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THE DIENE SYNTHESIS WITH β-NITROSTYRENE

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Our work on the use of β-nitrostyrene in the diene synthesis, interrupted on account of the illness of one of the authors, was recorded in a preliminary note a few years ago (1). It has since been concluded as time permitted, and is described in this paper.

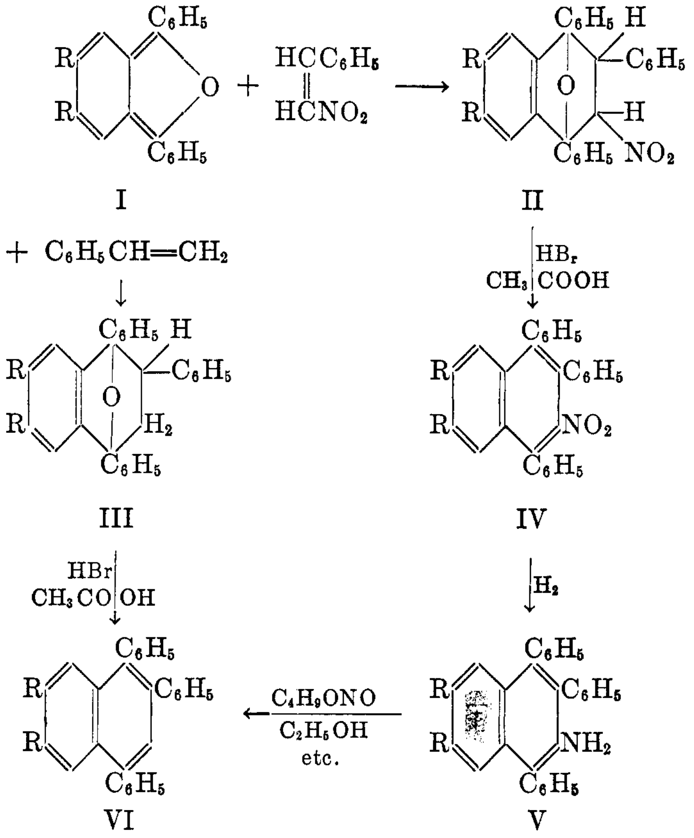
β-Nitrostyrene added readily to butadiene, isoprene, 2,3-dimethylbutadiene, 2,3-diphenylbutadiene, 1,4-diphenylbutadiene, phellandrene, cyclopentadiene, cyclohexadiene, 1,3-diphenylisobenzofuran, and 1,3-diphenyl-5,6-dimethylisobenzofuran. While it gave an addition product with 2,5-dimethyl-3,4-diphenylcyclopentadienone (2), secondary products were isolated from tetraphenylcyclopentadienone and methyleneanthrone; the latter gave *Bz*-1-phenylbenzanthrone, and the tetraphenylketone gave pentaphenylbenzene. It is very interesting to note that although it did not appear to enter into reaction with simple furans (1), it formed addition products very easily with isobenzofurans.

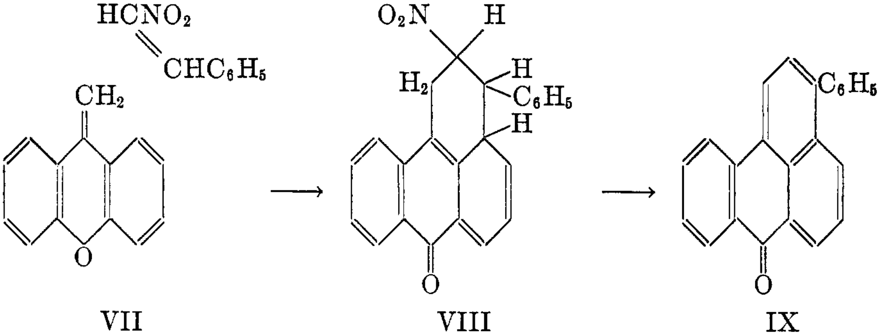
The addition and reactions used to prove the structure are conveniently illustrated by 1,3-diphenylisobenzofuran (I, R = H) and (a) nitrostyrene, and (b) styrene. Both of the addition products (II, III) were readily dehydrated by hydrogen bromide in acetic acid to give naphthalene derivatives, (IV, VI). The nitro compounds were reduced to the corresponding amines, (V), which, upon diazotization with butyl nitrite in acetic acid and reduction by alcohol, gave the same triphenylnaphthalenes, (VI), as were secured from the styrene addition products (III). The hydrocarbon, 1,2,4-triphenylnaphthalene, has been described in the recent literature (3); the properties agree in all respects.

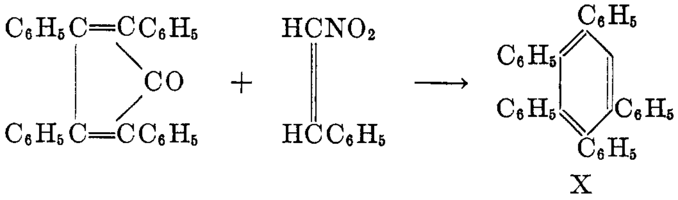
The same reactions were carried through with 1,3-diphenyl-5,6-dimethylisobenzofuran (I, R = CH_3); it was converted into 1,2,4-triphenyl-6,7-dimethylnaphthalene (VI, R = CH_3). These results show that the diene synthesis has taken place in normal fashion. The reactions afford a convenient method for the synthesis of polysubstituted naphthalene derivatives.

Additional evidence supporting the conclusion that the reaction has taken place in the manner expected is afforded by the production of *Bz*-1-phenylbenzanthrone from the addition product secured by the use of methyleneanthrone (VII–IX), and of pentaphenylbenzene (X), from the interaction with tetraphenylcyclopentadienone. In this last instance, the loss of carbon monoxide from the addition product is in accord with the behavior of the dimethyl homolog (2).

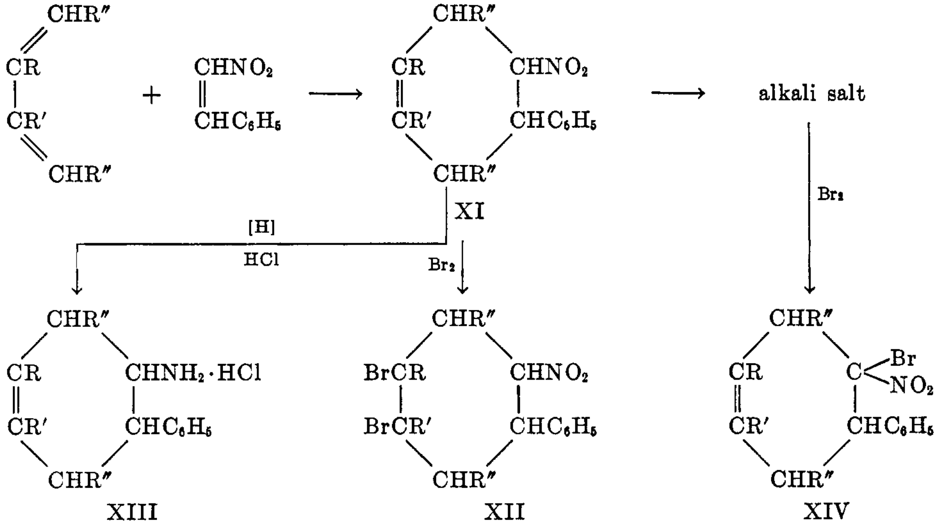
The aliphatic dienes gave derivatives of tetrahydrobiphenyl (XI). These exhibit the characteristic properties of such structures; thus, they dissolve in alkaline solutions by virtue of the acidic hydrogen in the position *alpha* to the nitro group, and these solutions take up one equivalent of bromine; they add one


I
II
III
IV
V
VI
+ C6H5CH═CH2
HCC6H5
HCNO2
HBr
CH3COOH
H2
C4H9ONO
C2H5OH
etc.
R
C6H5
NO2
NH2
O

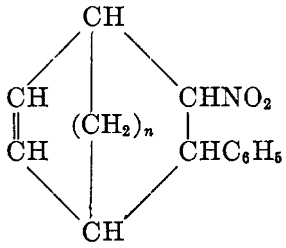

VII
VIII
IX
HCNO2
CHC6H5
CH2
O2N
H
H2
C6H5
O


X
C6H5C═CC6H5
CO
HCNO2
HCC6H5
C6H5

molecule of bromine to the double bond; they are reducible to amines.[1] The products are represented by structures XI–XIV.



The structures of the substances obtained by the use of the cyclic dienes were not determined, but by analogy with the above, it seems highly probable that they have the bridged-ring structure shown in XV.



XV

Most of the addition products can be distilled, but the one formed from 1,4-diphenylbutadiene dissociated into its components at the boiling point, and in solution below 100°; thus, on treatment with bromine, the tetrabromide of 1,4-diphenylbutadiene resulted.

Attempts to dehydrogenate some of the addition products by the use of sulfur or chloranil were unsuccessful; much hydrogen bromide was evolved when bromine was used, but the products were intractable black tars.

EXPERIMENTAL

I. The addition products. A. From dienes. The actual procedure was varied according to the nature of the diene. In some instances the use of alcohol as a solvent gave an increased yield. The properties are given in Table I.

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[1] The investigation of these amines was carried out by Dr. Nightingale at the University of Missouri.

TABLE I

Properties of the Addition Products

NO.	ADDEND	SOLVENT	YIELD %	M.P., °C.	FORMULA	CALC'D, %			FOUND, %		
						C	H	N	C	H	N
XI; R,R′,R″ = H	Butadiene	toluene	70	103	$C_{12}H_{13}NO_2$	70.9	6.4	6.9	71.3	6.6	6.7
XI; R = CH_3; R′,R″ = H or R′ = CH_3; R,R″ = H	Isoprene	—	58	52	$C_{13}H_{15}NO_2$	71.9	7.0	6.5	72.4	7.1	6.2
XI; R,R′ = CH_3; R″ = H	2,3-Dimethylbutadiene	—	82	96	$C_{14}H_{17}NO_2$	73.2	7.4		72.9	7.4	
XI; R,R′ = H; R″ = C_6H_5	1,4-Diphenylbutadiene	*o*-$Cl_2C_6H_4$	80	130	$C_{24}H_{21}NO_2$	81.1	5.9	3.9	80.9	5.8	4.2
XI; R,R′ = C_6H_5; R″ = H	2,3-Diphenylbutadiene	*o*-$Cl_2C_6H_4$	9	175	$C_{24}H_{21}NO_2$	81.1	5.9	3.9	81.2	6.0	3.8
XV; n = 1	Cyclopentadiene	—	quant.	145/1 mm.[a]	$C_{13}H_{13}NO_2$	72.6	6.1	6.5	72.6	6.1	6.4
XV; n = 2	Cyclohexadiene	—	25	138–142/1 mm.[a]	$C_{14}H_{15}NO_2$	73.3	6.6	6.1	72.9	6.4	6.3
	Phellandrene	—	45	85 195/1 mm.[a]	$C_{18}H_{23}NO_2$	75.8	8.4	4.9	76.3	8.1	4.5
VIII	Methyleneanthrone	acetic acid	3	255	$C_{23}H_{13}NO_3$	78.6	3.7	4.0	78.6	3.7	4.1
II; R = H	1,3-Diphenylisobenzofuran	ethanol	quant.	163	$C_{28}H_{21}NO_3$	80.2	5.0		80.1	4.9	
II; R = CH_3	1,3-Diphenyl-5,6-dimethylisobenzofuran	ethanol	quant.	182	$C_{30}H_{25}NO_3$	80.5	5.6		80.6	5.7	

[a] = boiling point.

1-Nitro-2-phenyl-1,2,3,6-tetrahydrobenzene (*XI; R,R′,R″ = H*). A mixture of 13 g. of butadiene, 22.5 g. of β-nitrostyrene, and 30 cc. of toluene was heated in a sealed tube for five hours at 150°. The product crystallized, and was cooled, filtered, and then recrystallized from methanol.

1-Nitro-2-phenyl-4,5-dimethyl-1,2,3,6-tetrahydrobenzene (*XI; R,R′ = CH₃; R″ = H*) was secured by refluxing equal weights of the components on the steam-bath for several hours; methanol was used for purification. 1-Nitro-2-phenyl-4(or 5)methyl-1,2,3,6-tetrahydrobenzenes could not be obtained by this procedure, but after standing in a warm (70–80°) place for five months, it yielded 58% of addition product.

The phenylated dienes were added in an indifferent medium, but the cyclic dienes served as their own solvent. Although 1-nitro-2,3,6-triphenyl-1,2,5,6-tetrahydrobenzene (XI; R,R′ = H; R″ = C_6H_5) dissociated into its components on attempted vacuum-distillation, it was easily isolated in the solid state after steam-distilling the solvent and treating the residue with ethanol. Oxides of nitrogen were evolved during the formation of 1-nitro-2,4,5-triphenylbenzene (XI; R,R′ = C_6H_5; R″ = H); the structure of a by-product, m.p. 76°, was not determined.

Tetraphenylcyclopentadienone did not react in the absence of a solvent, but in trichlorobenzene, oxides of nitrogen and carbon monoxide were given off; pentaphenylbenzene was formed. It was identified by comparison with a sample at hand.

Acetic acid was used to dissolve methyleneanthrone and nitrostyrene. During the sixteen-hour refluxing, oxides of nitrogen were evolved. The first product that crystallized was the known *Bz*-1-phenylbenzanthrone; it was identified by comparison with an authentic specimen. The second substance that separated was the addition product (VIII). When this was oxidized with chromium trioxide in acetic acid, it formed α-benzoylanthraquinone, m.p. and mixed m.p. 227°.

B. From furans. 1,2,4-Triphenyl-3-nitro-1,4-oxido-1,2,3,4-tetrahydronaphthalene (*II, R = H*) was prepared by refluxing a mixture of 7 g. of 1,3-diphenylisobenzofuran, 4 g. of β-nitrostyrene, and 200 cc. of alcohol for three hours, and working up by appropriate manipulation. The 6,7-dimethyl homolog was likewise obtained; in both instances the yield was practically quantitative. Furan, sylvan, and 2,5-dimethylfuran did not appear to react at 100° or in a sealed tube; the nitrostyrene was recovered unchanged.

II. The bromination products. A. 1-Nitro-2-phenyl-4,5-dibromo-4,5-dimethylcyclohexane (*XII, R,R′ = CH₃; R″ = H*). A solution of 2.3 g. of the addition product from 2,3-dimethylbutadiene in 10 cc. of chloroform was treated cold with 1.6 g. of bromine in 5 cc. of the same solvent. The bromine reacted at once, without evolution of hydrogen bromide [correction of statement in Note (1)]. After appropriate manipulation, a white dibromide, m.p. 69°, was obtained.

Anal. Calc'd for $C_{14}H_{17}Br_2NO_2$: Br, 40.9. Found: Br, 41.1.

In a similar manner, 1-nitro-2-phenyl-4,5-dibromocyclohexane (XII; R,R′R″ = H), m.p. 107°, was secured.

Anal. Calc'd for $C_{12}H_{13}Br_2NO_2$: Br, 44.1. Found: Br, 44.1, 44.1.

B. When the addition product from 1,4-diphenylbutadiene was submitted to a similar procedure, even though the temperature was prevented from rising above 0° at any time, the known 1,4-diphenyl-1,2,3,4-tetrabromobutane was the sole halogen-containing material. It was identified by comparison with a specimen prepared from the hydrocarbon directly (4).

C. 1-Bromo-1-nitro-2-phenyl-4,5-dimethyl-1,2,3,6-tetrahydrobenzene (*XIV; R,R′ = CH₃; R″ = H*). The sodium salt was obtained by shaking 2.3 g. of the nitro compound with 0.5 *N* alcoholic potassium hydroxide. To this was added 2 g. of bromine; the mixture was heated to boiling, and the potassium bromide filtered. The filtrate was diluted, extracted with ether, and the oil remaining after removal of the solvent allowed to crystallize. The bromonitro compound was recrystallized from dilute methanol; m.p. 68–69°.

Anal. Calc'd for $C_{14}H_{16}BrNO_2$: C, 54.2; H, 5.2; N, 4.5.
Found: C, 54.2; H, 5.1; N, 4.3.

On being heated, it decomposed almost explosively, with copious evolution of hydrogen bromide; the carbonaceous residue has a fragrant odor. This drastic decomposition was unexpected, for similar substances are tractable (5). With a view to decreasing the violence of the reaction, a *p*-cymene solution was used; it gave off gas from 100–165°. After one and one-half hours at the higher temperature, a vacuum distillation was attempted; even at 3 mm. there was a violent decomposition with production of carbonaceous material having a fragrant odor.

III. The aliphatic amines. 1-Amino-2-phenyl-1,2,3,6-tetrahydrobenzene hydrochloride (XIII; R,R′,R″ = H). A solution of 4.1 g. of the addition product from butadiene in 50 cc. of alcohol was reduced by hydrogen in the presence of a Raney nickel catalyst; after it was filtered, the solution was saturated with hydrogen chloride. The hydrochloride melted above 220°.

Anal. Calc'd for $C_{12}H_{16}ClN$: N, 6.7. Found: N, 6.7.

1-Amino-2-phenyl-4,5-dimethyl-1,2,3,6-tetrahydrobenzene was secured by a similar procedure. The free amine was an oil, b.p. 129–132°/3 mm. The hydrochloride melted at 173° with decomposition.

Anal. Calc'd for $C_{14}H_{20}ClN$: N, 5.9. Found: N, 6.2.

IV. The naphthalene series. A. Dehydration of the addition products. 1,2,4-Triphenyl-3-nitronaphthalene (IV; R = H). A suspension of 10 g. of the addition product in 50 cc. of acetic acid containing 30–32% hydrogen bromide was allowed to stand for four hours, heated to boiling, and cooled; 7 g. of the naphthalene derivative, m.p. 218–219°, was obtained. By the same procedure, 1,2,4-triphenyl-6,7-dimethyl-3-nitronaphthalene (IV; R = CH_3), m.p. 237–238°, was also prepared.

Anal. Calc'd for $C_{28}H_{19}NO_2$: C, 83.8; H, 4.7.
Found: C, 83.9; H, 4.7.
Calc'd for $C_{30}H_{23}NO_2$: N, 3.3. Found: N, 3.0.

B. The amines. 1,2,4-Triphenyl-3-aminonaphthalene (V; R = H). Reduction of the nitro compound by the use of zinc dust and acetic acid proceeded smoothly; the amine had the m.p. 256–257°. 1,2,4-Triphenyl-6,7-dimethyl-3-aminonaphthalene, m.p. 226–227°, was similarly prepared.

Anal. Calc'd for $C_{28}H_{21}N$: N, 3.8. Found: N, 3.6.
Calc'd for $C_{30}H_{25}N$: C, 90.2; H, 6.3; N, 3.5.
Found: C, 89.7; H, 6.5; N, 3.5.

C. Diazotization and reduction. 1,2,4-Triphenylnaphthalene. To a suspension of 0.8 g. of the amine in 10 cc. of acetic acid and 5 cc. of absolute ethanol at 0° was added 1.5 g. of butyl nitrite, and then 5 cc. of a solution of acetic acid saturated with hydrogen chloride. After three hours at 0° it was filtered and poured into 100 cc. of boiling absolute ethanol. After suitable manipulation, 0.4 g. of hydrocarbon was isolated; it melted at 158–159° in agreement with the literature (3). The dimethyl homolog exhibited the same behavior. Both hydrocarbons were synthesized and proved to be identical in all respects with the specimens prepared from the amines, as just described.

D. Synthesis. 1,2,4-Triphenylnaphthalene and 6,7-dimethyl-1,2,4-triphenylnaphthalene (VI). The addition products (III) were first obtained by refluxing a mixture of 8 g. of the isobenzofuran, 4 g. of styrene, and 20 cc. of xylene for two hours, and suitable manipulation. 1,2,4-Triphenyl-1,4-oxido-1,2,3,4-tetrahydronaphthalene (III; R = H), m.p. 116–117°, and the 6,7-dimethyl homolog (III; R = CH_3), m.p. 172–173°, crystallized from alcoholic benzene.

Anal. Calc'd for $C_{28}H_{22}O$: C, 89.8; H, 5.9.
Found: C, 89.6; H, 5.9.
Calc'd for $C_{30}H_{26}O$: C, 89.6; H, 6.5.
Found: C, 89.6; H, 6.5.

Dehydration was accomplished as described under the nitro compound, using an acetic acid solution of hydrogen bromide. 1,2,4-Triphenyl-6,7-dimethylnaphthalene had the m.p. of 167–168°.

Anal. Calc'd for $C_{30}H_{24}$: C, 93.8; H, 6.3.
Found: C, 93.6; H, 6.1.

1,2,4-Triphenylnaphthalene was also synthesized by this procedure.

Anal. Calc'd for $C_{28}H_{20}$: C, 94.4; H, 5.6.
Found: C, 94.3; H, 5.9.

SUMMARY

β-Nitrostyrene readily enters into the diene synthesis. It has been added to open-chain and cyclic aliphatic dienes, to unsaturated cyclic ketones, and to isobenzofurans.

The addition products, isolated in all but one instance, appear to have the properties expected.

The series of reactions affords a convenient method for securing polysubstituted naphthalenes.

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