DIENE SYNTHESES WITH NITRO COMPOUNDS

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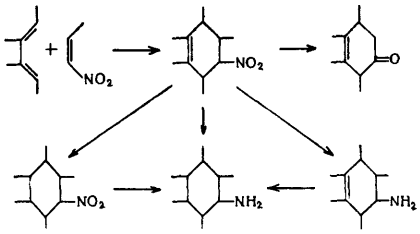
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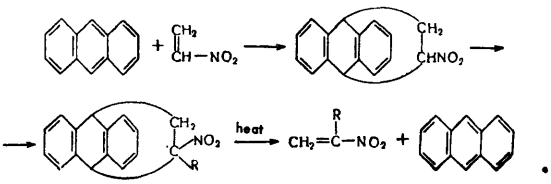
INTRODUCTION

From information available on diene syntheses with nitro compounds, it is evident that the introduction of a nitro group into the molecule of a diene or dienophile considerably changes their reactivity in the Diels–Alder reaction. Nitrophilodienes, containing a nitro group conjugated with a double bond, condense with dienes more readily than ordinary ethylenes. However, a nitro group has an inhibiting effect on the diene system and nitrodienes show reduced reactivity in the Diels–Alder reaction.

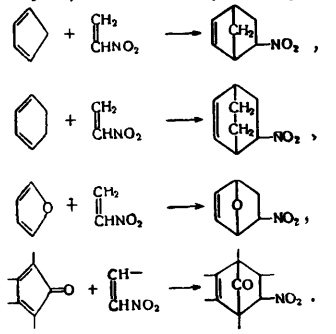
The diene condensation of unsaturated nitro compounds yields adducts with a nitro group and a double bond in the molecule, from which a series of interesting products can be synthesised, which are either unobtainable or obtainable only with difficulty by other methods. By the reduction of nitro-adducts under different conditions and in the presence of different catalysts, saturated alicyclic nitro compounds[1], and unsaturated and saturated amines[1,2] can be obtained. Using the Nef reaction the corresponding ketones[3,4] can be synthesised.



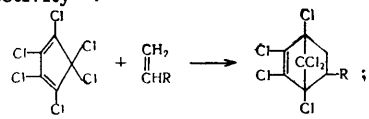
The saturated amines formed in this way can be used as starting materials for the synthesis of polynuclear heterocyclic compounds containing nitrogen[5]. Diene syntheses can be used in the synthesis of α-substituted nitro-olefines[6]:



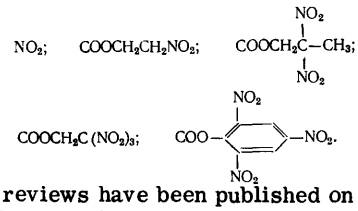
Diene reactions can further be used for preparing bicyclic nitro compounds, containing endomethylene[1,2,3], endoethylene[7], endo-oxy-[8], and carbonyl bridges[9]:



Compounds with insecticidal activity have been prepared by the condensation of *o*- or *m*-nitrostyrenes with hexachlorocyclopentadiene and the subsequent reduction of the nitro groups in the adducts to amino groups[10]. Condensations of hexachlorocyclopentadiene with nitroethylene, and with 2-nitroethyl, 2,2-dinitropropyl, 2,2,2-trinitroethyl, and 2,4,6-trinitrophenyl esters of acrylic acid yield adducts with insecticidal activity[11]:



where



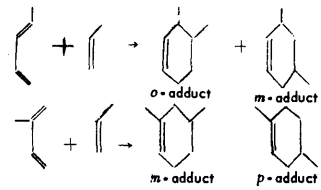
Although many reviews have been published on the diene synthesis, several stereochemical problems remain to be elucidated. Moreover, the chemical properties of the adducts obtained from the unsaturated nitro compounds have not yet been fully discussed. We have therefore dealt with these questions in this review.

Tables at the end of the paper summarise all the material on the diene synthesis of nitrodienes and nitrophilodienes, published up to the beginning of 1959.

THE MECHANISM OF THE DIELS–ALDER REACTION

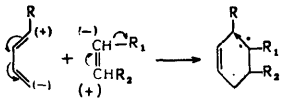
Despite a substantial volume of experimental data on diene reactions and several important theoretical generalisations on the stereochemistry of the products, there is at present no general agreement on the reaction mechanism[12–16].

When asymmetrical addends are used, the question of the mutual orientation of the diene and the philodiene arises. If a 1- or 2-substituted diene and a monosubstituted olefine are used, in each case two structurally different adducts can be formed, e.g.:

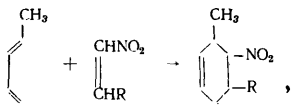


Since the condensation of dienes $CH_2=CH-CH=CHR$ (where

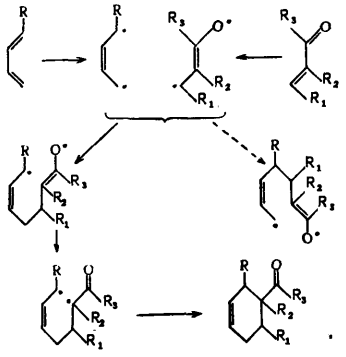
R = alkyl, *O*-alkyl, aryl) with philodienes $R_2CH=CHR_3$ (where R_2 = COOH, COOalkyl, CHO, $C\equiv N$, NO_2 . . . . , and R_3 = H, alkyl, aryl) in most cases yielded only the *o*-adduct, and the condensation of dienes $CH_2=CR_1-CH=CH_2$ with philodienes $R_2CH=CHR_3$ yielded mainly the *p*-adduct, an ionic reaction mechanism was suggested for the diene synthesis. In this mechanism, the anionoid end of the diene system adds to the cationoid end of the dienophile, forming a bipolar ion, which quickly cyclises to the adduct[17-21]:



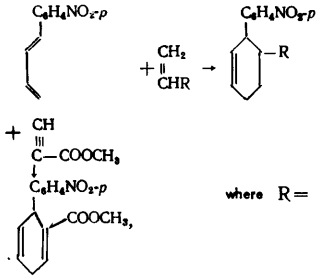
This hypothesis is fully consistent with the experimental data of Kataev and Matveeva, who by condensation of piperylene with 1-nitro-olefines of the type $NO_2CH=CHR$, obtained adducts in which the methyl and the nitro group are in *o*-position to each other[22]:



where R = $CH_2CH_2CH_3$, C_6H_5, and 2-furyl. According to this mechanism, the reaction of dienes containing an electronegative substituent in position 1 with philodienes also containing an electronegative substituent, should yield the adducts in which the electronegative substituents are *meta* to each other. However, in practice the *o*- and *p*-isomers are formed. This paradox may, according to some authors, be explained by assuming the diene synthesis to proceed via a reactive non-cyclised complex, or through the formation of a biradical intermediate and its subsequent cyclisation. Kataev[21], using the data of Alder, Schumacher, and Wolf[23], and also of Snyder and Poss[24], has suggested the following reaction path for the diene synthesis:



Kataev's scheme is consistent with the reaction of 1-(*p*-nitrophenyl)-1,3-butadiene with acrylic acid, acrylonitrile, and methyl propiolate to yield *o*-adducts, whereas by the ionic mechanism the *m*-adducts should be formed.

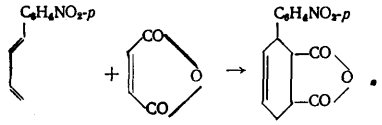


where R= COOH, CN .

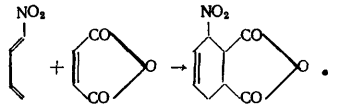
Most workers would now agree that the diene synthesis proceeds through an intermediate cyclic complex. In considering the direction of the reaction and the mutual orientation of the diene and the dienophile, one should remember that in the initial stage the electrostatic factors are of secondary importance, and that the conjugation in the intermediate stage plays a more important role. The presence of substituents may change the difference between the conjugation energy of the active complex and the initial stage, and this may manifest itself in the activation energy[25].

DIENE SYNTHESIS WITH NITRODIENES

Kataev, in his work, drew attention to the small reactivity of 1-(*p*-nitrophenyl)-1,3-butadiene. The yields of the corresponding adducts were usually in the 25–30% range; only with such an active philodiene as maleic anhydride did the yield reach 70%:[21]

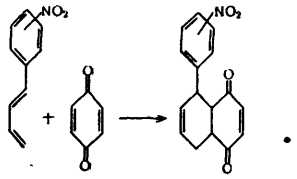


To elucidate more completely the effect of the nitro group on the diene synthesis, Kataev[21] studied the condensation of 1-nitrobutadiene with maleic anhydride, *p*-benzoquinone, acrolein, acrylonitrile, and dimethyl acetylene dicarboxylate. 1-Nitrobutadiene reacted only with maleic anhydride, giving merely 4% of the adduct.



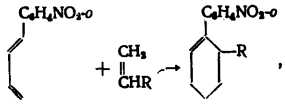
On the basis of these experimental data, Kataev[21] concluded that the α,β-double bond in 1-nitro-1,3-butadiene is considerably inactivated, and that the inactivating effect of the nitro group is diminished by the introduction of a benzene ring between it and the diene system, as in 1-(*p*-nitrophenyl)-1,3-butadiene.

Reactions of 1-(*o*-nitrophenyl)-, 1-(*m*-nitrophenyl)-, and 1-(*p*-nitrophenyl)-1,3-butadienes with *p*-benzoquinone were carried out by Goldberg and Scott[26]:



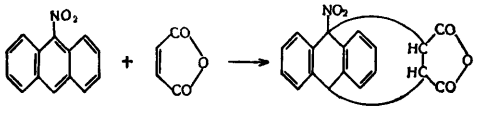
The adducts obtained can be used as amoebocides and fungicides.

1-(*o*-Nitrophenyl)-1,3-butadiene condenses with maleic anhydride, acrolein, and acrylic acid giving the corresponding adducts; the last two philodienes yield adducts with adjacent substituents[27]:

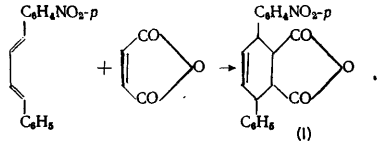


where R = CHO; COOH.

The introduction of a nitro group into the 9-position also has an inhibiting effect on the diene synthesis of anthracene with maleic anhydride. Whereas anthracene itself reacts within 10 min on boiling with maleic anhydride in xylene, giving the adduct in quantitative yield[28], the adduct of 9--nitroanthracene and maleic anhydride is formed in 56% yield by boiling the components for 2 h in xylene[29]:



1-(*p*-Nitrophenyl)-4-phenyl-1,3-butadiene reacts with maleic anhydride when heated in the absence of solvent at 100°, giving the adduct (I) in quantitative yield[30]:

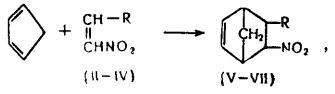


(I)

DIENE SYNTHESIS WITH NITROPHILODIENES

The presence in the philodiene of a nitro group conjugated with the double bond facilitates the diene synthesis, although the presence of a nitro group in the diene acts as an inhibitor, as shown above. The following unsaturated nitro compounds as philodienes in the Diels–Alder reaction have been used: nitroethylene and its homologues and derivatives, β-nitrostyrene and its homologues and derivatives, and 1,1-dinitroethylene.

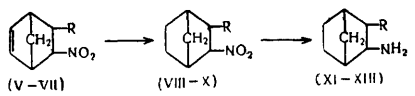
The condensation of nitro-olefines (nitroethylene, nitropropylene, and nitroamylene) with cyclopentadiene was first carried out by Alder and his collaborators. They showed, with nitroethylene as an example, that the condensation proceeded according to diene synthesis[1]:



(II–IV) (V–VII)

where R = H (II), R = CH_3 (III), R = C_3H_7 (IV), R = H(V), R = CH_3 (VI), and R = C_3H_7 (VII).

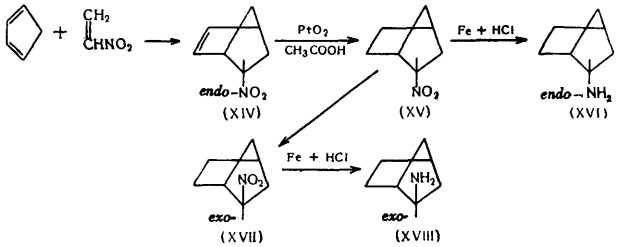
The structure of the adducts obtained was determined by transforming them into known products. The nitro-adducts (V), (VI), and (VII) were hydrogenated over platinum oxide to form the saturated nitro compounds (VIII), IX), and (X), which could be reduced by zinc or iron powder and hydrochloric acid to saturated amines (XI), (XII), and (XIII):



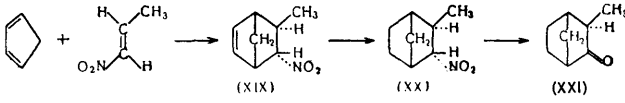
(V–VII) (VIII–X) (XI–XIII)

Amine (XI), prepared from nitro-adduct (V), was identical with *endo*-norbornylamine, already described in the literature. Similarly, (VIII) was identical with 2-nitronorcamphane, and (V) with 5-nitronorbornylene. These results indicated that the reaction of nitroethylene with cyclopentadiene proceeded with 1,4-addition. Adduct (V) showed that the diene synthesis with nitro-olefines followed the rule of the maximum accumulation of double bonds, formulated by Alder, and that the nitro-adduct had the *endo*-configuration.

Later work by Roberts, Lee, and Saunders[31] confirmed the stereospecific effect of the nitro group on the diene synthesis. In their opinion[31], the condensation of nitroethylene with cyclopentadiene yielded 90% of the adduct with the *endo*-configuration (XIV). They arrived at this conclusion because hydrogenation of adduct (XIV) gave *endo*-2--nitronorcamphane (XV), which was subsequently reduced to *endo*-norbornylamine (XVI). Isomerisation (heating with triethylamine) of *endo*-2-nitronorcamphane gave *exo*-2--nitronorcamphane (XVII), which was reduced to *exo*-norbornylamine (XVIII)[31].

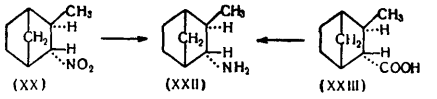


To establish the steric configuration of the substituents in the reaction product of nitropropylene and cyclopentadiene, van Tamelen and Thiede[32] carried out the selective hydrogenation of the nitro-adduct (XIX) over platinum oxide to (XX), and subsequently obtained the ketone (XXI) by the Nef reaction. Ketone (XXI) was shown to be identical with 3--*exo*-methylbicyclo[2,2,2]heptanone, already known:



(XIX) (XX) (XXI)

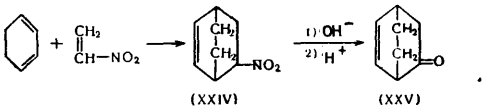
For conclusive confirmation of the *exo*-configuration of the methyl group, the nitro-adduct (XX) was reduced by means of iron and acetic acid to the amine (XXII):



(XX) (XXII) (XXIII)

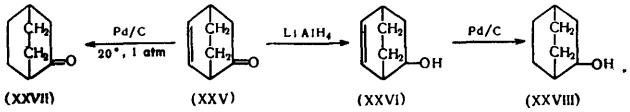
Amine (XXII) proved to be identical with the amine obtained by the Schmidt reaction from 2-*endo*-carboxy-3-*exo*-methylbicyclo[1,2,2]heptane (XXIII), whose configuration was known with certainty[32].

Wildman and Saunders observed the interesting case of the formation of an *endo*-ethylene bridge (XXIV) on boiling a mixture of nitroethylene and cyclo-1,3-hexadiene:[7]



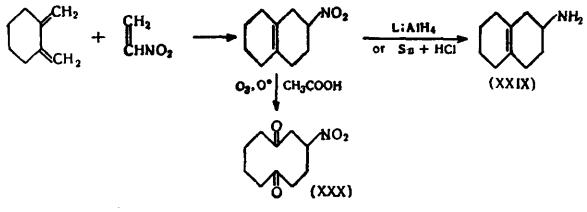
(XXIV) (XXV)

The adduct was subsequently subjected to the Nef reaction, the unsaturated ketone (XXV) thus formed was transformed into the unsaturated alcohol (XXVI). The ketone and alcohol were hydrogenated to the saturated compounds (XXVII) and (XXVIII)[7]:

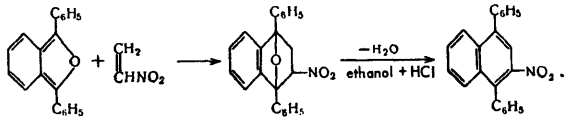


(XXVII) (XXV) (XXVI) (XXVIII)

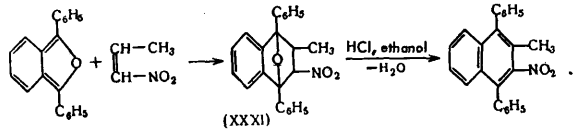
The reaction of nitroethylene with 1,2-dimethylenecyclohexane is highly exothermic, and yields 85% of 2-nitro--1,2,3,4,5,6,7,8-octahydronaphthalene, which can be reduced by $LiAlH_4$ or Sn + HCl to the unsaturated amine (XXIX), or oxidised by ozone to 3-nitrocyclodecane-1,6-dione (XXX)[33].



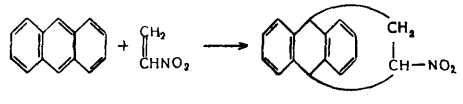
Nitroethylene reacts exothermically with 1,3-diphenylisobenzofuran giving quantitatively an adduct which, on dehydration with ethanol-HCl, is transformed into 1,4-diphenyl-2-nitronaphthalene[8]:



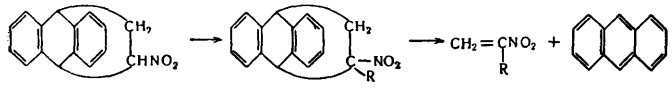
The reaction of 1-nitro-1-propene with 1,3-diphenylisobenzofuran yields two stereoisomeric adducts (XXXI), b.p. 188°–189° and 157°. Only the higher-boiling isomer eliminates water in the presence of ethanol-HCl to form an aromatic compound[8]:



Klager condensed nitroethylene with anthracene by heating them in *o*-dichlorobenzene solution at 145°–150° for 45 min:

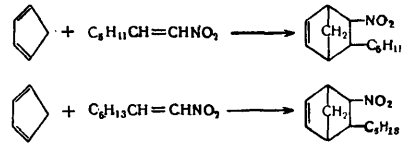


The adduct obtained was used for synthesising nitro-olefines[6]:

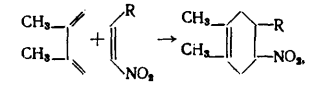


where R = CH_2OCOCH_3, $CH_2CH_2OCOCH_3$, CH_2CH_2CN.

The nature of the nitro-olefine has a considerable effect on the course of the diene synthesis. For instance, nitroethylene adds to cyclopentadiene at room temperature (67% yield)[3], whereas its homologues 1-nitroheptene and 1-nitrooctene condense with cyclopentadiene only at 100°:[34]

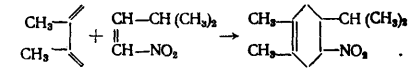


According to Drake and Ross[35], 2,3-dimethyl-1,3-butadiene condenses equally easily with all nitro-olefines, irrespective of their molecular weight:

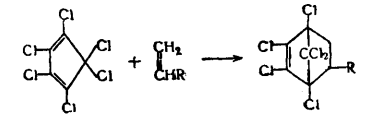


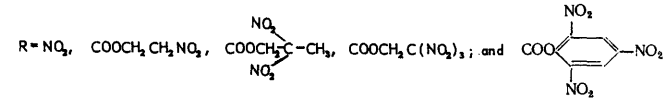
where R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, iso-C_4H_9, C_5H_{11}, C_6H_{13}.

However, if there is a bulky group (R = iso-C_3H_7) near the double bond of the nitro-olefine, condensation with 2,3--dimethyl-1,3-butadiene is considerably hindered and the yield of the adduct, under comparable conditions, is decreased[35]:



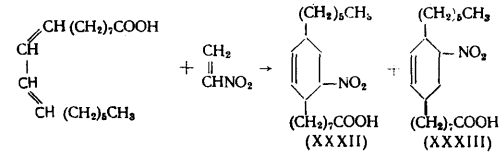
In some cases the steric hindrance is so pronounced that the diene synthesis is practically impossible. An example is encountered in the condensations of hexachlorocyclopentadiene with unsaturated nitro compounds of the structure $CH_2=CHR$ (where R = NO_2, $COOR'NO_2$) and $NO_2CH=$ $=CHR''$ (where R'' = alkyl, aryl, $COOCH_3$ and CN). The nitro-olefines of the latter type do not form adducts even when the components are heated above 100° for 20–30 h.[11] However, hexachlorocyclopentadiene condenses with nitrophilodienes of the type $CH_2=CHR$, giving the corresponding adducts in good yields[11]. Cyclopentadiene, as mentioned above, reacts quite easily with nitro-olefines $CH(NO_2)=CHR$ (where R = alkyl, aryl).





The steric hindrance, which has such a powerful effect on the condensation of hexachlorocyclopentadiene with nitrophilodienes $NO_2CH=CHR''$, apparently depends on two main factors. Firstly, the *trans*-position of the substituents in nitrophilodiene[32] probably inhibits the condensation with dienes, since the diene synthesis is considered to be exclusively a *cis*-addition. Secondly, the bulky chlorine atoms in the 5-position of hexachlorocyclopentadiene, hinders condensation with philodienes[36].

The condensation of nitroethylene with dienes containing different alkyl substituents in positions 1 and 4 is expected to form two stereoisomeric adducts. From the condensation of nitroethylene with 9,11-octadecadien-1-oic acid (the effect of COOH is negligible), it was possible to isolate the *meta*- and *ortho*-isomers[37] (XXXII) and (XXXIII).



One isomer, m.p. 85°–90°, was isolated in 16.2% yield, the other (a liquid, $n_D^{30°}$ = 1.4870) in 25.2% yield. The

authors did not ascribe structural formulae to the corresponding isomers.

The reaction of nitro-olefines with dienes is limited by their relative activity in the diene synthesis and by their ability to polymerise. 2-Nitro-1-alkenes, e.g. 2-nitro--1-propylene, are less reactive than 1-nitro-olefines. The former type react with cyclopentadiene only upon heating for several hours at 100°, and require careful preliminary purification and the presence of polymerisation inhibitors. Yields of the corresponding adducts are not large (30--40%)[38].

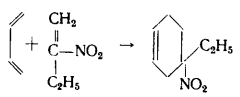


Study of the condensations of 2-nitro-1-butene with cyclopentadiene, butadiene, and 2,3-dimethylbutadiene[39] showed that reaction occurred more easily with the cyclic diene than with the acyclic ones, whereas 1-nitro-1-pentene condensed with both types of dienes with equal ease, and gave good yields of adducts[1].

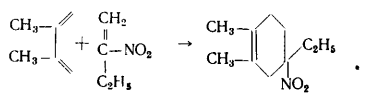
The condensation of 2-nitro-1-butene with cyclopentadiene in an autoclave, at 100°–115°, in the presence of hydroquinone, gave a 61% yield after 3 h[39]:



The adduct from butadiene and 2-nitro-1-butene formed in 37% yield after heating the mixture of components in an autoclave for 4 h at 120°–130°:[39]

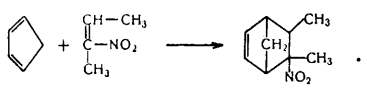


The reaction of 2-nitro-1-butene with 2,3-dimethylbutadiene proceeded more quickly than that with butadiene (under the same conditions it took 2 h). The yield of the product was 40%.[39]

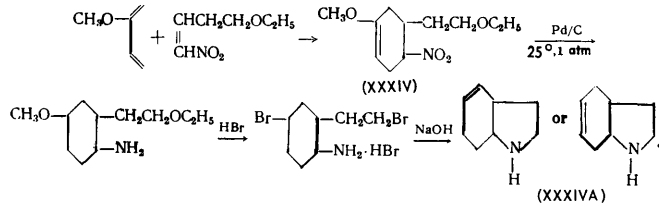


Nightingale and Janes[40] were unable to condense 2--nitro-2-alkenes (2-nitro-4-ethyl-2-hexene, 2-nitro-4--ethyl-2-pentene, and 3-nitro-3-hexene) with cyclopentadiene.

However, others authors later managed[38] to condense 2-nitro-2-butene with cyclopentadiene. The reaction proceeded (~100°) for 5 h and the yield of the nitro-adduct was 41%:



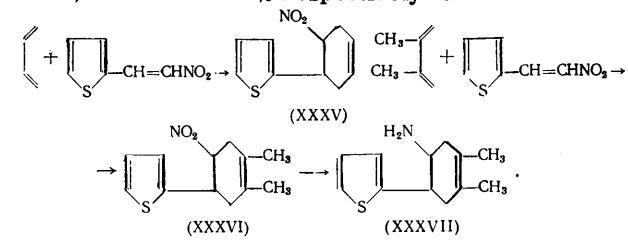
Drake and Ross[5] studied the condensation of 2-methoxy--1,3-butadiene with 4-ethoxy-1-nitro-1-butene and used the adduct obtained (XXXIV) for the synthesis of hexahydroindole (XXXIVA).



(XXXIV)

(XXXIVA)

2-(α-Thienyl)-1-nitroethylene condensed with butadiene and 2,3-dimethylbutadiene under the same conditions (140°, in autoclave, 6 h); the yields of the adducts (XXXV) and (XXXVI) were 61 and 84% respectively[39]:

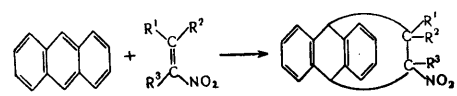


(XXXV)

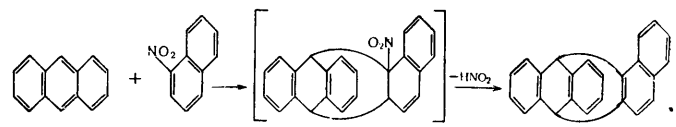
(XXXVI) (XXXVII)

The latter nitro-adduct can be reduced by means of $LiAlH_4$ to unsaturated amine (XXXVII).

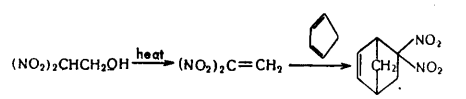
In condensations of anthracene with nitro-olefines of the types $RCH=CHNO_2$ (R = H, CH_3), $CH_2=C(R)NO_2$ (R = CH_3), $RCH=C(R)NO_2$ (R = CH_3), and $RRC=CHNO_2$ (R = CH_3), nitro-olefines of the last two types react with much the greater difficulty[41]:



Hurd and Juel[42] condensed anthracene with 1-nitronaphthalene at 300°, and obtained the adduct which, under the reaction conditions, split off a molecule of nitrous acid and was transformed into a benzotriptycene:



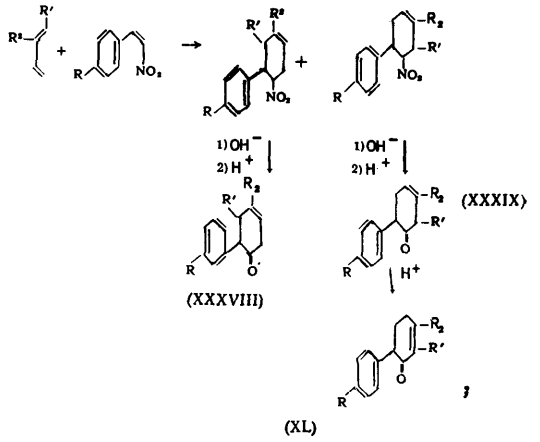
The interesting case of the formation of a *gem*-dinitro-adduct was described by Gold, Hamel, and Klager[43]. Heating cyclopentadiene with 2,2-dinitroethanol in chlorobenzene gave 1,1-dinitrobicyclo[2,2,1]-3-heptene. The authors correctly concluded that under the reaction conditions dinitroethanol is dehydrated to 1,1-dinitroethylene, which condenses with cyclopentadiene:



The behaviour of β-nitrostyrene and its homologues and derivatives in the diene synthesis has been studied very thoroughly. Condensations have been effected with butadiene, 2-ethoxybutadiene, piperylene, isoprene, 1,4-dimethylbutadiene, 2,3-dimethylbutadiene, 2,3-diphenylbutadiene, 1,4-diphenylbutadiene, cyclopentadiene, 3,4-diphenyl-2,5-dimethyl-2,4-cyclopentadien-1-one, 2,3,4,5--tetraphenyl-2,4-cyclopentadien-1-one, cyclohexadiene, phellandrene, 2-vinylcyclohexene, bicyclohexenyl, methyleneanthrone, anthracene, 1,3-diphenylisobenzofuran,

1,3-diphenyl-5,6-dimethylisobenzofuran. β-Nitrostyrene did not react with furan, silvan, and 2,5-dimethylfuran[4,41,44-53].

Butadienes which are substituted in positions 1 and 2 condense with β-nitrostyrene or its derivatives to give two isomers (except in the case of 2-ethoxybutadiene, which only yields one)[4]:

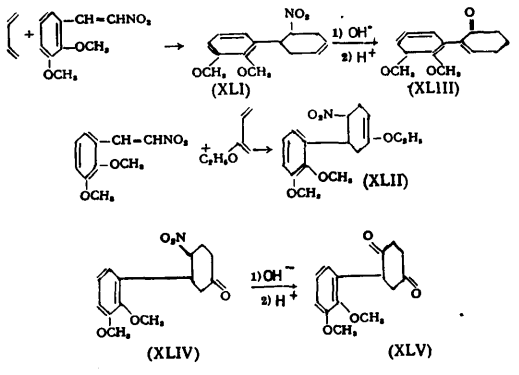


a) R = R' = H, $R_2 = OC_2H_5$; b) R = R' = H, $R_2 = CH_3$; c) R = OCH_3, R' = H, $R_2 = CH_3$; d) R = R_2 = H, R' = CH_3.

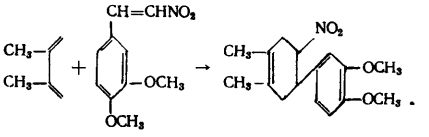
In reactions with isoprene and piperylene, a mixture of isomers is formed. In cases b) and d), namely in condensations of isoprene (b) and piperylene (d) with β-nitrostyrene, the relative quantities of isomers were determined from the quantities of ketones (XXXVIII) and (XXXIX) formed from them by the Nef reaction. Ketone (XXXIX) is isomerised under the action of acids into the conjugated ketone (XL).

Condensation of butadiene with β-nitrostyrene, and its derivatives (*m*-methoxy-, *p*-methoxy-, and 2,3-dimethoxy-β-nitrostyrene) in toluene at 100° for 48 h, gave adducts in 82–100% yield (see Table 3).[45]

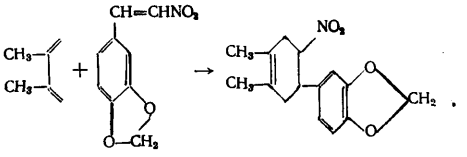
Barltrop and Nicholson[47], in their study of the preparation of intermediate compounds for the synthesis of the morphine series, condensed 2,3-dimethoxy-β-nitrostyrene with butadiene and 2-ethoxybutadiene at 200° for 15 h, using xylene as solvent. They subjected the resulting adducts (XLI) and (XLII) to a series of transformations in order to obtain the corresponding ketones (XLIII), (XLIV), and (XLV):



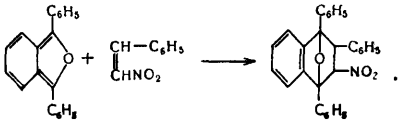
In 1939, 2,3-dimethylbutadiene was condensed with 3,4-dimethoxy-β-nitrostyrene by heating in xylene in a sealed tube at 175°–180° for 10 h[48]; 80% of the adduct was obtained.



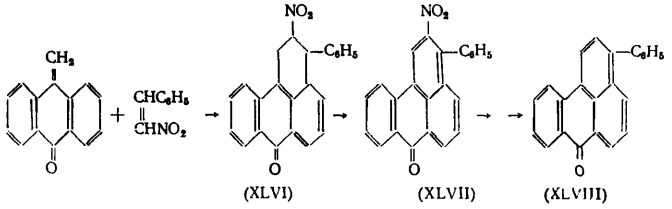
3,4-Methylenedioxy-β-nitrostyrene condenses with 2,3-dimethylbutadiene under the same conditions, yielding 70% of the corresponding adduct[48]:



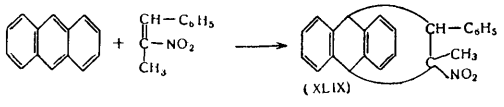
β-Nitrostyrene gives a quantitative yield of adduct when reacted with 1,3-diphenylisobenzofuran in boiling ethanol for 3 h[46]:



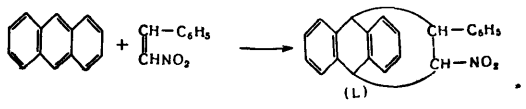
The addition of β-nitrostyrene to methyleneanthrone opened the way to the preparation of poly-condensed systems. The adduct thus formed, (XLVI), was dehydrogenated to form the polycyclic compound (XLVII), the nitro group of which was successively reduced and diazotised using butylnitrite and acetic acid. The diazo group was then replaced by hydrogen by decomposing the diazo compound with ethanol. Compound XLVIII was thus obtained[44,46].



By boiling β-methyl-β-nitrostyrene and anthracene in *o*-dichlorobenzene, a low yield (1.4%) of the corresponding adduct (XLIX)[41] was obtained:



However, β-nitrostyrene condenses with anthracene to give the adduct (L) in good yield[41]:



The sharp decrease in the yield of adduct (XLIX) as compared with that of adduct (L) can probably be accounted for by steric hindrance.

TABLE 1. Diene synthesis with nitrodienes.

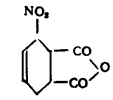
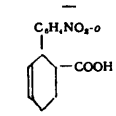
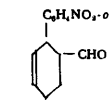
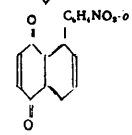
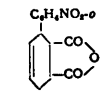
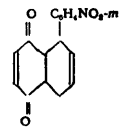
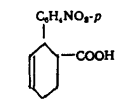
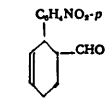
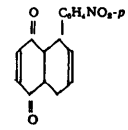
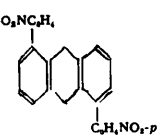
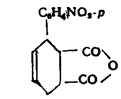
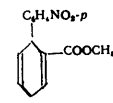
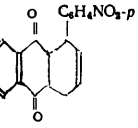
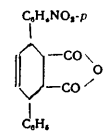
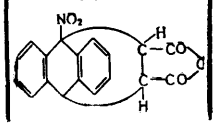
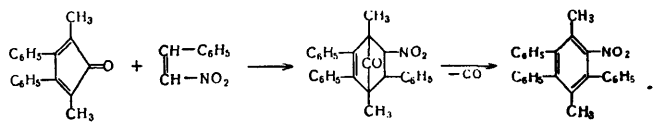
Diene	Philodiene	Adduct	Reaction conditions	Constants of the adduct	Yield, %	Reference
1-Nitro-1,3-butadiene	Acrylonitrile	—	90°—100°	—	0	21
1-Nitro-1,3-butadiene	Acrolein	—	90°—100°	—	0	21
1-Nitro-1,3-butadiene	Benzoquinone	—	90°—100°	—	0	21
1-Nitro-1,3-butadiene	Dimethyl acetylene dicarboxylate	—	90°—100°	—	0	21
1-Nitro-1,3-butadiene	Maleic anhydride		90°—100°	—	4	21
1-Nitro-1,3-butadiene	Naphthoquinone	—	90°—100°	—	0	21
1-(*o*-Nitrophenyl)-1,3-butadiene	Acrylic acid		refluxing for 18 h	m. p. 141°	78	27
1-(*o*-Nitrophenyl)-1,3-butadiene	Acrolein		refluxing for 5 h	m. p. 46° b. p. 100°/10 mm Hg	55	27
1-(*o*-Nitrophenyl)-1,3-butadiene	*p*-Benzoquinone		48 h in acetone without heating	m. p. 93°—97°	—	26
1-(*o*-Nitrophenyl)-1,3-butadiene	Maleic anhydride		15 min at 80° in benzene	m. p. 215°	quant.	27
1-(*m*-Nitrophenyl)-1,3-butadiene	*p*-Benzoquinone		48 h in acetone without heating	m. p. 120°—124°	—	26
1-(*p*-Nitrophenyl)-1,3-butadiene	Acrylic acid		refluxing for 2 h in xylene under nitrogen	m. p. 111°—114°	25—35 71	21 55
1-(*p*-Nitrophenyl)-1,3-butadiene	Acrolein		—	—	25—35	21
1-(*p*-Nitrophenyl)-1,3-butadiene	*p*-Benzoquinone		48 h in acetone without heating	m. p. 170°—174°	16	21 26
1-(*p*-Nitrophenyl)-1,3-butadiene	1,4-Dioxo-5-(*p*-nitrophenyl)-1,4,4',5,8,8'-hexahydronaphthalene		—	—	8	21
1-(*p*-Nitrophenyl)-1,3-butadiene	Maleic anhydride		15 min, 70°	m. p. 170.9°—172°	70	21 56
1-(*p*-Nitrophenyl)-1,3-butadiene	Methyl propiolate		—	—	25—35	21
1-(*p*-Nitrophenyl)-1,3-butadiene	Naphthoquinone		—	—	40	21

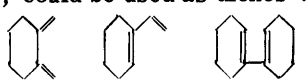
TABLE 1. contd.

Diene	Philodiene	Adduct	Reaction conditions	Constants of the adduct	Yield, %	Reference
1-(*p*-Nitrophenyl)-4-phenyl-1,3-butadiene	Maleic anhydride		2h, 100°	—	quant.	30
9-Nitroanthracene	Maleic anhydride		refluxing in xylene for 2 h	m. p. 244°–245°	56	29

To obtain polysubstituted phenylbenzenes, β-nitrostyrene was condensed with 3,4-diphenyl-2,5-dimethylcyclopentan-1-one:[9]

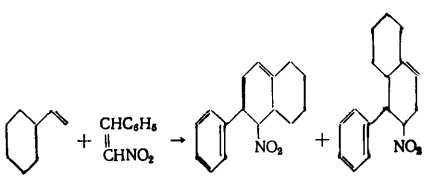


Alder showed that alicyclic compounds with both double bonds semicyclic (LI), as well as vinylcyclenes (LII) and bicyclenes (LIII), could be used as dienes[1]:



(LI) (LII) (LIII)

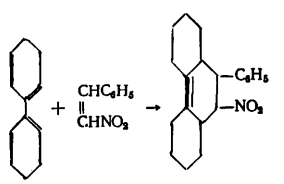
In the condensation of vinylcyclohexene with β-nitrostyrene, the formation of two structural isomers (LIV) and (LV)[48] is possible:



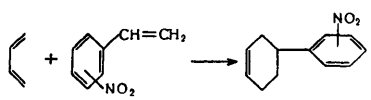
(LIV) (LV)

In the opinion of the authors, the formation of the first one is more probable[48].

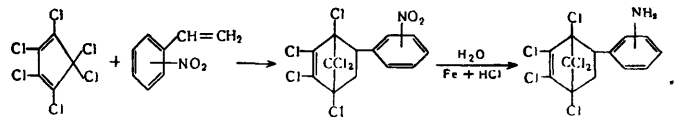
Bergmann and his collaborators[49] condensed β-nitrostyrene with bicyclohexenyl, obtaining 95% of the expected reaction product:



Other nitro-olefines studied were the isomeric *o*-, *m*-, and *p*-nitrostyrenes, which condensed with butadiene to form 44–60% of the corresponding adducts[50]:

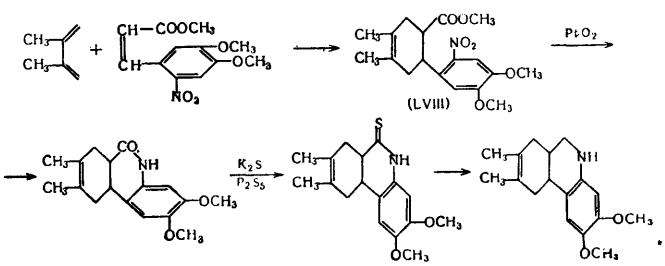


According to an American patent[10], the nitro-adducts (LVI), obtained from *o*- or *m*-nitrostyrenes and hexachlorocyclopentadiene, on reduction yield unsaturated amines (LVII), which possess fungicidal properties:



(LVI) (LVII)

Sugasawa, Kodama, and Hara[51] condensed 2,3-dimethylbutadiene with methyl 3,4-dimethoxy-6-nitrocinnamate, obtained adduct (LVIII), and studied its transformations:

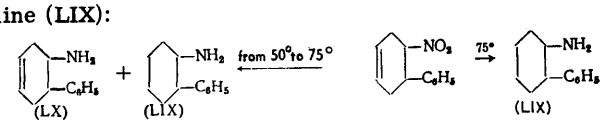


(LVIII)

METHODS FOR HYDROGENATION AND REDUCTION OF ADDUCTS

The adducts formed in the condensation of nitro-olefines with dienes contain a nitro group and a double bond. Therefore hydrogenation can lead to three different products, i.e. the saturated nitro compound, and the unsaturated and saturated amines. As the synthesis of these products is very important in determining the configuration of the adducts, we thought it necessary to include in this survey the methods for their selective hydrogenation.

It has been shown for a number of cases[52], that in hydrogenations over Raney nickel catalysts, NO_2 groups are reduced to amino groups at a lower temperature than that required for saturation of the double bond. For instance, the adduct obtained from butadiene and β-nitrostyrene was hydrogenated at 200 atm at 50°–75°. The analysis of the hydrogenation products showed that under these conditions a mixture of the saturated (LIX) and the unsaturated (LX) amines was formed, whereas at 75° the nitro-adduct was completely transformed into the saturated amine (LIX):



(LX) (LIX) (LIX)

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TABLE 2. Diene synthesis with nitrophilodienes, except *p*-nitrostyrene

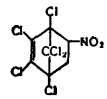
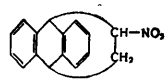
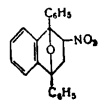
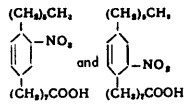
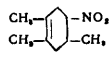
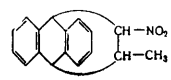
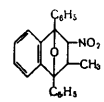
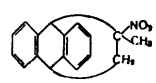
Diene	Philodiene	Adduct	Reaction conditions	Constants of the adduct	Yield %	Reference
Cyclopentadiene	Nitroethylene		8 h in a sealed tube in ether at 105°–100°; 8 h in benzene at 18°–20°	b. p. 70°–90°/15 mm Hg; 92°–94°/8 mm Hg	67	1 3
Hexachlorocyclopentadiene	Nitroethylene		14 h in chlorobenzene at 100°–102°, in the presence of glacial CH_3COOH	m. p. 160°–161.5°	73	11
1,3-Cyclohexadiene	Nitroethylene		refluxing for 1 h	b. p. 85°–87°/1 mm Hg	33	7
1,2-Dimethylenecyclohexane	Nitroethylene		stirring in cooled ether, then refluxing for 2 h	b. p. 128°–129°/5 mm Hg	85	33
Anthracene	Nitroethylene		8 h in benzene at 110°; 45 min in *o*-dichlorobenzene at 145°–150°	m. p. 113°–114°	76 71	6 39 41
1,3-Diphenylisobenzofuran	Nitroethylene		in $CHCl_3$ at 20°	m. p. 178°	99	8
9,11-Octadecadien-1--oic acid	Nitroethylene		heating in benzene in a sealed tube for 48 h	m. p. 85°–90°; liquid isomer $n_D^{20°}$ = 1.4835	16.2 25.2	37
2,3-Dimethyl-1,3--butadiene	1-Nitropropylene		8 h in acetonitrile; without solvent	b. p. 71°/0.6 mm Hg	68.5 72	35
Hexachlorocyclopentadiene	1-Nitropropylene	–	20–30 h at 100°–120°	–	0	11
Cyclopentadiene	1-Nitropropylene		8 h in glacial CH_3COOH at 113°; in glacial CH_3COOH at 40°–50°	b. p. 94°–95°/1 mm Hg; 91.5°–92.5°/11–12 mm Hg	55 59	1 32
Anthracene	1-Nitropropylene		in *o*-dichlorobenzene, refluxing for 45 min	m. p. 122.5°–123.5°	62	41
1,3-Diphenylisobenzofuran	1-Nitropropylene	 2 stereoisomers	5 h in $CHCl_3$ at 20°	m. p. 188°–189°, and 157°	41	8
Cyclopentadiene	2-Nitropropylene		in acetic acid at 98°; 90 min in autoclave	m.p. 104°, 84°–86°; b.p. 105°–110°/18 mm Hg	27 34	38 39
Hexachlorocyclopentadiene	2-Nitropropylene	–	20–30 h at 100°–120°	–	0	11
Anthracene	2-Nitropropylene		in benzene in a sealed tube at 110° for 12 h	m.p. 152°–153.5°	19	41

TABLE 2. contd.

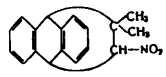
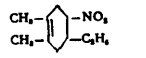
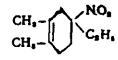
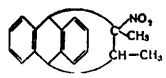
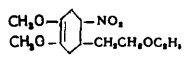
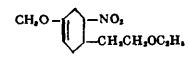
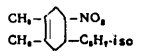
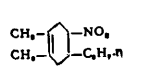
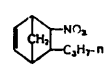
Diene	Philodiene	Adduct	Reaction conditions	Constants of the adduct	Yield %	Reference
Anthracene	2-Methyl-1-nitro-propylene		refluxing in *o*-dichlorobenzene for 4 h	m.p. 147.5–151.5°	0.6	41
2,3-Dimethyl-1,3--butadiene	1-Nitro-1-butene		refluxing in acetonitrile for 16 h	b.p. 105°/4 mm Hg	77.5	35
1,3-Butadiene	2-Nitro-1-butene		4 h in autoclave at 120°–130°	b.p. 82°–84°/5 mm Hg	37	39
2,3-Dimethyl-1,3--butadiene	2-Nitro-1-butene		2 h in autoclave at 140°	b.p. 94°–94.5°/8 mm Hg	40	39
Cyclopentadiene	2-Nitro-1-butene		3 h in autoclave at 103°–115°	b.p. 79°/5 mm Hg	61	39
Cyclopentadiene	2-Nitro-2-butene		5 h, 100°	m.p. 84.5°–86.5°; b.p. 65°/2 mm Hg	41	38
Anthracene	2-Nitro-2-butene		refluxing in *o*-dichlorobenzene for 3.25 h	m.p. 130.5°–132.5°	0.4	41
2,3-Dimethoxy-1,3--butadiene	4-Ethoxy-1-nitro-1--butene		in acetonitrile, refluxing for 34 h; in acetonitrile, refluxing for 40 h	b.p. 112°–114°/1 mm Hg	69	35
2-Methoxy-1,3-butadiene	4-Ethoxy-1-nitro-1--butene		6 h in acetonitrile at 100°	b.p. 137°–138°/2 mm Hg	52–53	5
2,3-Dimethyl-1,3--butadiene	1-Nitro-1-isopentene		in acetonitrile refluxing for 16 h; heating for 16 h at 100°	b.p. 105°/3 mm Hg	31.5 35	35
1,3-Butadiene	1-Nitro-1-pentene		6 h in a sealed tube, at 100°–110°	b.p. 118°/11 mm Hg	–	1
Piperylene	1-Nitro-1-pentene		15 h, 150°	b.p. 108°–110°/6 mm Hg	70	22
2,3-Dimethyl-1,3--butadiene	1-Nitro-1-pentene		6 h in a sealed tube at 100°–110°; 24 h at 100°	b.p. 146°–147°/12 mm Hg; b.p. 113°–114°/5 mm Hg	– 69.5	1 35
Cyclopentadiene	1-Nitro-1-pentene		in benzene, in a sealed tube at 105°–110°	b.p. 122°–125°/1 mm Hg	72	1

TABLE 2. contd.

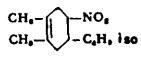
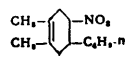
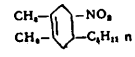
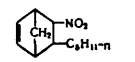
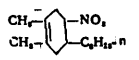
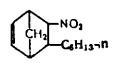
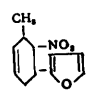
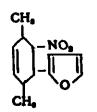
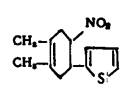
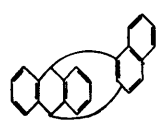
Diene	Philodiene	Adduct	Reaction conditions	Constants of the adduct	Yield, %	Reference
2,3-Dimethyl-1,3--butadiene	1-Nitro-1-isohexene		refluxing in acetonitrile for 32 h; 32 h at 100°	b.p. 115°–116°/3 mm Hg	68.5 65	35
2,3-Dimethyl-1,3--butadiene	1-Nitro-1-hexene		33 h, 100°	b.p. 124°–126°/3 mm Hg	73	35
2,3-Dimethyl-1,3--butadiene	1-Nitro-1-heptene		refluxing for 32 h in acetonitrile	b.p. 129°–130°/3 mm Hg	65	35
Cyclopentadiene	1-Nitro-1-heptene		5 h, 100°	b.p. 122°–123°/5 mm Hg	66	34
2,3-Dimethylbutadiene	1-Nitro-1-octene		24 h, 100°	b.p. 116°/0.3 mm Hg	77–78	35
Cyclopentadiene	1-Nitro-1-octene		4 h, 100°	b.p. 103°/0.5 mm Hg	33	34
Hexachlorocyclo-pentadiene	Methyl nitroacrylate	–	20–30 h, 100°–120°	–	0	11
Hexachlorocyclo-pentadiene	β-Nitroacrylonitrile	–	20–30 h, 100°–120°	–	0	11
Piperylene	2-(α-Furyl)nitro-ethylene		8 h at 150°, in a sealed tube	b.p. 120°–122°/4 mm Hg	55	22
1,4-Dimethyl-1,3-butadiene	2-(α-Furyl)nitro-ethylene		16 h at 150° in a sealed tube	b.p. 125°–127°/4 mm Hg	46	22
1,3-Butadiene	2-(α-Thienyl)nitro-ethylene		6 h in autoclave at 140°	m.p. 69°–70°	60	39
2,3-Dimethyl-1,3-butadiene	2-(α-Thienyl)nitro-ethylene		6 h in autoclave at 140°	m.p. 80.5°–81°	60	39
Anthracene	1-Nitronaphthalene		heating for 15 h at 300°	m.p. 207°–208°	44	42
Cyclopentadiene	1,1-Dinitroethylene		30 min in chlorobenzene at 100°–110°	m.p. 117°–118°	–	43

TABLE 2. contd.

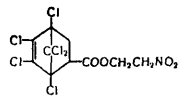
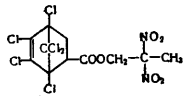
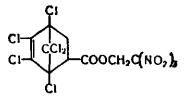
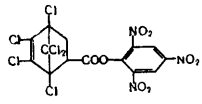
Diene	Philodiene	Adduct	Reaction conditions	Constants of the adduct	Yield %	Reference
Hexachlorocyclo-pentadiene	2-Nitroethyl acrylate		refluxing in chlorobenzene for 21 h	m.p. 93°–94°	89	11
Hexachlorocyclo-pentadiene	2,2-Dinitropropyl acrylate		10 h, 100°–110°	m.p. 114°–115°	quant.	11
Hexachlorocyclo-pentadiene	2,2,2-Trinitroethyl acrylate		refluxing for 20 h in chloro-benzene	m.p. 55°–51°	72	11
Hexachlorocyclo-pentadiene	2,4,6-Trinitrophenyl acrylate		28 h, 100°–110°	m.p. 116.5°–117.5°	65	11

TABLE 3. *Diene synthesis with β-nitrostyrene, its homologues and derivatives.*

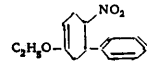
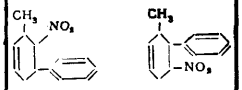
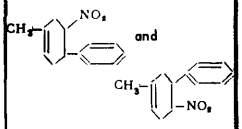
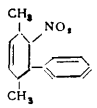
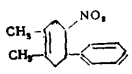
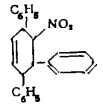
Diene	Philodiene	Adduct	Reaction conditions	Constants of the adduct	Yield, %	Reference
1,3-Butadiene	β-Nitrostyrene		48 h in toluene at 100°; 5 h in toluene at 150°	m.p. 103°	70	46
2-Ethoxy-1,3-butadiene	β-Nitrostyrene		refluxing for 3 h	m.p. 96.5°–97°	66	4
Piperylene	β-Nitrostyrene		10 h, 150°	m.p. 94°–95° and 98°–99°; m.p. 80°–82°	90 87	4 22
Isoprene	β-Nitrostyrene		in toluene at 100°	m.p. of the mixture of isomers 53.5°–54.5°; m.p. 52°	86 7 58	4 44 46
1,4-Dimethyl-1,3-butadiene	β-Nitrostyrene		16 h, 155°	b.p. 149°–151°/4 mm Hg	83	22
2,3-Dimethyl-1,3-butadiene	β-Nitrostyrene		24 h in toluene at 110° 2 h refluxing at 100°	m.p. 96°; m.p. 95°–96°	82 86	44 45 46
1,4-Diphenyl-1,3-butadiene	β-Nitrostyrene		in *o*-dichlorobenzene	m.p. 130°	40 80	44 46 48

TABLE 3. contd.

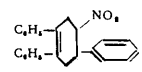
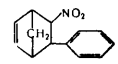
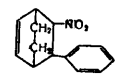
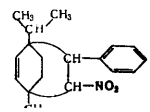
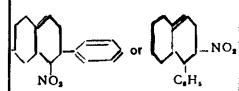
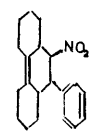
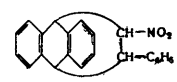
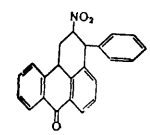
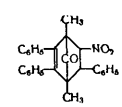
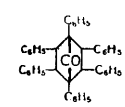
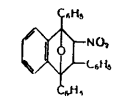
Diene	Philodiene	Adduct	Reaction conditions	Constants of the adduct	Yield, %	Reference
2,3-Diphenyl-1,3--butadiene	β-Nitrostyrene		refluxing in *o*-dichlorobenzene	m.p. 175°	9	44 46
Cyclopentadiene	β-Nitrostyrene		without solvent	b.p. 145°/1 mm Hg	95 quant.	44 46
Hexachlorocyclo-pentadiene	β-Nitrostyrene	–	20–30 h, 100°–150°	–	0	11
Cyclohexadiene	β-Nitrostyrene		without solvent	b.p. 138°–142°/1 mm Hg	20 25	44 46
Phellandrene	β-Nitrostyrene		without solvent	m.p. 85°; b.p. 190°/1 mm Hg	45	44 46
Vinylcyclohexene	β-Nitrostyrene		–	–	–	48
Bicyclohexenyl	β-Nitrostyrene		8 h, 100°	m.p. 187°	96	49
Anthracene	β-Nitrostyrene		refluxing in xylene for 20 h	m.p. 150°–151°	54	41
Methyleneanthrone	β-Nitrostyrene		refluxing in acetic acid for 16 h	m.p. 255°	3	44 46
3,4-Diphenyl-2,5--dimethylcyclo-2,4--pentadien-1-one	β-Nitrostyrene		in benzene	m.p. 176°	92	9
2,3,4,5-Tetraphenyl-cyclo-2,4-pentadien--1-one	β-Nitrostyrene		refluxing in trichlorobenzene	–	–	44
Furan	β-Nitrostyrene	–	100°	–	0	46
2-Methylfuran	β-Nitrostyrene	–	100°	–	0	46
2,5-Dimethylfuran	β-Nitrostyrene	–	100°	–	0	46
1,3-Diphenylisobenzo-furan	β-Nitrostyrene		refluxing in ethanol for 3 h	m.p. 163°	quant.	46

TABLE 3. contd.

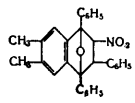
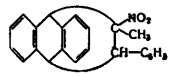
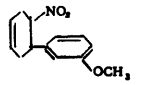
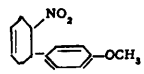
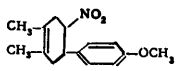
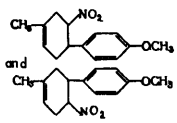
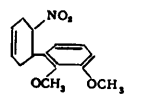
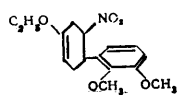
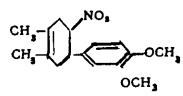
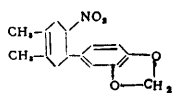
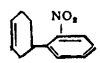
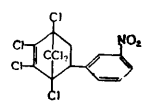
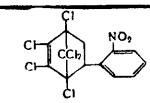
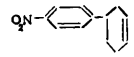
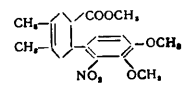
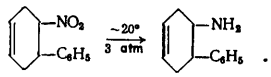
Diene	Philodiene	Adduct	Reaction conditions	Constants of the adduct	Yield, %	Reference
1,3-Diphenyl-5,6-dimethylisobenzofuran	β-Nitrostyrene		refluxing in ethanol for 3 h	m.p. 182°	quant.	46
Anthracene	β-Methyl-β-nitrostyrene		refluxing in *o*-dichlorobenzene for 4 h	m.p. 171.5°–172°	1.4	41
1,3-Butadiene	*m*-Methoxy-β-nitrostyrene		4.5 days in toluene at 100°	m.p. 67°–90°	97	45
1,3-Butadiene	*p*-Methoxy-β-nitrostyrene		4 days in toluene at 100°	m.p. 76.5°–77.5°	82	45
2,3-Dimethyl-1,3-butadiene	*p*-Methoxy-β-nitrostyrene		in toluene at 100°	m.p. 103.5°–104°	92	4
Isoprene	*p*-Methoxy-β-nitrostyrene		in toluene at 100°	m.p. 74°–75° and 97.5°–98.5°	63	4
1,3-Butadiene	2,3-Dimethoxy-β-nitrostyrene		3 days at 120°–130°; in xylene for 14 h at 200°; 10 h in xylene; 175°–180°, in autoclave	m.p. 81°–82°; 81°–83° 91°	100 70	45 47 48
2-Ethoxy-1,3-butadiene	2,3-Dimethoxy-β-nitrostyrene		15 h in xylene at 200°	b.p. 195°–205°/0.1 mm Hg	81	47
2,3-Dimethyl-1,3-butadiene	3,4-Dimethoxy-β-nitrostyrene		10 h in xylene at 175°–180°, in autoclave	m.p. 129°–130°	80	48
2,3-Dimethyl-1,3-butadiene	3,4-Methylenedioxy-β-nitrostyrene		10 h in xylene, 175°–180°, in autoclave	m.p. 91°	70	48
1,3-Butadiene	*o*-Nitrostyrene		40 h in a sealed tube at 123°–127°	m.p. 24°–25°	48	50
Hexachlorocyclopentadiene	*m*-Nitrostyrene		–	–	–	10
1,3-Butadiene	*m*-Nitrostyrene		40 h at 123°–127° in a sealed tube	m.p. 47.4°–47.6°	44	50

TABLE 3. contd.

Diene	Philodiene	Adduct	Reaction conditions	Constants of the adduct	Yield, %	Reference
Hexachlorocyclo-pentadiene	*o*-Nitrostyrene			–	–	10
1,3-Butadiene	*p*-Nitrostyrene		40 h at 123°–127° in a sealed tube	m.p. 87.2°–87.7°	60	50
2,3-Dimethyl-1,3--butadiene	Methyl-3,4-dimethoxy--6-nitrocinnamate		heating in xylene in a sealed tube	m.p. 155°–156°	–	51

The pure unsaturated amine (LX) can be obtained at low pressure and room temperature:



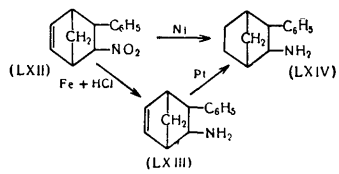
(LX)

The presence of two methyl group at the double bond considerably hinders its hydrogenation; for instance, in 1-nitro-2-phenyl-4,5-dimethylcyclohexene, the double bond is not hydrogenated below 165°.[52]

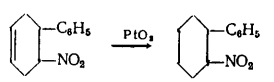
The degree of the selectivity of hydrogenation depends on the catalyst's "age" and the purity of the compound. Freshly prepared Raney nickel hydrogenates faster and more selectively than catalyst which has been standing for 2–3 months[52].

Methods are described in the literature for the selective reduction of either the nitro group[2] or the double bond[53] in nitro-adducts.

1-Nitro-2-phenylbicyclo[2,2,1]hexene (LXII) reduced with iron and hydrochloric acid gives in 47% yield the unsaturated amine (LXIII), which on hydrogenation over platinum yields the saturated amine (LXIV). LXIV can be obtained directly from (LXII) by hydrogenation over Raney nickel[2]:



If platinum oxide is used as a catalyst, selective hydrogenation of the double bond in 1-nitro-2-phenylcyclohexene (LXV) can be effected, while preserving the nitro group intact[53]:



(LXV)

On the basis of Arnold and Richardson's work[54], Zimmerman and Nevins[53] ascribed the *trans*-configuration to the adduct obtained from butadiene and β-nitrostyrene. This was in agreement with the fact that the hydrogenation of that adduct over platinum oxide in an ethyl acetate--acetic acid mixture, yielded *trans*-1-nitro-2-phenylcyclohexane.

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Δ^3-PIPERIDEINES

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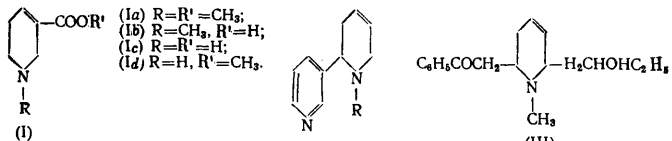
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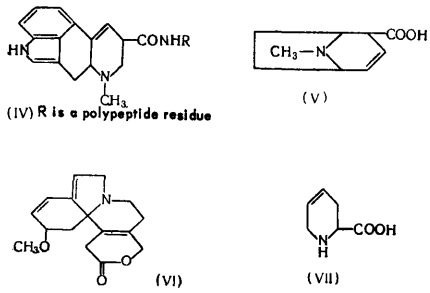
INTRODUCTION

Interest in the chemistry of 1,2,5,6-tetrahydropyridines (Δ^3-piperideines) is mainly due to the existence of a number of alkaloids which contain this structure. The fruit of the palm *Areca catechu*, which grows in India, Ceylon, and the Malay and Philippine Islands, is the source of a considerable number of alkaloids[1]. Jahns[2-5] obtained arecoline (*Ia*) and arecaidine (*Ib*) in a pure form from this fruit, and showed that they are both tetrahydropyridines methylated on the nitrogen and containing a carboxymethyl and a carboxy group respectively. Jahns believed that the double bond was in the 2,3-position, but Meyer[6,7] established that it is actually in the 3,4-position, and this has been confirmed synthetically by Wohl and Johnson[8]. Arecoline has been shown to be the methyl ester of 1-methyl--1,2,5,6-tetrahydronicotinic acid. Jahns also obtained guvacine and arecaine from the areca palm fruit; it was later shown[9-12] that guvacine is norarecaidine, i.e. 1,2,5,6--tetrahydronicotinic acid (*Ic*), and that arecaine is a mixture of arecaidine and guvacine. Hess[13] found another alkaloid related to arecoline, which has been named guvacoline (*Id*) and is norarecoline, i.e. 1,2,5,6-tetrahydronicotinic acid methyl ester.

The tobacco (*Nicotiana*) alkaloids anatabine (*IIa*)[14,15] and *N*-methyl anatabine (*IIb*)[16] are also Δ^3-piperideine derivatives; the secondary alkaloids from *Lobelia inflata* lobinine[17] and isolobinine[18-20] are stereoisomers of structure (III).[21]



The Δ^3-piperideine nucleus is found in the ergot (*Secale cornutum*) alkaloids ergotoxine, ergotamine, ergometrine, etc. of general formula (IV)[22,23], and in anhydroecgonine (V), of which the ethyl ester has been found in waste materials from the production of minor alkaloids of the leaves of *Erythroxylon coca*[24] and the methyl ester separated from Peruvian and Javanese coca seeds[25]. The *Erythrina* alkaloid β-erythroidine, to which Boekelheide and coworkers[26,27] give the formula (VI), also contain the Δ^3-piperideine nucleus. The amino-acid baikiain[28] (L-1,2,3,6-tetrahydropyridine-2-carboxylic acid) (VII) has been separated from Rhodesian teak (*Baikiaea plurijuga*).



The structure of certain alkaloids contains a piperidine ring substituted in the 3- or 4-position by a hydroxyl group, which is often esterified; dehydrating agents convert these compounds into the corresponding Δ^3-piperideines. Thus pseudoconiceine (IX) is obtained by the action of phosphorus