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SUCCESSIVE DIENE ADDITION AND DEHYDROGENATION IN NITROBENZENE SOLUTION WITHOUT ISOLATION OF THE HYDROAROMATIC INTERMEDIATE

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Occasionally the observation has been made that the diene reaction, when carried out in nitrobenzene solution, is accompanied by dehydrogenation of the primary hydroaromatic addition product. This behavior will be especially valuable if the addition product tends to dissociate again into its components; in this case, the dehydrogenation process removes the addition compound from the equilibrium mixture, and stabilizes the new product.

In a patent (1), the I. G. Farbenindustrie A. G. has shown that 2,3-dimethylbutadiene combines with naphthoquinone in nitrobenzene to give directly 2,3-dimethylanthraquinone. Clar (2) has reported that perylene and 2,3,10,11-dibenzperylene, which in xylene solution gave no trace of addition product with maleic anhydride, yielded the purely aromatic polycyclic system in nitrobenzene. The condensation between methyleneanthrone and maleic anhydride in the same solvent leads to the completely aromatic *bz*-benzanthrone-1,2-dicarboxylic acid with loss of four hydrogen atoms (3). More recently, Weizmann, E. Bergmann, and Berlin (4) have shown that a true benzoquinone derivative (I) is formed when phenylquinone acts upon bicyclohexenyl in nitrobenzene solution.

In the course of our synthetic experiments in the polycyclic series, we found it advisable to study the influence of nitrobenzene on the diene reaction more systematically. We have shown that nitrobenzene during these successive addition-dehydrogenation reactions is reduced to give water and aniline, which has been identified by the usual methods:

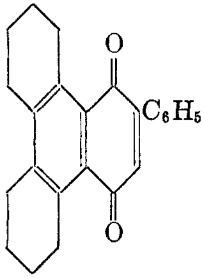
$$C_6H_5NO_2 + 3\ H_2 = C_6H_5NH_2 + 2\ H_2O.$$

Phenylated dienes, which have been investigated before with regard to their reactivity towards quinones (5), give, when the reaction is carried out in nitrobenzene solution, directly the anthraquinones: from 1-phenylbutadiene and benzoquinone, 1,5-diphenylanthraquinone is formed; from 1-phenylbutadiene and α-naphthoquinone, 1-phenylanthraquinone; from 1,4-diphenylbutadiene and benzoquinone, 1,4,5,8-tetraphenylanthraquinone; from 1,4-diphenylbutadiene and α-naphthoquinone, 1,4-diphenylanthraquinone.

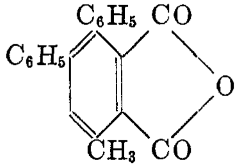
In the same way the condensation between dienes and maleic anhydride in nitrobenzene solution gives substituted phthalic anhydrides instead of the tetrahydro derivatives. From 1,2-diphenylpentadiene-(1,3), 3,4-diphenyl-6-methylphthalic anhydride (II) (6) was obtained; from 1,2,4-triphenylbutadiene, 3,4,6-triphenylphthalic acid (III); and from 9-(1′-cyclopentenyl) phenanthrene, 1,2-cyclopentenotriphenylene-3,4-dicarboxylic acid anhydride

(IV), which so far (7) has been accessible only in a more complicated manner from the primary hydroaromatic addition product.

But this addition-dehydrogenation reaction is not generally applicable. If crotonic or cinnamic acid is condensed with bicyclohexenyl, the dodecahydro products V and VI are isolated from the nitrobenzene solution, whereas maleic anhydride leads to the octahydrophenanthrene derivative VII. It appears, therefore, that dehydrogenation is achieved only when two carbonyl groups substitute the "dienophile" olefin, and one may assume that enolization always precedes the splitting off of the hydrogen atoms.[1] By this process, the two enolized hydrogen atoms are removed, as in quinone I. The removal of the two remaining "hydroaromatic" hydrogens depends then on the stability of the intermediary dihydrobenzene nucleus, which is in most cases dehydrogenated spontaneously by a hydrogen acceptor in the reaction mixture, or by air.



I



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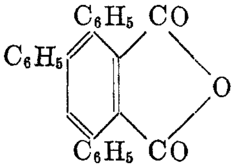

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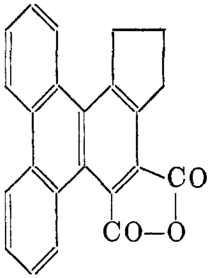

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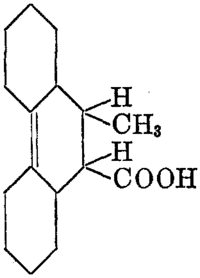

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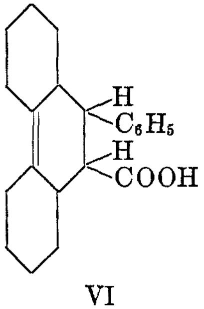

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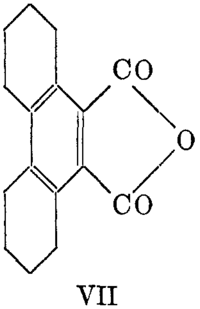

VII

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[1] Weidlich (8), however, failed to obtain the aromatized condensation product from 1,1-bidialin and maleic anhydride in boiling nitrobenzene.

EXPERIMENTAL

1,5-Diphenylanthraquinone.[2] 1-Phenylbutadiene (13 g.), benzoquinone (5.5 g.), and nitrobenzene (20 cc.) were heated at 200° for 3 hours. The black, viscous mass was diluted with glacial acetic acid (20 cc.) and, after cooling, the quinone filtered. From nitrobenzene, greenish-yellow needles, m.p. 355°; yield, 7 g.

1-Phenylanthraquinone. 1-Phenylbutadiene (5 g.) and α-naphthoquinone (5 g.) in nitrobenzene (5 cc.), when heated at 180° in an oil-bath, reacted violently. The heating was continued for 5 minutes, then methyl alcohol (8 cc.) was added, the reaction product cooled and filtered. After distillation *in vacuo* (b.p. 180° at 0.2 mm.), the quinone had the m.p. 177°; yield, 5 g.

1,4,5,8-Tetraphenylanthraquinone. 1,4-Diphenylbutadiene (20 g.) and benzoquinone (5 g.) in nitrobenzene (25 cc.) were heated under slightly reduced pressure at the boiling point of the solvent. After 6 hours standing, the reaction product was cooled, filtered, washed with glacial acetic acid, and recrystallized from nitrobenzene; m.p. 355°; yield, 14 g.

1,4-Diphenylanthraquinone. 1,4-Diphenylbutadiene (5 g.) and α-naphthoquinone (2.2 g.) were boiled in nitrobenzene (10 cc.) for 2 hours. The reaction product crystallized on cooling and was purified as described previously (5); yield, 70%.

3,4-Diphenyl-6-methylphthalic anhydride (II). 1,2-Diphenylpentadiene-(1,3) (6) (5 g.) and maleic anhydride (3 g.) were heated for 3 hours in boiling nitrobenzene (15 cc.). The reaction product began to separate during the heating; after 48 hours standing it was collected and recrystallized from light petroleum (b.p. 130°); m.p. 161°.

Anal. Calc'd for $C_{21}H_{14}O_3$: C, 80.3; H, 4.5.
Found: C, 80.1; H, 4.3.

3,4,6-Triphenylphthalic acid (III). 1,2,4-Triphenylbutadiene-(1,3) (6) and maleic anhydride (1.5 g.) were heated at 100° in nitrobenzene (15 cc.) for 2 hours. On cooling, the reaction product separated, and was recrystallized from xylene; long rods, m.p. 172°. Analysis showed that the water formed during the reaction had hydrolyzed the anhydride system.

Anal. Calc'd for $C_{26}H_{18}O_4 + H_2O$: C, 75.7; H, 4.9.
Found: C, 75.7; H, 4.9.

1,2-Cyclopentenotriphenylene-3,4-dicarboxylic acid anhydride (IV) (7). 9-(1'-Cyclopentenyl)phenanthrene (0.5 g.) and maleic anhydride (0.5 g.) were heated for 2 hours in boiling nitrobenzene (10 cc.). The nitrobenzene was removed with steam, the residue isolated with chloroform and distilled *in vacuo*. The oil boiling under 0.1 mm. pressure at 300–310° solidified on trituration with acetone, and was recrystallized from ethyl benzoate; needles, m.p. 284°, which were identified by mixed melting point.

1,2,3,4,5,6,7,8,9,10,11,14-Dodecahydro-9-methylphenanthrene-10-carboxylic acid (V). Crotonic acid (4 g.) and bicyclohexenyl (8 g.) in nitrobenzene (25 cc.) were heated for 2 hours at 130–140°, then boiled for 6 hours. The solvent was removed with steam and the residue treated with ether, from which the acid was separated by extraction with sodium hydroxide. The crude acid was air-dried and distilled *in vacuo;* b.p. 180–200° at 3.5 mm. On trituration with acetone and ligroin, the syrup crystallized. From butyl acetate long rods were obtained, from petroleum ether (130°) and xylene, beautiful rhombohedra, m.p. 164°.

Anal. Calc'd for $C_{16}H_{24}O_2$: C, 77.4; H, 9.7.
Found: C, 76.8; H, 10.0.

1,2,3,4,5,6,7,8,9,10,11,14-Dodecahydro-9-phenylphenanthrene-10-carboxylic acid (VI). Bicyclohexenyl (8 g.) and cinnamic acid (7 g.), after boiling for 5 hours in nitrobenzene

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[2] For the discussion of the structural formula, see Weizmann, Bergmann, and Haskelberg (5).

(35 cc.), yielded a mixture of unreacted cinnamic acid and the condensation product. The latter was recrystallized from a mixture of xylene and petroleum ether (130°), m.p. 221°.

Anal. Calc'd for $C_{21}H_{20}O_2$: C, 81.3; H, 8.4.
Found: C, 81.2; H, 8.8.

1,2,3,4,5,6,7,8-Octahydrophenanthrene-9,10-dicarboxylic acid anhydride (VII). Bicyclohexenyl (3.2 g.) and maleic anhydride (2 g.) were boiled in nitrobenzene (10 cc.) for 5 hours. The solvent was removed *in vacuo* and the residue distilled, b.p. 220–240° at 1.5 mm. The syrup crystallized by trituration with acetone. From acetic anhydride the substance crystallized in needles of m.p. 305°, and was identified by mixed melting point with an authentic sample.

SUMMARY

The diene addition-dehydrogenation reaction, carried out in nitrobenzene solution, is described and discussed.

Phenylated dienes, with α-naphthoquinones and benzoquinones, give directly phenylated anthraquinones. With maleic anhydride, the phthalic anhydrides are obtained directly. Bicyclohexenyl with crotonic and cinnamic acid in nitrobenzene, however, yields the hydroaromatic compounds.

REHOVOTH, PALESTINE.

REFERENCES

(1) French Patent 39,333, Oct. 12, 1931.
(2) CLAR, *Ber.*, **65**, 846 (1932).
(3) CLAR, *Ber.*, **69**, 1686 (1936).
(4) WEIZMANN, E. BERGMANN, AND BERLIN, *J. Am. Chem. Soc.*, **60**, 1331 (1938).
(5) WEIZMANN, E. BERGMANN, AND HASKELBERG, *J. Chem. Soc.*, **1939**, 391.
(6) F. BERGMANN AND E. BERGMANN, *J. Am. Chem. Soc.*, **62**, 1699 (1940).
(7) E. BERGMANN AND F. BERGMANN, *J. Am. Chem. Soc.*, **60**, 1805 (1938).
(8) WEIDLICH, *Ber.*, **72**, 1203 (1938).