21. *Some Perhydrophenanthrenecarboxylic Acid Derivatives.*

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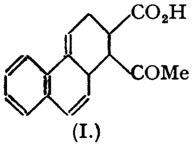
The Diels–Alder reaction between 1-vinylnaphthalene and β-acetylacrylic acid yields an adduct consisting of a mixture of the two possible structural isomers, which rearrange readily to the naphthalene analogues.

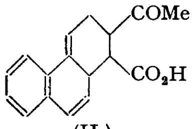
Citraconic anhydride failed to condense satisfactorily with 1-vinylnaphthalene, but with 6-methoxy-1-vinyl-3 : 4-dihydronaphthalene it gives an adduct, from which on hydrolysis two acids, shown to be 7-methoxy-1-methyl- and 7-methoxy-2-methyl-hexahydrophenanthrene-1 : 2-dicarboxylic acids, have been obtained.

COHEN and WARREN (*J.*, 1937, 1315) showed that maleic anhydride condensed readily with 1-vinylnaphthalene, yielding 1 : 2 : 3 : 11-tetrahydrophenanthrene-1 : 2-dicarboxylic acid anhydride, which rearranged under acid conditions to give 1 : 2 : 3 : 4-tetrahydrophenanthrene-1 : 2-dicarboxylic acid anhydride. The same series of reactions was successful with 6-methoxy-1-vinylnaphthalene.

β-Acetylacrylic acid would be expected to function likewise as a dienophile, although two possible structural isomers (I) and (II) might result. This expectation has now been realised, condensation occurring in boiling xylene solution, but the resulting adduct could not be purified because of its insolubility in organic solvents. However, on treatment with boiling glacial acetic acid, a more soluble, lower-melting product was obtained, which is a mixture of the two possible acetyl-1 : 2 : 3 : 4-tetrahydrophenanthrenecarboxylic acids (III) and (IV). This isomerisation occurred more easily than the similar transformation described by Cohen and Warren (*loc. cit.*), since both the adduct and the rearranged material showed identical ultra-violet light absorption of the naphthalene type, rearrangement of the adduct apparently occurring on effecting solution. Moreover, after being left in solution in 0·1N-alkali for an hour, followed by precipitation with acid, the adduct was completely converted into the lower-melting product. This latter was finally obtained as prisms, m. p. 160·5—161·5°, not changed by further crystallisation, although subsequent experiments showed that it was still a mixture of (III) and (IV). Reduction of the carbonyl group, either directly by the Clemmensen method, or, more satisfactorily, by the modified Wolff–Kischner procedure described by Cook and Linstead (*J.*, 1934, 946), gave the corresponding ethyl 1 : 2 : 3 : 4-tetrahydrophenanthrenecarboxylic acid mixture, but here again no satisfactory separation into the two components could be effected by crystallisation. The reduction product underwent simultaneous dehydrogenation and decarboxylation when heated with selenium at 300°, to give a product, m. p. 47°, with the composition of ethylphenanthrene. Construction of melting-point curves using known mixtures of synthetic 1-ethylphenanthrene (Haworth, *J.*, 1932, 1125; 1934, 454) and 2-ethylphenanthrene (Mosettig and Van de Kamp, *J. Amer. Chem. Soc.*, 1930, **52**, 3704; Haworth and Mavin, *J.*, 1933, 1012), and their corresponding picrates, indicated that the material, m. p. 47°, contained some 80% of 1-ethylphenanthrene and 20% of 2-ethylphenanthrene, thus showing that the original adduct contained the two possible forms (I) and (II). When the original adduct was heated with selenium, pure 1-ethylphenanthrene was easily obtained from (I). Since transformation involves loss of the carboxyl group, reduction of the carbonyl group, and aromatisation of the ring system, it would appear that a break at some stage in the sequence of reactions in the case of (II) may have occurred.



(I.)



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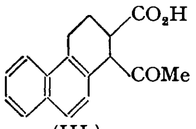
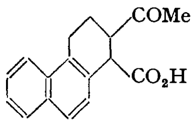


(III.)



(IV.)

The behaviour of acraldehyde, α-methyl-β-ethylacraldehyde, ethyl β-ethylacrylate, α-methyl-β-ethylacrylic acid, β-acetyl-α-methylacrylic acid, and citraconic anhydride as possible dienophiles in the Diels–Alder reaction with 1-vinylnaphthalene was also examined. Of these, only citraconic anhydride showed signs of condensation, but the product was polymeric. The anticipated products were obtained with citraconic anhydride and 6-methoxy-1-vinyl-3 : 4-dihydronaphthalene; in the latter reactant the diene system is not also part of an aromatic nucleus. Breitner has been reported (*C.I.O.S. Report Item No.* 24, *File No.* XXV—54, p. 20) to have found that only one of the two possible products was formed. After our examination of this reaction had been completed, a full account was published by Heer and Miescher (*Helv. Chim. Acta*, 1948, **31**, 219), and, consequently, our findings are only given in outline.

6-Methoxy-1-vinyl-3 : 4-dihydronaphthalene was prepared by a modification of the method described by Breitner (*loc. cit.*) involving the condensation of 6-methoxy-1-tetralone with acetylene in dioxan in presence of sodium acetylide. The unreacted ketone was, however, more conveniently removed with the Girard reagent, and partial hydrogenation of the triple bond effected catalytically over a palladium–calcium carbonate catalyst (Heilbron, Jones, McCombie, and Weedon, *J.*, 1945, 84).

This naphthalene reacted exothermally with citraconic anhydride, and treatment of the reaction mixture with alkali gave a mixture of two isomeric acids, separated by fractional crystallisation into (*A*) and the less soluble (*B*). Heating of (*A*) or (*B*) with selenium established the fundamental structure of these two acids, (*A*) giving 7-methoxy-2-methylphenanthrene, while (*B*) gave 7-methoxy-1-methylphenanthrene, identical with a synthetic specimen prepared by the method of Short, Stromberg, and Wiles, (*J.*, 1936, 319). 7-Methoxy-2-methylphenanthrene has been reported by Dane (*Annalen*, 1938, **536**, 183) as arising by dehydrogenation of the product of condensation of propiolic ester and 6-methoxy-1-ethynyl-3 : 4-dihydronaphthalene, while Heer and Miescher (*loc. cit.*) obtain it by dehydrogenation of 7-methoxy-2-methyl-1 : 2 : 3 : 4-tetrahydrophenanthrene-2-carboxylic acid, but an unambiguous synthesis is now recorded. Clemmensen reduction of β-(5-bromo-6-methoxy-2-naphthoyl)-*n*-butyric acid gave α-(5-*bromo*-6-*methoxy*-2-*naphthyl*)iso*valeric acid*, the nuclear bromine being then removed catalytically to give α-(6-*methoxy*-2-*naphthyl*)iso*valeric acid*. Ring closure of the acid chloride of the last compound with stannic chloride gave 4-*keto*-7-*methoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, which on Clemmensen reduction followed by selenium dehydrogenation gave 7-methoxy-2-methylphenanthrene, identical with the material obtained from acid (*A*). Acid (*A*) must, consequently, be a 7-methoxy-2-methylhexahydrophenanthrene-1 : 2-dicarboxylic acid, and (*B*) is the corresponding 1-methyl compound, conclusions which are in agreement with those reached by Heer and Miescher.

Partial dehydrogenation is shown to be readily accomplished in this type of compound, since, when the dimethyl ester of (*A*) was dehydrogenated with palladium–charcoal, two isomeric *tetrahydrophenanthrenedicarboxylic esters* were produced.

EXPERIMENTAL.

All melting points are uncorrected. Microanalyses by Drs. Weiler and Strauss. Light absorption data by Dr. Strauss.

Condensation of 1-*Vinylnaphthalene with β-Acetylacrylic Acid.*—A solution of 1-vinylnaphthalene (8·33 g., Cohen and Warren, *loc. cit.*) and β-acetylacrylic acid (9·2 g., Wolff, *Ber.*, 1887, **20**, 425; *Annalen*, 1891, **264**, 245) in dry xylene (13 c.c.) was refluxed for 1 hour, cooled, and diluted with benzene (20 c.c.). Unchanged β-acetylacrylic acid (0·9 g.) was removed and the filtrate extracted with sodium hydroxide (100 c.c., N). Acidification of the aqueous layer with acetic acid gave a gummy precipitate, which was collected and treated with boiling ethanol. The colourless microcrystalline adduct (5·25 g.) which remained undissolved was collected. It had m. p. 245—247° (decomp.), and was virtually insoluble in the common organic solvents except acetic acid (Found: C, 75·1; H, 5·9. Calc. for $C_{17}H_{16}O_3$: C, 76·1; H, 6·0%).

Rearrangement was effected by boiling a solution of the adduct (5 g.) in glacial acetic acid (50 c.c.)

for 30 minutes. The cooled solution was poured into water (500 c.c.) and the mixture kept for 48 hours. The precipitated mixture of acetyl-1 : 2 : 3 : 4-tetrahydrophenanthrenecarboxylic acids (5 g.) had m. p. 157—159°, and, after several crystallisations from ethanol and finally from ethyl acetate, formed colourless prisms, m. p. 160·5—161·5°, not altered by further crystallisation (Found : C, 76·0; H, 5·9. Calc. for $C_{17}H_{16}O_3$: C, 76·1; H, 6·0%). Both the adduct and the rearranged material rapidly decolourised alkaline permanganate solution. The mixture of semicarbazones crystallised from ethanol–benzene (2 : 1 by vol.) in colourless prisms, m. p. 254·5° (decomp.) (Found : C, 66·6; H, 6·0; N, 13·0. Calc. for $C_{18}H_{19}O_3N_3$: C, 66·4; H, 5·9; N, 12·9%). The 2 : 4-dinitrophenylhydrazones of the ethyl esters formed prisms, m. p. 184—185° (Found : C, 62·5; H, 5·0; N, 11·6. Calc. for $C_{25}H_{24}O_6N_4$: C, 63·0; H, 5·1; N, 11·8%). The same 2 : 4-dinitrophenylhydrazones were obtained from the condensation product of 1-vinylnaphthalene and ethyl β-acetylacrylate.

Light absorption.	λ max., A.	Log ε max.
Adduct and isomerised product	2840	3·75
	3220	2·43
1 : 2 : 3 : 11-Tetrahydrophenanthrene-1 : 2-dicarboxylic acid anhydride	2500	4·28
	3000	3·65
1 : 2 : 3 : 4-Tetrahydrophenanthrene-1 : 2-dicarboxylic acid anhydride	<2200	>4·29
	2715	3·71
	2805	3·74

Ethyl 1 : 2 : 3 : 4-*Tetrahydrophenanthrenecarboxylic Acids.*—Clemmensen reduction of the above keto-acid mixture (2 g.) yielded a mixture of ethyl 1 : 2 : 3 : 4-tetrahydrophenanthrenecarboxylic acids (0·3 g.) as colourless prisms, m. p. 148°, from benzene (Found : C, 80·3; H, 7·2. Calc. for $C_{17}H_{18}O_2$: C, 80·3; H, 7·1%). The modified Wolff–Kischner procedure described by Cook and Linstead (*loc. cit.*) was more successful. A melt of the semicarbazones, m. p. 245° (2·1 g.), and potassium hydroxide (2·0 g.) was heated at 200—210° for 1 hour. The reaction mixture was cooled and acidified, and the precipitated acid collected and dried in a vacuum at room temperature. The crude product (1·7 g.), which melted over a wide range, was crystallised from aqueous ethanol and finally from ethyl acetate–light petroleum (b. p. 60—80°) to give prisms (0·52 g.), m. p. 150—151°, not depressed on admixture with material prepared by the Clemmensen method.

Selenium Treatment.—The crude reduced material (0·5 g.) was heated at 280—300° for 24 hours with selenium (0·75 g.), and the mixture was cooled and extracted with ether (no acidic material was obtained on washing the extract with alkali). The solvent was removed, the residue distilled under reduced pressure from sodium, and the distillate crystallised from ethanol to give colourless plates, m. p. 47°, not altered by sublimation in high vacuum (Found : C, 93·6; H, 6·5. Calc. for $C_{16}H_{14}$: C, 93·2; H, 6·8%). The picrate had m. p. 105—106°.

The purified reduced acids, m. p. 150—151°, treated in similar manner, gave 1-ethylphenanthrene, m. p. 59°, after crystallisation from ethanol.

The adduct when similarly treated gave, after one crystallisation from ethanol, 1-ethylphenanthrene, m. p. 62·5°, not depressed on admixture with an authentic sample (Found : C, 92·6; H, 7·0. Calc. for $C_{16}H_{14}$: C, 93·2; H, 6·8%).

Mixed Melting Points of 1- *and* 2-*Ethylphenanthrene.*—The melting-point curve of authentic specimens of 1- and 2-ethylphenanthrene was obtained by melting the required amount of the two components together. Samples of the melts, which all resolidified readily, were then observed in an ordinary melting-point apparatus, the point of final clearance being recorded in the Table. For the melting points of the mixed picrates, homogeneous, known compositions were obtained by dissolving the two components in a small volume of methanol and removing the solvent at room temperature in a vacuum over concentrated sulphuric acid.

1-Ethylphenanthrene, %	100	95	92	90	83·4	80	75	70
M. p.	62°	54°	52·5°	52·5°	47°	46·5°	47°	47·5°
1-Ethylphenanthrene, %	64	56	50	40	33·3	25	15	0
M. p.	48·5°	48°	49·5°	53°	53·5°	57·5°	62°	64°
1-Ethylphenanthrene picrate, %	100	80	65	50	35	20	0	
M. p.	112°	106°	103°	98·5°	95°	93°	94·5°	

β-Acetyl-α-methylacrylic Acid.—This was prepared in low yield from α-methyl-lævulinic acid by a procedure based on that of Wolff (*loc. cit.*) for β-acetylacrylic acid. It crystallised from benzene in colourless needles, m. p. 102—102·5° (Found : C, 56·6; H, 6·3. Calc. for $C_6H_8O_3$: C, 56·3; H, 6·3%). Ajello and Cusmano (*Gazzetta*, 1940, **70**, 512) report β-acetyl-α-methylacrylic acid, m. p. 98°, as a degradation product of 5-nitroso-2 : 4-dimethylpyrrole.

Condensation of 6-*Methoxy*-1-*vinyl*-3 : 4-*dihydronaphthalene with Citraconic Anhydride.*—On mixing the naphthalene (6 g.) with citraconic anhydride (4 g.) a deep-yellow colour developed, and after the mixture had been warmed to 70—75° the temperature rose to 125°. The viscous product could not be induced to crystallise on cooling. It was extracted with boiling sodium hydroxide solution (200 c.c., 2N), the insoluble material removed with ether, and the alkaline extract acidified with dilute sulphuric acid. A red oil separated which solidified on standing. It was collected and treated with hot ethanol (50 c.c.); part dissolved, and, on cooling, the ethanolic extract deposited an acid (*A*) (1·1 g.), m. p. 165—170°, which after 3 crystallisations from ethanol formed prismatic needles, m. p. 180—181°, containing 1 mol. of water of crystallisation lost at 100° in a high vacuum (Found : C, 68·5; H, 6·2. Calc. for $C_{18}H_{20}O_5$: C, 68·3; H, 6·4%). The material insoluble in ethanol (1 g.) had m. p. 200—220°. After 2 crystallisations from 2-ethoxyethanol, acid (*B*) formed small colourless needles, m. p. 235° (decomp.) (Found : C, 68·1; H, 6·5. Calc. for $C_{18}H_{20}O_5$: C, 68·3; H, 6·4%).

On treatment with acetyl chloride or acetic anhydride acid (*A*) yielded an anhydride, m. p. 164—165°, as needles from chloroform–light petroleum (b. p. 60—80°) (Found : C, 72·7; H, 6·3%). Heer and Miescher (*loc. cit.*) give m. p. 148° for this anhydride. (*B*) similarly formed an anhydride, m. p. 125° (Found : C, 72·0; H, 6·0. Calc. for $C_{18}H_{18}O_4$: C, 72·5; H, 6·1%). Both (*A*) and (*B*) gave crystalline dimethyl esters, m. p. 104—105° (Found : C, 69·9; H, 7·3%), and m. p. 160—161° (Found : C, 69·8; H, 7·0. Calc. for $C_{20}H_{24}O_5$: C, 69·8; H, 7·0%), respectively, when treated with diazomethane.

Selenium Dehydrogenations.—(*A*) (0·2 g.) was heated with selenium (0·25 g.) at 300—320° for 18 hours. The residue was extracted with chloroform, and the oil thus obtained distilled from a little sodium in a high vacuum. The solid distillate was further purified by passage of its benzene solution through a short column of activated alumina; after crystallisation from methanol it formed blades or needles, m. p. 142—143°, not depressed on admixture with the synthetic specimen of 7-methoxy-2-methylphenanthrene described below.

When (*B*) (0·2 g.) was similarly treated with selenium (0·25 g.), 7-methoxy-1-methylphenanthrene, m. p. 129—130°, was obtained as colourless needles showing no depression in melting point when mixed with a synthetic specimen prepared by the method of Short, Stromberg, and Wiles (*loc. cit.*). A mixture of the isomeric methoxymethylphenanthrenes obtained from the two acids melted at 115—120°.

Synthesis of 7-*Methoxy*-2-*methylphenanthrene.*—β-(5-Bromo-6-methoxy-2-naphthoyl)-*n*-butyric acid (5 g., Haworth and Sheldrick, *J.*, 1934, 864) was refluxed vigorously with a mixture of amalgamated zinc wool (12 g.), hydrochloric acid (20 c.c.), water (7 c.c.), and toluene (10 c.c.) for 12 hours. The mixture was diluted with water and extracted with ether, from which the product was obtained by shaking with 2N-sodium hydroxide solution and acidification of the alkaline layer.

α-(5-*Bromo*-6-*methoxy*-2-*naphthyl*)iso*valeric acid* (3·5 g.) separated and crystallised as colourless plates from aqueous ethanol, m. p. 130—131° (Found : C, 56·6; H, 5·2. $C_{16}H_{17}O_3Br$ requires C, 57·1; H, 5·1%). This bromo-acid (1 g.) was dissolved in methanolic potassium hydroxide (100 c.c., 5%) and shaken with hydrogen in presence of palladium–calcium carbonate catalyst (2 g., Busch and Stöve, *Ber.*, 1916, **49**, 1064). The theoretical amount of hydrogen was absorbed in 25 minutes. Acidification of the solution obtained by filtration of the catalyst and distillation of most of the methanol gave α-(6-*methoxy*-2-*naphthyl*)iso*valeric acid* (0·6 g.) as plates from aqueous methanol, m. p. 114—115° (Found : C, 73·8; H, 7·2. $C_{16}H_{18}O_3$ requires C, 74·4; H, 7·0%). This acid (3 g.) was treated with phosphorus pentachloride (3 g.) in benzene (10 c.c.). After being warmed to complete the reaction, the solution was diluted with benzene (10 c.c.) and cooled to solidification point; stannic chloride (4 c.c.) in benzene (4 c.c.) was then added. The mixture was kept at room temperature for 3 hours and then treated with ether and dilute hydrochloric acid. The organic layer was separated, washed with water, dilute sodium carbonate and again with water, dried, and the solvents distilled. The residue, crystallised from methanol, gave 4-*keto*-7-*methoxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (2 g.) as plates, m. p. 111°, readily subliming at 100°/10^{-3} mm. (Found : C, 79·7; H, 6·6. $C_{16}H_{16}O_2$ requires C, 80·0; H, 6·7%). A mixture of the cyclic ketone (2 g.), amalgamated zinc (15 g.), hydrochloric acid (20 c.c.), glacial acetic acid (20 c.c.), and toluene (15 c.c.) was refluxed for 18 hours. After addition of water and ether, the organic layer was separated, and washed with water and then with two portions of 2N-sodium hydroxide (25 c.c. each). The alkaline extract was warmed with methyl sulphate (2 c.c.) on the steam-bath. This solution was then re-extracted with ether and the extract combined with the previous extract. After drying and removal of the solvents, the residue (1·6 g.) partly crystallised but was not further purified. This material (0·5 g.) was heated with selenium (0·75 g.) at 300° for 18 hours. The 7-methoxy-2-methylphenanthrene, isolated with chloroform and distilled from sodium, after crystallisation from methanol formed colourless blades or needles, m. p. 142—143°, not depressed on admixture with the material obtained by dehydrogenation of acid (*A*) (Found : C, 86·3; H, 6·4. Calc. for $C_{16}H_{14}O$: C, 86·6; H, 6·4%).

Partial Dehydrogenation of the Dimethyl Ester of (*A*).—The ester (0·2 g.) was heated in a sealed tube with palladium–charcoal (0·3 g., 15%) in acetone (10 c.c.) at 200° for 5 hours. The filtered solution was evaporated to dryness and crystallised from a little methanol; needles of the *dimethyl tetrahydrophenanthrenedicarboxylate* separated which, after 3 crystallisations from methanol, had m. p. 167° (Found : C, 70·25; H, 6·6. $C_{20}H_{22}O_5$ requires C, 70·2; H, 6·5%). The original mother liquor on standing deposited an *isomer* as feathery needles, which after crystallisation from light petroleum (b. p. 60—80°) had m. p. 97°, depressed to 80—85° when mixed with the dimethyl ester of (*A*) (Found: C, 70·1; H, 6·6%).

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