

Taylor and Rosenblum¹⁴ and Herr and Noyes¹⁰ and their changes with temperature are consistent with equations (5) and (6). Because of the experimental difficulties, nothing in the nature of direct evidence can be applied to the formation of acetyl iodide. However, if we assume its presence and calculate it by difference, then we find that the log $[\text{CH}_3\text{CO}]$ against $1/T$ gives a straight line with an activation energy of 6 kcal./mole. If there is a rapid equilibrium between acetyl iodide and iodide atoms as suggested by Gorin²



then this value represents the difference in activation energy between (2) and the forward reaction in (7) which gives a value of 9 kcal. for the latter. This value is quite reasonable and can be compared with the value of 12 kcal./mole found for the reaction of $\text{ICH}_2\text{-CH}_2\text{-}$ with iodine¹⁶ and a similar value found for the reaction of $\text{ICH}_2\text{-CH}_2\text{CH}_2\text{-}$ and iodine.¹⁷ It is this relatively high value, in our opinion, that explains the small amounts of acetyl iodide found by Gorin² and by us, and also the large quantities of biacetyl found by the former at 3130 Å., in the presence of iodine.

Acknowledgment.—We are indebted to Dr. J. J. Lingane for the use of his apparatus in the electrometric titrations for iodine.

Summary

1a. A description has been given of a versatile

(16) Arnold and Kistiakowsky, *J. Chem. Phys.*, **1**, 166 (1933).

(17) Ogg and Priest, *ibid.*, **7**, 77 (1939).

apparatus especially designed for the study of the flow photolysis of mixed vapors.

1b. A low pressure system for the micro-analysis of hydrocarbon vapors is described.

2. The photolysis of acetone by λ 2537 Å. in the presence and absence of iodine has been investigated over the range 60–140°.

3. In the absence of iodine the main products are ethane and carbon monoxide with small amounts of methane and biacetyl, and relative yields are in good agreement with the values found by other investigators.

4. In the presence of iodine the products are carbon monoxide and methyl iodide with small amounts of acetyl iodide and traces of methane formed.

5. The primary process at 2537 Å. is exclusively a splitting of the acetone into methyl and acetyl radicals accompanied by a spontaneous decomposition of at least 22% of the acetyl radicals formed. The efficiency of the primary process is close to unity.

6. The formation of methane is probably accompanied by the disappearance of two methyl radicals and the formation of methyl ethyl ketone.

7. Minimum activation energies are found of 16 kcal./mole for the decomposition of acetyl radicals and 9 kcal./mole for the formation of acetyl iodide from acetyl radicals and iodine.

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The Sterical Course and the Mechanism of the Diene Reaction

BY FELIX BERGMANN AND H. EMILE ESCHINAZI*

Since the discovery of the Diels–Alder reaction, there have been found in numerous cases two isomeric addition compounds,¹ which are usually explained as stereoisomers. During a study of the adducts of dicyclohexenyl, we have made some observations, which we believe make it possible to draw several general conclusions about the steric course of the diene reaction.

From the interaction of dicyclohexenyl with cinnamic acid, we isolated, in addition to the one

already known adduct (Ia),² a second isomer Ib. The possibility of *cis-trans* isomerism with regard to the phenyl and carboxyl groups could be excluded by the fact that both acids could be recovered unchanged after saponification of their methyl esters with sodium butylate. This procedure is known to isomerize *cis*-esters bearing an α -hydrogen atom.³ Both isomers, therefore, are derived from the *trans*-cinnamic acid. Condensation of dicyclohexenyl with benzalacetone yielded only one form of II, which corresponds to acid

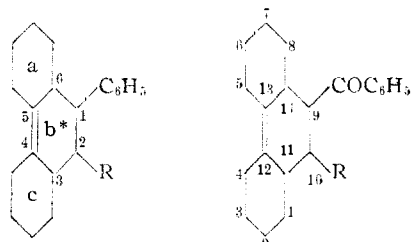
* The material of this article forms a portion of a thesis to be submitted by Mr. Eschinazi to the Hebrew University, Jerusalem.

(1) (a) Fieser and Fieser, *THIS JOURNAL*, **57**, 1679 (1935); (b) Adams and Geissman, *ibid.*, **61**, 2083 (1939); (c) Goldberg and Müller, *Helv.*, **23**, 831 (1940).

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

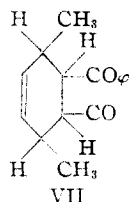
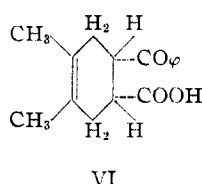
(3) Hüchel and Goth, *Ber.*, **58**, 447 (1925); Bickel, *THIS JOURNAL*, **60**, 927 (1938).

Ia, as the ester of the latter could be converted into II by means of methylmagnesium iodide. Benzalacetophenone leads to two isomeric adducts (III). In the case of *trans*-dibenzoyl ethylene the second form of IV was very unstable and could be converted gradually into the main product by repeated recrystallizations. *trans*-Benzoylacrylic acid yielded only one condensation product (V). The results of the different experiments have been summarized in Table I.



I (a) and (b), R = COOH
 II, R = COCH₃
 III(a) and (b), R = COC₆H₅

IV, R = COC₆H₅
 V, R = COOH



* For the sake of simplicity in the following discussion only ring (b) has been numbered.

TABLE I

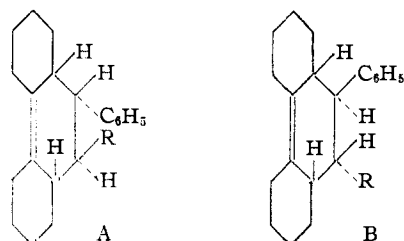
Philodienic compound	M. p. of isomer first, ^a °C.	M. p. of isomer second, ^a °C.	Remarks
<i>trans</i> -Cinnamic acid	231	282	No isomerization of the esters by saponification with sodium butylate
<i>trans</i> -Benzalacetone	135	154	
<i>trans</i> -Benzalacetophenone	216	154	
<i>trans</i> -Dibenzoyl ethylene	182	162	First easily converted into second during recrystallization.
<i>trans</i> -Benzoylacrylic acid	259	..	

^a This designation is arbitrary, assuming that the main isomer represents the "normal" addition product.

The occurrence of isomers in the diene reaction has been explained in different ways. Diels and Alder⁴ considered the two products obtained from cyclopentadiene and crotonaldehyde to be derived from the *cis*- and *trans*-forms of the aldehyde, and the same explanation has obviously been adopted by Fieser^{1a} for the adduct VI, as in this case the only possibility of stereoisomerism is given by the relative position of the benzoyl and carboxyl groups. On the other hand, Adams, *et al.*,^{1b} assumed that in their adduct VII the two forms are characterized by the relative posi-

tion of the methyl groups. The *cis*-position of the methyl groups was proved for the main product, and the remaining one is assumed to be one of the two possible *trans*-isomers.

From the observations of Alder,⁵ Kuhn⁶ and from our own experiments on dicyclohexenyl the general conclusion seems justified, that the relative position of the substituents in the olefinic component is retained in the adduct, in contradistinction to the assumption of Diels⁴ and Fieser.^{1a} On the other hand, in the addition products of dicyclohexenyl no stereoisomerism on carbon atoms 3 and 6 in the newly formed six-ring (b) (compare formula I) should be considered possible for sterical reasons. An inspection of the model shows that the three rings of the hydrophenanthrene must be arranged in one plane.⁷ To the two forms of I or III one is, therefore, inclined to ascribe the remaining possible structures A and B



which differ only in the relative position of the pair of substituents at carbon atom 1 and 2, *e. g.*, phenyl at carbon atom 1 and hydrogen at 2, and the pair of hydrogen atoms at carbon 3 and 6 in the adduct-ring (b) of I. However, it has been demonstrated by Alder, *et al.*,⁸ that all adducts of cyclopentadiene show the same relative arrangement at C_{3,6} and C_{1,2}.⁹ Moreover, the position with regard to Fieser's condensation product VI cannot be explained even by a formulation corresponding to A and B. The only assumption which is consistent with all experimental observations is the shift of the double bond between C₄₋₅.¹⁰ Especially in the case of bicyclic

(5) Alder, Stein, *et al.*, *Ann.*, **514**, 1 (1934).

(6) Kuhn and Wagner-Jauregg, *Ber.*, **63**, 2662 (1930).

(7) As in the case of decalin, *cis-trans*-connection of adjacent rings is possible in perhydrophenanthrene. The peculiar double bond at C₁₂₋₁₃ in the dicyclohexenyl adducts, however, causes the C₄₋₁₂ and C₆₋₁₃ bonds to lie in the plane of ring (b). Hence it is hardly possible to construct models with *trans*-arrangement of the links C₈₋₁₄ and C₄₋₁₁ (compare formula IV).

(8) Alder, Stein, Liebmann and Rolland, *Ann.*, **514**, 197 (1934); compare also footnote 5.

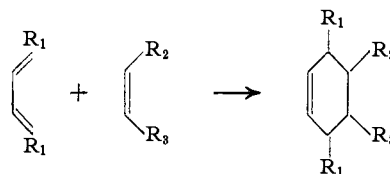
(9) The only exception is the dimerization product of cyclopentadiene, which at a reaction temperature of 170° is obtained in an α - and β -form. This isomerism corresponds to formulas A and B.

(10) Such a possibility has already been considered by Kuhn (see footnote 6).

(4) Diels and Alder, *Ann.*, **470**, 67 (1929).

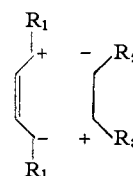
dienes like dicyclohexenyl, 3,4,3',4'-tetrahydro-1,1'-binaphthyl¹¹ and 3,4,3',4'-tetrahydro-7,7'-dimethyl-1,1'-binaphthyl¹² the ready shift of the double bond from an internuclear position into an intranuclear one is easily understood from the general behavior of these cyclic systems. Wallach¹³ found that cyclohexenylcyclohexanone represents a mixture of VIII and IX, with IX predominant, although in IX conjugation of the double bond with the carbonyl group is abolished. In the diene condensation products the assumed shift is probably further enhanced by the attraction of the double bond by the substituents at C₁ and C₂ of I (CO, CN, COOH, CHO, C₆H₅, etc.). The two isomeric adducts are regularly obtained in different yields and the main product has always been shown to contain the "normal" 4,5-double bond. It is also noteworthy that under slightly different conditions the second isomer may sometimes be entirely absent. Thus the acid I(b) was obtained in appreciable amounts when the reaction was carried out in a sealed tube. In an open vessel at the same temperature, however, the lower-melting isomer I(a) was formed exclusively. Finally, it seems probable that the two forms of IV are not isomers, but polymorphic modifications. A re-shift of a double bond by simple recrystallization is not very reasonable, and such an explanation would be entirely inadequate for a similar observation by Dufraisse.¹⁴ All the experimental facts discussed above lead to the following general rules about the sterical course of the diene reaction; but it should be borne in mind that only the first one has been proved, whereas the others are formulated tentatively and have to await further investigations to be settled definitely: (1) The structure of the philodienic component is preserved unchanged in the adduct. No *cis-trans* isomerization occurs. (2) No isomerism is caused by different spatial arrangements at carbon atoms 3 and 6 of the newly formed ring. (3) No isomerism is caused by the relative arrangement of substituents at carbon atoms 1 and 6 (or 2 and 3). (4) Isomeric adducts differ in the position of the double bond only. It follows from these rules that only one out of the

eight racemates which are possible in a diene condensation product according to the equation comes actually into existence.



Discussion

The first rule, which appears satisfactorily established, permits some further conclusions to be drawn about the mechanism of the reaction concerned. If the olefinic component is not isomerized, no intermediate like X, which would allow at least a partial isomerization of the olefin, can exist. This means that no unipolar approach of the two reacting molecules precedes the ring closure, but the two ends of the olefinic double bond reach the carbon atoms 1 and 4 of the butadiene simultaneously. This argument is supported by the observation that non-reactive dienes sometimes cause the isomerization of maleic into fumaric acid.¹⁵ In such cases, the approach of the other ends may be sterically hindered. The quadrupole system, represented for example by



requires that the mesomeric form of the philodienic component contribute remarkably to the structure of the olefin and now it can be understood why unsubstituted butadiene is able to undergo the Diels-Alder reaction, whereas ethylene and its simple aliphatic homologs are not. It is known, that resonance gives the 2,3-bond of butadiene about 20% double-bond character,¹⁶ whereas ethylene must be substituted by "resonance-promoting" substituents (CO, CN, COOH, etc.). The structural conditions which are necessary for the diene reaction are, therefore, intimately connected with the ability of unsaturated molecules to couple with diazo compounds. Butadiene readily yields a coupling product,¹⁷ whereas ethyl-

(11) Weidlich, *Ber.*, **71**, 1203 (1938); compare also footnote 1c.

(12) Newman, *THIS JOURNAL*, **62**, 1683 (1940).

(13) Wallach, *Ann.*, **381**, 95 (1911); Kon and Nutland, *J. Chem. Soc.*, 3101 (1926).

(14) Dufraisse and Priou, *Bull. soc. chim.*, [5] **5**, 502 (1938); the authors assume again an isomerism corresponding to formulas A and B. A shift of the double bond at C₄₋₅ is impossible in this case, because it belongs at the same time to a benzenoid ring.

(15) See the case of 9-cyclohexenylphenanthrene: E. Bergmann and F. Bergmann, *THIS JOURNAL*, **59**, 1443 (1937).

(16) Cf. Pauling, "Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N. Y., 1940, p. 217.

(17) Meyer, *Ber.*, **52**, 1468 (1919).

ene requires "activation" by the above-mentioned substituents.¹⁸

The same theoretical principle offers a ready explanation for the different ability of vinyl substituted aromatic systems to function as diene, *i. e.*, vinylbenzene (XI) is inert toward all philodienic compounds, whereas α -(and β -)-vinyl-naphthalenes (XII)^{19,20} and still more 9-vinyl-phenanthrenes (XIII)¹⁵ easily give addition products. It appears that XI has a very small tendency to resonate, *e. g.*, with XIa, whereas the same mesomerism in the other cases (XII \rightarrow XIIa; XIII \rightarrow XIIIa) does not interfere with the benzenoid structure of the remaining rings.

Remarks on the Chemical Behavior of the Dicyclohexenyl Adducts

The addition products of dicyclohexenyl are characterized by their resistance to various reagents. The esters of Ia and b were recovered unchanged after six hours of boiling with sodium ethylate, but were saponified by sodium butylate. In this way it could be shown that the adduct with ethyl cinnamate² was derived from the lower melting form Ia.

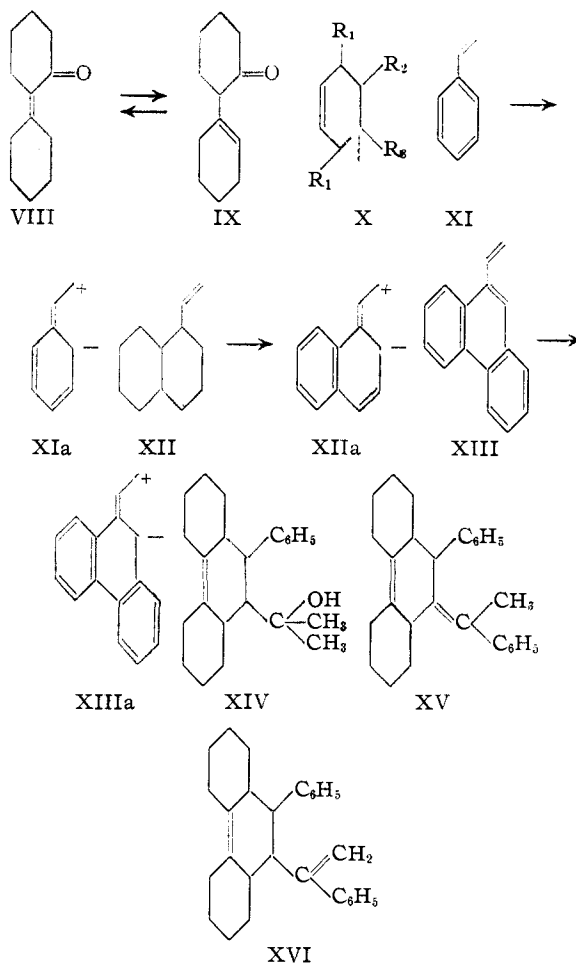
The ketones II and III yielded no carbonyl derivative, nor could they be reduced by aluminum isopropylate. None of the adducts reacted with Grignard compounds under the normal conditions (a boiling mixture of ether and benzene). The ester of acid Ia was, however, converted into II by methylmagnesium iodide in boiling toluene, but was not attacked at all by phenylmagnesium bromide. The isomeric ester gave no reaction with either Grignard compound. Therefore the isomeric forms of I and III could not be related to each other. Compound II, however, could be converted into the carbinol XIV by a Grignard reaction. Hence we tried to link II with III by permitting the former to react with phenylmagnesium bromide and the latter with methylmagnesium iodide. The lower-melting form of III gave no definite product at all, whereas the higher-melting one yielded an olefin XV or XVI,²¹ which was different from the corresponding product from II. No conclusion can, of course, be drawn from these negative results.

(18) Meerwein and co-workers, *J. prakt. Chem.*, **152**, 237 (1939).

(19) Cohen, *Nature*, **136**, 869 (1935).

(20) Cohen and Warren, *J. Chem. Soc.*, 1318 (1937); Bachmann and Kloetzel, *THIS JOURNAL*, **60**, 2204 (1938).

(21) Formula XVI is preferred because of the very strong absorption of bromine. The double bond at C₄-5 is inert toward bromine. The absorption of bromine by XVI proves at the same time, that no spontaneous cyclization has occurred.



Experimental Part

1,2,3,4,5,6,7,8,9,10,11,14-Dodecahydro-9-phenylphenanthrene-10-carboxylic acid (I; for numerals see II).—The reaction between dicyclohexenyl (12 g.) and cinnamic acid (11 g.) was carried out in a sealed tube as described,² and the reaction mass triturated with cold methanol. The crude product (17 g.) was extracted twice with 60 cc. of boiling ethanol. The ethanolic solution deposited the main product (about 10 g.) in form of needles; m. p. 231°²² (Ia). It was recrystallized from high-boiling petroleum ether. The residue (about 1 g.) was dissolved in 60 cc. of butanol, from which the second isomer (Ib) was obtained as long prisms; m. p. 282°.

Anal. Calcd. for C₂₁H₂₆O₂: C, 81.3; H, 8.4. Found: C, 81.1; H, 8.1.

The acid Ia was not decarboxylated by basic copper carbonate in boiling quinoline or by heating with soda lime at 350°.

The methyl ester of the isomer Ia was prepared by means of diazomethane. Recrystallization from methanol yielded white needles; m. p. 111–112°.

Anal. Calcd. for C₂₂H₂₈O₂: C, 81.5; H, 8.6; OCH₃, 9.6. Found: C, 81.2; H, 8.2; OCH₃, 9.8.

(22) The m. p. is given in the literature as 221°.

The ester was not attacked by alcoholic sodium hydroxide solution or by sodium ethylate. Sodium butylate in boiling butanol, however, produced the sodium salt of the original acid, which crystallized on standing overnight. The precipitate was filtered off, acidified, and the resulting acid recrystallized from ethanol; m. p. and mixed m. p. 231°.

The same result was obtained by saponification of the ethyl ester, m. p. 85°, which had been prepared directly by condensation of dicyclohexenyl with ethyl cinnamate and was reported to resist normal saponification methods extraordinarily well.² The acid Ib reacted much more slowly with diazomethane than its isomer. The ester was obtained from petroleum-ether (80°) as short needles; m. p. 147°.

Anal. Calcd. for $C_{22}H_{28}O_2$: OCH_3 , 9.6. Found: OCH_3 , 9.6.

The ester was again saponified with sodium butylate in four hours, as described above, and yielded the original acid of m. p. 282°.

Variations of the Condensation Reaction with Cinnamic Acid.—(a) Dicyclohexenyl (20 g.) and cinnamic acid (18 g.) were heated together in an open vessel to 175° for eight hours. The isomer Ia was obtained exclusively; yield 15 g., 40%. (b) The same amounts were heated together at 205–210° for six hours. Again no trace of the isomer Ib was detected; yield of Ia 18 g., 47%. (c) When 3 g. of the acid, m. p. 231°, was heated in a sealed tube for five hours to 200°, no isomerization occurred. (d) When 3 g. of the same acid was heated in a sealed tube to 250° for one hour, no trace of the second isomer was detectable.

9-Phenyl-10-acetyldodecahydrophenanthrene (II).—Dicyclohexenyl (10 g.) and benzalacetone (12 g.) were heated together for three hours at 175°. The reaction was then interrupted because of the occurrence of drops of water, which indicated the onset of self-condensation of the ketone. By fractionated distillation 5 g. of a fraction, b. p. 180–190° (0.5 mm.), was obtained, which crystallized on trituration with methanol. An ethanolic solution of this material deposits clusters of needles; m. p. 135°; yield, 27%.

Anal. Calcd. for $C_{22}H_{28}O$: C, 85.7; H, 9.1. Found: C, 85.7, 85.4; H, 8.9, 8.8.

The same results were obtained in a sealed tube and in an open flask.

The head of the distillation (16 g.), which passed over at 120° (2.5 mm.), represented the starting mixture. It was again heated under the same conditions as described above and yielded a further crop of 2 g. of the adduct II. It was not advisable to continue by the same method because of the increase in self-condensation products of the ketone. The adduct II gave no hydrazone or semicarbazone and was not reduced by aluminum isopropylate, even in boiling xylene.

9-Phenyl-10-benzoyldodecahydrophenanthrene (III).—Dicyclohexenyl (9 g.) and benzalacetophenone (11 g.) were heated together in an open vessel at 180–185° for six hours. The reaction mixture crystallized partially with ethanol, yielding 7 g. of the isomer IIIa. After filtration, it was necessary to wash with petroleum-ether, which removed the second isomer. Recrystallization from petroleum-ether (130°) gave needles; m. p. 216°; yield, 6 g.

Anal. Calcd. for $C_{27}H_{30}O$: C, 87.6; H, 8.1. Found: C, 87.6; H, 8.3.

The mother liquors of IIIa were distilled *in vacuo*. At 220–240° (0.4 mm.) a fraction was obtained which was difficultly induced to crystallization by treatment with methanol; from isopropanol as needles, m. p. 153–154° (IIIb); yield, 1 g. The material, which was easily soluble in petroleum-ether, gave no ketone derivative, like the isomer IIIa.

Anal. Calcd. for $C_{27}H_{30}O$: C, 87.6; H, 8.1. Found: C, 87.2; H, 8.2.

9,10-Dibenzoyl-dodecahydrophenanthrene (IV).—(a) *trans*-Dibenzoyl-ethylene (2.5 g.) and dicyclohexenyl (2.5 g.) in xylene (15 cc.) were boiled for three hours, and the solution left overnight in an ice-box. A small amount of crystals was deposited (IVb), showing a m. p. of 162°. To the filtrate of IVb an equal volume of ligroin was added to precipitate a reddish-yellow material (IVa). This was recrystallized from petroleum-ether (130°) or butanol and formed brownish blocks; m. p. 182°; yield 2.0 g. The substance dissolved in cold concentrated sulfuric acid with brown color.

Anal. Calcd. for $C_{28}H_{30}O_2$: C, 84.4; H, 7.5. Found: C, 84.3; H, 7.6.

The first crystallize (IVb), when recrystallized from the same solvent, gave a mixture of white plates and yellow-brown prisms. These were separated mechanically. The prisms proved to be identical with IVa, whereas the plates were recrystallized several times from petroleum-ether. After each recrystallization the mixture of crystals was separated. However, the form IVa appeared again and again, whereas the first form IVb disappeared gradually.

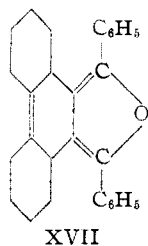
(b) A solution of 1 g. of each of the components in ethanol (10 cc.) was boiled for six hours. During reaction, yellowish crystals appeared (crystallize I). The solution was filtered while hot, and deposited on cooling the crystallize II. The filtrate was then evaporated, and the crystallize III was obtained. All three fractions proved to be the pure substance IVa, of m. p. 182°; yield 1.45 g., 85%. No trace of the form of m. p. 162° was detectable in this experiment.

(c) Dicyclohexenyl (3.3 g.) and dibenzoyl-ethylene (4.7 g.) in nitrobenzene (30 cc.) were heated to 150° for one hour, to 175° for one hour, and finally boiled for ten minutes. The solvent was removed by steam, and the residue treated with alcohol. After repeated recrystallization from butanol (with addition of charcoal), we obtained 5 g. of the material with a melting point of 182°.

Reactions of the Adduct IV.—(a) Adduct IV (1.6 g.) was dissolved in boiling acetic anhydride (25 cc.) and 5 drops of sirupy phosphoric acid (d. 1.75) was added. The color changed immediately to red-brown. After ten minutes, the solution was cooled and deposited a crystalline mass, which was recrystallized from butanol. The solution showed intense green fluorescence and deposited yellow rods; m. p. 179–180°, yield 1.4 g. Fluorescence was observed in solvents, containing oxygen or halogen, but not in hydrocarbons.

Anal. Calcd. for $C_{28}H_{30}O$: C, 88.4; H, 7.4. Found: C, 88.3; H, 7.6.

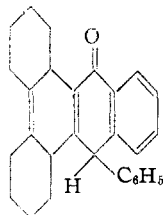
This substance represents the dihydroisobenzofuran derivative XVII:



It gave no addition compound with maleic anhydride, in concordance with the observation of Adams.²³ With concentrated sulfuric acid a curious reaction was observed. When 0.2 g. of XIV and 1 cc. of sulfuric acid were heated to about 80°, complete solution took place, the color changing from initial yellow with green fluorescence to red, then to brown. On pouring onto ice, a grayish powder was obtained which could be recrystallized satisfactorily from ethanol or butanol. These solutions showed no fluorescence at all: sharp plates; m. p. 141°; yield quantitative. In contrast to XIV, the substance dissolved easily in petroleum ether.

Anal. Calcd. for C₂₈H₂₈O: C, 88.4; H, 7.4. Found: C, 88.3, 88.1; H, 7.4, 7.4.

The substance is isomeric with XVII. Reaction with maleic anhydride gave unclear results. A structure like



is to be considered. It is possible that the substance contains the double bonds in other positions than XVII, but this point was not elucidated.

9-Benzoyldodecahydrophenanthrene-10-carboxylic Acid (V).—(a) Dicyclohexenyl (8 g.) and *trans*-benzoylacrylic acid (10 g.) were heated together to 170–180° for four hours. The red sirup was treated with methanol and yielded about 4 g. of crystalline material, 24%; from butyl acetate as tablets, m. p. 258–259° (V). The substance was resistant to bromine.

Anal. Calcd. for C₂₇H₂₆O₂: C, 78.0; H, 7.7. Found: C, 77.9; H, 7.6.

(b) Ten grams of the diene and 12.5 g. of the acid in xylene (50 cc.) were boiled for seven hours and left overnight in an icebox; yield, 4.5 g. of adduct V, 22%.

(c) A mixture of 3.2 g. of the diene and 3.6 g. of the acid in ethanol (20 cc.) was boiled for eight hours. Crystals already had appeared at the boiling temperature. The total yield of entirely uniform product (V) was 1.8 g. (27%).

The methyl ester of V, which was prepared by means of diazomethane, crystallized from petroleum ether (130°) in clusters of needles; m. p. 159–160°.

(23) Adams and Gold, *This Journal*, **62**, 56 (1940).

Anal. Calcd. for C₂₂H₂₀O₂: C, 78.4; H, 8.0; OCH₃, 8.8. Found: C, 78.4; H, 8.1; OCH₃, 8.8.

No esterification occurred in boiling methanol with gaseous hydrochloric acid.

The acid V gave a clear, red-brown solution in concentrated sulfuric acid. On pouring onto ice, a white precipitate was obtained, which could be recrystallized from methanol with large losses; m. p. 124–125°.

Anal. Calcd. for C₂₂H₂₀O₄: C, 74.1; H, 7.9. Found: C, 73.9; H, 7.5.

This points to a hydration product of the adduct V. The adduct V could not be cyclized by sulfuric acid in benzoyl chloride, to yield the corresponding derivative of 1,2,3,4-dibenzanthraquinone.²⁴ Apparently this method is not suitable for partially hydrogenated *o*-benzoylbenzoic acids.

Grignard Reactions.—1. Methyl ester of Ia with methylmagnesium iodide: In ethereal solution, no reaction occurred. A 2-g. portion of the ester, m. p. 111°, was added to a Grignard solution from methyl iodide (4 g.) and magnesium (0.7 g.). After distilling off the solvent, the residue was heated on a steam-bath for ten hours. After the usual decomposition, the ether left a thick oil, which was induced to crystallize by methanol and a few drops of ethyl acetate; from ethanol, needles, m. p. 135°. The product is identical with the ketone II.

The ester did not react with phenylmagnesium bromide in boiling xylene. The isomeric ester of Ib showed no reaction with either of the Grignard compounds.

2. Reaction of ketone II with methylmagnesium iodide: The reaction was brought about in boiling toluene and yielded a thick oil; b. p. 190–200° (4 mm.); yield 60% (XIV). This carbinol could not be cyclized by sulfuric acid in acetic anhydride.

Anal. Calcd. for C₂₂H₃₂: C, 85.2; H, 10.0. Found: C, 85.2; H, 10.4.

3. Reaction of ketone II with phenylmagnesium bromide: The reaction had to be carried out in boiling xylene. After decomposing the mixture with sulfuric acid, we obtained directly an olefin (XV or XVI). It was purified by vacuum distillation; b. p. 190–200° (0.05 mm.). Recrystallization from methanol and water yielded aggregated plates; m. p. 106–107°.

Anal. Calcd. for C₂₆H₃₂O: C, 91.3; H, 8.7. Found: C, 91.3; H, 8.7.

Bromine was rapidly absorbed, but the bromination product was an oil, which could not be purified.

4. Reaction of ketone IIIa with methylmagnesium iodide was accomplished by boiling in toluene for eight hours. The product crystallized without vacuum distillation from isopropanol as needles; m. p. 156°; 4 g. of ketone yielded 2 g. of hydrocarbon (corresponding to XV or XVI).

Anal. Calcd. for C₂₈H₃₂: C, 91.3; H, 8.7. Found: C, 91.4; H, 8.6.

5. Reaction of ketone IIIb with methylmagnesium iodide: 0.5 g. of the adduct IIIb and 5 equivalents of methylmagnesium iodide in toluene were heated in an oil-bath for ten hours. The reaction product was distilled in

(24) Compare Waldmann, *J. prakt. Chem.*, **160**, 121 (1938).

a high vacuum (0.05 mm.), bath-temperature 280–300°. A drop of yellowish oil was obtained which could not be induced to crystallize. Because of the small amount of material available, the oil could not be purified satisfactorily; therefore, no definite conclusions can be drawn regarding the sterical relation of the ketone II to IIIa or IIIb.

Summary

The steric aspects of the Diels–Alder reaction have been studied as regards the formation of stereoisomers, particularly in the condensation of dicyclohexenyl with ketonic compounds. Certain general rules are proposed, the first being well established: (1) the structure of the philodienic component is preserved unchanged in the adduct

with no *cis-trans* isomerization; (2) no isomerism is caused by different spatial arrangements at carbons 3 and 6 of the new ring; (3) no isomerism is caused by the relative arrangement of substituents at carbons 1 and 6 (or 2 and 3); (4) isomeric adducts differ in the position of the double bond only. Dicyclohexenyl has been condensed with cinnamic acid, benzalacetone, benzalacetophenone, *trans*-dibenzoyl ethylene, *trans*-benzoylacrylic acid, and the properties and reactivities of the addition products studied. In general, they proved to be very resistant to attack by ordinary ketone reagents.

REHOVOTH, PALESTINE

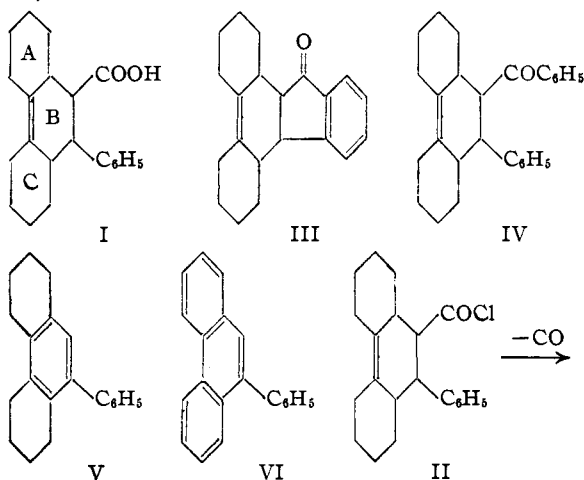
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[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE]

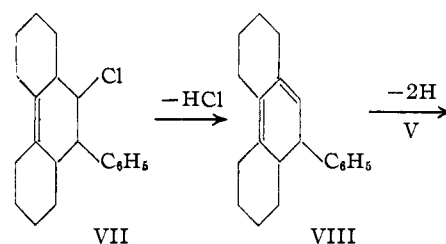
Friedel–Crafts Reactions of 9-Phenyl-dodecahydrophenanthrene-10-carboxylic Acid

BY H. EMILE ESCHINAZI AND FELIX BERGMANN

In continuation of our previous experiments with the adduct of dicyclohexenyl and cinnamic acid (I),¹ we attempted to cyclize the acid (I) to the dibenzfluorenone derivative III. When the acid chloride II² was treated with aluminum chloride in boiling benzene solution, the benzoyl derivative IV of m. p. 198–199° was isolated as the only reaction product. IV proved to be different from both the isomeric condensation products of dicyclohexenyl with benzalacetophenone, of m. p. 216 and 153°, respectively.¹ The most probable explanation for the occurrence of a third isomer is that aluminum chloride causes a shift of the 12,13-double bond in IV.



(1) F. Bergmann and Eschinazi, *THIS JOURNAL*, **64**, 1405 (1942).
 (2) Previous attempts to prepare this chloride by means of thionyl chloride were unsuccessful: T. Berlin, Dissertation, Jerusalem, 1939.



In boiling carbon disulfide no clear results were obtained and no definite reaction product could be isolated. In boiling petroleum ether (80°), however, stannic chloride gave immediately a green-blue complex with the acid chloride II. After decomposition with sodium hydroxide, a hydrocarbon C₂₀H₂₂ was isolated, which is derived from the acid I by elimination of carbon dioxide and aromatization of ring B. Its structure as 9-phenyl-1,2,3,4,5,6,7,8-octahydrophenanthrene (V) is proved by its dehydrogenation to 9-phenylphenanthrene (VI)³ by means of sulfur or selenium.

Although the exact mechanism for the formation of V was not elucidated, we believe that first CO is split off and that the remaining chloride VII loses a molecule of hydrogen chloride to yield the dihydrobenzene derivative VIII. This intermediate stage may then be converted to V by disproportionation or autoxidation.

It is of interest that the selective dehydrogenation of ring B in I, which is effected by reaction with stannic chloride, could not be achieved with sulfur or selenium, the former agent leading directly

(3) Koelsch, *THIS JOURNAL*, **56**, 480 (1934); E. Bergmann and F. Bergmann, *ibid.*, **59**, 1443 (1937).