and amino derivatives, (3) anhydrogossypol and its derivatives, (4) the esters, (5) the ethers and their degradation products, (6) apogossypol and its degradation products, (7) desapogossypol and its degradation products lead to the postulation that gossypol is 2,2-bi-1,6,7-trihydroxy-3-methyl-5-isopropyl-8-aldehydonaphthyl.

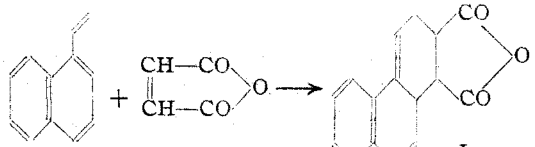
URBANA, ILLINOIS RECEIVED JUNE 27, 1938

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

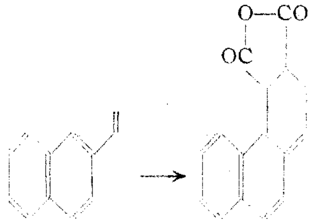
The Diels-Alder Reaction between Naphthylcyclopentenes and Maleic Anhydride

BY W. E. BACHMANN AND M. C. KLOETZEL[1]

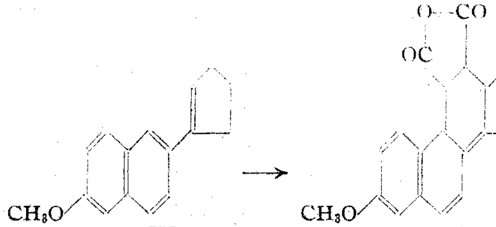
Cohen and Warren[2] have shown recently that 1-vinylnaphthalene and 2-vinylnaphthalene undergo the Diels-Alder reaction with maleic anhydride to give 1,2,3,10a-tetrahydrophenanthrene-1,2-dicarboxylic acid anhydride (I) and 2,3,4,4a-tetrahydrophenanthrene-3,4-dicarboxylic acid anhydride (II), respectively. A similar addition of maleic anhydride to 1-(6′-methoxy-2′-naphthyl)-cyclopentene-1 (III) would be expected to form a compound (IV) having the sterol skeleton, but it has been reported by Bergmann and Bergmann[3] that maleic anhydride reacts neither with 1-(α-naphthyl)-cyclopentene-1 (V) nor with (III). We have now found that (III) and (V) can be made to react practically quantitatively with maleic anhydride. Similarly, 1-(β-naphthyl)-cyclopentene-1 (VI) can be made to react with maleic anhydride to the extent of 92%.



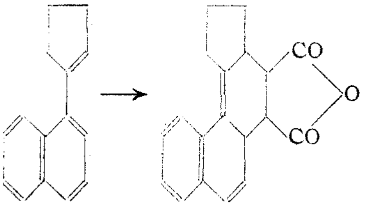
I



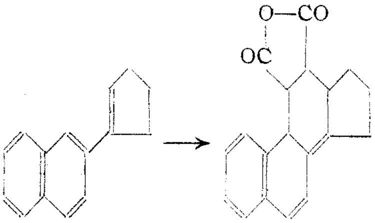
II



III IV



V Va



VI VIa

When a xylene solution of equimolecular proportions of (V) and maleic anhydride was refluxed for two hours and allowed to cool, a mixture of 3,4-cyclopentano-1,2,3,10a-tetrahydrophenanthrene-1,2-dicarboxylic acid and the corresponding acid anhydride (Va) was deposited. Under these conditions, reaction was found to have gone to the extent of 63%. A quantitative yield of the adduct could be obtained by fusing (V) with ten mole equivalents of maleic anhydride for twenty hours on a steam-bath.

When 1-(β-naphthyl)-cyclopentene-1 (VI) was refluxed for two hours in xylene solution with maleic anhydride and the solution was allowed to cool, 1,2-cyclopentano-2,3,4,4a-tetrahydrophenanthrene-3,4-dicarboxylic acid anhydride (VIa) was deposited as a resin, but (VIa) and (IV) were best prepared by fusing (VI) or (III), respectively, with ten mole equivalents of maleic anhydride on a steam-bath for twenty hours, dissolving the adduct in aqueous potassium hydroxide and precipitating by acidification with hydrochloric acid.

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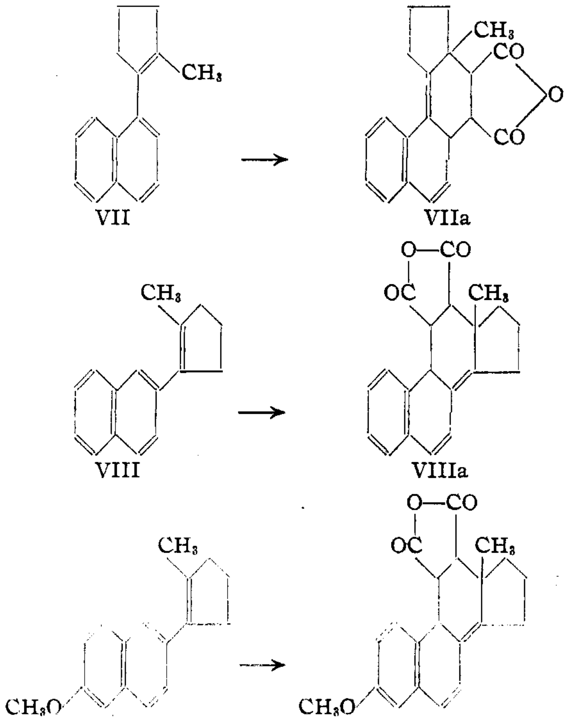
[1] Du Pont Post-Doctorate Fellow.

[2] Cohen and Warren, *J. Chem. Soc.*, 1318 (1937).

[3] Bergmann and Bergmann, THIS JOURNAL, **59**, 1443 (1937).

We have shown recently[4] that methyl groups in the *meso* positions of anthracene derivatives markedly activate the diene systems involved in the reaction with maleic anhydride. We therefore prepared 1-(α-naphthyl)-2-cyclopentene-1 (VII), 1-(β-naphthyl)-2-methylcyclopentene-1 (VIII) and 1-(6′-methoxy-2′-naphthyl)-2-methylcyclopentene-1 (IX) and tested their reactivity with maleic anhydride. These naphthylcyclopentenes reacted to give (VIIa), (VIIIa) and (IXa), respectively, but, contrary to expectation, the presence of the methyl groups actually decreased the rates of reaction.



VII VIIa

VIII VIIIa

IX IXa

The compounds (IV), (Va), (VIa), (VIIa), (VIIIa) and (IXa) are in each instance proposed as the primary addition products with the realization that they may be isomerized to the corresponding naphthalenic isomers. This isomerization was actually demonstrated by Cohen and Warren,[2] who converted (I) into (X) by the action of hot acetic acid saturated with hydrogen chloride.

The extent of reaction of each of these naphthylcyclopentenes with maleic anhydride was determined by refluxing a xylene solution (2 cc. of xylene/g. of cyclopentene) containing equimolecular proportions of the reactants for periods of one and two hours, respectively. In each instance, also, the naphthylcyclopentene was fused with ten mole equivalents of maleic anhydride on a steam-bath for twenty hours. The results, which are based upon the weight of unreacted cyclopentene recovered, are presented in Table I. It is important, however, that in most instances of long refluxing, although the extent of reaction is greater, the adduct is contaminated with decomposition products, so that a shorter period of reflux is generally desirable for preparative purposes.

TABLE I

THE EXTENT OF REACTION OF NAPHTHYLCYCLOPENTENES WITH MALEIC ANHYDRIDE

	Percentage of reaction after		
	Period of reflux		Fusion
Naphthylcyclopentene	1 hour	2 hours	20 hours
1-(α-Naphthyl)-cyclopentene-1 (V)	45	63	98
1-(α-Naphthyl)-2-methylcyclopentene-1 (VII)	9	16	32
1-(β-Naphthyl)-cyclopentene-1 (VI)	55	58	92
1-(β-Naphthyl)-2-methylcyclopentene-1 (VIII)	18	19	77
1-(6′-Methoxy-2′-naphthyl)-cyclopentene-1 (III)	45	56	98
1-(6′-Methoxy-2′-naphthyl)-2-methyl-cyclopentene-1 (IX)	12	14	94

The naphthylcyclopentenes necessary for this investigation were all prepared in a similar manner. First of all, the tertiary cyclopentanols were prepared by means of the Grignard reaction: thus, α-naphthylmagnesium bromide with cyclopentanone and 2-methylcyclopentanone gave 1-(α-naphthyl)-cyclopentanol-1 and 1-(α-naphthyl)-2-methylcyclopentanol-1, respectively; β-naphthylmagnesium iodide with the same two ketones gave 1-(β-naphthyl)-cyclopentanol-1 and 1-(β-naphthyl)-2-methylcyclopentanol-1, respectively; and 6-methoxy-2-naphthylmagnesium bromide gave 1-(6′-methoxy-2′-naphthyl)-cyclopentanol-1 and 1-(6′-methoxy-2′-naphthyl)-2-methylcyclopentanol-1, respectively. These carbinols were then dehydrated to the corresponding naphthylcyclopentenes by warming for a short time with anhydrous formic acid.

It may be observed that the use of (VIII) and (IX) in the reaction with maleic anhydride offers a convenient method of obtaining compounds containing angular methyl groups; thus, (IXa) is an isomer of the methyl ether of deoxoequilenin-11,12-dicarboxylic acid anhydride. It was therefore of interest to attempt the decarboxylation of our adducts with the hope of obtaining derivatives closely related to naturally occurring compounds.

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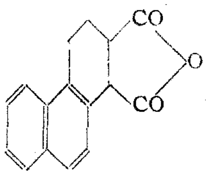
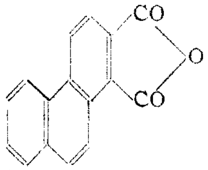
[4] Bachmann and Kloetzel, THIS JOURNAL, **60**, 481 (1938).

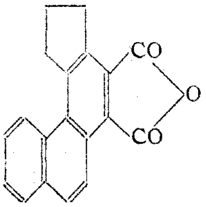
When a mixture of (I) or (Va) with the theoretical amount of sulfur necessary to remove four hydrogen atoms was heated to 250–270° for a period of thirty to forty-five minutes, phenanthrene-1,2-dicarboxylic acid anhydride (XI) or 3,4-cyclopentenophenanthrene - 1,2 - dicarboxylic acid anhydride (XII) were obtained, respectively. Dehydrogenation of (IV), (VIa), (VIIa), (VIIIa) or (IXa) with sulfur did not proceed smoothly under these same conditions.



X



XI

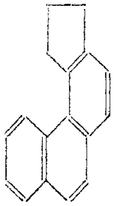


XII

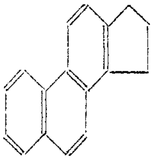
An attempt then was made to decarboxylate (XII) by refluxing in quinoline solution with basic copper carbonate. This method gave erratic results, however, and in no case was the yield of 3,4-cyclopentenophenanthrene (XIII) greater than 19%. Dry distillation of the dipotassium salt of 3,4 - cyclopentenophenanthrene - 1,2 - dicarboxylic acid with potassium hydroxide at 430° likewise gave 3,4-cyclopentenophenanthrene in extremely poor yield. When, however, the calcium salt of (XI) was dry distilled with a mixture of calcium oxide and zinc dust, a 30% yield of phenanthrene was obtained.

When the latter method of decarboxylation was applied to the adducts themselves it was found that dehydrogenation as well as decarboxylation took place, even when no zinc dust was employed in the distillation of the calcium salts. Dry distillation of the calcium salt of 1,2,3,10a-tetrahydrophenanthrene - 1,2 - dicarboxylic acid (from I) with calcium oxide alone gave a 67% yield of phenanthrene. When zinc dust was included in the distillation mixture, the yield of phenanthrene was reduced to 28%, and the product, moreover, was contaminated with impurities which were difficult to remove. The calcium salt of 3,4-cyclopenteno-1,2,3,10a-tetrahydrophenanthrene-1,2-dicarboxylic acid (from Va) was distilled with a mixture of calcium oxide and zinc dust, resulting in a 62% yield of 3,4-cyclopentenophenanthrene (XIII). Addition of 1-(α-naphthyl)-cyclopentene-1 to maleic anhydride, followed by decarboxylation of the resulting adduct, therefore offers a second convenient synthesis of 3,4-cyclopentenophenanthrene.[5]

In like manner, the addition of 1-(β-naphthyl)-cyclopentene-1 to maleic anhydride, followed by decarboxylation of the resulting adduct, offers a convenient synthetic route to 1,2-cyclopentenophenanthrene (XIV), for the dry distillation of the calcium salt of 1,2-cyclopentano-2,3,4,4a-tetrahydrophenanthrene-3,4-dicarboxylic acid (from VIa) with a mixture of calcium oxide and zinc dust resulted in an 80% yield of 1,2-cyclopentenophenanthrene, even when crude adduct was employed.



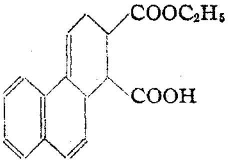
XIII



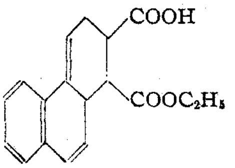
XIV

When this method of decarboxylation was extended to 2-methyl-1,2-cyclopentano-2,3,4,4a-tetrahydrophenanthrene-3,4-dicarboxylic acid anhydride (VIIIa), a good yield of distillate was obtained. Although the product formed a picrate (m. p. 123–124°), its identity was not ascertained. Similarly, the distillation of the calcium salts of those adducts containing methoxyl or angular methyl groups produced no identifiable products.

The reaction of 1-vinylnaphthalene with ethyl hydrogen maleate was investigated in the hope of obtaining an adduct which might be readily decarboxylated without simultaneous aromatization. When a mixture of equimolecular proportions of the hydrocarbon and ester was heated on the steam-bath for fifteen hours, addition took place to the extent of 72%, and the adduct, (XV) or (XVI), was isolated as a colorless solid. Dehydrogenation of this with sulfur gave phenan-



XV



XVI

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[5] Bachmann and Kloetzel, THIS JOURNAL, 59, 2207 (1937).

threne-1,2-dicarboxylic acid anhydride (XI). Attempted decarboxylation by refluxing in quinoline solution with basic copper carbonate gave, however, only an unidentified, crystalline product.

Experimental

The effect of concentration, time and temperature on the yields of adducts was determined by means of a procedure outlined in a previous paper.[4] Xylene solutions containing equivalent quantitites of the reactants (2 cc. of xylene/g. of naphthylcyclopentene) were heated to the boiling points of the solutions for periods of one hour and two hours, respectively. Forty per cent. potassium hydroxide solution was then added to hydrolyze the addition product (anhydride) and the potassium salt of the dicarboxylic acid was dissolved in hot water. Benzene was added to dissolve unreacted naphthylcyclopentene and the two solutions were separated. Evaporation of the benzene in a weighed container gave the amount of unreacted naphthylcyclopentene; acidification of the aqueous solution with dilute hydrochloric acid precipitated the dicarboxylic acid.

Experiments also were carried out in which the naphthylcyclopentene and ten mole equivalents of maleic anhydride were fused together on a steam-bath for twenty hours without the addition of any solvent. These reaction mixtures were worked up as before in order to determine the extent of reaction. The results of these experiments, which are accurate to a few per cent., are presented in Table I.

1-Vinylnaphthalene and Maleic Anhydride.—The adduct of 1-vinylnaphthalene was prepared according to the method of Cohen and Warren[2] with some modifications. The yellow solution obtained by heating 8.5 g. of 1-vinylnaphthalene, 5.7 g. of maleic anhydride and 17 cc. of anhydrous xylene on a steam-bath began to deposit the adduct within ten minutes. Heating was continued for three hours, after which the mixture was allowed to stand at 0° for twelve hours and the precipitate was filtered off; yield 13.0 g. This crude product began to sinter at 130° and finally melted with decomposition at 185–190°. A portion of the product was soluble in hot acetic acid, and on being cooled the solution deposited colorless crystals of **1,2,3,10a-tetrahydrophenanthrene-1,2-dicarboxylic acid.** The portion insoluble in acetic acid was presumably the corresponding dicarboxylic acid anhydride (I).[3]

Decarboxylation and Dehydrogenation of 1,2,3,10a-Tetrahydrophenanthrene-1,2-dicarboxylic Acid to Phenanthrene.—A 2.5-g. sample of the crude adduct from 1-vinylnaphthalene and maleic anhydride was dissolved by warming in 80 cc. of water containing 1.0 g. of sodium hydroxide, 1.5 g. of calcium oxide was added, and the mixture was boiled for five minutes in order to form the calcium salt of 1,2,3,10a-tetrahydrophenanthrene-1,2-dicarboxylic acid. The suspension was evaporated to dryness and the calcium salt was mixed intimately with 8.5 g. of calcium oxide and dry distilled in a hard glass test-tube. The yellow, crystalline product (1.2 g.) which condensed in the cold part of the tube was sublimed in vacuum (130° at 0.6 mm.) and crystallized from ethanol, yield 0.8 g., m. p. 97–98°, giving no depression of melting point when mixed with an authentic sample of phenanthrene. The picrate (m. p. 144–145°) was likewise identical with phenanthrene picrate.

In a similar experiment, when the calcium salt of the dicarboxylic acid was dry-distilled with a mixture of 8.5 g. of calcium oxide and 6.3 g. of zinc dust, the phenanthrene obtained (0.5 g.) was contaminated with other products.

Phenanthrene-1,2-dicarboxylic Acid Anhydride (XI).—A mixture of 1.0 g. of the crude adduct obtained from 1-vinylnaphthalene and maleic anhydride was mixed with 260 mg. of sulfur and heated to 255° for forty minutes. The product was sublimed in vacuum (240° at 1 mm.) and recrystallized from chlorobenzene; yield, 320 mg. of yellow needles; m. p. 310–311° (Fieser and Hershberg[6] give 311–312°).

The **diethyl ester of phenanthrene-1,2-dicarboxylic acid** was prepared by refluxing for six hours a mixture of 200 mg. of phenanthrene-1,2-dicarboxylic acid anhydride, 10 cc. of absolute ethanol and 1 cc. of concentrated sulfuric acid. A clear yellow solution was obtained within one hour. Most of the alcohol was evaporated and the ester was precipitated with water. When the precipitate was warmed with a small quantity of ethanol the ester dissolved, leaving behind some unchanged dicarboxylic acid anhydride which was filtered off. The ester was vacuum sublimed (140° at 0.6 mm.) and crystallized from ethanol in pale yellow needles, m. p. 132°; yield, 63 mg.

Anal. Calcd. for $C_{20}H_{18}O_4$: C, 74.5; H, 5.6. Found: C, 74.0; H, 5.8.

Decarboxylation of Phenanthrene-1,2-dicarboxylic Acid.—A 0.47-g. sample of phenanthrene-1,2-dicarboxylic acid was converted to the calcium salt in the same manner as described for the conversion of 1,2,3,10a-tetrahydrophenanthrene-1,2-dicarboxylic acid, and was then dry distilled with a mixture of 1.7 g. of calcium oxide and 1.3 g. of zinc dust. The crude **phenanthrene** (100 mg.) was purified by picration, and was identical with an authentic sample.

1-Vinylnaphthalene and Ethyl Hydrogen Maleate.—A mixture of 2.6 g. of 1-vinylnaphthalene and 2.5 g. of ethyl hydrogen maleate[7] was heated on a steam-bath for fifteen hours. Water, potassium carbonate and benzene were then added and the layers were separated. Evaporation of the benzene left 0.74 g. of unreacted vinylnaphthalene, indicating 72% reaction. Acidification of the aqueous layer with dilute hydrochloric acid precipitated the adduct (XV or XVI) as a pale yellow solid (4 g.), which was digested with warm ether and filtered. The colorless powder so obtained is very soluble in ethyl acetate, chloroform, acetic acid or hot ethanol; insoluble in ether, hot benzene or hot *n*-butyl ether. Partial purification of the adduct was accomplished by solution in hot acetone (in which it is slightly soluble) and reprecipitation with ether, but the compound was not successfully crystallized.

When a sample of the aforementioned adduct (1.5 g.) was heated at 250–260° for thirty minutes with sulfur (330 mg.) and the product vacuum sublimed, there was obtained 100 mg. of **phenanthrene-1,2-dicarboxylic acid anhydride** (XI).

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(6) Fieser and Hershberg, THIS JOURNAL, **57**, 1508, 1853 (1935).

(7) Shields, *J. Chem. Soc.*, **59**, 740 (1891).

A solution of the aforementioned adduct (2 g.) in quinoline (20 cc.) was refluxed with basic copper carbonate (400 mg.) for thirty minutes, and after being cooled was diluted with ether and filtered. The ethereal solution was washed with dilute hydrochloric acid, dilute sodium carbonate and finally with water. Evaporation of the ether left only a yellow crystalline compound which crystallized from acetic acid in broad, yellow needles; m. p. 246–247°; yield 600 mg. The compound (C, 81.1; H, 4.3) gives a red-orange color with concentrated sulfuric acid, and is soluble in hot, aqueous potassium hydroxide with difficulty.

1-(α-Naphthyl)-cyclopentanol-1 was prepared by adding 42 g. of cyclopentanone dropwise to a solution of α-naphthylmagnesium bromide prepared from 116 g. of α-bromonaphthalene, 12.5 g. of pure magnesium ribbon and 300 cc. of anhydrous ether. The cyclopentanone was added at such a rate that the mixture refluxed gently from heat of reaction. The crystalline addition product which separated after standing at 0° for twelve hours was filtered off and hydrolyzed with ice water and ammonium chloride. When an ethereal solution of the hydrolyzed product was allowed to evaporate spontaneously at room temperature the carbinol was obtained in colorless crystals which were then washed with petroleum ether (60–70°); yield, 50 g. (42%). From 30–40° petroleum ether **1-(α-naphthyl)-cyclopentanol-1** crystallized in colorless, rectangular prisms, m. p. 75.5–76°. Concentrated sulfuric acid gives a purple-red color with this carbinol.

Anal. Calcd. for $C_{15}H_{16}O$: C, 84.9; H, 7.6. Found: C, 84.5; H, 7.1.

1-(α-Naphthyl)-cyclopentene-1 (V) was obtained when the corresponding naphthylcyclopentanol was dehydrated with either potassium acid sulfate or anhydrous formic acid.

A mixture of 5 g. of the carbinol and 7.5 g. of potassium acid sulfate was heated in a Pyrex test-tube at 165° for forty-five minutes. Water and benzene were then added, the benzene layer was separated and evaporated and the residual oil was distilled in vacuum (165–168° at 1 mm.); yield, 3.7 g. (81%) of a colorless oil which solidified when placed in a refrigerator at −2°.

Dehydration with anhydrous formic acid was accomplished by dissolving 20 g. of finely powdered 1-(α-naphthyl)-cyclopentanol-1 in 50 cc. of the acid at room temperature. Within several minutes the solution became cloudy and the hydrocarbon separated as an oil. After warming the mixture on a steam-bath for five minutes to complete the reaction, 200 cc. of water was added and the 1-(α-naphthyl)-cyclopentene-1 was extracted with benzene; yield, 18 g. (98%).

The naphthylcyclopentene prepared by either method yielded a picrate which crystallized from methanol in vermilion needles, m. p. 79–80°.[3]

Anal. Calcd. for $C_{21}H_{17}O_7N_3$: N, 9.93. Found: N, 9.98.

1-(α-Naphthyl)-cyclopentene-1 and Maleic Anhydride.—A solution of 8.5 g. of 1-(α-naphthyl)-cyclopentene-1 and 4.5 g. of sublimed maleic anhydride in 17 cc. of anhydrous xylene was refluxed for two hours, the solvent was evaporated and the residue was dissolved in 13 cc. of hot acetic acid. After standing for twelve hours the solution deposited 2.8 g. of a mixture of **3,4-cyclopentano-1,2,3,10a-tetrahydrophenanthrene-1,2-dicarboxylic acid** and the corresponding acid anhydride (Va). The dicarboxylic acid crystallizes from acetic acid in colorless, diamond-shaped plates, m. p. 211–213° dec. (in nitrogen).

Anal. Calcd. for $C_{19}H_{18}O_4$: C, 73.5; H, 5.8. Found: C, 73.2; H, 5.9.

The dicarboxylic acid is soluble in acetone, dioxane or hot benzene, slightly soluble in cold benzene, and insoluble in ether. It dissolves in dilute potassium hydroxide and the cold alkaline solution reduces potassium permanganate instantaneously. Acidification of the alkaline solution yields the dicarboxylic acid as a yellow gum. Recrystallization from acetic acid or from acetic anhydride partially converted the acid to the corresponding anhydride, as was shown by analysis.

3,4-Cyclopentenophenanthrene-1,2-dicarboxylic Acid Anhydride (XII).—A mixture of 500 mg. of 3,4-cyclopentano-1,2,3,10a-tetrahydrophenanthrene-1,2-dicarboxylic acid and 100 mg. of sulfur was heated to 230–240° for forty-five minutes in an atmosphere of carbon dioxide. The product was sublimed in vacuum (250–280° at 0.4 mm.) and crystallized from chlorobenzene (65 cc./g.) in yellow needles; m. p. 321°; yield, 270 mg. (54%).

Anal. Calcd. for $C_{19}H_{12}O_3$: C, 79.1; H, 4.2. Found: C, 78.9; H, 4.2.

3,4-Cyclopentenophenanthrene (XIII). (a) Decarboxylation and Dehydrogenation of 3,4-Cyclopentano-1,2,3,10a-tetrahydrophenanthrene-1,2-dicarboxylic Acid.—A 1.2-g. sample of 3,4-cyclopentano-1,2,3,10a-tetrahydrophenanthrene-1,2-dicarboxylic acid was converted to the calcium salt as in the case of 1,2,3,10a-tetrahydrophenanthrene-1,2-dicarboxylic acid, and dry distilled with 4 g. of calcium oxide and 3 g. of zinc dust. The yellow distillate obtained (0.56 g.) was dissolved in 4 cc. of absolute ethanol and 0.6 g. of picric acid was added to the hot solution. When the solution was cooled, 1.0 g. of **3,4-cyclopentenophenanthrene picrate** crystallized; m. p. 133–134° alone and when mixed with an authentic sample of the same melting point.

The picrate was decomposed with dilute ammonium hydroxide, and the **3,4-cyclopentenophenanthrene** liberated was crystallized from acetone–methanol, m. p. 69–71° alone and when mixed with an authentic sample.[5]

(b) Decarboxylation of 3,4-Cyclopentenophenanthrene-1,2-dicarboxylic Acid Anhydride.—A mixture of 70 mg. of 3,4-cyclopentenophenanthrene-1,2-dicarboxylic acid anhydride, 14 mg. of basic copper carbonate and 2 cc. of quinoline was refluxed for thirty minutes, a large volume of ether was added and the solution was filtered from a dark sludge. The ethereal solution was shaken with dilute hydrochloric acid, dilute potassium hydroxide and finally with water. Evaporation of the ethereal solution left a residue which, when dissolved in acetone–alcohol, yielded 10 mg. of yellow needles of m. p. 240°. These were discarded and the remaining residue was sublimed in vacuum (up to 150° at 0.4 mm.) and crystallized from acetone–alcohol; yield, 10 mg. of **3,4-cyclopentenophenanthrene** in colorless plates, m. p. 71.5–72° alone and when mixed with an authentic sample. The picrate of the hydrocarbon obtained was likewise identical with an authentic sample of 3,4-cyclopentenophenanthrene picrate.

3,4-Cyclopentenophenanthrene-1,2-dicarboxylic acid also was decarboxylated with poor yield by dry distillation of its dipotassium salt. A mixture of 100 mg. of 3,4-cyclopentenophenanthrene-1,2-dicarboxylic acid anhydride, 100 mg. of potassium hydroxide and 5 cc. of water was heated in a test-tube until complete solution was obtained. The solution was then evaporated to dryness and the residue was heated for thirty minutes at 430°. The white sublimate obtained from the cool part of the tube was dissolved in ethanol and picric acid was added; yield, 5 mg. of **3,4-cyclopentenophenanthrene picrate**, m. p. 134–135°.

1-(α-Naphthyl)-2-methylcyclopentene-1 (VII).—To the cooled solution of α-naphthylmagnesium bromide prepared from 31 g. of α-bromonaphthalene, 3.8 g. of pure, powdered magnesium and 100 cc. of anhydrous ether, was added dropwise a solution of 15 g. of 2-methylcyclopentanone[8] in 15 cc. of anhydrous benzene. The clear green solution obtained was refluxed on a steam-bath for two hours, cooled and then hydrolyzed with cold, aqueous ammonium chloride. To the residual 1-(α-naphthyl)-2-methylcyclopentanol-1 obtained when the organic layer was evaporated was added 85 cc. of anhydrous formic acid, and the resulting blue-green solution was warmed on a steam-bath for ten minutes. The solution was poured into 400 cc. of water, ether was added and the ethereal extract was washed with 10% sodium carbonate. After removal of the ether the residue was fractionated three times in vacuum, and the fraction boiling at 165–168° (1 mm.) finally was collected as **1-(α-naphthyl)-2-methylcyclopentene-1**; yield, 6 g. of pale yellow oil. Concentrated sulfuric acid gives a red color with this hydrocarbon. The compound was not obtained analytically pure.

1-(α-Naphthyl)-2-methylcyclopentene-1 and Maleic Anhydride.—A mixture of 1.0 g. of 1-(α-naphthyl)-2-methylcyclopentene-1 and 4.7 g. of maleic anhydride was heated on a steam-bath for twenty hours. **3-Methyl-3,4-cyclopentano-1,2,3,10a-tetrahydrophenanthrene-1,2-dicarboxylic acid** (0.25 g.) was obtained in the form of a brown gum when the reaction mixture was extracted with aqueous potassium hydroxide and the extract was acidified with dilute hydrochloric acid.

1-(β-Naphthyl)-cyclopentene-1 (VI).—To the solution of Grignard reagent prepared by refluxing 25.4 g. of β-iodonaphthalene, 2.5 g. of pure magnesium powder and 75 cc. of anhydrous ether for three hours, was added dropwise a solution of 8.5 g. of cyclopentanone in 10 cc. of ether. The mixture was allowed to warm up from heat of reaction, and then allowed to stand at room temperature for two hours. To the crude 1-(β-naphthyl)-cyclopentanol-1 obtained by hydrolysis of the Grignard reaction mixture was added 50 cc. of anhydrous formic acid, and the solution was heated on a steam-bath for ten minutes. **1-(β-Naphthyl)-cyclopentene-1** separated in crystalline form when the solution was cooled. The crude hydrocarbon was crystallized twice from ethanol (separating from a yellow, insoluble by-product) and formed thin, colorless plates, m. p. 85–86°; yield, 5.2 g. The compound gives a rose-red color with concentrated sulfuric acid.

Anal. Calcd. for $C_{15}H_{14}$: C, 92.7; H, 7.3. Found: C, 92.6; H, 7.35.

1-(β-Naphthyl)-cyclopentene-1 and Maleic Anhydride.—A mixture of 1.0 g. of 1-(β-naphthyl)-cyclopentene-1 and 5 g. of maleic anhydride was fused on a steam-bath for twenty hours. A red color was produced immediately when the reactants were mixed. The reaction product was hydrolyzed with water and potassium hydroxide, the aqueous solution was extracted with benzene to remove unreacted hydrocarbon, and was then acidified with dilute hydrochloric acid; yield, 1.4 g. (92%) of cream-colored adduct.

Decarboxylation and Dehydrogenation of 1,2-Cyclopentano-2,3,4,4a-tetrahydrophenanthrene-3,4-dicarboxylic Acid.—The calcium salt of 1,2-cyclopentano-2,3,4,4a-tetrahydrophenanthrene-3,4-dicarboxylic acid was prepared as before from a 2.0-g. sample of the crude adduct, and was dry distilled with 8 g. of calcium oxide and 6 g. of zinc dust. **1,2-Cyclopentenophenanthrene** (1.2 g.) crystallized in the cold part of the tube, and was recrystallized from ethanol; yield, 0.6 g. of nearly colorless leaflets, m. p. 135–136° alone and when mixed with an authentic sample of hydrocarbon melting at 134°. **1,2-Cyclopentenophenanthrene picrate** was prepared and crystallized from ethanol in orange-yellow needles, m. p. 130–132°.

1-(β-Naphthyl)-2-methylcyclopentene-1 (VIII) was prepared in the same manner as its α-naphthyl isomer, from β-naphthylmagnesium iodide and 2-methylcyclopentanone. The crude hydrocarbon was fractionated four times in vacuum, and the fraction boiling at 180–182° (1 mm.) finally was collected as **1-(β-naphthyl)-2-methylcyclopentene-1**; yield, 5.5 g. of yellow oil (from 38 g. of β-iodonaphthalene). Concentrated sulfuric acid produces a red color with this hydrocarbon. Like its α-naphthyl isomer, the hydrocarbon was not obtained analytically pure.

1-(β-Naphthyl)-2-methylcyclopentene-1 and Maleic Anhydride.—The adduct was prepared by fusing the naphthylmethylcyclopentene with ten mole equivalents of maleic anhydride on a steam-bath for twenty hours, as described for 1-(β-naphthyl)-cyclopentene-1; yield, 58% of cream-colored powder.

1-(6′-Methoxy-2′-naphthyl)-cyclopentene-1 (III).—1-(6′-Methoxy-2′-naphthyl)-cyclopentanol-1 was prepared from 6-methoxy-2-naphthylmagnesium bromide and cyclopentanone, and then dehydrated with anhydrous formic acid as described in the preparation of 1-(β-naphthyl)-cyclopentene-1. The crude product was fractionated in vacuum, and the fraction boiling at 200–240° (1 mm.) was crystallized from ethanol. Boiling for fifteen minutes with an equivalent weight of maleic anhydride in xylene solution removed the last traces of colored impurities, and the **1-(6′-methoxy-2′-naphthyl)-cyclopentene-1** finally crystallized from ethanol in colorless leaflets, m. p. 141–142°; yield, 10 g. from 22 g. of 6-bromo-2-methoxynaphthalene. Bergmann and Bergmann,[3] who prepared this hydrocarbon by dehydrating the carbinol with potassium acid sulfate, reported a melting point of 148° for this compound.

1-(6′-Methoxy-2′-naphthyl)-cyclopentene-1 and Maleic Anhydride.—When 1.0 g. of 1-(6′-methoxy-2′-naphthyl)-cyclopentene-1 and 4.4 g. of maleic anhydride were melted together on a steam-bath the mixture quickly became brown-red. Heating was continued for twenty hours and

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[8] Cornubert and Borrel, *Bull. soc. chim.*, (*IV*) **47**, 310 (1930).

the reaction mixture was hydrolyzed as previously described. Acidification of the alkaline solution precipitated 0.52 g. of **7-methoxy-1,2-cyclopentano-2,3,4,4a-tetrahydrophenanthrene-3,4-dicarboxylic acid** in the form of a cream-colored solid. The adduct was not crystallized successfully, but was partially purified by solution in cold acetic acid and reprecipitation with xylene. It then formed a colorless powder which sintered and darkened at 280° and finally melted at 310°, dec. The compound is nearly insoluble in hot xylene or hot chlorobenzene, but is readily soluble in cold acetic acid. Molecular weight (by neutralization) was 300; calculated, 340.

1-(6′-Methoxy-2′-naphthyl)-2-methylcyclopentene-1 (IX).—This compound was prepared in the usual manner by dehydrating the carbinol obtained from 6-methoxy-2-naphthylmagnesium bromide and 2-methylcyclopentanone. The crude product was distilled twice in vacuum, and the fraction boiling at 200–205° (0.9 mm.) was crystallized from ethanol. Boiling for one hour with an equivalent weight of maleic anhydride removed the colored impurities and the **1-(6′-methoxy-2′-naphthyl)-2-methylcyclopentene-1** finally crystallized from methanol in clusters of colorless needles; m. p. 74–75°; yield 4.0 g. The compound gives an orange-red color with concentrated sulfuric acid.

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.7; H, 7.6. Found: C, 85.6; H, 7.7.

1-(6′-Methoxy-2′-naphthyl)-2-methylcyclopentene-1 and Maleic Anhydride.—When a mixture of 0.7 g. of the methoxy derivative and 2.94 g. (ten mols) of maleic anhydride was heated on a steam-bath for twenty hours and the alkaline solution of the hydrolyzed product was acidified with dilute hydrochloric acid, 0.9 g. (92%) of **7-methoxy-2-methyl-1,2-cyclopentano-2,3,4,4a-tetrahydrophenanthrene-3,4-dicarboxylic acid** was obtained in the form of a colorless, granular precipitate. The adduct is practically insoluble in hot xylene but is readily soluble in cold acetic acid. It was partially purified by solution in cold acetic acid, and reprecipitation with xylene: the colorless powder so obtained sintered and darkened at 275° and finally melted at 292°, dec.

Summary

Maleic anhydride reacts with 1-(α-naphthyl)-cyclopentene-1, 1-(α-naphthyl)-2-methylcyclopentene-1, 1-(β-naphthyl)-cyclopentene-1, 1-(β-naphthyl)-2-methylcyclopentene-1, 1-(6′-methoxy-2′-naphthyl)-cyclopentene-1 and 1-(6′-methoxy-2′-naphthyl)-2-methylcyclopentene-1. In these reactions one of the double bonds of the diene system is part of the aromatic naphthalene ring.

Dry distillation of the calcium salt of 3,4-cyclopentano-1,2,3,10a-tetrahydrophenanthrene-1,2-dicarboxylic acid or 1,2-cyclopentano-2,3,4,4a-tetrahydrophenanthrene-3,4-dicarboxylic acid with a mixture of calcium oxide and zinc dust produces excellent yields of 3,4-cyclopentenephenanthrene or 1,2-cyclopentenophenanthrene, respectively. This reaction offers a convenient route to the synthesis of these two hydrocarbons.

ANN ARBOR, MICHIGAN RECEIVED JULY 14, 1938

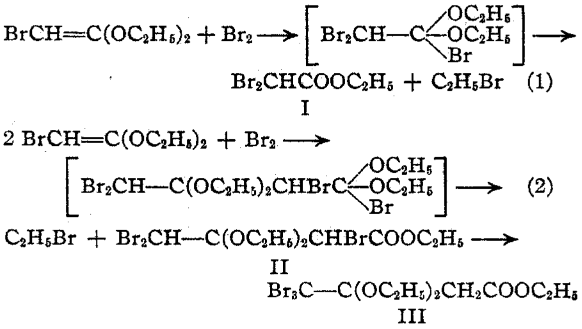
[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Ketene Acetals. III. The Bromination of Bromoketene Diethylacetal. Other Halogenated Ketene Acetals

BY ARTHUR MAGNANI[1] AND S. M. MCELVAIN

A continuation of the study of various halogenated ketene acetals led to an investigation of the bromination of bromoketene diethylacetal.[2] Although the bromination did not prove to be of any value from the standpoint of preparing other ketene acetals, it seems to be of sufficient interest to report at this time.

Bromoketene diethylacetal absorbs bromine rapidly at 0–5° but the absorption stops abruptly after approximately 0.7 of an equivalent of bromine has reacted. No further absorption of bromine occurs even if the temperature of the reactants is allowed to rise to 25°. The products that were isolated from the resulting reaction mixture can be explained on the basis that slightly less than one-half of the bromoketene acetal reacts according to reaction (1) while somewhat more than one-half of the acetal follows the course shown in reaction (2)



$$\mathrm{BrCH{=}C(OC_2H_5)_2 + Br_2 \longrightarrow \left[Br_2CH{-}C\begin{matrix}OC_2H_5\\ OC_2H_5\\ Br\end{matrix} \right] \longrightarrow \underset{I}{Br_2CHCOOC_2H_5} + C_2H_5Br} \quad (1)$$

$$\mathrm{2\,BrCH{=}C(OC_2H_5)_2 + Br_2 \longrightarrow \left[Br_2CH{-}C(OC_2H_5)_2CHBrC\begin{matrix}OC_2H_5\\ OC_2H_5\\ Br\end{matrix} \right] \longrightarrow} \quad (2)$$

$$\mathrm{C_2H_5Br + \underset{II}{Br_2CH{-}C(OC_2H_5)_2CHBrCOOC_2H_5} \longrightarrow \underset{III}{Br_3C{-}C(OC_2H_5)_2CH_2COOC_2H_5}}$$

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[1] Du Pont Post-doctorate Research Assistant, 1937–1938.

[2] Beyerstedt and McElvain, THIS JOURNAL, **59**, 2266 (1937).