[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

The Diels–Alder Reaction of 1-Vinylnaphthalene with α,β- and $\alpha,\beta,\gamma,\delta$-Unsaturated Acids and Derivatives

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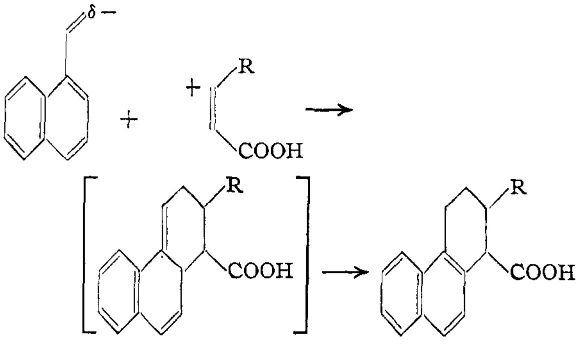
The reaction of 1-vinylnaphthalene as a diene in the Diels–Alder reaction[2] was extended recently to the addition of fumaric acid, citraconic anhydride, and mesaconic acid.[3] We have now studied the addition of a number of α,β- and $\alpha,\beta,\gamma,\delta$-unsaturated acids and derivatives. In general, the yields of adducts were low on account of two competing reactions: homopolymerization of the 1-vinylnaphthalene and copolymerization with the dienophile. In most of the reactions two structural isomers were possible of formation, since the diene and the dienophile were unsymmetrically substituted. The structural isomer which was formed in each reaction was that expected from an application of the general principle of the English school that the most nucleophilic carbon atom will bond to the most electrophilic carbon atom.[4] In applying this principle to 1-vinylnaphthalene, the terminal carbon atom of the vinyl group was assumed to be the most potentially nucleophilic carbon atom by analogy with styrene.[5]

In the usual type of Diels–Alder reaction which involves a hydrocarbon diene and an α,β-unsaturated carbonyl compound as the dienophile, we prefer to consider that the attack is initiated by the strongly electrophilic β-carbon atom of the dienophile upon the easily polarizable diene. A second type of reaction suggests itself in which the polarities are reversed. A strongly electrophilic diene (such as sorbic acid) could attack an easily polarizable nucleophilic olefin. Apparently no unequivocal examples of this type involving unsymmetrical reactants have been mentioned; the closest approach appears to be the reaction of cyclones with unsaturated hydrocarbons. Three examples are reported in this paper. The cyclic dimerization of dienes does not fall cleanly into either category, but represents an intermediate type where both the diene and the dienophile are easily polarizable.

1-Vinylnaphthalene as the Diene. Formation of Hydrophenanthrene Derivatives.—1-Vinylnaphthalene reacted with α,β-unsaturated acids in acetic acid or propionic acid to yield 1,2,3,4-tetrahydrophenanthrene-1-carboxylic acids (I).



I

The initial adducts (shown in brackets) were isomerized to the compounds with a naphthalene nucleus by the action of the acidic medium in accordance with previous experience.[3]

Acrylic acid yielded 1,2,3,4-tetrahydrophenanthrene-1-carboxylic acid (I, R = H) whose structure was proved by the ultraviolet absorption spectrum (Fig. 1), which showed the presence of a naphthalene ring, by the failure of the compound to decolorize neutral permanganate, and by sulfur dehydrogenation to the known phenanthrene-1-carboxylic acid. Acrylic acid was the only dienophile of those studied which polymerized extensively with itself.

Crotonic acid (*trans*-β-methylacrylic acid) and β-ethylacrylic acid gave 2-methyl and 2-ethyl-1,2,3,4-tetrahydrophenanthrene-1-carboxylic acids (I, R = CH_3; I, R = CH_3CH_2), respectively. Both stereoisomers (*cis* and *trans*) of I (R = CH_3) were isolated in a 1:4 ratio, but the configurations were not established. This result is not considered to be an exception to the rule of *cis* addition, but is attributed to partial isomerization of the crotonic acid to isocrotonic acid under the conditions of the reaction. The structures were proved by decarboxylation and dehydrogenation of I (R = CH_3) to 2-methylphenanthrene and of I (R = CH_3CH_2) to 2-ethylphenanthrene. Neither dienophile showed much tendency to copolymerize with 1-vinylnaphthalene.

A study of the factors affecting the yields of adduct was made with crotonic acid. When the reaction was carried out in air, total polymerization of the 1-vinylnaphthalene resulted. For this reason all of the reactions were conducted in an inert atmosphere of nitrogen or carbon dioxide. Strong acids such as *p*-toluenesulfonic acid promoted complete polymerization of the 1-vinylnaphthalene. The addition of small amounts of picric acid or *sym*-trinitrobenzene, which have been found to act as inhibitors of

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[1] From the Ph.D. dissertation of N. C. Deno (present address: Department of Chemistry, The Ohio State University). The dissertation, which is available on microfilm, contains more detailed directions for some of the experiments.

[2] Cohen, *Nature*, **136**, 869 (1935); Cohen and Warren, *J. Chem. Soc.*, 1315 (1937).

[3] Bachmann and Scott, THIS JOURNAL, **70**, 1458 (1948).

[4] See Hudson and Robinson, *J. Chem. Soc.*, 715 (1941), for a discussion of this principle in the Diels–Alder reaction.

[5] Wheland, "The Theory of Resonance and Its Application to Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 246.

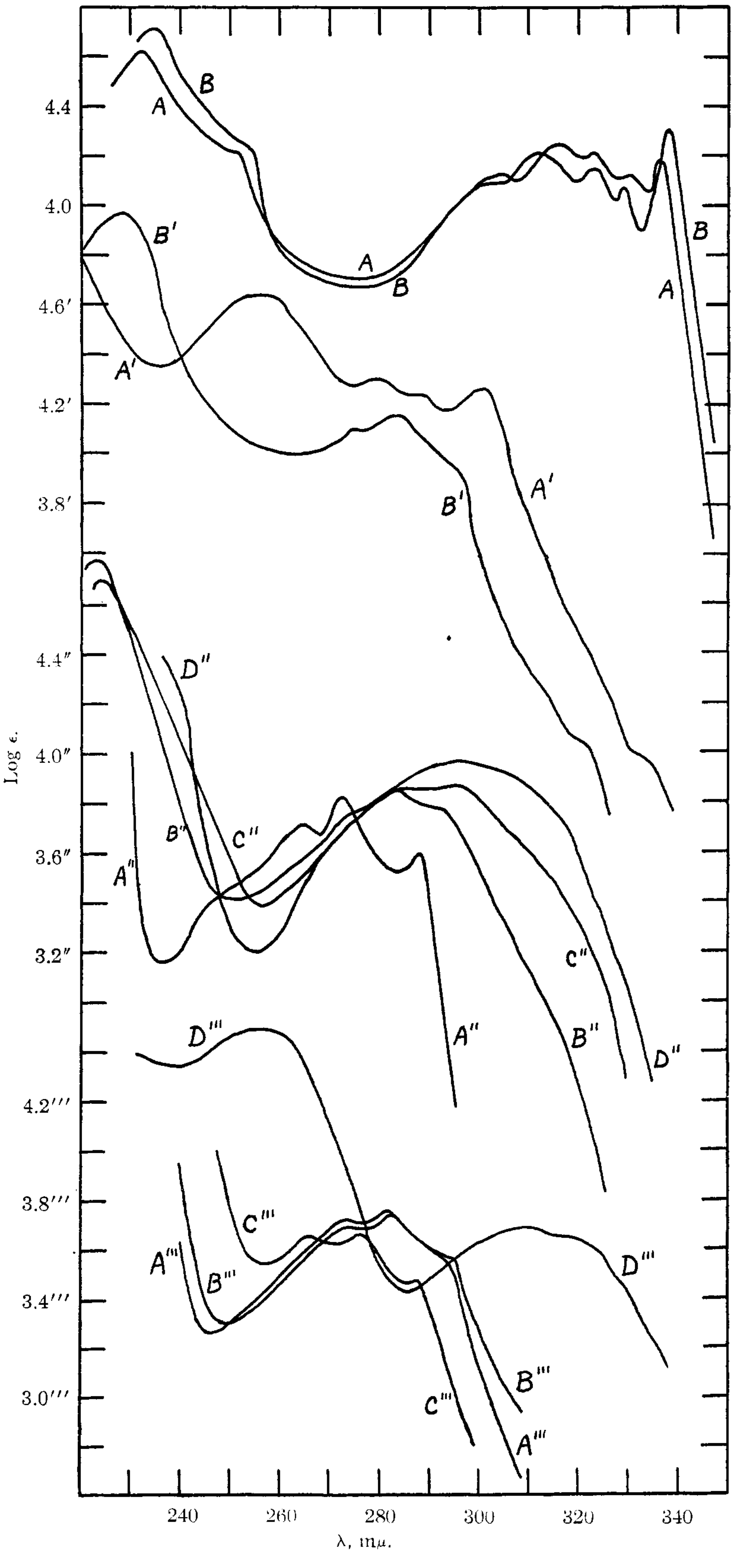
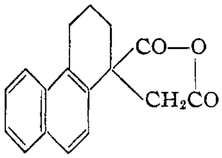


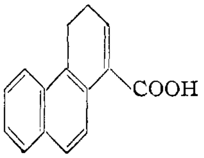
Fig. 1.—A, 3,4-Benzfluorene (XIII, R = H); B, 6-methyl-3,4-benzfluorene (XIII, R = CH_3); A′, 1-(1′-naphthyl)-phenanthrene; B′, 1-(1′-naphthyl)-1,2,3,4-tetrahydrophenanthrene (XVI); A″, naphthalene (Askew, *J. Chem. Soc.*, 512 (1935); B″, 1-(1′-cyclohexenyl)-naphthalene; C″, 1-(1′-cyclopentenyl)-naphthalene; D″, 1-propenylnaphthalene [Pestemer and Manchen, *Monatsh.*, **68**, 97 (1936)]. A‴, 1,2,3,4-Tetrahydrophenanthrene-1-carboxylic acid (I, R = H); B‴, 1-carboxymethyl-1,2,3,4-tetrahydrophenanthrene-1,2-dicarboxylic anhydride (IV); C‴, *trans*-1,2,3,4-tetrahydrophenanthrene-1,2-dicarboxylic acid; [3] D‴, 3,4-dihydrophenanthrene-1-carboxylic acid (III).

certain polymerizations,[6] resulted in very low yields of adduct. Hydroquinone was employed in many runs as a precautionary measure, although it had no effect on the yield of the adduct from crotonic acid.

Itaconic acid yielded the anhydride of 1-carboxy-1,2,3,4-tetrahydrophenanthrene-1-acetic acid (II) in addition to copolymer. The structure of the adduct was proved by decarboxylation and dehydrogenation to 1-methylphenanthrene.



II



III

The adduct from α-bromoacrylic acid split out hydrogen bromide during the reaction and formed 3,4-dihydrophenanthrene-1-carboxylic acid (III). The acid rapidly decolorized permanganate in aqueous acetone, and the ultraviolet absorption spectrum (Fig. 1) clearly showed the double bond conjugated with the naphthalene ring. Addition of a mole of hydrogen to the unsaturated acid yielded 1,2,3,4-tetrahydrophenanthrene-1-carboxylic acid (I, R = H), which confirmed the structures of both acids.

Aconitic acid yielded the anhydride of 1-carboxymethyl-1,2,3,4-tetrahydrophenanthrene-1,2-dicarboxylic acid to which the structure IV has been assigned. The degradation of the compound with various reagents is of interest. Sulfur dehydrogenation eliminated the acetic acid group with the formation of phenanthrene-1,2-dicarboxylic anhydride (V), while treatment with palladium at 310° yielded 1-methylphenanthrene. Unexpectedly, the acetic acid moiety was removed also by dry distillation of a mixture of the sodium salt of the acid and calcium hydroxide, and phenanthrene was the sole volatile product. The monomethyl ester anhydride, the free triacid, and the trimethyl ester were prepared from the adduct.

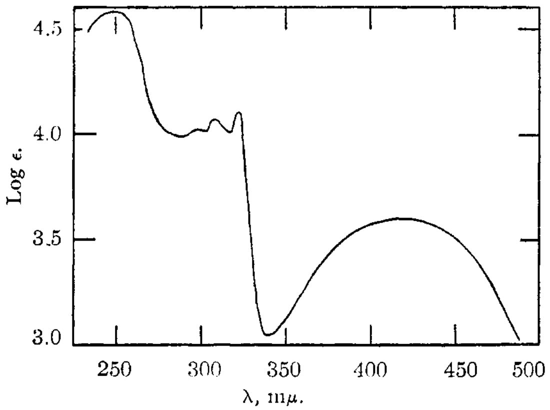
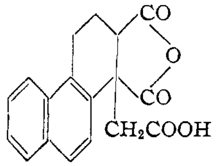
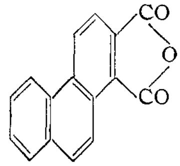


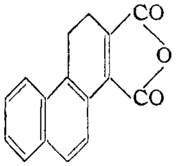
Fig. 2 —1.4-Chrysoquinone (VIII).



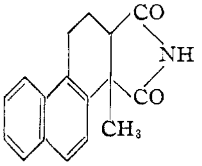
IV



V



VI

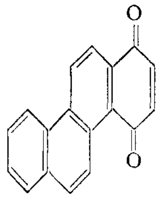


VII

Chloromaleic anhydride reacted with 1-vinylnaphthalene with elimination of hydrogen chloride, for the product was 3,4-dihydrophenanthrene-1,2-dicarboxylic anhydride (VI). Mesacon-β-amidic acid, $CH_3(COOH)C{=}CHCONH_2$, gave 1-methyl-1,2,3,4-tetrahydrophenanthrene-1,2-dicarboxylic imide (VII), whose structure was established by independent synthesis of the imide from the corresponding acid of Bachmann and Scott.[3] The same imide was obtained from 1-vinylnaphthalene and *cis*- and *trans*-ethyl β-cyanocrotonate after the reaction mixture had been submitted to hydrolytic conditions. The major product from 1-vinylnaphthalene and fumaronitrile was copolymer.

Under the usual conditions acetylenedicarboxylic acid gave only copolymer. In dibutyl ether, however, phenanthrene-1,2-dicarboxylic anhydride was produced in low yield, the intermediate adduct having been dehydrogenated apparently by the excess dienophile.

1,2-Chrysoquinone (VIII, absorption spectrum in Fig. 2) was formed in high yield from *p*-benzoquinone. The intermediate adduct was dehydrogenated by the excess quinone. Methyl vinyl ketone gave an adduct which from theoretical considerations is probably 1-acetyl-1,2,3,4-tetrahydrophenanthrene, although its structure has not been established.



VIII

Under the conditions that were successful with crotonic acid, aconic acid, β-angelica lactone, and β-acetylacrylic acid gave low yields of products that were not investigated further; 1,2-diacetylethylene and mucobromic acid gave chiefly copolymer; and β,β-dimethylacrylic acid, β-furylacrylic acid, 5-methylcyclohexene-1,5-dicarboxylic acid, and butadiene monoxide failed to react.

1-Vinylnaphthalene as the Dienophile. Formation of 1-Cyclohexenylnaphthalene Deriva-

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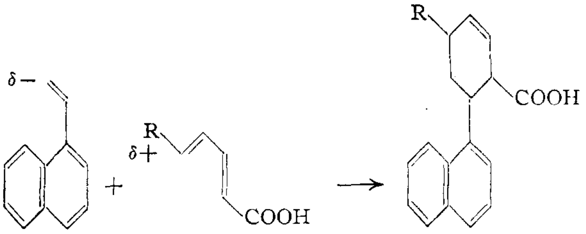
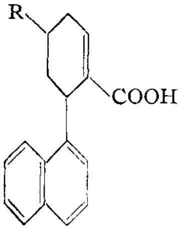
(6) Frank and Adams, This Journal, 68, 908 (1946).

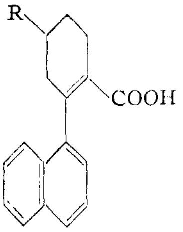
tives.—1-Vinylnaphthalene reacted as the dienophile with butadiene-1-carboxylic acid, sorbic acid, and muconic acid and formed 1-cyclohexenylnaphthalene derivatives. This represents a new synthesis of hydrobiaryl acids. We found no evidence for the formation of tetrahydrophenanthrene derivatives.



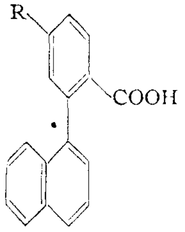
IX



X



XI



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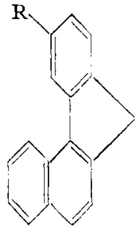
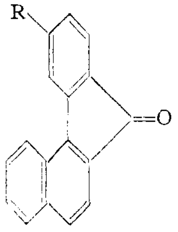
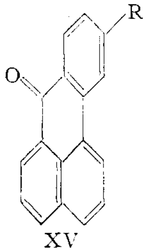


XIII



XIV



XV

Each of the three diene acids yielded a mixture of adducts from which crystalline isomeric (called α and β) 1-cyclohexenylnaphthalene-2′-carboxylic acids were isolated, in which the location of the double bond has not been established with certainty. The six adducts behaved toward bromine in carbon tetrachloride more like α,β-(slow decolorization) than β,γ-unsaturated acids (IX); this implied that the double bond had shifted toward the carboxyl group (as in X and XI) during the reaction. The β adducts were isomerized to the α adducts by alkali; with R = H or CH_3, the conversion was quantitative. In agreement with the interpretation that this might represent a further shift of the double bond from its position in the β adduct (X) to a position in conjugation with the aromatic ring in the α adduct (XI)[7] was the greater reactivity of the α adducts to 3% sodium amalgam and water. On the basis of the available information, these structures seem more likely than IX for the β adducts and X or an epimer of IX for the α adducts. The ultraviolet absorption spectra (Fig. 3) do not distinguish between the various possibilities, because the absorption due to the conjugation of the double bond with the carboxyl group is masked by the strong absorption of the naphthalene ring, and the conjugation with the naphthalene ring is not manifested apparently on account of steric inhibition of resonance.[8]

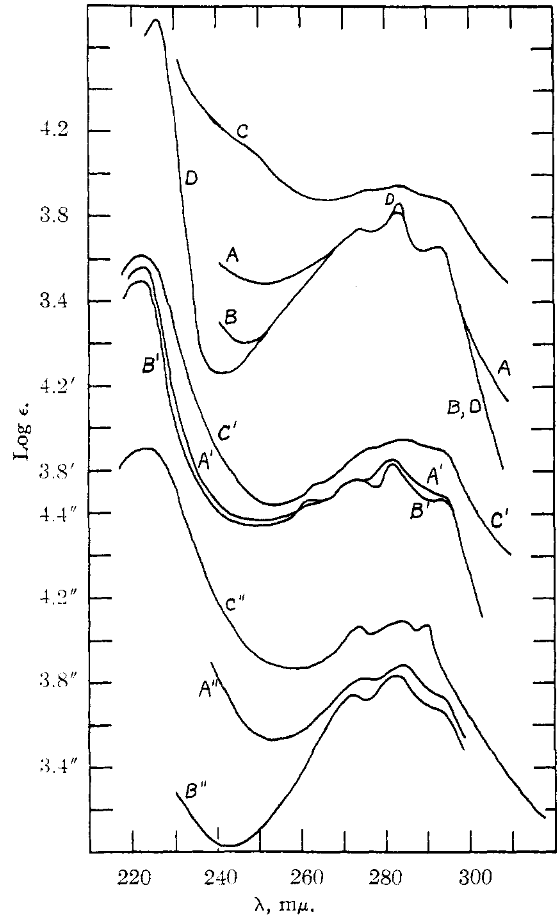


Fig. 3.—A, α-1-Cyclohexenylnaphthalene-2′,5′-di-carboxylic acid (probably XI, R = COOH); B, β-1-cyclohexenylnaphthalene-2′,5′-dicarboxylic acid (probably X, R = COOH); C, 1-phenylnaphthalene-2′,5′-dicarboxylic acid (XII, R = COOH); D, presumably 1-cyclohexylnaphthalene-2′,5′-dicarboxylic acid. A′, α-1,1-Cyclohexenylnaphthalene-2′-carboxylic acid (probably XI, R = H); B′, β-1-cyclohexenylnaphthalene-2′-carboxylic acid (probably X, R = H); C′, 1-phenylnaphthalene-2′-carboxylic acid (XII, R = H). A″, α-5′-Methyl-1-cyclohexenylnaphthalene-2′-carboxylic acid (probably XI, R = CH_3); B″, β-5′-methyl-1-cyclohexenylnaphthalene-2′-carboxylic acid (probably X, R = CH_3); C″, 5′-methyl-1-phenylnaphthalene-2′-carboxylic acid (XII, R = CH_3).

The cyclohexenylnaphthalene structure of the adducts from butadiene-1-carboxylic acid was proved by sulfur dehydrogenation to the known 1-phenylnaphthalene-2′-carboxylic acid (XII, R

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[7] Linstead, *J. Chem. Soc.*, 2498 (1929).

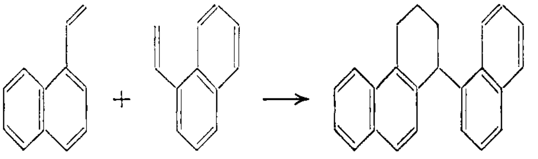
[8] Compare the spectrum of 1-(1′-cyclohexyl)-naphthalene in Fig. 8 with that of 1-phenylnaphthalene [Jones, *Chem. Rev.*, **32**, 34 (1942)].

= H; absorption spectrum in Fig. 3). Dry distillation of a mixture of the sodium salt of the adduct and calcium hydroxide followed by palladium treatment of the distillate at 300° gave the known 3,4-benzfluorene (XIII, R = H). This unexpected result apparently involved cyclization in the alkaline medium to tetrahydrobenzfluorenone followed by internal dehydrogenation–reduction to the hydrocarbon. After the structure of the product had been elucidated, it was learned that *o*-phenylbenzoic acid yields fluorenone when heated with soda–lime.[9]

In a similar manner sulfur dehydrogenation of the adducts from sorbic acid yielded 5′-methyl-1-phenylnaphthalene-2′-carboxylic acid (XII, R = CH_3), which was cyclized to the known 10-methyl-7-oxo-7-benz(de)anthracene (XV, R = CH_3). Likewise, 6-methyl-3,4-benzfluorene (XIII, R = CH_3) was obtained by the procedure which gave 3,4-benzfluorene; the similarity in absorption spectra of these two hydrocarbons (Fig. 1) was evidence for the structure of the methyl derivative.[10]

The adducts from muconic acid were dehydrogenated to 1-phenylnaphthalene-2′,5′-dicarboxylic acid (XII, R = COOH) with palladium. Apparently some disproportionation took place, for a compound was isolated whose analysis and absorption spectra (Fig. 3) corresponded to those of 1-cyclohexylnaphthalene-2′,5′-dicarboxylic acid.[11] The best method of preparation of 1-phenylnaphthalene-2′,5′-dicarboxylic acid (36% yield from 1-vinylnaphthalene) was dehydrogenation of the dimethyl ester of the crude adduct with sulfur followed by hydrolysis. The ring system was established by decarboxylation of the diacid to 1-phenylnaphthalene and by cyclization to the known 7-oxo-7-benz(de) anthracene-10-carboxylic acid (XV, R = COOH).

1-Vinylnaphthalene as the Diene and Dienophile. Dimerization.—When 1-vinylnaphthalene alone was refluxed in propionic acid, polymerization occurred; from the product 1-(1′-naphthyl)-1,2,3,4-tetrahydrophenanthrene (XVI) was isolated. The absorption curve (Fig. 1) showed the presence of two naphthalene rings and the complete structure was proved by sulfur dehydrogenation to 1-(1′-naphthyl)-phenanthrene.



XVI

The resemblance of the spectrum of the latter hydrocarbon with that calculated for a mole of naphthalene and one of phenanthrene may be interpreted in terms of steric inhibition of conjugation between the two ring systems in the molecule.

Observations on the Reactions.—Our results are in agreement with the view that a strongly electrophilic carbon atom of an olefin or diene attacks the potentially nucleophilic terminal carbon atom of 1-vinylnaphthalene. They also demonstrate a close correlation between the reaction of an electrophilic olefin or diene in the Diels–Alder reaction and the reaction of the olefin or diene with strongly nucleophilic anions. For example, the anion of malonic ester attacks diethyl citraconate at the β-position[12] and the ester of sorbic acid and of butadiene-1-carboxylic acid at the δ-carbon atom.[13] Analogously, it is the β-carbon atom of citraconic anhydride[3] and the δ-carbon atom of the two diene acids that bond to the terminal carbon atom of 1-vinylnaphthalene.

In connection with the study of the derivatives of phenylnaphthalenes, the absorption curves of 1-(1′-cyclohexenyl)-naphthalene and of 1-(1′-cyclopentyl)-naphthalene were recorded (Fig. 1). Calvin[14] had noticed a correlation between nonplanarity (as evidenced by steric inhibition of resonance in the ultraviolet spectra) and decreased reactivity of certain dienes in the Diels–Alder reaction. This effect may explain the low reactivity of 1-(1′-cyclohexenyl)-naphthalene[15] compared to the reactivity of 1-(1′-cyclopentenyl)-naphthalene,[16] for the absorption curves seem to indicate a lesser tendency for the cyclohexenyl derivative to be planar.

Experimental

1-Vinylnaphthalene and Acrylic Acid.—A mixture of 20 cc. of an 85% aqueous solution of acrylic acid,[17] 0.4 g. of hydroquinone and 3 cc. of 1-vinylnaphthalene (prepared by dehydration of β-1-naphthylethyl alcohol[2]) was refluxed for one hundred hours in an atmosphere of carbon dioxide. The clear brown gum was dissolved in aqueous potassium hydroxide, the solution was extracted with benzene, and the aqueous layer was acidified. The precipitated gum was evaporatively distilled up to 250° at 0.1 mm., and the distillate (2.68 g.) was again evaporatively distilled at 200° and 0.1 mm. Crystallization of the distillate from ethyl acetate gave 0.53 g. (12%) of **1,2,3,4-tetrahydrophenanthrene-1-carboxylic acid (I, R = H)**; m. p. 155–159°, which was raised to 159–161° by several recrystallizations.

Anal. Calcd. for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.48; H, 6.34.

Only 1.5% of the 1-vinylnaphthalene was accounted for as neutral homopolymer. A 6% yield of the acid (I, R =

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[9] Fittig and Schmitz, *Ann.*, **193**, 115 (1878); Fittig and Ostermayer, *ibid.*, **166**, 372 (1873).

[10] These spectra differed from the spectrum of 7-benz(de)-anthracene [Clar and Furnari, *Ber.*, **65**, 1420 (1932)], which had been a ring system under consideration.

[11] Cook and Lawrence, *J. Chem. Soc.*, 1431 (1936), observed disproportionation of 1-cyclohexenylnaphthalene under similar conditions.

[12] Hope, *J. Chem. Soc.*, 892 (1912); Ingold, Shoppee and Thorp, *ibid.*, 1477 (1926).

[13] Kohler and Butler, This Journal, **48**, 1036 (1926).

[14] Calvin, *J. Org. Chem.*, **4**, 256 (1939).

[15] Bergmann and Bergmann, This Journal, **59**, 1443 (1937); Bergmann and Szmuszkovicz, *ibid.*, **69**, 1367 (1947); Henri and Bergmann, *Nature*, **143**, 278 (1939).

[16] Bachmann and Kloetzel, This Journal, **60**, 2204 (1938).

[17] Kaszuba, *ibid.*, **67**, 1227 (1945).

H) was obtained from a solution of methyl acrylate in acetic acid that had been refluxed for six hours with 0.5 g. of *p*-toluenesulfonic acid. After the addition of 0.5 g. of sodium acetate, 1-vinylnaphthalene was added and the mixture was refluxed for two hundred hours.

Dehydrogenation of the Adduct.—A mixture of 55 mg. of I (R = H) and 30 mg. of sulfur was heated at 235–245° under nitrogen for fifteen minutes, and the product was separated into neutral and acidic fractions with alkali and benzene. The resulting phenanthrene-1-carboxylic acid (40 mg., m. p. 217–225°), after two recrystallizations from ethanol, had the m. p. 229–230° (reported, 232–233°,[18] 228°[19]); the m. p. of its methyl ester was not depressed when mixed with an authentic sample.

1-Vinylnaphthalene and Crotonic Acid.—A mixture of 1.5 cc. (0.01 mole) of 1-vinylnaphthalene, 4.3 g. (0.05 mole) of crotonic acid, and 0.2 g. of hydroquinone in 10 cc. of propionic acid was refluxed for two hundred hours under carbon dioxide. By means of alkali the product was separated into 1-vinylnaphthalene homopolymer (1.14 g. or 74%) and acidic material; the latter on evaporative distillation at 200° and 0.1 mm. yielded a colorless solid (0.63 g. or 26%; m. p. 151–158°), which was separated into the *cis* and *trans* forms of **2-methyl-1,2,3,4-tetrahydrophenanthrene-1-carboxylic acid** (**I, R = CH_3**) by numerous fractional recrystallizations from benzene. Both isomers formed colorless prisms; one (21% yield) with m. p. 156–157°, the other (5%) with m. p. 211–212°.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.97; neut. equiv., 240. Found: (lower melting isomer) C, 79.91; H, 6.97; neut. equiv., 241; (higher melting isomer) C, 79.91; H, 6.78; neut. equiv., 241.

When the reaction was carried out in the presence of air, 5% of *p*-toluenesulfonic acid, 5% of *sym*-trinitrobenzene, or in pyridine as the solvent, only the homopolymer of 1-vinylnaphthalene was formed. The presence of 5% of picric acid or of water lowered the yield; the addition of hydroquinone had no effect.

The **methyl ester** of the 156–157° acid, formed in quantitative yield with diazomethane, crystallized from methanol in colorless prisms; m. p. 57–57.5°.

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.29; H, 7.14. Found: C, 80.50; H, 7.38.

The ester yielded the original acid when refluxed with 20% aqueous-methanolic sodium hydroxide for twenty-four hours.

Degradation of the Adducts to 2-Methylphenanthrene.—To a solution of 240 mg. of the 156–157° acid in 5 cc. of 0.5 *N* sodium hydroxide was added 0.5 g. of calcium oxide. After thorough mixing, the mixture was evaporated and the residue was ground with 0.5 g. of calcium oxide. Dry distillation in a nitrogen atmosphere gave a liquid distillate, which was heated with 50 mg. of 5% palladium on charcoal catalyst under nitrogen. Evaporative distillation of the product at 150° and 0.01 mm. yielded 170 mg. of a colorless liquid which gave the picrate of 2-methylphenanthrene (56% yield based on the original acid); m. p. 115.5–116.5° (reported,[20] 118–119°). The hydrocarbon generated from the picrate had the m. p. 54.5–55.5° (reported,[20] 55–56°). In a similar manner, 42 mg. of the 211–212° acid yielded 22 mg. (66%) of 2-methylphenanthrene. When the methyl ester of the lower melting acid was heated with 5% palladium on charcoal under nitrogen at 310–320° for fifteen minutes, 2-methylphenanthrene was formed in 70% yield.

1-Vinylnaphthalene and β-Ethylacrylic Acid.—The unsaturated acid was prepared by the method of Auwers.[21] When the malonic acid was completely dissolved in the pyridine before the addition of the propionaldehyde, the yield of β-ethylacrylic acid was 59%; the yield was much lower when a small amount of piperidine[22] was added.

The reaction with 1-vinylnaphthalene, carried out in the manner described for crotonic acid, gave 28% of adduct and 68% of neutral homopolymer. After several recrystallizations from ethyl acetate, the **2-ethyl-1,2,3,4-tetrahydrophenanthrene-1-carboxylic acid** (**I, R = CH_3-CH_2**) had the m. p. 129.5–131°; yield, 18%.

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.22; H, 7.11.

By the procedure described for the methyl homolog, 2-ethylphenanthrene (52%; m. p. 52–55°) was obtained; after several recrystallizations from ethanol the hydrocarbon melted at 65–65.5° (reported,[23] 64–65°); m. p. of the picrate, 92–93.5° (reported,[23] 92–93°).

1-Vinylnaphthalene and Itaconic Acid.—The procedure was similar to that with crotonic acid except that 2.6 g. (0.02 mole) of itaconic acid[24] was used. After being poured into excess dilute potassium hydroxide, the mixture was heated for thirty minutes at 100° in order to hydrolyze anhydrides. Evaporative distillation of the acidic portion up to 200° at 0.1 mm. gave 1.41 g. of distillate, a solution of which in acetone–petroleum ether deposited 1.26 g. (47%) of **the anhydride of 1-carboxy-1,2,3,4-tetrahydrophenanthrene-1-acetic acid** (**II**); m. p. 145.5–148°, raised by further recrystallization to 147.5–148°.

Anal. Calcd. for $C_{17}H_{14}O_3$: C, 76.68; H, 5.30. Found: C, 76.94; H, 5.40.

The diacid obtained by alkaline hydrolysis did not have a sharp melting point; at about 190° it changed to the anhydride. The **dimethyl ester of 1-carboxy-1,2,3,4-tetrahydrophenanthrene-1-acetic acid**, formed in nearly quantitative yield with diazomethane, crystallized from methanol–petroleum ether in large, glistening prisms; m. p. 60–62°.

Anal. Calcd. for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45. Found: C, 72.84; H, 6.33.

The picrate of the dimethyl ester crystallized from methanol in yellow needles; m. p. 90.5–91.5°.

Degradation of the Adduct to 1-Methylphenanthrene.—A mixture of 100 mg. of II and 400 mg. of 5% palladium–charcoal catalyst was heated at 310–320° under nitrogen for fifteen minutes. The 1-methylphenanthrene obtained on distillation at 15 mm. crystallized from ethanol in glistening flakes (16 mg.); m. p. 119–119.5° alone and when mixed with an authentic sample. Of interest is the observation that the melting point (135–136°) of the picrate of 1-methylphenanthrene is not depressed by the picrate (m. p. 142–143°) of phenanthrene.

When less catalyst was used or when II was dry-distilled with soda-lime, the m. p. of the 1-methylphenanthrene could not be raised above 110°, although its picrate melted sharply at 135–136°.

1-Vinylnaphthalene and α-Bromoacrylic Acid.—The acidic adduct (from 2 g. of α-bromoacrylic acid, 1.5 cc. of 1-vinylnaphthalene, 10 cc. of acetic acid, fifty hours refluxing under nitrogen), after separation from the neutral homopolymer (1.14 g.), was evaporatively distilled up to 210° at 0.1 mm., and the solid distillate (0.4 g. or 18%, m. p. 194–204°) after several recrystallizations from ethanol gave colorless, glistening prisms of 3,4-dihydro-1-phenanthrenecarboxylic acid (III); m. p. 211–212° (reported,[25] 213–214°). The product immediately decolorized a solution of potassium permanganate in aqueous acetone.

Hydrogenation of the Unsaturated Acid.—A mixture of 95 mg. of 3,4-dihydrophenanthrene-1-carboxylic acid and 20 mg. of Adams catalyst in 15 cc. of ethanol was shaken for two hours under two atmospheres of hydrogen. The colorless needles of 1,2,3,4-tetrahydrophenanthrene-1-carboxylic acid (80 mg.) after recrystallization from aqueous ethanol melted at 157–159.5°, alone and when mixed with the adduct from acrylic acid.

1-Vinylnaphthalene and Aconitic Acid.—The reaction mixture (3 cc. 1-vinylnaphthalene, 7 g. aconitic acid, 20

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[18] Fieser, This Journal, **54**, 4110 (1932).

[19] Bachmann, *ibid.*, **57**, 555 (1935).

[20] Haworth, *J. Chem. Soc.*, 1133 (1932).

[21] Auwers, *Ann.*, **432**, 63 (1923).

[22] Goldberg and Linstead, *J. Chem. Soc.*, 2351 (1928).

[23] Haworth and Mavin, *ibid.*, 1015 (1933).

[24] Kindly supplied by Chas. Pfizer and Co.

[25] Bachmann and Fujimoto, unpublished results.

cc. acetic acid, one hundred hours refluxing under nitrogen) was concentrated at 100° in a current of air and the acidic adduct was separated from the neutral homopolymer (2 g.) with alkali. The adduct was evaporatively distilled up to 270° at 0.1 mm.; addition of benzene to a solution of the distillate (1.07 g.) in hot ethyl acetate gave 0.86 g. (14%) of colorless prisms of the **anhydride of 1-carboxymethyl-1,2,3,4-tetrahydrophenanthrene-1,2-dicarboxylic acid** (IV); m. p. 215–219°, which was raised to 218–219° by recrystallization.

Anal. Calcd. for $C_{17}H_{12}O_5$: C, 68.91; H, 4.08. Found: C, 68.92; H, 4.48.

The **monomethyl ester** of the anhydride acid, formed with diazomethane in ether, crystallized from benzene–petroleum ether in colorless prisms; m. p. 178.5–179.5°.

Anal. Calcd. for $C_{19}H_{16}O_5$: C, 70.36; H, 5.00. Found: C, 70.61; H, 5.11.

The **trimethyl ester of 1-carboxymethyl-1,2,3,4-tetrahydrophenanthrene-1,2-dicarboxylic acid**, formed from the triacid (obtained by alkaline hydrolysis of IV) and diazomethane in ether–methanol, crystallized from methanol in colorless prisms; m. p. 95–97°.

Anal. Calcd. for $C_{20}H_{20}O_6$: C, 68.09; H, 5.98. Found: C, 67.73; H, 5.97.

When a mixture of acetic acid (15 cc.) and acetic anhydride (5 cc.) was used as the solvent, the distilled product contained phenanthrene-1,2-dicarboxylic anhydride (V), isolated as yellow needles (1%, m. p. 304–306°) on recrystallization from acetone. This surprising result was checked repeatedly. When propionic acid was employed, the higher temperature caused decarboxylation of some of the aconitic acid to itaconic acid with the resultant formation of the itaconic acid adduct (II) in 14% yield in addition to the aconitic acid adduct (IV) in 8% yield.

Degradation of the Adduct from Aconitic Acid.—Palladium–charcoal treatment of the adduct in the manner described for II gave 1-methylphenanthrene (m. p. 115–116°) in 18% yield. After recrystallization from ethanol the hydrocarbon melted at 118–119°, alone and when mixed with an authentic specimen.

A mixture of 74 mg. of IV and 17.6 mg. of sulfur was heated at 310–320° under nitrogen for fifteen minutes and then sublimed under reduced pressure. Two recrystallizations from acetic anhydride gave 10 mg. (16%) of phenanthrene-1,2-dicarboxylic anhydride (V); m. p. 305–308°, alone and when mixed with an authentic specimen.

A solution of 0.1 g. of the anhydride acid (IV) and 0.3 g. of sodium hydroxide in 5 cc. of water was treated with calcium oxide and worked up as described for the itaconic acid adduct; yield of phenanthrene, 20 mg. (32%). The product obtained from the soda-lime pyrolysis before the treatment with palladium was chiefly phenanthrene.

1-Vinylnaphthalene and Chloromaleic Anhydride.—The cooled mixture (1.5 cc. of 1-vinylnaphthalene, 2.64 g. of chloromaleic anhydride, 10 cc. acetic acid, twenty-five hours refluxing under nitrogen) deposited 3,4-dihydrophenanthrene-1,2-dicarboxylic anhydride (VI, 1.12, g., m. p. 270–272°), which was separated mechanically from adhering brown powder and recrystallized from 40 cc. of acetic anhydride; yield, 1.01 g. (40%); m. p. 270–271°, alone and when mixed with an authentic sample.[26]

1-Vinylnaphthalene and Mesacon-β-amidic Acid.—From 1.55 g. of mesacon-β-amidic acid[27] 37% of evaporatively distilled adduct was obtained by the procedure used with crotonic acid. Recrystallization of the adduct from ethyl acetate gave 0.49 g. (19%) of colorless prisms of **1-methyl-1,2,3,4-tetrahydrophenanthrene-1,2-dicarboxylic imide** (VI); m. p. 209–212° which was raised to 211.5–212.5° by recrystallization.

Anal. Calcd. for $C_{17}H_{15}O_2N$: C, 76.96; H, 5.70; N, 5.28. Found: C, 77.06; H, 5.63; N, 5.26.

The same imide was formed by shaking 50 mg. of *cis*-1-methyl-1,2,3,4-tetrahydrophenanthrene-1,2-dicarboxylic anhydride[3] with 20 cc. of concentrated aqueous ammonia for five hours, acidifying the concentrated solution, and subliming the precipitate at 170° and 0.1 mm. Recrystallization of the sublimate from ethyl acetate gave the imide; m. p. 210–212°, alone and when mixed with the adduct described previously.

1-Vinylnaphthalene and *cis* and *trans* Ethyl β-Cyanocrotonate.—To the propionic acid solution of the adduct from 1.8 cc. of *cis*-ethyl β-cyanocrotonate[28] obtained by the procedure used with crotonic acid was added 5 cc. of concentrated hydrochloric acid and 5 cc. of acetic acid, and the mixture was refluxed for forty-eight hours. Evaporative distillation of the acidic fraction at 0.1 mm. and fractional crystallization of the distillate from ethyl acetate–petroleum ether and from benzene yielded 1-methyl-1,2,3,4-tetrahydrophenanthrene dicarboxylic anhydride (4.5%) and its imide (VI, 9.5%). Under similar conditions *trans*-ethyl β-cyanocrotonate[28] gave 10% of the anhydride and 7.5% of the corresponding imide (VI).

1-Vinylnaphthalene and Fumaronitrile.—By the procedure used in the preceding experiment, 0.41 g. of crystalline sublimate (m. p. 187–226°) was obtained from 1.56 g. of fumaronitrile; the chief product was copolymer (1.74 g.). Two recrystallizations of the sublimate from ethyl acetate gave 40 mg. (1.5%) of phenanthrene-1,2-dicarboxylic anhydride (V); m. p. 305–307°.

1-Vinylnaphthalene and Acetylenedicarboxylic Acid.—A solution of 1.55 cc. of 1-vinylnaphthalene, 2.28 g. of acetylenedicarboxylic acid, and 0.2 g. of hydroquinone in 20 cc. of dibutyl ether was kept at 100° under carbon dioxide for one hundred and fifty hours. The yellow precipitate was isolated and sublimed at 220° and 0.1 mm. and the sublimate (0.31 g.) was recrystallized from acetic anhydride; yield of phenanthrene-1,2-dicarboxylic anhydride (V), 0.2 g. (8%); m. p. 307.5–310°.

When the reaction was run in boiling acetic acid only copolymer was formed. The product obtained at room temperature in acetic acid was the phenanthrene derivative in low yield.

1-Vinylnaphthalene and Methyl Vinyl Ketone.—The ketone which separated on addition of excess potassium carbonate to 15 cc. of the 85% azeotrope[29] at 0° was decanted into a solution of 3 cc. of 1-vinylnaphthalene in 50 cc. of acetic acid, and the solution was refluxed under nitrogen for seventy hours. The viscous liquid (2 g., b. p. 112–185° at 0.1 mm.) obtained by fractional distillation formed yellow needles, presumably the **picrate of 1-acetyl-1,2,3,4-tetrahydrophenanthrene**, when treated with 1 g. of picric acid in 10 cc. of methanol; yield, 0.48 g. (5%); m. p. 90–91°.

Anal. Calcd. for $C_{16}H_{16}O \cdot C_6H_3N_3O_7$: C, 58.22; H, 4.22. Found: C, 58.12; H, 4.10.

1-Vinylnaphthalene and *p*-Benzoquinone.—The precipitate in the cooled mixture (6 cc. of 1-vinylnaphthalene, 24 g. of *p*-benzoquinone, 100 cc. of acetic acid, five hours at 100°) was collected and washed with three 10-cc. portions of acetic acid and two of ether; yield, 8.23 g. (78%); m. p. 200–207°. After several recrystallizations from acetic acid the glistening golden-bronze flakes of **1,4-chrysoquinone** (VIII) melted at 206.5–207.5°.

Anal. Calcd. for $C_{18}H_{10}O_2$: C, 83.71; H, 3.90. Found: C, 83.47; H, 4.15.

In an attempt to isolate the intermediate in the formation of 1,4-chrysoquinone, several solvents were tried; only in diethyl ether did the solution remain bright yellow. When the isolated yellow solid was heated in acetic acid, the solution became red and the golden flakes of 1,4-chrysoquinone crystallized.

1-Vinylnaphthalene and Butadiene-1-carboxylic Acid.—A solution of 3 g. of butadiene-1-carboxylic acid (prepared from acrolein and malonic acid[30]), 3 cc. of 1-vinylnaphthalene and 0.5 g. of hydroquinone in 20 cc. of acetic acid was

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[26] Fieser and Hershberg, This Journal, **57**, 1853 (1935).

[27] Anschütz, *Ann.*, **353**, 139 (1907).

[28] Mowry and Rossow, This Journal, **67**, 926 (1945).

[29] Kindly furnished by E. I. du Pont de Nemours and Co.

[30] Doebner, *Ber.*, **35**, 1137 (1902).

heated at 100° under nitrogen for two hundred hours, and then added with good stirring to 100 cc. of benzene. The clear solution which was decanted from the precipitated gum was washed well with dilute sodium sulfate solution and then extracted with 50 cc. of 5% aqueous potassium hydroxide. The acid obtained on acidification of the alkaline extract with acetic acid was evaporatively distilled up to 230° at 0.1 mm., and the distillate (1.6 g.) was crystallized from aqueous methanol. Repeated recrystallization of the prisms (1 g., m. p. 143–182°) from aqueous methanol gave 0.23 g. (5%) of the α adduct, probably **1-(1′-cyclohexenyl)-naphthalene-2′-carboxylic acid (XI, R = H)**; m. p. 180–185°. The highest m. p. obtained was 184–185°. This acid and most of the others were dried at 100° and 0.1 mm. for analysis.

Anal. Calcd. for $C_{17}H_{16}O_2 \cdot CH_3OH$: C, 75.53; H, 6.67. Found: C, 75.97; H, 6.24.

The β adduct was obtained by refluxing a solution of 9.5 g. of butadiene-1-carboxylic acid, 15 cc. of 1-vinylnaphthalene and 0.1 g. of hydroquinone in 100 cc. of propionic acid for two hundred hours under nitrogen. After removal of the solvent at 100° and 15 mm. the residue was stirred with 50 cc. of benzene, 150 cc. of water and 20 g. of sodium bicarbonate. The benzene layer was separated and extracted twice with 50 cc. of saturated sodium bicarbonate solution. Extraction with dilute aqueous potassium hydroxide followed by acidification of the extract gave an acid which was evaporatively distilled up to 210° at 0.1 mm.; crystallization of the distillate (3.58 g.) from ethanol gave massive prisms of the β adduct, probably **1-(3′-cyclohexenyl)-naphthalene-2′-carboxylic acid (X, R = H)**; yield, 1.35 g. with m. p. 135.5–136° and 0.11 g. with m. p. 133–134°.

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 80.62; H, 6.44.

Isomerization of the β-Adduct to the α-Adduct.—A solution of the β-adduct in 10% aqueous potassium hydroxide was kept at 100° for four days. Acidification and ether extraction gave the α adduct (m. p. 178–184°) in quantitative yield.

Dehydrogenation of the Adducts.—A mixture of 111 mg. of the α-adduct from butadiene-1-carboxylic acid and 30 mg. of sulfur was heated at 250–260° under nitrogen for twenty minutes, and then evaporatively distilled up to 220° at 0.1 mm. The acidic fraction, after purification through its salt, was dissolved in benzene–petroleum ether; slow evaporation of the solution gave 20 mg. (18%, m. p. 147–150°) of 1-phenylnaphthalene-2′-carboxylic acid. After two recrystallizations from methanol the acid melted at 154–155°, alone and when mixed with an authentic specimen prepared from diazotized methyl anthranilate and naphthalene.[31]

Formation of 3,4-Benzofluorene.—A solution of 370 mg. of the β-adduct from butadiene-1-carboxylic acid and 60 mg. of sodium hydroxide in 10 cc. of water was stirred at 100° with 1.8 g. of calcium oxide for five minutes and evaporated. The residue was ground with 1.8 g. of calcium oxide and heated under nitrogen with a free flame. The yellow distillate was heated with 30 mg. of 5% palladium–charcoal catalyst at 310–320° under nitrogen for ten minutes and evaporatively distilled up to 145° at 0.1 mm. The nearly colorless distillate (170 mg.) when treated with an equal weight of picric acid in ethanol gave 80 mg. of the picrate of 3,4-benzfluorene as red needles; m. p. 113–116°. Further recrystallization raised the m. p. to 120–123°, not depressed when mixed with an authentic specimen.[32] The hydrocarbon, generated from the picrate, after two recrystallizations from aqueous ethanol formed glistening flakes; m. p. 120–122° alone and when mixed with 3,4-benzfluorene.[32] There was excellent agreement in the ultraviolet absorption spectra of the two samples.

Anal. Calcd. for $C_{17}H_{12}$: C, 94.40; H, 5.60. Found: C, 94.42; H, 5.50.

1-Vinylnaphthalene and Sorbic Acid.—A solution of 10.5 g. of sorbic acid (prepared from crotonaldehyde and malonic acid[30]) and 11.3 cc. of 1-vinylnaphthalene in 50 cc. of propionic acid was refluxed under carbon dioxide for two hundred hours, and then worked up as described for X (R = H). The crystalline distillate (6.41 g.) obtained by evaporative distillation up to 240° at 0.1 mm. of the potassium hydroxide extracted material was triturated with benzene and with 30–60° alkanes, and the fine, colorless needles of the α adduct, probably **5′-methyl-1-(1′-cyclohexenyl)-naphthalene-2′-carboxylic acid (XI, R = CH_3)**, were collected; m. p. 175–178°. The acid was recrystallized from ethyl acetate or aqueous ethanol; m. p. 180–181°. Usually another crystalline modification crystallized in colorless prisms with m. p. 168–168.5°; when this was mixed with the 180–181° form, the mixture sintered at 168°, resolidified and melted at 181°. A similar result was obtained with a third modification which was obtained as long colorless needles with m. p. 160–161°.

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.17; H, 6.8; neut. equiv., 266. Found: C, 80.82, 80.94; H, 6.83, 6.91; neut. equiv., 265.

The colorless crystals (0.73 g., m. p. 145–151°) recovered from the benzene and alkanes digestion appeared to be a mixture of the α- and β-adducts.

The β-adduct was obtained by refluxing a solution of 22.4 g. of sorbic acid and 15 cc. of 1-vinylnaphthalene in 100 cc. of acetic acid under nitrogen for one hundred and twenty hours. The solution was diluted with 200 cc. of benzene and 100 cc. of ether and extracted with three 200-cc. portions of dilute aqueous sodium sulfate, then with 130 cc. of saturated sodium bicarbonate solution (to remove sorbic acid), and finally with 200 cc. of 5% aqueous potassium hydroxide. Acidification of the last extract gave a gum which was rinsed well with water and heated with 200 cc. of ethanol. The cooled solution, after being filtered to remove some copolymer, yielded 5.81 g. of crystals (m. p. above 140°) which crystallized from ethanol–water in colorless prisms; yield 3.83 g.; m. p. 149.5–152° (which was depressed to 134–148° by the α adduct). The β adduct, probably **5′-methyl-1-(3′-cyclohexenyl)-naphthalene-2′-carboxylic acid (X, R = CH_3)**, crystallized from benzene–alkanes in colorless needle-like blades; m. p. 152.5–153.5°.

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.27; H, 6.86.

Additional β-adduct was isolated from the aqueous alcoholic filtrate; it was purified by evaporative distillation up to 210° at 0.1 mm. followed by recrystallization. The total yield of β-adduct was 14%. Both the α- and β-adducts showed typical naphthalenic absorption in the ultraviolet (Fig. 3). They decolorized permanganate rapidly at *p*H 10; neither showed any evidence of decomposition when heated to 250°.

Isomerization of the β-Adduct to the α-Adduct.—After a solution of the β-sorbic acid adduct in 10% aqueous potassium hydroxide had been kept at 100° for six days, acidification and ether extraction gave the α adduct in quantitative yield; m. p. 179–181°. After a single day's treatment a mixture of acids (m. p. 78–92°) was obtained.

Dehydrogenation of the Adducts to 5′-Methyl-1-phenylnaphthalene-2′-carboxylic Acid (XII, R = CH_3).—A mixture of 250 mg. of the adduct (α or β) and 70 mg. of sulfur was kept at 260–270° under nitrogen for forty-five minutes, and then evaporatively distilled up to 190° at 0.1 mm. After a separation from neutral material with alkali, the acidic portion was dissolved in ethanol–water; slow spontaneous evaporation to dryness gave yellowish granules (110 mg. or 44%, m. p. 164–169°), which were separated mechanically from a brittle gum. By recrystallization from benzene–alkanes and then from methanol the dehydrogenated acid was obtained as colorless needles; m. p. 174–174.5°.

Anal. Calcd. for $C_{18}H_{14}O_2$: C, 82.84; H, 5.38. Found: C, 82.80; H, 5.85.

Cyclization to 10-Methyl-7-oxo-7-benz(de)anthracene (XIV, R = CH_3).—A mixture of 60 mg. of 5′-methyl-1-

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[31] Grieve and Hey, *J. Chem. Soc.*, 108 (1938).

[32] Cook, Dansi, Hewett, Iball, Mayneord and Roe, *ibid.*, 1319 (1935).

phenylnaphthalene-2′-carboxylic acid and 60 mg. of phosphorus pentachloride in 4 cc. of benzene was kept at 60° for thirty minutes; 300 mg. of aluminum chloride was added and the mixture kept at 60° for eight hours. The product was extracted from the hydrolyzed mixture with ether, the ether solution was washed with water and dilute alkali, the solvent was removed and a solution of the residue in 10 cc. of benzene was passed through a $^3/_8''$ × 12″ alumina column. Development into a dark brown upper band, an orange-red middle band, and a yellow lower band was accomplished with benzene (100 cc.). Elution of the yellow band with hot ethanol yielded 10 mg. (18%) of yellow needles of 10-methyl-7-oxo-7-benz(de)anthracene; m. p. 155–157°. After one recrystallization the cyclic ketone melted at 157–158°, alone and when mixed with a sample prepared by the Scholl reaction from 1-naphthyl *p*-tolyl ketone,[33] but purified more efficiently by chromatographic adsorption than by recrystallization from ethanol alone.

Elution of the orange-red band with hot ethanol gave 3 mg. (5%) of orange-red blades (m. p. 155–156°), which may be the isomeric 6-methyl-3,4-benzfluorenone.

6-Methyl-3,4-benzfluorene (XIII, R = CH_3).—The reaction with 230 mg. of the adduct (α or β) from sorbic acid was carried out as described for 3,4-benzfluorene. The liquid (90 mg.) obtained by evaporative distillation gave 30 mg. of deep red needles of the **picrate of 6-methyl-3,4-benzfluorene** in alcohol; m. p. 116–116.5°, raised to 119–120.5° by recrystallization.

Anal. Calcd. for $C_{18}H_{14}{\cdot}C_6H_3N_3O_7$: N, 9.17. Found: N, 9.14.

The hydrocarbon, generated from the picrate, crystallized from ethanol in glistening colorless flakes; m. p. 72–72.5°. Its absorption curve (Fig. 1) agrees with that of 3,4-benzfluorene. The ***sym*-trinitrobenzene complex** crystallized from ethanol in fine, yellow needles; m. p. 147.5–148.5°.

Anal. Calcd. for $C_{18}H_{14}{\cdot}C_6H_3N_3O_6$: C, 65.16; H, 3.87; N, 9.50. Found: C, 65.52; H, 3.50; N, 9.48.

Hydrogenation, Oxidation, and Bromination of the α-Adduct.—A solution of 110 mg. of the adduct in 15 cc. of ethanol and 1 cc. of acetic acid (necessary for reaction) with 30 mg. of platinum oxide catalyst absorbed a mole of hydrogen in one hour. Crystallization of the product from ethyl acetate gave 20 mg. of colorless needles; m. p. 201–202.5°, raised to 202–202.5° by recrystallization from ethanol–water. The analysis corresponds to a **tetrahydro derivative** of the adduct.

Anal. Calcd. for $C_{18}H_{22}O_2$: C, 79.96; H, 8.15. Found: C, 79.58; H, 8.02.

The ultraviolet absorption curve corresponded to a benzenoid system without conjugation with a double bond. The acid slowly decolorized permanganate in aqueous acetone.

A solution of 130 mg. of the α adduct and 1.3 g. of potassium permanganate in 50 cc. of water was kept at 100° for six hours. The manganese dioxide was removed by filtration and washed with water, and the filtrate was acidified and evaporated to dryness. Sublimation at 200° in a slow current of air gave 30 mg. of sublimate which after trituration with water yielded 15 mg. (20%) of phthalic anhydride (m. p. 127.5–128.5°), identified by mixed m. p. and through its imide and anilide. Oxidation with potassium dichromate in acetic acid likewise gave phthalic acid.

A crystalline bromo derivative was obtained in one experiment. A solution of 266 mg. of α adduct, 1 cc. of thionyl chloride and a drop of pyridine was allowed to stand for six hours. After removal of the excess thionyl chloride at 15 mm., bromine (0.2 g.) was added. After six hours the mixture was heated with aqueous alkali and the acidic product was sublimed at 0.1 mm., and recrystallized several times from aqueous ethanol; yield of colorless needles, 190 mg. (55%); m. p. 201°, raised to 208–209° by further recrystallization. The compound is considered to be **4-bromo-5′-methyl-1-(1′-cyclohexenyl)-naphthalene-2′-carboxylic acid,** for the absorption curve indicated the presence of the bromine on the naphthalene ring.

Anal. Calcd. for $C_{18}H_{17}O_2Br$: C, 62.62; H, 4.96. Found: C, 62.20; H, 4.90.

1-Vinylnaphthalene and Muconic Acid.—A mixture of 8.5 g. of muconic acid (prepared from α,α′-dibromoadipic acid and alkali[34]), 7.5 cc. of 1-vinylnaphthalene and 0.2 g. of hydroquinone in 300 cc. of propionic acid was refluxed under carbon dioxide for two hundred hours. The chilled solution was filtered from unchanged muconic acid and evaporated at 100° and 25 mm. The residue was warmed with 100 cc. each of benzene and water and an excess of sodium bicarbonate, the layers were separated and the benzene solution extracted again with 50 cc. of saturated sodium bicarbonate solution. The gum obtained on acidification of the aqueous extracts was heated with 150 cc. of methanol containing 1 g. of benzenesulfonic acid hydrate for eighteen hours. After the addition of sodium acetate and the removal of the methanol, acidic material was removed with alkali, and the dimethyl ester of the adduct was evaporatively distilled up to 205° at 0.1 mm.; yield, 9.73 g. Treatment of the acidic fraction with diazomethane, followed by evaporative distillation yielded an additional 0.42 g. of the ester; total yield, 10.15 g.

A solution of the ester in 50 cc. of benzene was added to an alumina column, $^1/_2''$ × 24″; the first 10 cc. of eluate contained practically no product; the next 30 cc. contained 6.38 g. of colorless oil, which was hydrolyzed by heating with 30 cc. of acetic acid and 15 cc. of concentrated hydrochloric acid at 100° for twenty-four hours. After several recrystallizations of the product from acetic acid, 3.13 g. (19%) of the β-adduct, probably **1-(3′-cyclohexenyl)-naphthalene-2′,5′-dicarboxylic acid** (X, R = COOH), containing one-half mole of acetic acid of crystallization was obtained as colorless, granular crystals; m. p. 271–274°, raised to 274–275° by further recrystallization. The acetic acid is not removed at 65° and 0.1 mm.

Anal. Calcd. for $2(C_{18}H_{16}O_4){\cdot}CH_3COOH$: C, 69.92; H, 5.56; neut. equiv., 130. Found: C, 70.06; H, 5.68; neut. equiv., 126.

When the compound is heated to 150° the acetic acid is eliminated.

Anal. Calcd. for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44; neut. equiv., 148. Found: C, 72.75; H, 5.56; neut. equiv., 147, 149.

When the residues from the β-adduct were recrystallized from acetone–ethyl acetate, 0.27 g. of the α adduct, probably **1-(1′-cyclohexenyl)-naphthalene-2′,5′-dicarboxylic acid** (XI, R = COOH) was obtained; m. p. 275–275.5° (depressed to 248–256° by the β adduct). The α adduct crystallized from acetic acid with one mole of acetic acid that was not lost at 65° and 0.1 mm.

Anal. Calcd. for $C_{18}H_{16}O_4{\cdot}CH_3COOH$: C, 67.40; H, 5.65. Found: C, 67.77; H, 5.65.

Both adducts are little soluble in most solvents except hot ethanol and acetic acid. They sublime unchanged at 180–210° and 0.1 mm. and show no evidence of decomposition even at 300°. Decolorization of permanganate is slow in aqueous acetone but is rapid in aqueous solution at *p*H 10. The absorption curves (Fig. 3) are nearly identical with the curve for naphthalene.

In addition to the adducts described above 0.01 g. of 1-phenylnaphthalene-2′,5′-dicarboxylic acid (XII, R = COOH; m. p. 299–301°) was isolated. This result showed that some dehydrogenation took place.

Isomerization of the β-Adduct to the α-Adduct.—The dimethyl ester, prepared from 1 g. of the β adduct and diazomethane in methanol–ether followed by removal of the solvents, was added to a suspension of sodium methoxide (prepared from 0.3 g. of sodium) in 15 cc. of dry benzene, and the mixture was refluxed for five hours. After the addition of acetic acid to the cooled mixture, the benzene solution was washed with bicarbonate solution

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[33] Fieser and Martin, THIS JOURNAL, **58**, 1443 (1936).

[34] Ingold, *J. Chem. Soc.*, 952 (1921).

and evaporated. Hydrolysis of the ester by refluxing with 10 cc. of acetic acid and 5 cc. of concentrated hydrochloric acid for twelve hours gave the acid from which 0.29 g. of the α adduct (m. p. 274–275°) was obtained by recrystallization from acetic acid.

Dehydrogenation of the Adducts to 1-Phenylnaphthalene-2′,5′-dicarboxylic Acid (XII, R = COOH).—The dimethyl ester (from 0.45 g. of the β-adduct) and 50 mg. of 5% palladium–charcoal catalyst was heated under nitrogen at 310–320° for thirty minutes. The product obtained by evaporative distillation up to 190° at 0.1 mm. was heated with 8 cc. of acetic acid and 4 cc. of concentrated hydrochloric acid at 100° for twenty-four hours. Crystallization of the isolated diacid from 3 cc. of acetic acid gave 0.1 g. (22%) of cream-colored granules of XII (R = COOH); m. p. 304–304.5°, raised to 304.5–305° by further recrystallization.

Anal. Calcd. for $C_{18}H_{12}O_4$: C, 73.97; H, 4.13. Found: C, 73.43; H, 4.04.

The diacid failed to decolorize permanganate even at a *p*H of 10.

A mixture of 0.45 g. of sulfur and 2.07 g. of the dimethyl ester of the crude adducts (part of the 10.15 g.) was heated at 250–260° under nitrogen for fifty minutes and evaporatively distilled up to 220° at 0.1 mm. A solution of the distillate in 40 cc. of acetic acid and 20 cc. of concentrated hydrochloric acid was refluxed for fifty hours, concentrated to 20 cc. and cooled, whereupon 1.1 g. (58%, or 36% based on 1-vinylnaphthalene) of 1-phenylnaphthalene-2′,5′-dicarboxylic acid (m. p. 299–301°) precipitated.

When the crude dimethyl ester was heated with palladium, a 16% yield of XII (R = COOH) was obtained; in addition, 9% of a new diacid (colorless needles from ethyl acetate–benzene) was isolated; m. p. 242–244.5°, raised to 247.5–248° by further recrystallization. The diacid does not decolorize permanganate even at *p*H 10; its analysis corresponds to that of **1-cyclohexylnaphthalene-2,5′-dicarboxylic acid.**

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08. Found: C, 72.42; H, 6.34.

Decarboxylation of 1-Phenylnaphthalene-2′,5′-dicarboxylic Acid.—A mixture of 0.2 g. of the acid, 0.2 g. of copper bronze, and 0.6 g. of barium hydroxide octahydrate was thoroughly mixed and dry-distilled. After the removal of water in the distillate by reduced pressure, the nearly colorless liquid (100 mg.) was dissolved in 0.5 cc. of acetic acid and treated with 0.2 cc. of 100% nitric acid in 0.5 cc. of acetic acid. After two hours, seeding induced immediate crystallization of 4-nitro-1-phenylnaphthalene (23 mg., m. p. 121–124°); after one recrystallization from ethanol it melted at 124–125°, alone and when mixed with a sample (m. p. 124–126°) prepared by the method of Weiss and Woidlich,[35] who report a m. p. of 132°.

10-Carbomethoxy-7-oxo-7-benz(de)anthracene (XV, R = $COOCH_3$).—A solution of 100 mg. of 1-phenylnaphthalene-2′,5′-dicarboxylic acid in 3 cc. of acetic anhydride was refluxed for one hour. The acetic anhydride was removed slowly by distillation, the temperature was raised to 300°, and the pressure was lowered to 0.1 mm. After two hours at 320°, sublimation was complete. The yellow-orange crystals (60 mg. or 64%, m. p. 285–298°) were converted to the methyl ester by diazomethane and a solution of the ester in benzene was passed through an alumina column, where it was developed with benzene (400 cc.). Elution of the yellow band with hot methanol gave 7 mg. of bright yellow needles of XV (R = $COOCH_3$); m. p. 168–169° (reported,[36] 167–168°). Cyclization of 100 mg. of the acid with 10 cc. of anhydrous hydrogen fluoride at 25° gave similar results.

Dimerization of 1-Vinylnaphthalene.—A solution of 10 cc. of 1-vinylnaphthalene in 67 cc. of propionic acid was refluxed under nitrogen for two hundred hours. The chilled solution was filtered from precipitated gum, the propionic acid was removed under reduced pressure, and a solution of the residue in 50 cc. of benzene was passed through a 30″ × 1/2″ column of alumina and followed with more benzene. The first 50 cc. was collected and evaporated, and the residue was evaporatively distilled at 160–240° and 0.1 mm. The colorless crystalline distillate (2.16 g. or 21%; m. p. 140–145°) of **1-(1′-naphthyl)-1,2,3,4-tetrahydrophenanthrene** (XVI) was recrystallized from benzene–ethanol; m. p. 147–148°.

Anal. Calcd. for $C_{24}H_{20}$: C, 93.46; H, 6.54; mol. wt., 308. Found: C, 93.34; H, 6.44; mol. wt. (Rast method), 325.

1-(1′-Naphthyl)-phenanthrene.—A mixture of 100 mg. of the tetrahydro compound and 25 mg. of sulfur was heated in a narrow tube at 240–250° for fifteen minutes; the sides of the tube were washed down with a few drops of acetone and the process repeated. The product obtained by evaporative distillation up to 250° at 15 mm. was dissolved in acetone and heated with 0.5 g. of zinc dust. After removal of the zinc, a little ethanol was added and the solution was concentrated by boiling on a steam-bath. On cooling 25 mg. of 1-(1′-naphthyl)-phenanthrene crystallized in glistening, colorless blades; m. p. 113–115°, raised to 115–116.5° by further recrystallization. The second crop (60 mg., m. p. 112–115°) was converted to the picrate, which was recrystallized from ethanol; m. p. 135–136°.

The hydrocarbon and its picrate were identical with those prepared from 2 g. of 1-keto-1,2,3,4-tetrahydrophenanthrene and 1-naphthylmagnesium bromide.[37] The carbinol, which was not obtained crystalline, was dehydrated when heated at 200° and above under reduced pressure and evaporatively distilled. The resulting **1-(1′-naphthyl)-3,4-dihydrophenanthrene** crystallized from alcohol–acetone in colorless plates or hexagonal prisms, yield, 0.6 g.; m. p. 134–134.5°. The hydrocarbon gives a blue color with concentrated sulfuric acid.

Anal. Calcd. for $C_{24}H_{18}$: C, 94.1; H, 5.9. Found: C, 94.4; H, 5.9.

The **1-(1′-naphthyl)-phenanthrene**, obtained in 80% yield by treatment of the dihydro derivative with palladium-charcoal at 320° for one-half hour, crystallized from alcohol–acetone in colorless plates; m. p. 117.5–118°.

Anal. Calcd. for $C_{24}H_{16}$: C, 94.7; H, 5.3. Found: C, 94.5; H, 5.2.

The **picrate** crystallized from absolute ethanol in light orange plates; m. p. 135.5–136°.

Anal. Calcd. for $C_{24}H_{16}\cdot C_6H_3N_3O_7$: N, 7.9. Found: N, 7.9.

Summary

1-Vinylnaphthalene reacted as the diene component in the Diels–Alder reaction with twelve olefinic dienophiles. The adducts were derivatives of 1,2,3,4-tetrahydrophenanthrene except in two examples in which the adduct was dehydrogenated to the phenanthrene derivative during the reaction.

With two olefinic dienophiles containing an α-halogen atom, the halogen acid was eliminated during the reaction with the formation of a dihydrophenanthrene derivative. The single acetylenic dienophile that was tried gave a phenanthrene derivative.

1-Vinylnaphthalene acted as the dienophile component with three diene acids and gave 1-cyclohexenylnaphthalene compounds, representing a new synthesis of partially hydrogenated biaryl acids as well as the first unequivocal examples of the combination of an electrophilic diene and a nucleophilic dienophile.

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(35) Weiss and Woidlich, *Monatsh.*, **46**, 453 (1925).

(36) Copp and Simonson, *J. Chem. Soc.*, 209 (1942).

(37) Bachmann and Wilds, unpublished results (dissertation of Wilds, 1939).

1-Vinylnaphthalene acted both as diene and dienophile in undergoing a Diels–Alder type of dimerization to 1-(1′-naphthyl)-1,2,3,4-tetrahydrophenanthrene.

The results of the reactions have added support to current electronic interpretations of the Diels–Alder reaction.

ANN ARBOR, MICHIGAN RECEIVED MARCH 11, 1949

[CONTRIBUTION FROM THE SUGAR RESEARCH FOUNDATION LABORATORY, DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Preparation and Proof of Structure of 1,2:5,6-Dicyclohexylidene-D-glucofuranose[1]

BY ROBERT C. HOCKETT,[2] ROBERT ELLSWORTH MILLER[3] AND ALLEN SCATTERGOOD

Acetone is the only ketone whose reaction products with D-glucose have been fully characterized and determined structurally.[4] The products of the reaction, the water-soluble and non-reducing "monoacetoneglucose" and "diacetoneglucose" have been unequivocally shown to be 1,2-isopropylidene-D-glucofuranose and 1,2:5,6-diisopropylidene-D-glucofuranose, respectively.[5]

We have now found that the acid-catalyzed condensation of D-glucose with cyclohexanone forms a crystalline non-reducing dicyclohexylidene-glucose (I) which, in contrast to "diacetoneglucose," is water-insoluble. A 14-experiment yield study in which the variables were mole ratio of cyclohexanone to glucose, sulfuric acid concentration, and time, indicated that the best crude yield that could be secured under anhydrous conditions at room temperature was about 40%.

Structure

One hydroxyl group was shown to be present in I by the preparation in crystalline form of a monobenzoate (IIa), a benzenesulfonate (IIb) and a *p*-toluenesulfonate (tosylate, IIc). We were unable to secure the acetylation product or the methylation product of I in the crystalline condition. The preparation of these monoesters of non-reducing I showed that four of the five hydroxyl groups of a hemiacetal form of the D-glucose were blocked, probably by the formation of two heterocyclic rings. When compound IIb was heated under reflux with sodium iodide in acetic anhydride, practically no insoluble sodium benzenesulfonate was formed. This indicated that the benzenesulfonate group of IIb would undergo a displacement reaction only with considerable difficulty. In the absence of a neighboring hydroxyl group, an arylsulfonate group reluctant to undergo a displacement reaction is usually considered to be attached to a secondary carbon atom[6] or to have the back side approach of the replacing group blocked.[7] Thus it seemed probable that the hydroxyl group of I was on a ring which was blocked by other attached groups so that the approach of a replacing group was made difficult.

The location of the hydroxyl group of I was ascertained by an acid-catalyzed methanolysis of tosylate IIc followed by an acetylation of the sirupy product (III). Crystalline methyl 3-tosyl-2,4,6-triacetyl-β-D-glucopyranoside (IV) resulted, and demonstrated that carbon atom number three of I was the site of the hydroxyl group. Compound IV had previously been obtained by Peat and Wiggins[8] through a similar series of reactions starting with 1,2:5,6-diisopropylidene-D-glucofuranose (diacetoneglucose).

The location and size of the acetal rings of I was determined by the discovery that one of the two cyclohexylidene groups of I could be removed selectively. Controlled acid-catalyzed methanolysis of I gave a non-reducing crystalline monocyclohexylidene-D-glucose (V). Product V, obtained in good yield, could readily be recrystallized from water in contrast to 1,2-isopropylidene-D-glucofuranose ("monoacetone-glucose") which is very soluble in water.

The benzoylation of V gave a crystalline tribenzoate (VI) demonstrating the presence of three hydroxyl groups in V. The acid-catalyzed hydrolysis of VI gave 3,5,6-tribenzoyl-D-glucofuranose (VII) previously obtained by Fischer and Rund[9] from 1,2-isopropylidene-D-glucofuranose ("monoacetoneglucose"). Compound VII was isolated as its carbon tetrachloride addition product first observed by Fischer.

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[1] A portion of the material in this paper was presented before the Division of Sugar Chemistry and Technology at the 115th meeting of the American Chemical Society, San Francisco, California, March 27, 1949.

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[3] The material presented in this paper is taken from a thesis submitted to the Department of Chemistry of the Massachusetts Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Philosophy by Robert Ellsworth Miller whose present address is: The American Sugar Refining Company, Research and Development Division, Philadelphia 48, Pennsylvania.

[4] Kranslein, Dickhauser and Voss, U. S. Patent 1,902,866 (March 28, 1933) reported a "dicyclohexanoneglucose of m. p. 134°" which they formulated as a 1,2:5,6-dicyclohexylidene-D-glucofuranose in the patent. No analytical results, specific rotation, yield, or proof of structure were given.

[5] (a) K. Freundenberg and A. Doser, *Ber.*, **56**, 1243 (1923); (b) Anderson, Charlton and Haworth, *J. Chem. Soc.*, 1329 (1929).

[6] (a) Bell, Friedmann and Williamson, *ibid.*, 252 (1937); (b) Oldham and Rutherford, THIS JOURNAL, **54**, 366 (1932).

[7] Bartlett and Knox, *ibid.*, **61**, 3184 (1939).

[8] Peat and Wiggins, *J. Chem. Soc.*, 1092 (1938).

[9] Fischer and Rund, *Ber.*, **49**, 88 (1916).