

chromate content of each solution was checked by electro-metric titration according to the method described by Kelley.<sup>4</sup> All weighings were made in air and calculated to weights *in vacuo*.

It will be noted that the specific gravity determinations made with technical  $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  in tap water<sup>5</sup> are in good agreement with the data for c. p.  $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  and consequently the data may be used for determining the dichromate content of solutions of technical sodium dichromate without introducing any appreciable error.

TABLE I

| $\text{Na}_2\text{Cr}_2\text{O}_7$ ,<br>wt. per cent. | Specific gravity<br>15.6°/15.6°C. (60°/60°F.) |
|---|---|
| 1.50  | 1.0105  |
| 4.50  | 1.0344  |
| 13.41   | 1.1076  |
| 22.61   | 1.1921  |
| 31.44   | 1.2833  |
| 39.48   | 1.3763  |
| 44.10   | 1.4356  |
| 47.38   | 1.4790  |
| 48.10   | 1.4886  |
| 53.07 <sup>a</sup>                                    | 1.5683 <sup>a</sup>                           |
| 56.28 <sup>a</sup>                                    | 1.6200 <sup>a</sup>                           |
| 56.68 <sup>a</sup>                                    | 1.6259 <sup>a</sup>                           |
| 57.23   | 1.6352  |
| 60.25 <sup>a</sup>                                    | 1.6849 <sup>a</sup>                           |
| 61.40 <sup>a</sup>                                    | 1.7056 <sup>a</sup>                           |
| 63.92   | 1.7464  |

<sup>a</sup> These values obtained by using technical grade sodium dichromate in tap water.

(4) Kelley and co-workers, *Ind. Eng. Chem.*, **9**, 780 (1917).

(5) These determinations were made by W. H. Hartford of this Laboratory.

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## On the Mechanism of "Aromatizing" Diene Reactions in Nitrobenzene

BY F. BERGMANN

Diels-Alder reactions in nitrobenzene allow one to obtain in a single step an aromatic condensation product.<sup>1</sup> The mechanism and the general applicability of this modified method of diene synthesis have now been investigated with the following results.

(a) If the isolated tetrahydro product, which is obtained in the usual solvents, is boiled in nitrobenzene for different periods, aromatization occurs. Therefore, no active intermediary stage, as has been observed in diene reactions, is responsible for the easy dehydrogenation with nitrobenzene.

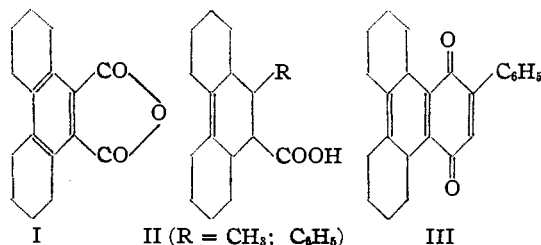
(b) Other nitro compounds, *e. g.*, *p*-chloro-, *p*-bromonitrobenzene and *m*-dinitrobenzene, when

(1) E. Bergmann, L. Haskelberg and F. Bergmann, *J. Org. Chem.*, in press.

added to the xylene solution of the two components, do not influence the results of the condensation in the instances investigated so far.

(c) Dicyclohexenyl and maleic anhydride are easily condensed in nitrobenzene with simultaneous aromatization (I). However, with cinnamic or crotonic acid the tetrahydro products (II) were obtained. It is evident that nitrobenzene acts only on systems capable of double ortho-enolization, as in the adducts with quinones or maleic anhydrides. In these cases the di-enolic form is dehydrogenated and one new double bond established in the newly formed six-membered ring. The removal of the remaining two "hydroaromatic" hydrogen atoms now depends on the stability of the intermediary dihydrobenzene nucleus, which in most cases undergoes spontaneous dehydrogenation. At times the intermediary stage can be isolated, as in the condensation of dicyclohexenyl and phenylquinone (III).<sup>2</sup> The possibility of double enolization is, however, not sufficient for the aromatizing effect of nitrobenzene, as anthracene endosuccinic anhydride is not affected by this solvent. Here only the two hydrogens in  $\alpha$ -position to the carboxyls would be removable for steric reasons and the intermediary IV would not be stable under the experimental conditions, but would be converted into V.<sup>3</sup> The only other case recorded in literature where nitrobenzene failed to dehydrogenate the addition product, is the work of Weidlich<sup>4</sup> on *bis*-(1,1'-dialin). This latter reaction is now under investigation.

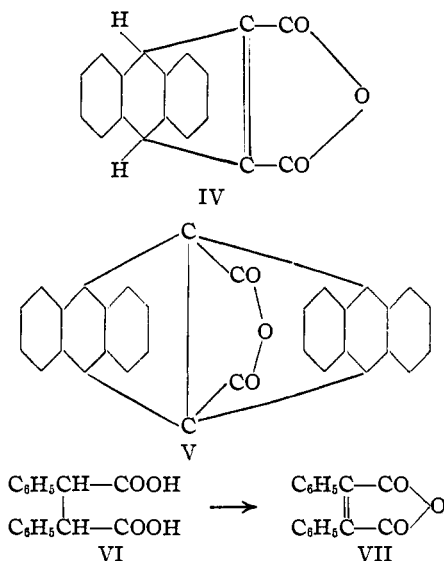
As a final proof for the above assumed reaction mechanism, we have now found that *meso*-diphenylsuccinic acid (VI), when heated for twelve hours in nitrobenzene, yields diphenylmaleic anhydride (VII) in about 40% yield. The di-enolic system involved in all these reactions,  $-\text{C}(\text{OH})=\text{C}=\text{C}(\text{OH})-$ , may be regarded as the vinylog



(2) Ch. Weizmann, E. Bergmann and T. Berlin, *THIS JOURNAL*, **60**, 1331 (1938).

(3) Diels and Friedrichsen, *Ann.*, **513**, 145 (1934).

(4) Weidlich, *Ber.*, **71**, 1203 (1938).



of the grouping  $-\text{C}(\text{OH})=\text{C}(\text{OH})-$ . As a matter of fact, benzoin is nearly quantitatively converted into benzil by the same procedure as above.

### Experimental Part

**Dehydrogenation of Isolated Diene Addition Products.**—(a) Seven grams of 1,2,3,6-tetrahydro-3,6-diphenylphthalic anhydride<sup>6</sup> was dissolved in nitrobenzene (35 cc.) and slowly heated to 200° during two hours, then kept boiling for one hour, whereby drops of water distilled into the condenser. After two days crystals with m. p. 220° were deposited. These did not depress the m. p. of 3,6-diphenylphthalic anhydride (m. p. 221–222°). The yield was low (45%) apparently because of partial dissociation of the adduct at the high temperature of the reaction.

(b) 1,2,3,4,5,6,7,8,9,10,11,14-Dodecahydrophenanthrene-9,10-dicarboxylic acid anhydride (4 g.) was warmed in nitrobenzene (25 cc.) for twelve hours at 170–175°. After removal of the solvent, the residue was distilled at 220–240° (1.5 mm.). The distillate crystallized on trituration with acetone and was recrystallized from acetic anhydride; m. p. 305°. It does not depress the m. p. of the authentic octahydrophenanthrene derivative I.<sup>2</sup>

**Dehydrogenation with Other Nitro Compounds.**—1,4-Diphenylbutadiene (10.3 g.), maleic anhydride (5 g.) and *p*-bromonitrobenzene (6.6 g.) were refluxed for four hours in xylene (50 cc.). After cooling the whole mass became solid; recrystallization from xylene gave m. p. 214°; mixed m. p. with the tetrahydro product,<sup>5</sup> 212°.

Likewise with *p*-chloronitrobenzene or *m*-dinitrobenzene no dehydrogenation occurred. The same results were obtained in an analogous experiment with dicyclohexenyl.

**Diene Reactions of Dicyclohexenyl with Various Philediolic Components.**—(a) Dicyclohexenyl (3.2 g.) and maleic anhydride (2 g.) were boiled in nitrobenzene (10 cc.) for five hours and the reaction mixture worked up as described above. The product had a m. p. 305°.

(b) 1,2,3,4,5,6,7,8,9,10,11,14-Dodecahydro-9-methylphenanthrene-10-carboxylic acid (II, R = CH<sub>3</sub>).—Cro-

tonic acid (4 g.) and dicyclohexenyl (8 g.) in nitrobenzene (25 cc.) were heated for six hours and the mixture worked up as in the foregoing example, to give a product of b. p. 180–200° (3.5 mm.). The sirup crystallized on trituration with acetone and ligroin; long rods from butyl acetate, from xylene beautiful rhombohedra, m. p. 164°.

*Anal.* Calcd. for C<sub>16</sub>H<sub>24</sub>O<sub>2</sub>: C, 77.4; H, 9.7. Found: C, 76.8; H, 10.0.

(c) 1,2,3,4,5,6,7,8,9,10,11,14-Dodecahydro-9-phenylphenanthrene-10-carboxylic Acid (II, R = C<sub>6</sub>H<sub>5</sub>).—Cinnamic acid (7 g.) and dicyclohexenyl (8 g.) were heated for five hours in nitrobenzene solution (35 cc.). On cooling a mixture of unreacted cinnamic acid and the condensation product settled down. The latter was recrystallized from a mixture of xylene and petroleum ether (130°), m. p. 224°. It gave no depression with an authentic sample.<sup>2</sup>

*Anal.* Calcd. for C<sub>21</sub>H<sub>28</sub>O<sub>2</sub>: C, 81.3; H, 8.4. Found: C, 81.2; H, 8.8.

**Miscellaneous Reactions.**—Anthracene endosuccinic anhydride<sup>6</sup> (4 g., m. p. 264°) was heated in nitrobenzene (25 cc.) for twelve hours. Part of the substance crystallized directly, part only after removal of the solvent. After one crystallization from ethyl benzoate, the substances were identified as starting material.

Three grams of *meso*-diphenylsuccinic acid (m. p. 245–246°) was heated in nitrobenzene (25 cc.) for twelve hours, whereupon the solution became dark. The solvent was driven off by steam and the residue filtered while hot in order to remove a black tar on the bottom. From the filtrate white crystals were obtained on cooling. Recrystallization from dilute alcohol gave m. p. 242° and mixed m. p. with the starting material, 245–246°; yield 1.5 g. The black tar was pulverized in a mortar with the aid of ethanol and then recrystallized in rods from glacial acetic acid or xylene; m. p. 157°; yield, 1.2 g.

For identification of this diphenylmaleic anhydride, it was converted into the anil<sup>7</sup> by heating in aniline for five minutes to 150° and pouring into hydrochloric acid. The yellow precipitate was recrystallized from xylene and high-boiling petroleum ether, m. p. 172°.

*Anal.* Calcd. for C<sub>22</sub>H<sub>15</sub>O<sub>2</sub>N: N, 4.3. Found: N, 4.5.

Benzoin (6 g.) was heated in nitrobenzene (25 cc.) for three hours and the black solution distilled with steam. After the solvent, long yellow needles appeared in the distillate, which were identified as benzil by mixed m. p.

(6) Diels and Alder, *Ann.*, **486**, 191 (1931).

(7) Anschütz and Bendix, *ibid.*, **259**, 65 (1890).

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### Statistics of Intramolecular Aldol Condensations in Unsaturated Ketone Polymers

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When pairs of neighboring substituents of a long chain polymer molecule condense intramolecularly with one another, some of the substituents fail to react because they become isolated

(5) Diels and Alder, *Ber.*, **62**, 2081 (1929).