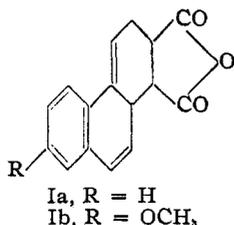


[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

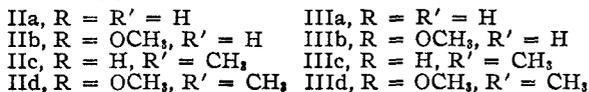
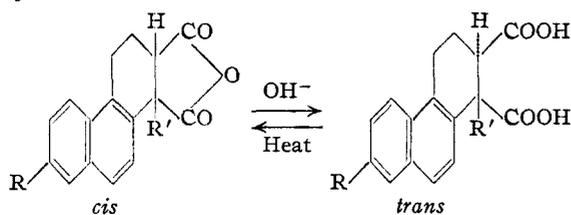
## The Reaction of 1-Vinylnaphthalene and 6-Methoxy-1-vinylnaphthalene with Citraconic Anhydride, Fumaric Acid and Mesaconic Acid<sup>1</sup>

BY W. E. BACHMANN AND L. B. SCOTT<sup>2</sup>

Cohen<sup>3</sup> made the interesting discovery that 1-vinylnaphthalene can function as a diene in the Diels-Alder reaction. From the reaction of this hydrocarbon with maleic anhydride in xylene, *cis*-1,2,3,10a-tetrahydrophenanthrene-1,2-dicarboxylic anhydride (Ia) was obtained.<sup>4</sup> The product was isomerized to the naphthalenic compound 1,2,3,4-tetrahydrophenanthrene-1,2-dicarboxylic anhydride (IIa) by treatment with glacial acetic acid saturated with dry hydrogen chloride.



We have investigated this reaction and similar ones and have examined the by-products. It was found that when 1-vinylnaphthalene and maleic anhydride reacted in toluene at 90–100° a mixture of monomeric and copolymeric addition products was formed.<sup>5</sup> The monomeric portion which was essentially the non-naphthalenic anhydride (Ia) could be isolated from the mixture in 16% yield by recrystallization. When the crude mixture was subjected to evaporative distillation at low pressure, the distillate was the *cis*-naphthalenic anhydride IIa.



Various procedures were tried to separate the maximum amount of monomeric product from the mixture. The best procedure consisted in

(1) Presented by W. E. Bachmann in Basel, Zürich, and Geneva, Switzerland, May 9–16, 1947, under the auspices of the American-Swiss Foundation for Scientific Exchange.

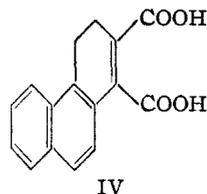
(2) From the Ph.D. dissertation of L. B. Scott, 1944. Present address: Shell Development Company, Emeryville, California.

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

(4) Cohen and Warren, *J. Chem. Soc.*, 1315 (1937).

(5) In the light of our present results, the products reported by Bachmann and Kloetzel, *THIS JOURNAL*, **60**, 2204 (1938), as powders and melting over a wide range may have contained polymeric material.

hydrolysis of the crude mixture, esterification of the resulting diacid with diazomethane, and evaporative distillation. In this manner the dimethyl ester of *cis*-1,2,3,4-tetrahydrophenanthrene-1,2-dicarboxylic acid (acid corresponding to IIa) was obtained in 60% yield. Recently, Cohen's structure for this ester was confirmed by Fujimoto<sup>6</sup> in this Laboratory, who obtained the same ester by esterifying the acid prepared by sodium amalgam reduction of the acid IV derived from the 3,4-dihydrophenanthrene-1,2-dicarboxylic anhydride of Fieser and Hershberg.<sup>7</sup> The formation of the *cis* acid showed that *cis* addition of hydrogen to the double bond had taken place.



When vinylnaphthalene and maleic anhydride were refluxed in acetic or propionic acid, the monomeric addition product was entirely naphthalenic and consisted of a mixture of anhydride and diacid that contained some of the *trans*-isomer. It is considered that the primary product Ia is isomerized under the conditions of the experiment.

Of considerable interest is the result with the *trans*-dienophile, fumaric acid. Although fumaric acid reacts more slowly than maleic anhydride (110 hours required compared with 3 hours for maleic anhydride), it was found to be superior: the yield of monomeric adduct was higher and that of copolymer was lower. The addition product from fumaric acid and vinylnaphthalene in boiling propionic acid was entirely naphthalenic. After esterification with diazomethane and evaporative distillation of the product, an 89% over-all yield of *trans*-diester (ester of IIIa) containing some *cis*-diester was obtained. The presence of the *cis*-isomer may have been the result of a conversion of some of the fumaric acid to maleic anhydride during the long reflux period at elevated temperatures.

Pure *trans*-diacid (IIIa) can be prepared by treating either the *cis*-diacid or diester (or *cis-trans*-mixtures) with methanolic potassium hydroxide, while pure *cis*-diacid can be obtained by gentle alkaline hydrolysis of distilled and recrystallized *cis*-anhydride (IIa). Both the *cis*- and

(6) From the Ph.D. dissertation of George Fujimoto, 1947.

(7) Fieser and Hershberg, *THIS JOURNAL*, **57**, 1851 (1935).

*trans*-diacids can be recrystallized unchanged but each is converted to the *cis*-anhydride by evaporative distillation at 160–200° under reduced pressure. The pure diesters were prepared by treating the corresponding diacids with diazomethane; *cis*-dimethyl ester was also obtained by refluxing pure *cis*-anhydride with methanol and treating the resultant acid-ester with diazomethane. Both esters can be evaporatively distilled unchanged. The above results indicate that the best preparative procedure for this group of compounds involves the addition of fumaric acid to vinylnaphthalene in acetic or propionic acid followed by conversion of the *cis*-*trans*-mixture so obtained to either a pure *cis*- or a pure *trans*-addition product by the methods outlined above.

The results from 6-methoxy-1-vinylnaphthalene and maleic anhydride to give IIb and with fumaric acid to yield IIIb were entirely analogous. Here, too, the *cis*-*trans* and *trans*-*cis* interconversions could be carried out. The only previous work with these compounds was that of Cohen and Warren,<sup>4</sup> who obtained the methoxy derivative Ib from the reaction of 6-methoxy-1-vinylnaphthalene and maleic anhydride in xylene.

It has been reported<sup>8</sup> that citraconic anhydride does not react with 1-vinylnaphthalene. We found that reaction did occur in benzene, toluene, xylene, and dioxane but only alkali-soluble copolymers were formed. However, when the reaction was carried out in boiling acetic or propionic acid, the product was a mixture of copolymeric material and *cis*-naphthalenic monomer (44–49%). The Diels-Alder reaction followed by isomerization could give rise to two *cis*-naphthalenic anhydrides, one with the methyl group in the 1-position (IIc) and the isomer with the methyl group in the 2-position. Only a single isomer was isolated and all the evidence indicates that it is the product with the methyl group in the 1-position, namely, *cis*-1-methyl-1,2,3,4-tetrahydrophenanthrene-1,2-dicarboxylic anhydride (IIc).<sup>9</sup> The *trans*-diacid (IIIc) was prepared directly in yields as high as 57% from mesaconic acid and 1-vinylnaphthalene in propionic acid.

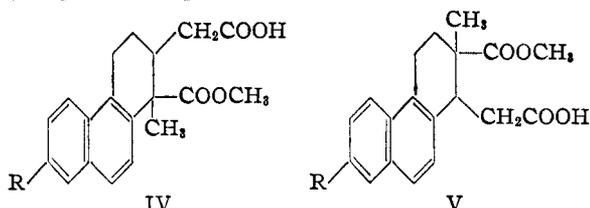
The *cis*- and the *trans*-diacids were both converted to the *cis*-anhydride by evaporative distillation. When the *cis*-diester was refluxed with methanolic potassium hydroxide for twenty-four hours, a *cis*-*trans*-diacid mixture was obtained.

The evidence for the location of the methyl group in the 1-position is three-fold. A methyl group was introduced into the alicyclic ring of the dimethyl ester of *trans*-1,2,3,4-tetrahydrophenanthrene-1,2-dicarboxylic acid (ester of IIIa) by forming a sodio derivative with triphenylmethylsodium and adding methyl iodide. It was expected that the  $\alpha$ -H adjacent to the naphthalene ring would be the one to be replaced by the methyl

group in this reaction. The complex mixture of *cis*- and *trans*-compounds that resulted was converted to a totally *cis*-mixture and was fractionally crystallized. The only product isolated in pure form was the dimethyl ester of *cis*-1-methyl-1,2,3,4-tetrahydrophenanthrene-1,2-dicarboxylic acid (ester of acid of IIc).

The calcium salt of the *cis*-diacid (derived from IIc) was dry-distilled and the distillate was dehydrogenated. The product was a mixture but it gave a single, pure picrate: the picrate of 1-methylphenanthrene.

The *trans*-diester of IIIc was half-hydrolyzed in 99% yield by refluxing its methanolic solution with one equivalent of sodium hydroxide. Since esters of secondary carboxyl groups are saponified much more rapidly than esters of tertiary carboxyl groups, the half-ester probably has the free carboxyl group in the 2-position. When a sample of *cis*-diester was similarly half-hydrolyzed a *cis*-*trans*-acid ester mixture resulted. An Arndt-Eistert synthesis was carried out on the *trans*-acid ester. The product, which is considered to be IV (R = H) depressed the melting point of both the *cis*- and *trans*-forms of V<sup>10</sup> (R = H) one of which was expected if the original adduct had the methyl group in the 2-position.



The addition of 1-vinyl-6-methoxynaphthalene in boiling acetic or propionic acid to citraconic anhydride gave IIId (60% yield isolated as the ester) and to mesaconic acid yielded IIIId (72% yield isolated as the ester). The properties of the products were similar to those of the desmethoxy compounds. The *cis* and *trans* forms of the dimethyl ester of 7-methoxy-1-methyl-1,2,3,4-tetrahydrophenanthrene-1,2-dicarboxylic acid were obtained by C-methylation of the ester of IIIb. The product (probably IV, R = OCH<sub>3</sub>) obtained by an Arndt-Eistert reaction on the half-ester differed from the *cis* and *trans* forms of V (R = OCH<sub>3</sub>). Further confirmation of the structures is being sought by synthesis by other methods.

## Experimental

### Reactions of 1-Vinylnaphthalene

**With Maleic Anhydride.** (a) **In Toluene.**—A solution of 4.45 g. (0.0289 mole) of freshly prepared and distilled 1-vinylnaphthalene<sup>4</sup> (b. p. 93–99° at 9–10 mm.), 3.36 g. (0.0342 mole) of freshly sublimed maleic anhydride and 10 cc. of dry toluene was warmed on a steam-cone for three hours. Light-yellow solid began to precipitate almost immediately. The mixture was cooled and the precipitate was filtered and washed with 10 cc. of toluene; yield, 6.63 g. of a mixture of monomeric and copolymeric

(8) Bergmann and Bergmann, *THIS JOURNAL*, **59**, 1443 (1937).

(9) The preparation of the isomer with the methyl group in the 2-position is described in the paper by Bachmann and Chemersda which follows.

(10) Bachmann and Wilds, *THIS JOURNAL*, **62**, 2084 (1940).

addition products, which sintered at 125°, softened at 170° and melted at 177–191° dec. It was soluble in warm, dilute sodium hydroxide but not in dilute sodium bicarbonate, and it reacted with neutral permanganate and 5% bromine in carbon tetrachloride, in agreement with results previously reported. The solvent was removed from the filtrate in a current of air on a steam cone and the residue was treated with 45% potassium hydroxide, water and benzene (in that order). A minimum of gentle warming was used to effect solution, the clear layers were separated, and an additional 0.34 g. of almost completely copolymeric product and 0.15 g. (3% of the charged diene) of viscous, brown oil were isolated from the aqueous and benzene phases, respectively. The hydrocarbon fraction, which reacted instantly with permanganate, was presumably 1-vinylnaphthalene and its homopolymers.

A portion of the initial 6.63 g. of product was dissolved in dilute sodium hydroxide with a minimum of gentle warming and was added to excess hydrochloric acid. The resultant diacid mixture was treated with diazomethane and was evaporatively distilled at 160–200° and *ca.* 0.05 mm. A light-yellow distillate of the dimethyl ester of *cis*-1,2,3,4-tetrahydrophenanthrene-1,2-dicarboxylic acid (ester of IIa) was obtained in what corresponded to a 60% yield based on 1-vinylnaphthalene; a residue, presumably polymeric, remained undistilled after two hours at 200°. The diester distillate which was inactive toward neutral permanganate and 5% bromine in carbon tetrachloride crystallized from methanol in stout colorless prisms, *m. p.* 105.5–106.5° *cor.* Cohen<sup>3,4</sup> prepared this compound by the action of methanolic hydrogen chloride on the naphthalenic anhydride and by the action of dilute sodium hydroxide and dimethyl sulfate on the non-naphthalenic anhydride (Ia).

A second portion of the initial product was dissolved in glacial acetic acid saturated with dry hydrogen chloride and was refluxed for ninety minutes with the constant addition of a slow stream of hydrogen chloride.<sup>4</sup> It was then converted to the diacid, esterified with diazomethane, and evaporatively distilled as above. Approximately the same over-all yield of monomeric product was obtained as above, but it proved to be a mixture of the *cis*- and *trans*-naphthalenic dimethyl esters; *m. p.* 92–96.5° with previous softening at 90° after one crystallization from methanol. Fractional recrystallization using seeds of pure *cis*- and *trans*-diesters (*m. p.* 106° and 68°, respectively) resulted in the isolation of pure, colorless samples of each of these compounds.

A third portion was treated with acetic acid–hydrogen chloride as above and was evaporatively distilled without further treatment at 180–200° and *ca.* 0.05 mm. Yellow *cis*-1,2,3,4-tetrahydrophenanthrene-1,2-dicarboxylic anhydride (IIa) distilled in what corresponded to a 36% over-all yield based on 1-vinylnaphthalene. The *cis*-anhydride showed no activity toward neutral permanganate or 5% bromine in carbon tetrachloride and crystallized from ethyl acetate in light-yellow prisms melting at 168.5–170° *cor.* After treatment with Norit in acetone and recrystallization from acetone–ethyl acetate, the pale-yellow prisms melted at 170.3–170.8° *cor.* (reported,<sup>3,4</sup> 167–168° for a sample of adduct treated with acetic acid–hydrogen chloride; 169–170°<sup>8</sup> for a solid treated with hot glacial acetic acid and recrystallized from acetic acid–acetic anhydride and from toluene). A portion of the recrystallized *cis*-anhydride was converted to the *cis*-diacid which crystallized from glacial acetic acid in colorless, powdery crystals melting at 228–229° dec. (reported,<sup>4</sup> 220° dec.). Another portion of the anhydride was refluxed in methanol for twenty hours. After about one and one-half hours the pale-yellow crystals had completely dissolved to form a faintly yellow solution, which became colorless during the next few hours. The solution was cooled and treated with diazomethane without the isolation of the intermediate acid-ester. The *cis*-dimethyl ester melted at 108.5–109° *cor.*

When a portion of the initial addition product was evaporatively distilled without prior treatment of any kind, much decomposition occurred and some maleic

anhydride was collected; over-all yield of *cis*-anhydride (IIa), *ca.* 10%.

With the rest of the initial product it was shown that the polymeric material was more soluble than the monomeric in toluene, in ethyl acetate, in glacial acetic acid and in acetone. Accordingly, the above Diels–Alder reaction was duplicated on a 0.13-mole scale and the initially precipitated addition product was recrystallized once from toluene and twice from acetone. The colorless crystals of *cis*-1,2,3,10a-tetrahydrophenanthrene-1,2-dicarboxylic acid anhydride (Ia) weighed 5.3 g. (16%); *m. p.* 187.5–190° dec. with previous softening at 186° (reported,<sup>4</sup> 186–189° for a product obtained in a similar manner).

(b) **In Acetic or Propionic Acid.**—A solution of 4.2 g. (0.027 mole) of 1-vinylnaphthalene and 3.35 g. (0.034 mole) of maleic anhydride in 10 cc. of acetic acid was warmed on a steam cone for three hours. The clear, yellow solution was cooled and the colorless precipitate was filtered and washed, yield 2.91 g. (39%). The solvent was removed from the filtrate and the residue was warmed with 45% potassium hydroxide, water and benzene as before. The aqueous layer gave 3.38 g. (45%) of product; the hydrocarbon fraction weighed 0.61 g. (14%). Experiments similar to those conducted above established the following facts: (a) the product was a mixture of monomeric and copolymeric solids that reacted sluggishly and to only a slight extent with neutral permanganate and 5% bromine in carbon tetrachloride; (b) the monomeric product, a mixture of anhydride and diacid, was essentially *cis* but contained some *trans*; (c) by esterification of the total addition product, followed by evaporative distillation, the naphthalenic diester (ester of IIa) could be obtained in 45% over-all yield.

**With Fumaric Acid.**—A solution of 5.2 g. (0.034 mole) of 1-vinylnaphthalene and 15 g. (0.129 mole) of recrystallized fumaric acid in 250 cc. of propionic acid and 2.5 cc. of propionic anhydride was refluxed for 110 hours. The solvent was removed and the residue was treated with 45% potassium hydroxide, water and benzene as before. The aqueous layer was added with stirring to an excess of hot, dilute hydrochloric acid and the mixture was filtered hot (to keep fumaric acid in solution). The product was esterified with diazomethane and was fractionally and evaporatively distilled at *ca.* 0.05 mm., a small dimethyl fumarate fraction being discarded. The main fraction, which came over at 180–220°, was the dimethyl ester of *trans*-1,2,3,4-tetrahydrophenanthrene-1,2-dicarboxylic acid mixed with 20–30% of the *cis*-diester, yield, 8.95 g. (39% yield based on 1-vinylnaphthalene). The diester mixture crystallized from methanol in large, stout prisms, *m. p.* 88–93.5° *cor.*

***cis*- to *trans*-Inversion.**—A mixture of 2 g. of the *cis*-*trans*-diester product from the fumaric acid experiment and 1.56 g. of *cis*-diacid from distilled *cis*-anhydride when refluxed with 20 cc. of 45% potassium hydroxide and 40 cc. of methanol for twenty-four hours gave 3.2 g. (95%) of *trans*-1,2,3,4-tetrahydrophenanthrene-1,2-dicarboxylic acid (IIIa), *m. p.* 222–223° dec. *cor.* with previous softening at 221°. The acid crystallized from glacial acetic acid in powdery, colorless crystals, *m. p.* 225–227° dec. *cor.*

*Anal.* Calcd. for C<sub>18</sub>H<sub>14</sub>O<sub>4</sub>: C, 71.09; H, 5.22; neut. equiv., 135. Found: C, 70.97; H, 5.39; neut. equiv., 136.

A portion of the above recrystallized *trans*-diacid was esterified with diazomethane and the *trans*-dimethyl ester was recrystallized from methanol. The colorless mixture of glistening prisms and clusters of needles melted at 67.8–68.6° *cor.*

*Anal.* Calcd. for C<sub>18</sub>H<sub>18</sub>O<sub>4</sub>: C, 72.47; H, 6.08. Found: C, 72.32; H, 6.13.

***trans*- to *cis*-Inversion.**—One gram of recrystallized *trans*-diacid (XVII) was evaporatively distilled at *ca.* 0.05 mm. and 160–200° (residue, 0.02 g.). The light-yellow distillate was triturated with dilute sodium bicarbonate and with water and dried, yield, 0.895 g. (96%) of the *cis*-anhydride (IIa). Its identity was established

by mixed melting points of the anhydride and the derived *cis*-dimethyl ester.

**Reduction of 3,4-Dihydrophenanthrene-1,2-dicarboxylic Acid by Sodium Amalgam.**<sup>6</sup>—A solution of the disodium salt of the acid, prepared by warming 0.78 g. of the anhydride<sup>7</sup> with 0.28 g. of sodium hydroxide and 2.8 cc. of water, was swirled with 28 g. of 2% sodium amalgam for twenty-five minutes while the mixture was warmed on a steam-bath. Acidification yielded 0.69 g. of acid which crystallized from acetic acid in colorless prisms, m. p. 219–221°. The dimethyl ester, prepared by means of diazomethane, crystallized from methanol in colorless prisms, m. p. 102–104°, and, after evaporative distillation, 104–105.5° alone and when mixed with the dimethyl ester of *cis*-1,2,3,4-tetrahydrophenanthrene-1,2-dicarboxylic acid.

**With Citraconic Anhydride.**—In twenty-one different experiments in which 1 g. of freshly prepared 1-vinylnaphthalene and various weights of citraconic anhydride<sup>11</sup> were brought into reactive relationship with or without a solvent of low dipole moment, no monomeric product was isolated. These experiments involved reaction temperatures of 25° to 215°, reaction periods of one hour and twenty minutes to fourteen days, solvents such as benzene, toluene and xylene, and the use of sulfur, an atmosphere of nitrogen, hydroquinone and a commercial rubber-polymerization inhibitor. The copolymeric addition products that were obtained reacted sluggishly or not at all with neutral permanganate, gave indefinite neutral equivalents ranging from 165–220 (calculated for the monomer, 142), had molecular weights of more than 400 (calculated for the monomer, 284) as determined in camphor by the Rast method, and did not evaporatively distil at 240° and 0.05 mm.

A subsequent series of ten experiments conducted in acetic, propionic and valeric acids gave addition mixtures of monomeric and copolymeric addition products from which a single *cis*-naphthalenic monomer was isolated by means of evaporative distillation or fractional crystallization in yields up to 49%. In a typical run a clear solution of 8 g. (0.052 mole) of 1-vinylnaphthalene and 17.5 g. (0.156 mole) of citraconic anhydride in 50 cc. of propionic acid was refluxed for seventeen hours. The solvent was removed on a steam cone in a current of air, excess citraconic anhydride was distilled at 0.3–0.4 mm., and the residue was warmed gently with 45% potassium hydroxide, water and benzene (in that order). The benzene layer contained 1.75 g. (22%) of viscous, brown oil which reacted instantly with neutral permanganate. The dark-brown, gummy diacid addition product isolated from the aqueous layer was evaporatively distilled at 0.05 mm. and 160–200°. The light-yellow distillate of *cis*-1-methyl-1,2,3,4-tetrahydrophenanthrene-1,2-dicarboxylic anhydride (IIc) weighed 6.1 g. A sample after decolorization in acetone, crystallized from acetone-ethyl acetate in fine, colorless prisms, m. p. 140.8–141.1° cor.

*Anal.* Calcd. for C<sub>17</sub>H<sub>14</sub>O<sub>3</sub>: C, 76.67; H, 5.30. Found: C, 76.64; H, 5.42.

Distilled anhydride was dissolved in a moderate excess of warm sodium hydroxide and the solution was added to an excess of hydrochloric acid. The precipitated *cis*-diacid was isolated and 1 g. was esterified with diazomethane, yield, 1.08 g. (98%), m. p. 100–101°. The dimethyl ester of *cis*-1-methyl-1,2,3,4-tetrahydrophenanthrene-1,2-dicarboxylic acid crystallized from methanol in fine, colorless needles, m. p. 101–101.5 cor.

*Anal.* Calcd. for C<sub>19</sub>H<sub>20</sub>O<sub>4</sub>: C, 73.06; H, 6.45. Found: C, 72.97; H, 6.26.

**With Mesaconic Acid.**—A solution of 9.6 g. (0.062 mole) of 1-vinylnaphthalene and 20 g. (0.154 mole) of mesaconic acid<sup>12</sup> in 60 cc. of propionic acid was refluxed for one hundred and six hours. The solvent was removed on a steam cone in a current of air and the residue was treated with warm potassium hydroxide, water and

benzene. Undissolved copolymeric material (3.35 g.) was filtered off and the clear layers were worked up as before; neutral oil in benzene layer, 1.85 g. (19%); unpurified diacid addition product, 10.35 (59%). An aliquot of the product was esterified with diazomethane and the ester was evaporatively distilled at 0.01 mm. and 160–190°; yield 57% based on 1-vinylnaphthalene. The dimethyl ester of *trans*-1-methyl-1,2,3,4-tetrahydrophenanthrene-1,2-dicarboxylic acid, after decolorization in acetone, crystallized from acetone-methanol in large, colorless prisms, m. p. 118.8–119.5° cor.

*Anal.* Calcd. for C<sub>19</sub>H<sub>20</sub>O<sub>4</sub>: C, 73.06; H, 6.45. Found: C, 73.18; H, 6.35.

The rest of the addition product was treated with Norit in acetic acid solution and was recrystallized from acetic acid. The *trans*-diacid (IIIc) crystallized in small, colorless prisms; m. p. 251–252° dec. cor.

*Anal.* Calcd. for C<sub>17</sub>H<sub>16</sub>O<sub>4</sub>: C, 71.81; H, 5.67. Found: C, 72.07; H, 5.69.

***cis* to *trans*-Inversion.**—A solution of 0.5 g. of *cis*-dimethyl ester in 25 cc. of 45% potassium hydroxide and 50 cc. of methanol was refluxed for twenty-four hours, and the resulting mixture of *cis*- and *trans*-diacids was esterified with diazomethane. A 30% yield of *trans*-diester melting at 112–114° was isolated from the mixture.

***trans* to *cis*-Inversion.**—Evaporative distillation of 2 g. of unpurified *trans*-diacid at 190–200° and 0.01 mm. gave 1.78 g. (95%) of the *cis*-anhydride (IIc), m. p. 136.5–138.5°. The distillate was insoluble in dilute sodium bicarbonate; its identity was established by mixed melting points of the anhydride and the derived *cis*-dimethyl ester.

**Introduction of a Methyl Group into the Alicyclic Ring.**—A solution of triphenylmethylsodium (prepared from 1.1 g. of triphenylchloromethane in 40 cc. of ether-benzene) was added dropwise to an ether-benzene solution of 0.75 g. of the dimethyl ester of *trans*-1,2,3,4-tetrahydrophenanthrene-1,2-dicarboxylic acid in a nitrogen atmosphere. The blood-red solution reacted immediately with the ester and a yellow-green solid precipitated. The addition was continued until a blood-red color persisted for fifteen minutes. The mixture was then shaken with 15 g. of methyl iodide for twenty-four hours. A slight excess of dilute acid was added, the solvent was removed and the residual oil was refluxed with methanolic potassium hydroxide for six hours. Preliminary crystallizations indicated that the resulting diacids were a complex mixture of *cis*- and *trans*-compounds. In order to reduce this complexity, the *cis*- and *trans*-diacids were converted to the *cis*-anhydride by evaporative distillation at 0.01 mm. and 160–200°. The light-yellow distillate was refluxed in methanol and the solution was treated with diazomethane. Fractional crystallization yielded 0.47 g. (60% yield based on starting diester) of the dimethyl ester of *cis*-1-methyl-1,2,3,4-tetrahydrophenanthrene-1,2-dicarboxylic acid; m. p. 96–99°. Recrystallization of this fraction from methanol gave colorless prisms; m. p. 99.5–100.5° alone and when mixed with an authentic sample. The m. p. was depressed by the original diester.

**Degradation to 1-Methylphenanthrene.**—The calcium salt of IIc prepared from 1 g. of recrystallized *cis*-anhydride was intimately mixed with 1.5 g. of calcium oxide and a little water, and the mixture was distilled. The gummy distillate was triturated with warm, dilute sodium hydroxide and was evaporatively distilled at 110–135° and ca. 0.05 mm. The light-yellow oil (0.35 g.) proved to be a mixture, at least a part of which contained active double bonds. Accordingly, 90 mg. of the oil was treated with 10 mg. of 30% palladium-charcoal catalyst<sup>13</sup> at 310° for thirty minutes in an atmosphere of nitrogen, and the aromatized product was redistilled. From the colorless distillate (m. p. 98–105°) and picric acid in absolute ethanol was obtained the picrate of 1-methylphenanthrene in fine, yellow needles; m. p. 135.7–136.2°; mixed melting point with the picrate of authentic 1-methylphe-

(11) Shriner, Ford and Roll, *Org. Syntheses*, **11**, 28, 70 (1931).

(12) Shriner, Ford and Roll, *ibid.*, **11**, 74 (1931).

(13) Zelinsky and Turowa-Pollak, *Ber.*, **58**, 1295 (1925).

nanthrene (136–136.5°), 136–136.5°. The hydrocarbon, regenerated from the picrate by treatment with ammonium hydroxide, crystallized from ethanol in thin, colorless plates, m. p. 116–118°; mixed melting point with 1-methylphenanthrene (120–121°), 118.5–120.5° with previous softening at 117°. A portion of the regenerated hydrocarbon was converted to the trinitrobenzene complex, which crystallized from ethanol in fine, yellow needles melting at 157.5–158.5° alone and when mixed with an authentic sample (m. p. 157.5–158.5°). 2-Methylphenanthrene melts at 55–56°; its picrate at 118–119°.

**Hydrolysis to the Acid Ester.**—A solution of 1.5 g. of recrystallized *trans*-dimethyl ester, 9.7 cc. of 0.5 *N* sodium hydroxide (1.01 equivalents) and 35 cc. of methanol was refluxed for twenty-four hours. From the solution was isolated 1.425 g. (99.5%) of the acid ester, presumably *trans*-1-methyl-1-carbomethoxy-1,2,3,4-tetrahydrophenanthrene-2-carboxylic acid, melting at 186–189.5°. The acid ester crystallized from methanol in colorless prisms, m. p. 193–195° cor.; after another recrystallization from acetone, 194.2–195° cor.

*Anal.* Calcd. for C<sub>18</sub>H<sub>18</sub>O<sub>4</sub>: C, 72.47; H, 6.08; neut. equiv., 298. Found: C, 72.47; H, 6.11; neut. equiv., 301.

When the above hydrolysis was carried out on the *cis*-dimethyl ester, the product was a mixture of *cis*- and *trans*-acid esters, m. p. 169.5–181° with previous softening at 162°. Esterification of this acid ester mixture with diazomethane and fractional crystallization of the product gave crystals of pure *cis*-diester and of pure *trans*-diester.

**Arndt-Eistert Reaction on the Acid Ester.**—A mixture of 4.54 g. of unpurified *trans*-acid ester, 5 cc. of dry ether, 5 cc. of dry benzene and 4 cc. of oxalyl chloride (a large excess) was allowed to react for six hours. A solution was obtained in three hours and gassing ceased after about five and one-half hours. Volatile compounds were removed completely *in vacuo*, the acid chloride was dissolved in dry ether-benzene, and the solution was added dropwise with swirling to a 3-mole excess of ice-cold, ethereal diazomethane. After two hours at room temperature, the solvents were removed and the crystalline yellow diazoketone was refluxed with silver oxide in absolute methanol for six hours. A total of seven 0.05-g. portions of silver oxide was added during this period; no evolution of nitrogen was noted after the first three hours. The diester isolated from the filtered mixture was evaporatively distilled at 175–195° and *ca.* 0.05 mm. Since the viscous, yellow oil (4.28 g.) did not crystallize readily, it was dissolved in methanol and refluxed for two and one-half hours with 1.01 equivalents of *N* methanolic sodium hydroxide.<sup>10</sup> The acid ester (4.05 g.), presumably 1-methyl-1-carbomethoxy-1,2,3,4-tetrahydrophenanthrene-2-acetic acid (IV, R = H), after decolorization in acetone, crystallized from acetone-methanol in colorless prisms; yield, 2.48 g. (52%), m. p. 148–149.5° cor. After a second recrystallization, a sample melted at 150.9–151.7° cor.

*Anal.* Calcd. for C<sub>19</sub>H<sub>20</sub>O<sub>4</sub>: C, 73.06; H, 6.45. Found: C, 73.27; H, 6.43.

This compound depressed the melting points of samples of  $\alpha$ - (m. p. 133–134°) and  $\beta$ - (m. p. 158–160°) 2-methyl-2-carbomethoxy-1,2,3,4-tetrahydrophenanthrene-1-acetic acid.<sup>10</sup>

#### Reactions of 1-Vinyl-6-methoxynaphthalene

**With Maleic Anhydride.**—Two grams (0.011 mole) of freshly prepared and recrystallized 1-vinyl-6-methoxynaphthalene (obtained in 68–79% yield<sup>4</sup>) and 2.2 g. (0.022 mole) of sublimed maleic anhydride were refluxed in 8 cc. of glacial acetic acid for two and one-half hours. The yellow color that appeared at the instant of mixing gradually deepened to a red-orange. The solvent was removed from the clear solution and the reaction mixture was treated with 45% potassium hydroxide, water and benzene. The mixture was filtered and the clear layers were separated and worked up as in the case of desmethoxy experiments. From the benzene layer was isolated 0.98 g. (49%) of a brown oil (presumably the starting

vinyl compound and/or its homopolymers) that reacted instantly with neutral permanganate and from the aqueous phase there was obtained 1.27 g. of red-orange diacid that showed little double bond activity, m. p. indefinite. A portion of the diacid evaporatively distilled at 185–225° and *ca.* 0.03 mm. gave yellow *cis*-anhydride (26% over-all yield). After treatment with Norit in acetone solution, the *cis*-7-methoxy-1,2,3,4-tetrahydrophenanthrene-1,2-dicarboxylic anhydride (IIb) crystallized from ethyl acetate in glistening yellow prisms, m. p. 160.5–161° cor. A recrystallization from acetone did not change the color or the melting point.

*Anal.* Calcd. for C<sub>17</sub>H<sub>14</sub>O<sub>4</sub>: C, 72.33; H, 5.00. Found: C, 72.37; H, 4.95.

Cohen and Warren reported 171–175° for the non-naphthalenic adduct (Ib). The rest of the diacid was esterified with diazomethane and the *cis*-dimethyl ester (30% over-all yield) was evaporatively distilled, m. p. 117.5–118° after recrystallization from methanol. There was some indication that a small impurity of *trans*-diester was present.

When distilled *cis*-anhydride was refluxed with methanol for five hours, the yellow crystals dissolved to give a solution which gradually became colorless. Upon cooling, thin, colorless flakes of *cis*-acid ester precipitated, m. p. 208.5–210.5° cor. The mixture was treated with diazomethane; the dimethyl ester of *cis*-7-methoxy-1,2,3,4-tetrahydrophenanthrene-1,2-dicarboxylic acid crystallized from methanol in large, colorless prisms, m. p. 119.5–120° cor.

*Anal.* Calcd. for C<sub>19</sub>H<sub>20</sub>O<sub>6</sub>: C, 69.50; H, 6.14. Found: C, 69.50; H, 6.24.

Several other similar runs were made with quantities of reactants identical to the above but varying one or more of the reaction conditions. In an experiment in which only half as much acetic acid (4 cc.) and a reaction temperature of only 90–95° was used, solid began to precipitate after six minutes of the two and one-half hour reaction period. The addition product (2.38 g.) was mainly copolymeric and only a 9% over-all yield of *cis*-diester distilled. When 4 cc. of toluene was used as a solvent only 7% yield of *cis*-diester was obtained. When additional maleic anhydride was used as the solvent in a two and one-half hour run at 90–95°, the addition product was one-half monomeric (15% yield).

**With Fumaric Acid.**—A solution of 2 g. (0.011 mole) of 1-vinyl-6-methoxynaphthalene and 1.5 g. (0.013 mole) of recrystallized fumaric acid in 10 cc. of glacial acetic acid was refluxed for eighteen hours, and the reaction mixture was worked up as above; 0.42 g. (21%) of brown oil with active double bonds was isolated from the benzene layer. The aqueous suspension of the nearly colorless diacid addition product was filtered while hot; yield 2.44 g. A portion of the diacid was esterified with diazomethane and was fractionally and evaporatively distilled at *ca.* 0.05 mm. After traces of dimethyl fumarate had distilled at 100–140°, the *trans*-dimethyl ester came over at 170–225° in what corresponded to a 71% over-all yield, m. p. 117–118° after recrystallization from methanol. Fractional crystallization of the diester indicated that it contained about 5–12% of the *cis*-isomer.

In a second experiment identical with the preceding one except that a fifty-six hour reflux period was used, a 72% over-all yield of distilled diester (80–90% *trans*- and 10–20% *cis*-) was obtained. Addition had taken place to the extent of 90%, but more copolymeric material was produced.

Part of the diacid addition product from the first experiment was dissolved in methanol and was refluxed for ten hours with 45% potassium hydroxide to isomerize the *cis*-impurity. The resultant *trans*-7-methoxy-1,2,3,4-tetrahydrophenanthrene-1,2-dicarboxylic acid, after decolorization with Norit and recrystallization from glacial acetic acid, crystallized from acetone in colorless prisms; m. p. 220.5–221.5° dec. cor.

*Anal.* Calcd. for C<sub>17</sub>H<sub>16</sub>O<sub>6</sub>: C, 67.99; H, 5.37; neut.

equiv., 150. Found: C, 68.16; H, 5.45; neut. equiv., 152.5.

The *trans*-dimethyl ester prepared by means of diazomethane crystallized from methanol in fine, colorless crystals; m. p. 118.5–119° cor.; after another recrystallization from methanol–acetone, 119.4–119.8° cor.

*Anal.* Calcd. for  $C_{19}H_{20}O_5$ : C, 69.50; H, 6.14. Found: C, 69.50; H, 6.15.

The mixed melting point of the *cis*- (m. p. 119.5–120° cor.) and *trans*- (m. p. 118.8–119.3° cor.) dimethyl esters was 100–115° with previous softening at 98°.

*cis*- to *trans*-Inversion.—A solution of 1 g. of the *cis*-diester in 10 cc. of 45% potassium hydroxide and 20 cc. of methanol was refluxed for twenty-three hours. The diacid was treated with diazomethane and the resultant *trans*-diester was crystallized from methanol; yield, 95%; m. p. 118.8–119.5° cor. alone or when mixed with an authentic sample.

*trans*- to *cis*-Inversion.—Evaporative distillation of the unpurified *trans*-diacid at 100–225° and ca. 0.03 mm. yielded the *cis*-anhydride as shown by mixed melting points of the recrystallized anhydride and of the derived *cis*-dimethyl ester.

**With Citraconic Anhydride.**—A solution of 4.75 g. (0.026 mole) of 1-vinyl-6-methoxynaphthalene and 6.2 g. (0.055 mole) of citraconic anhydride in 50 cc. of propionic acid was refluxed for twenty-one hours. The diacid (5.84 g.), which showed no olefinic activity, was divided into two portions. One part on evaporative distillation at 200–225° and ca. 0.02 mm. gave *cis*-1-methyl-7-methoxy-1,2,3,4-tetrahydrophenanthrene-1,2-dicarboxylic anhydride (II<sub>d</sub>) (56% yield), which crystallized from ethyl acetate in fine, colorless prisms; m. p. 127.5–128.5°, and after two more recrystallizations, 129–129.7° cor.

*Anal.* Calcd. for  $C_{18}H_{16}O_4$ : C, 72.96; H, 5.44. Found: C, 72.74; H, 5.28.

The rest of the diacid was treated with excess diazomethane, and the *cis*-dimethyl ester was evaporatively distilled (60% yield) and crystallized from methanol in fine, colorless needles; m. p. 165–166°, and after another recrystallization from acetone, 168.3–168.8° cor.

*Anal.* Calcd. for  $C_{20}H_{22}O_5$ : C, 70.16; H, 6.48. Found: C, 70.32; H, 6.55.

**With Mesaconic Acid.**—A solution of 4.75 g. (0.026 mole) of 1-vinyl-6-methoxynaphthalene and 7.07 g. (0.055 mole) of mesaconic acid in 40 cc. of propionic acid was refluxed for four days. Considerable copolymeric material insoluble in both warm benzene and warm base was filtered off during the isolation procedure. Grayish-white *trans*-diacid (5.43 g.) was esterified with diazomethane and the ester was evaporatively distilled under reduced pressure, 64% yield. The dimethyl ester of the *trans*-acid after two recrystallizations from methanol and two from acetone–methanol formed colorless platelets; m. p. 134.4–135° cor.

*Anal.* Calcd. for  $C_{20}H_{22}O_5$ : C, 70.16; H, 6.48. Found: C, 70.47; H, 6.54.

The *trans*-1-Methyl-7-methoxy-1,2,3,4-tetrahydrophenanthrene-1,2-dicarboxylic acid (III<sub>d</sub>), obtained by methanolic alkaline hydrolysis of the distilled ester, after decolorization with Norit in glacial acetic acid, crystallized in fine, colorless crystals; m. p. 227–232° dec. with previous softening; after further recrystallization from acetic acid and then from acetone, 243–244° dec. cor.

*Anal.* Calcd. for  $C_{18}H_{18}O_5$ : C, 68.78; H, 5.77; neut. equiv., 157. Found: C, 68.96; H, 5.81; neut. equiv., 158.

*cis*- to *trans*-Inversion.—When 0.5 g. of the *cis*-diester 30 cc. of 45% potassium hydroxide and 60 cc. of methanol were refluxed for thirty-six hours, the diacid (0.44 g., m. p. 195–199.5° dec.) was mainly *trans* as judged by fractional crystallization of the *cis*-*trans*-diester mixture obtained by esterification. About a 40% yield of *trans*-dimethyl ester melting at 130–132.5° was isolated.

*trans*- to *cis*-Inversion.—Evaporative distillation of a

sample of crude *trans*-diacid at 180–225° and ca. 0.01 mm. gave the *cis*-anhydride in about 90% yield.

**Introduction of a Methyl Group into the Alicyclic Ring.**—The reaction between 1 g. of the dimethyl ester of *trans*-7-methoxy-1,2,3,4-tetrahydrophenanthrene-1,2-dicarboxylic acid and a solution of triphenylmethylsodium was carried out as described for the desmethoxy analog; much dark-green solid precipitated. The mixture was then shaken with 20 g. of methyl iodide for fourteen hours and was worked up as before. The diacid mixture (from which 0.2 g. of the *cis*- and a few mg. of the *trans*-diester can be isolated if it is esterified) was evaporatively distilled at ca. 0.01 mm. and the resultant *cis* anhydride was refluxed with methanol for ten hours. The *cis*-acid ester was treated with diazomethane and the product was recrystallized from methanol; yield, 0.79 g. (76% over-all yield) of the dimethyl ester of *cis*-1-methyl-7-methoxy-1,2,3,4-tetrahydrophenanthrene-1,2-dicarboxylic acid; m. p. 163.5–165°, and after another recrystallization 164.5–165.5° alone or when mixed with an authentic sample.

**Hydrolysis of the *trans*-Dimethyl Ester to the Acid Ester.**—Two grams of *trans*-dimethyl ester, 5.46 cc. of 1.07 *N* sodium hydroxide and 75 cc. of methanol were refluxed for twenty-four hours. An aqueous suspension of the sparingly soluble sodium salt of the acid ester was added slowly with stirring to an excess of hydrochloric acid, stirring was continued for three hours, and the mixture was left overnight before filtering; yield 1.81 g. (95%), m. p. 186.5–188.5° with previous softening. The acid ester, presumably *trans*-1-methyl-1-carbomethoxy-7-methoxy-1,2,3,4-tetrahydrophenanthrene-2-carboxylic acid, was decolorized with Norit and recrystallized from acetone; m. p. 194.5–195.5° cor.

*Anal.* Calcd. for  $C_{18}H_{20}O_5$ : C, 69.50; H, 6.14; neut. equiv., 328. Found: C, 69.52; H, 5.98; neut. equiv., 328.

**Arndt-Eistert Reaction on the Acid Ester.**—By the method described for the desmethoxy analog, the acid ester (2.5 g.) gave yellowish crystals of the diazoketone; m. p. 151–153° dec. This was refluxed for five hours with absolute methanol and several portions of silver oxide, and the resulting dimethyl ester was evaporatively distilled at 170–190° and ca. 0.03 mm.; yield of light-yellow, glassy solid, 2.39 g. This was refluxed in methanolic solution with one equivalent (+1.5% excess) of *N* sodium hydroxide for two and one-half hours; yield, 2.11 g. The acid ester, presumably *trans*-1-methyl-1-carbomethoxy-7-methoxy-1,2,3,4-tetrahydrophenanthrene-2-acetic acid (IV, R = OCH<sub>3</sub>), after decolorization in acetone, crystallized from methanol in colorless prisms; yield, 1.16 g. with m. p. 171–172° and 0.52 g. with m. p. 169–170.5°; total, 64% over-all yield. After a recrystallization from ethyl acetate, the acid ester crystallized from acetone–methanol in stout, colorless plates; m. p. 173.4–173.8° cor.

*Anal.* Calcd. for  $C_{20}H_{22}O_5$ : C, 70.16; H, 6.48. Found: C, 70.47; H, 6.51.

This compound markedly depressed the melting points of samples of  $\alpha$ - (m. p. 137–138°) and  $\beta$ - (m. p. 211–212°) 2-methyl-2-carbomethoxy-7-methoxy-1,2,3,4-tetrahydrophenanthrene-1-acetic acid.<sup>14</sup>

The dimethyl ester prepared by means of diazomethane, after one crystallization from ligroin–benzene and two recrystallizations from acetone–methanol, formed colorless prisms; m. p. 85.2–86.3° cor.

*Anal.* Calcd. for  $C_{21}H_{24}O_5$ : C, 70.77; H, 6.79. Found: C, 70.73; H, 6.59.

This compound depressed the melting points of samples of  $\alpha$ - (m. p. 126–126.5°) and  $\beta$ - (m. p. 114–114.5°) dimethyl ester of 2-methyl-2-carbomethoxy-7-methoxy-1,2,3,4-tetrahydrophenanthrene-1-acetic acid.<sup>14</sup>

## Summary

The addition of fumaric acid to 1-vinylnaphtha-

(14) Bachmann, Cole and Wilds, THIS JOURNAL, 62, 824 (1940).

lene gave a higher yield of monomeric adduct than did maleic anhydride.

Citraconic anhydride and mesaconic acid add to 1-vinylnaphthalene and to 1-vinyl-6-methoxynaphthalene to give the *cis* and *trans* forms of

adducts in which the methyl group is in the 1-position of the hydrophenanthrene nucleus.

*cis-trans* Interconversions of the products are described.

ANN ARBOR, MICHIGAN

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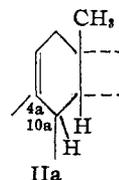
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

## The Diels-Alder Reaction of 1-Vinyl-6-methoxy-3,4-dihydronaphthalene with Citraconic Anhydride<sup>1</sup>

BY W. E. BACHMANN AND J. M. CHEMERDA<sup>2</sup>

1-Vinyl-6-methoxy-3,4-dihydronaphthalene has been allowed to react with a number of dienophiles in order to obtain estrogens or suitable intermediates for the synthesis of estrone.<sup>3,4,5</sup> In 1941 we began an investigation<sup>6</sup> of the reaction of this diene with citraconic anhydride.<sup>7</sup> Theoretically, two sets of products were possible: I, with the methyl group in the 1-position, and II, with the methyl group in the 2-position. In virtue of the three asymmetric carbon atoms, each of the structures can exist in eight stereoisomeric forms (four racemic mixtures). However, the principle of *cis* addition reduces the number to two racemic mixtures for each structure; and, if the rule of the "maximum accumulation of double bonds" prior to addition is applicable, only one racemic mixture for each structural isomer should be obtained. The configuration of the 2-methyl derivative should be IIa; similarly, the single racemic mixture of I would have the H's on C<sub>2</sub> and C<sub>10a</sub> and the methyl group on C<sub>1</sub> *cis* to each other.

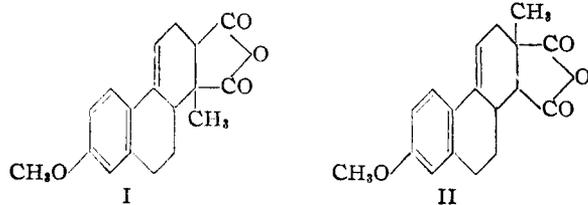
Citraconic anhydride reacted with 1-vinyl-6-methoxy-3,4-dihydronaphthalene in boiling benzene to give a mixture of adducts in 70% yield, from which two pure, crystalline anhydrides were isolated. The anhydrides, m. p. 128° (one part)



IIa

and m. p. 163° (two parts), comprised at least 60% of the mixture.<sup>8</sup> These results illustrate the pronounced steric selectivity of the Diels-Alder addition. For convenience in isolation, the crude product was hydrolyzed, and the acid portion was separated from neutral material and reconverted to anhydrides by fusion at 190–200°. It was not determined whether the original compounds were regenerated or whether this treatment shifted the double bond (for example, to the 4a-10a position).<sup>9</sup>

The 128° anhydride is *cis*-1-methyl-7-methoxyhexahydrophenanthrene-1,2-dicarboxylic anhydride (I), since treatment of it or the corresponding acid with palladium on charcoal<sup>10</sup> at 315° for a short time yielded 1-methyl-7-methoxyphenanthrene and (after hydrolysis) the *cis*-1-methyl-7-methoxy-1,2,3,4-tetrahydrophenanthrene-1,2-dicarboxylic acid (V) of Bachmann and Scott.<sup>7</sup> The 163° anhydride is *cis*-2-methyl-7-methoxyhexahydrophenanthrene-1,2-dicarboxylic anhydride (II); it and the acid (IV) derived from it were transformed smoothly into 2-methyl-7-methoxyphenanthrene<sup>11</sup> and the anhydride of



(1) Presented by W. E. Bachmann in Basel, Zürich, and Geneva, Switzerland, May 9–16, 1947, under the auspices of the American-Swiss Foundation for Scientific Exchange.

(2) Research Associate supported by a grant from the Horace H. Rackham Fund at the University of Michigan, 1941–1942. Present address: Merck and Co., Rahway, N. J.

(3) Dane and co-workers, *Ann.*, **532**, 29, 39 (1937); **536**, 183, 196 (1938); **537**, 246 (1939).

(4) Goldberg and Müller, *Helv. Chim. Acta*, **23**, 831 (1940).

(5) Bockemüller, U. S. Patent 2,179,809; *C. A.*, **34**, 1823 (1940).

(6) This investigation, which was interrupted by the war, is now being resumed. Further work on the reaction of the diene with citraconic anhydride and a study of the reaction with mesaconic acid are in progress.

(7) See Bachmann and Scott, *THIS JOURNAL*, **70**, 1458 (1948), for the addition of citraconic anhydride and of mesaconic acid to 1-vinyl-6-methoxynaphthalene.

(8) Cf. Breitner, *Med. u. Chem.*, **4**, 317 (1942); *Chem. Zentr.*, **114**, I, 2688 (1943); *C. A.*, **38**, 4953 (1944). The German abstract appeared after most of our experimental work had been completed. Breitner obtained a potent estrogen from an anhydride adduct (m. p. 210°) prepared from the diene and citraconic anhydride. Later the Government Intelligence Team (Report No. 248, Pharmaceuticals at the I. G. Farbenindustrie Plant, Elberfeld, Germany, Office of the Publication Board, Department of Commerce, Washington, D. C.) reported that Breitner's product was prepared from an adduct melting at about 125° and at 160° after several recrystallizations.

(9) The structures I, II, III, and IV are written with the double bond in the 4-4a position until more information is available.

(10) Hartung, *THIS JOURNAL*, **50**, 3370 (1928); **66**, 888 (1944).

(11) Heer and Miescher, *Experientia*, **3**, 322 (1947), recently reported the formation of 1-methyl- and 2-methyl-7-methoxyphenanthrene from the adducts which they obtained from the diene and citraconic anhydride. An example of a 1-methyl-1-carboxyhydrophenanthrene derivative which has been decarboxylated and dehydrogenated is abietic acid (Ruzicka, *et al.*, *Helv. Chim. Acta*, **6**, 692 (1923); **16**, 842 (1933)) and of a 2-methyl-2-carboxy derivative is estric acid (Butenandt, Weidlich and Thompson, *Ber.*, **66**, 601 (1933)).