

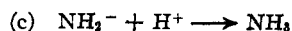
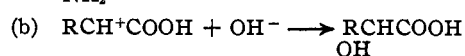
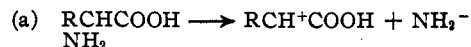
agree very well with theory (hygroscopicity?): Calcd. for  $C_4H_5O_3$ ; C, 35.8; H, 4.5. Found: C, 36.2; H, 5.5.

### Summary

1. In water solution glycine, alanine, betaine and aspartic acid are hydrolyzed under the influence of ultraviolet light, giving the corresponding hydroxy acids.

2. The kinetics and quantum yields of these reactions have been measured.

3. The following mechanism has been suggested.



4. The hydrolysis of optically active aspartic acid is accompanied by racemization, which is in accordance with the above mechanism.

5. The behavior of tyrosine has been studied qualitatively.

REHOVOTH, PALESTINE

RECEIVED APRIL 9, 1936

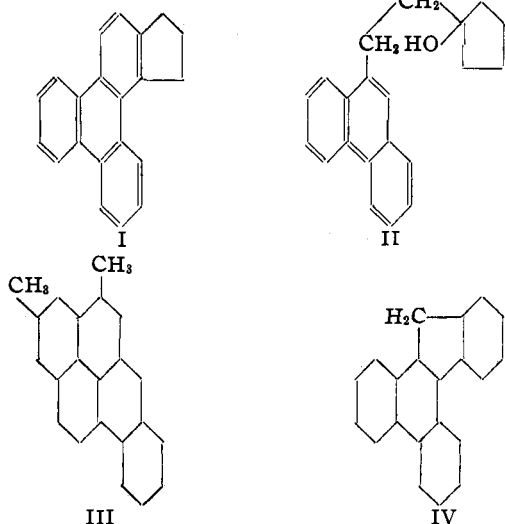
[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE]

## Cyclopentenotriphenylene

BY ERNST BERGMANN AND OTTILIE BLUM-BERGMANN

Jacobs and Elderfield<sup>1</sup> obtained by dehydrogenation of strophanthidin, *inter alia*, a hydrocarbon, the analysis of which gave figures corresponding to the formula  $C_{21}H_{16}$ . On the basis of a strophanthidine formula which has since been abandoned, the authors suggested the structure of cyclopentenotriphenylene (I). In connection with other experiments we thought it interesting to synthesize the above hydrocarbon; its properties were quite different from those of the hydrocarbon obtained by the American authors. Our synthesis parallels the preparation of cyclopentenophenanthrene by Cook and co-workers.<sup>2</sup> Their work gave us some valuable information about the formation and structure of various by-products.

$\beta$ -(9-Phenanthryl)-ethanol was easily prepared from 9-phenanthrylmagnesium bromide and ethylene oxide or ethylene chlorohydrin and converted into the corresponding chloride. Its magnesium derivative reacted with cyclopentanone to give (9-phenanthrylethyl)-cyclopentanol (II). In accordance with the observations of Cook, we tried to convert (II) directly into (I) with glacial acetic acid and concentrated sulfuric acid, but without success, and also none of the two crystalline hydrocarbons resulting from the crude reaction product by subsequent dehydrogenation was the desired product (I). The first had the formula  $C_{21}H_{14}$  and was characterized by a vermilion picrate. It is most probable that it corresponds to 2-methylpyrene<sup>2a</sup> obtained by Cook in the corresponding experiment in the naphthalene series, and therefore is 7-methyl-1,2-benzpyrene (III). We hope to confirm this suggestion, by spectroscopic comparison of our product with benzpyrenes of known structure, as 1,2- and 4,5-benzpyrene recently described by Cook and Hewett<sup>3</sup> and Fieser and Fieser,<sup>4</sup> respectively. The second isolated hydrocarbon, which occurred only in minor quantities, turned yellow on keeping. It resembles in this respect the complex fluorene derivatives prepared by Cook and Hewett;<sup>2b</sup> we therefore assume that it has the structure of 1,2,3,4-dibenzofluorene (IV) and is analogous to chrysofluorene isolated by Cook in his experiments in the naphthalene series. The corresponding fluorenone has recently



(1) Jacobs and Elderfield, *J. Biol. Chem.*, **107**, 143 (1934).

(2) Cook, *et al.*, *J. Chem. Soc.*, (a) 1098 (1933); (b) 365 (1934).

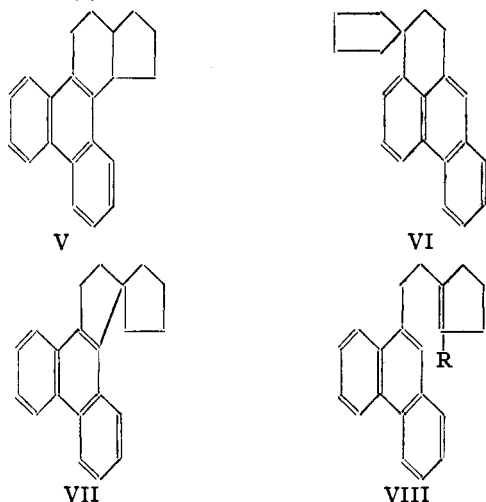
(2a) Barry, Cook, *et al.*, *Proc. Roy. Soc. (London)*, **B117**, 321 (1935).

(3) Cook and Hewett, *J. Chem. Soc.*, 398 (1933).

(4) Fieser and Fieser, *THIS JOURNAL*, **57**, 782 (1935).

been described by Koelsch.<sup>5</sup> These hydrocarbons cannot be formed by dehydrogenation of the normal compound (V) which we expected from the treatment of II with concentrated sulfuric acid, as an intermediate product; they must derive from the two spirans (VI) and (VII), respectively, by thermal rearrangement and subsequent dehydrogenation.<sup>5a</sup> As a matter of fact we succeeded in isolating, from the crude product of the above treatment of (II), a crystalline substance  $C_{21}H_{20}$  which was not identical with (V) and, since under our experimental conditions the *cis* isomer of (V) would not be stable,<sup>6</sup> must be one of the spirans (VI) or (VII).

After this failure, we had to proceed by the way suggested by the formulas (II)  $\rightarrow$  (VIII)  $\rightarrow$  (V)  $\rightarrow$  (I).



The dehydration of (II) was effected easily by heating with potassium bisulfate and the conversion of (VIII, R = H) into (V) by means of aluminum chloride. We prefer the olefinic double bond in (VIII, R = H) in the five-membered ring, rather than in the semicyclic position; but that question is of no importance for the course of the reaction.

Cook and his co-workers observed in several cases that 2-methylcyclopentanone is more suitable for syntheses of this kind, since the condensation with Grignard compound and subsequent dehydration and dehydrogenation gives more uniform products.<sup>7</sup> A series of experiments starting with the methylated ketone was unsuccessful,

since 9-ethylphenanthrene formed prevented the easy isolation of the expected ethylene (VIII, R =  $CH_3$ ).

The cyclopentenotriphenylene obtained by dehydrogenation of (V) is a well-crystallized compound characterized by its dark brown-red picrate. It is isomeric with methylcholanthrene and the melting points and those of their picrates show a striking resemblance; but the mixtures show a depression of the m. p. Obviously, methylcholanthrene could not be formed in our synthetical process. The spectroscopic analysis of cyclopentenotriphenylene and its comparison with similar hydrocarbons is now in progress.

### Experimental

$\beta$ -(9-Phenanthryl)-ethanol.—(a) An ethereal solution of ethylene oxide (10 g.) was added to 9-phenanthrylmagnesium bromide, prepared according to Bachmann<sup>8</sup> from magnesium (5 g.), 9-bromophenanthrene (48.5 g.) in a mixture of benzene (120 cc.) and ether (120 cc.). The rather violent reaction was completed by boiling for two hours; the reaction mixture was decomposed with ice and acid, washed with soda solution, dried and evaporated. The oily residue crystallized, on trituration with light petroleum and acetone; from benzene clusters of needles; m. p. 92°; yield 15–21 g. Calcd. for  $C_{18}H_{14}O$ : C, 86.5; H, 6.3. Found: C, 86.7, 86.7; H, 6.7, 6.6.

(b) According to Grignard<sup>9</sup> an ethereal solution of 9-phenanthrylmagnesium bromide (from 102 g. of bromophenanthrene and 11 g. of magnesium) was added to a solution obtained by addition of ethylene chlorohydrin (22.4 cc.) to ethylmagnesium bromide (8.1 g. of magnesium and 25.4 cc. of ethyl bromide). Since no reaction took place, the solvents were distilled off; at the end of the distillation reaction occurred, causing the mass to foam and swell violently. After addition of fresh ether the mass was treated as above and the product isolated by distillation (1 mm.). At 145–170° some phenanthrene passed over, then at 200° the reaction product, which crystallized quickly (40–50 g.).

$\beta$ -(9-Phenanthryl)-ethyl Chloride.—The above alcohol (20 g.) was mixed with dimethylaniline (11.7 cc.) and benzene (24 cc.) and the mixture cooled with ice water. Then thionyl chloride (7.6 cc.) was added drop by drop and the dark red solution heated until the evolution of sulfur dioxide ceased. On addition of water a dark oil separated and was isolated with ether. The residue crystallized at once and was triturated with ethyl acetate and recrystallized from benzene mixed with a little benzene; m. p. 82–84°; yield, 15–17 g. Calcd. for  $C_{18}H_{18}Cl$ : C, 79.7; H, 5.4. Found: C, 79.9; H, 5.4.

(9-Phenanthryl-ethyl)-cyclopentanol (II).—The above chloride (29.6 g.) reacted smoothly with magnesium (3.2 g.) when activated with iodine and methyl iodide. After

(5) Koelsch, *THIS JOURNAL*, **56**, 480 (1934).

(5a) See Fieser, "Chemistry of Natural Products Related to Phenanthrene," Reinhold Publishing Corp., New York, N. Y., 1936, p. 162.

(6) Zelinsky and Turowa-Pollak, *Ber.*, **65**, 1299 (1932).

(7) Compare Bergmann and Weiss, *Ann.*, **480**, 65 (1930).

(8) Bachmann, *THIS JOURNAL*, **56**, 1363 (1934).

(9) Grignard, *Ann. chim.*, [8] **10**, 23 (1907). Compare Schlenk, O. Bergmann and E. Bergmann, *J. Soc. Chem. Ind.*, **52**, 209T (1933).

two hours of boiling, cyclopentanone (10.8 cc.) was added; it reacted markedly and gave a crystalline precipitate. The mass was boiled for a further two hours and then decomposed with ice and ammonium chloride or ice and acid. An insoluble compound separated and was filtered off after some time (1.75 g.); it was recrystallized from xylene. The yellowish leaflets, m. p. 214–216°, exhibit a strong violet fluorescence and consist, according to the analysis, of  $\alpha,\beta$ -di-(9-phenanthryl)-butane,  $C_{14}H_9CH_2CH_2CH_2CH_2C_{14}H_9$ . Calcd. for  $C_{32}H_{26}$ : C, 93.7; H, 6.3. Found: C, 93.8, 94.1; H, 6.1, 6.5. The residue of the ethereal filtrate crystallized on trituration with benzene. This carbinol was recrystallized from benzene and cyclohexane as transparent prisms, m. p. 108–109°; yield, 17.1 g. Calcd. for  $C_{21}H_{27}O$ : C, 86.9; H, 7.6. Found: C, 86.5; H, 7.6.

**Reactions with Concentrated Sulfuric Acid.**—(a) The carbinol (II) (4 g.) was heated for two hours on the water-bath with glacial acetic acid (40 cc.) and concd. sulfuric acid (4 cc.); a violet color and smell of sulfur dioxide was observed. Then water was added and the oily product, after isolation with ether, directly heated with selenium (10 g.) to 320–340° for sixteen hours. The mass was extracted with benzene and ethyl acetate and purified by distillation at 0.8 mm. (bath temperature 240–280°). The reddish oil (1.2 g.), on trituration with benzene, gave a crystalline powder (0.5 g.) melting at 132–142°; from propyl alcohol, then from glacial acetic acid, silky needles, m. p. 157.5–159.5°. Calcd. for  $C_{21}H_{14}$  (III): C, 94.7; H, 5.3. Found: C, 94.3, 94.3, 94.6, 95.0, 94.6; H, 5.3, 5.6, 5.4, 5.6, 5.3. The picrate, prepared from equivalent amounts of the components in benzene and isolated by evaporation of the solvent, was recrystallized from alcohol, containing picric acid, as beautiful vermilion needles of m. p. 153–155°. Calcd. for  $C_{27}H_{17}O_7N_3$ : C, 65.5; H, 3.4; N, 8.5. Found: C, 66.0, 66.0; H, 4.1, 3.6; N, 7.6. From the benzene mother liquors of the above hydrocarbon (III), there separated, on standing, a second hydrocarbon (0.2 g.), which melted at 115–116°, after repeated recrystallization from benzene, and after purification through the picrate; needles turning yellow on exposure to air and light. The picrate prepared in hot alcohol, crystallized on cooling as orange-yellow needles, m. p. 165–167°. Calcd. for  $C_{27}H_{16}N_3O_7 = C_{21}H_{16}$  (IV) +  $C_6H_4N_3O_7$ : C, 65.2; H, 3.8; N, 8.4. Found: C, 65.4; H, 4.2; N 8.0.

(b) The experiment was repeated as before but the crude oily product left for some time. A small amount of a crystalline powder separated which was triturated with ethyl acetate, filtered, washed with alcohol and recrystallized from the same solvent as leaflets of m. p. 117–120°. Undoubtedly, the substance is one of the spirans (VI) or (VII). Calcd. for  $C_{21}H_{20}$ : C, 92.6; H, 7.4. Found: C, 92.3; H, 8.2.

**1'- $\beta$ -(9-Phenanthryl)-ethyl-cyclopentene-(1) (VIII).**—The carbinol (17 g.) and potassium bisulfate (25.5 g.) were heated at 160–170° for one hour; the mixture was poured into water, the product extracted with ether and distilled; b. p. 206–207° (1.3 mm.). The distillate (14.3 g.) was a viscous oil unsaturated toward bromine, which crystallized immediately; it melted at 50–54.5°, but it was impossible to recrystallize it and therefore it was converted into tetra-

hydro-cyclopenteno-triphenylene (V) by dissolving in carbon disulfide and adding finely powdered aluminum chloride (14 g.), at room temperature. After twelve hours the violet mass was decomposed with ice and hydrochloric acid and the product distilled; b. p. 210–215° (1 mm.). The oil crystallized spontaneously; on recrystallization from ethyl or propyl alcohol it gave beautiful prisms (6.9 g.) m. p. 105.5–107°. Calcd. for  $C_{31}H_{26}$ : C, 92.6; H, 7.4. Found: C, 92.6; H, 7.6. (Picrate, see below.)

**Cyclopentenotriphenylene (I).**—The tetrahydro compound (5 g.) was mixed with selenium (12 g.) and heated for twenty hours at 330–340°. The mass was powdered and extracted with ether in a Soxhlet apparatus. The solution was evaporated and the residue distilled at 1 mm. The yellow oil (2.5 g.) on trituration with acetone and benzene gave 0.4 g. of cyclopentenotriphenylene as a yellow powder which was recrystallized several times from glacial acetic acid and propyl alcohol as yellowish, small needles, m. p. 171–172.5°. Calcd. for  $C_{31}H_{14}$ : C, 94.0; H, 6.0. Found: C, 94.2, 94.1; H, 5.7, 5.8. The picrate, prepared in propyl alcohol, was recrystallized from a mixture of benzene and propyl alcohol, containing picric acid; it formed brownish-red needles; m. p. 172–173°. Calcd. for  $C_{37}H_{19}O_7N_3$ : C, 65.2; H, 3.8. Found: C, 65.4, 65.7; H, 4.1, 4.1. The mother liquor of the cyclopentenotriphenylene was treated with picric acid in benzene solution. The precipitate consisted of the above dark picrate and a small proportion of a yellow picrate which, after recrystallization from alcohol containing picric acid, proved to be the picrate of some unchanged tetrahydro compound (V); needles, m. p. 161–162°. Calcd. for  $C_{27}H_{23}O_7N_3$ : C, 64.7; H, 4.6. Found: C, 64.1, 64.1, 64.4; H, 4.7, 4.4, 5.0.

**Experiments with 2-Methylcyclopentanone.**—Methylcyclopentanone (7.6 g.; b. p. 135–136°; prepared according to Cornubert and Borrell,<sup>10</sup> was added to phenanthryl-ethylmagnesium chloride (from magnesium (2.1 g.) and the chloride (19.2 g.)); during the vigorous reaction a white product crystallized. After boiling for one hour, the mass was decomposed with ice and ammonium chloride (or ice and dilute sulfuric acid), the precipitate of 1,4-di-(9-phenanthryl)-butane (1.2 g.) filtered off and the reaction product isolated as usual. It could not be obtained in a crystalline state and free of 9-ethylphenanthrene and was therefore heated with twice its weight of potassium bisulfate at 160–170° for one hour. The product isolated as above was fractionated at 1.5 mm. The *first fraction*, b. p. 162–170°, crystallized spontaneously and was recrystallized from alcohol, containing a little light petroleum as white, silky prismatic needles, m. p. 62–64°. The melting point and the analysis showed that the substance was 9-ethylphenanthrene. Calcd. for  $C_{18}H_{14}$ : C, 93.2; H, 6.8. Found: C, 93.4, 93.3; H, 7.1, 7.0. The *second fraction*, b. p. 180–195° (0.8 mm.) was an unsaturated (bromine) yellow oil,  $n_D$  1.6499, which crystallized after some time; from alcohol as needles, exhibiting blue fluorescence, m. p. 73–75°. The analysis showed that the desired 1-(phenanthryl-ethyl)-2-methyl-cyclopentene-(1) (IX) had been formed but the yield was so poor that further experiments with this substance had to be abandoned.

(10) Cornubert and Borrell, *Bull. soc. chim.* (IV), 47, 304 (1930).

Calcd. for  $C_{22}H_{22}$ : C, 92.3; H, 7.7. Found: C, 92.3; H, 8.2. In view of the violence of the Grignard reaction, it is improbable that the ethylphenanthrene derives from unchanged Grignard compound. It could have been formed by dismutation of the expected carbinol, or when methylcyclopentanone inclines to react in an enolic form.<sup>11</sup>

(11) Compare Grignard and Savard, *Bull. soc. chim. Belg.*, **86**, 97 (1927).

### Summary

1. Cyclopentenotriphenylene has been prepared, starting with  $\beta$ -(9-phenanthryl)-ethyl chloride and cyclopentanone.

2. The nature of several by-products has been discussed.

REHOVOTH, PALESTINE

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[CONTRIBUTION FROM THE UNIVERSITY OF MARYLAND]

## Cerin and Friedelin. III. A Study of the Oxidative Degradation of Friedelin<sup>1</sup>

BY NATHAN L. DRAKE AND WILLIAM P. CAMPBELL

Our previous study of cerin and friedelin<sup>2</sup> has shown that these substances are polycyclic in nature, the former a hydroxy ketone, the latter a ketone, both derived from the same nucleus. From evidence now available<sup>3</sup> it is apparent that this polycyclic nucleus contains five fused rings, and that cerin and friedelin are derived from a completely hydrogenated picene, and should be classed as derivatives of a triterpene.

It is the purpose of this communication to describe certain degradation experiments in which the attack on the friedelin molecule is at the carbonyl group.

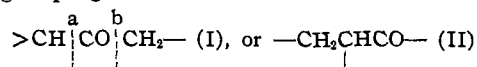
Sodium and amyl alcohol reduce friedelin to the corresponding alcohol, friedelinol, whose benzoate can be prepared readily by the action of benzoyl chloride on the alcohol in pyridine solution. This benzoate, when heated in an atmosphere of nitrogen to 300°, is converted into a hydrocarbon friedelene,  $C_{30}H_{50}$ , and benzoic acid. Similar unsaturated hydrocarbons with alkyl or aryl groups attached to the carbon which, in the original friedelin molecule, held the carbonyl oxygen, can be prepared by the action of the Grignard reagent on friedelin. Phenylmagnesium bromide yields such a hydrocarbon directly; the tertiary alcohol first produced undergoes spontaneous dehydration. Two products are obtained when methylmagnesium iodide reacts with friedelin. One is the expected methyl-substituted tertiary alcohol, the other methylfriedelene. The tertiary alcohol is readily dehydrated by acetic anhydride to methylfriedelene. All of these unsaturated substances give a pronounced yellow

color with tetranitromethane, but the *purest* friedelin gives no color.

The ready dehydration which these alcohols undergo, and the formation of benzoic acid from the benzoate, prove the presence of a hydrogen atom adjacent the carbonyl group of friedelin, and indicate that this hydrogen is probably tertiary.

Because friedelene is so easily accessible it was chosen for further study. Oxidation of friedelene by chromic anhydride in glacial acetic acid yields a neutral substance,  $C_{30}H_{48}O$ . This compound gives a color with tetranitromethane and yields no methane when treated with methylmagnesium iodide. The substance  $C_{30}H_{48}O$  must, therefore, be an unsaturated ketone, and since no methylene group of friedelin behaves in a similar fashion during oxidative degradations, it is reasonable to assume that the ketone  $C_{30}H_{48}O$ , which we have called friedelene, owes its formation to the activating effect of the double bond on the hydrogens of an adjacent methylene group. The formation of  $\alpha,\beta$ -unsaturated ketones by oxidation is a common reaction in the terpene series. Pinene can be oxidized to verbenone by treatment with chromic acid<sup>4</sup> and cedrin<sup>4</sup> and limonene can also be converted to  $\alpha,\beta$ -unsaturated ketones by oxidation.<sup>5</sup> Similarly cholestene is converted to cholestenone under the influence of chromic anhydride.<sup>6</sup>

On the basis of this evidence the existence of the grouping



in friedelin is postulated. Evidence obtained from the oxidation of friedelin makes it possible

(1) From the Ph.D. dissertation of William P. Campbell.  
(2) Drake and Jacobsen, *THIS JOURNAL*, **57**, 1570; Drake and Shrader, *ibid.*, **1854** (1935).

(3) Cf. the fourth article in this series, *ibid.*, **58**, 1684 (1936).

(4) Semmler and Jakubowicz, *Ber.*, **47**, 1143 (1914).

(5) Blumann and Zeitschel, *ibid.*, **47**, 2624 (1914).

(6) Windaus, *ibid.*, **53**, 488 (1920).