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Organometallic Derivatives of Diazoalkanes

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The methods of synthesis and properties of organometallic derivatives of diazo-compounds are examined, attention being concentrated on the influence of the metal or the organometallic fragment on the structure and reactivity of the diazo-compounds. Studies on the use of metal-containing diazoalkanes as precursors of carbynes and α-metallated carbenes as well as studies on the reactivity of the latter are discussed.
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I. INTRODUCTION

Two types of organometallic derivatives of diazoalkanes are known. The first includes only two compounds: 1-diazo-3-triethylsilyl-2-propanone and ferrocenyl(phenyl)diazomethane[1,2]; in these compounds the metal atom and the diazo-group are separated by hydrocarbon fragments. The second type includes α-metallated diazoalkanes in which one of the carbon atoms is linked both to the diazo-group and to the metal atom. The chemistry of these compounds is developing vigorously, because, apart from their continuously expanding applications in organometallic synthesis, they are a potential source of carbynes—unstable derivatives of univalent carbon. Furthermore, they are used extensively as precursors of α-metallated carbenes—short-lived species with a high and unusual reactivity. For example, singlet α-silylcarbenes frequently isomerise to sila-alkanes $R_2Si{=}CR'_2$—unstable intermediates with a $(p{-}p)\pi$ bond between the carbon and silicon atoms.

The considerable advances in the studies on the structure and reactivity of carbynes, α-metallated carbenes, and sila-alkanes are closely related to the progress in the chemistry of organometallic derivatives of diazo-compounds. The most complete compilation of data on the chemistry of α-metallated diazoalkanes (up to 1969) is given in Lappert and Poland's review[3]. Latest advances in the chemistry of organophosphorus diazo-compounds are discussed in other reviews[4,5].

II. METHODS OF SYNTHESIS

1. Metallation of Aliphatic Diazo-Compounds

In consequence of the enhanced CH acidity of diazoalkanes of the type $HC(N_2)R$, the latter are readily metallated by methyl-, n-butyl-, and phenyl-lithium. Diazomethyl-lithium[6-9], which is involved in a tautomeric equilibrium with lithium isocyanamide[10,11], trimethylsilyldiazomethyl-lithium[12-15], ethyl lithiodiazoacetate[16-20], and dialkyl lithiodiazomethylphosphonates[15] have been obtained in this way:

$$R'Li + HC(N_2)R \rightarrow LiC(N_2)R + R'H \quad ;$$
$$R{=}H,\ Me_3Si,\ COOEt,\ (MeO)_2P(O){-},\ \text{or}\ (EtO)_2P(O){-}$$

The metallation of diazoacetic ester requires low temperatures (between −110° and −65°C), while Me_3SiCHN_2 is smoothly metallated at 0 °C. The reaction of methyl-lithium with diazoethane in ether at 20 °C leads to a complex mixture of products[21]. Lithium diisopropylamide smoothly metallates α-diazoketones[17]. The reaction of the latter with butyl-lithium is complex:

$$\text{iso-}Pr_2NLi + HC(N_2)COR \xrightarrow[-70^\circ]{THF} LiC(N_2)COR \quad .$$

$Me_3SiC(N_2)K$ and $(EtO)_2P(O)C(N_2)K$ have been obtained by treating diazoalkanes with potassium t-butoxide[15].

Silver oxide metallates diazoacetic ester[22-24], diazoketones, and phosphorus-containing diazoalkanes[25,26], but the yield of silver derivatives depends greatly on the quality of the oxide[17]:

$$Ag_2O + 2HC(N_2)R \rightarrow H_2O + 2AgC(N_2)R \quad .$$

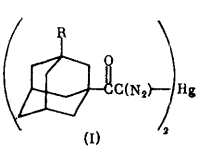
The reaction of silver acetylacetonate with dimethyl diazomethylphosphonate leads to a quantitative yield of $AgC(N_2)P(O)(OMe)_2$.[27] Treatment of silver acetate with an excess of CH_2N_2 in ether in the presence of pyridine at −5 °C yielded the complex $Ag_2CN_2.C_6H_5N$. When the complex is kept in vacuo at 25 °C, Ag_2CN_2, an explosive light-sensitive compound, is formed[28].

Diazoacetic ester is metallated at −70 °C by alkylmagnesium halides and dialkylmagnesium compounds[17], while at 0 °C Grignard reagents attack the diazo-group[29,30].

Yellow mercury(II) oxide reacts under mild conditions with the nitrile and esters of diazoacetic acid, diazoketones, and ethyl diazomethylphosphonate[25,31-37]:

$$HgO + 2HC(N_2)R \rightarrow H_2O + Hg[C(N_2)R]_2$$

Mercury derivatives of adamantoyldiazomethane (I) were obtained recently by this procedure[38]:



(I)

R = H, Cl, or Br .

Mercuration of dimethyl diazomethylphosphonate by mercury acetylacetonate leads to $Hg[C(N_2)P(O)(OMe)_2]_2$ in 80% yield[27].

Asymmetric alkyl- and aryl-mercuridiazoalkanes have been obtained by the reaction of diazo-compounds with arylmercury hydroxides[39], arylmercury silylamides[40], and organomercury

ethoxides[39]. The last compounds were synthesised *in situ* by treating RHgCl with alcoholic potassium ethoxide:

$$PhHgOH + HC(N_2)COMe \xrightarrow{-H_2O} PhHgC(N_2)COMe$$

$$RHgN(SiMe_3)_2 + HC(N_2)COOEt \rightarrow RHgC(N_2)COOEt + (Me_3Si)_2NH$$

$$RHgCl + EtOK \xrightarrow{+EtOH} RHgOEt \xrightarrow[-EtOH]{+HC(N_2)R'} RHgC(N_2)R' \quad ;$$

R = Me, t-Bu, $PhCH_2$, or Ph; R′ = CN, Me, Ph, COMe, COOMe, or COOEt.

We may note that the reactions of diazomethane with $RHgN(SiMe_3)_2$ and RHgOEt lead to crystalline readily detonated disubstituted derivatives of diazomethane regardless of the reactant ratio[39,40], for example:

$$2\,RHgN(SiMe_3)_2 + CH_2N_2 \rightarrow (RHg)_2CN_2 + 2\,(Me_3Si)_2NH \quad .$$

When bis[bis(trimethylsilyl)amide]mercury or mercury acetate is treated with diazomethane[40,41] in ether, the highly explosive polymeric diazomethylenemercury $(HgCN_2)_n$ is formed. According to Wright et al.[41], the latter reaction also leads to bis(diazomethyl)mercury $Hg(CHN_2)_2$, but attempts to repeat the synthesis of this diazomethane derivative were unsuccessful[33,40]. Polymeric diazomethylenezinc and diazomethylenecadmium have been obtained similarly[40]:

$$M[N(SiMe_3)_2]_2 + CH_2N_2 \rightarrow (MCN_2)_n + 2\,(Me_3Si)_2NH \quad ;$$

M = Hg, Zn, or Cd.

The above method of synthesis is fairly universal. Thus the interaction of diazomethane with organometallic compounds containing metal–nitrogen bonds leads to diazomethane derivatives of the type $(Me_nM)_2CN_2$, where M = germanium, arsenic, and their analogues, as well as thallium[6,40,42–45], for example:

$$(Me_2TlNMe_2)_2 + CH_2N_2 \rightarrow (Me_2Tl)_2CN_2 + 2Me_2NH \quad ;$$

$$2Me_2BiN(Me)SiMe_3 + CH_2N_2 \rightarrow (Me_2Bi)_2CN_2 + 2Me_3Si(Me)NH \quad .$$

Monometallated diazomethane derivatives Me_3GeCHN_2 and Me_2AsCHN_2 have been obtained in the same way but at controlled temperatures, using Me_3SnCl as the complex-forming agent and in the prsence of a large excess of diazomethane[44,46], for example:

$$Me_3GeNMe_2 + CH_2N_2 + Me_3SnCl \xrightarrow[-80°]{Et_2O} Me_3GeCHN_2 + Me_3SnCl \cdot Me_2NH \quad .$$

Diazo-compounds with two different organometallic fragments have been obtained analogously[47]:

$$R_nM{-}NR_2' + Me_2AsCHN_2 \rightarrow \begin{matrix} Me_2As \\ \diagdown \\ R_nM \end{matrix}\!\!>CN_2 + R_2'NH \quad ;$$

$R_nM = Me_3Si$, Me_3Ge, Me_3Sn, Me_3Pb, Me_2Sb, or Me_2Bi;

$$Hg[N(SiMe_3)_2]_2 + 2Me_2AsCHN_2 \rightarrow Hg[C(N_2)AsMe_2]_2 + 2\,(Me_3Si)_2NH \quad .$$

A large series of α-metallated diazocarbonyl compounds, derivatives of zinc-subgroup elements[40,48], germanium[40,45,49–53], and arsenic[43,54], have been obtained by treating compounds having metal–nitrogen bonds with α-diazoketones and diazoacetate esters, for example[50]:

$$R_{4-n}Sn(NR_2')_n + n\,HC(N_2)COOEt \rightarrow R_{4-n}Sn[C(N_2)COOEt]_n + n\,R_2'NH \quad ;$$

R = Me, Et, t-Bu, or Ph; R′ = Me or Et; $n = 1, 2$.

Methyl diazoacetate is readily metallated by trialkylmethoxystannanes[52], but this reaction requires more severe conditions than the previous ones (≥100 °C):

$$R_3SnOMe + HC(N_2)COOMe \rightarrow \underset{(85\%)}{R_3SnC(N_2)COOMe} + MeOH \quad ;$$

R = Et or n-Bu.

Bromotrimethylsilane silylates diazoacetate esters in the presence of amines[52], while chlorotrimethylsilane does not enter into similar reactions[6]:

$$Me_3SiBr + HC(N_2)COOR + Et_3N \xrightarrow[C_6H_6]{80°} Me_3SiC(N_2)COOR + Et_3N \cdot HBr \quad ;$$

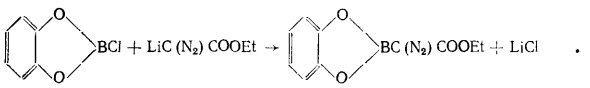
R = Me or Et.

2. Synthesis from α-Metallated Diazoalkanes

Ethoxycarbonyldiazomethyl-lithium reacts under mild conditions (below −50 °C) with halogenotrimethylsilanes, halogenotrimethylplumbanes, and chlorotributylstannane[16,17,49]:

$$R_3MCl + LiC(N_2)COOEt \xrightarrow{THF} R_3MC(N_2)COOEt + LiCl \quad .$$

A boron-containing diazoacetic ester has been obtained analogously[17]:



The interaction of trimethylsilyldiazomethyl-lithium $Me_3SiC(Li)N_2$ with Me_3SiCl in a pentane–hexane mixture at temperatures between −90° and −100 °C leads to bis(trimethylsilyl)diazomethane[14]. The reactions of diazomethyllithium with Ph_3GeCl, Me_3SnCl, and Ph_3SnBr also lead to dimetallated derivatives of diazomethane $(R_3N)_2CN_2$ (M = Ge or Sn).[6] It has been suggested[6] that the R_3MCHN_2 formed initially is metallated by a second mole of diazomethyl-lithium, this being followed by the reaction of $R_3MC(Li)N_2$ with the initial organogermanium or organotin halide. The attempts to obtain diazomethyl derivatives of zinc and cadmium by treating $ZnCl_2$ or $CdCl_2$ with diazomethyl-lithium were unsuccessful[33].

α-Mercurated diazoalkanes have been used widely for the synthesis of metal-containing diazo-compounds. Thus lithium-,[16,55] silicon-,[56–59] germanium-[49] and tin-containing[49,58] derivatives of diazoacetic ester have been obtained by transmetallation:

$$Hg[C(N_2)COOEt]_2 + 2RLi \xrightarrow[-70°]{THF} R_2Hg + 2LiC(N_2)COOEt$$

R = n-Bu, Ph, EtS, t-BuS.

$$Hg[C(N_2)COOEt]_2 + (R_3M)_2S \rightarrow HgS + 2R_3MC(N_2)COOEt \quad ;$$

$R_3M = Me_3Si$, Me_3Sn, or Ph_3Sn.

$$Hg[C(N_2)COOEt]_2 + 2R_3SiI \rightarrow HgI_2 + 2R_3SiC(N_2)COOEt \quad .$$

However the method of synthesis of $LiC(N_2)COOEt$ examined in the previous section is preferable.

A general method of the synthesis of α-metallated diazocarbonyl compounds which are derivatives of Group IVB elements is based on radical exchange reactions between bis(triethylsilyl)mercury or its analogues and mercurated diazocarbonyl compounds. In this case the exchange reactions are accompanied by demercuration[60–63]:

$$(R_3M)_2Hg + Hg[C(N_2)C(O)R']_2 \rightarrow 2R_3M{-}Hg{-}C(N_2)C(O)R' \rightarrow$$

$$\rightarrow 2Hg + 2R_3MC(N_2)C(O)R' \quad ;$$

$R_3M = Et_3Si$, $MePh_2Si$, Et_3Ge, or $(Me_3CCH_2)_3Sn$; R′ = Me, Et, OMe, OEt, or Ph.

The esters of stannylated diazoacetic acids react exothermically with trialkylhalogenosilanes, forming the corresponding silyl derivatives (yields 75–90%):[52]

$$R_3SnC(N_2)COOMe + R_3'SiBr \rightarrow R_3'SiC(N_2)COOMe + R_3SnBr \quad ;$$

R = Et or n-Bu; R′ = Me or Et.

3. Other Methods of Synthesis

Trimethylsilyldiazomethane can be obtained by treating with alkali *N*-(trimethylsilylmethyl)-*N*-nitrosourea[64,65,66] (a procedure analogous to the synthesis of diazomethane[67]) and

methyl[68] or ethyl[65] *N*-(trimethylsilylmethyl)-*N*-nitrosocarbamates and also by the decomposition of *N*-(trimethylsilylmethyl)-*N*-nitrosoacetamide with β-phenylethylamine[13,55]:

$$Me_3SiCH_2N(NO)CONH_2 \xrightarrow{20\%\ KOH} Me_3SiCHN_2 \quad (53—70\%) \quad ;$$

$$Me_3SiCH_2N(NO)COOR \xrightarrow[Et_2O,\ 20^\circ]{NaOH} Me_3SiCHN_2 \quad (\sim 25\%) \quad ;$$

$$Me_3SiCH_2N(NO)COMe \xrightarrow{PhCH_2CH_2NH_2} Me_3SiCHN_2 \quad .$$

Like the usual diazoalkanes[69], their α-silylated analogues have been obtained by oxidising hydrazones by metal oxides[57,70] and by treating *N*-tosylhydrazines with alkali[71]:

$$Ph_3SiCOPh + N_2H_4 \rightarrow Ph_3SiC(Ph)=NNH_2 \xrightarrow[or\ HgO]{MnO_2} Ph_3SiC(N_2)Ph \quad ;$$

$$Ph_3SiCOR + TsNHNH_2 \rightarrow Ph_3SiC(R)=NNHTs \xrightarrow[or\ MeONa]{n\text{-}BuLi} Ph_3SiC(N_2)R \quad ;$$

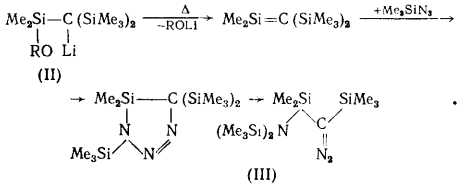
R=Me, Et, Ph, 4-FC_6H_4, 4-ClC_6H_4, 4-BrC_6H_4, or $PhCH_2$.

Phenyl(triphenylgermyl)diazomethane, phenyl(trimethylsilyl)-diazomethane[71], and phenyl(trimethylsilyl)diazomethane labelled with ^{13}C at the diazo carbon atom have also been obtained using tosylhydrazine[72-74].

γ-Triethylsilylacetyldiazomethane has been synthesised by treating triethylsilylacetyl chloride with diazomethane[1]:

$$Et_3SiCH_2COCl + CH_2N_2 \xrightarrow[-5—0^\circ]{Et_2O} Et_3SiCH_2\underset{\underset{O}{\|}}{C}CHN_2 \quad .$$

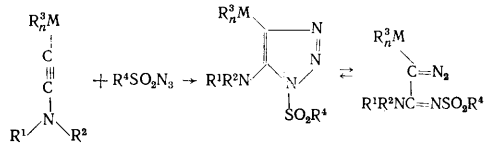
According to the data of Wiberg and coworkers[75], the thermolysis of compound (II) involves the intermediate formation of 1,1-dimethyl-2,2-bis(trimethylsilyl)-1-silaethylene. Its reaction with trimethylsilyl azide leads to a silicon-containing diazomethane (III) in a yield up to 50%:



(II) (III)

The second product of this unusual reaction is bis(trimethylsilyl)diazomethane.

It has been shown[76-78] that the reaction of sulphonyl azides with organometallic ynamines proceeds regiospecifically and leads to 5-amino-1,2,3-triazoles, which, depending on the nature of the substituents R^1, R^2, R^3, R^4, either wholly isomerise to α-metallated diazoacetamidines or are involved in a tautomeric equilibrium with the latter:



R^1, R^2, R^4 = alkyl, or aryl; $R^3_nM = R^1_2As$, R^1_2Sb, $Ph_2P(O)$—, $Ph_2P(S)$—, R^1_3Si, R^1_3Ge, or R^1_3Sn.

III. REACTIONS WITHOUT THE EVOLUTION OF NITROGEN

1. Reactions not Involving the Diazo-Group

Trimethylsilyldiazomethyl-lithium reacts with D_2O, forming Me_3SiCDN_2, which is of preparative interest[12]. Reactions with ketones in a mixture of tetrahydrofuran (THF) and pentane at −100 °C lead to 1-diazo-1-(trimethylsilyl)-2-alkanols—a new type of organosilicon bifunctional compound[13]:

$$Me_3SiC(Li)N_2 + RCOR' \xrightarrow[-100^\circ]{hydrolysis} Me_3SiC(N_2)C(OH)RR' \quad (65—85\%) \quad ;$$

R=H, Me; R'=Me, Ph; or R, R'=$(CH_2)_5$.

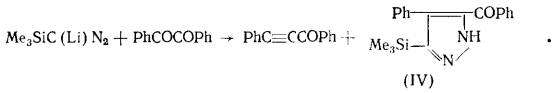
Benzophenone, whose reaction with $Me_3SiC(Li)N_2$ leads to diphenylacetylene (yield up to 85%), is an exception[15,79].

The reactions of the lithio-derivative of diethyl diazomethylphosphonate with diaryl ketones and with 2-benzoylthiophen and 3-benzoylpyridine proceed analogously:

$$(EtO)_2P(O)C(Li)N_2 + 4\text{-}RC_6H_4COPh \xrightarrow[-78\rightarrow 20^\circ]{THF} \xrightarrow{H_2O} 4\text{-}RC_6H_4C{\equiv}CPh \quad (66—94\%) \quad ;$$

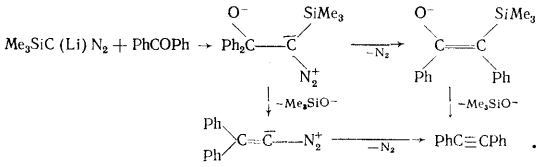
R=H, Cl, or MeO .

One of the products of the reaction of trimethylsilyldiazomethyl-lithium with benzil is pyrazole (IV)†:



(IV)

It has been suggested[15] that in these reactions the nucleophilic addition of the anion [for example, $Me_3SiC(N_2)^-$] to the carbonyl group is accompanied by the Wolff rearrangement, which involves the evolution of nitrogen and the elimination of the Me_3SiO^- anion (the sequence of these stages has not been elucidated):



A series of diazo-esters have been obtained in reactions of ethoxycarbonyldiazomethyl-lithium with alkyl halides, benzoyl chloride, benzaldehyde, and certain ketenes in THF at −50 °C or lower temperatures[16-18], for example:

$$LiC(N_2)COOEt + PhCOCl \rightarrow LiCl + PhCOC(N_2)COOEt \quad ;$$

$$LiC(N_2)COOEt + RCOR' \rightarrow RR'C(OH)C(N_2)COOEt \quad .$$

The yield of diazoesters $RR'C(OH)C(N_2)COOEt$ can be significantly increased when the reaction is carried out without the isolation of $LiC(N_2)COOEt$, by adding n-butyl-lithium to an equimolar mixture of diazoacetic ester and the carbonyl compound[17,19,20]:

$$HC(N_2)COOEt + RCOR' \xrightarrow[-60^\circ]{+BuLi} RR'C(OH)C(N_2)COOEt \quad ;$$

R=H or Me, R'=Me or Ph; R, R'=$(CH_2)_4$, $(CH_2)_5$ or $(CH_2)_6$.

An analogous procedure has been proposed for the synthesis of β-hydroxy-α-diazoketones (yields up to 95%). In this case the lithio-derivative of the diazoketone is formed *in situ* on treatment with lithium diisopropylamide:

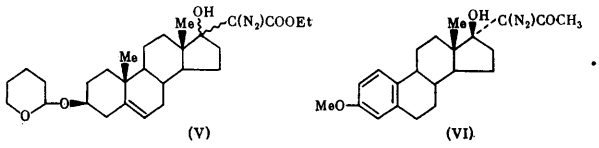
$$HC(N_2)\underset{\underset{O}{\|}}{C}R + R^1COR^2 \xrightarrow[-70^\circ]{iso\text{-}Pr_2NLi} R^1R^2C(OH)C(N_2)\underset{\underset{O}{\|}}{C}R$$

R=Me, Ph, 4-$MeOC_6H_4$, or t-Bu; R^1 = H or Me; R^2=Me, Ph, or PhCH=CH.

The diazoester (V) has been obtained in this way[17], i.e. by

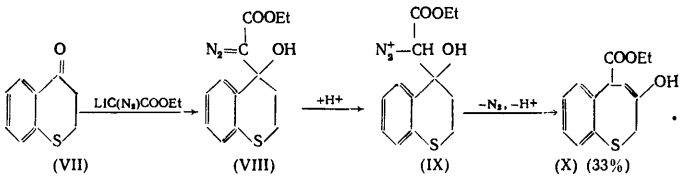
† The structure of a silylated enol was erroneously attributed to this product in a preliminary communication[79].

treating a mixture of 3β-(tetrahydro-2-pyranyloxy)-5(6)-androsten-17-one and diazoacetic ester with n-butyl-lithium, while treatment of a mixture of 3-methoxy-1,3,5,(10)-oestratrien-17-one and diazoacetone with lithium diisopropylamide leads to the diazoketones (VI):



(V) (VI)

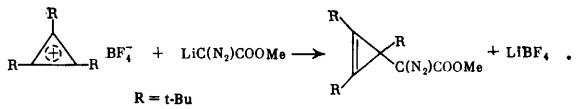
It has been shown recently[19] that the nucleophilic addition to $LiC(N_2)COOEt$ to the carbonyl group of 4-thiochromanone (VII) leads to the diazoester (VIII). Its treatment with a methanol solution of HCl generates the diazonium ion (IX)#, which then eliminates a nitrogen molecule and a proton, being converted into ethyl 2,3-dihydro-4-hydroxy-1-benzothiepin-5-carboxylate (X):



(VII) (VIII) (IX) (X) (33%)

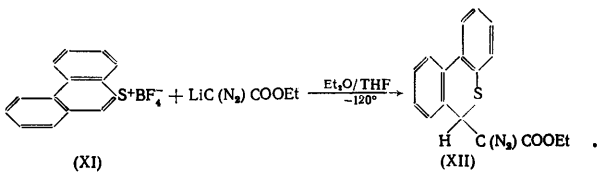
The ester of 1,3-dihydro-4-hydroxy-2-benzothiepine-5-carboxylic acid was synthesised similarly[19].

It is known[17] that the reactions of $LiC(N_2)COOEt$ with alkyl halides give low yields of compounds of the type $RC(N_2)COOEt$. On the other hand, tri-t-butylcylcopropenylium tetrafluoroborate reacts smoothly with methoxycarbonyldiazomethyllithium[81]:



R = t-Bu

A new synthesis of dienzo[*b*,*d*]thiepin[82,83], involving the reaction of dibenzothiopyrylium tetrafluoroborate (XI) with $LiC(N_2)COOEt$, has been described[82,83]; the diazo-compound (XII) is formed in 32% yield:



(XI) (XII)

The silver derivatives of diazoacetic ester[22,24], diazoketones[22], and diphenyl(diazomethyl)phosphorane[4] are readily alkylated by alkyl halides:

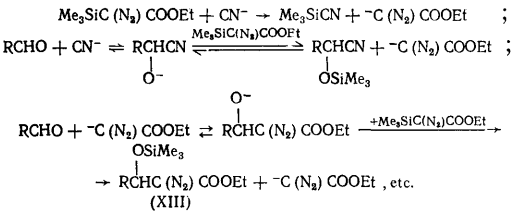
$$AgC(N_2)COOEt + BrCN \xrightarrow{Et_2O} BrC(N_2)COOEt + AgCN \quad .$$

The reactions of iodine or bromocyanogen with $AgC(N_2)$. .COOEt and $AgC(N_2)P(O)(OMe)_2$ also do not involve the diazo-group[5,22], for example:

$$AgC(N_2)COR + R'X \rightarrow AgX + R'C(N_2)COR \quad .$$

Diazoesters of the $XC(N_2)COOEt$ (X = Cl, Br, or I) series have been obtained in addition by treating mercuribisdiazoacetic ester with thionyl chloride, bromine, or iodine[23,84]. However, the treatment of mercuribis(adamantoyldiazomethane) with a solution of ICl in chloroform (at ~10 °C) yielded adamantyl chlorodi-iodomethyl ketone as a result of the substitution of the diazo-group and the mercury atom by halogen atoms[85]. The reaction of $Hg[C(N_2)COOEt]_2$ with bromotriphenylmethane leads to the ethyl ester of 2-diazo-3,3,3-triphenylpropionic acid[22].

It has been shown recently[86] that ethyl α-(trimethylsilyl)-diazoacetate reacts exothermically with aliphatic and aromatic aldehydes, forming adducts (XIII) in nearly quantitative yields. The reaction is catalysed by the complex KCN.18-crown-6- and includes initiation and catalytic stages:



When trimethylsilyldiazoacetic acid ester interacts with ethyl chlorocarbonate at 100 °C, the Si–C bond is cleaved selectively[52]:

$$Me_3SiC(N_2)COOEt + ClCOOEt \rightarrow Me_3SiCl + N_2C(COOEt)_2 \quad .$$

The reaction of stannylated diazoketones with methanol results in the selective heterolysis of the Sn–C bond[52]:

$$Bu_3SnC(N_2)COR + MeOH \rightarrow Bu_3SnOMe + HC(N_2)COR \quad ;$$

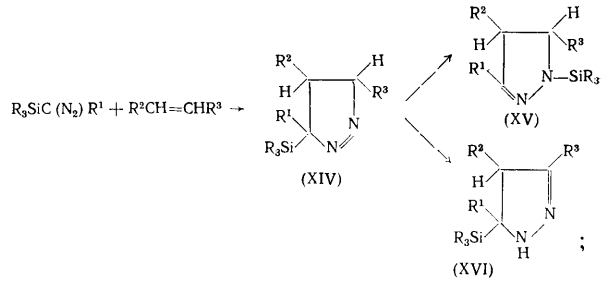
R = Me or Ph.

2. 1,3-Dipolar Cycloaddition Reactions

The formation of five-membered heterocycles in reactions with dipolarophiles is characteristic of the usual diazoalkanes[87,88] as well as their α-metallated analogues. In particular the cycloaddition of α-silyldiazoalkanes to diethyl fumarate, acrylonitrile, methyl acrylate, and analogous compounds with activated C=C bonds has been most thoroughly investigated[59,64,65,89–92]. It has been shown by ^1H NMR [89,92] that the primary products are 3-organosilyl-Δ^1-pyrazolines (XIV). The majority of Δ^1-pyrazolines are known to isomerise readily to Δ^2-pyrazolines[87,88,93]. The isomerisation of the heterocycles (XIV) leads to compounds (XV) as a result of the 1,3-migration of the R_3Si group or to their analogues (XVI) if the process is accompanied by the 1,3-transfer of a hydrogen atom. A rearrangement of the first type is characteristic of the diazoalkanes $R_3SiC(N_2)R^1$ with R^1 = Ph or COOEt, while that of the second type is characteristic of the

For details of the methods for the generation and reactions of aliphatic diazonium ions, see Kirmse's review[80].

diazoalkanes with $R^1 = H$ or Me:[65,89,92]



(XIV) (XV) (XVI)

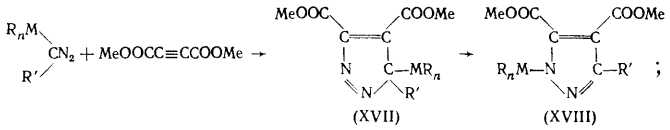
R = Me or Ph; R^1=Ph, COOEt, Me, or H;
R^2 = H or COOEt; R^3=CN, COMe, COOMe, or COOEt.

It has been shown for diethyl fumarate[92] that the relative rates of cycloaddition of diazoalkanes decrease in the sequence

$$\underset{1}{Me_3SiC(N_2)Me} > \underset{2\cdot10^{-2}}{Me_3SiC(N_2)Ph} > \underset{25\cdot10^{-4}}{Ph_3SiC(N_2)Me} > \underset{\sim2.5\cdot10^{-6}}{Ph_3SiC(N_2)Ph} > \underset{\sim2.5\cdot10^{-7}}{Me_3SiC(N_2)COOEt}.$$

The authors[92] believe that the rates of these reactions are determined by the degree of $(p \rightarrow d)_\pi$ interaction of the silicon and diazo-carbon atoms in the compound $R_3SiC(N_2)R^1$ (which was confirmed by CNDO/2 calculations) and also by the resonance-stabilising properties of R^1 and the steric conditions in the transition state of the cycloaddition reaction[92]. The rate of the isomerisation (XIV) → (XV) increases with enhancement of the electron-accepting properties of R^1: COOEt > Ph ≫ Me. The 1,3-migration of the hydrogen atom in the process (XIV) → (XVI) is accelerated under the influence of electron-accepting groups R^3 and in addition is catalysed by traces of water and amines[89,92].

The reactions of ethyl triethylplumbyldiazoacetate with acrylonitrile, dimethyl maleate, tetracyanoethylene, and related compounds are analogous to those discussed above[94]. It has been shown[94,95] that the reactions of metallated diazoalkanes $R_nMC(N_2)R'$ with dimethyl acetylenedicarboxylate lead to isopyrazoles (XVIII) with 1,3-migration of the R_nM fragment:

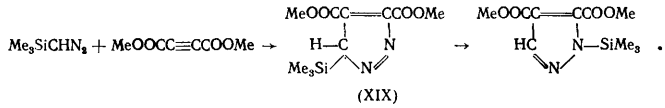


(XVII) (XVIII)

R_nM=Me_3Sn, Me_3Pb, Me_2Sb, Me_2Bi, MeHg.

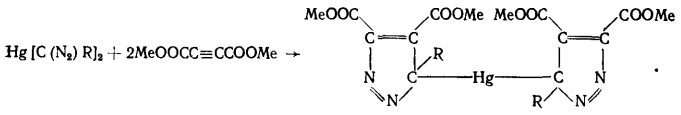
HgC(N2)COOEt, or HgC (N2) COMe; R′=R_nM, COOEt, COMe, or COPh.

Me_2AsCHN_2, $(Me_2As)_2CN_2$, and $Me_2AsC(N_2)COOEt$ do not enter into this reaction, which can be explained by steric hindrance[95], nor does bis(dimethylthallium)diazomethane, which has an ionic structure[42]. Sigmatropic rearrangements of the type (XVII) → (XVIII) accompany also reactions involving the 1,3-dipolar cycloaddition of diazoalkanes $(Me_3Sn)_2CN_2$ and $Me_3SiC(N_2)R$ to MeOOCC≡CCOOMe, while the capacity of R for migration diminishes in the sequence[56,59] $Me_3Sn > Me_3Si > H > COOEt$. For example[14,91], in the isomerisation of isopyrazole (XIX) the Me_3Si group migrates and not the hydrogen atom as suggested previously[90]:

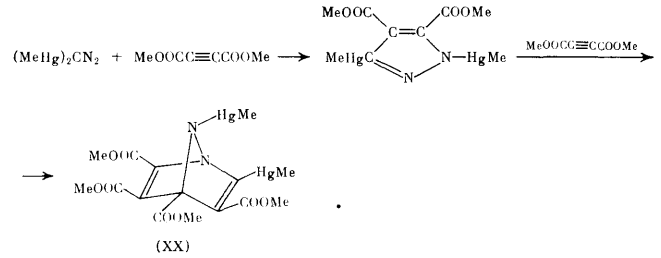


(XIX)

The reactions of mercuribis(diazoalkanes) of the type $Hg[C(N_2)R]_2$, where R = COOEtCOMe, with MeOOCC≡CCOOMe also proceed via the 1,3-cycloaddition mechanism[95]:



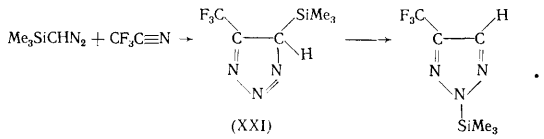
Bis(methylmercuri)diazomethane is converted in an analogous reaction into a mercurated pyrazole, which undergoes the Diels–Alder reaction with a second mole of MeOOCC≡CCOOMe, forming adduct (XX). On the basis of mass-spectrometric data, the structure of bis(methylmercuri)diazanorbornadiene was attributed to the latter[95]:



(XX)

Dipolarophiles such as phenylacetylene, diphenylacetylene, sodium acetylenedicarboxylate[6,94], and bis(trimethylstannyl)-acetylene[95] do not react with α-metallated diazoalkanes or react sluggishly.

According to Crossman et al.[66], the reaction of trimethylsilyldiazomethane with trifluoroacetonitrile leads to adduct (XXI), which is converted into 4-trifluoromethyl-2-trimethylsilyl-1,2,3-triazole as a result of the migration of the Me_3Si group:



(XXI)

3. The Staudinger Reaction

It has been shown recently[44,46] that organometallic derivatives of diazo-compounds react with tris(dimethylamino)phosphine, which is highly basic, to form the corresponding phosphazines. In this reaction, discovered by Staudinger[96,97] for non-metallated analogues, the reactivity of the α-metallated diazoalkanes is determined by steric factors. Derivatives of diazomethane in the series Me_nMCHN_2 (M = Si, Ge, or As; $n = 3$ or 2) reacts spontaneously with $(Me_2N)_3P$; in the case of M = Si or As, a mixture of *cis*- and *trans*-phosphazines is formed:

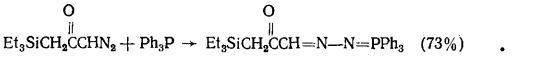
$$Me_nMCHN_2 + (Me_2N)_3P \xrightarrow{Et_2O} Me_nMCH{=}N{-}N{=}P(NMe_2)_3 .$$

The analogous reaction with the compounds MeHgC(N2)R, where R = COOEt, COMe, or COPh, takes place under mild conditions, while the interaction of mercuribisdiazoacetic ester can be carried out in stages:

In the series of diazoesters $Me_2MC(N_2)COOEt$ (M = As, Sb,

or Bi) phosphazines have been obtained only for the first two representatives. On the other hand, diazoalkanes with bulky substituents, for example compounds of the type $(Me_2M)_2CN_2$ (M = As or Sb), $(Me_3M)_2CN$, and $Me_3MC(N_2)$.COOEt (M = Si, Ge, Sn, or Pb) do not react with tris-(dimethylamino)phosphine[44,46]. Bis(dimethylthallium)diazomethane also does not react with $P(NMe_2)_3$, but this is due to the ionic structure of the diazoalkane[42].

We may note that 1-diazo-3-(trimethylsilyl)-2-propanone, in which the diazo-group is not shielded by the organometallic fragment, readily reacts with triphenylphosphine[1], like the usual diazo-compounds:



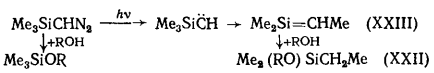
It has been suggested that in the transition states of these reactions the phosphine attacks the electrophilic α-N atom with subsequent rearrangement to Staudinger's β-N-adduct[44].

IV. REACTIONS INVOLVING THE INTERMEDIATE FORMATION OF CARBENES AND CARBYNES

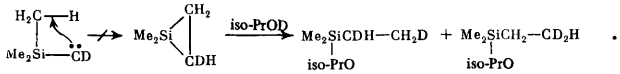
1. Intramolecular Rearrangement of Carbenes

Kinetic and chemical evidence was obtained in 1967 [98,99] for the existence of the short-lived sila-alkenes $R_2Si{=}CR'_2$, in which the silicon atom has a coordination number of 3. This stimulated an intense development of methods for the generation of sila-alkenes as well as the study of their structure and reactivity (see the relevant reviews[100-102]). In particular, it was found that α-silyated diazoalkanes are available as precursors of sila-alkenes.

Thus photolysis of trimethylsilyldiazomethane in alcohols leads to alkoxydimethylethylsilanes (XXII).[12,103,104] Me_3SiOR is formed via a side reaction (non-photochemically):

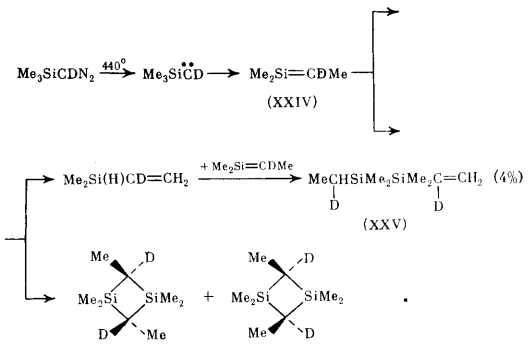


It has been suggested that the photolysis generates trimethylsilylcarbene, whose isomerisation leads to the sila-alkene (XXIII) as a result of the 1,2-shift of the methyl group to the carbene centre. The formation of the intermediate (XXIII) has been confirmed by the reaction with deuterated alcohols. For example, the photolysis of Me_3SiCDN_2 in iso-PrOD yielded isopropoxysilane $Me_2(iso\text{-}PrO)SiCD_2Me$, in which deuterium atoms are present only in the methylene group of the Et fragment[12]. This rules out the alternative mechanism—via the silacyclopropane intermediate:

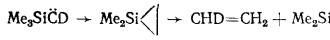


It has also been shown[103] that the photolysis of $Me_2PhSiCHN_2$ and $Me_2(PhCH_2)SiCHN_2$ in methanol leads to the carbenes $Me_2PhSi\ddot{C}H$ and $Me_2(PhCH_2)Si\ddot{C}H$. They isomerise to sila-alkenes via the 1,2-shift of one of the groups from silicon to the carbene centre. The ease of migration varies in the sequence Me > Ph ≅ $PhCH_2$.

Judging from the composition of the products and their yield, the pyrolysis of Me_3SiCHN_2 (or Me_3SiCDN_2) in a flow system generates trimethylsilylcarbenes, which isomerise preferentially to a sila-alkene[12,104], for example:

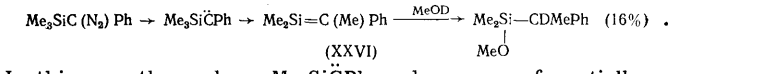


The sila-alkene (XXIV) dimerises to *cis*- and *trans*-disilacyclobutanes (overall yield >40%) and to a lesser extent rearranges to dimethylvinylsilane. The reaction of the latter with compound (XXIV) leads to adduct (XXV) in 4% yield. Furthermore, thermolysis gives rise to traces of ethylene and dimethylsilene as a result of a side reaction[104]:



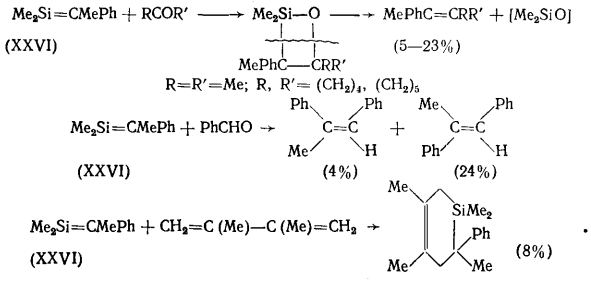
The intermediate formation of compound (XXIV) was confirmed by the pyrolysis of Me_3SiCHN_2 in the presence of 2-propanol. The latter traps sila-alkene with the formation of 2-propoxydimethylethylsilane (yield more than 67%).[12,104]

On the other hand, in the pyrolysis of phenyl(trimethylsilyl)diazomethane in the presence of alcohols the yield of sila-alkene (XXVI) was low[73]:

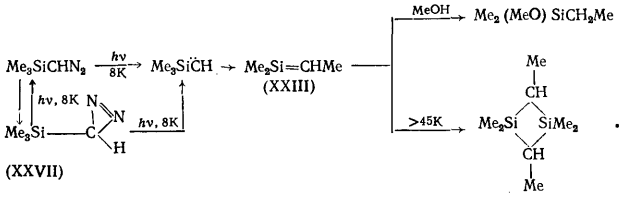


In this case the carbene $Me_3Si\ddot{C}Ph$ undergoes preferentially *carbene–carbene rearrangement* (see below).

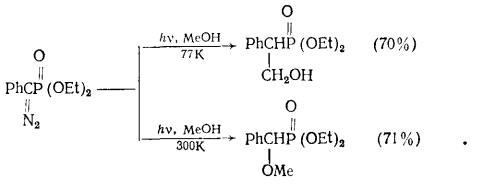
The intermediate formation of sila-alkenes[105,106], including the intermediate (XXVI),[73,107] has been confirmed in addition by the reaction with ketones, which leads to olefins, by the reaction with aldehydes, in which mixtures of *cis*- and *trans*-alkenes are formed, and by the reaction with 2,3-dimethylbutadiene, which is known to trap sila-alkenes effectively[101] with formation of Diels–Alder adducts:



In 1967 two groups of investigators[104,108,109] obtained simultaneously data for the mechanism of the photolysis of trimethylsilyldiazomethane, isolated in an argon matrix at 8 K:

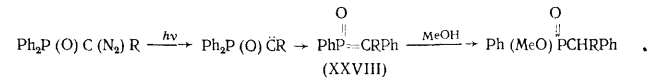


It was shown by ultraviolet, ^1H NMR, and infrared spectroscopy that the primary photolysis product is trimethylsilyldiazirine (XXVII), which is stable at room temperature. Further photolysis of the mixture of Me_3SiCHN_2 and compound (XXVII) proceeds via the carbene to the sila-alkene (XXIII). The infrared spectra of compound (XXIII) (not entirely identical) were also published in other communications[108,109]. Furthermore, compound (XXIII) was identified on the basis of the formation of a mixture of *cis*- and *trans*-disilacyclobutanes by the reaction with methanol. It has been found by EPR that trimethylsilylcarbene has a triplet ground state[108]. This was confirmed by the formation of triplet carbenes in the photolysis of Me_3SiCDN_2, $Me_2(H)SiCHN_2$, and $(Me_3Si)_2CN_2$ in argon matrices at 8 K. At the same time it has been suggested that thermolysis of Me_3SiCHN_2 at ~420 °C and its photolysis at 25 °C leads to singlet trimethylsilylcarbene[108]. Two recently published interesting examples of the dependence of the spin state of carbenes on the conditions of their generation are consistent with this finding. Thus the photolysis of α-diazobenzylphosphonate in a methanol matrix at 77 K leads to triplet carbene and its photochemical decomposition in alcohols at 300 K leads to singlet carbene[110]. In the former case the reaction with the alcohol yields preferentially the C–H insertion product, while in the latter case the O–H insertion product is formed, in agreement with Kirmse's data[111]:



Similarly[112] the photolysis of phenyldiazomethane in 2-propanol at 20 °C results in the formation of benzyl 2-propyl ether (77%) as a result of the insertion of singlet phenylcarbene in the O–H bond of the alcohol molecule. On the other hand, if the photolysis is carried out in a 2-propanol matrix at −196 °C, then triplet phenylcarbene is generated (cf. Refs. 113–115) and reacts with the alcohol preferentially via the C–H insertion mechanism.

In conclusion of the discussion of the methods for the generation of sila-alkenes, we may note that the photolysis of the derivatives of diphenylphosphoryldiazomethane generates carbene which, like silylcarbenes, isomerise to unstable alkylideneoxophosphoranes (XXVIII) as a result of the 1,2-shift of the pH group from the hetero-element to the carbene centre[116,117]:

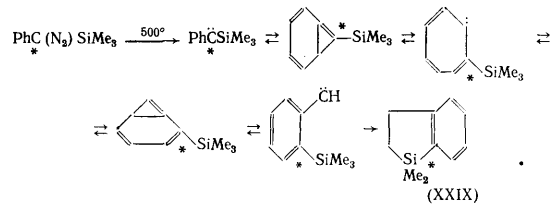


(XXVIII)

The intermediates (XXVIII) belong to a new class of heterocumulenes containing quinquevalent phosphorus having a coordination number of 3. They have been trapped successfully with methanol, aldehydes, and ketones[116,117].

The reactions of phosphorylcarbenes, including their intramolecular rearrangements, have been discussed in reviews[4,118].

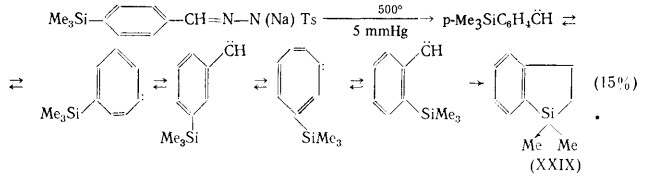
In the pyrolysis of $Me_3SiC(N_2)Ph$ and $Me_3SiC(Ph)=N-N(Li)Ts$ in the gas phase[72–74,107,119] one of the products is 1,1-dimethyl-1-silaindan (XXIX) (yield up to 37%). It is assumed that the carbene Me_3SiCPh formed is in equilibrium with trimethylsilylheptatrienylidene and *o*-trimethylsilylbenzylidene (carbene–carbene rearrangement). The pyrolysis of the labelled compounds $Me_3Si^{13}C(N_2)Ph$ and $Me_3Si^{13}C(Ph)=N-N(Li)Ts$ leads to indan (XXIX) with the label in the benzene ring, which confirms the following mechanism[72,73]:



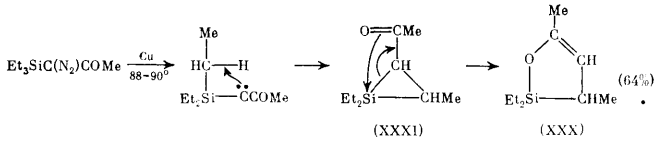
(XXIX)

Side reactions lead to the isomerisation of the carbene $PhCSiMe_3$ to the sila-alkene (XXVI) (again see above) and to a lesser extent to 1,1-dimethyl-2-phenyl-1-silacyclopropane.

It is of interest that silaindan (XXIX) has also been obtained by the pyrolysis of the sodium salt of *p*-trimethylsilylbenzaldehyde tosylhydrazone[120], which generates the carbene $p\text{-}Me_3SiC_6H_4CH$, differing in structure from $PhCSiMe_3$. The reaction mechanism is analogous to that discussed above:

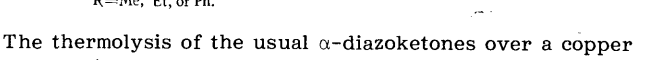


The copper-catalysed thermolysis of triethylsilyldiazoacetone in hexane leads to 1,1-diethyl-3,5-dimethyl-1-sila-2-oxa-3-cyclopentene (XXX). The carbenoid§ $Et_3SiCCOMe$ formed is probably inserted intramolecularly into the C–H bond of the $Si-CH_2$ fragment. This is followed by ring expansion[63,121,122] in the intermediate (XXXI):



(XXXI) (XXX)

The intermediate formation of silacyclopropanes in the rearrangements of carbenes has also been postulated in other studies[73,104]. On the other hand, the thermolysis of triethylgermyldiazoacetone and its analogues over copper generates the carbenoids $Et_3GeCCOR$, which undergo the Wolff rearrangement with formation of germylated ketens[63,123]:

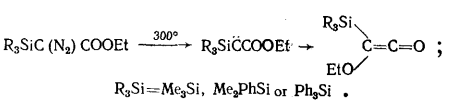


The thermolysis of the usual α-diazoketones over a copper catalyst is known to lead to ketocarbenoids which do not undergo the Wolff rearrangement[125], with a few exceptions[124].

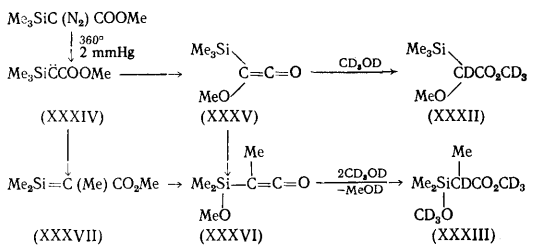
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§ Following Marchand and MacBrockway[126], here and henceforth the term carbenoids is applied to the carbenes formed in the thermocatalytic decomposition of diazoalkanes on metals or their salts. There are data showing that the carbenoid is usually coordinated to the catalyst; as a result, the properties of the carbenoid can differ from those of the corresponding carbene.

We may note that the pyrolysis of α-silyldiazoacetates in a flow system leads to the Wolff rearrangement[127];

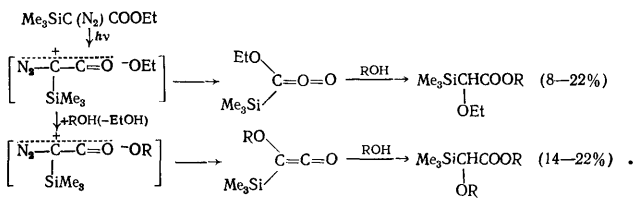


Ando and coworkers[128,129] showed that the esters (XXXII) and (XXXIII) are formed, together with other products, in the pyrolysis of methyl trimethylsilyldiazoacetate in a flow system in the presence of alcohols (for example, CD_3OD). They suggested that the pyrolysis leads to the carbene (XXXIV), which undergoes the Wolff rearrangement to the alkoxyketen(XXXV) and the latter can isomerise to the ketone (XXXVI). The reactions of (XXV) and (XXXVI) with the alcohol lead to esters:



Later the authors[129] suggested that the keten (XXXVI) is formed as a result of the rapid isomerisation of the silaalkene (XXXVII), which fails to react with the alcohol.

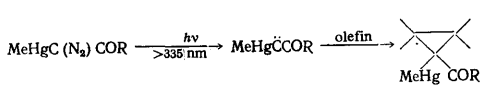
In its photochemical decomposition in alcohols[130,131] ethyl trimethylsilyldiazoacetate undergoes the Wolff rearrangement without the intermediate formation of carbenes (cf.Refs.132 and 133):



The photolysis of $MeHgC(N_2)COOMe$ [39] and $MeHgC(N_2)COMe$ [134] generates carbenes; the Wolff rearrangement is not typical for these compounds.

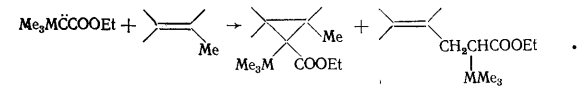
2. Addition to Multiple Bonds

The photolysis of α-metallated diazo-compounds under the usual conditions leads to carbenes in a singlet form. If the rate of their reaction with olefins is greater than the rate of their intercombination transition to the triplet state, stereospecific cycloaddition to the C=C bond and insertion in the C–H bond take place. The relative contributions of these reactions depend on many factors. For example[39,134], the yield of cyclopropanes is 70–90% in the photolysis of MeHgC.(N$_2$)COR (R = Me or OMe) in but-1-ene, 2-methylpropene, *cis*- or *trans*-but-2-ene, and buta-1,3-diene:



The reaction mixtures contain virtually no CH insertion products and the yield of products corresponding to the Wolff rearrangement is less than 4%.

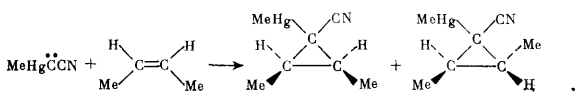
On the other hand, the photolysis of the diazoesters $Me_3MC(N_2)COOEt$ (M = Si, Ge, Sn, or Pb) leads to carbenes, which react with olefins less selectively: the formation of cyclopropanes is accompanied by the CH insertion[49,58,59,135]:



Steric factors have a considerable influence. Thus the interaction of the carbene $Me_3SiCCOOEt$ with isobutene entails the formation of only the cycloaddition product, while the reaction with the sterically hindered tetramethylethylene yields to the CH insertion product only[59]. The photolysis of Me_3SiCHN_2 generates trimethylsilylcarbene, whose reactions with ethylene and *trans*-but-2-ene give a low yield of cyclopropanes[136]. At the same time the carbene dimerises with formation of *trans*-1,2-bis(trimethylsilyl)ethylene. The latter reaction becomes the main one in the photolysis of Me_3SiCHN_2 in the presence of sterically hindered tetramethylethylene, tetrafluoroethylene, and perfluoropropene[136].

It has been shown by ^{1}H NMR that, on direct photochemical generation of the carbenes MeHgCCOMe, MeHgCCOOMe, Me_3SiCH, and $Me_3MCCOOEt$ (M = Si, Ge, Sn, or Pb),[49,59,134,136] their cycloaddition to *cis*- and *trans*-but-2-enes is mainly *cis*-stereospecific. This is evidence for the singlet state of the carbenes[111,137]. The contribution of the non-stereospecific cycloaddition of $Me_3SiCCOOEt$ is only 5%. The introduction of even small amounts of benzophenone into the reaction mixture[59] increases this contribution to 15% as a result of the sensitisation of the photolysis[111].

It has been shown recently[53] that the cyanocarbene HCCN, obtained by the direct photolysis of diazoacetonitrile, adds mainly *cis*-stereospecifically (to the extent of 94%) to *cis*-but-2-ene. Consequently, the contribution of triplet cyanocarbenes to this reaction is also low. On the other hand, both the direct benzophenone-sensitised photolysis of $MeHgC(N_2)CN$ in *cis*-but-2-ene leads to 1:1 mixtures of *cis*- and *trans*-dimethylcyclopropanes, which indicates the non-stereospecificity of the reaction

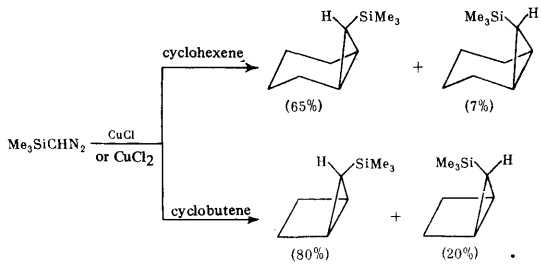


The difference between the properties of the carbenes HCCN and MeHgCCN has been explained[53] by the heavy atom effect. Both kinds of carbenes are generated in the singlet form, but, under the influence of the α-mercury atom, there is a rapid intercombination transition of MeHgCCN to the triplet state and the steady-state concentration of triplet carbenes increases.

The catalytic decomposition of trimethylsilyldiazomethane over copper salts in the presence of olefins leads to the carbenoid¶ Me_3SiCH. It is stabilised by cycloaddition to olefins and by dimerisation to *trans*- and *cis*-1,2-bis(trimethylsilyl)ethylenes[64,65,136,138]. The reaction with *trans*-but-2-ene takes place stereospecifically and leads to 1-trimethylsilyl-2,3-*trans*-dimethylcyclopropane (yield 13%).[136] The interaction with cyclohexene results in the formation of *anti*- and *syn*-7-trimethylsilylnorcarane[64,65]; the reaction with cyclobutene gives a mixture of *exo*- and *endo*-5-trimethylsilylbicyclo[2,1,0]pentanes[138], while the reaction with cyclohexa-1,3-diene leads to *exo*-7-trimethylsilylbicyclo[4,1,0]-hept-2-ene.[139] In the first two instances the cycloaddition

¶ For the role of the catalysts in the carbenoid decomposition of aliphatic diazo-compounds, see Mandel'shtam[140].

takes place with the preferential formation of the *exo*-isomers:

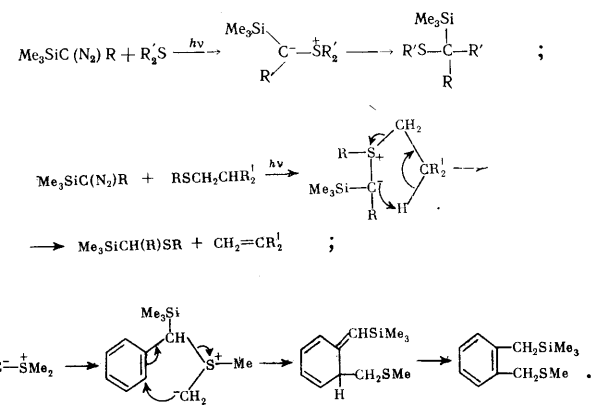


3. The Insertion of α-Metallated Carbenes in the O–H, C–H, C–O, C–S, C–Cl, Si–H, Si–Hg, and Ge–Hg σ-Bonds

Reactions of this type were investigated in relation to a large number of examples. It has been shown[39,23,71,119] that, in their reaction with alcohols, carbenes are usually selectively inserted in the O–H bonds, which makes it possible to use methanol and its deuterated derivatives for the identification of carbenes in the singlet state. For example, the photolysis of $MeHgC(N_2)COOMe$ in methanol leads to $MeHgCH(OMe)COOMe$ in 98% yield. The structure of the product was confirmed by its reduction (with $NaBH_4$ in ethanol) to $MeOCH_2COOEt$ and the photolysis of the initial diazoester in CD_3OD.[39]

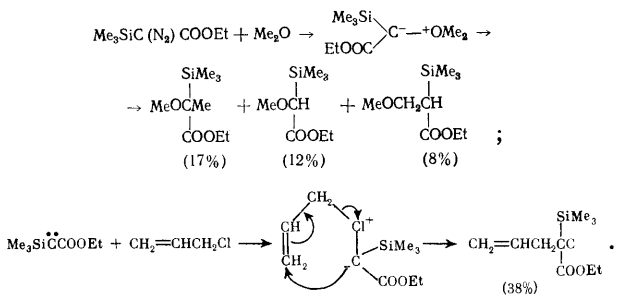
There is yet another reaction specific to singlet α-metallated carbenes—the insertion in the C–H bond[49,59,136]. Thus the photolysis ($\gamma > 300$ nm) of $Me_3SiC(N_2)COOEt$ in cyclohexane leads to ethyl cyclohexyltrimethylsilylacetate (yield 49%) while in n-butane at −30 °C a mixture of ethyl 2-trimethylsilylcaproate and ethyl 3-methyl-2-trimethylsilylvalerate is formed (overall yield 52%).[59] Furthermore, the rearrangements of certain carbenes, for example $Me_3SiC\ddot{}Ph$ [72,119] and p-$Me_3SiC_6H_4$–$\ddot{C}H$ [120] include a stage involving the intramolecular insertion of the carbene group in the C–H bond (see Section IV).

It has been shown recently[131,141] that the photolysis of the diazoalkanes $Me_3SiC(N_2)R$ (R = COOEt or Ph) in dialkyl sulphides at ~20 °C leads to the carbenes $Me_3SiC\ddot{}R$, which react with R'_2S to form sulphonium ylids. This can be followed by stages involving insertion in the C–S bond, elimination, and the Sommelet–Hauser rearrangement (cf. Hauser et al.[142]):



The photolysis of $Me_3SiC(N_2)COOEt$ in dimethyl sulphide[141] at −78 °C leads to the stable ylid $Me_2S^+-^-C(COOEt)SiMe_3$ (m.p. 40 °C). Other evidence in support of the intermediate formation of ylids in such reactions has been presented in a review[143].

The reactions of α-silylated carbenes with ethers and alkyl halides also includes the ylid formation stage[131]:



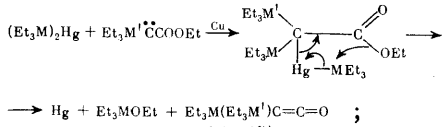
The insertion of the unusual carbenes[140,144,145] and their α-metallated analogues[136,147,148] in the Si–H bond is of synthetic interest. In the general case this bond is more carbenophilic than the C–H bond[136,146]. However, the yield of the Si–H insertion product can depend on the method of generation of the carbene. Thus the liquid-phase photolysis of a mixture of trimethylsilyldiazomethane and trimethylsilane leads to the Si–H insertion product $Me_3SiCH_2SiMe_3$ (yield 66%). On the other hand, this product is not formed in the liquid-phase thermolysis (in the photolysis of the same mixture in the gas phase)[136].

The catalytic decomposition of $Et_3GeC(N_2)COOEt$ over copper in benzene in the presence of triethylsilane or triethylgermane proceeds with the selective insertion of the resulting carbenoid in the Si–H or Ge–H bonds[147], for example:

$$Et_3Ge\ddot{C}COOEt + Et_3SiH \rightarrow Et_3Si\,(Et_3Ge)\,CHCOOEt\ .$$

In the analogous reaction with $Me(C_6F_5)_2SiH$ the insertion of $Et_3Ge\ddot{C}COOEt$ in the more inert Si–H bond does not occur[148]. The reaction leads to the azene $Et_3Ge(EtOOC)C{=}N{-}N{=}C(COOEt)GeEt_3$ (yield ~90%), which is known to be formed[60] via the addition of carbenoid $Et_3Ge\ddot{C}COOEt$ to a molecule of the initial diazoester.

It has been shown[149,150] that dihalogenocarbenes react non-selectively with bis(trimethylsilyl)- and bis(trimethylgermyl)-mercury. Dihalogenocarbenes are inserted both in the mercury–Group IVB element bond and in the newly formed Hg–C bond. On the other hand, the carbenoid $Et_3MCCOOEt$, formed in the catalytic decomposition of α-metallated diazoesters of the $Et_3M'C(N_2)COOEt$ (M' = Si, Ge, or Sn) series over copper in hexane or toluene in the presence of bis(triethylsilyl)- or bis(triethylgermyl)-mercury, is inserted in the Si–Hg or Ge–Hg bond. Successive demercuration ketens[61–63]:

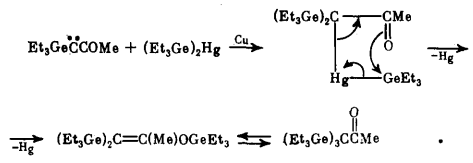


$$\rightarrow Hg + Et_3MOEt + Et_3M(Et_3M')C{=}C{=}O\ ;$$

(58–92%)

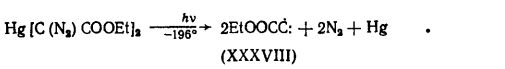
M = Si or Ge; M' = Si, Ge, or Sn.

The acetyltriethylgermylcarbenoid, generated by the thermocatalytic decomposition of $Me_3GeC(N_2)COMe$, is inserted selectively in the Ge–Hg bond in the reaction with bis(triethylgermyl)mercury. The reaction is also accompanied by demercuration[147]:



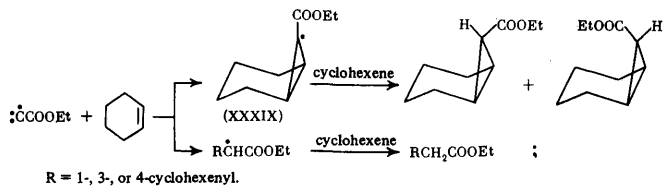
4. Methods of Generation and Reactivities of Carbynes

The chemistry of carbynes, which are derivatives of univalent carbon, has been developing vigorously in two directions. Studies have been made on the methods of synthesis and reactivities of transition metal complexes in which one of the ligands is a carbyne (see Fischer's review[111] review[151]). Methods for the generation of carbynes as kinetically independent species are being developed (see the short review of Strausz er al.[152]). In particular, ethoxycarbonylmethine (XXXVIII) is generated in the short-wavelength photolysis ($\lambda > 2100$ Å) of mercuribis(ethyl diazoacetate)[33,152] or alkylmercuridiazoacetates[39]:



(XXXVIII)

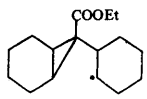
It was established that the carbyne (XXXVIII) is in the $^2\Pi$ ground state (↑↓↑ CCOOEt). Two parallel processes are characteristic of its reaction with cyclohexene: (1) addition to the double bond (concerted mechanism forbidden by orbital symmetry rules), leading to the formation of 7-ethoxycarbonyl-7-norcaranyl radicals (XXXIX); (2) insertion in the C–H bond (preferentially the allylic bond) with formation of alkyl radicals (XL):



(XXXIX)

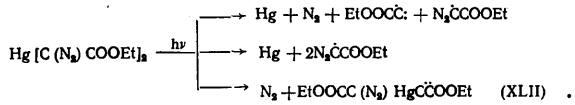
R = 1-, 3-, or 4-cyclohexenyl.

The radicals (XXXIX) and (XL) abstract hydrogen from cyclohexene. For (XXXIX), this process takes place stereospecifically with the preferential formation of the less stable ethyl *endo*-norcarane-7-carboxylate. Furthermore, the radicals (XXXIX) add to the double bond of cyclohexane and the resulting radicals (XLI) then disproportionate:



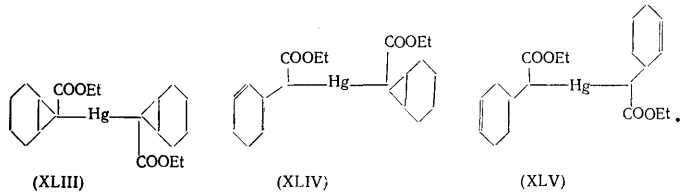
(XLI)

With increase of λ (for $\lambda > 2800$ Å), the yield of the carbyne (XXXVIII) falls owing to photolysis via competing pathways:



(XLII)

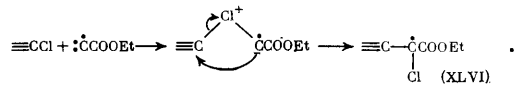
Under these conditions, the overall yield of the organomercury products (XLIII)–(XLV) increases to 38% with a simultaneous decrease of the yield of the non-mercurated products from 31 to 5%. Consequently the relative contribution of the mercury-containing carbenes [for example, (XLII)] in reactions with the solvent (cyclohexene) greatly increases:



(XLIII) (XLIV) (XLV)

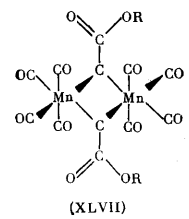
The regioselective insertion of the carbyne (XXXVIII) and the mercurated carbene (XLII) in the C–H bonds in the α-position with respect to the heteroatom has been observed in the photolysis of $Hg[C(N_2)COOEt]_2$ in heterocyclic compounds (tetrahydrofuran, tetrahydrothiophen, or pyrrolidine).[153] Judging from the proportions of the insertion products, the principal intermediate is the carbene (XLII), while the yield of the carbyne (XXXVIII) is 10–20%.

According to Patrick and Kovith[154], the photolysis of $Hg[C(N_2)COOEt]_2$ in the chloroalkanes $Me_{4-n}CCl_n$ ($n = 1$–4) at $\lambda < 2900$ Å leads to derivatives of ethyl chloroacetate and ethyl chloroacrylate. In this case the ethoxycarbonylmethine (XXXVIII) formed is inserted preferentially in the C–Cl bond with the intermediate formation of the chlorine-containing radical (XLVI). By analogy with the chemistry of the carbenes[126], it is suggested that the insertion step is preceded by the formation of an ylid radical:



(XLVI)

It is of interest to note that, in the reaction of $Mn(CO)_5Br$ with $Hg[C(N_2)COOR]_2$ (R = Et or t-Bu) in boiling ether, one of the products is the dimeric complex (XLVII) in which ethoxycarbonylmethine and t-butoxycarbonylmethine function is neutral three-electron bridge ligands[155,156].



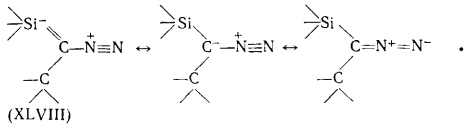
(XLVII)

The analogous complex is not formed in the reaction with $AgC(N_2)COOEt$. So far no analogies for this reaction are known[156].

V. STRUCTURAL AND SPECTROSCOPIC STUDIES

According to X-ray diffraction data[157], the $Ph_3SiC(N_2)Ph$ molecule is monomeric. It contains the linear C–N–N group and the planar Si–C(N_2)C fragment. The C–N bond is somewhat shorter and the N–N bond somewhat longer than in diazomethane (cf. Cox et al.[158]). The Si–C bond in the fragment is single (1.88 Å), which has been explained by the low contribution of structure (XLVIII) to the resonance

hybrid:



(XLVIII)

According to the same data[157], phenyl(triphenylgermyl)diazomethane has the same structure as its silicon analogue.

It has been shown[159,160] that all seven atoms of the $HgC(N_2)CO_2$ fragment in the crystals of t-BuHgC(N_2)COOEt and $Hg[C(N_2)COOEt]_2$ lie in the same plane. In the t-butyl derivative the carbonyl group is in the *cis*-position with respect to the diazo-group. This conformation is in general more stable than the transoid conformation[161]. It is particularly characteristic of aliphatic α-diazoalkanes[162].

It has been shown by NMR and infrared (IR) and Raman spectroscopic methods that bis(dimethylthallium)diazomethane is an ionic compound and that the anion $[CN_2]^{2-}$ has a linear structure[42]. In other compounds of the type $(R_nM)_2CN_2$ the metal–diazo-carbon bonds are covalent. The diazo-group gives rise to a distinct band in the IR spectra of these compounds in the range 1950–2050 cm^{-1}, due to the asymmetric stretching vibrations of the N–N bond[40,47]. The diazo-group in the compounds $(R_3Sn)_2CN_2$ absorbs in the region of 2000 cm^{-1} regardless of the nature of R. However, in the $(Me_3M)_2CN_2$ series the frequency $\nu_{as}(CN_2)$ decrease on average by 50 cm^{-1} in the following sequence of M: Si > Ge > Sn > Pb, which reflects the inductive effect of the Me_3M groups[40]. An analogous shift of the absorption band in the region of low frequencies has been observed in the spectra of the following series of compounds: $Me_2As(Me_3Ge)CN_2$ (2020 cm^{-1}), $Me_2As(Me_3Sn)CN_2$ (2000 cm^{-1}), and $Me_2As.(Me_3Pb)CN_2$ (1985 cm^{-1}).[47]

The introduction of the Me_2M fragment (M = As, Sb, or Bi) at the α-carbon atom of ethyl diazoacetate reduces the frequency by 45–55 cm^{-1}. It has been suggested[43] that this effect is due to the mass of the substituent and to a lesser extent the nature of the metal. An analogous conclusion was reached in the analysis of the IR spectra of $Me_3MC(N_2)$COOEt (M = Si, Ge, Sn, or Pb) and certain related compounds[40].

As regards the stretching vibrations of the carbonyl group, an appreciable bathochromic shift is observed only after the introduction of the Me_3Sn, Me_3Pb, MeHg, and EtHg fragments, whereupon, according to the authors[40,43], the carbonyl group is coordinated intramolecularly to the metal atom. On the other hand, if such coordination does not occur in the compounds $Me_nMC(N_2)$COOEt (M = Si, Ge, As, Sb, or Bi), the band shifts only very slightly[40,43].

Analogous effects are characteristic also of α-metallated diazoketones. For example, the carbonyl absorption band in the spectra of the compounds $Hg[C(N_2)COR]_2$ (R = alkyl, adamantyl, or aryl)[33,35,38] undergoes a 25–45 cm^{-1} bathochromic shift relative to the non-mercurated analogues.

The ultraviolet spectra of mercuridiazoacetates $RHgC(N_2).COOR'$ (R and R' = alkyl) contain two absorption bands: at 374–377 nm ($\varepsilon \cong 44$–59) and at 268–274 nm ($\varepsilon \cong 8600$–10 000). The introduction of the alkylmercuri-group in $HC(N_2)COOR'$ causes a 20–25 nm shift of the short-wavelength maximum and reduces its intensity by 40%. The position of the long-wavelength maximum changes only slightly (by 2–3 nm), but its intensity increases by a factor of three[39]. Similar features are characteristic of α-mercurated diazoketones[33,35].

Organometallic derivatives of diazo-compounds are also widely investigated by pulse $^{13}C\{^1H\}$ Fourier transform NMR.[43,163] In particular, $^1J(H-C)$ and the chemical shifts $\delta(^{13}CN_2)$ of the diazo-carbon atom in the compounds Me_nMCHN_2, $(Me_nM)_2CN_2$, and $Me_nMC(N_2)$COOEt (M = Hg, Si, Ge, Sn, Pb, As, Sb, or Bi; $n = 1$, 2, or 3) have been determined. It has been found[163] that the substitution of the hydrogen atom in diazomethane or ethyl diazoacetate by the Me_3M fragment entails a downfield shift of the $^{13}CN_2$ signal, the magnitude of the signal increasing in the sequence Si < Ge < Sn < Pb.

In their analysis of the $^{13}C\{H\}$ NMR spectra of compounds in the $(Me_3M)_2CN_2$ series (M is a silicon subgroup element), Lorberth and coworkers[43,163] established that the carbon atom linked to the diazo-group is shielded owing to the diamagnetic influence of the neighbouring Me_3M fragments. The atom is particularly strongly shielded in bis(trimethylstannyl)diazomethane [$\delta(^{13}CN_2) = 5.8$ p.p.m.] and bis(trimethylplumbyl)diazomethane [$\delta(^{13}CN_2) = 1.9$ p.p.m.]. To account for this effect, the compound $(Me_3Sn)_2CN_2$ was investigated in detail by photoelectron spectroscopy, ^1H, ^{13}C, ^{15}N, and ^{119}Sn NMR, as well as ^{119} ^{119}Sn-Mössbauer spectroscopy[164]. It was established that the Me_3Sn groups function in this case as very powerful electron donors, as a result of which the CN_2 fragment acquires an enhanced electron density, which is distributed fairly uniformly over all three atoms of this group. Analysis of the Mössbauer spectra of solid specimens of $(Me_3Sn)_2CN_2$ led to the conclusion that tetracoordinate tin atoms, deshielded by the CN_2 group, are present[164].

A similar effect of the Me_3M groups (M = Si, Ge, or Sn) had been observed previously by ^{13}C NMR in dimetallated ketens $(Me_3M)_2C{=}C{=}O$.[165] In the diazoesters $Me_3MC(N_2)$COOEt the shielding of the α-carbon atom is less marked [$\delta(^{13}CN_2) = 37.8$–42.9 p.p.m.].[163,164]

REFERENCES

1. Yu.I.Baukov, A.S.Kostyuk, O.S.Sytina, and I.F.Lutsenko, Zhur.Obshch.Khim., **44**, 955 (1974).
2. P.Ashkenazi, S.Lupan, A.Schwartz, and M.Gais, Tetrahedron Letters, 817 (1969).
3. M.F.Lappert and J.S.Poland, Adv.Organomet.Chem., **9**, 397 (1970).
4. M.Regitz, Angew.Chem., **87**, 259 (1975); Int.Ed.Engl., **14**, 222 (1975).
5. M.Regitz, Synthesis, 351 (1972).
6. M.F.Lappert, J.Lorberth, and J.S.Poland, J.Chem. Soc.A, 2954 (1970).
7. E.Müller and D.Ludsteck, Chem.Ber., **87**, 1887 (1954).
8. E.Müller and W.Rundel, Chem.Ber., **88**, 917 (1955).
9. E.Müller and W.Rundel, Chem.Ber., **90**, 1299 (1957).
10. E.Müller and R.Beutler, Annalen, **719**, 72 (1968).
11. R.Beutler, B.Zeeh, and E.Müller, Chem.Ber., **102**, 2636 (1969).
12. R.L.Kreeger and H.Shechter, Tetrahedron Letters, 2061 (1975).
13. U.Schöllkopf and H.U.Scholz, Synthesis, 271 (1976).
14. D.Seyferth and T.C.Flood, J.Organomet.Chem., **29**, C 25 (1971).
15. E.W.Colvin and B.J.Hamill, J.Chem.Soc., Perkin Trans. I, 869 (1977).
16. U.Schöllkopf and H.Frasnelli, Angew.Chem., **82**, 291 (1970); Int.Ed.Engl., **9**, 301 (1970).
17. U.Schöllkopf, B.Banhidai, R.Meyer, H.Beckhaus, and H.Frasnelli, Annalen, 1767 (1974).
18. U.Schöllkopf, H.Frasnelli, B.Banhidai, and R.Meyer, BRD.P.2 245094 (1974); Chem.Abs., **81**, 104 755 (1974).
19. R.Pellicciari and B.Natalini, J.Chem.Soc., Perkin Trans Trans.I, 1822 (1977).
20. E.Wenkert and C.A.McPherson, J.Amer.Chem.Soc., **94**, 8084 (1972).

21. E.Müller and W.Rundel, Chem.Ber., **89**, 1065 (1956).
22. U.Schöllkopf and N.Rieber, Chem.Ber., **102**, 488 (1969).
23. U.Schöllkopf, F.Gerhart, M.Reetz, H.Frasnelli, and H.Schumacher, Annalen, **716**, 204 (1968).
24. U.Schöllkopf and N.Rieber, Angew.Chem., **79**, 238 (1967); Int.Ed.Engl., **6**, 261 (1967).
25. M.Regitz, A.Liedenheger, U.Eckstein, M.Martin, and W.Anschutz, Annalen, **748**, 207 (1971).
26. U.Felcht and M.Regitz, Chem.Ber., **108**, 2040 (1975).
27. D.Seyferth, R.S.Marmor, and P.Hilbert, J.Org.Chem., **36**. 1379 (1971).
28. E.T.Blues, D.Bryce-Smith, J.G.Irvin, and I.W.Lawston, Chem.Comm., 466 (1974).
29. N.Eistert, M.Regitz, G.Heck, and H.Schwall, in "Methoden der organischen Chemie (Houben-Weyl), Aufl.*Bd 10/4*, Verl.Thieme, Stuttgart, 1968, p.473.
30. R.Huisgen, Angew.Chem., **67**, 439 (1955).
31. E.Buchner, Chem.Ber., **28**, 215 (1895).
32. T.Curtius and E.Buchner, J.prakt.Chem., [2], **38**, 411 (1888).
33. T.DoMinh, O.P.Strausz, and H.E.Gunning, Tetrahedron Letters, 5237 (1968).
34. T.DoMinh, H.E.Gunning, and O.P.Strausz, J.Amer. Chem.Soc., **89**, 6785 (1967).
35. P.Yates, F.X.Garneau, and J.P.Lokensgard, Tetrahedron, **31**, 1979 (1975).
36. P.Yates and F.X.Garneau, Tetrahedron Letters, 71 (1967).
37. P.Demaree, M.C.Doria, and J.M.Muchowski, Canad.J. Chem., **55**, 243 (1977).
38. A.A.Fridman, N.A.Kolobov, V.S.Zelesov, and M.P.Sivkova, Zhur.Org.Khim., **10**, 884 (1974).
39. S.J.Valenty and P.S.Skell, J.Org.Chem., **38**, 3937 (1973).
40. J.Lorberth, J.Organomet.Chem., **27**, 303 (1971).
41. A.N.Wright, K.A.W.Kramer, and G.Steel, Nature, **199**, 903 (1963).
42. P.Krommes and J.Lorberth, J.Organomet.Chem., **120**, 131 (1976).
43. P.Krommes and J.Lorberth, J.Organomet.Chem., **93**, 339 (1975).
44. P.Krommes and J.Lorberth, J.Organomet.Chem., **127**, 19 (1976).
45. R.Grüning and J.Lorberth, J.Organomet.Chem., **78**, 221 (1974).
46. P.Krommes and J.Lorberth, J.Organomet.Chem., **110**, 195 (1976).
47. E.Glozbach and J.Lorberth, J.Organomet.Chem., **132**, 359 (1977).
48. J.Lorberth, F.Schmock, and G.Lange, J.Organomet. Chem., **54**, 23 (1973).
49. U.Schöllkopf, B.Banhidai, and H.U.Scholz, Annalen, **761**, 137 (1972).
50. J.Lorberth, J.Organomet.Chem., **15**, 251 (1968).
51. M.F.Lappert and J.Lorberth, Chem.Comm., 836 (1967).
52. A.S.Kostyuk, I.B.Ruderfer, Yu.I.Baukov, and I.F.Lutsenko, Zhur.Obshch.Khim., **45**, 819 (1975).
53. P.S.Skell, S.J.Valenty, and P.W.Humer, J.Amer.Chem. Soc., **95**, 5041 (1973).
54. P.Krommes and J.Lorberth, J.Organomet.Chem., **97**, 59 (1975).
55. U.Schöllkopf, M.Reetz, B.Banhidai, and H.U.Scholz, "The XIIIth International Congress on Pure and Applied Chemistry, Boston", p.11.
56. K.D.Kaufmann and K.Rühlmann, Z.Chem., **8**, 262 **(1968).**
57. K.D.Kaufmann, "Abstracts of Reports at the IVth International Conference on Organometallic Chemistry, Bristol, 1969", p.D9.
58. U.Schöllkopf and N.Rieber, Angew.Chem., **79**, 906 (1967); Int.Ed.Engl., **6** 884 (1967).
59. U.Schöllkopf, D.Hoppe, N.Rieber, and V.Jacobi, Annalen, **730**, 1 (1969).
60. O.A.Kruglaya, I.B.Fedot'eva, B.V.Fedot'ev, and N.S.Vyazankin, Izv.Akad.Nauk SSSR, Ser.Khim., 2790 (1975).
61. O.A.Kruglaya, I.B.Fedot'eva, B.V.Fedot'ev, and N.S.Vyazankin, Izv.Akad.Nauk SSSR, Ser.Khim., 199 (1975).
62. O.A.Kruglaya, I.B.Fedot'eva, B.V.Fedot'ev, V.V.Keiko, and N.S.Vyazankin, Zhur.Obshch.Khim., **46**. 930 (1976).
63. O.A.Kruglaya, I.B.Fedot'eva, B.V.Fedot'ev, I.D.Kalikhman, E.I.Brodskaya, and N.S.Vyazankin, J.Organomet.Chem., **142**, 155 (1977).
64. D.Seyferth, A.W.Dow, H.Menzel, and T.C.Flood, J.Amer.Chem.Soc., **90**, 1080 (1968).
65. D.Seyferth, H.Menzel, A.W.Dow, and T.C.Flood, J.Organomet.Chem., **44**, 279 (1972).
66. J.M.Crossman, R.N.Haszeldine, and A.E.Tipping, J.Chem.Soc., Dalton Trans., 483 (1973).
67. F.Arndt, in "Organic Syntheses" (Translated into Russian), Inostr.Lit., Moscow, 1949, Vol.2, p.174.
68. V.D.Sheludyakov, G.D.Khatuntsev, and V.F.Mironov, Zhur.Obshch.Khim., **39**, 2785 (1969).
69. J.Mathieu and R.Panico, "Reaction Mechanisms in Organic Chemistry" (Translated into Russian), Izd.Mir, Moscow, 1975, p.218.
70. K.D.Kaufmann, B.Auräth, P.Träger, and K.Rühlman, Tetrahedron Letters, 4973 (1968).
71. A.G.Brook and P.F.Jones, Canad.J.Chem., **47**, 4353 (1969).
72. T.J.Barton, J.A.Kilgour, R.R.Gallucci, A.J.Rothschild, J.Slutsky, A.D.Wolf, and M.Jones, J.Amer. Chem.Soc., **97**, 657 (1975).
73. W.Ando, A.Sekiguchi, A.J.Rothschild, R.R.Gallucci, M.Jones, T.J.Barton, and J.A.Kilgour, J.Amer.Chem. Soc., **99**, 6995 (1977).
74. J.A.Kilgour, Ph.D.Thesis, Iowa State Univ., 1976; Diss.Abs., **B**, **36**, 5054 (1976).
75. N.Wiberg and G.Preiner, Angew.Chem., **89**, 343 (1977).
76. G.Himbert, D.Frank, M.Regitz, Chem.Ber., **107**, 2513 (1974).
77. G.Himbert, D.Frank, and M.Regitz, Chem.Ber., **109**, 370 (1976).
78. D.Frank, G.Himbert, and M.Regitz, Chem.Ber., **111**, 183 (1978).
79. E.W.Colvin and B.J.Hamill, Chem.Comm., 151 (1973).
80. W.Kirmse, Angew.Chem., **88**, 273 (1976).
81. S.Masamune, N.Nakamura, M.Suda, and H.Ona, J.Amer.Chem.Soc., **95**, 8481 (1973).
82. K.Nakasuji, K.Kawamura, T.Ishihara, and I.Murata, Angew.Chem., **88**, 650 (1977).
83. K.Nakasuji, K.Kawamura, T.Ishihara, and I.Murata, Heterocycles, **4**, 1835 (1976).
84. F.Gerhart, U.Schöllkopf, and H.Schumacher, Angew. Chem., **79**, 50 (1967).
85. A.L.Fridman and N.A.Kolobov, Zhur.Org.Khim., **12**, 233 (1976).
86. D.A.Evans, L.K.Truesdale, and K.G.Grimm, J.Org. Chem., **41**, 3335 (1976).
87. R.Huisgen, Angew.Chem., **75**, 742 (1963); Int.Ed. Engl., **2**, 633 (1963).
88. R.Huisgen, Angew.Chem., **75**, 604 (1963); Int.Ed. Engl., **2**, 565 (1963).

89. A.G.Brook and P.F.Jones, Canad.J.Chem., **49**, 1841 (1971).
90. M.F.Lappert and J.S.Poland, Chem.Comm., 156 (1969).
91. M.F.Lappert and J.S.Poland, J.Chem.Soc.C, 3910 (1971).
92. A.R.Bassindale and A.G.Brook, Canad.J.Chem., **52**, 3474 (1974).
93. G.W.Cowell and A.Ledwith, Quart.Rev., **24**, 119 (1970).
94. R.Grüning and J.Lorberth, J.Organomet.Chem., **69**, 213 (1974).
95. R.Grüning and J.Lorberth, J.Organomet.Chem., **129**, 55 (1977).
96. H.Staudinger and G.Luscher, Helv.Chim.Acta, **5**, 75 (1922).
97. H.J.Bestmann, H.Buckschewski, and H.Leube, Chem. Ber., **92**, 1345 (1959).
98. L.E.Gusel'nikov and M.C.Flowers, Chem.Comm., 864 (1967).
99. M.C.Flowers and L.E.Gusel'nikov, J.Chem.Soc.B, 419, 1396 (1968).
100. L.E.Gusel'nikov, N.S.Nametkin, and V.M.Vdovin, Acc.Chem.Res., **8**, 18 (1975).
101. L.E.Gusel'nikov, N.S.Nametkin, and V.M.Vdovin, Uspekhi Khim., **43**, 1317 (1974) [Russ.Chem.Rev., No.7 (1974)].
102. H.Sadurai, Kagaku no Ryoiki, **29**, 50 (1975).
103. W.Ando, A.Sekiguchi, and T.Migita, Chem.Letters, 779 (1976).
104. R.L.Kreeger, Ph.D.Thesis, Ohio State University, 1976; Diss.Abs., Int.B, **37**, 3961 (1977).
105. D.N.Roark and L.H.Sommer, Chem.Comm., 167 (1973).
106. R.D.Bush, C.M.Golino, G.D.Homer, and L.H.Sommer, J.Organomet.Chem., **80**, 37 (1974).
107. W.Ando, A.Sekiguchi, J.Hagiwara, and T.Migita, Chem.Comm., 145 (1975).
108. M.R.Chedekel, M.Skoglund, R.L.Kreeger, and H.Shechter, J.Amer.Chem.Soc., **98**, 7846 (1976).
109. O.L.Chapman, C.C.Chang, J.Kolc, M.E.Jung, J.A.Love, T.J.Barton, and M.L.Tumey, J.Amer.Chem. Soc., **98**, 7844 (1976).
110. H.Tomioka, T.Inagaki, and Y.Izawa, Chem.Comm., 1023 (1976).
111. W.Kirmse, "Carbene Chemistry", Acad.Press, New York, 1971
112. H.Tomioka and Y.Izawa, J.Amer.Chem.Soc., **99**, 6128 (1977).
113. M.Jones and R.A.Moss, "Carbenes", Wiley-Intersci., New York, 1973.
114. R.A.Moss and M.A.Joyce, J.Amer.Chem.Soc., **99**, 1262 (1977).
115. A.M.Trozzolo, Acc.Chem.Res., **1**, 329 (1968).
116. M.Regitz, W.Illger, and G.Mass, Chem.Ber., **111**, 705 (1978).
117. G.Maas, M.Regitz, and W.Illger, Chem.Ber., **111**, 726 (1978).
118. M.Regitz, New Synth.Methods, **2**, 145 (1965); Chem. Abs., **86**, 155 721 (1977).
119. W.Ando, A.Sekiguchi, T.Hagiwara, and T.Migita, Chem.Comm., 372 (1974).
120. A.Sekiguchi and W.Ando, Bull.Chem.Soc.Japan, **50**, 3067 (1977).
121. O.A.Kruglaya, B.V.Fedot'ev, I.B.Fedot'eva, and N.S.Vyazankin, "Abstracts of Reports at the VIIIth International Conference on Organometallic Chemistry, Kyoto, Japan, 1977", p.120.
122. O.A.Kruglaya, B.V.Fedot'ev, I.B.Fedot'eva, I.D.Kalikhman, and N.S.Vyazankin, Zhur.Obshch. Khim., **48**, 472 (1978).
123. O.A.Kruglaya, I.B.Fedot'eva, B.V.Fedot'ev, and N.S.Vyazankin, Izv.Akad.Nauk SSSR, Ser.Khim., 2646 (1976).
124. P.Yates and R.J.Crawford, J.Amer.Chem.Soc., **88**, 2646 (1966).
125. H.Maier and K.P.Zeller, Angew.Chem., **87**, 52 (1975).
126. A.P.Marchand and N.MacBrockway, Chem.Rev., **74**, 431 (1974).
127. E.R.Matjeka, Ph.D.Thesis, Iowa State Univ., 1974; Diss.Abs., Int.B, **35**, 5339 (1975).
128. W.Ando, A.Sekiguchi, T.Migita, S.Kammula, M.Green, and J.Jones, J.Amer.Chem.Soc., **97**, 3818 (1975).
129. W.Ando and A.Sekiguchi, see Ref.121, p.124.
130. W.Ando, T.Hagiwara, and T.Migita, J.Amer.Chem.Soc., **95**, 7518 (1973).
131. A.Sekiguchi and W.Ando, J.Synth.Org.Chem.Japan, **35**, 897 (1977).
132. O.P.Strausz, T.DoMinh, and H.E.Gunning, J.Amer. Chem.Soc., **90**, 1660 (1968).
133. T.DoMinh, O.P.Strausz, and H.E.Gunning, J.Amer. Chem.Soc., **91**, 1261 (1969).
134. P.S.Skell and S.J.Valenty, J.Amer.Chem.Soc., **95**, 5042 (1973).
135. M.Weidenbruch, Chem.Ztg, **97**, 355 (1973).
136. R.N.Haszeldine, D.L.Scott, and A.E.Tipping, J.Chem. Soc., Perkin Trans.I, 1440 (1974).
137. P.S.Skell and R.C.Woodworth, J.Amer.Chem.Soc., **78**, 4496 (1956).
138. A.J.Ashe, J.Amer.Chem.Soc., **95**, 818 (1973).
139. R.T.Taylor and L.A.Paquette, J.Org.Chem., **43**, 242 (1978).
140. T.V.Mandel'shtam, Symposium, "Sovremannye Problemy Organicheskoi Khimii" (Modern Problems of Organic Chemistry), Leningrad, 1976, p.87.
141. W.Ando, T.Hagiwara, and T.Migita, Tetrahedron Letters, 1425 (1974).
142. C.R.Hauser, S.W.Kantor, and W.R.Brasen, J.Amer. Chem.Soc., **75**, 2660 (1953).
143. W.Ando, Acc.Chem.Res., **10**, 179 (1977).
144. D.Seyferth, R.Damrauer, R.M.Turkel, and L.J.Dodd, J.Organomet.Chem., **17**, 367 (1969).
145. H.Watanabe, T.Nakano, K.I.Araki, H.Matsumoto, and Y.Nagai, J.Organomet.Chem., **69**, 389 (1974).
146. D.Seyferth and J.M.Burlitch, J.Amer.Chem.Soc., **85**, 2667 (1963).
147. O.A.Kruglaya, I.B.Fedot'eva, B.V.Fedot'ev, I.D.Kalikhman, E.I.Brodskaya, and N.S.Vyazankin, Izv.Akad.Nauk SSSR, Ser.Khim., 1887 (1976).
148. L.I.Belousova, O.A.Kruglaya, V.V.Neretin, I.D.Kalikhman, N.A.Ivanova, A.A.Tatarinova, and N.S.Vyazankin, Izv.Akad.Nauk SSSR, Ser.Khim., 2070 (1977).
149. D.Seyferth, R.J.Cross, and B.Prokai, J.Organomet. Chem., **7** P 20 (1967).
150. D.Seyferth, E.M.Hanson, B.Prokai, and R.J.Cross, J.Organomet.Chem., **24**, 33 (1970).
151. E.O.Fischer, Adv.Organomet.Chem., **14**, 1 (1976).
152. O.P.Strausz, G.J.A.Kennepohl, F.X.Garneau, T.DoMinh, B.Kim, S.Valenty, and P.S.Skell, J.Amer. Chem.Soc., **96**, 5723 (1974).
153. T.B.Patrick and T.T.Wu, J.Org.Chem., **43**, 1506 (1978).
154. T.B.Patrick and G.H.Kovith, J.Org.Chem., **40**, 527 (1975).
155. W.A.Herrmann, Angew.Chem., **86**, 895 (1974); Int. Ed.Engl., **13**, 812 (1974).
156. W.A.Herrmann, J.Organomet.Chem., **97**, 1 (1975).

157. C.Glidewell and G.M.Sheldrick, J.Chem.Soc., Dalton Trans., 2409 (1972).
158. A.P.Cox, L.F.Thomas, and J.Sheridan, Nature, **181**, 1000 (1958).
159. R.A.Smith, M.Torres, and O.P.Strausz, Canad.J. Chem., **55**, 2752 (1977).
160. R.A.Smith, M.Torres, and O.P.Strausz, Canad.J. Chem., **55**, 3527 (1977).
161. J.G.Csizmadia, H.E.Gunning, R.K.Gosavi, and O.P.Strausz, J.Amer.Chem.Soc., **95**, 133 (1973).
162. F.Kaplan and G.K.Meloy, J.Amer.Chem.Soc., **88**, 950 (1966).
163. R.Grüning, P.Krommes, and J.Lorberth, J.Organomet. Chem., **128**, 167 (1977).
164. A.Fadini, E.Glozbach, P.Krommes, and J.Lorberth, J.Organomet.Chem., **149**, 297 (1978).
165. Yu.K.Grishin, S.V.Ponomarev, and S.A.Lebedev, Zhur.Org.Khim., **10**, 404 (1974).

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