[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE]

ON THE MECHANISM OF THE DIENE REACTION

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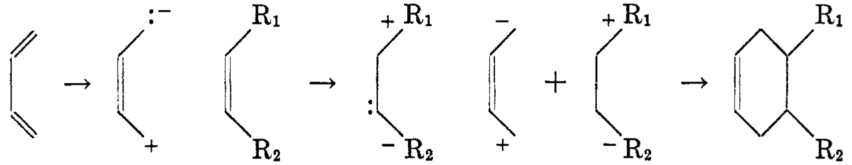
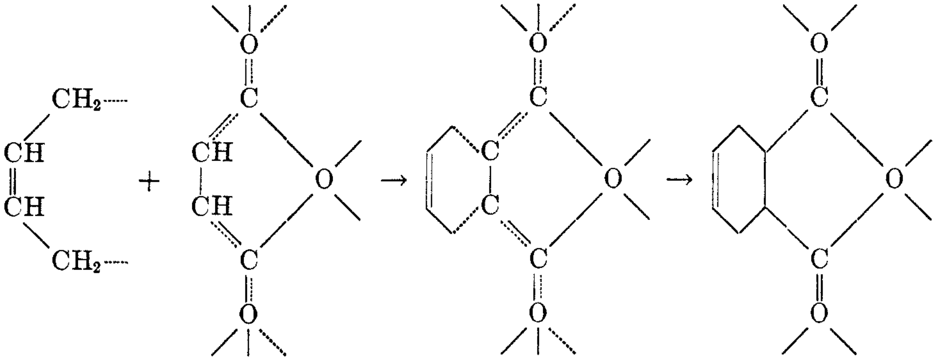
In a recent publication from this laboratory (1) the following scheme A was formulated for the Diels-Alder reaction, involving resonance forms of both components. According to this scheme each partner shows at one pole an electron deficit which is remedied by the lone pair of the other partner.



Scheme A

At the same time, a paper by Hudson and Robinson (2) presented scheme B for the same reaction, assuming that both the α- and δ-carbon atoms of the diene function successively as electron donors, whereas the philodienic component serves as electron acceptor at both ends of its olefinic bond. The addition proceeds, therefore, in two phases, allowing a monopolar approach of the two reacting molecules. This scheme was based on the successful condensation of isoeugenol and isosafrole, and can easily be applied to other reactions such as bromination of ethylenic compounds, avoiding the breakdown of the Br_2-molecule into a positive and negative ion, which is assumed in almost all other theories.



Scheme B. A dotted line represents a single electron.

It is, however, evident, as the authors already recognized, that scheme B cannot be applied to philodienic compounds possessing only one substituent. Diene additions must therefore proceed by different mechanisms depending on the structure of the philodiene. Furthermore, according to scheme B, the reactivity in a series of olefins $R_1CH{=}CHR_2$ should decrease gradually with increased difference in negativity between R_1 and R_2. The end-points of such a series would be represented by $R_1 = R_2$ on one side, and by $R_1 = H$ on the other. Investigation of such complete series of olefins in the same type of reaction would shed light on the general mechanism of the Diels-Alder reaction, whether proceeding along two different ways or on a common path.

Several cases of Diels-Alder reactions seem to support the former possibility. In Tables I and II the results of a systematic study of condensations with bicyclohexenyl and 3,4,3′,4′-tetrahydro-1,1′-binaphthyl (bis-dialin) are summarized. Two groups of philodienic components are clearly discernible: with equal and different substituents.

TABLE I

Adducts with Bicyclohexenyl

PHILODIENIC COMPONENT	RATIO $\frac{\text{DIENE}}{\text{PHILODIENE}}$	SOLVENT	YIELD %	REFERENCE
Maleic anhydride	1:10		95	Present authors
trans-Dibenzoylethylene	1.5:1	Ethanol	85	(1)
trans-Cinnamic acid	1:1		50	(1)
Indene	1.5:1		43	(15)
Benzalacetophenone	1:1		30	(1)
Benzalacetone	1:1.3		27	(1)
trans-Benzoylacrylic acid	1:1	Ethanol	25	(1)
Acrolein	1:1	Benzene	20	(16)

TABLE II

Adducts with bis-Dialine

PHILODIENIC COMPONENT	RATIO $\frac{\text{DIENE}}{\text{PHILODIENE}}$	YIELD %	REFERENCE
Maleic anhydride	1:2	87 (nitrobenzene)	(11)
"	1:10	95	Present authors
Quinone	1:10	80	"
trans-Dibenzoylethylene	1:1	50	"
α-Naphthoquinone	1:2	50	"
Cinnamic acid Benzoylacrylic acid Benzalacetone Benzalacetophenone	1:1		"

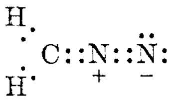
It is seen, however, that the yields vary with changes in the ratio of components, solvents etc. In many cases, the drastic conditions cause side reactions, *e.g.*, with ketones and quinones. In view of the reversibility of the diene reaction, and in order to get a sound basis for comparison, it is necessary to use a large excess of one component. This, naturally, could only be the diene, which serves as solvent and diluent for the olefin. Bicyclohexenyl was chosen because of its excellent reactivity and its being a liquid of high solvent power. Results, now obtained in 5:1 reaction mixtures, are given in Table III.

It is obvious at once, that no difference is detectable between symmetrical and unsymmetrical philodienes. Even the reaction temperature does not indicate any group difference: Fumaric acid, which should behave like its *cis* isomer, can be brought into reaction only at 200°,[1] whereas β-nitrostyrene (4) reacts as easily as quinone or maleic anhydride at 80°. If we add the recent observation of Joshel and Butz (5), that even ethylene undergoes the Diels-Alder reaction, when suitably activated, then we can safely conclude that scheme A represents satisfactorily the general reaction mechanism. This scheme has also the advantage of revealing the complete formal analogy of the Diels-Alder condensation with the reaction between philodienes and diazomethane. In certain cases, the primary addition product with diazomethane has been isolated (6, 7). The formula CH_2N_2 can be best represented as a resonance hybrid mainly between a, b, and c (besides other, less contributing, forms), and evidently form c (or b) is able to explain the cyclization in a way corresponding to scheme A.

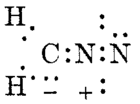
TABLE III

ADDUCTS WITH BICYCLOHEXENYL, RATIO DIENE/PHILODIENE = 5:1

PHILODIENIC COMPONENT	TEMP. °C	YIELD, %
Maleic anhydride	80	95
Quinone	80	85
α-Naphthoquinone	100	99
Fumaric acid	200	80
Benzalacetone	180	76
Dibenzalacetone	180	95
Cinnamic acid	180	75
β-Nitrostyrene	80	95



a



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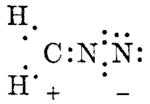

c

On the other hand, it must be conceded that scheme B may apply in extraordinary cases such as styrene derivatives, because styrene itself is entirely incapable of functioning as diene (it may, on the contrary, serve as philodienic component!). A resonance form of styrene as diene in accordance with scheme A apparently requires too great a disturbance of the aromatic nucleus.[2]

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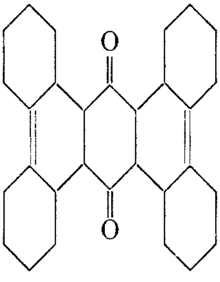
[1] As far as we are aware, this is the first case of direct condensation of free fumaric acid with dienes. Compare reference 3.

[2] When this paper was ready for publication, Allen and van Allan [*J. Am. Chem. Soc.*, **64**, 1260 (1942)] published certain experiments on the Diels-Alder reaction comprising a complete series from maleic anhydride to acetylene and showing likewise the equality of symmetrically and unsymmetrically substituted and monosubstituted ethylenes as philodienes.

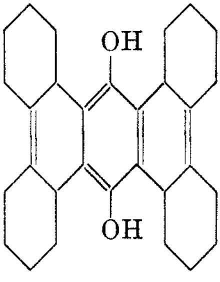
CHEMICAL REMARKS

1. Especially with quinones, the use of an excess of diene gives superior results because it avoids the dehydrogenating action of free quinone on the adduct. *E.g.*, the reaction between bicyclohexenyl and benzoquinone has been reported to yield one single and five double addition products. Barnett (8) obtained from a boiling solution of one mole of benzoquinone in 2 moles of the diene only one product of m.p. 315°. Weizmann and co-workers (9), working with the same mixture at 140°, reported an adduct of m.p. 247° (I) in 25% yield and a partially dehydrogenated product of m.p. 297° (II ?). Finally Backer (10), who used different solvents, isolated two further addition products of m.p. 217° and 137°, respectively, and one (isomerization ?) product of m.p. 304°. Under the mild conditions used in the present work, the two isomers of m.p. 248° and 217° were isolated (the large excess of bicyclohexenyl allows of course only for the formation of bis-adducts), making up together an almost quantitative yield. Ethanolic potash enolizes the higher-melting adduct to an isomer of m.p. 327° (III), and the lower-melting form to a corresponding compound of m.p. 310–312°, apparently identical with the last-mentioned product of Backer. Both enols are resistant to alcoholic ferric chloride, which would dehydrogenate them, if they were the hydroquinones II. The experiment of Barnett was repeated and the product, obtained in about 10% yield, proved to be identical with the isomerization product of m.p. 312°. This is not surprising, since spontaneous enolization of adducts has already been reported (7). The situation can, therefore, be somewhat clarified by the following statement:

Bicyclohexenyl and benzoquinone have, so far, given three bis-addition products of m.p. 137°, 217°, 248° resp. The last two give enolization products of m.p. 310° and 327° resp. under a variety of conditions.



I



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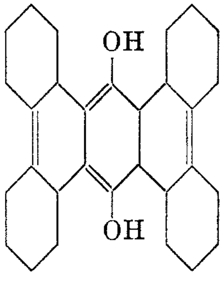
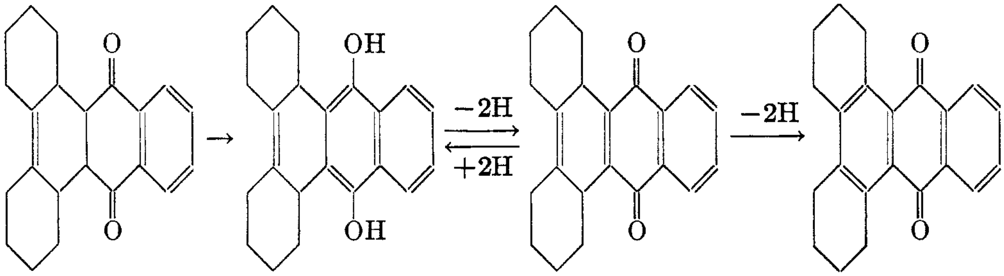


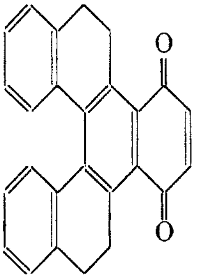
III

Similarly, α-naphthoquinone gave a quantitative yield of the primary addition compound (IV), without even a trace of dehydrogenation products. When enolization is effected by alcoholic potash or by hydrobromic-acetic acid, the intermediary hydroquinone V is extremely unstable and passes already during recrystallization into the naphthoquinone VI by autoxidation. Curiously enough, during reaction with hydrobromic acid, about 50% of the material is dehydrogenated further to the anthraquinone VII. Apparently, part of VI functions as hydrogen acceptor for the other part according to the following scheme, and V then regenerates VI by autoxidation.

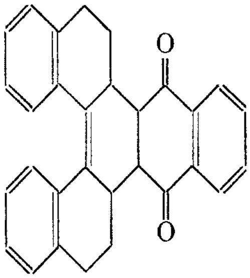


IV V VI VII

It is significant that both VI and VII were isolated by Weizmann and coworkers (9) directly in the diene reaction at a temperature of 200°, whereas Barnett (8), from a boiling mixture, obtained the primary product V. It has already been shown in other examples (7), that enolization and dehydrogenation are favored by an excess of the quinone. Bis-dialin gave, by use of an excess of benzoquinone, exclusively the compound VIII by loss of four hydrogen atoms from the primary adduct. In accordance with this structure, the compound is unable to undergo enolization. α-Naphthoquinone under the same conditions yielded the primary addition product IX, and dibenzoylethylene gave XII.

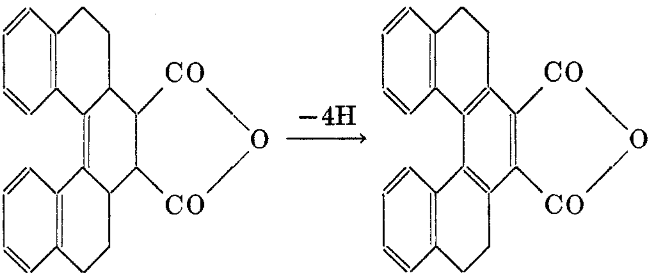


VIII

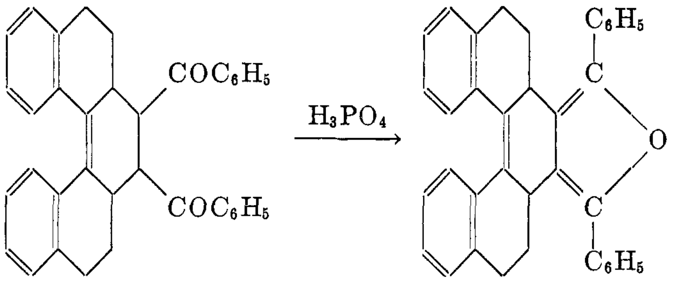


IX

2. Condensation between bis-dialin and maleic anhydride in nitrobenzene was reported by Weidlich (11) to give the "tetrahydro" product X, in contradiction to the common dehydrogenating action of this solvent (12). It has now been found, that extending the reaction time from two to ten hours gives the expected "aromatized" compound XI, thus confirming our previous statement, that nitrobenzene oxidizes the already-formed adduct and does not act on some hypothetical intermediate.



X XI



XII XIII

EXPERIMENTAL PART

I. REACTIONS WITH BICYCLOHEXENYL

Reactions which mainly represent repetitions of previous experiments under altered conditions, are not recorded.

1. *With benzoquinone.* The quinone (1.1 g; 1/100 mole) and the diene (8 g.; 1/20 mole) were warmed on a water-bath for five hours. The clear solution started crystallization after three hours. The crystals (2.5 g.) showed the m.p. 235–240°. This substance was dimorphic; from butanol it crystallized in prismatic rods, m.p. 233–235°, from high-boiling petroleum ether in needles, m.p. 247° (I). The mother liquor deposited, after 24 hours, a second crop (0.8 g.), of m.p. 190–195°. From high-boiling petroleum ether, clusters of rectangular prisms, m.p. 212° (Ia).

Anal. Calc'd for $C_{30}H_{40}O_2$: C, 83.3; H, 9.3.
Found: C, 82.8; H, 9.2.

On concentrating the mother liquors, a further crop (0.4 g.) of the first isomer, (m.p. 247°) was obtained, bringing the total yield to 86%.

Enolization: 0.5 g. of I was suspended in ethanolic potassium hydroxide and left at room temperature for 24 hours. The filtered material was recrystallized twice from nitrobenzene; clusters of colorless needles, m.p. 327° (III). The substance was recovered unchanged after boiling its butanolic solution with ferric chloride.

Anal. Calc'd for $C_{30}H_{40}O_2$: C, 83.3; H, 9.3.
Found: C, 83.5; H, 8.9.

Adduct Ia, when treated in the same way, gave colorless needles (from butyl acetate), m.p. 310–312° (IIIa).

Anal. Calc'd for $C_{30}H_{40}O_2$: C, 83.3; H, 9.3.
Found: C, 83.5; H, 9.6.

According to Barnett (8), a solution of quinone (0.6 g.) in bicyclohexenyl (2 g.) was boiled for two minutes, and the mixture treated with alcohol and acetone. From butyl acetate, white needles were obtained (0.2 g., 10%); m.p. 308°, mixed m.p. with the foregoing compound (IIIa), 308–310°.

The mother liquors were concentrated and yielded, upon treatment with ligroine, 0.1 g. of a mixture of I and Ia.

2. *With α-naphthoquinone.* The quinone (1.2 g., 1/130 mole) and the diene (6 g., 1/26 mole), when heated on a water-bath, gave a clear solution, which solidified after two hours. Treatment with alcohol gave 2.5 g. (100%) of adduct, which crystallized from butanol in colorless plates, m.p. 207–208° (IV).

(a) Five-tenths gram of IV was suspended in hot alcohol and alcoholic potash added. The solution turned immediately red-yellow, and on cooling a red solid crystallized. On recrystallization, first a heterogeneous material (yellow needles, red prismatic rods) appeared, which, however, gradually changed into a pure red substance; prismatic rods (from butyl acetate), m.p. 248° (VI).

Anal. Calc'd for $C_{22}H_{22}O_2$: C, 83.0; H, 6.9.
Found: C, 82.7; H, 7.1.

(b) Five-tenths gram of IV was dissolved in glacial acetic acid (25 cc.), and at 80° five drops of conc'd hydrobromic acid were added. The colorless solution turned immediately yellow and deposited, on cooling, yellow needles (VII). From acetic acid, m.p. and mixed m.p. with a previous sample (9) 234–235°. Conc'd sulfuric acid gave a beautiful red color.

Anal. Calc'd for $C_{22}H_{20}O_2$: C, 83.6; H, 6.3.
Found: C, 83.8; H, 6.1.

From the filtrate of VII, water precipitated a brown-black material (quinhydrone of V + VI ?). Repeated recrystallization from butyl acetate gave red rods, m.p. and mixed m.p. with VI 248°.

3. *With fumaric acid.* The acid (1.25 g. 1/92 mole), suspended in the diene (8.5 g., 1/18 mole) did not react at 100°. However, reaction took place at 190–200°. The excess of bicyclohexenyl was distilled off, and the residue extracted with boiling sodium hydroxide solution. The adduct acid, which was precipitated from the filtered extract, was amorphous (2.5 g., 80%) and was therefore converted into its di-anilide. The adduct was dissolved in benzene (25 cc.) and phosphorus pentachloride (2.2 g.) added at once. An exothermic reaction occurred, and was completed by refluxing for half an hour. Solvent and phosphorus oxychloride were removed *in vacuo*, and the residue boiled with aniline (2 cc.) for two minutes. Hydrochloric acid precipitated a sirupy product, which crystallized on treatment with alcohol. From glacial acetic acid long, colorless, slender needles, m.p. 312°, were obtained.

Anal. Calc'd for $C_{28}H_{32}N_2O_2$: C, 77.8; H, 7.4; N, 6.5.
Found: C, 78.2; H, 7.8; N, 6.8.

4. *With β-nitrostyrene.* Nitrostyrene (1 g., 1/150 mole) and the diene (5 g., 1/30 mole) were warmed on a water-bath for eight hours. On cooling, the product crystallized, and was triturated with methanol. Yield, 1.9 g., 95%; from butanol beautiful rods, m.p. 187°. With hot conc'd sulfuric acid a golden-yellow solution was obtained.

Anal. Calc'd for $C_{20}H_{26}NO_2$: C, 77.2; H, 8.0; N, 4.5.
Found: C, 77.2; H, 8.3; N, 4.6.

The adduct was not attacked by catalytic hydrogenation, in accordance with observations of Alder (13). (The $C_{12,13}$ double bond in these adducts is known to be entirely refractive).

5. *With dibenzalacetone.* The ketone (1.2 g., 1/200 mole) and the diene (4 g., 1/40 mole) were heated to 180–190° during five hours. The sirupy mass crystallized on trituration with ethanol (2 g., 95%); from butanol thin long needles, m.p. 208–209°.

Anal. Calc'd for $C_{41}H_{50}O$ (double adduct): C, 88.2; H, 9.0.
Found: C, 88.5; H, 8.6.

II. REACTIONS WITH 3,4,3′,4′-TETRAHYDRO-1,1′-BINAPHTHYL

1. *Preparation of bis-dialin.* For the preparation of tetralone we used the method of Thompson (14). Contrary to this author's experience, we did not find the described treatment sufficient to remove peroxides. Eventually, the following changes were introduced: treatment with sodium hydroxide at 60° was continued for 4 hours, and shaking with ferrous sulfate at room temperature was extended at least for 24 hours.[3] The average yield was two-thirds of that reported by Thompson. Pinacolization of tetralone was best effected in the following way: to 200 cc. of dry benzene, absolute ethanol (10 cc.) was added, and about 25 cc. was distilled off. Thin aluminum foil (7 g.) was added, care being taken to expose a fresh surface of the metal, then 1 g. of mercuric chloride, and finally tetralone

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[3] The tetralin-tetralone mixture was shaken with half of its volume of a saturated solution of $FeSO_4$. Practically no emulsions were formed, if this solution was filtered before use, and the layers separated within a few minutes. The absence of peroxides was proved by the negative reaction with KI in glacial acetic acid.

(20 g.). The mixture was refluxed overnight. The liquid was now decanted, the metal dissolved in dilute HCl and ice, and the solution extracted with ether. The ether extracts were combined with the benzene solution, the solvents removed, and the residue refluxed for three hours with a 1:1 mixture of acetic acid and acetic anhydride. On cooling, bis-dialin (15 g.) crystallized. Recrystallization from ethanol containing 10% benzene, gave 12 g. of pure diene, m.p. 141°. The pinacol itself, when isolated, crystallized from butyl acetate in beautiful prisms, m.p. 191–192° (8).

2. *Condensation with maleic anhydride.* The anhydride (24 g., 1/4 mole) and bis-dialine (6 g., 1/40 mole) were heated together on a water-bath for four hours. The clear solution solidified completely. The excess anhydride was removed by water. The residue, m.p. 233°, (8 g., 95%) was fractionally crystallized from xylene. The main product formed thick rectangular plates, m.p. 256° (X).

Anal. Calc'd for $C_{24}H_{20}O_3$: C, 80.9; H, 5.6.
Found: C, 81.1; H, 5.5.

The mother liquors yielded a second adduct, clusters of fine needles, m.p. 260° (Xa). Mixed m.p. with the foregoing 232°.

Anal. Calc'd for $C_{24}H_{20}O_3$: C, 80.9; H, 5.6.
Found: C, 81.0; H, 5.8.

Adduct X was transformed with diazomethane into its di-ester, which formed tetragonal pyramids from high-boiling petroleum ether; m.p. 168°.

This ester (0.9 g.) was isomerized with sodium (0.5 g.) in boiling butanol (25 cc.) during three hours (1). The sodium salt of the isomeric acid crystallized on cooling. It was decomposed with dil. sulfuric acid at 0°, and the product recrystallized from butyl acetate, m.p. 239°.

Anal. Calc'd for $C_{24}H_{22}O_4$: C, 77.0; H, 5.9.
Found: C, 76.7; H, 5.7.

Adduct Xa, on the other hand, resisted all attempts, to convert it into the free acid. Therefore the same chain of reactions could not be carried out here.[4]

3. *Condensation in nitrobenzene.* The diene (2.5 g.) and maleic anhydride (15 g.) were boiled in nitrobenzene (25 cc.). After 3 hours, the product which crystallized on cooling was identical with the above adduct X, m.p. 256°. Then boiling was extended to 10 hours, the solvent removed by steam, and the black residue dissolved in 30% aqueous KOH with addition of some alcohol, the extract boiled with charcoal and filtered. The filtrate was nearly neutralized with HCl, a small amount of tar which settled down was removed, and then excess HCl added. The orange-yellow product was recrystallized from ethyl benzoate (red solution with green fluorescence), m.p. 275° (yellow eicosihedra, XI).

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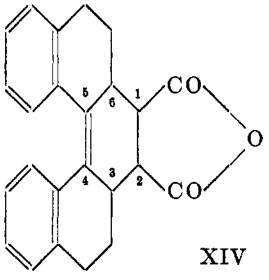
[4] The isomerization of adduct Xa was attempted in order to settle definitely the question of isomeric adducts (1). If it is assumed that the two anhydrides can be represented, *e.g.*, by formulas XIV and XV, then isomerization with sodium butoxide should give two different *trans* acids. On the other hand, if the isomerism of XIV and XV is based on the position of hydrogens at C_3 and C_6 relative to C_1 and C_2, then the same *trans* acids would be obtained from both adducts.



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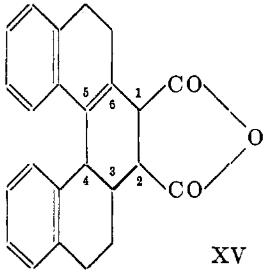
XIV



XV

Anal. Calc'd for $C_{24}H_{16}O_3$: C, 81.8; H, 4.55.
Found: C, 81.8; H, 4.2.

4. *With benzoquinone.* The diene (2.6 g.) and benzoquinone (11 g., 10 equiv.) were heated together at 125–150° for three hours. At first, a homogeneous liquid resulted, which, however, solidified later completely. After steam distillation, a dark red residue was left; crude yield, 3 g. (80%). Recrystallization from butyl acetate and acetic anhydride gave red plates, m.p. 268° (VIII).

Anal. Calc'd for $C_{26}H_{18}O_2$: C, 86.2; H, 5.0.
Found: C, 86.0; H, 4.7.

The substance was not altered when treated with HBr in acetic acid solution. No addition was observed, when 4 equiv. of the diene were heated with 1 mole of quinone, or when the components were dissolved in boiling benzene or xylene.

5. *With α-naphthoquinone.* Two moles of the quinone was heated with 1 mole of the diene at 130° for 3 hours. After steam distillation, the residue was triturated with chloroform-ethanol. From butanol, fine yellow needles, m.p. 226° (IX); yield 50%.

Anal. Calc'd for $C_{30}H_{24}O_2$: C, 86.5; H, 5.8.
Found: C, 86.6; H, 6.0.

6. *With* trans-*dibenzoylethylene.* No reaction took place in boiling benzene. If, however, the diene (2 g.) and the ethylene (2 g.) were heated to 200° for 10 hours, about 2 g. (50%) of yellow crystals was obtained by treating the reaction mixture with ethanol-acetone. From butyl acetate, quadrangular prisms, m.p. 236–238° (XII). Near the end of the crystallization a second isomer appeared in the form of needles, which, however, was not isolated.

Anal. Calc'd for $C_{36}H_{30}O_2$: C, 87.4; H, 6.1.
Found: C, 87.1; H, 6.4.

Dehydration: The adduct (1.7 g.) was dissolved in boiling acetic anhydride (25 cc.). When five drops of phosphoric acid (sp. gr. 1.75) were added, the color changed from yellow to red. The product was recrystallized from nitrobenzene, then from acetic anhydride. Yellow prismatic rods, m.p. 272–273° (XIII).

Anal. Calc'd for $C_{36}H_{28}O$: C, 90.8; H, 5.9.
Found: C, 90.2; H, 6.0.

When the product was dissolved in conc'd H_2SO_4 at 50°, no isomer analogous to the corresponding derivative of bicyclohexenyl (1) could be detected.

SUMMARY

1. High yields of adducts can be obtained from bicyclohexenyl with both symmetrically and unsymmetrically substituted ethylenes. This finding is discussed with reference to two schemes (A and B) for the mechanism of the Diels-Alder reaction.

2. The use of excess diene gives superior yields and clearer results, especially in the case of quinones.

REHOVOTH, PALESTINE

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