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Catalytic decomposition of diazomethane as a general method for the methylenation of chemical compounds

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Contents

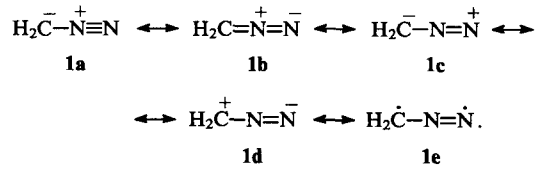
I.	Introduction	799
II.	Interaction of diazomethane with metal salts and complexes	800
III.	Catalytic conversion of unsaturated compounds into cyclopropane derivatives	802
IV.	Catalytic interaction of diazomethane with aromatic compounds	827
V.	Synthesis of ketones by converting carbonyl compounds into higher homologues	830
VI.	Catalytic methylation of alcohols and amines by diazomethane	832
VII.	Conclusion	835

Abstract. The principal advances and trends in the application of diazomethane as a methylenating agent in synthetic chemistry using transition and non-transition metal compounds as catalysts are surveyed and analysed. The catalytic reactions of diazomethane with olefins, acetylenes, aromatic compounds, ketones, alcohols, and amines are examined. A systematic account is given of data concerning the influence of the structure of the initial substrates and of the nature of the catalyst components on the regio- and stereo-selectivity of the reactions considered. The possibilities of the catalytic conversion by diazomethane (generated *in situ*) of unsaturated compounds into cyclopropane derivatives are considered. The bibliography includes 284 references.

I. Introduction

Diazomethane, which is the simplest representative of diazo-compounds, was first obtained by Pechmann[1] in 1894 and since then it has been firmly established as one of the popular reagents in synthetic organic chemistry, which are widely used to effect under mild conditions reactions involving the conversion of unsaturated compounds into cyclopropane derivatives, the conversion of carbonyl compounds into higher homologues, and the methylation of carboxylic acids, alcohols, and phenols. The present review is devoted mainly to the reactions of diazomethane with various organic compounds which occur as a rule in the presence of homogeneous metal complex catalysts.

Depending on the conditions, diazomethane can be regarded as an acid or base, as an electrophile or a nucleophile, and as a 1,3-dipole or a source of carbene (methylene). The linear structure of diazomethane has been established by electron diffraction[2] and by microwave spectroscopy.[3] It has a dipole moment of 1.4 D and carbon–nitrogen and nitrogen–nitrogen bond lengths of 0.132 and 0.112 nm respectively. These values are averages of the C–N and C=N bond lengths and the N=N and N≡N bond lengths respectively. Thus the structure of diazomethane can be represented by the following resonance structures, among which structures **1a** and **1b** make the greatest contribution:



1a **1b** **1c** **1d** **1e**

Other structural characteristics and spectroscopic data for diazomethane have been fairly fully presented in another review.[4]

The constant interest of investigators in diazomethane despite its high toxicity and explosive nature is due to the fact that it is a unique source of the simplest carbene—methylene, the high reactivity of which makes it possible to regard it as a promising one-carbon synthon for the creation of non-traditional chemical technologies. Furthermore, the development of the chemistry of diazomethane in relation to the problem of the synthesis and investigation of the reactivity of methylene has assisted in many respects in the understanding and determination of the mechanisms of important processes such as the metathesis of olefins, the Fischer–Tropsch reaction, the activation of alkanes, etc.[5–7] Finally, the majority of the methods of synthesis of diazomethane itself are based on the use of readily available compounds, in particular *N*-methyl-*N*-nitrosoamides, and extremely simple procedures for its generation.[4,8]

Diazo-compounds can be decomposed by three main methods—thermal, photochemical, and catalytic.[9,10] However, the first two are relatively unsuitable for preparative purposes, primarily because such processes are unsafe and there is an increased likelihood of side reactions, for example, those involving insertion in various C–H bonds. The progress in the chemistry of diazomethane during the last 10–15 years has been indissolubly linked with the application of metal complex

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catalysts, which not only promote the formal generation of methylene under mild conditions but also make it possible to regulate its reactivity within wide limits. The results have made, in particular, a significant contribution to the development of modern highly efficient methods of synthesis of many cyclopropane derivatives from readily available olefins and the factual data accumulated make it possible to elucidate in greater depth the mechanistic aspects of the catalytic cyclomethylenation of various unsaturated compounds.

It is noteworthy that the use of diazomethane in catalytic reactions involving the conversion of various unsaturated compounds into cyclopropane and cyclopropene derivatives has developed virtually in parallel with the application for such purposes of well-known aliphatic diazo-compounds such as diazoacetic acid esters. Whereas in the 1950s–1960s, mainly copper compounds were used as the traditional catalysts for the decomposition of the above diazo-compounds, since the middle of the 1970s catalysts based on rhodium and palladium have begun to be vigorously introduced into laboratory practice. A series of monographs and reviews[10–22] devoted to the synthetic possibilities of the catalytic methods for the conversion of unsaturated substrates into cyclopropane derivatives with the aid of diazo-compounds and to the consideration of the probable mechanisms of these processes appeared during this period. However, the majority of the publications do not yield a complete picture concerning the use of metal complex catalysis in the chemistry of diazomethane and do not deal with the specific features of diazomethane itself which distinguish it from other aliphatic diazo-compounds.

On the basis of the factual data accumulated, an attempt is made in the present review to present as fully as possible the advances and prospects in the application of metal complex catalysis in the chemistry of diazomethane.

II. Interaction of diazomethane with metal salts and complexes

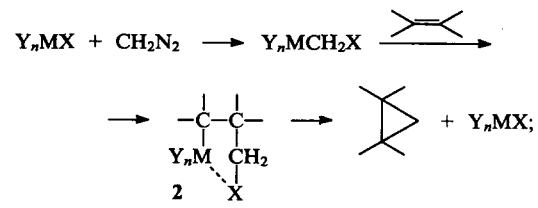
Diazomethane readily decomposes on treatment with many transition and non-transition metal compounds.[15,22–26] This includes its decomposition on the active surface centres of pure metals (Ni, Pd, Cu, Fe, Co, Ru, U),[27–28] heterogeneous catalysts, and various sorbents,[29,30] which by no means always involves the transfer of methylene to the double bonds of olefins or other substrates and this process is extremely sensitive to the nature of both the substrate and the catalyst. In most cases the decomposition of CH_2N_2 is accompanied by the liberation of ethylene and other volatile products, although it can also lead to the preferential formation of polymethylene.[31–33] For example, the dediazotisation of CH_2N_2 by nickelocene yields polymethylene almost quantitatively even in the presence of olefins.[31]

The interaction of CH_2N_2 with compounds of the majority of the elements in the Periodic Table with the properties of Lewis acids and primarily with their halides leads to the initial formation of organometallic (organoelement) compounds via the insertion of methylene in M–X bonds.

$$MX_n \xrightarrow{CH_2N_2} MX_{n-m}(CH_2X)_m \xrightarrow{CH_2N_2} M(CH_2X)_n.$$

According to data surveyed in a number of reviews[15–23], Zn, Cd, Hg, Al, In, Tl, Sn, Pb, Sb etc. interact via this mechanism and compounds of the Group IV and V elements in the highest oxidation states, for example Sn(IV), Pb(IV), and Sb(V), are initially reduced by diazomethane to the corresponding Sn(II), Pb(II), and Sb(III) compounds.

The conversion of olefins into cyclopropane derivatives by halomethylmetal compounds of this kind has been investigated most thoroughly for Zn and Al derivatives:[34–36] these compounds are relatively unstable and are in essence intermediates capable of adding to the double bond of olefins. Since the three-carbon ring is formed stereospecifically, the reaction mechanism implies the selectivity of the stages involving the addition of the halomethyl derivative and the γ-elimination of the metal halide, as well as the stability of the steric configuration of the organometallic intermediate **2**.



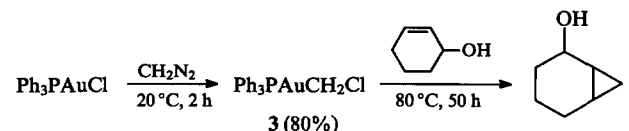
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Y = Alk, Ar, Hal; X = Cl, I.

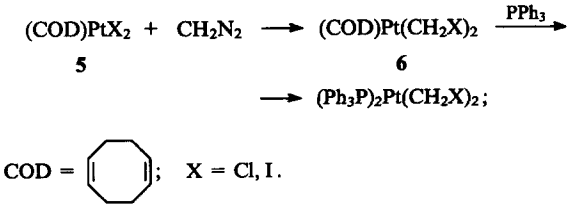
Thus, according to Hoberg's data,[36] diethylaluminium iodide reacts with CH_2N_2 in pentane at −80 °C with the evolution of nitrogen and the formation of crystalline Et_2AlCH_2I. By interacting with olefins, this compound affords the corresponding cyclopropane (for example, norcarane in the case of cyclohexene). Zinc compounds react via the same mechanism and the regeneration of the initial metal halide makes it possible to use it in catalytic amounts. The conversion of olefins into cyclopropane derivatives by CH_2N_2 in the presence of ZnX_2 is one of the versions of the Simmons–Smith method, various aspects of which have been considered in another review.[37]

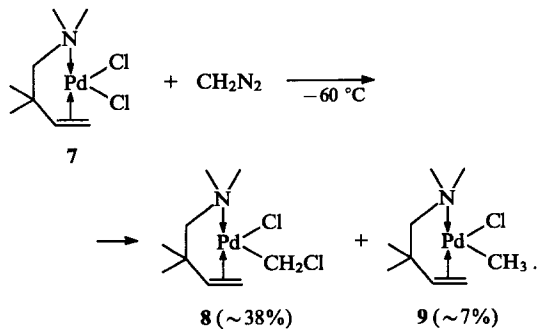
It is noteworthy that virtually all the reactions involving the conversion of olefins into cyclopropane derivatives by diazomethane in the presence of zinc- or aluminium-containing catalysts are carried out under anhydrous conditions—mainly in ether. A disadvantage of the above catalysts is their high reactivity in relation to the initial olefins, which induces their oligomerisation or conversion into the corresponding halides.

The insertion of methylene, generated from CH_2N_2, in the M–X bond occurs also when transition metal compounds are used. In certain cases, it was then possible not only to isolate the products of such insertion but also to demonstrate the possibility of converting olefins into cyclopropane derivatives by such products. Thus, according to Nesmeyanov et al.,[38] the interaction of Ph_3PAuCl with CH_2N_2 at 20 °C leads to the chloromethyl derivative **3**, which is capable of subsequently methylenating cyclohexenol to form 2-hydroxynorcarane **4**, albeit in low yield.

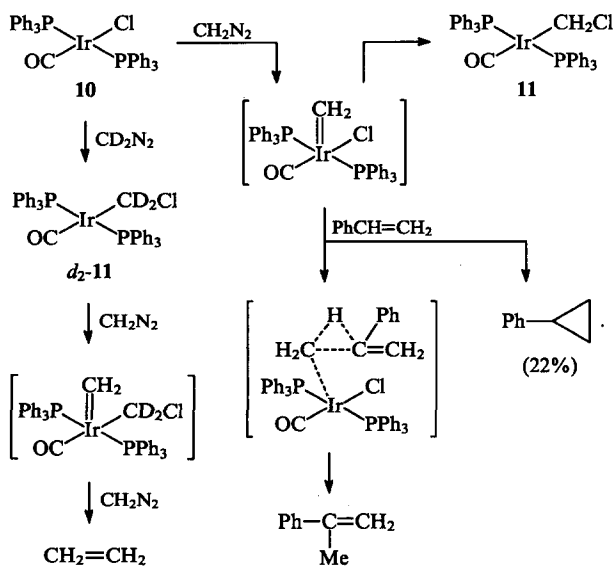


Halomethyl derivatives have also been obtained when complex palladium and platinum dihalides were used. The interaction of the platinum complex **5** with an excess of CH_2N_2 then affords a high yield of the bishalomethyl derivative **6**,[39] while the palladium complex **7** unexpectedly affords also the methyl complex **9** together with the chloromethyl derivative **8**.[40]

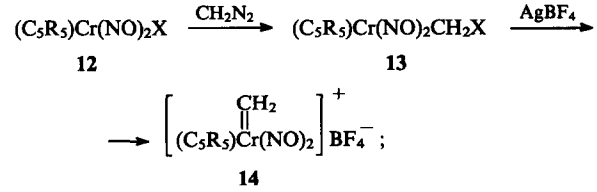




It is noteworthy that, apart from the halomethyl derivatives of transition metals, products may be obtained in which the methylene fragment is coordinated to the metal atom. Thus the addition of CH_2N_2 to the iridium complex **10** at −30 °C leads to the adduct **11** (or d_2-**11**).[41] The formation of ethylene on subsequent addition of CH_2N_2 to the deuteriated complex d_2-**11** as well as the formation of phenylcyclopropane and α-methylstyrene on interaction of compound **11** with styrene have been attributed[41] in this instance to the involvement in the reaction of the methylene complexes of pentacoordinate iridium.



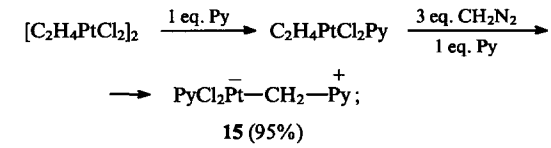
The complex chromium halides **12** interact with CH_2N_2, affording a high yield of the corresponding halomethyl derivatives **13**, which are converted in the presence of $AgBF_4$ into the cationic complexes **14**.[42] The attempt to convert cyclohexene into a cyclopropane derivative by compounds **14** proved successful only in the case of the pentamethylcyclopentadienyl ligand, the yield of norcarane not exceeding 5% under these conditions.

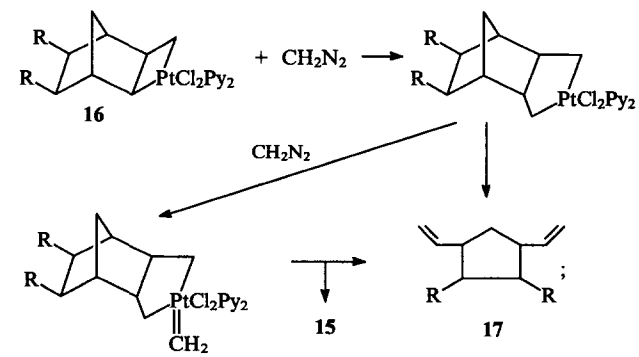


R = H, Me; X = Cl, Br.

The possible methods of the synthesis of cationic methylene complexes of transition metals not involving the use of CH_2N_2 as well as certain reactions with transfer of the methylene fragment from these complexes to the substrate, including the conversion of olefins into cyclopropane derivatives by such complexes, have been considered in a review.[43]

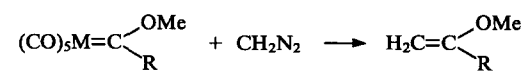
In contrast to complexes **5**, the pyridineplatinum complex, formed on controlled addition of pyridine to bis(ethyleneplatinum dichloride), interacts with a threefold excess of CH_2N_2, affording not the halomethyl derivatives of platinum but two enantiomeric forms of the ylide **15**.[44] The same compound is obtained also in the reaction of CH_2N_2 with the derivatives of platinacyclobutanes **16**, but in this case the main process reduces, according to Jennings et al.,[45] to the insertion of methylene into the Pt−C bond with subsequent conversion of the resulting platinacyclopentanes into *cis*-divinylcyclopentanes **17**.

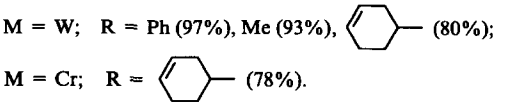




R = H, R−R is a chemical bond or CH_2.

The dediazotisation of CH_2N_2 by stable methoxycarbene complexes of chromium and tungsten is accompanied by the transfer of methylene to the carbene ligand, which results in the formation of the vinyl ethers **18** in satisfactory yields.[46,47]





Copper and palladium compounds constitute another group of transition metal compounds catalysing the decomposition of CH_2N_2 and ensuring the successful transfer of methylene to the substrate (in particular, the conversion of

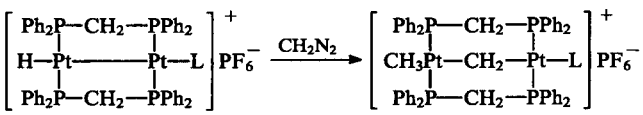
olefins into cyclopropane derivatives under mild conditions). The involvement of carbene complexes of metals in these reactions with the methylene generated from CH_2N_2 has so far been only postulated. However, despite the absence of direct experimental evidence for the formation of these complexes under the real conditions of the conversion of olefins into cyclopropane derivatives by CH_2N_2, their participation in the reactions is indicated by the existence of stable carbene complexes of other transition metals[6,43,48] as well as the detection of complexes of CH_2N_2 and methylene with atomic copper at 11 K in an argon matrix.[49]

Catalysts based on transition metals can be regarded as centres on which CH_2N_2 is coordinated and methylene is generated from it. The nature of the metal and the ligand environment of the central catalyst atom, which influence the strength of the bond linking the coordinated methylene, make it possible to vary its reactivity under these conditions, which leads in its turn to the possibility of regulating the regio- and stereoselectivity of the addition of methylene to various substrates.

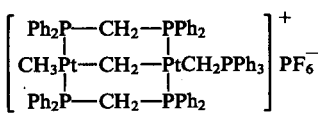
Finally, the reactions of CH_2N_2 with di- and poly-nuclear transition metal complexes, leading to the formation of μ-methylene complexes as a result of the addition of methylene to the metal–metal bond, are of independent interest:

Compound	Ref.
$(\mu\text{-}CH_2)[C_5H_5(NO)Fe]_2$	50
$(\mu\text{-}CH_2)[C_5Me_5(CO)Co]_2$	51
$(\mu\text{-}CH_2)[(C_5H_4Me)Mn(CO)_2]_2$	52, 53
$(\mu\text{-}CH_2)[C_5Me_5(CO)Rh]_2$	54, 55
$(\mu\text{-}CH_2)(\mu\text{-}CF_3C{\equiv}CCF_3)[ClRh(Ph_2PCH_2PPh_2)]_2$	56
$(\mu\text{-}CH_2)[ClPt(Ph_2PCH_2PPh_2)]_2$	57
$(\mu\text{-}CH_2)H_2Os_3(CO)_{10}$	58
$(\mu\text{-}CH_2)Os_3PtH_2(CO)_{10}\{P(C_6H_{11})_3\}$	59

The structural features of the μ-methylene complexes of transition metals have been analysed and the methods of their synthesis have been described in a review.[60] It is of interest to note that in the case of the hydridoplatinum complexes **19**, the insertion of CH_2 into the Pt–H bond with formation of complexes **20**, and into the Pt–P bond on interaction of compound **19c** with an excess of diazomethane, was observed simultaneously with its insertion in the Pt–Pt bond.[61]



19 **20a, b**



20c

L = CO (**a**), PMe_2Ph (**b**), PPh_3 (**c**).

The dinuclear complex $Mn_2(CO)_{10}N_2CH_2$, in which the Mn atoms are linked by a nitrogen bridge, while the methylene fragment is attached to one of the nitrogen atoms, was synthesised by the reaction of CH_2N_2 with $Mn(CO)_5H$ in tetrahydrofuran (THF) at −85 °C.[62]

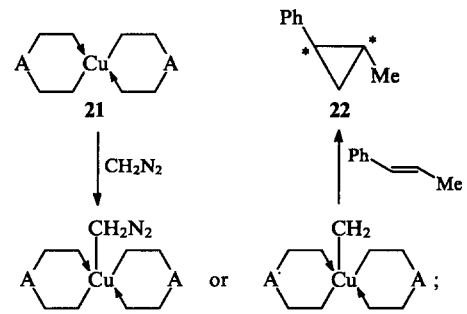
It is noteworthy that the interest in the stable μ-methylene complexes of transition metals has been mainly induced by the possibility of the involvement of such complexes as intermediates in the Fischer–Tropsch reaction. Unfortunately the reactions involving the transfer of the methylene fragment from these complexes to various substrates have been scarcely investigated.

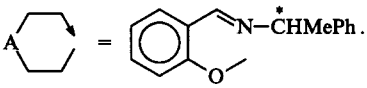
III. Catalytic conversion of unsaturated compounds into cyclopropane derivatives

1. The mechanism of the catalytic conversion of olefins into cyclopropane derivatives by diazomethane

Despite the abundance of compounds inducing the decomposition of diazomethane, copper and palladium compounds are the commonest and most effective agents for the catalytic conversion of olefins into cyclopropane derivatives by diazoalkanes. The experimental data accumulated hitherto have shown[63–66] that, among copper compounds, the salts of copper(I) are catalytically active in these reactions. The copper(II) salts, in particular $CuCl_2$ or $Cu(OSO_2CF_3)_2$, are initially reduced by diazomethane to the corresponding univalent copper compounds.[34,65]

According to Nefedov et al.,[66] when $Cu(acac)_2$ is used for the conversion of alkenes into cyclopropane derivatives, it is initially reduced by diazomethane to the relatively unstable Cu(acac), which is characterised primarily by the disappearance of the initial colour of the catalyst as a consequence of the conversion of Cu(II) into Cu(I). In view of this, one can assume that copper(I) compounds with one singly charged chelate anion are catalytically active in the case of other copper chelate compounds, in particular those with optically active ligands. Nevertheless, the pentacoordinate state of copper(II) has been considered[67] as an intermediate and the induction of the optical activity in the resulting cyclopropane **22** (yield 62%, optical yield 8%) is explained by the influence of the two optically active ligands in the initial complex **21**.

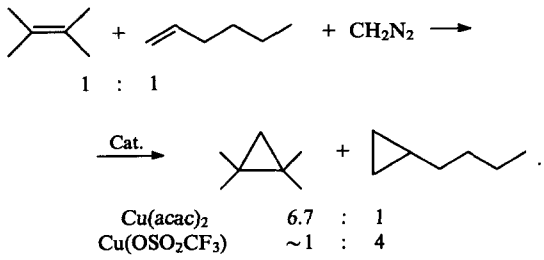




When palladium(II) compounds are used as the catalysts in the dediazotisation of CH_2N_2, a catalytically active species involving a change in the valence state of the palladium is also formed initially. Thus palladium halides or acetate are reduced to zerovalent palladium, which is either precipitated as a black deposit or is present in solution in the form of complexes stabilised by suitable ligands.[68] Under particular conditions, certain olefins, affording the corresponding π-olefin complexes, can also play the same role. However, the thermal stability of zerovalent palladium complexes is as a rule low[69] and depends significantly on the nature of the double bonds in the unsaturated compound. Inner complexes of palladium, for example $Pd(acac)_2$, apparently form more complex catalytically active structures with formally univalent palladium.[25]

There are two possible mechanisms of the catalytic conversion of olefins into cyclopropane derivatives by diazocompounds, in particular by diazomethane, in the presence of copper and palladium derivatives, the principal difference between which consists in the different sequences of the stages involving the interaction of the catalyst with the diazocompound and the olefin.[17,65,70,71]

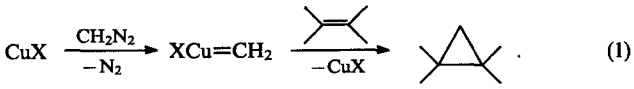
In relation to the conversion of mono- and tetra-substituted alkenes into cyclopropane derivatives, Salomon and Kochi[65] showed that regioselectivity in the conversion of various double bonds into cyclopropane groups differs depending on whether copper acetylacetonate or triflate is used as the catalyst. The more substituted double bond is converted into a cyclopropane group in the presence of $Cu(acac)_2$, whereas in the presence of $Cu(OSO_2CF_3)_2$ the terminal double bond undergoes such conversion.

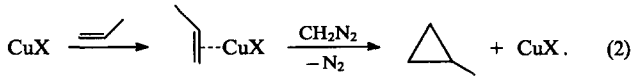


On these grounds, it was claimed that the change in the basicity of the anion affects the ability of the copper ion to form π-complexes with particular double bonds of olefins and is therefore capable of altering the sequence of the stages in the interaction of the catalyst with the diazo-compound and the olefin.

According to the first and commonest mechanism of the conversion of olefins into cyclopropane derivatives by diazoalkanes, a complex between the catalyst and the diazo-compound is formed initially. This is followed by the formation of a complex with the carbene, after which the double bond of the unsaturated compound is converted into a cyclopropane group by this complex.[17,65,70,71]

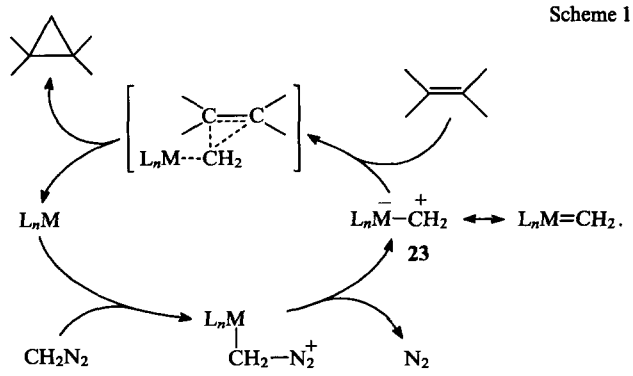
According to the other mechanism, a π-complex of the active form of the catalyst with the unsaturated compound is formed initially, interacting subsequently with the diazo-compound.[17,65,70]





In our view, the conversion of olefins into cyclopropane derivatives in the presence of copper compounds should be considered within the framework of one mechanism, because the key stage in both cases is the generation of the carbene complex (Scheme 1). The electrophilicity of the metal (Cu^+) induces, by analogy with the protonation of diazo-compounds, a shift of electron density towards the formation of an unstable diazonium cation, which readily eliminates a nitrogen molecule. The electrophilicity of the carbene species is in its turn largely determined by the contribution of the polarised structure **23**. Next, this complex reacts preferentially either with the more nucleophilic tetraalkyl-substituted double bonds, if the catalyst is incapable of effecting selectively the coordination of any one of the double bonds, or with monosubstituted double bonds. The latter reaction is less vigorous, but such bonds are present in excess in the coordination sphere of the metal as a consequence of complex formation. Here one should note that the regioselectivity of the conversion of double bonds into cyclopropane groups in the presence of copper catalysts is not high and the observed differences are of the same order of magnitude.

Scheme 1

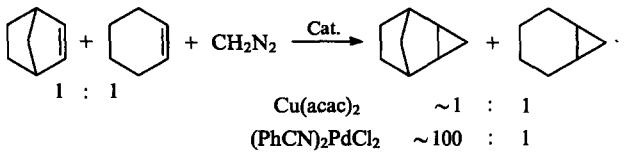


On the other hand, the effectiveness of the cyclopropane formation reaction is influenced very greatly in both cases by the competing side reaction between the methylene complex and yet another diazomethane molecule. This process involves the intermediate formation of organocopper compounds, which readily decompose with liberation of active metallic copper on which unsaturated compounds are scarcely converted into cyclopropane derivatives by diazomethane.[66] Obviously the ease of such reactions depends both on the nature of the olefin to be converted into a cyclopropane derivative and on the nature of the catalyst. The probability of the insertion of the methylene generated into the Cu–X bond of the catalyst is then found to be highest for nucleophilic anions. Thus, in the case of CuCN or CuI, this side reaction apparently plays a dominant role, which virtually rules out the possibility of the transfer of methylene to the olefin.[66] Furthermore, in order to reduce the probability of side reactions in catalysis by copper compounds, a very slow addition of CH_2N_2 to a mixture of the olefin and the catalyst is essential.

Within the framework of the mechanism considered, the possibility of the reverse polarisation of the carbene complex $L_nM{=}CH_2 \longleftrightarrow L_nM^+ - {}^-CH_2$ has been postulated in order to account for the preferential conversion of the electron-deficient double bond into a cyclopropane group.[72] Thus, in the interaction of CH_2N_2 with methyl acrylate, styrene, cyclohexene, and hex-1-ene, catalysed by zerovalent nickel complexes, the formation of a cyclopropane adduct was observed only for methyl acrylate. However, in such cases one must not apparently fail to take into account the active formation of complexes between the electron-deficient alkenes themselves and the central atom of the catalyst, which can influence significantly the nature of their interaction with CH_2N_2. The conversion of unsaturated compounds into cyclopropane derivatives by diazomethane in the presence of zerovalent nickel and especially zerovalent palladium complexes, which exhibit a series of significant and fundamental differences from the catalysis by copper compounds, should in fact be regarded as an alternative mechanism, in which the initial formation of π-olefin complexes is indeed an important stage of the entire process.

In contrast to the copper compounds, catalysts based on palladium compounds display an extremely high regio-selectivity in the conversion of individual double bonds into cyclopropane groups. This has no analogue among other methods for the conversion of unsaturated compounds into cyclopropane derivatives (without taking into account the influence of steric factors). The use of various palladium compounds as catalysts under these conditions hardly affects the regioselectivity of the cyclopropane formation reaction.

Instances of reactions exhibiting different stereoselectivities in the conversion of the same cycloolefins into cyclopropane derivatives under the influence of copper or palladium catalysts have also been observed (see Section III.3.b).



Finally, in contrast to copper catalysts, the conversion of double bonds into cyclopropane groups in the presence of palladium compounds proceeds without special complications up to the total conversion of the olefin into the corresponding cyclopropane even when the order in which the reactants are mixed is altered, for example when the catalyst is added to a mixture of the unsaturated compound and an excess of CH_2N_2.

Thus the results show that the mechanism of the action of palladium catalysts differs significantly from that of the catalysis of the cyclopropane formation reaction by copper compounds.

As mentioned above, the palladium compounds used as catalysts are initially reduced by diazomethane to low-valence palladium complexes stabilised in solution by suitable olefin ligands. In contrast to the olefin copper(I) complexes, where the coordinated ligand undergoes only slight changes compared with the initial olefin, in the π-olefin complexes of zerovalent palladium considerable changes occur in the coordinated ligand: the double bond is lengthened, the bond angles of the substituents are altered, and there is intense reverse donation of electrons from the metal to the olefin.

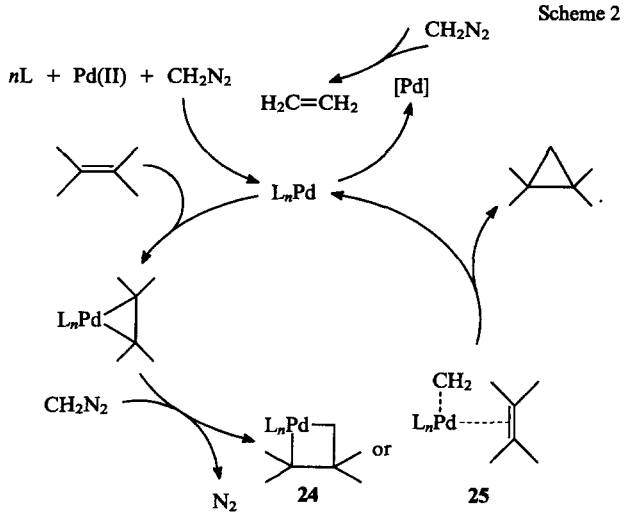
Thus the observed high selectivity in the conversion of various double bonds into cyclopropane groups by diazomethane in the presence of palladium compounds is undoubtedly due to their high selectivity in the formation and stabilisation of π-olefin complexes of zerovalent palladium.[68] According to Green et al.,[69] these complexes contain three equivalent olefin ligands. Furthermore, one can imagine two versions of the interaction of the π-olefinpalladium complexes with CH_2N_2.

In the first case, CH_2N_2 reacts directly with the polarised Pd–C bond of the π-olefin complex, affording the unstable palladiacyclobutane **24**, from which the cyclopropane adduct is eliminated and the initial π-olefin complex is regenerated under the influence of the next olefin molecule. Other complex-forming groups, for example the triphenyl phosphite or acetylacetonate groups, can also be present under these conditions as one or two ligands.

In the second version, CH_2N_2 substitutes one of the olefin ligands, eliminating the N_2 molecule and affording the metal–olefin–carbene complex **25**, from which the cyclopropane adduct is obtained either directly or via the palladiacyclobutane intermediate **24** (Scheme 2). The involvement of the latter in the reaction actually makes it possible to account for certain regio- and stereo-specific features of the conversion of olefins into cyclopropane derivatives by diazomethane in the presence of palladium catalysts. The existence of both metal–olefin–carbene complexes and metallacyclobutanes is now known.[73,74] However, the involvement of these intermediates in the conversion of olefins into cyclopropane derivatives, catalysed by copper and palladium compounds, is as yet tentative.

Unfortunately, under real experimental conditions, the yields of the cyclopropane adducts are determined not only by the contributions of the above mechanisms of the cyclopropane formation reaction but also by the possibility of the occurrence of side reactions associated primarily with the change in the active form of the catalyst. Thus the principal cause of the loss of catalytic activity by both copper and palladium compounds in the cyclopropane formation reaction is the liberation of the free metal and, as noted above, in the former case this is determined by the ease of the formation and α-decomposition of the organocopper intermediates, whilst in the latter it is due to the use of olefins with a low complex-forming capacity. The

Scheme 2



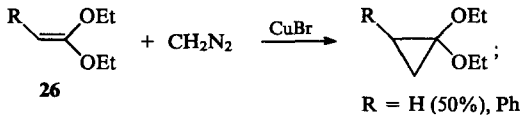
principal product of the decomposition of CH_2N_2 under these conditions is ethylene, which means that even the use of CH_2N_2 in manyfold excess does not lead to the complete conversion of olefins into the corresponding cyclopropane adducts.

2. Conversion of olefins into cyclopropane derivatives by diazomethane in the presence of copper catalysts

Copper compounds, in particular, CuCl and CuBr, were some of the first and commonest catalysts of the conversion of olefins into cyclopropane derivatives by diazomethane. Universality and the ability to catalyse the conversion of monosubstituted and polysubstituted olefins of different structure into cyclopropane derivatives are characteristic features of the above catalysts. In the copper salt-catalysed decomposition of CH_2N_2, the possibility of side reactions of the initial olefins and the resulting cyclopropanes is almost completely ruled out and there is also no insertion of the methylene fragment into the C–H bonds of these compounds.[11,12,71] However, the degree of conversion of olefins into cyclopropanes varies within wide limits even in the presence of an excess of the added diazomethane and depends significantly on the nature of the double bonds and the experimental conditions.

a. Conversion of unsaturated aliphatic compounds into cyclopropane derivatives

The conversion of unsaturated compounds into cyclopropane derivatives by diazomethane using copper catalysts was first achieved in 1959 by Dull and Abend,[75] who investigated the interaction of CH_2N_2 with ketene acetals **26** in the presence of CuBr in hexane.

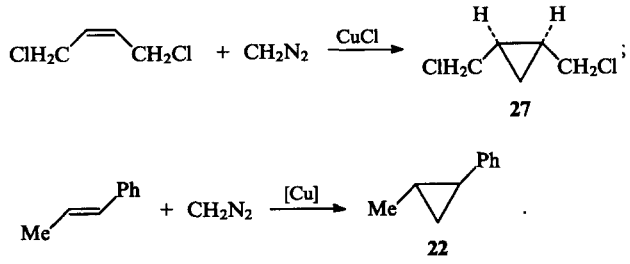


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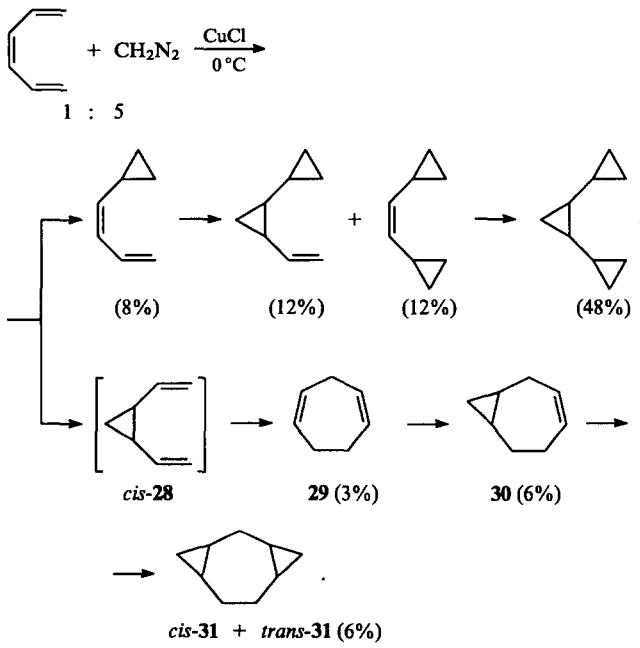
R = H (50%), Ph (12%).

Numerous studies, in which the method involving the catalytic conversion of multiple bonds into cyclopropane groups by diazomethane in the presence of copper compounds had been applied to a wide variety of unsaturated compounds containing both isolated and conjugated double bonds, were published in the 1960s. In order to eliminate or diminish the amount of solvent employed, particularly in the conversion of polyene compounds into polycyclopropane derivatives, which requires a large amount of CH_2N_2, the Gaspard–Roth method was frequently resorted to.[76] It consists in passing CH_2N_2 diluted with an inert gas into the olefin or its solution in a saturated hydrocarbon containing a catalytic amount of the copper salt at a temperature of about 0 °C.

The catalytic conversion of olefins into cyclopropane derivatives by diazomethane in the presence of various copper compounds proceeds stereospecifically with retention of the configuration of the initial unsaturated compound. Thus the interaction of CH_2N_2 with *cis*-1,4-dichlorobut-2-ene [77] in the presence of CuCl leads exclusively to *cis*-1,2-bis(chloromethyl)-cyclopropane **27**, while the conversion of *trans*-propenylbenzene into cyclopropane [67] in the presence of the copper complex **21** leads to *trans*-2-methyl-1-phenylcyclopropane **22**.

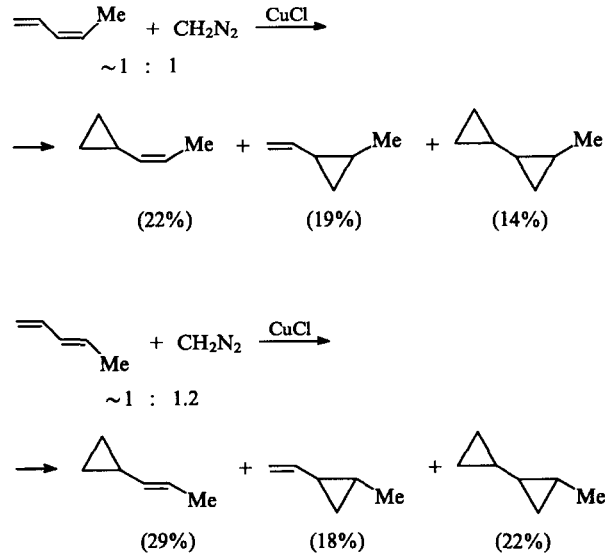


The regioselectivity of such reactions is as a rule low, which has been noted in relation to the conversion of a highly unsaturated hydrocarbon, namely hexa-1,3,5-triene, into a cyclopropane derivative.[76] Thus the interaction of *cis*-hexatriene with CH_2N_2 in the presence of CuCl leads to the formation of all the possible products of the addition of methylene to the double bonds in both the initial triene and in the mono- and di-adducts formed from it. The absence of *cis*-1,2-divinylcyclopropane **28** from the reaction mixture and the formation of the cyclic hydrocarbons **29–31** under these conditions has been explained[76] by the ready rearrangement of *cis*-**28** to the cyclodiene **29** and its subsequent conversion into cyclopropane derivatives.

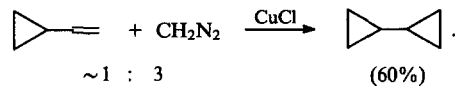


In contrast to the *cis*-isomer, *trans*-hexatriene affords only the expected linear cyclopropane formation reaction adducts, including also *trans*-1,2-divinylcyclopropane.[76] Despite the excess of CH_2N_2, the complete conversion of the hexatrienes is not then attained in both cases.

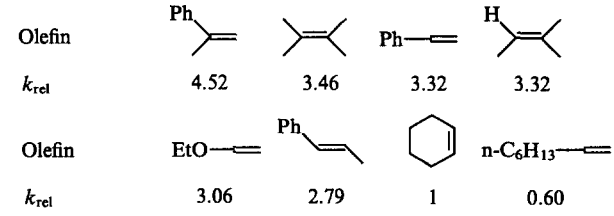
The interaction of *cis*- and *trans*-penta-1,3-dienes with CH_2N_2† in the presence of CuCl also takes place non-selectively[78] (but, as in the case of other olefins, with retention of the configuration of the double bond) and leads to a mixture of different products of the cyclopropane formation reaction. Despite the postulated electrophilic nature of the carbene intermediate, the conversion of the less substituted double bond into a cyclopropane group is somewhat preferred.



As was to be expected, the conversion of vinylcyclopropane itself by an excess of CH_2N_2 into bicyclopropyl proceeds fairly smoothly, which makes it possible to regard this method of synthesis of bicyclopropyl as preparative.[79]



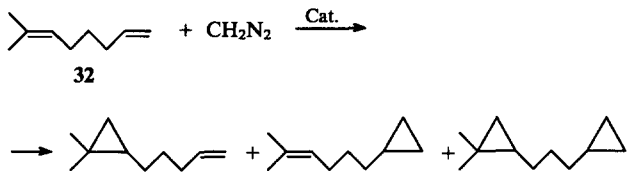
The constants of the relative reactivity of olefins of different structure in relation to CH_2N_2 have been published[67] (the reaction was carried out in the presence of copper salicylaldiminate **21**; the degree of conversion of the olefins was ~10%):



Interesting results as regards the relative reactivity of the double bonds have been obtained using copper catalysts containing anions with different basicities.[65] Thus passage of CH_2N_2 into a mixture of 2,3-dimethylbut-2-ene and hex-1-ene in proportions of 1 : 1 in the presence of a catalytic amount of $Cu(acac)_2$ leads to tetramethylcyclopropane and butylcyclopropane in proportions of 6.7 : 1. The same reaction in the presence of $Cu(OSO_2CF_3)_2$ leads to the formation of the above cyclopropanes in the reverse proportions (~1 : 4) (see Section III.1).

† Instead of the absolute amount of CH_2N_2, the amount of *N*-methyl-*N*-nitrosourea used to generate it has been stated in a number of communications. Therefore here and henceforth in specifying the olefin : CH_2N_2 molar ratio it is postulated that CH_2N_2 is formed in a yield of 55% – 60% on average.[66]

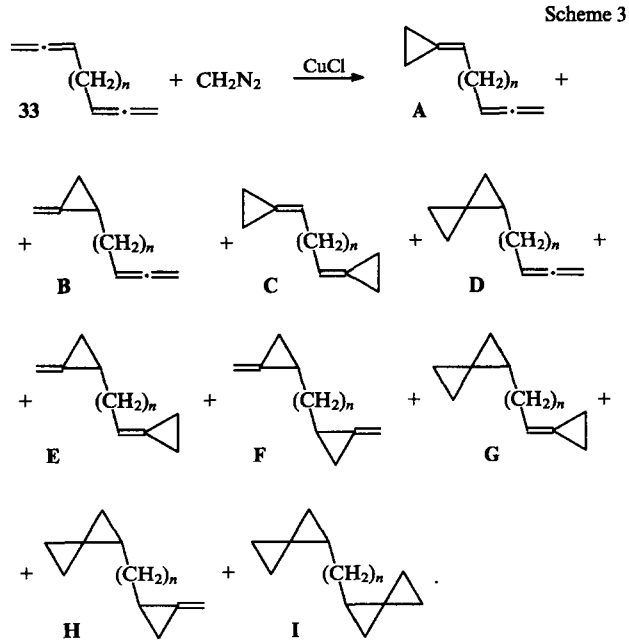
A similar dependence of the mode of the cyclopropane formation reaction on the degree of substitution of the double bond and the copper salt employed is manifested also in the conversion of 2-methylocta-2,7-diene **32** into a cyclopropane derivative.[65] In the presence of copper acetylacetonate, the more substituted double bond is converted into a cyclopropane group, while in the presence of copper triflate the terminal double bond is thus converted.



Cat.	Conversion of diene (%)	Adducts ratio
$Cu(acac)_2$	~10	6.1 : 1 : ~0.1
	90	10 : 1 : 6
$Cu(OSO_2CF_3)_2$	10	1 : 2 : ~0.1
	50	1 : 2.5 : 0.4

The results are probably associated with the unequal abilities of the catalyst to effect the coordination of different double bonds: copper ions coordinated to the acetylacetonate ligand are hardly involved in the formation of π-olefin complexes by reaction with the double bonds, whereas copper ions containing only the weak nucleophilic $CF_3O_2SO^-$ anion are capable of the selective formation of complexes by reacting with the less substituted (or strained) double bonds.[80,81] For this reason, the electrophilic methylene complex formed on decomposition of CH_2N_2 in the coordination sphere of copper reacts preferentially with the more nucleophilic (i.e. alkylated) C=C bonds in the former case, while in the latter case it reacts with the unsubstituted or strained double bonds, which, although less nucleophilic, show instead a greater tendency towards the formation of complexes with the metal atom and are therefore more accessible.

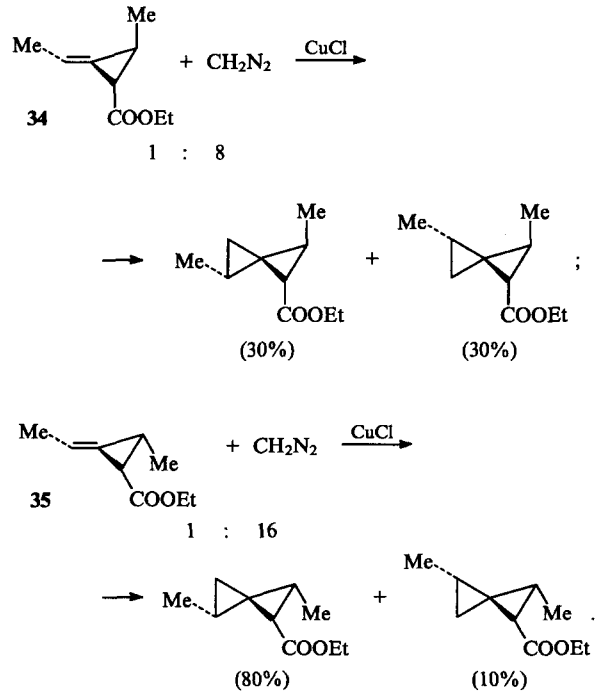
Scheme 3



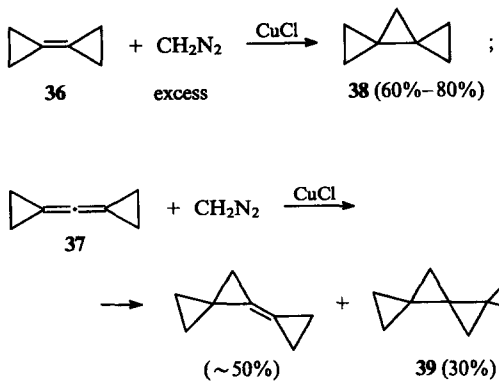
n	Reagents ratio	Yield of products (%)								
		A	B	C	D	E	F	G	H	I
0	1 : 5	8	13	3	15	9	8	13.5	17	11.5
2	1 : 8	8	9	4	10	7	6	14	14	14

The copper salt-catalysed interaction of CH_2N_2 with allenes and methylenecyclopropanes has been investigated in a number of studies.[82–88] Although this method is fairly general for the synthesis of spiropentanes which are difficult to obtain, it nevertheless frequently leads to the formation of a complex mixture of compounds in relatively low yields or requires the use of a large excess of CH_2N_2. Thus a more than tenfold excess of CH_2N_2 has been used to convert tetradeuterioallene into the corresponding spiropentane at −80° C,[82] while the conversion of hexa-1,2,4,5- or octa-1,2,6,7-tetraenes **33** with a fivefold to eightfold molar excess of CH_2N_2 in the presence of CuCl led to the formation of a complex mixture of hydrocarbons containing all the possible products of the conversion of the double bonds into cyclopropane groups (Scheme 3).[83,84]

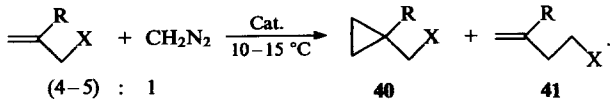
The conversion of methylenecyclopropanes into the corresponding spiropentane derivatives takes place significantly more smoothly under these conditions. Thus (in the presence of CuCl) the catalytic conversion of the esters of propylidenecyclopropanecarboxylic acid esters into cyclopropane derivatives by a large excess of CH_2N_2 was used as the basis of the synthesis of ethoxycarbonylspiropentanes.[85,86] Each individual isomer of the initial methylenecyclopropanes, for example compounds **34** and **35**, then forms two stereoisomeric spiropentanes. The steric disposition of the substituents can affect the degree of addition of the methylene attacking the double bond from different sides of the latter.



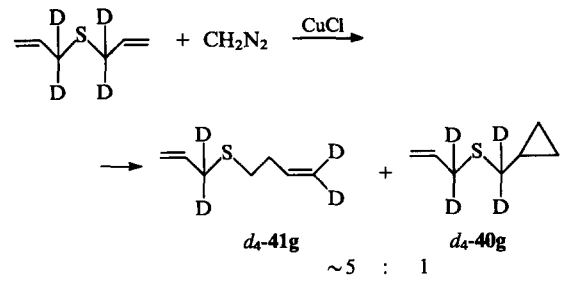
Fitjer and Conia[87,88] synthesised the polyspirane hydrocarbons **38** and **39**, consisting exclusively of cyclopropane fragments, from the bicyclopropylidene **36** and the allene **37** in 80% and 30% yields respectively. However, according to the data of Zefirov et al.,[89] who repeated the conversion of compound **36** into tercyclopropyl **38** in the presence of CuCl, the maximum yield of the latter was only 60%. As in all the previous cases, when copper compounds are used as catalysts, the target cyclopropane formation reaction proves to be extremely sensitive to the conditions under which it is carried out. One of the causes of the loss of catalytic activity of CuCl on transfer of methylene to the double bond of the olefin is probably its reduction to metallic copper.



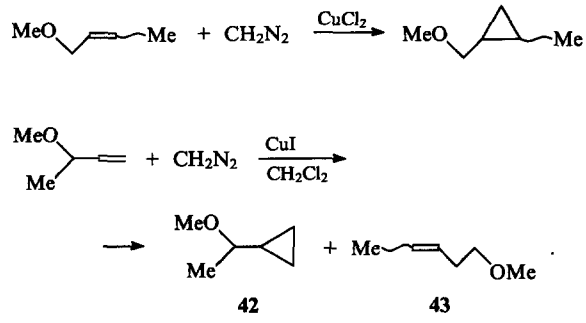
The catalytic interaction of CH_2N_2 with allyl derivatives in the presence of copper salts has been widely investigated by Kirmse and coworkers.[77,90–94] It was found that in the case of allyl halides as well as *O*- and *S*-allyl derivatives, the reaction leads to both the products of the conversion of the double bond into a cyclopropane group with formation of methylcyclopropanes **40** and to the products of formal insertion into the carbon–heteroatom bond with formation of 4-X-but-1-enes **41**, the yield and proportions of which depend significantly on the nature of the heteroatom and the reaction conditions (Table 1). Thus, when the reaction is carried out in pentane, allyl chloride affords predominantly chloromethylcyclopropane **40a**, whereas allyl bromide in CH_2Cl_2 gives rise to 4-bromobut-1-ene **41b**.



According to some data,[77,92] the formation of the homoallyl derivatives **41** proceeds via the stage involving the allyl rearrangement of the metastable ylide produced as a result of the addition of methylene to the heteroatom, which agrees well, in particular, with experimental data concerning the interaction of the deuteriated diallyl sulfide with CH_2N_2, as a result of which two deuterium atoms in compound d_4-**41g** formed are attached to the double bond.



It has also been noted[92] that the interaction of 1-methoxybut-2-ene with CH_2N_2 leads only to the conversion of the double bond into a cyclopropane group, whereas both the cyclopropane adduct **42** and a considerable proportion of the products of the allyl rearrangement—the isomeric 1-methoxypent-3-enes **43**—are formed from 2-methoxybut-3-ene.



The interaction of CH_2N_2 with allyl azide in the presence of CuCl affords 1,3,5-triallylhexahydro-*s*-triazine **44** together with cyclopropylmethyl azide.[93] This elegant synthesis of the *N*-allylaldimine trimer probably also proceeds via the intermediate formation of the ylide **45**.

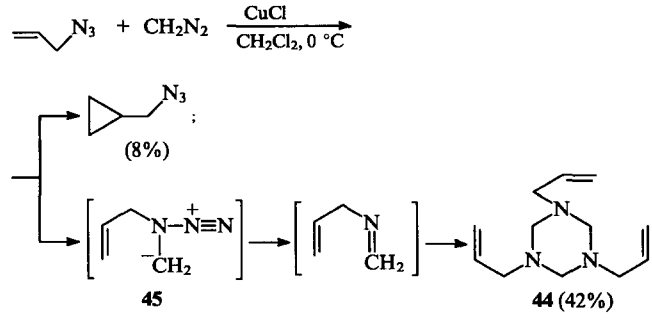
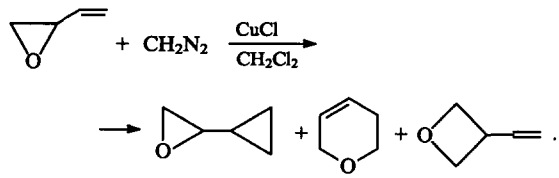


Table 1. Composition of the products of the interaction of CH_2N_2 with allyl derivatives ($H_2C=CRCH_2X : CH_2N_2 :$ Cat. ~5 : 1 : 0.6).

	$H_2C=CRCH_2X$		Catalyst (Cat.)	Solvent	Overall yield (%)	Content (%)		Ref.
	R	X				**40**	**41**	
a	H	Cl	CuCl	C_5H_{12}	30	83	14	77
			$CuCl_2$	C_5H_{12}	30	85	13	77
			$CuCl_2$	CH_2Cl_2	31	76	19	77
b	H	Br	$CuCl_2$	C_5H_{12}	17	21	79	77
			$CuCl_2$	CH_2Cl_2	29	6	90	77
			$(PhO)_3PCuCl$	CH_2Cl_2	79 [a]	2	98	95
c	Me	Cl	$CuCl_2$	CH_2Cl_2	30	34	59	77
d	Cl	Cl	$CuCl_2$	CH_2Cl_2	25	24	74	77
e	H	OMe	$CuCl_2$	C_5H_{12}	20	90	10	92
f	H	OC_3H_5	$CuCl_2$	C_5H_{12}	25	95	5	92
g	H	SC_3H_5	CuCl	C_5H_{12}	35	17	83	92
h	H	NMe_2	CuCl	CH_2Cl_2	26	100	–	93
i	H	$ONMe_2$	CuCl	Et_2O	7	100	–	93

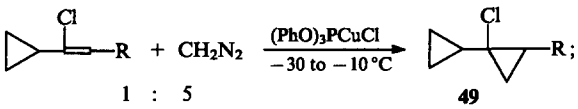
[a] Molar ratio $H_2C=CHCH_2Br : CH_2N_2 :$ Cat. ~1 : 3 : 0.01.

Under analogous conditions, vinyloxiran and CH_2N_2 give rise to the cyclopropane adduct **46**, the product of the allyl rearrangement—5,6-dihydropyran **47**, and also 3-vinyloxetan **48**, formed as a result of the formal insertion of methylene into the C–O bond of the initial epoxide.[94]



46 (64%) **47** (7%) **48** (29%)

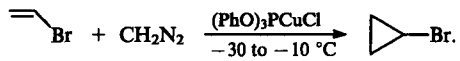
The catalytic interaction of CH_2N_2 with vinyl halides in the presence of CuCl or $(PhO)_3P \cdot CuCl$ leads to the corresponding cyclopropanes **49**, but, even in the presence of a fivefold molar excess of CH_2N_2, the degree of conversion of the vinyl halides into compounds **49** did not exceed 35%. An appreciable amount of CH_2N_2 then decomposed with formation of volatile products (mainly ethylene).[95]



1 : 5 **49**

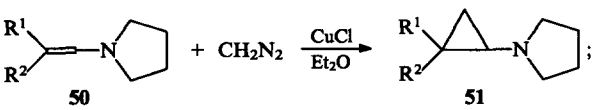
R = H (35%), CH(cyclo-C_3H_5)Me (24%), CH_2CH_2Cl (19%).

The conversion of vinyl bromide into a cyclopropane under the same conditions proceeds with a much lower degree of conversion.[95]



1 : 5 (13%)

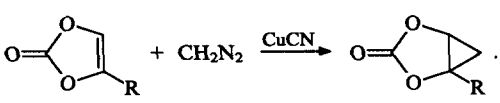
The conversion of vinylamines into cyclopropane derivatives occurred much more successfully. It was then noted[96] that the addition of CH_2N_2 to a mixture of the corresponding vinylamine **50** and 20 mol% of CuCl was accompanied by the appearance of a red colour, which vanished as CH_2N_2 was consumed. When a three–four-fold molar excess of CH_2N_2 was used, the yields of cyclopropylamines **51** were 69%–80% after isolation.



50 **51**

$R^1 = R^2 = H$ (73%), Me (69%);
$R^1 = H$, $R^2 = Et$ (80%);
$R^1 + R^2 = (CH_2)_4$ (70%).

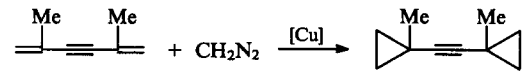
The conversion of ethylene carbonates **52** into cyclopropane derivatives was achieved under unusual conditions. In this case, the vapour of a mixture of CH_2N_2 with ether was passed into the unsaturated compounds **52** heated to 110–120 °C and containing CuCN as the catalyst.[98]



52

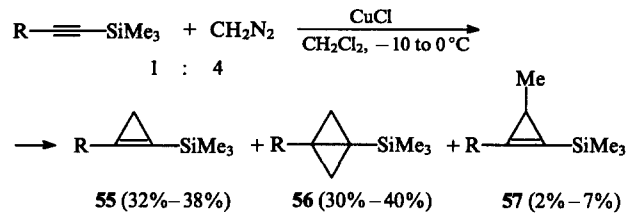
R	Reagents ratio	Yield of product (%)
H	4.2 : 1	28
Me	1.3 : 1	19

The simultaneous presence in the molecule of double and triple carbon–carbon bonds makes it possible under certain conditions to direct cyclopropane formation processes selectively to the double bonds. Thus a preparative method of synthesis of bis(1-methylcyclopropyl)acetylene **54** by the reaction of CH_2N_2 with the dienyne **53** in the presence of copper salicylaldiminate has been proposed.[99]. The triple bond in the product **54** is not involved despite the excess of diazomethane.



53 1 : 10 **54** (60%)

Nevertheless we were able to achieve for the first time the direct cyclomethylenation of the carbon–carbon triple bond with diazomethane in alkyl(trimethylsilyl)acetylenes using CuCl or $(PhO)_3P \cdot CuCl$ as the catalyst.[100,101] The reaction did not then stop with the formation of the cyclopropenes **55** but proceeded further, leading to the accumulation of the corresponding bicyclobutanes **56** in the mixture. Furthermore, the formation of methylcyclopropenes **57** as a result of the insertion of methylene in a C–H bond in the cyclopropenes **55** formed was an unexpected feature for the given reaction.

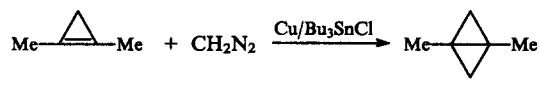


1 : 4

55 (32%–38%) **56** (30%–40%) **57** (2%–7%)

R = Me, Pr, cyclo-C_3H_5.

Before the above study, the only example of the catalytic cyclomethylenation of cyclopropenes by diazomethane was the interaction of 1,2-dimethylcyclopropene with CH_2N_2 in the presence of the modified bimetallic catalyst Cu/Bu_3SnCl.[102]

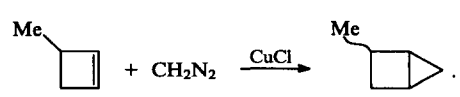


(13%)

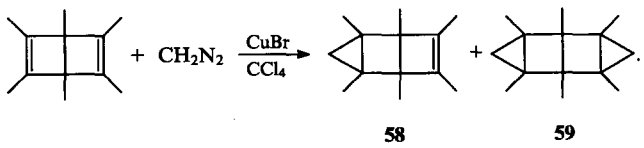
b. Conversion of cyclic unsaturated compounds into cyclopropane derivatives

The catalytic decomposition of CH_2N_2 on copper catalysts has been used widely for the conversion of cyclic and bicyclic hydrocarbons with one or several double bonds (conjugated and non-conjugated, endocyclic and exocyclic) into cyclopropane derivatives and also for the specific synthesis of compounds which are relatively unstable or difficult to obtain.

The possibility of the catalytic conversion of the C=C bond in cyclopropenes into a cyclopropane group was already mentioned above. Several examples of the conversion of the double bonds present in a four-membered ring into cyclopropane groups have been described.[103–105] Thus the interaction of CH_2N_2 with 3-methylcyclobutene leads to a mixture of *cis*- and *trans*-2-methylbicyclo[2.1.0]pentanes.[103]



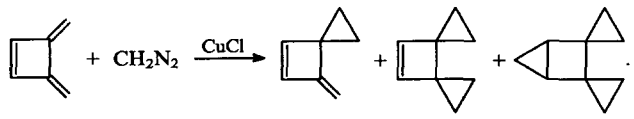
The tricyclic and tetracyclic hydrocarbons **58** and **59** have been synthesised by the reaction of hexamethylbicyclo[2.2.0]-hexa-2,5-diene with an excess of CH_2N_2 in the presence of CuBr.[104]



58 **59**

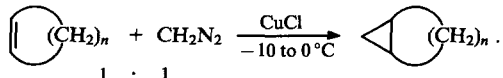
Reagents ratio	Yield of **58** (%)	Yield of **59** (%)
1:2	30	5
1:5	57	22

The spiro hydrocarbons **60–62** have been obtained by the reaction of 1,2-dimethylenecyclobut-3-ene with CH_2N_2 (in the proportions **60** : **61** : **62** = 5.8 : 1 : 1.7).[105] The absence of the mono- and di-adducts, produced by the conversion of the endocyclic double bond into a cyclopropane group, among the reaction products indicates the preferential conversion of the exocyclic bonds in the initial triene into cyclopropane groups.



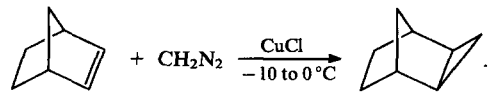
1 : 10 **60** **61** **62**

The interaction of C_6-C_8 cycloalkenes and norbornene with CH_2N_2 in the presence of CuCl leads to the corresponding bicyclo[*n*.1.0]alkanes **63** or the tricyclooctane **64**.[66] The yields of the cyclopropane derivatives under the same conditions increase on passing from cyclohexene to cyclooctene and norbornene, which is probably due to the ability of the strained cycloolefins to stabilise the catalyst in the form of π-olefin complexes.



1 : 1 **63a–c**

Product	*n*	Yield (%)
63a	4	20–25
63b	5	50–55
63c	6	75–80



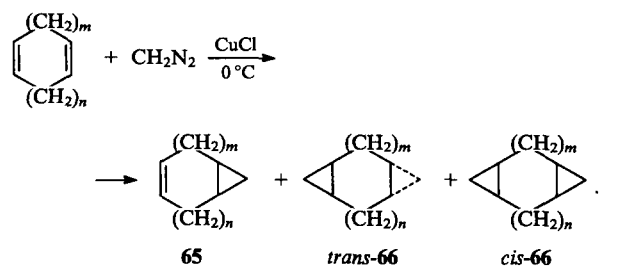
1 : 1 **64** (80%–85%)

This difference is manifested also in the competing reactions (CuCl, −5 °C) of norbornene and cyclohexene with CH_2N_2 (molar ratios 1 : 1 : 0.1)—the degree of conversion of the former into a cyclopropane derivative is greater by a factor of 2.7 than that of the latter. On the other hand, the conversion of the same mixture of cycloolefins into cyclopropanes in the presence of $Cu(acac)_2$ results in the formation of equal amounts of the cyclic adducts **64** and **63a** at any stage of the reaction, their yields amounting to 50%–55% for reactant ratios of ~1 : 1 : 2. In all cases, the cyclopropane formation reaction proceeds most effectively at the beginning of the addition of CH_2N_2, after which it is sharply retarded, particularly when the reaction mixture blackens.[66]

The conversion of cyclopentadiene,[106,107] cyclohexa-1,3-diene,[108] cycloheptа-1,3-diene, and cyclohepta-1,4-diene,[76] as well as cycloocta-1,5-diene [66] in the presence of CuCl into cyclopropane derivatives leads, as expected, to a mixture of mono- and di-adducts, namely to the bicycloalkenes **65** and the tricycloalkanes **66** (Table 2). The tricycloalkanes **66** are formed from the non-conjugated dienes in the form of a mixture of the *cis*- and *trans*-isomers (~1 : 1), whereas the *trans*-isomers predominate in the products of the reaction involving the double cyclopropane formation from conjugated dienes.

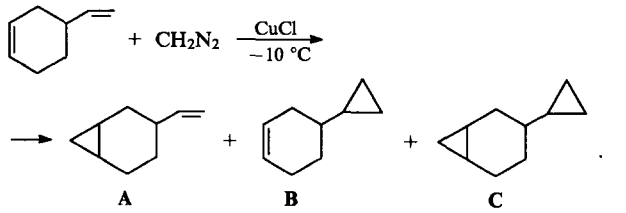
Table 2. Composition of the products of the conversion of cyclic dienes into cyclopropane derivatives by diazomethane in the presence of 5–6 mol% CuCl.

Cycloolefin		Molar ratio olefin : CH_2N_2	Yield of product (%)			Ref.
m	*n*		**65**	*trans*-**66**	*cis*-**66**	
0	1	1:3	40	45	11	106
0	2	1:3.5	7	54	32	108
0	3	1:5	45	35	10	76
1	2	1:3	45	20	20	76
2	2	1:2	35	24	27	66



65 *trans*-**66** *cis*-**66**

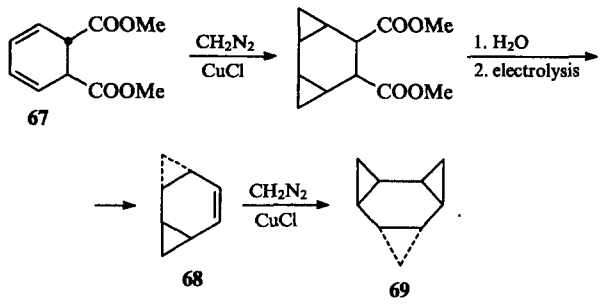
The catalytic conversion of 4-vinylcyclohexene into cyclopropane derivatives in the presence of CuCl proceeds via both the endocyclic and exocyclic double bonds, leading to mono- and di-adducts, the yields of which were found to be determined not only by the ratio of the olefin and CH_2N_2 but also by the amount of the catalyst employed.[66]



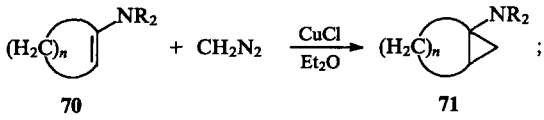
A **B** **C**

Olefin : CH_2N_2 : CuCl	Yield (%)		
	A	**B**	**C**
1:1:0.03	10	~8	2–3
1:2:0.03	13	10	3–4
1:2:0.40	17	21	~20

The diazomethane method for the catalytic conversion of cyclic double bonds into cyclopropane groups has been used successfully for the specific synthesis of trishomobenzene **69** from dimethyl *trans*-dihydrophthalate **67**, which cannot be obtained by the direct conversion of benzene into a cyclopropane derivative because of the ready isomerisation of the norcaradiene formed initially (see Section IV). For this purpose, the cyclodiene **67** was converted into the corresponding product of the double cyclopropane formation reaction by treatment with an excess of CH_2N_2 in the presence of CuCl, the ester groups were split off, and the resulting *trans*-tricyclooctene **68** was again subjected to the cyclopropane formation reaction by treatment with diazomethane and was converted into *trans*-**69**.[109]

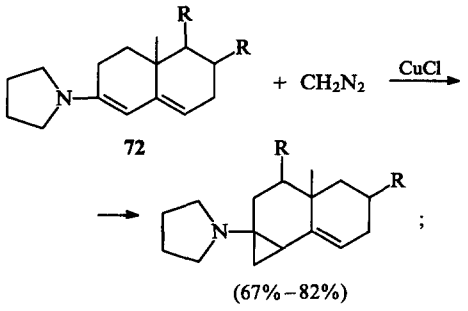


Like their aliphatic analogues **50**, the cyclic enamines **70** can also be fairly successfully converted into cyclopropane derivatives by treatment with an excess of CH_2N_2, which leads to high yields of the corresponding 1-aminobicyclo[*n*.1.0]alkanes **71**.[96,110]



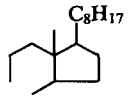
R = Me, Et; n = 3 (65%–72%);
R + R = $(CH_2)_4$; n = 3, 4 (72%–75%);
R + R = $CH_2CH_2OCH_2CH_2$; n = 3, 4 (86%–87%).

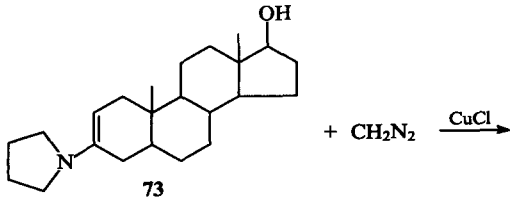
Under analogous conditions, the conversion of cyclic dienamines **72** into cyclopropane derivatives proceeds regioselectively despite the presence of an excess of CH_2N_2 and involves mainly the C=C bond conjugated with a nitrogen atom. As in the formation of a cyclopropane from the enamine **73**, one of the geometrical isomers is formed preferentially.[110]

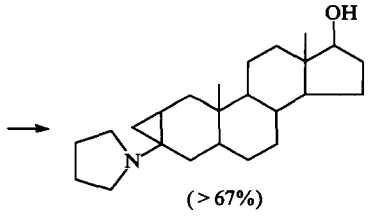


(67%–82%)

72:CH_2N_2 = ~1:(2.5–3);

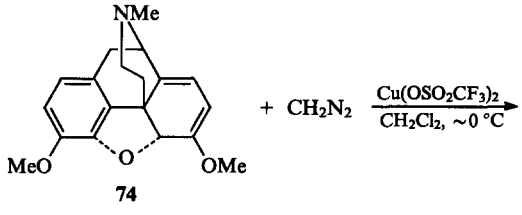
R = H or R + R = 

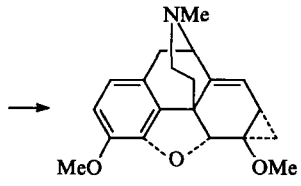




(>67%)

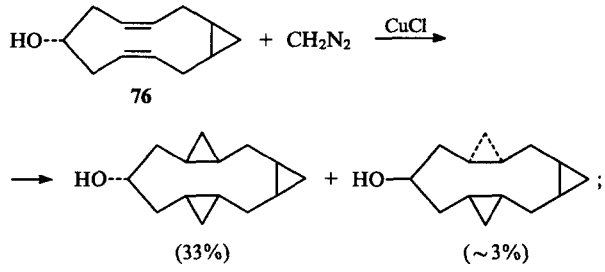
Generally speaking, the presence of bulky substituents and the configuration of the ring in the unsaturated compound can influence significantly the reactivity of the substrate and the stereochemical result of the addition of the methylene fragment to the double bond. Furthermore, the presence in the molecule of heteroatomic substituents capable of being coordinated to the catalyst also apparently affects the mode of addition of CH_2 to the double bond. Thus, in the reaction of thebaine **74** with an excess of CH_2N_2 in the presence of copper triflate, a high regio- and stereo-selectivity of the addition of the CH_2 fragment to the $C^6=C^7$ bond of thebaine **74** with formation of the previously unknown hydrophenanthrene alkaloid **75** was observed.[111]

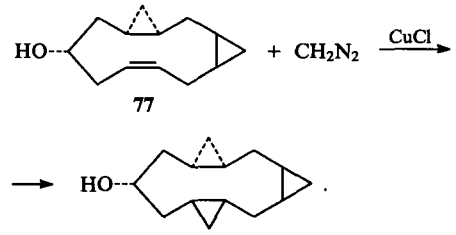




75 (~96%)

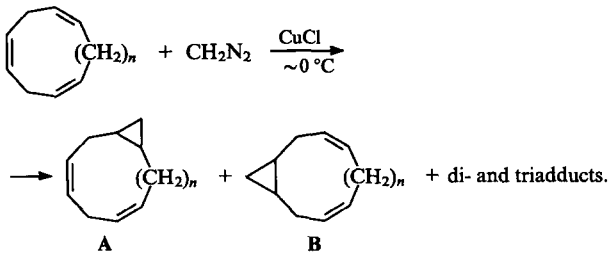
The high stereoselectivity of the conversion of endocyclic double bonds into cyclopropane groups has also been observed in the reaction of the unsaturated alcohols **76** and **77** with an excess of CH_2N_2 in the presence of CuCl.[112]





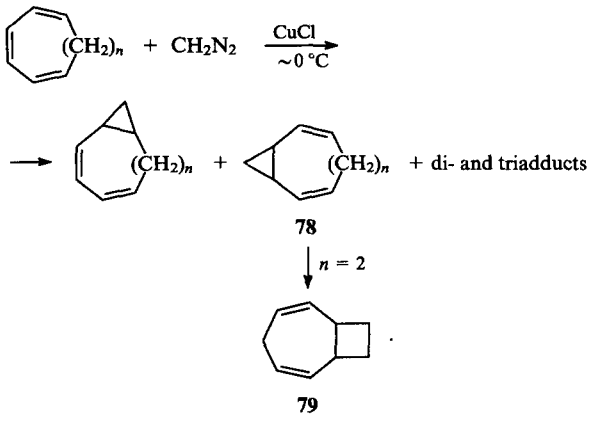
one isomer
(yield has not been given)

Cyclic trienes are converted into cyclopropane derivatives by treatment with diazomethane in the presence of CuCl similarly to cyclic dienes, the ratios and yields of the mono-, di-, and tricyclic adducts being determined mainly by the amount of the CH_2N_2 employed.[76,113]



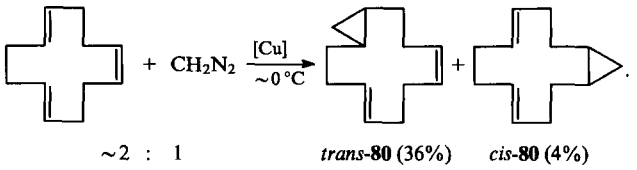
n	triene : CH_2N_2	Yield of adducts (%)		
		mono	di	tri
1	1 : 2.8	34	34	13

Furthermore, it has been shown[113] that the adduct **78** ($n = 2$), formed in 3% – 4% yield in the cyclopropane formation reaction from cycloocta-1,3,5-triene, isomerises to the bicyclic diene **79** (yield 8%) already during the course of the reaction.

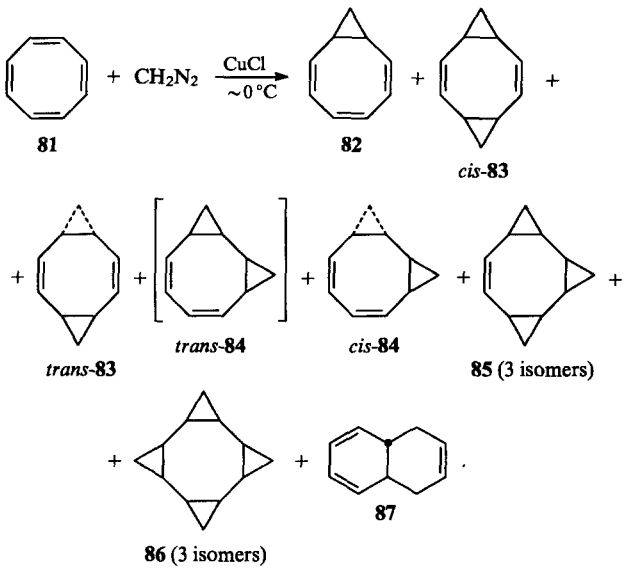


n	triene : CH_2N_2	Yield of adducts (%)		
		mono	di	tri
1	~1 : 4	18	45	28
2	1 : 2	34	31	8

In the cyclopropane formation reactions of unsaturated compounds with different configurations of the double bonds, the preferential conversion of the *trans*-C=C bond into a cyclopropane group has been noted. Thus the reaction of an excess of (*E*,*Z*,*Z*)-cyclododeca-1,5,9-triene with CH_2N_2 in the presence of the chelate copper complex **21** leads to the monocyclopropane derivatives **80** with a ratio *trans* : *cis* ≃ 9 : 1.[67]

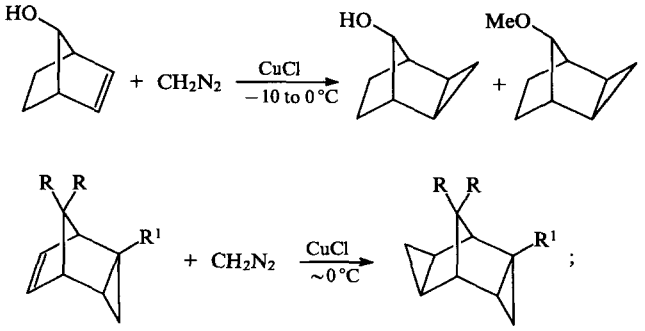


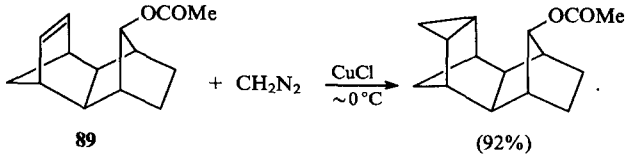
The catalytic conversion of cyclooctatetraene **81** into a cyclopropane derivative by treatment with diazomethane in the presence of CuCl was first achieved as early as the middle 1960s,[114,115] but only bicyclo[6.1.0]nona-2,4,6-triene **82** was isolated in ~30% yield and identified together with some products of the double cyclopropane formation reaction — *cis*-tricyclo[7.1.0.0^{4,6}]deca-2,7-diene (*cis*-**83**) and tricyclo[7.1.0.0^{2,4}]-deca-5,7-diene **84**, in which the configuration of the cyclopropane fragments was not established. Later the catalytic interaction of compound **81** with CH_2N_2 was investigated in detail by Nefedov and coworkers[116] and the stereochemistry of the cyclopropanes formed was established. In order to achieve a higher degree of conversion of compounds **81** and **82** into the tri- and tetra-cyclic adducts **85** and **86**, the reaction mixture was filtered twice under argon, as CH_2N_2 was added, and a fresh portion of CuCl (3 – 4 mol%) was introduced. It is of interest to note that the conjugated diene *trans*-**84** could not be detected in the double cyclopropane formation products **83** and **84** probably because of its ready isomerisation to the triene **87**, which was isolated in 2% – 3% yield.



81 : CH_2N_2	Yield of adducts (%)						
	82	*cis*-**83**	*trans*-**83**	*cis*-**84**	**85**	**86**	**87**
1 : 1	44	3 – 4	2 – 3	8	5	1 – 2	~2
1 : 3	13	~7	~5	14	36	15 – 17	~3

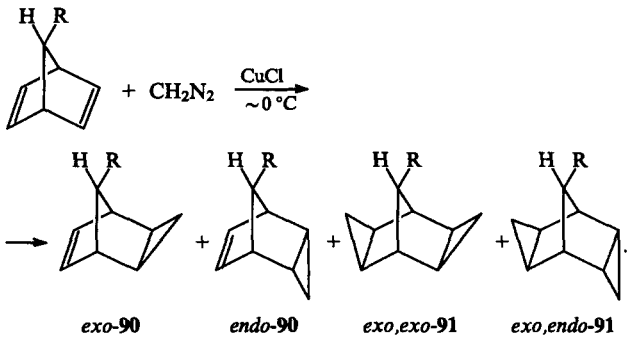
The fairly effective conversion of norbornene into a cyclopropane derivative by treatment with diazomethane in the presence of CuCl has already been mentioned.[66] It has been established recently[117] that, regardless of the nature of the catalyst [Cu(OTf)$_2$, CuCl, Cu(acac)$_2$], the main product is the *exo*-isomer **64**, while the fraction of the *endo*-isomer does not exceed 2%. The exclusive *exo*-addition of methylene to the norbornene double bond was observed also in the catalytic conversion into cyclopropanes of norbornene derivatives as well as other polycyclic compounds, for example compounds **88** and **89**, containing this fragment, on treatment with diazomethane.[118 – 122] It is striking that the *exo*-conversion of the





double bond into a cyclopropane group occurs for both *anti*- and *syn*-orientations of the substituent in the 7-position of the bicyclo[2.2.1]heptene fragment and that the partial (~10%) formation of the corresponding methoxy-derivatives has been observed, together with conversion into a cyclopropane, for the hydroxy-derivatives.[119,121]

In contrast to norbornenes, the interaction of CH_2N_2 with norbornadiene and its derivatives in the presence of copper catalysts proceeds non-selectively and leads to a mixture of the mono- and di-adducts **90** and **91** containing both *exo* and *endo*-isomers.[117-119,123,124]

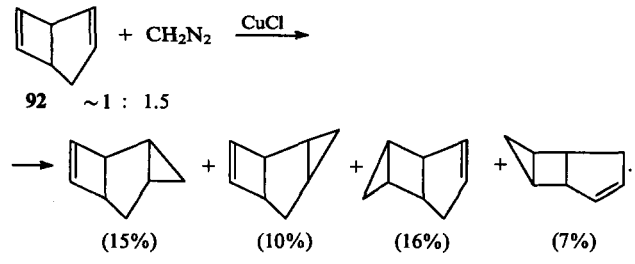


For a 1 : 1 norbornadiene (R = H) : CH_2N_2 ratio, the yields of the monoadducts (*exo*- and *endo*-) and triadducts (*exo,exo*- and *exo,endo*-) were respectively 33%, 15%, 8%, and ~4%. For R = OCOMe and OCOPh, the ratio *exo*-90 : *endo*-90 is ~5:1.

It was found that the partial formation of the *endo*-isomer is characteristic not only of norbornadienes but also of *exo*-tricyclo[3.2.1.$0^{2,4}$]octene (*exo*-**90**, R = H).[117] Whereas the subsequent conversion of *endo*-**90** (R = H) into a cyclopropane derivative in the presence of copper compounds leads exclusively to *exo,endo*-**91** (the *endo,endo*-isomer was not detected at all), the conversion of *exo*-**90** (R = H) into a cyclopropane derivative under the same conditions affords a mixture of the isomeric diadducts **91** in proportions of ~6:1.

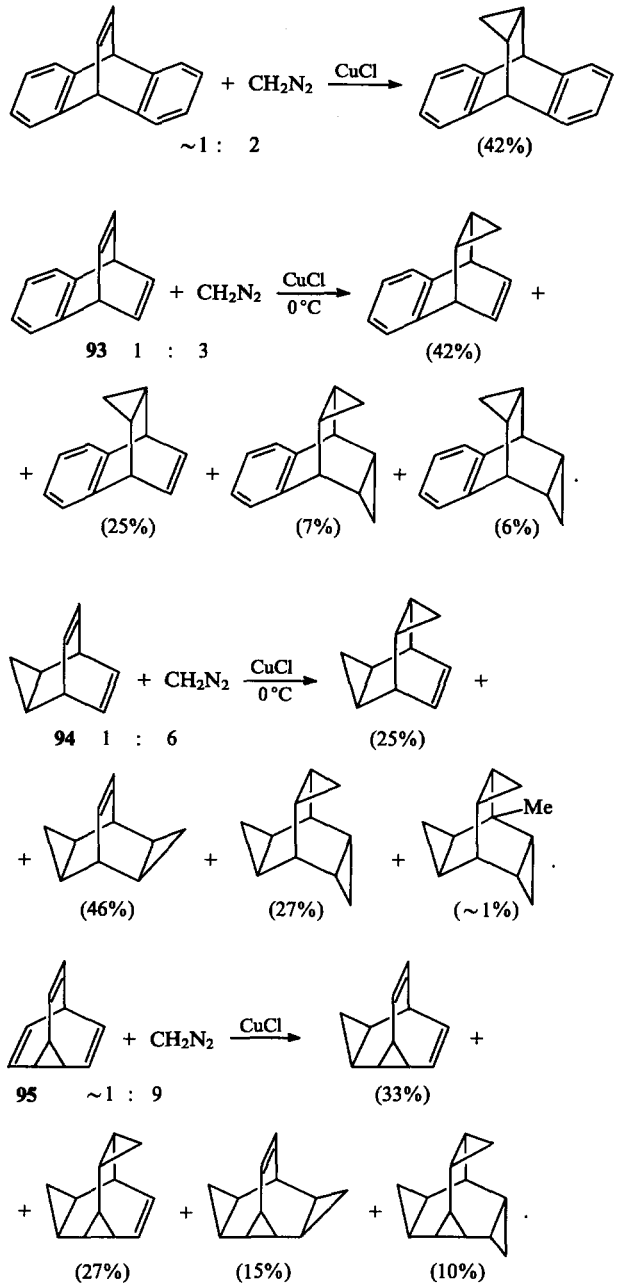
The increased content of the *endo*-isomer, compared with norbornenes, on conversion of norbornadiene into a cyclopropane derivative in the presence of copper catalysts is apparently associated with the characteristics of the geometry of the double bonds. Thus, according to calculations,[125] the angle of the *endo*-deformation of the vinyl C–H bonds in norbornadiene is smaller than in norbornene (2.3° and 4.9° respectively), so that the probability of the attack on the double bond by the carbene complex from the side of the *endo*-position is greater for the former compound. The detailed stereochemical aspects of the addition of methylene to the norbornene double bond in the presence of various catalysts will be examined in Section III.3.b (Table 5).

The conversion of the asymmetric bicyclo[3.2.0]hepta-2,6-diene **92** into a cyclopropane derivative in the presence of CuCl involves both double bonds and affords mixtures of the corresponding *syn*- and *anti*-isomers. The authors[126] observed the formation of four diadducts, in an overall yield of ~27%, together with the monoadducts.



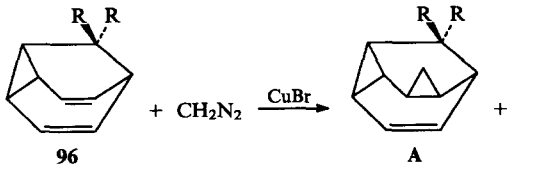
The mild conditions for the conversion of unsaturated compounds into cyclopropanes by diazomethane in the presence of copper compounds have been used widely for the synthesis and study of the chemical reactions of cyclopropane derivatives of bicyclo[2.2.2]octa-2,5,7-triene (barrelene),[127-130] tricyclo-[3.3.0.$0^{2,8}$]octa-3,6-diene (semibullvalene),[128] tricyclo[3.3.2.$0^{2,8}$]-deca-3,6,9-triene (bullvalene),[130] tricyclo[3.3.1.$0^{2,8}$]nona-3,6-diene (barbaralane),[131,132] and tricyclo[5.2.1.$0^{4,10}$]deca-2,5,8-triene (triquinacene).[133]

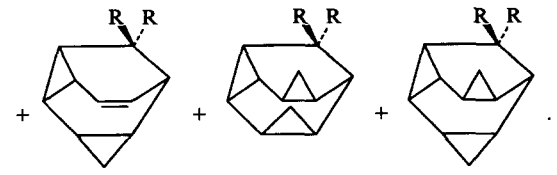
It is striking that, among the products of the conversion of benzobarrelene **93**, homobarrelene **94**, and also bullvalene **95** into cyclopropane derivatives, no *endo,endo*-isomers corresponding to the addition of methylene fragments oriented in opposition to one another were detected. However, in the case of the diene **94** deMeijere et al.[130] observed, in addition to the expected adduct, the appearance of a minor product corresponding to the formal insertion of methylene into the angular C–H bond.



The high selectivity of the addition of methylene to the endocyclic double bonds is also characteristic of the structure of barbaralane, as for norbornene. Thus the interaction of the

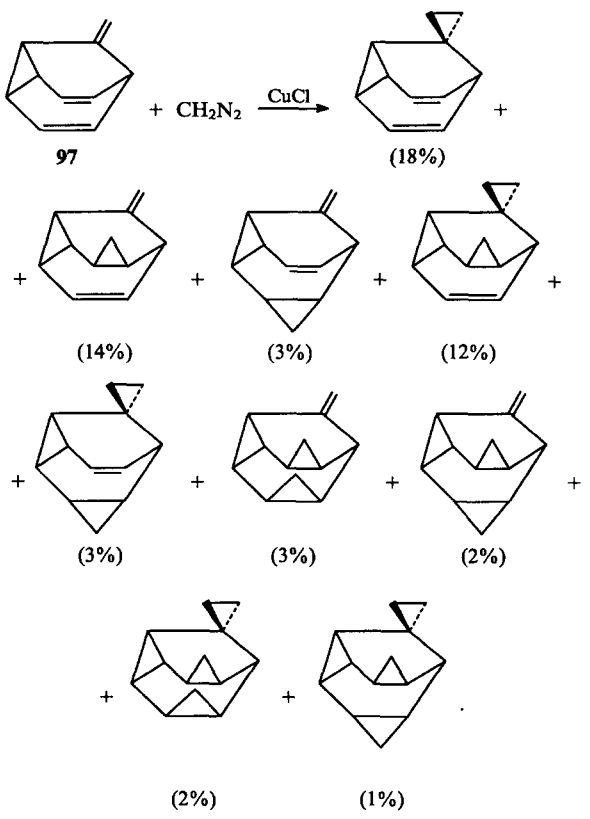
tricyclodienes **96** with an excess of CH_2N_2 in the presence of CuBr leads to the mixture of the mono- and di-adducts with an appreciable predominance of the *exo*-isomers.[131]



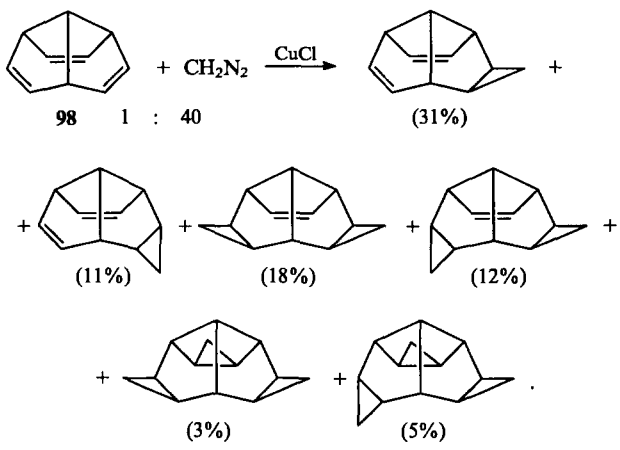


CR_2	Yield of adducts (%)			
	A	B	C	D
C=O	43.5	0.6	43.5	2.5
	~63	2.1	4.2	0.2

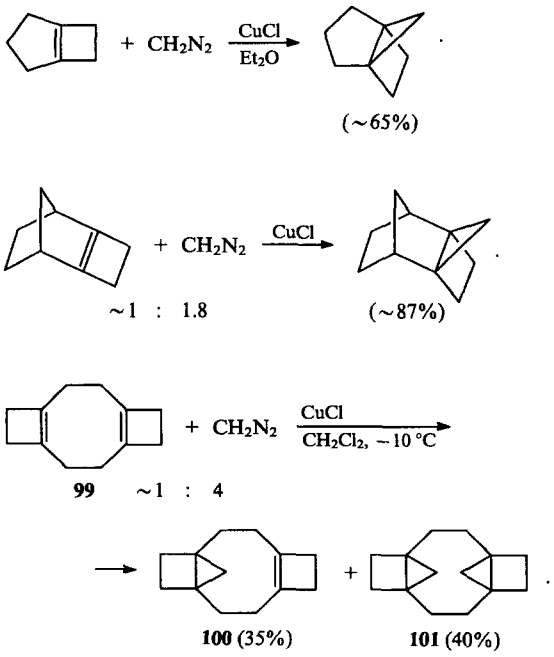
The conversion of 9-methylenebarbaralane **97** into a cyclopropane derivative proceeds in a more complex manner owing to the possibility of the conversion into cyclopropane groups of both endocyclic and exocyclic double bonds and leads to a mixture of nine cyclic adducts with different numbers and disposition of the cyclopropane fragments.[132] However, as in the case of norbornadiene, hydrocarbons with two *endo,endo*-oriented cyclopropane rings in the molecule were not detected in the products of the catalytic conversion of the polycyclenes **96**–**98** into cyclopropanes.



In many instances, the yields of cyclopropane adducts (particularly the products of the double and triple cyclopropane formation reactions) are significantly lower than might have been expected on the basis of the amount of CH_2N_2 employed and the structure of the unsaturated compounds. In particular, an unjustifiably large (40-fold) excess of CH_2N_2 was used in the formation of a cyclopropane derivative from triquinacene **98** [133] (cf the interaction of CH_2N_2 with cyclo-octatetraene[116]). The low degree of conversion of olefins into cyclopropanes is probably associated with the rapid change during the reaction of the nature of the catalyst, for example, with a gradual conversion of copper(I) salts by diazomethane into organometallic compounds or metallic copper, which, according to Nefedov et al.,[66] is reflected significantly in the target cyclopropane formation reaction.

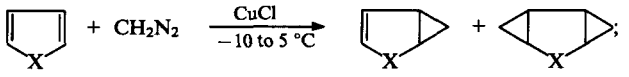


The ability of copper compounds to catalyse the formation of cyclopropanes on treating with diazomethane olefins with different degrees of substitution of double bonds, including tetrasubstituted olefins, proved useful for the synthesis of carbocyclic propellanes which are difficult to obtain and are highly strained.[134–136] In particular, isomeric polycyclic hydrocarbons **101**, containing two propellane fragments in the molecule (isomer ratio ~6 : 1), were synthesised, together with the monoadduct **100**, by the reaction of the diene **99** with CH_2N_2 in the presence of CuCl.[136]



c. Conversion of unsaturated heterocyclic compounds into cyclopropane derivatives

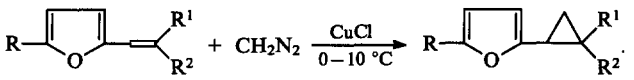
In the presence of copper salts, diazomethane is also capable of converting the double bonds in heterocyclic compounds into cyclopropane groups. Five-membered unsaturated heterocyclic compounds (furan, thiophene, pyrrole, and their derivatives) are then converted into the corresponding bicyclic and tricyclic compounds.[137-139] Thus the interaction of CH_2N_2 with an excess of furan in the presence of CuBr or CuCl leads to 2-oxabicyclohexene **102a** in 50%–65% yield; for the stoichiometric reactant ratio, the diadduct **103a** is formed in ~5% yield together with compound **102a**. The conversion of thiophene into a cyclopropane derivative proceeds less effectively probably owing to the lower stability of the adduct **102b**, the yield of which ranges from 6% to 22% according to different estimates.[137,138]



102 **103**

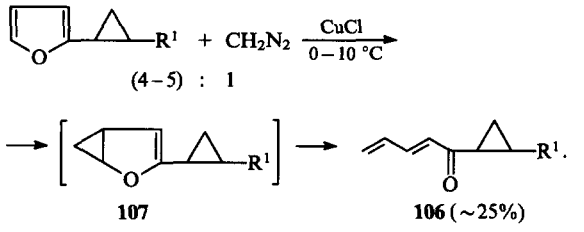
X = O (**a**), S (**b**).

The presence of substituents in the furan ring influences both the regioselectivity in the conversion of the double bonds into cyclopropane groups and the stability of the resulting adducts. Thus the interaction of CH_2N_2 with 2-alkenylfurans **104** leads in the first place to the conversion of the exocyclic double bonds into cyclopropane groups with formation of the corresponding 2-cyclopropylfurans **105**.[140] However, the subsequent interaction of compound **105** (R = H) with CH_2N_2 in the presence of CuCl affords 1-cyclopropylpenta-2,4-diene-1-ones **106**, apparently as a result of the addition of CH_2 to the unsubstituted double bond of the furan ring and the subsequent opening of the oxabicyclic adduct **107**.[140]



104 (3–4) : 1 **105** (21%–40%)

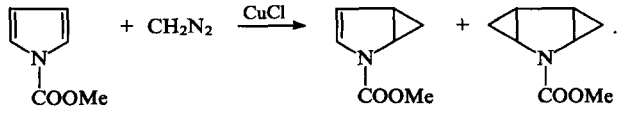
R, R^1, R^2 = H and/or Me.



107 **106** (~25%)

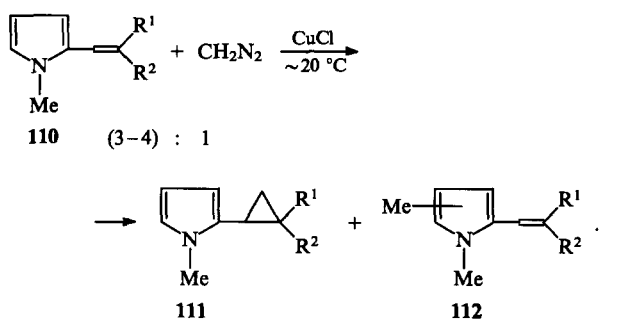
R^1 = Me, cyclo-C_3H_5.

In the catalytic reaction of CH_2N_2 with *N*-methylpyrrole in the presence of CuCl, the products of the formal insertion of methylene into the C–H bonds of the pyrrole ring were obtained instead of the cyclopropane adduct (see Section VI). On the other hand, *N*-methoxycarbonylpyrrole forms the bicyclic and tricyclic compounds **108** and **109** in moderate yields under similar conditions, the *trans*-isomer of the diadduct **109** predominating appreciably.[141,142]



~1 : 3 **108** (39%) **109** (12%)

In the reactions with 2-alkenylpyrroles **110**, diazomethane leads to the formation, in the presence of CuCl, of both the cyclopropane adducts **111** involving the exocyclic double bond and of the products **112** of the insertion of methylene into the C–H bonds of the pyrrole ring.[143] Together with the monoadducts **111** and **112**, a complex mixture of products of the addition (or insertion) of a second CH_2 fragment to the monoadducts formed was then obtained in an overall yield of 6%–10%.

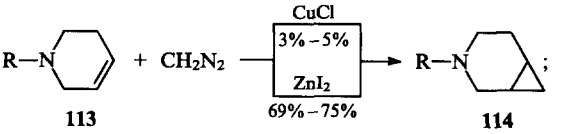


110 (3–4) : 1

111 **112**

R^1	R^2	Yield of **111** (%)	Yield of **112** (%)
H	H	18	6
H	Me	6	15
Me	Me	8	18

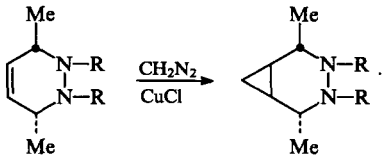
The interaction of CH_2N_2 with *N*-alkyldehydropiperidines **113** in the presence of 20 mol% of CuCl leads to the corresponding cyclopropanes **114** in a yield of only 3%–5%.[144] The reaction of compound **113** with an excess of an ethereal solution of the organozinc reagent obtained from CH_2N_2 and ZnI_2 makes it possible to synthesise the adduct **114** in preparative yields (69%–75%).[145]



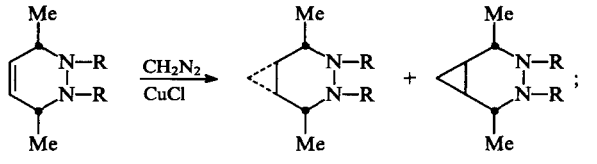
113 **114**

R = Me, Et, Pr.

The conversion of the 1,2-diazacyclohexene **115**, containing electron-accepting substituents at the nitrogen atoms, into a cyclopropane derivative by treatment with diazomethane proceeds more successfully and leads in the case of *trans*-**115** to only the isomer **116a** and in the case of *cis*-**115** to the isomers **116b** and **116c** in proportions of ~8 : 1.[146]



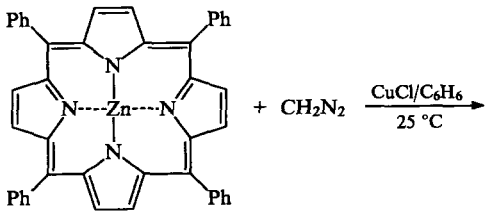
trans-**115** **116a**



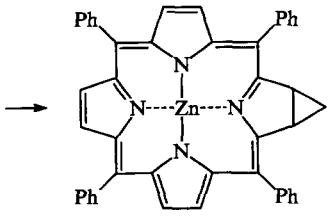
cis-**115** **116b** **116c**

R = COOMe.

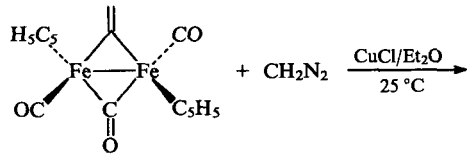
Finally one should note that, in the presence of CuCl, diazomethane is capable of converting into cyclopropane groups the double bonds in unsaturated ligands forming part of the composition of mononuclear or dinuclear metal complexes, for example compounds **117** and **118**.[147,148]



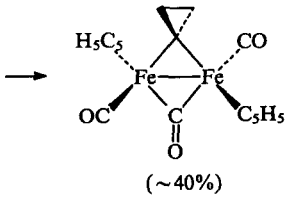
117



(~28%)



118



(~40%)

It follows from the results presented above that, in the presence of copper compounds, diazomethane is capable of converting into cyclopropane derivatives an extremely wide range of unsaturated compounds containing C=C bonds of different nature and with different degrees of substitution. However, the tendency of copper compounds to be readily 're-reduced' by diazomethane with the formation of highly active metallic copper, which leads to a vigorous side reaction involving the decomposition of CH_2N_2 and hence results in a low degree of conversion of the olefins into the corresponding cyclopropanes and limits the preparative use of this reaction.

3. Conversion of olefins into cyclopropane derivatives by diazomethane in the presence of palladium catalysts

One can say without exaggerating that the wide scale preparative use of diazomethane in the synthesis of cyclopropane derivatives from olefins has been recently associated with the employment of various palladium compounds as catalysts of the decomposition of CH_2N_2. The available literature data give grounds for the assertion that the nature of the cycloaddition of methylene to the double bonds is associated to a large extent with the ability of the initial olefins to be coordinated to the palladium atom, the regio- and stereo-selectivity in the conversion of various double bonds into cyclopropane groups differing significantly from those in their conversion into cyclopropane derivatives in the presence of copper compounds.[10,19,68,70] $Pd(OAc)_2$, $Pd(acac)_2$, and $(PhCN)_2PdCl_2$ are most often employed as palladium catalysts.

The catalytic activity of palladium compounds in the conversion of olefins into cyclopropanes was first noted in 1968 by Kirmse and Kapps,[92] who investigated the interaction of diallyl ether with CH_2N_2 in the presence of bis[η-allylpalladium chloride]. They then obtained the cyclopropane adduct **40f** in 38% yield without an admixture of the product **41f**, in contrast to catalysis by copper salts. In the next year, the same workers[94] reported the interaction of vinyloxiran with CH_2N_2, leading to the formation of the adducts **46** and **47** in proportions of ~6 : 1. However, at that time the above studies still failed to encourage investigators to employ palladium catalysts on a wider scale in the conversion of olefins into cyclopropanes.

Appreciable progress in the conversion of unsaturated compounds into cyclopropanes by treatment with diazomethane in the presence of palladium compounds and primarily in the presence of $Pd(OAc)_2$ is associated with the work of Teysie and coworkers,[149] who converted styrene into phenylcyclopropane in ~90% yield, and with the work of Vorbruggen and coworkers,[150,151] who demonstrated the possibility of the effective conversion into cyclopropanes of norbornene and norbornadiene as well as monosubstituted α,β-unsaturated carbonyl compounds by this method. Since then, the number of studies in this field began to increase sharply.

In the first place, it was established that the nature of the palladium catalyst {$PdCl_2$, $Pd(OAc)_2$, $[\eta\text{-}C_3H_5PdCl]_2$, $(PhCN)_2PdCl_2$} does not influence significantly the nature of the reaction of olefins when the latter is carried out in CH_2Cl_2, while the yields of the cyclopropane formation products are determined under identical conditions mainly by the nature of the C=C bonds.[68,152] Nevertheless, more detailed differences in the nature of the catalysts,[25] influencing the yield of the products of the cyclopropane formation reaction, in particular the formation of tricyclooctane **64** from norbornene, were discovered under conditions where the ethereal solution of CH_2N_2 was rapidly mixed with the olefin and the catalyst. Thus the introduction into $Pd(acac)_2$, which affords the highest yield of compound **64** under these conditions, of electron-donating ligands, for example NEt_3, Me_2S, PPh_3, etc., in the proportions $Pd(acac)_2$: L = 1 : 2 lowers the yield of the cyclopropane adducts from 72% to 23%.[25]

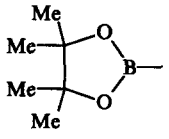
The observed dependence of the yields of compound **64** on the structure of the palladium compounds can be explained by the increasing hindrance by the ligands to the coordination of the olefin and also by the retardation of the formation of the catalytically more active low-valence palladium complexes when palladium(II) compounds are reduced by diazomethane (see Section III.1).

a. Conversion of aliphatic unsaturated compounds into cyclopropane derivatives

It has been established by numerous investigations that in the series of unsaturated aliphatic compounds those with terminal double bonds are most successfully converted into cyclopropane derivatives by diazomethane. The yields of the cyclopropane adducts are then determined by the amount of the added CH_2N_2 and in some cases are 88%–97% when a two–three-fold excess of CH_2N_2 is employed (Table 3).

It is noteworthy that the nature of the substituents at the C=C bond affects appreciably the nature of its conversion into a cyclopropane group. Thus the conversion of olefins with electron-donating substituents attached directly to the C=C bond, for example ethyl vinyl ether,[158] into cyclopropanes proceeds with an extremely low degree of conversion, whereas the conversion of oxygen- and nitrogen-containing allyl derivatives into cyclopropanes takes place fairly successfully. Furthermore, the results concerning the relative reactivities of various unsaturated compounds have demonstrated[159] that styrene and allyl alcohol are 15–20 times less reactive than alk-1-enes in their conversion into cyclopropanes by diazomethane.

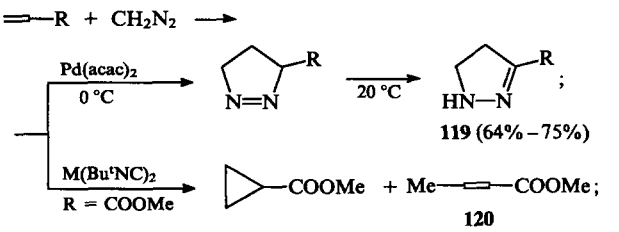
Table 3. Conversion of the monosubstituted olefins $CH_2=CHR$ into cyclopropane derivatives by treatment with diazomethane in the presence of 0.4–1.0 mol% of palladium compounds.

R	$CH_2=CHR:CH_2N_2$	Catalyst	Reaction conditions[a]	Yield of cyclo-C_3H_5R (%)	Ref.
n-C_4H_9–n-C_9H_{19}	1:1	$Pd(acac)_2$	A	44–60	25
n-C_8H_{17}	1:3	$Pd(OAc)_2$	A	89	153
cyclo-C_6H_{11}	1:1	$Pd(acac)_2$	A	41	25
Ph, CH_2Ph	1:1	$Pd(acac)_2$	A	43–46	25
CH_2CH_2COMe	1:1	$Pd(acac)_2$	A	60	25
$CH_2(CH_2)_7COOMe$	–	$Pd(OAc)_2$	B	>60	154
CMe_2CH_2COOEt	1:3	$Pd(OAc)_2$	A	89	153
CH_2OH, CH_2OMe	1:2	$(PhCN)_2PdCl_2$	B	72–74	155, 156
CH_2OPh, $CH_2OC_6H_4Br$-*m*	1:2	$(PhCN)_2PdCl_2$	B	88	155, 156
CH_2OPh	1:3	$Pd(OAc)_2$	A	97	153
CH_2OAc	1:2	$(PhCN)_2PdCl_2$	B	80	155, 156
CH_2NMe_2, CH_2NHPh	1:2	$(PhCN)_2PdCl_2$	B	62–68	155, 156
$CH(OEt)_2$	1:2	$(PhCN)_2PdCl_2$	B	77–80	155, 156
$CH_2NHCOMe$	1:1.9[b]	$(PhCN)_2PdCl_2$	C	73	157
OEt	1:3	$(PhCN)_2PdCl_2$	A	12–15	158
COOEt	~1:3	$Pd(OAc)_2$	B	82	160
	1:4	$Pd(OAc)_2$	B	98	161
	–	$Pd(OAc)_2$	B	92	162

[a] **Method A.** A solution of CH_2N_2 and the olefin was treated with 0.6–1.0 mol% of the catalyst at 10–0 °C. **Method B.** A mixture of the olefin and 0.4–0.8 mol% of the catalyst in ether or CH_2Cl_2 was treated with CH_2N_2. **Method C.** A mixture of the olefin, a 40%–50% solution of KOH, 0.2 mol% of the catalyst, ether, and CH_2Cl_2 was treated with *N*-methyl-*N*-nitrosourea.
[b] The ratio of the olefin to *N*-methyl-*N*-nitrosourea is indicated.

In contrast to allyl alcohol and its ethers, allyl halides (allyl chloride, allyl bromide, methylallyl chloride) are not converted into cyclopropanes by diazomethane in the presence of palladium compounds and do not afford the products of the formal insertion of methylene in the C–Hal bond, as happens when copper compounds are used as catalysts.

The interaction of CH_2N_2 with unsaturated compounds containing strong electron-accepting substituents (CN, COOR) at the double bond takes place in a more complex manner. In this case, there is competition between the possible formation of cyclopropanes and the readily occurring 1,3-dipolar cycloaddition of CH_2N_2. The nature of the palladium catalyst can then influence significantly the composition of the reaction products. Thus, in the presence of $Pd(OAc)_2$, ethyl acrylate and CH_2N_2 afford a high yield of ethyl cyclopropanecarboxylate,[160] whereas acrylonitrile and methyl acrylate react with CH_2N_2 in the presence of $Pd(acac)_2$ to form the pyrazolines **119**.[25]



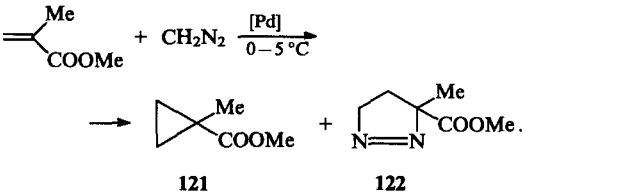
R = CN, COOMe.

M	Yield of C_3H_5COOMe (%)	Yield of **120** (%)
Pd	0.9	24.4
Ni	66.5	20.4

Finally, it has been noted[72] that methyl crotonate **120** is formed together with the cyclopropane adduct in the reaction of CH_2N_2 with methyl acrylate in the presence of $Pd(Bu^tNC)_2$.

It is noteworthy that a decrease in the polarity of the double bond in α,β-unsaturated ethers favours the formation of cyclopropane adducts.

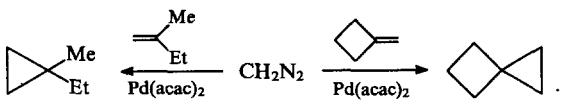
The interaction of CH_2N_2 with methyl methacrylate containing both electron-donating and electron-accepting substituents at the same carbon atom proceeds mainly with formation of the cyclopropane adduct **121** and even in the presence of $Pd(acac)_2$ its yield is fairly high compared with that of the 1-pyrazoline **122** formed simultaneously.[25,151]



121 **122**

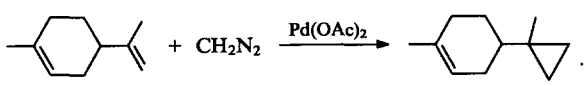
Reagents ratio	[Pd]	Yield of **121** (%)	Yield of **122** (%)
1:2.5	$Pd(OAc)_2$	88	–
1:1	$Pd(acac)_2$	76	15

The conversion of 1,1-disubstituted double bonds into cyclopropane groups occurs also in the case of *gem*-dialkylethylenes, but, in order to attain a high yield of cyclopropanes it is necessary to use a large excess of CH_2N_2 in virtually all cases.[25,89,151,153]



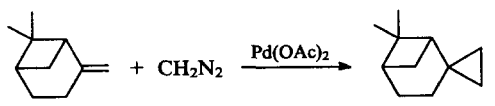
(18%) (48%)

Olefin : CH_2N_2 = 1 : 1



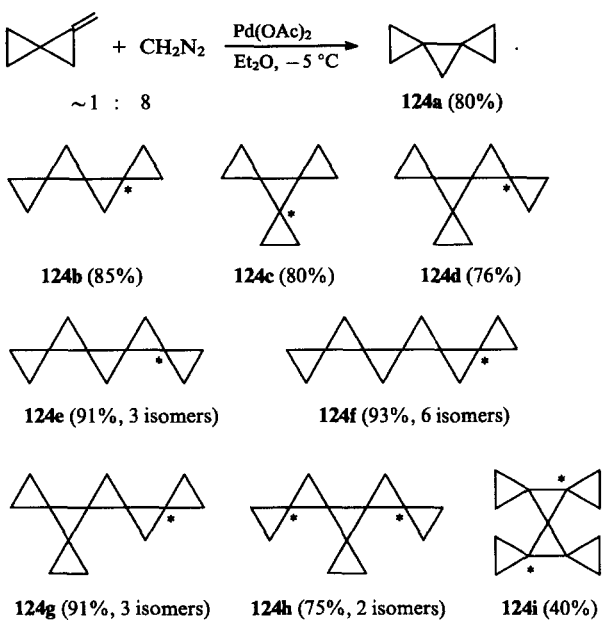
~1 : 3 (82%)

It is of interest to note that β-pinene **123** reacts with CH_2N_2, affording the cyclopropane adduct in 63% yield,[153] whereas derivatives of 2-methylenenorbornane are hardly converted into cyclopropanes even in the presence of a four–six-fold excess of CH_2N_2.[25, 163]



123 ~1 : 3 (63%)

The cyclomethylenation of methylenecyclopropanes by treatment with diazomethane in the presence of $Pd(OAc)_2$ is one of the stages in the general method of synthesis of linear and branched triangulanes **124**, made up of spiroannelated cyclopropane fragments. It was developed by Zefirov and coworkers.[89, 164–168]



~1 : 8 **124a** (80%)

124b (85%) **124c** (80%) **124d** (76%)

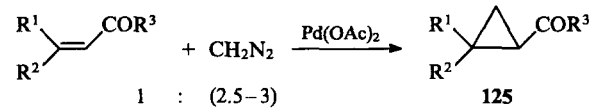
124e (91%, 3 isomers) **124f** (93%, 6 isomers)

124g (91%, 3 isomers) **124h** (75%, 2 isomers) **124i** (40%)

(The asterisks designate the carbon atoms constituting the methylene fragment in the initial methylenecyclopropanes.)

As a rule, the conversion of the corresponding olefins into cyclopropanes was then carried out under isotypical conditions using a large excess of an ethereal solution of CH_2N_2 and 4–5 mol% of $Pd(OAc)_2$ as the catalyst.

In the presence of palladium compounds, diazomethane is also capable of converting 1,2-disubstituted double bonds into cyclopropane groups, but in this case the reaction is even more sensitive to the nature of the substituents than in the case of terminal olefins. Thus hept-3-ene, *cis*- and *trans*-1,2-dichloroethylenes, as well as tri- and tetra-substituted alkenes (3-methylhept-3-ene, tetramethylethylene) do not give rise to cyclopropanes on reaction with CH_2N_2 in the presence of palladium compounds.[25] On the other hand, α,β-unsaturated carbonyl compounds afford satisfactory yields of the corresponding cyclopropanes **125** in the presence of $Pd(OAc)_2$.

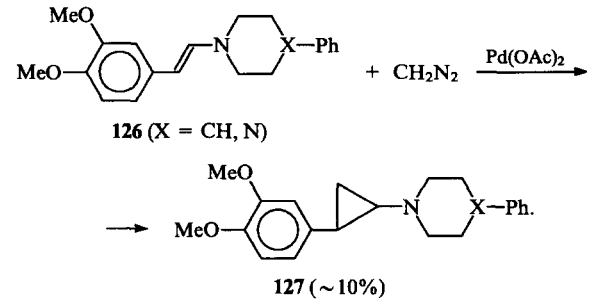


1 : (2.5–3) **125**

R^1	R^2	R^3	Yield of **125** (%)	Ref.
H	Ph	Ph (Me)	85–98	151
H	Ph (Me)	OEt (OMe)	89–90	151
Ph	H	OEt	85	151
H	$(CH_2)_3COOMe$	H	80	169
H	$(CH_2)_{18}Me$	OMe	99	154
H	$MeOC_6H_4$	OMe	84–99	170
H	$(RO)_2C_6H_3$	OMe	75–97	171
Me	Me	Me (OMe)	0	151

In contrast to internal alkenes, the esters of non-conjugated unsaturated carboxylic acids are also capable of being converted into cyclopropanes by treatment with diazomethane in the presence of palladium acetate and their reactivity depends on the configuration of the double bond. Thus methyl elaidate, containing a *trans*-C=C bond, is more reactive than methyl oleate containing a *cis*-C=C bond.[154]

In contrast to the esters of unsaturated carboxylic acids, the conversion of β-arylvinylamines into cyclopropane derivatives in the presence of palladium catalysts proceeds less successfully and in the case of the enamine **126** leads to the cyclopropane adduct **127** in only 10% yield.[172]

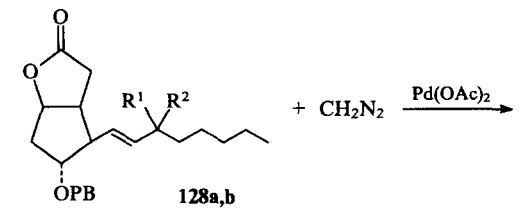


126 (X = CH, N)

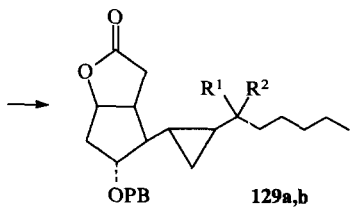
127 (~10%)

In this reaction, palladium compounds are apparently less effective than CuCl.[110]

The catalytic interaction of CH_2N_2 with unsaturated compounds makes it possible to synthesise certain prostaglandin preparations containing a cyclopropane ring.[173] Under these conditions, the reaction involving the formation of a cyclopropane from the hydroxy-derivative **128b**, containing, in contrast to allyl alcohol, a disubstituted double bond,[155] leads to the formation, together with the cyclopropane adduct **129b** (yield ~20%), of the methoxy-derivative **129** (R^1 = H, R^2 = OMe).

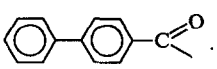


128a,b

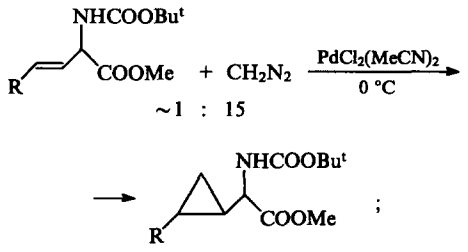


129a,b

CR^1R^2 = C=O (**a**) (92%);
R^1 = H, R^2 = OH (**b**) (20%);

PB = 

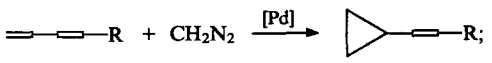
A method of synthesis of cyclopropyl-L-alanines and their derivatives—intermediates in the synthesis of food additives, medicinal drugs, and pesticides—has also been developed on the basis of the catalytic conversion of unsaturated compounds into cyclopropanes by diazomethane in the presence of palladium compounds.[174,175]



R = H (98%), CH_2OAc (68%).

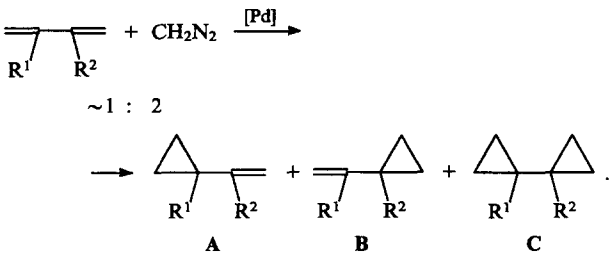
The regioselectivity of the conversion of various double bonds into cyclopropane groups and the possibility of obtaining polycyclopropane adducts are manifested most clearly in the interaction of CH_2N_2 with dienes and trienes.

The conversion of 1,3-dienes such as piperylene[25,68] as well as 1-cyclopropyl- and 1-alkoxy-butadienes[25,156,158] into cyclopropane derivatives in the presence of $Pd(acac)_2$ or $(PhCN)_2PdCl_2$ involves the terminal double bond and leads to the corresponding vinylcyclopropanes in high yields already in the presence of a (1.5–2)-fold excess of CH_2N_2.



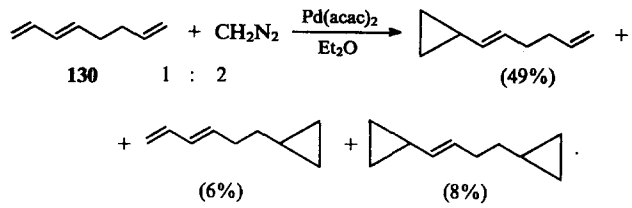
1 : 2 R = Me (90%), cyclo-C_3H_5 (91%), OMe, OEt, OAc, $OSiMe_3$ (80%–86%).

Under analogous conditions, the conversion of isoprene into a cyclopropane derivative proceeds less selectively, although a tendency towards the preferential formation of cyclopropanes from the less substituted C=C bond is retained.[68] In this case and also in the interaction of butadiene with 2,3-dimethylbutadiene[25] with an excess of diazomethane, the second double bond is converted into a cyclopropane group, which is accompanied by the partial formation of the corresponding bicyclopropyls, in agreement with the general tendency in the conversion of the terminal double bonds of alkenes into cyclopropyl groups.



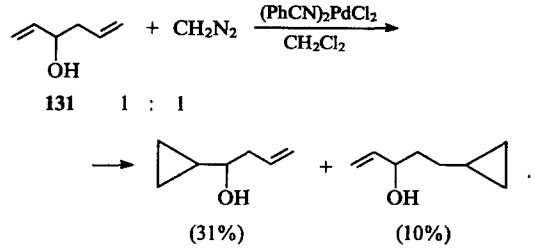
R^1	R^2	Yield of adducts (%)		
		A	B	C
H	H	67	–	29
H	Me	70	12	9
Me	Me	65	–	15

A terminal vinyl group conjugated with a double bond, as happens, for example, in octa-1,3,7-triene **130**, is approximately eight times more reactive than a terminal non-conjugated double bond.[25]



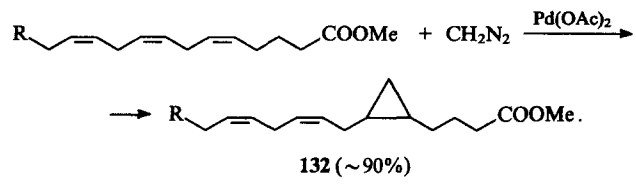
130 1 : 2 (49%) (6%) (8%)

The catalytic reaction of CH_2N_2 with hexa-1,5-dien-3-ol **131**, containing different terminal double bonds, gives rise to the preferential conversion of the allyl C=C bond into a cyclopropyl group, in contrast to the homoallyl bond.[155]

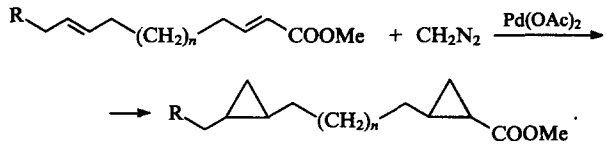


131 1 : 1 (31%) (10%)

The reactivity of vicinally substituted double bonds depends both on their position in the linear hydrocarbon chain and on their configuration. Thus the conversion of derivatives of arachidonic acid, containing *cis*-double bonds, into cyclopropanes involves only the C=C bond closest to the carboxy-group with formation of the cyclopropane adduct **132**, whereas the conversion into cyclopropanes of the esters of the *trans*-polyunsaturated acids affords satisfactory yields of the polycyclopropane adducts **133**.[176]

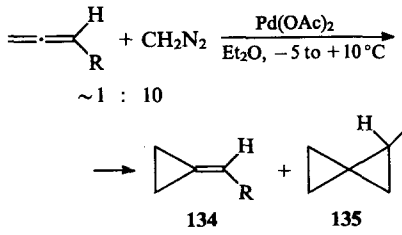


132 (~90%)



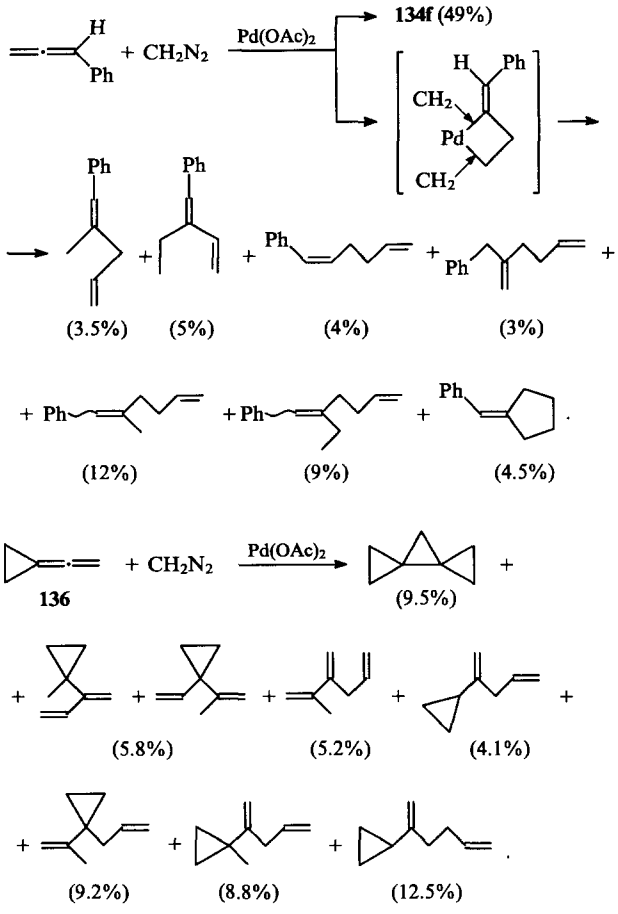
133 (80%–90%)

The conversion of allenes into cyclopropanes by treatment with diazomethane in the presence of $Pd(OAc)_2$ takes place most successfully when the catalyst is added to an ethereal solution of the allene and CH_2N_2, taken in a large excess.[177] The reaction then takes place fairly selectively with formation of adducts involving the least substituted double bond. However, in the conversion of alka-1,2-dienes into cyclopropanes, the corresponding spiropentanes **135** (yields up to 60%) are also formed together with the monoadducts **134**,[177,178] which indicates the possibility of the conversion into cyclopropyl groups of tri-substituted double bonds in the presence of palladium compounds.

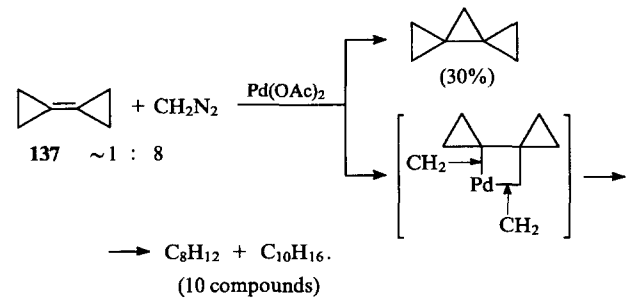


Compound	R	Yield of **134** (%)	Yield of **135**(%)
a	Bu	67	25
b	CH_2CH_2OH	~2	60
c	CH_2CH_2OAc	34	56
d	CH_2CH_2Br	63	27
e	CH_2CH_2OTs	78	–
f	Ph	49	–

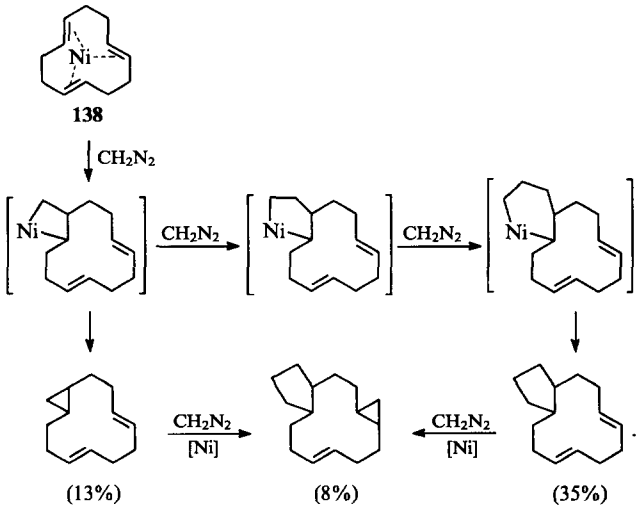
In a study of the interaction of CH_2N_2 with phenylallene (~10:1) and vinylidenecyclopropane **136** (~20:1) in the presence of $Pd(OAc)_2$, an unusual oligomethylenation reaction was discovered. It leads to the incorporation of several equivalents of methylene into the molecule with formation of a complex mixture of unsaturated hydrocarbons.[179,180] The use of a smaller relative amount of CH_2N_2 then affords the same mixture of products in approximately the same proportions as in the presence of an excess of CH_2N_2,[179] which is probably due to the possibility of their formation from the same intermediates.



A similar oligomethylenation reaction takes place also in the case of bicyclopropylidene **137**, which indicates, on the one hand, the possibility of the conversion of a tetrasubstituted double bond into a cyclopropyl group by diazomethane in the presence of palladium compounds,[181] and, on the other, the possibility of the existence of palladiacyclic intermediates stabilised by the spiro-linked cyclopropane ring and capable of reacting subsequently with several equivalents of methylene until their decomposition into the corresponding hydrocarbons, in which the bicyclopropyl fragment is largely retained.



The results agree with the non-trivial reaction of CH_2N_2 with *trans, trans, trans*-cyclododeca-1,5,9-trienenickel **138**, discovered previously, which resulted in the formation not only of cyclopropane derivatives but also of trimethylenation products, which are converted into compounds with a condensed five-membered ring.[182]



The formation of cyclopentane derivatives indicates that the reaction proceeds via a stage involving the formation of a metallacyclobutane fragment, the subsequent insertion of methylene in the Ni–C bond of which actually leads to the cyclopentane derivatives. The absence of a cyclobutane adduct is apparently due to the different stabilities of the four-, five-, and six-membered metallacycles and, in particular, the greater stability of nickelacyclopentanes (the reaction of which with CH_2N_2 goes to completion) compared with the other two metallacycles containing an odd number of carbon atoms in the ring, which they can readily eliminate in the form of the corresponding cycloalkane adducts.

b. Conversion of cyclic unsaturated compounds into cyclopropane derivatives

The possibility of the conversion of cyclic unsaturated compounds into cyclopropanes by treatment with diazomethane has led to extensive prospects for the synthesis of various cyclopropanes. The nature of the double bonds, determined primarily by the degree of strain in the cyclic system, exerts a significant influence on the nature of their conversion into cyclopropyl groups.

Thus, in the series of cycloolefins cyclohexene, cycloheptene, cyclooctene, and norbornene, the yields of cyclopropanes increase from 15% to 95% respectively under the same conditions (for example, when an equimolar amount of CH_2N_2 is passed at a uniform rate into the solution of the olefin in the

Table 4. Conversion of norbornene derivatives into cyclopropane derivatives by treatment with diazomethane in the presence of 0.3–1.2 mol% of palladium compounds in ether.

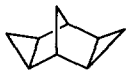
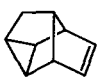
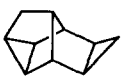
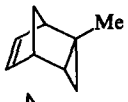
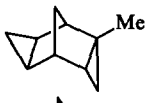
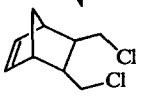
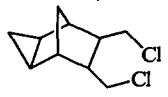
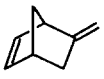
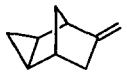
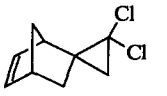
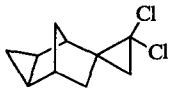
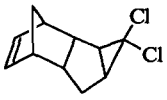
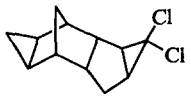
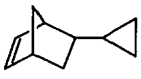
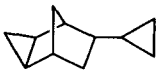
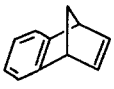
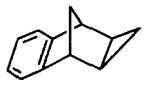
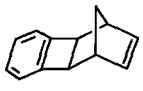
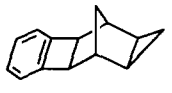
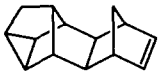
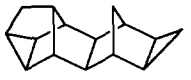
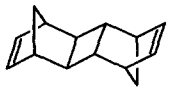
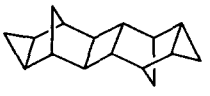
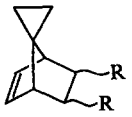
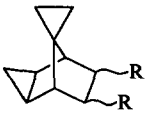
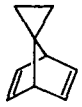
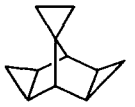
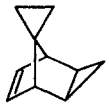
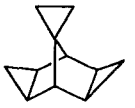
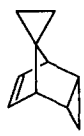
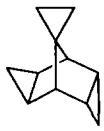
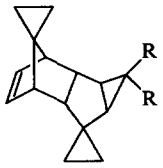
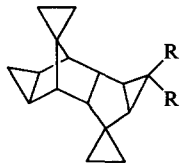
Unsaturated compounds	Olefin : CH_2N_2	Catalyst	Reaction product	Yield (%)	Ref.
	1:4.6[a]	$Pd(OAc)_2$		63	150
	1:1	$(PhCN)_2PdCl_2$[b]	*exo,exo*-**91a**	94	68
	1:7[a]	$Pd(OAc)_2$		~90	184
	1:1	$Pd(acac)_2$		54	25
	1:2	$Pd(acac)_2$[b]		~100	109
	~1:3[a]	$Pd(OAc)_2$		88	185
	~1:7[a]	$Pd(OAc)_2$		70	163
	1:2	$Pd(acac)_2$		88	25
	~1:7[a]	$Pd(OAc)_2$		80	163
	~1:9[a]	$Pd(OAc)_2$		85	186
	~1:6[a]	$Pd(OAc)_2$		90	187
	–	$[\eta\text{-}C_3H_5PdCl]_2$		~100	188
	1:10	$[\eta\text{-}C_3H_5PdCl]_2$		95	188
 (*exo,exo*-**139**)	1:3	$Pd(acac)_2$		78	189
endo,exo-**139**	1:3	$Pd(acac)_2$		93	189
exo,endo-**139**	1:3	$Pd(acac)_2$		82	189
endo,endo-**139**	1:3	$Pd(acac)_2$		60	189
 (*exo,exo*-**140**)	1:6	$Pd(acac)_2$		~65	189
exo,endo-**140**	1:6	$Pd(acac)_2$		80	189
endo,endo-**140**	1:6	$Pd(acac)_2$		87	189
					
R = H	1:1	$Pd(acac)_2$[b]	*exo*-**141** (R = H)	62	25
R = Cl	1:7[a]	$Pd(OAc)_2$		85	190
	1:7[a]	$Pd(OAc)_2$		65	190
	1:7[a]	$Pd(OAc)_2$		70	190

Table 4 (continued).

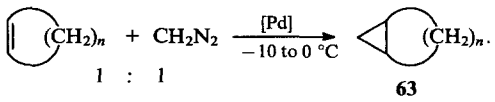
Unsaturated compounds	Olefin : CH_2N_2	Catalyst	Reaction product	Yield (%)	Ref.
	1 : 7[a]	$Pd(OAc)_2$		75	190
	1 : 7[a]	$Pd(OAc)_2$		80–85	191

R = H, Cl.

[a] The olefin : *N*-methyl-*N*-nitrosourea molar ratio is indicated.
[b] Solvent — CH_2Cl_2.

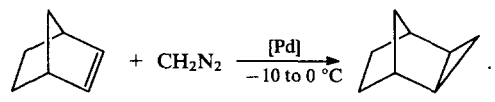
presence of 0.1–0.5 mol% of the palladium catalyst in CH_2Cl_2 at −10 to 0 °C).[68] As in the case of monosubstituted olefins, the use of $PdCl_2$, $Pd(OAc)_2$, $(PhCN)_2PdCl_2$, and $[\eta\text{-}C_3H_5PdCl]_2$ in these reactions hardly exerts a significant influence on the yields of the cyclic adducts.

The interaction of a mixture of cyclohexene and norbornene with CH_2N_2 in the presence of $(PhCN)_2PdCl_2$ proceeds, in contrast to copper compounds, regioselectively and leads to the almost complete conversion of norbornene into the adduct **64** without an appreciable conversion of cyclohexene into a cyclopropane derivative. Furthermore, a characteristic feature of palladium catalysts is their ability to propagate the reaction at a high CH_2N_2 concentration and to retain a high activity in the conversion of strained olefins into cyclopropanes virtually up to the completion of the reaction. These results undoubtedly indicate the preferential formation of π-olefin complexes in the conversion of unsaturated compounds into cyclopropanes with participation of palladium catalysts.[68]



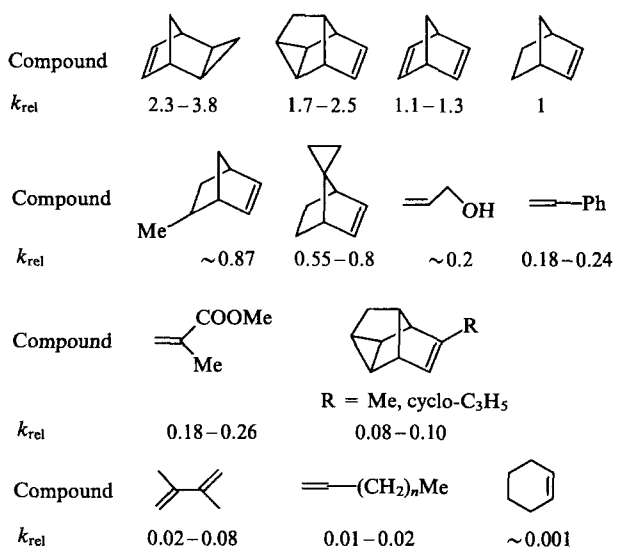
1 : 1 **63**

Product	*n*	Yield (%)
63a	4	10–15
63b	5	78–82
63c	6	90–92

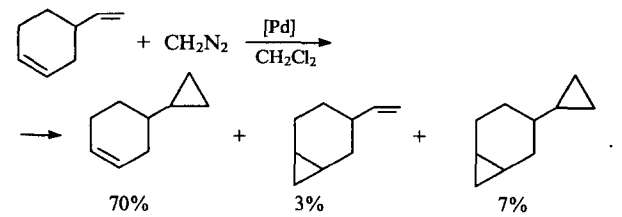


~1 : 1 **64** (93%)

One can now say without exaggeration that the conversion of polycyclenes into cyclopropanes by treatment with diazomethane, catalysed by palladium compounds, is one of the most promising methods of synthesis of polycyclic hydrocarbons of the norbornane series with a condensed cyclopropane fragment in the molecule (Table 4). The relative reactivities of certain unsaturated compounds in the reaction with CH_2N_2 in the presence of the palladium catalysts $Pd(OAc)_2$, $Pd(acac)_2$, and $(PhO)_3P \cdot PdCl_2$ have been investigated[159] and a significant difference between the rates of conversion of the norbornene and aliphatic mono- and di-substituted double bonds into cyclopropyl groups has been demonstrated.



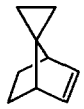
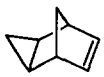
The substituted norbornene double bond proves to be more reactive than the terminal aliphatic double bond,[159,183] which is in its turn an order of magnitude more reactive than cyclohexene. This is clearly illustrated by the catalytic conversion of 4-vinylcyclohexene into the cyclopropyl derivative.[68]



70% 3% 7%

The stereochemistry of the addition of methylene, generated by the catalytic decomposition of CH_2N_2, to certain norbornene hydrocarbons has been investigated;[117] comparative estimates of the degrees of *exo*- and *endo*-conversion of the double bonds into cyclopropyl groups are given in Table 5. The results combined with other data for the conversion of norbornene derivatives into cyclopropanes in the presence of various catalysts based on palladium compounds confirm the high stereoselectivity in the formation of the *exo*-adducts (the fraction of the *endo*-isomers does not exceed 1.5%). On the other hand, when copper compounds and especially $Rh_2(OCOCF_3)_4$ are used as catalysts, the formation of *endo*-isomers is observed. Their amount increases significantly on passing from norbornene to norbornadiene and reaches 36%–42%.[117]

Table 5. Stereochemistry of the conversion of norbornene hydrocarbons into cyclopropane derivatives by treatment with diazomethane in the presence of various catalysts (0.5 – 1.0 mol%).

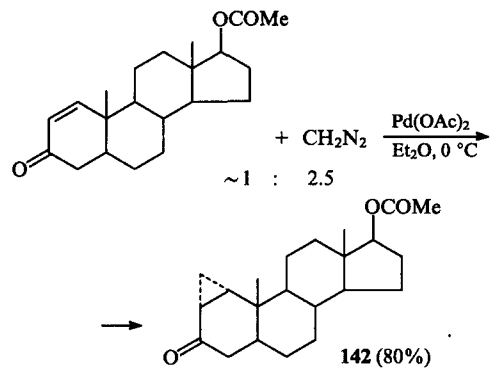
Original olefin	Reaction products	Ratio of *exo*- and *endo*-isomers [overall yield of isomers (%)]						
		$Pd(acac)_2$	$(PhCN)_2PdCl_2$	$Pd(OAc)_2$	$Cu(OTf)_2$	CuCl	$Cu(acac)_2$	$Rh_2(OCOCF_3)_4$
	*exo*- and *endo*-**64**	100:0 (87)	100:0 (81)	100:0 (78)	98:2 (73)	97:3 (58)	97:3 (38)	90:10 (18)
	*exo*- and *endo*-**141**	100:0 (32)	100:0 (36)	99:1 (18)	99:1 (23)	97:3 (38)	98:2 (18)	77:23 (20)
	*exo,exo*- and *exo,endo*-**91** (R = H)	99:1 (83)	100:0 (90)	99:1 (71)	95:5 (56)	86:14 (78)	96:4 (55)	74:26 (20)
	*exo*- and *endo*-**90** (R = H)	99:1 (52)	99:1 (54)	99:1 (48)	75:25 (34)	70:30 (48)	64:36 (36)	58:42 (19)
	exo,exo- and *exo,endo*-**91** (R = H)	98:2 (16)	99:1 (16)	98:2 (14)	72:28 (9)	65:35 (12)	62:38 (9)	53:47 (4)

The *exo*-stereoselectivity in the conversion of norbornenes into cyclopropanes under the influence of palladium catalysts is probably associated with the ability of norbornenes to form initially coordinated π-complexes with the central metal atom, which react subsequently with CH_2N_2.[68,70] In view of the *endo*-deformation of the vinyl hydrogen atoms (the angle of deviation of the C–H bonds from the C–CH=CH–C plane of the norbornene fragment is 3°–5°),[125,192] this coordination is undoubtedly extremely sensitive to the electronic state of the double bond and takes place exclusively in the *exo*-position. In the case of copper and particularly rhodium catalysts, the double bond is attacked by metal–carbene complexes, as a result of which the interaction of the carbene centre with the double bond is less sensitive to the electronic state of the latter and takes place partially in the *endo*-position.

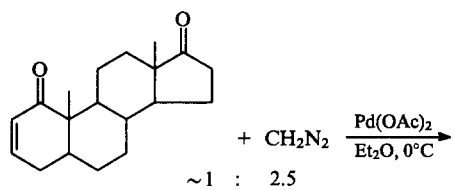
The increased content of the *endo*-isomers in the conversion of the norbornadiene into cyclopropane derivatives compared with norbornenes) in the presence of copper and rhodium catalysts is also apparently associated with the characteristic features of the geometry of the double bonds. Thus, according to calculations,[125] the angle of the *endo*-deformation of the vinyl C–H bonds in norbornadiene is smaller than in norbornene (2.3° and 4.9° respectively) and the probability of the attack on the double bond by the carbene complex from the direction of the *endo*-position is therefore increased for the former compound. This explanation is apparently valid also for many other cycloaddition reactions involving norbornadiene, accompanied by the formation of *exo*- and *endo*-isomers.

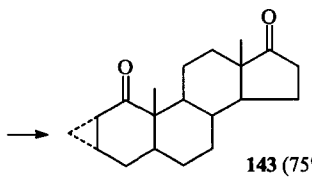
The conversion of an unsubstituted double bond in five-membered and six-membered rings into cyclopropyl groups, which is ineffective for the hydrocarbons themselves, is significantly activated by the presence of a conjugated carbonyl group. Thus the use of a comparatively small excess of CH_2N_2 led to the synthesis in high yields of the steroids **142**–**144** containing the cyclopropane ring in the molecule.[151]

It has been established recently[176] that, when $Pd(acac)_2$ is used as the catalyst, it is possible to achieve the conversion into a cyclopropyl group, also of a non-conjugated endocyclic double bond in a six-membered ring, which is illustrated, in particular, by the formation of the isomeric adducts **145**. Trisubstituted double bonds in Δ^5-, Δ^7-, Δ^{11}-, and Δ^{14}-steroids do not give rise to cyclopropyl groups under the chosen conditions.

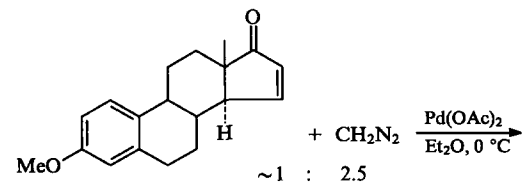


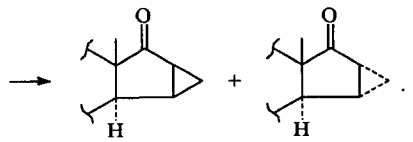
142 (80%)



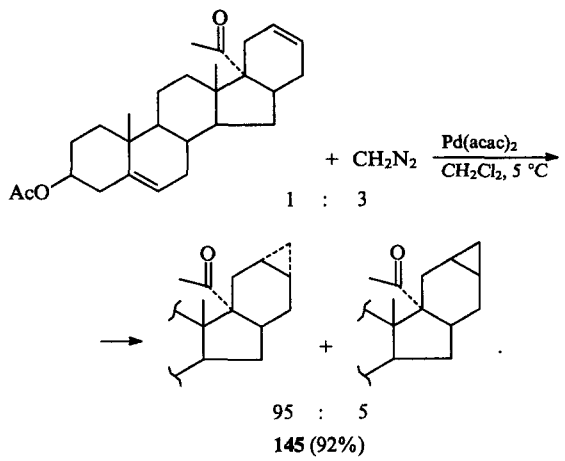


143 (75%)



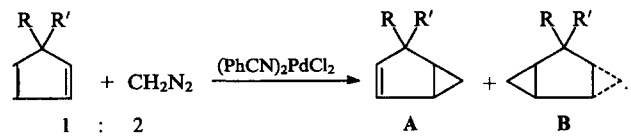


144 (~100%)

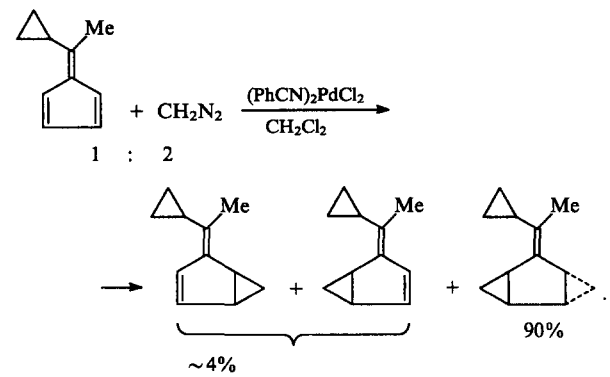


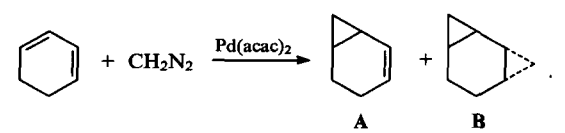
145 (92%)

The double bonds in cyclopentadiene,[68] spiro[2,4]heptadiene,[193] 6,6-disubstituted fulvenes,[68] cyclohexa-1,3-diene,[25,194] and cycloocta-1,5-diene[68,194] are fairly readily converted into cyclopropyl groups by diazomethane in the presence of palladium compounds and the formation of a cyclopropyl group from one of the double bonds sometimes accelerates the similar conversion of the second double bond, which is probably due to the increase in its strain as a result of the additional introduction of a cyclopropane fragment into the cyclic structure. The conversion of the second double bond in five- and six-membered cyclic dienes into a cyclopropyl group then occurs with formation of only the corresponding *trans*-isomers,[68,194] whereas in the case of cycloocta-1,5-diene, small amounts of the *cis*-isomer are also produced (*trans* : *cis* ≃ 7 : 1).



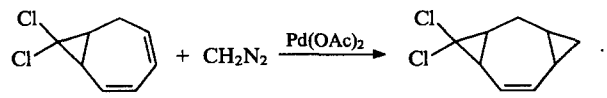
R	R′	Yield of A (%)	Yield of B (%)
H	H	15	75
$-CH_2CH_2-$		12	77

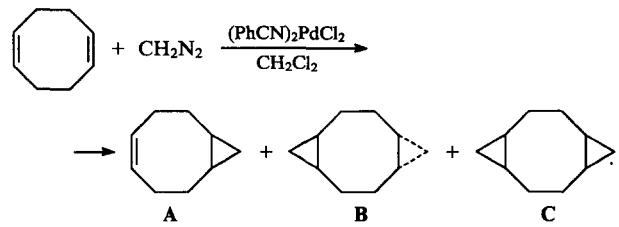




Reagents ratio	Yield of A (%)	Yield of B (%)
1:1	43	1
1:2	53	13

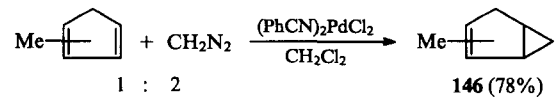
It is of interest to note that neither cyclohepta-1,3,5-triene[194] nor cycloocta-1,3,5,7-tetraene[116] are converted into cyclopropane derivatives by diazomethane in the presence of $Pd(OAc)_2$ despite the use of an excess of CH_2N_2.





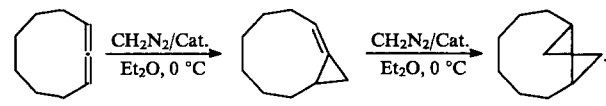
Reagents ratio	Yield of products (%)		
	A	B	C
1:1	5	38	5.5
1:2	6	72	10

The substituents in the cyclodienes exert the same influence on the regioselectivity of the addition of methylene as in alkenes. Thus the conversion of a mixture of methylcyclopentadienes into cyclopropane derivatives in the presence of palladium compounds involves only the unsubstituted double bond with formation of 2- and 3-methylbicyclohexenes **146**.[68]



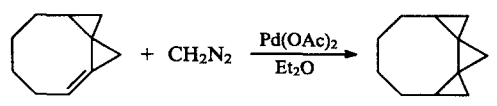
146 (78%)

The allene group in cyclonona-1,2-diene is converted into a cyclopropyl group by an excess of CH_2N_2 in the presence of the palladium catalysts $Pd(OAc)_2$ and $(PhCN)_2PdCl_2$, affording bicyclodecene **147** in a preparative yield (~60%). Repeated treatment of the reaction mixture with diazomethane leads to the partial formation of the spiran adduct **148**, the yield of which does not, however, exceed 10%.[177]

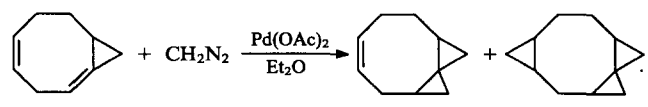


147 (~60%) **148** (~10%)

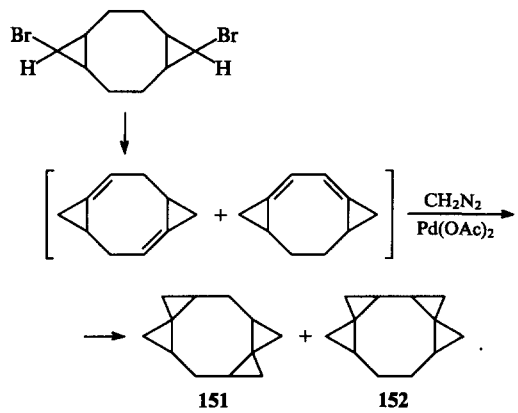
A similar approach, involving the catalytic introduction of an additional cyclopropyl group into alkylidenecyclopropanes, has been used recently to synthesise the polyspiran hydrocarbons **149**–**152** containing several three-membered rings in the molecule.[195]



149

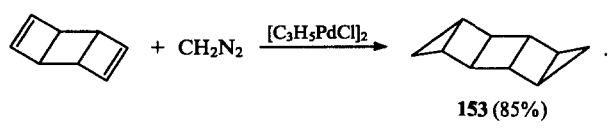


150

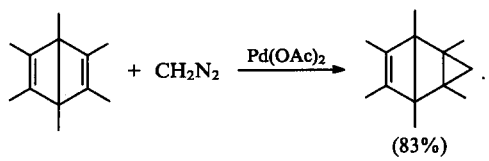


151 152

Polycyclic structures containing a C=C bond in a four-membered ring are also converted into cyclopropane derivatives by treatment with diazomethane in the presence of palladium compounds and the nature of the cyclopropane formation reaction involving such substances has a number of specific features. Thus, whereas the formation of the diadduct **153** in a high yield in the cyclopropane formation reaction involving tricyclo[4.2.0.0^{2,5}]octa-3,7-diene appears fairly evident,[188] the conversion of the tetrasubstituted double bond of the permethylated Dewar benzene into a cyclopropyl group using a palladium catalyst appears to be non-trivial.[150]

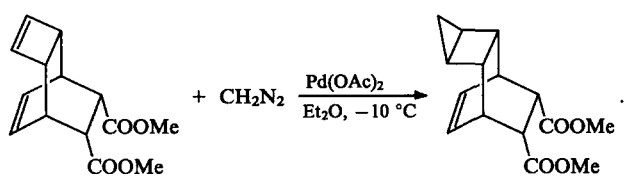


153 (85%)



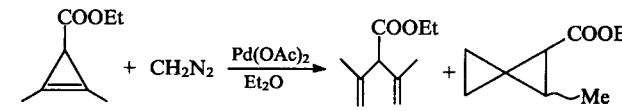
(83%)

The cyclobutene fragment in the polycyclic diene **154** is converted into a cyclopropyl group less effectively, which leads to the monoadduct **155** in a yield of ~30% even in the presence of a large excess of CH_2N_2.[196] The absence of the formation of a cyclopropane adduct from the second double bond is apparently associated with the steric hindrance generated by the four-membered ring and the methoxycarbonyl substituents. It is noteworthy that, according to Dzhemilev et al.,[25] bicyclo-[2.2.2]oct-2-ene itself affords the cyclopropane adduct in 64% yield.



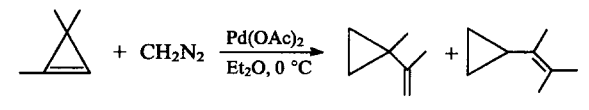
154 ~1 : 12 **155** (30%)

In contrast to the unsaturated compounds examined, the interaction of cyclopropenes with CH_2N_2 catalysed by palladium compounds proceeds in a more complex manner and is accompanied by the formation of appreciable amounts of oligomeric products. The nature of the compounds synthesised then depends to a large extent on the degree of substitution of the cyclopropenes, the electron-accepting properties of the substituents, and the reaction conditions.[197–199] Thus ethyl 1,2-dimethylcyclopropenecarboxylate reacts with an excess of CH_2N_2 to form the diene **156** and the spiropentane **157** in an overall yield of ~25%.[197,199] The appearance of the spiropentanes **157** (isomer ratio ~1 : 1.2) can be explained by the partial isomerisation of the initial cyclopropene ester to the corresponding ester of 2-methylene-3-methylcyclopropenoic acid and its subsequent conversion into a cyclopropane derivative.

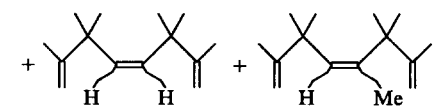


156 (15%) **157** (10%)

The addition of a catalytic amount of $Pd(OAc)_2$ to a mixture of an ethereal solution of CH_2N_2 and 1,3,3-trimethylcyclopropene leads to the vinylcyclopropanes **158** and **159** and the trienes **160** and **161** in an overall yield of ~40% (for the total conversion of the initial cyclopropene).[198,199]

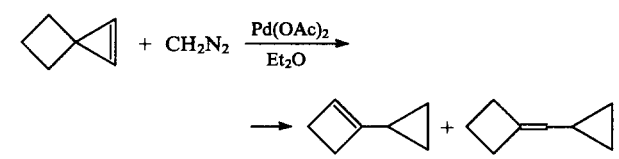


158 (7%) **159** (10%)



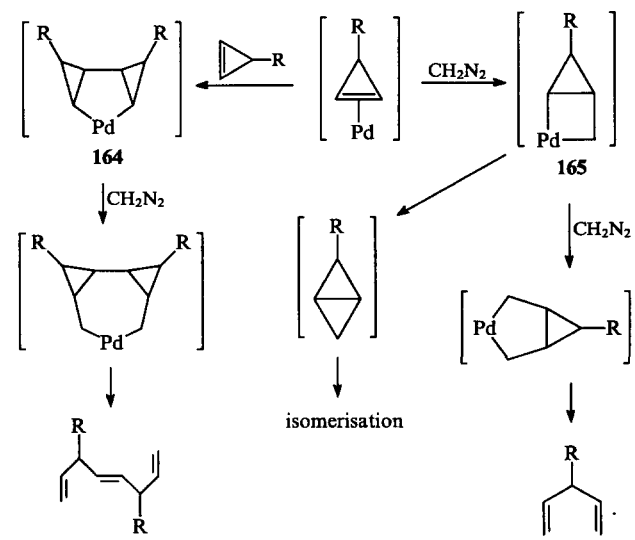
160 (8%) **161** (15%)

The monomeric products **162** and **163** are obtained in an even lower yield in the catalytic reaction of CH_2N_2 with spirohex-1-ene.[199]



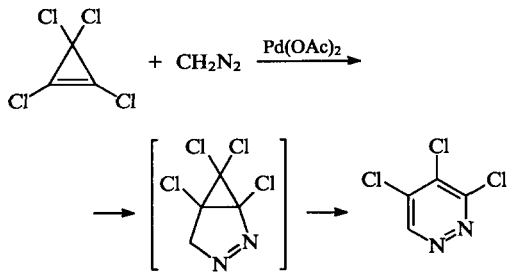
162 (3%) **163** (5%)

A probable mechanism of the observed reactions has been proposed.[197–199] It explains the formation of compounds **158–163** as a result of the catalytic conversion of the bicyclobutanes and/or metallacycles formed initially. The difference between the coordinating capacities of trimethylcyclopropene and the cyclopropenecarboxylate ester is then attributed to the possibility of the formation of two different intermediates—the metallacycles **164** and **165**. The subsequent



insertion of methylene in the Pd–C bonds leads to the expansion of the metallacycles and is completed by their decomposition with the opening of the cyclopropane fragment and the elimination of palladium.

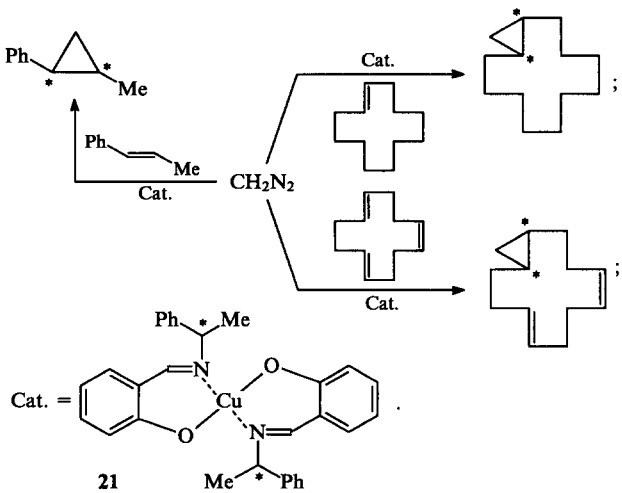
In contrast to the cyclopropenes mentioned above, the interaction of tetrachlorocyclopropene with CH_2N_2 leads to trichloropyridazine **166**. Owing to the combination of the low coordinating capacity of the tetrasubstituted cyclopropene with its high electron deficiency, the only reaction pathway in this instance is 1,3-dipolar addition with subsequent conversion of the resulting adduct **167** into the pyridazine **166**.[199]



167 **166** (75%)

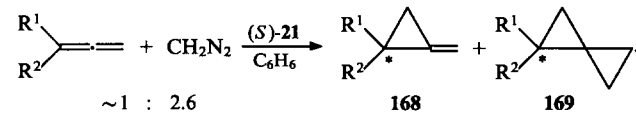
4. Asymmetric conversion of olefins into cyclopropane derivatives by diazomethane

The catalytic chiral [1 + 2]-cycloaddition of methylene, generated from CH_2N_2, to olefins with formation of optically active cyclopropanes was achieved for the first time in 1968 by Nozaki et al.,[67] who used salicylideneaminecopper complexes (*R*)- or (*S*)-**21**, obtained from chiral 1-phenylethylamines, as the catalyst. Thus (*E*)-propenylbenzene is converted on treatment with compound **21** into *trans*-2-methyl-1-phenylcyclopropane **22** in 62% yield with an enantiomeric excess of ~8%. Partial optical activity of the products formed in the presence of the optically active catalysts **21** has been observed also in the conversion of *trans*-cyclododecane and *Z*,*Z*,*E*-cyclododeca-1,5,9-triene into cyclopropane derivatives.[67]



21

Asymmetric induction has been observed also in the decomposition of CH_2N_2 on treatment with (*S*)-**21** as catalyst in the presence of phenyl-, 1-methyl-1-phenyl-, and hexylallenes.[200,201] Both the methylenecyclopropanes **168** and the corresponding spiropentanes **169** were then obtained in satisfactory yields. In the case of phenylallene,[201] the absolute configuration of the methylenecyclopropane **168a** was determined and the optical yield of compounds **168a** and **169a** was estimated as ~12%.

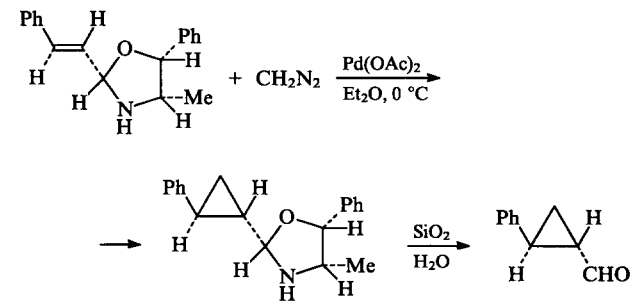


~1 : 2.6 **168** **169**

Compound	R^1	R^2	Yield of **168** (%)	Yield of **169** (%)
a	Ph	H	30	45
b	Ph	Me	43	52
c	C_6H_{13}	H	7	43

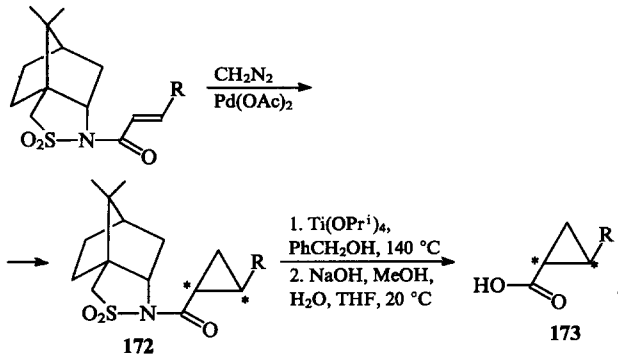
After the publication of these studies, which demonstrated only the possibility, in principle, of the induction of optical activity in the cyclopropanes produced, there were virtually no publications concerning the use of catalysts containing optically active ligands for the conversion of unsaturated compounds into cyclopropane derivatives by diazomethane. On the other hand, studies on the synthesis and use of chiral catalysts, in the first place rhodium compounds, for the decomposition of other diazo-compounds, especially alkyl diazoacetates, developed extensively.[202]

Nevertheless the interest in the synthesis of optically active compounds based on the catalytic conversion of olefins into cyclopropane derivatives by diazomethane has persisted in connection with the possibility of the effective conversion of suitable chiral substrates into cyclopropanes. The usual palladium catalysts, especially $Pd(OAc)_2$, are used in this instance and the optical activity is induced in the resulting *trans*-1,2-disubstituted cyclopropane by the presence in the initial olefin of an optically active substituent, which can be transformed, when necessary, into a suitable functional group. Thus a method of synthesis of (1*R*,2*R*)-phenylformylcyclopropane **171** with an optical purity not less than 90% from cinnamaldehyde and L-ephedrine has been proposed. The key stage of the reaction is the synthesis of the oxazolidine derivative **170**.[203]



170 (~100%) (1*R*,2*R*)-**171** (ee > 90%)

It has been shown recently[204] that *trans*-*N*-enoylsultams—derivatives of α,β-unsaturated carboxylic acids and bornane[10.2]sultam—undergo the stereoselective cyclopropane formation reaction on treatment with diazomethane in the presence of $Pd(OAc)_2$, forming the corresponding *trans*-disubstituted cyclopropanes **172** in high yields (the enantiomeric excess of the nonrecrystallised reaction products is 67%–91%). The subsequent hydrolysis of the cyclopropanes **172** in the presence of titanium tetraisopropoxide leads to the optically active cyclopropanecarboxylic acids **173**.[204]



R	Ph	2-MeOC$_6$H$_4$	3-MeOC$_6$H$_4$	Me	C$_{10}$H$_{21}$
Yield of **172** (%)	73	73	63	72	62

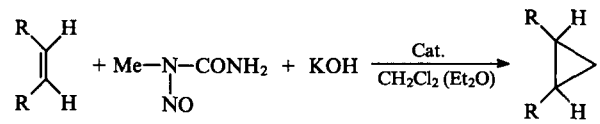
R	3,4,5-(MeO)$_3$C$_6$H$_2$		
Yield of **172** (%)	62	67	67

The authors [204] also noted that the diastereomeric excess of the cyclopropane products, for example **172** (R = Ph), increases from 53% to 87% when the reaction temperature is raised from −30 to 0 °C and remains almost unchanged on its further increase (from 0 to +30 °C).

5. Conversion of unsaturated compounds into cyclopropane derivatives by diazomethane generated *in situ*

The results presented above show that the catalytic reaction of diazomethane with unsaturated compounds constitutes a universal and fairly simple (from the standpoint of the initial reactants) method of synthesis of various cyclopropanes and that the use of palladium catalysts is especially promising. However, the standard procedure in the cyclopropane formation reaction suffers from a number of significant disadvantages and limitations, the main ones being the necessity for the preliminary preparation and transport of the toxic and explosive diazomethane, which renders it suitable only for laboratory purposes.

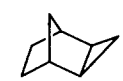
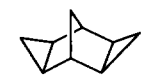
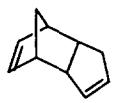
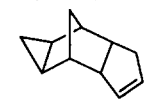
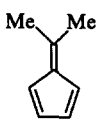
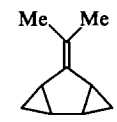
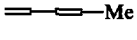
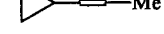
In 1987 we showed for the first time [205] that the conversion of allyl alcohol and allyl ethers into cyclopropane derivatives can be carried out successfully with the direct generation of CH_2N_2 by the alkaline hydrolysis of *N*-methyl-*N*-nitrosourea in the presence of the unsaturated compound and the palladium catalyst. In our subsequent studies [157,206] this method was developed further. In particular, it proved extremely effective for the conversion into cyclopropane derivatives of the majority of unsaturated compounds containing monosubstituted and strained endocyclic double bonds. In the method proposed, *N*-methyl-*N*-nitrosourea is added gradually at 10–20 °C to a mixture of the unsaturated compound, the palladium catalyst, an organic solvent, and 40%–50% KOH solution.



Cat. = $(PhCN)_2PdCl_2$, $Pd(OAc)_2$, $Pd(acac)_2$, $[(PhO)_3P]_2PdCl_2$, $[(PhO)_3P]_4Pd$.

The successful use of palladium catalysts in this method for conversion into cyclopropane derivatives, which involves the use of a concentrated solution of alkali, is apparently due to the involvement in the reaction of non-hydrolysable low-valence π-olefinpalladium complexes. The activity of the catalytic system hardly diminishes under these conditions and makes it possible to achieve conversion into cyclopropane in preparative yields,

Table 6. Catalytic conversion of unsaturated compounds into cyclopropane derivatives by the diazomethane generated *in situ* from *N*-methyl-*N*-nitrosourea (MNU) and KOH [catalyst : 0.2 mol% $(PhCN)_2PdCl_2$, temperature 12–15 °C].

Unsaturated compound	MNU : substrate	Solvent	Product	Yield (%)
	1.5 : 1	CH_2Cl_2		95
	2.9 : 1	CH_2Cl_2		92
	1.5 : 1	CH_2Cl_2–hexane		94
	3 : 1	CH_2Cl_2–Et_2O		84
	1.6 : 1	CH_2Cl_2		92
	1.9 : 1	Et_2O		92
	1.7 : 1	CH_2Cl_2		91
	1.8 : 1	CH_2Cl_2–Et_2O		88
	1.9 : 1	CH_2Cl_2–Et_2O		88

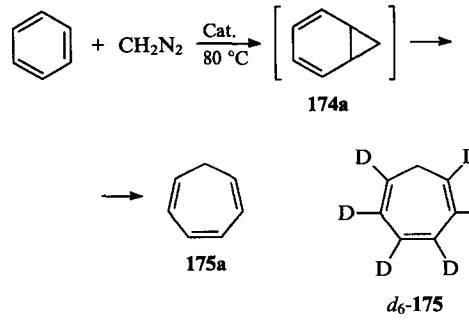
which are the same as in the *ex situ* procedure.[157] Table 6 presents the results of the conversion into cyclopropanes of certain unsaturated hydrocarbons and alkenes with functional group substituents under the conditions of the simultaneous generation and catalytic decomposition of diazomethane.

Thus the creation of a convenient and safe method for the conversion of unsaturated compounds into cyclopropane derivatives by diazomethane generated *in situ* has provided a powerful instrument in synthetic organic chemistry for the formation of cyclopropanes from the corresponding olefins (predominantly monosubstituted and disubstituted). Furthermore, the elimination of the need to employ large quantities of diazomethane to maintain the efficiency of the cyclopropane formation stage itself makes this method promising for application on an industrial scale.

IV. Catalytic interaction of diazomethane with aromatic compounds

The transition metal complex-catalysed interaction of diazomethane with aromatic compounds is accompanied by the dediazotisation of CH_2N_2 and the addition of the methylene fragment to the aromatic system. In the case of compounds of the benzene series, the main products of these reactions are cyclohepta-1,3,5-trienes.[207-213] The reaction involving the expansion of a six-membered ring to a seven-membered one is characteristic also of the catalytic decomposition of other diazo-compounds (for example, alkyl diazoacetates[214]) in different benzene derivatives. This leads to extensive possibilities in the synthesis of cyclohepta-1,3,5-trienes, which are otherwise difficult to obtain. Among the large number of metal salts and complexes tested as catalysts of the methylenation of aromatic compounds by diazomethane, those based on rhodium and copper are the most effective [$Rh_2(OCOCF_3)_4$, $Rh_2(OAc)_4$, Rh/C, $CuCl_2$, CuCl, CuBr].[207-210] On the other hand, the mononuclear rhodium complexes [$RhCl_3$, $Rh(acac)_3$, $Rh(PPh_3)_3Cl$] as well as palladium compounds and copper *N*-(1-phenylethyl)salicylaldiminate proved to be altogether inactive in this reaction.[210]

The catalytic interaction of CH_2N_2 with benzene was first achieved by Müller and coworkers.[207,208] Cycloheptatriene **175a** was obtained in this reaction in 85% yield (relative to CH_2N_2) by adding a benzene solution of CH_2N_2 to a suspension of CuCl or CuBr in benzene at 80 °C. The use of $Rh_2(OCOCF_3)_4$ instead of copper halides with the ratios C_6H_6 : CH_2N_2 : Cat. = 4000 : 200 : 1 makes it possible to increase the yield of compound **175a** to 95% and to carry out the process under milder conditions (~20 °C).



d_6-175

According to the data of Dzhemilev et al.,[210] the catalytic cycle in the formation of cycloheptatrienes by the reaction of CH_2N_2 with benzene in the presence of rhodium catalysts presupposes the involvement of dinuclear rhodium complexes,[215] which facilitate the multistage addition of CH_2 to the aromatic system via the formation of metallacyclic intermediates. The subsequent reductive elimination of the dinuclear rhodium complexes from complex **176** is accompanied by the formation of bicyclo[4.1.0]hepta-2,4-dienes (norcaradienes), which are converted into the corresponding cycloheptatrienes under the reaction conditions as a result of the synchronous electrocyclic opening of the cyclopropane ring (Scheme 4). This mechanism has been confirmed by the selective distribution of deuterium in the adduct d_6-**175**, obtained by the reaction of CH_2N_2 with perdeuteriobenzene in the presence of $Rh_2(OCOCF_3)_4$.[210]

Scheme 4

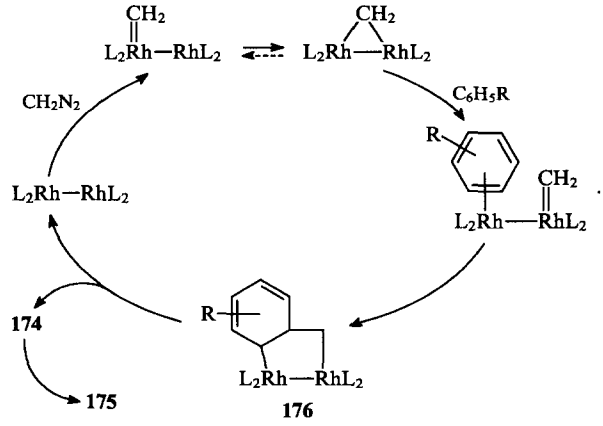
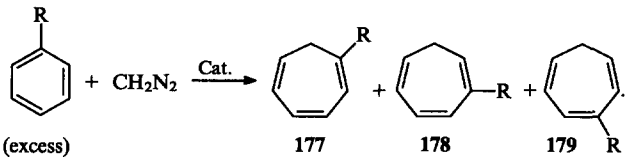


Table 7. The formation of substituted cyclohepta-1,3,5-trienes in the reaction of monosubstituted benzenes with CH_2N_2 in the presence of CuBr or $Rh(OCOCF_3)_4$.

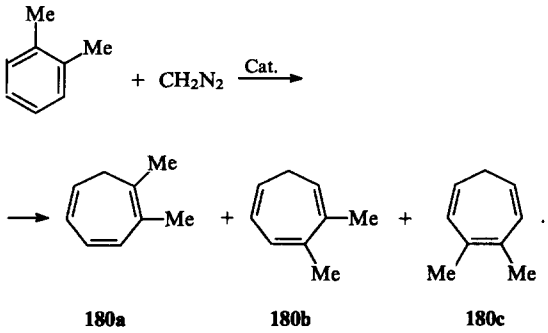
Catalyst (0.5-2 mol%)	Substituent R	Overall yield (%)	k_{rel} (PhR/PhH)	Proportions of isomeric products (%)		
				177	178	179
CuBr	Me	75	–	21	43	36
	Et	68	–	20	38	42
	Pr^i	64	–	17	37	46
	Bu^t	50	–	13	35	52
	F	41	–	23	25	52
	Cl	50	–	15	43	42
	Br	25	–	8	54	38
	OMe	75	–	30	25	45
$Rh_2(OCOCF_3)_4$	Me	98	1.02	24	26	50
	Ph	92	0.93	23	28	49
	Cl	20	0.16	25	11	64
	Br	8	0.06	19	27	54
	COOEt	7	0.07	12	33	55

Benzene derivatives react with CH_2N_2 similarly to benzene itself and in the presence of both copper and rhodium catalysts a mixture of isomeric 1-, 2-, and 3-substituted cycloheptatrienes **177–179** is then formed from monosubstituted benzenes (Table 7).[210–213]



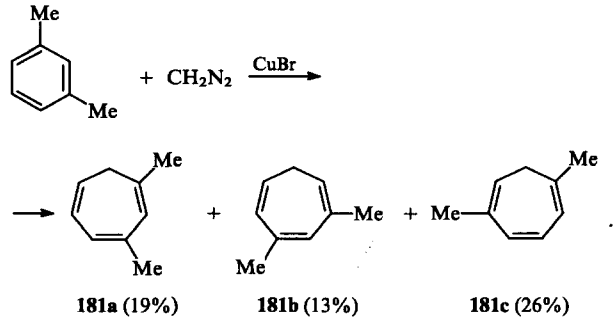
The introduction of bulky and electron-accepting substituents into the benzene ring lowers significantly the overall yield of the reaction products. Whereas in the case of halobenzenes the use of CuBr is preferred in this reaction, for benzene derivatives with electron-donating substituents a greater activity is shown by $Rh_2(OCOCF_3)_4$. It is striking that the preferential formation of 3-substituted cycloheptatrienes **179** is observed in virtually all instances. It has been suggested[210] that the cycloaddition of methylene to the six-electron π-system of substituted aromatic compounds largely involves the C(3)–C(4) bond of the benzene ring, where, according to Dewar,[216] the highest electron density is concentrated. Benzaldehyde, benzonitrile, nitrobenzene, and pyridine do not react with CH_2N_2 in the presence of $Rh_2(OCOCF_3)_4$; surprisingly, anisole behaves in the same way.[210]

Preparative methods of synthesis of isomeric dimethylcycloheptatrienes **180–182**, with a fixed relative disposition of the methyl groups, and of individual 1,3,5-trialkylcyclohepta-1,3,5-trienes **183** have been developed on the basis of the catalytic interaction of diazomethane with xylenes and 1,3,5-trialkylbenzene.[210–212] As was to be expected, the overall yield of cycloheptatrienes increases appreciably under these conditions when $Rh_2(OCOCF_3)_4$ is used as the catalyst.

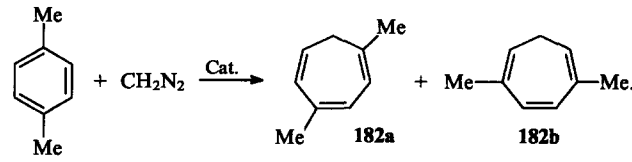


180a **180b** **180c**

Cat.	Yield of **180** (%)		
	a	**b**	**c**
CuBr	8	31	12
$Rh_2(OCOCF_3)_4$	18	29	51

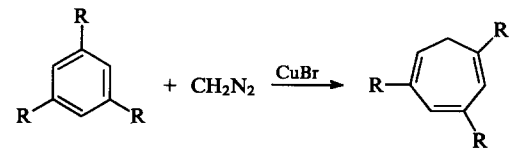


181a (19%) **181b** (13%) **181c** (26%)



182a **182b**

Cat.	Yield of **182** (%)	
	a	**b**
CuBr	25	37
$Rh_2(OCOCF_3)_4$	73	24

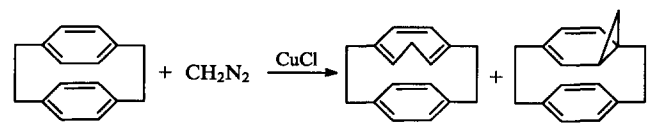


183

R = Me (75%), Et (59%), Pr^i (45%).

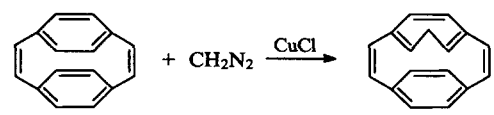
Like *p*-xylene, 1,4-dimethoxybenzene interacts with CH_2N_2, affording in the presence of CuCl two isomers — 1,4- and 2,5-dimethoxycyclohepta-1,3,5-trienes in an overall yield of ~65%.[213]

The catalytic methylenation of the aromatic ring by diazomethane occurs also in the case of cyclophanes.[217–220] Thus the interaction of CH_2N_2 with [2,2]paracyclophane **184** in the presence of CuCl leads to a mixture of different methylenation products, among which monoadducts are formed as a mixture of approximately equal amounts of compounds **185** and **186** containing both the cycloheptatriene and norcaradiene fragments.[217,218]



184 **185** (~10%) **186** (~10%)

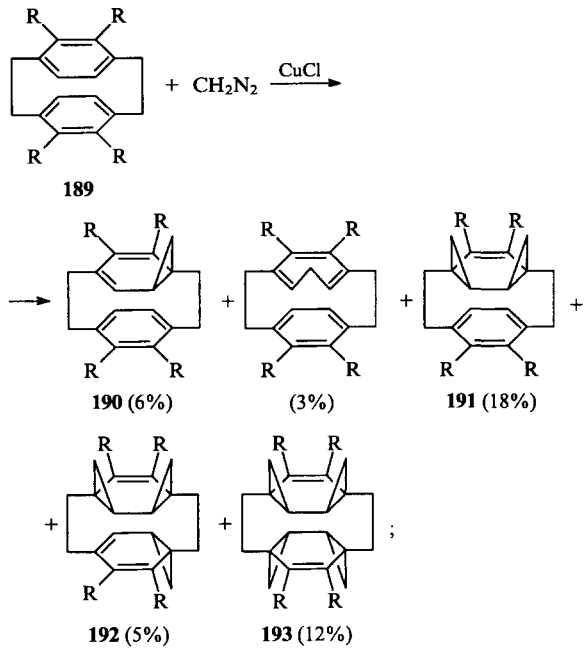
The methylenation of [2,2]paracyclophane-1,9-diene **187** takes place unexpectedly selectively under similar conditions; methylene then attacks benzene rings much faster than the double bond, adding preferentially to the unsubstituted bond with formation of the cycloheptatriene derivative **188**.[217]



187 **188**

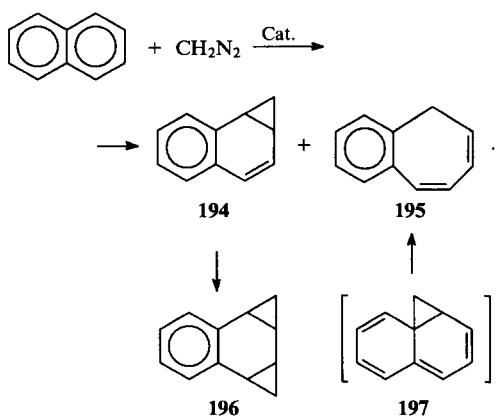
On the other hand, tetrakis(methoxycarbonyl)paracyclophane **189** reacts with a large excess of CH_2N_2 in the presence of CuCl and affords mainly the CH_2N_2 adducts **190–193** as a result of the addition of methylene to the monosubstituted bonds of the benzene ring.[219,220]

In contrast to benzene and its derivatives, the interaction of polynuclear aromatic compounds with CH_2N_2 in the presence of both copper and rhodium catalysts leads mainly to the formation of fairly stable cyclopropane adducts and in a number of instances the reaction proceeds with a high regioselectivity. Thus the interaction of CH_2N_2 with an excess of naphthalene at 80 °C in the presence of $Rh_2(OCOCF_3)_4$ affords 2,3-benzobicyclo[4.1.0]hepta-2,4-diene **194** in a yield of 98%, the relative reactivity of naphthalene in this reaction being higher by a factor

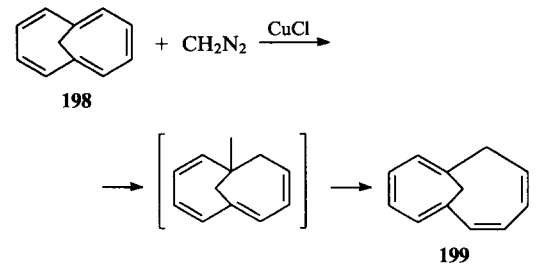


R = COOMe.

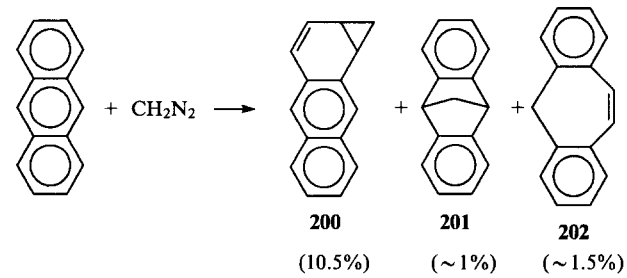
of 1.7 than that of benzene.[210] The same reaction in the presence of CuBr leads to an overall yield of about 30% of a mixture of the cyclopropane **194** and benzocycloheptatriene **195**, the ratio of which varies from 95 : 5 at 120–140 °C to 40 : 60 at 170–190 °C.[221] When a fourfold molar excess of CH_2N_2 was used, the product **196** of the double cyclopropane formation reaction was obtained with a yield of 18%. Since all attempts to isomerise compound **194** to compound **195** were unsuccessful,[210] one may assume that compound **195** is formed as a result of the isomerisation of another cyclic methylene–naphthalene adduct, for example compound **197**, formed at an elevated temperature as a consequence of the decrease in the regioselectivity of the reaction.



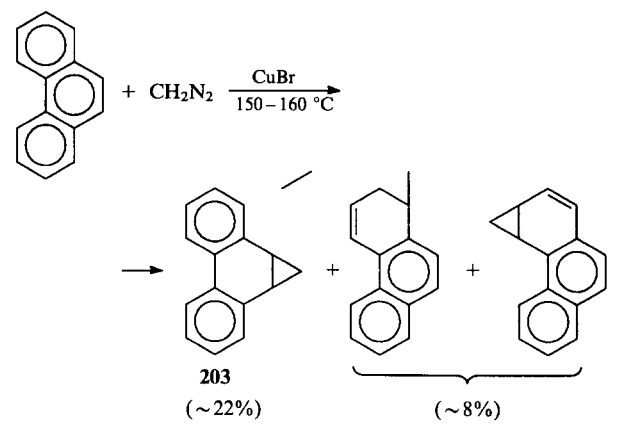
The catalytic interaction of diazomethane with another 10-electron aromatic system—bicyclo[4.4.1]-undeca-1,3,5,7,9-pentaene **198**[222,223]—apparently involves wholly the most substituted double bond, since, according to the data of Vogel et al.,[223] the reaction results in the formation of only bicyclo[5.4.1]dodeca-2,4,7,9,11-pentaene **199**.

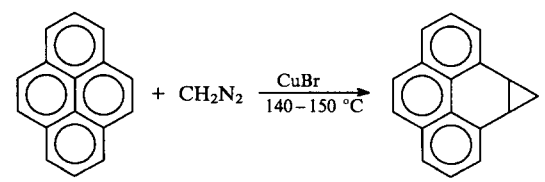


The interaction of CH_2N_2 with anthracene in the presence of CuBr has been carried out at 25 °C using CH_2Cl_2 as the solvent. A mixture of the products **200**–**202**, in which the cyclopropane adduct **200** predominated, was then obtained in an overall yield of 13%.[224]

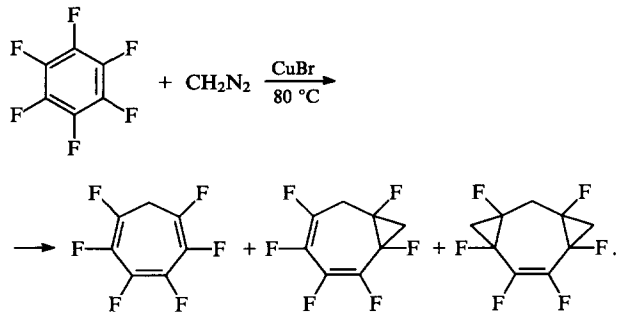


The catalytic addition of methylene to phenanthrene also leads to a mixture of compounds,[221,225] in which, according to the data of Müller et al.,[225] the dominant component is the cyclopropane adduct **203** formed as a result of the addition of methylene to the C(9)–C(10) bond. The higher reactivity of the bonds in the central rings of condensed aromatic systems compared with the bonds in the peripheral benzene rings is indicated also by the formation of only one isomer **204** in the catalytic conversion of pyrene into a cyclopropane derivative.[226]



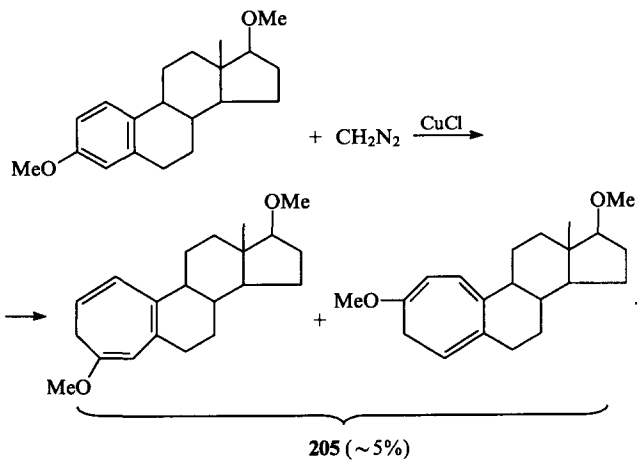


When diazomethane reacted with a boiling solution of hexafluorobenzene in the presence of CuBr, a complex mixture of compounds was obtained in which hexafluorocyclohepta-1,3,5-triene and the products of its further conversion into cyclopropane derivatives—hexafluorobicyclo[5.1.0]octa-2,4-diene and hexafluorotricyclo[6.1.0.$0^{3,5}$]-non-6-ene—were identified.[227]



The catalytic conversion of the benzene ring into the cycloheptatriene system in the series of steroids on treatment with CH_2N_2 has been achieved by Müller and coworkers[212,228] as early as 1963 in relation to the dimethyl ether of β-oestradiol.

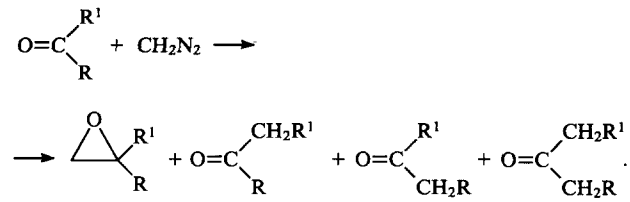
The low yield of the steroids **205** and the lack of other similar data did not promote further research on these lines. However, one may be optimistic about the possibility of converting complex aromatic compounds into higher homologues by varying the substituents in the aromatic ring and by using other catalytic systems, in particular rhodium compounds.



205 (~5%)

V. Synthesis of ketones by converting carbonyl compounds into higher homologues

The study of the reactions of diazomethane with aldehydes and ketones began with the discovery of diazomethane itself and embraced virtually all classes of organic compounds containing the carbonyl group—aliphatic, alicyclic, aromatic, and heterocyclic ketones, aldehydes,[229-234] ketosteroids,[235-238] and polycyclic ketones.[239] As a rule, the non-catalytic interaction of CH_2N_2 with aldehydes leads to ketones and epoxides, while its interaction with ketones leads to the higher homologues of the latter and/or the corresponding epoxides, ketones reacting with CH_2N_2 more slowly than aldehydes. The reaction is carried out predominantly in methanol and lasts from several hours to several days.



In this section, the results of catalytic reactions of diazomethane with carbonyl compounds will be briefly described. Interest in such reactions arose for the first time in the 1960s.

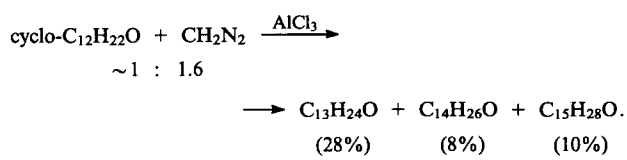
In 1960, two groups of investigators[240-242] established independently that boron trifluoride etherate increases appreciably the yield of higher homologues of ketones and the corresponding carbonyl compounds in the reactions of diazomethane with carbonyl compounds, suppressing at the same time the formation of epoxides. For example, the yield of cyclononanone, obtained from cyclooctanone and CH_2N_2 in the ring expansion reaction catalysed by $BF_3 \cdot OEt_2$, increases from 20% to 46% compared with the noncatalytic version.[243]

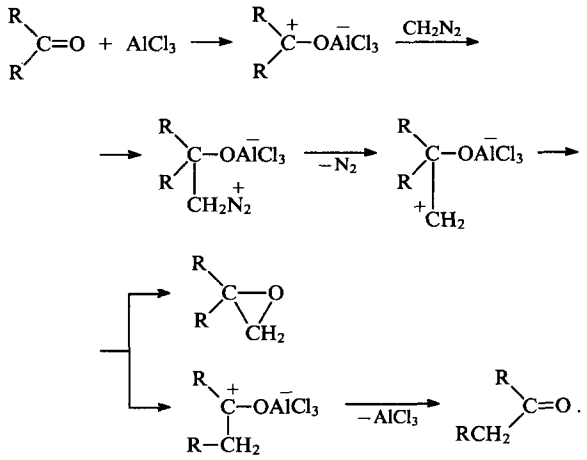
Together with boron trifluoride etherate, effective catalysts of the conversion of carbonyl compounds into higher homologues by diazomethane are also $ZnCl_2$, AlX_3 (X = Cl, Br, I), $GaCl_3$, $ZrCl_4$, HBF_4.[240-243] Table 8 presents examples of the catalytic conversion of cyclooctanone into its higher homologues on treatment with CH_2N_2.[243]

Table 8. Catalytic interaction of cyclooctanone with diazomethane.

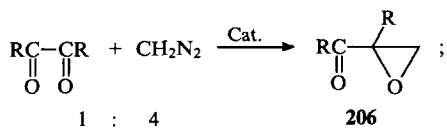
Catalyst		Yield of cycloalkanones (%)	
(2–4 mol%)	Ketone : CH_2N_2	C_9	C_{10}
$ZnCl_2$	1 : 1.2	25	–
AlX_3 (X = Cl, Br, I)	1 : 1.3	48–49	11–14
$AlEt_3$	1 : 1.3	49	19
$GaCl_3$	1 : 1.4	42	5
$ZrCl_4$	1 : 1.3	49	13
HBF_4	1 : 1.2	33	–
$TiCl_4$	1 : 1.2	10	–

It has been noted[243] that the reactivity of cyclic ketones falls appreciably on passing from cyclohexanone to cycloundecanone. Starting with the latter, ketones with an odd number of carbon atoms in the ring are less reactive than ketones with an even number of carbon atoms. This rule is illustrated, in particular, by the reaction of CH_2N_2 with cyclododecanone, as a result of which cyclopentadecanone is actually formed in a somewhat higher yield than cyclotetradecanone.





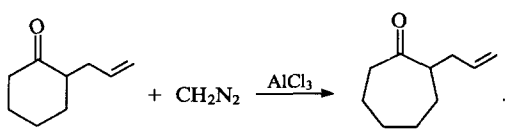
Depending on the nature of the carbonyl compound, the primary carbenium ion may be stabilised also by the carbonyl oxygen atom, which leads to the formation of the corresponding oxiran. In particular, the interaction of CH_2N_2 with α-diketones in the presence of both BF_3 and $AlCl_3$ leads mainly to the ketooxirans **206**.[242,243]



1 : 4 **206**

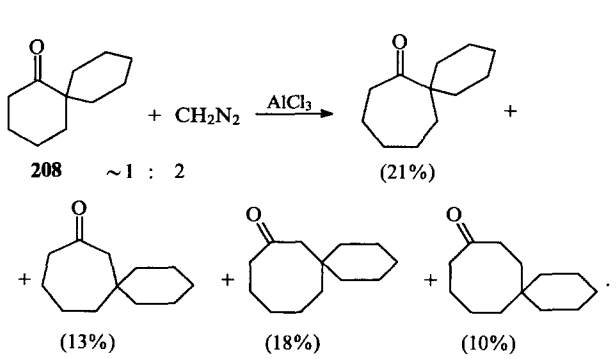
R = Ph, Me (54%, Cat. = $BF_3 \cdot OEt_2$).

The proposed mechanism has been confirmed also by the fact that the interaction of CH_2N_2 with 2-allylcyclohexanone in the presence of $AlCl_3$ involves predominantly the carbonyl group with formation of 2-allylcycloheptanone **207**, whereas the products of the conversion of the double bond into a cyclopropyl group were not detected.[243]



207 (~60%)

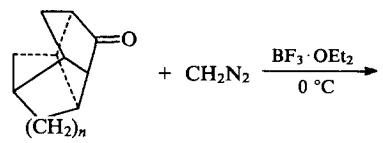
It is noteworthy that the insertion of methylene in the α-C–C bond takes place mainly from the side without substituents. However, in a number of instances such regioselectivity is not maintained. For example, the conversion of the spiran ketone **208** into a higher homologue leads to a mixture of cyclic ketones containing a carbonyl group in different positions relative to the spiran carbon atom.[244]



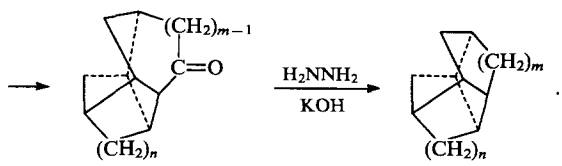
208 ~1 : 2 (21%)

(13%) (18%) (10%)

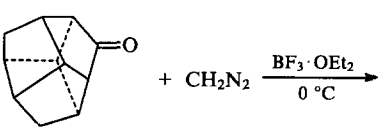
An example of the use of the ring expansion reaction on treatment with CH_2N_2 in the series of polycyclic ketones is provided by the synthesis of triblattanes—analogues of the D_3-twist-form of bicyclo-[2.2.2]octane, linked by different numbers of diagonal bridging groups. Thus the interaction of tetracyclo[4.3.0.$0^{2,5}$.$0^{3,8}$]nonan-9-one **209a** with an excess of CH_2N_2 in the presence of 1 equivalent of $BF_3 \cdot OEt_2$ and the subsequent Wolff–Kishner reduction of the resulting ketones leads to [*m*.0]-triblattanes **210a** (*m* = 2–4).[245] A mixture of [*m*.1]triblattanes **210b** (*m* = 2–7) and [*m*.1.1]-triblattanes **212** (*m* = 2–7) and [*m*.1.1]-triblattanes **212** (*m* = 2–6) has been obtained similarly from tetracyclodecanone **209b** and trishomocubanone **211** and it has been noted that in the absence of a catalyst the ketone **209b** does not react with diazomethane.[245,246]



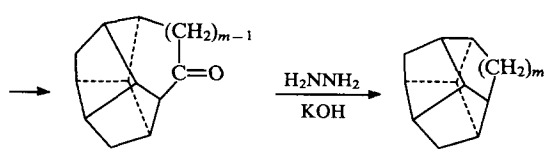
209 *n* = 0 (**a**), 1 (**b**)



210

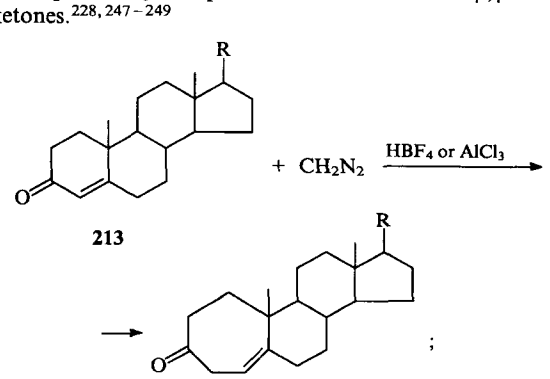


211



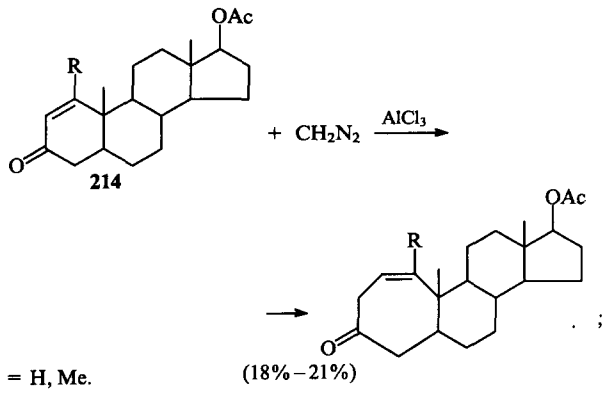
212

The non-catalysed reaction of diazomethane with α,β-unsaturated ketones usually proceeds as 1,3-dipole cycloaddition and leads to the formation of pyrazolines. On the other hand, the catalytic interaction of CH_2N_2 with conjugated ketones, carried out for the 3-ketosteroids **213** and **214**, proceeds as in the case of cycloalkanones—with ring expansion accompanied by the preferential formation of β,γ-unsaturated ketones.[228,247–249]



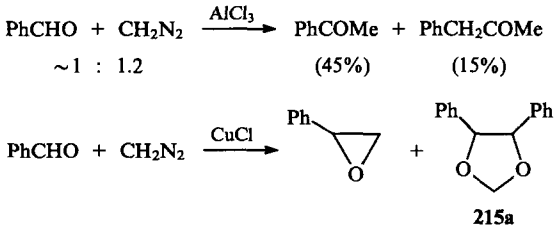
213

R = C_8H_{17} (40%); OAc (20%–30%); Ac (29%); $COCH_2OAc$ (31%).

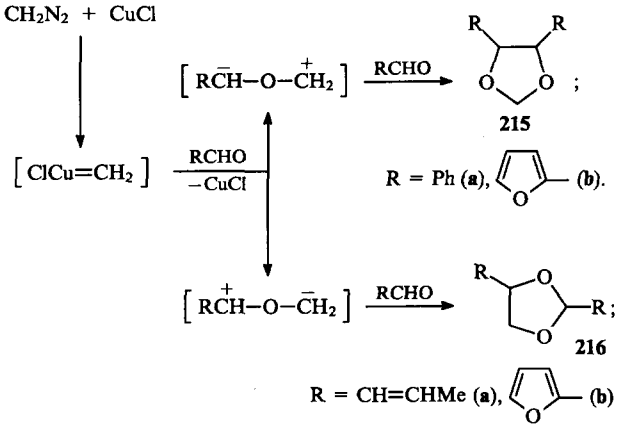


R = H, Me.

In certain cases, the use of transition metal Lewis compounds instead of acids alters significantly the mode of reaction of carbonyl compounds with CH_2N_2. Thus the interaction of benzaldehyde with CH_2N_2 in the presence of $AlCl_3$ leads to acetophenone and phenylacetone,[250] whereas in the presence of CuCl diazomethane reacts with an excess of benzaldehyde to form phenyloxiran and a mixture of isomeric 4,5-diphenyl-1,3-dioxolans **215a**.[251]



Crotonaldehyde and furfural react similarly with CH_2N_2 in the presence of CuCl, affording respectively the isomeric 2,4-dipropenyl-1,3-dioxolans **216a** in 18% yield, on the one hand, and 2,4-difuryl-1,3-dioxolans **216b** and 4,5-difuryl-1,3-dioxolans **215b** in an overall yield of 7%, on the other.

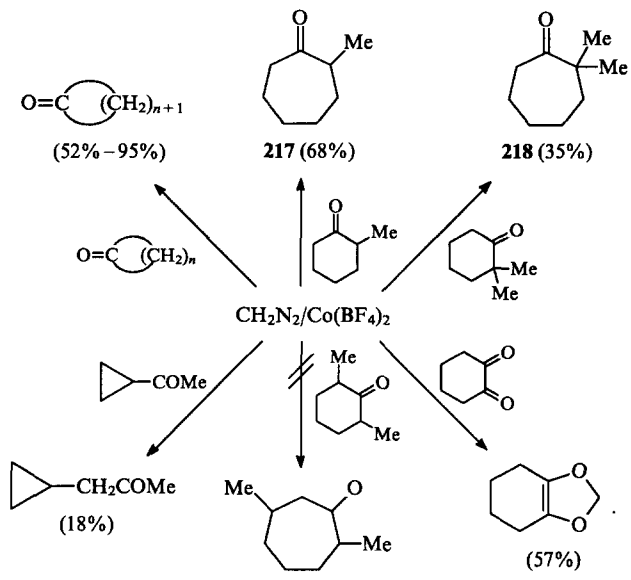


The formation of 1,3-dioxolans presupposes the addition of the methylene complex $[ClCu{=}CH_2]$ to the carbonyl group of the aldehydes and then the addition of a second aldehyde molecule to the intermediate 1,3-dipoles.[251]

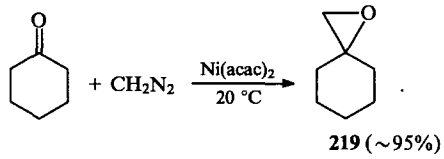
Cobalt tetrafluoroborate also behaves as an effective catalyst of the conversion of linear and cyclic carbonyl compounds into higher homologues by reaction with diazomethane. It makes it possible to obtain ketones with a specified number of carbon atoms in the chain under mild conditions, in one stage, with a high selectivity, and in high yields.[252] Thus the reaction of cyclohexanone with a threefold excess of CH_2N_2 in the presence of $Co(BF_4)_2$ at 0 °C leads to cycloheptanone in 81% yield. The formation of only an insignificant amount of polymethylene was noted under these conditions.

The catalytic activity of $Co(BF_4)_2$ depends extremely significantly on the structure of the initial cyclic ketone. The formal insertion of methylene, accompanied by ring expansion, involves the sterically least hindered C–C bond in the initial carbonyl compound. Thus α-methylcyclohexanones afford only α-methylcycloheptanones, for example compounds **217** and **218**, while α,α′-disubstituted cyclic ketones, for example 2,6-dimethylcyclohexanone, do not react at all under these conditions (Scheme 5).[252]

Scheme 5



The interaction of CH_2N_2 with cyclohexanone in the presence of $Ni(acac)_2$ takes place in a completely different manner. In this case, the only reaction product is oxiranylcyclohexane **219**, the yield of which reaches 95%.[252,253]



Thus the catalytic conversion of ketones into higher homologues with the aid of diazomethane is of preparative importance—especially in the synthesis of macrocyclic ketones.

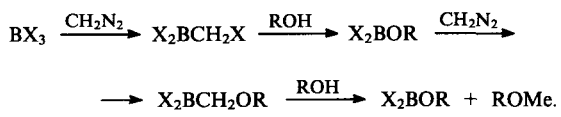
VI. Catalytic methylation of alcohols and amines by diazomethane

In this section we do not claim to provide a complete description of the available data on the reactions of diazomethane with compounds containing a mobile hydrogen atom at the nitrogen and oxygen atoms. Only a general assessment of the catalytic interaction of CH_2N_2 with alcohols and amines is given.

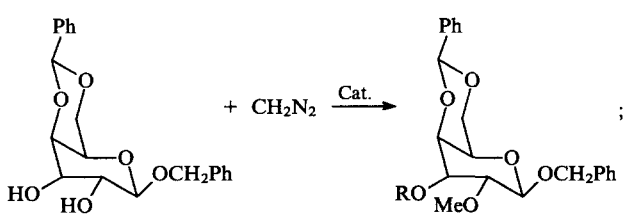
Alcohols are as a rule inert to CH_2N_2, but in the presence of Lewis acids such as $BF_3 \cdot OEt_2$, HBF_4, $AlCl_3$, $SnCl_2$, etc. they form methyl ethers in fairly satisfactory yields (40%–92%).[254–272] The effectiveness of the methylation is then to a large extent determined by the nature of the hydrocarbon substituents. In particular, it has been shown in relation to the methylation of pentyl and butyl alcohols in the presence of HBF_4 and $BF_3 \cdot OEt_2$ that the yield of the corresponding methyl ethers falls on passing from primary to tertiary alcohols ($k_{rel} \simeq 2 : 1.5 : 1$).[255–258] The shielding influence of the substituents is manifested to an even greater extent in the

methylation of cyclic alcohols. Thus in the presence of BF_3 or $AlCl_3$, unhindered cycloalkanols afford the methyl ethers in 80%–84% yields,[259] while, for example, isoborneol is not methylated at all under these conditions.[258]

According to the data of Bawn and Ledwith,[260] the mechanism of the methylation of alcohols by diazomethane in the presence of boron compounds involves the formation of boron alkoxides and the insertion of methylene in the B–O bond with the subsequent cleavage of the boron–carbon bond by the alcohol.



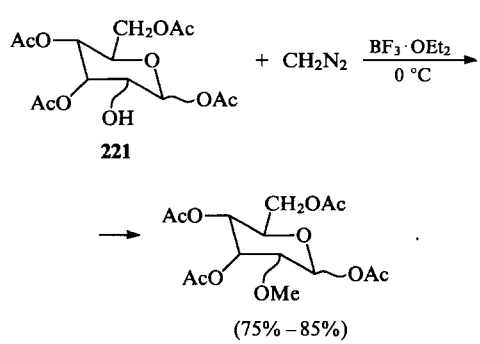
Diazomethane combined with boron trifluoride etherate or $SnCl_2 \cdot 2H_2O$ has been used in the carbohydrate chemistry for the complete or partial methylation of the hydroxy-groups.[261–265] For example, the methylation of the galacto-pyranoside **220** in the presence of $SnCl_2 \cdot 2H_2O$ involves preferentially one of the OH groups, whereas in the presence of $BF_3 \cdot OEt_2$ both hydroxy-groups are methylated.[261]



220

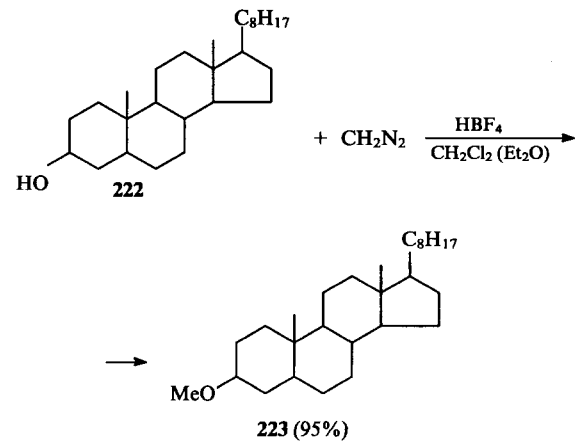
Cat. = $SnCl_2 \cdot 2H_2O$, R = H (91%);
Cat. = $BF_3 \cdot OEt_2$, R = Me (84%).

In the presence of $BF_3 \cdot OEt_2$, diazomethane proved to be an effective reagent also for the methylation of partially acylated carbohydrates, for example compound **221**, which in the case where the usual methylating agents (MeI, Me_2SO_4) are employed are readily hydrolysed by the bases used for this purpose.[263–265]



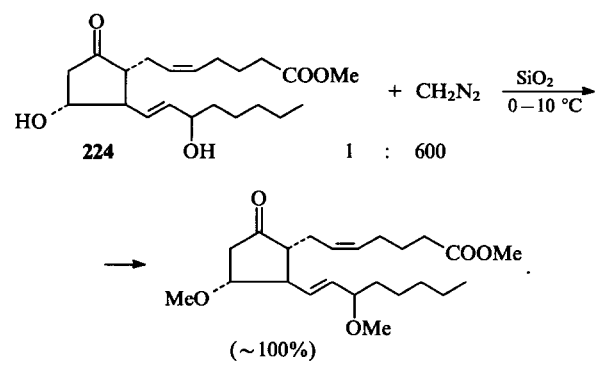
(75%–85%)

Catalytic methylation of steroid alcohols by diazomethane also takes place with high degrees of conversion.[258,266] Thus the interaction of cholestanol **222** with an excess of CH_2N_2 in the presence of HBF_4 leads to the formation of the methyl ether **223** in 95% yield.[266]



223 (95%)

Alcohols, including prostaglandins, terpene alcohols, and carbohydrates, are fairly successfully methylated by an excess of CH_2N_2 when acted upon by silica gel suspended in ether.[267] Despite the large excess of CH_2N_2, methylene is inserted selectively in the O–H bonds of prostaglandin **224** without affecting the keto-group and the double bonds.

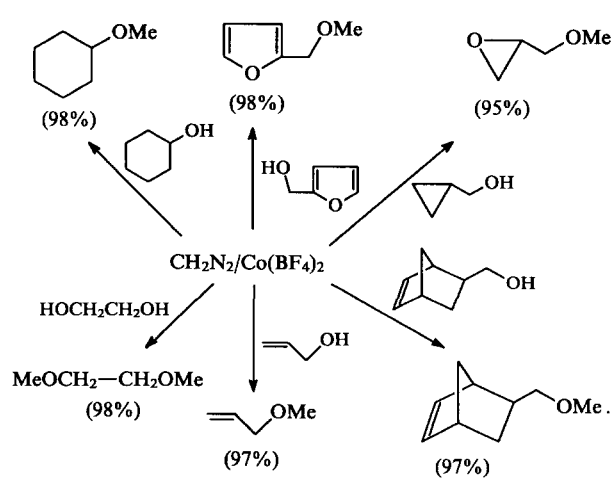


(~100%)

Later another method was proposed, according to which the alcohol adsorbed on silica gel was treated with gaseous diazomethane.[268] Even tertiary alcohols or sterically hindered phenols, such as 1-methylcyclohexanol or 2,6-di-isopropyl-phenol, afforded the corresponding methyl ethers in 99% and 79% yields on treatment with a large excess of CH_2N_2 (68 and 34 molar equivalents respectively) under these conditions.

Cobalt tetrafluoroborate also exhibits a high catalytic activity in the methylation of alcohols.[269,270] The use of 3–4 equivalents of CH_2N_2 then leads to *O*-methyl derivatives in high yields (Scheme 6). Reactivity of alcohols in the presence of

Scheme 6

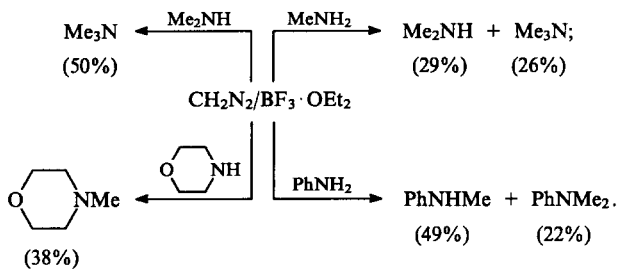


$Co(BF_4)_2$, can be arranged in the following sequence: secondary > primary > tertiary.[269] The double bonds of the unsaturated aliphatic or cyclic alcohols are then hardly involved, whereas under similar conditions palladium compounds catalyse mainly the conversion of double bonds into cyclopropyl groups.[155,156]

Like alcohols, primary and secondary amines are methylated by diazomethane in the presence of $BF_3 \cdot OEt_2$ or HBF_4, affording the corresponding methylamines in yields not exceeding 50%. The *N*-methylation of primary amines results in the formation as a rule of a mixture of the corresponding mono- and di-methylamines.[271-275]

Certain examples of the methylation of various amines by an excess of CH_2N_2 in the presence of $BF_3 \cdot OEt_2$ are presented in Scheme 7.

Scheme 7



Copper compounds (CuCN, CuCl) are also capable of catalysing the methylation of amines by diazomethane. The yields of the corresponding *N*-methylamines are then 32% and 25% respectively in the case of piperidine and morpholine.[276]

The use of $CF_3SO_3H-NEt_3$ as the catalyst of the methylation of secondary amines makes it possible to increase the yields of the methylamines to 68%–98%.[277,278]

$$R^1R^2NH + CH_2N_2 \xrightarrow[CH_2Cl_2]{CF_3SO_3H/Et_3N} R^1R^2NMe;$$

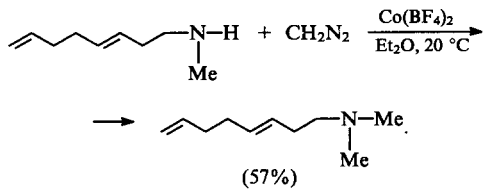
$R^1 = PhCH_2, Me_2CH, Me$; $R^2 = MeC_6H_4, PhCH_2, Ph$.

Cobalt compounds exhibit a high effectiveness in reactions of this kind. One of the best catalysts of the methylation of amines available at present is apparently $Co(BF_4)_2$, the use of which increases the yield of the methylated amines to 86%–98% even in the presence of a comparatively small excess of diazomethane.[269,279]

$$R^1R^2NH + CH_2N_2 \xrightarrow[Et_2O,\ 10-30\ ^\circ C]{Co(BF_4)_2} R^1R^2NMe;$$

1 : (1–4)

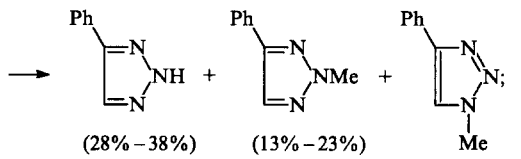
$R^1 = R^2 = Et$ (89%), Pr^i (86%);
$R^1 = Me$, $R^2 = Ph$ (98%);
$R^1 + R^2 = (CH_2)_5$ (88%),
$(CH_2)_2O(CH_2)_2$ (97%).



There are few data concerning other reactions of heteroatomic compounds with diazomethane, including those involving the use of catalysts, and they date back mainly to the 1950s–1960s.

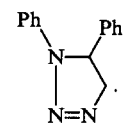
For example, it has been noted that the interaction of CH_2N_2 with benzonitrile or benzylideneaniline in the presence of alkylalanes ($AlEt_3$, Et_2AlCl, etc.) is accompanied by the addition of CH_2N_2 to the C≡N and C=N bonds with formation of five-membered heterocycles — triazoles and triazolines.[280]

$$PhC{\equiv}N + CH_2N_2 \xrightarrow[-78\ ^\circ C]{Et_2AlX}$$



$PhC{\equiv}N : CH_2N_2 : Et_2AlX = 2 : 1 : 1$

$$PhN{=}CHPh + CH_2N_2 \xrightarrow[-78\ ^\circ C]{Et_2AlX}$$



(35%–48%)

According to the results of a number of studies,[281-284] diazomethane interacts with silanes, germanes, and stannanes in the presence of copper powder, affording the products of the insertion of methylene in Si–Cl, Ge–Cl, Si–H, and Sn–H bonds, the reactions with chlorogermanes and hydrostannanes being much more effective than those with the corresponding silanes.

$$MCl_4 + CH_2N_2 \xrightarrow[Et_2O,\ -60\ ^\circ C]{Cu} Cl_3MCH_2Cl;$$

1 : 1 M = Ge (93%); Si (45%–47%).

$$MeMCl_3 + CH_2N_2 \xrightarrow[Et_2O,\ -60\ ^\circ C]{Cu} MeCl_2MCH_2Cl;$$

1 : 1 M = Ge (78%); Si (13%).

$$Et_3MH + CH_2N_2 \xrightarrow[Et_2O,\ -0\ ^\circ C]{Cu} Et_3MMe;$$

M = Sn (75%);
Ge (9%); Si (~1%).

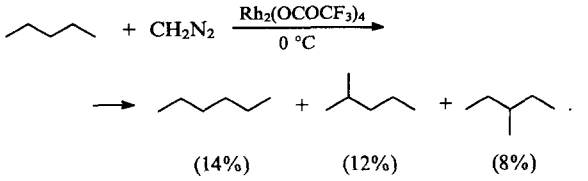
$$Cl_3Si{-}SiCl_3 + CH_2N_2 \xrightarrow[-30\ ^\circ C]{Cu} ClCH_2SiCl_2SiCl_2CH_2Cl.$$

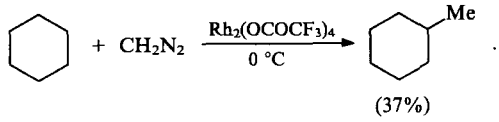
1 : 3 (28%)

$$Cl_3C{-}SiCl_3 + CH_2N_2 \xrightarrow[-60\ ^\circ C]{Cu} Cl_3C{-}SiCl_2CH_2Cl.$$

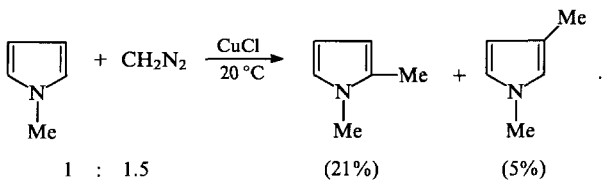
1 : 1 (22%)

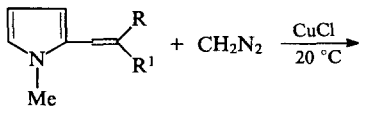
Despite the fact that the catalytic decomposition of CH_2N_2 does not generally yield the products of the insertion of methylene in the C–H bonds, nevertheless there is a possibility of the occurrence of such reactions. Thus the decomposition of CH_2N_2 in pentane or cyclohexane catalysed by $Rh_2(OCOCF_3)_4$, leads to the partial methylation of the latter.[252]



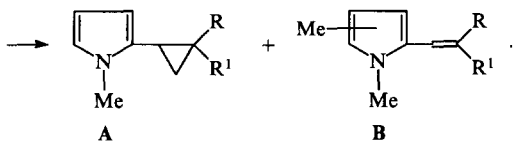


The formation of an appreciable amount of the products of the insertion of methylene in the C–H bonds in the CuCl-catalysed decomposition of CH_2N_2 has been observed also in the case of *N*-methylpyrroles.[143] Even when CH_2N_2 interacts with 2-alkenyl-*N*-methylpyrroles **225**, the products of the insertion of methylene into the vinyl C–H bonds of the pyrrole ring are formed together with the cyclopropane adducts.[143]





225



A **B**

R	R^1	Yield of **A** (%)	Yield of **B** (%)
H	H	18	6
H	Me	6	15
Me	Me	8	18

VII. Conclusion

The data presented demonstrate the great potential possibilities of the use of diazomethane in laboratory practice for the modification of various classes of organic compounds. Furthermore, convincing evidence has been obtained recently for the possibility of the simultaneous generation and catalytic decomposition of diazomethane, which significantly enhances the prospect for its application in fine organic synthesis. In the first place, this applies to the reactions involving the direct conversion of unsaturated compounds into cyclopropane derivatives, which leads to the formation of cyclopropane synthons. Systematic study of these reactions in the presence of a number of catalytic systems made it possible not only to establish the characteristic features of the conversion of various double bonds into cyclopropyl groups, to estimate the effectiveness of the catalysts based on transition and non-transition metals, and to put forward the mechanisms of their reaction with diazomethane, but it has also been possible to develop a safe method for the conversion of many unsaturated compounds, including those with functional groups in the molecule, into cyclopropane derivatives.

Considerable advances in the attainment of this aim have been associated with the use of palladium compounds as process catalysts, which ensure a high degree of conversion of the initial olefins into cyclopropanes combined with a minimal consumption of diazomethane and hence of *N*-methyl-nitrosoamides used for its generation *in situ*.

The employment of metal complex catalysis in the chemistry of diazomethane has also made it possible to achieve the conversion of benzenes into cyclohepta-1,3,5-trienes and the selective conversion of ketones into higher homologues and the methylation of alcohols and amines. Apart from the copper compounds and Lewis acids put forward for these purposes as early as the end of the 1950s, other more effective catalysts are being used nowadays, for example $Rh_2(OCOCF_3)_4$ for the synthesis of cycloheptatrienes and $Co(BF_4)_2$ for the conversion of ketones into higher homologues and the methylation of alcohols and amines.

The successive development of studies on these lines will be determined by the further search for active and highly selective catalysts of the decomposition of diazomethane and of the transfer of the methylene fragment to the substrate molecule, including procedures involving the modification of the ligand sphere of transition metal compounds, and also by the advances in the elucidation of the mechanisms of the catalytic reactions with participation of diazomethane.

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