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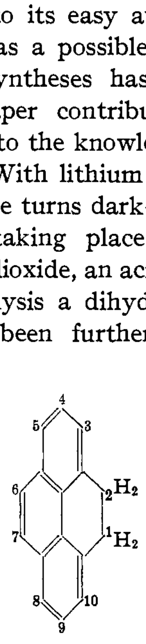
Some Reactions of Pyrene

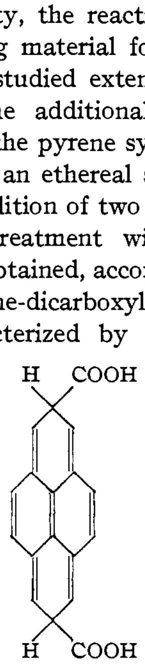
BY ERNST BERGMANN AND ELIAHU BOGRACHOV

Due to its easy availability, the reactivity of pyrene as a possible starting material for polycyclic syntheses has been studied extensively.[1] This paper contributes some additional observations to the knowledge of the pyrene system.

(a) With lithium metal,[2] an ethereal solution of pyrene turns dark-red, addition of two lithium atoms taking place. On treatment with dry carbon dioxide, an acid was obtained, according to the analysis a dihydro-pyrene-dicarboxylic acid. It has been further characterized by a well-crystallized dimethyl ester. When the dilithium compound, however, was hydrolyzed, only pyrene could be isolated from the resulting solution, the dihydro hydrocarbon primarily formed being autoxidizable. It cannot be identical, therefore, with the stable 1,2-dihydropyrene (I), obtained by Coulson[3] by catalytic hydrogenation of pyrene. It follows that addition of lithium does not take the same course as that of catalytically activated hydrogen, which concords with observations made by Schlenk and Bergmann.[4] This most probably is due to the addition of alkali metal being an addition of ions.[5] The structure of the dicarboxylic acid is the subject of further investigation. Both of the possible formulas (II) and (III) would account for the non-formation of an anhydride. In the formation of (II) pyrene would react as a substituted biphenyl,[6] while the observation of Vollmann and co-workers[7] that pyrene adds most easily in positions 3 and 10, would lead to formula (III) for the dicarboxylic acid.



I



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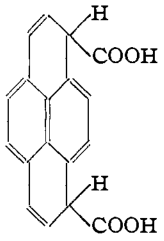
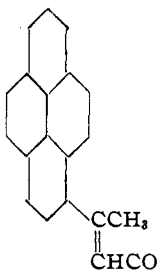
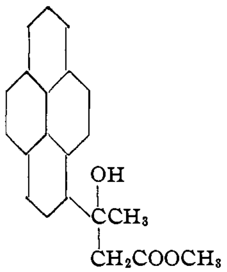


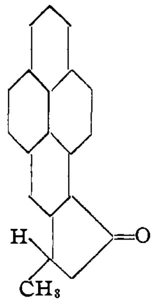
III



IV



V



VI

(b) From pyrene-3-aldehyde, pyrenyl-3-acrylic acid is obtained more easily than according to Vollmann and co-workers[7] by direct heating with malonic acid in presence of pyridine and piperidine.[8] The ester of pyrenyl-3-acrylic acid is prepared without difficulties by means of methyl alcoholic hydrochloric acid and can be hydrogenated to give the ester of β-(pyrenyl-3)-propionic acid. When, however, the unsaturated acid is methylated by means of diazomethane, besides the expected ester (60%), a second product (30%) is secured which proved to be methyl β-(3-pyrenyl)-crotonate (IV). Its structure is indicated by the observation that the same ester was obtained when 3-acetylpyrene was treated with methyl bromo-acetate and the hydroxy-ester (V) so formed dehydrated by means of formic acid. A methylation of the type by

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(1) Compare, *e. g.*, Vollmann, *et al.*, *Ann.*, **531**, 1 (1937).

(2) The behavior of polycyclic systems toward alkali metals has been studied recently by Bachmann, *J. Org. Chem.*, **1**, 347 (1936); Bachmann and Pence, THIS JOURNAL, **59**, 2339 (1937); Fieser and Hershberg, *ibid.*, **59**, 2502 (1937). For the reaction of chrysene, studied in our laboratories, see Mohler and Sorge, *Helv. chim. acta*, **22**, 229 (1939).

(3) Coulson, *J. Chem. Soc.*, 1298 (1937).

(4) Schlenk and Bergmann, *Ann.*, **463**, 1 ff. (1928).

(5) For the mechanism of catalytic hydrogenation, see Farkas and Farkas, *Trans. Faraday Soc.*, **33**, 837 (1937).

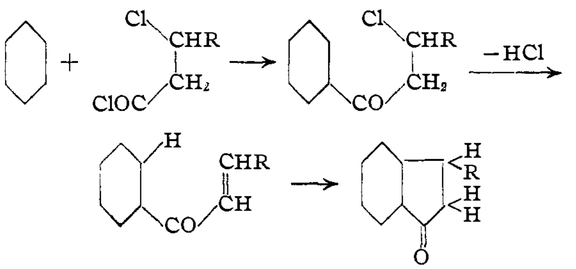
(6) Fieser, "Chemistry of Natural Products Related to Phenanthrene," New York, 1937, p. 17. For the lithium addition to biphenyl, see Schlenk and Bergmann, *Ann.*, **463**, 83 (1928); Hueckel and Bretschneider, *ibid.*, **540**, 157 (1939).

(7) Vollmann and co-workers, *ibid.*, **531**, 1 (1937).

(8) Compare, *e. g.*, Callow, Gulland and Haworth, *J. Chem. Soc.*, 1444 (1929); Reichert and auf dem Kampe, *Arch. Pharm.*, **277**, 26 (1939).

which (IV) is formed from methyl pyrenyl-3-acrylate has been observed in other cases, too, *e. g.*, that of ethyl cinnamate, ethyl α-methylcinnamate[9] and α-naphthoquinones.[10]

(c) According to F. Mayer[11] a cyclopenteno-system can be adnexed to a naphthalene derivative in reacting with β-chloro-acyl chlorides by the scheme



The unsaturated ketone is not always isolated, as it undergoes easily the cyclo-isomerization characteristic for allylbenzenes.[12] Pyrene gives, under the standard conditions of this synthesis, with β-chlorobutyryl chloride, a single reaction product, m. p. 101°, for which formula (VI) is most probable, as pyrene is usually substituted at C_3.[7]

The structures of the two isomeric saturated ketones, m. p. 113 and 82.5°, which are formed analogously from anthracene and β-chloro-butyryl chloride, are now under investigation.

Experimental

Pyrene and Lithium.—Pyrene (5 g.) in ether (125 cc.) was shaken with lithium turnings (about 0.5 g.) in a Schlenk tube for several days; the dark-red color of the lithium compound appeared after some hours. On saturation with dry gaseous carbon dioxide, a brownish-yellow precipitate was obtained, which was dissolved in water (about 200 cc.) and acidified. The dihydro-pyrene-dicarboxylic acid (II or III) was extracted with ether and, after evaporation of this solvent, recrystallized from nitrobenzene or ethyl malonate, m. p. 310°. *Anal.* Found: C, 73.9; H, 3.4. Calcd. for $C_{18}H_{12}O_4$: C, 73.9; H, 4.1.

Dimethyl Ester.—The foregoing acid (1 g.) was added to a 1% ethereal solution of diazomethane (1 g.). The acid dissolved easily, and the ethereal solution, on evaporation, left the ester, which was distilled at 0.1 mm. pressure (b. p. 240°), triturated with methyl alcohol and recrystallized from isopropyl alcohol, m. p. 134°. *Anal.* Found: C, 75.1; H, 4.8. Calcd. for $C_{20}H_{16}O_4$: C, 75.0; H, 5.0.

3-Pyrenyl-acrylic Acid.—3-Pyrene-aldehyde[7] (19 g.), malonic acid (7.5 g.), pyridine (12 cc.) and piperidine (1 cc.) were heated for two hours on the steam-bath. The mixture, which at first became rapidly homogeneous, crystallized spontaneously during this time. It was heated to 150° for five minutes and treated with dilute hydrochloric acid. Pyrenyl-3-acrylic acid (16 g.) after recrystallization from ethyl malonate, formed long needles, m. p. 280°.

Methyl 3-pyrenyl-acrylate was obtained from the acid by heating it with methyl alcohol, while a stream of gaseous hydrochloric acid passed through the solution. The reaction product was diluted with water, extracted with ether and the ether residue recrystallized from benzene or glacial acetic acid; needles, m. p. 146°. *Anal.* Found: C, 84.0; H, 4.7. Calcd. for $C_{20}H_{14}O_2$: C, 83.9; H, 4.9.

Methyl β-(3-Pyrenyl)-propionate.—The foregoing ester (1.5 g.) was hydrogenated in glacial acetic acid at room temperature in presence of barium sulfate–palladous hydroxide. The absorption of the required amount of hydrogen proceeded smoothly (140 cc. at 27° and 760 mm.) and the reaction product distilled constantly at 200° under 2.5 mm. pressure. It was triturated with and recrystallized from methyl alcohol; m. p. 81°. *Anal.* Found: C, 83.8; H, 5.4. Calcd. for $C_{20}H_{16}O_2$: C, 83.3; H, 5.5.

3-Pyrenyl-acrylic Acid and Diazomethane.—The acid (10 g.) was added in small portions to a 1.4% solution of diazomethane in ether (250 cc.)[13] and kept at room temperature for several days. A solid phase (A) was filtered off and the solution (B) after removal of the solvent distilled under 0.03 mm. pressure. At 228°, a yellowish distillate was obtained, which was triturated with and then recrystallized from methyl alcohol. The crystals, m. p. 105–106°, were identified with methyl β-(3-pyrenyl)-crotonate (IV); yield, 3 g. *Anal.* Found: C, 83.9; H, 5.2. Calcd. for $C_{21}H_{16}O_2$: C, 84.0; H, 5.3.

The solid phase (A) was also distilled under 0.035 mm. pressure, and the fraction boiling at 180–200° isolated. It solidified spontaneously and was recrystallized from benzene; yield, 6 g.; m. p. (146°) and mixed m. p. proved the identity with methyl 3-pyrenyl-acrylate.

Synthesis of β-(3-Pyrenyl)-crotonic Acid.—3-Acetylpyrene prepared according to Vollmann and co-workers[14] (11 g.), zinc (4.6 g., "Zinkflitter fein," Kahlbaum), methyl bromo-acetate (9 cc.) and benzene (100 cc.) were boiled for ten hours. The reaction product was decomposed with ice and dilute sulfuric acid and the benzene evaporated from the organic layer after washing and drying. The crude hydroxy-ester (V, 13 g.) was heated at 140° for three hours with 85% formic acid (30 g.). The reaction product was diluted with water, extracted with ether and the ethereal solution washed with sodium carbonate solution, dried and distilled. Methyl β-(3-pyrenyl)-crotonate (IV) distilled at 215–217° under 0.025 mm. pressure; it was triturated with methyl alcohol and recrystallized from the same solvent and from light petroleum; yield, 40%, m. p. 105.5°. *Anal.* Calcd. for $C_{21}H_{16}O_2$: C, 84.0; H, 5.3; OCH_3, 10.3. Found: C, 83.9; H, 5.3; OCH_3, 11.3. This substance was identified with the product obtained above from β-(3-pyrenyl)-acrylic acid. When the ester was boiled with three times the theoretical amount of potassium hydroxide in the form of a 15% methyl alcohol solution for five to six

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(9) Auwers and Koenig, *Ann.*, **496**, 252 (1932); Auwers and Ungemach, *Ber.* **66**, 1198 (1933).

(10) E. Bergmann and F. Bergmann, *J. Org. Chem.*, **3**, 128 (1938). Compare Kawai, Sugimoto and Sugiyama, *Ber.*, **72**, 953 (1939).

(11) F. Mayer and Mueller, *ibid.*, **60**, 2278 (1927).

(12) See also for references, Ch. Weizmann and E. Bergmann, *Scripta Academica Hierosolymitana*, **1**, 12 (1938).

(13) Prepared according to Adamson and Kenner, *J. Chem. Soc.*, 1554 (1937).

(14) Vollmann and co-workers, ref. 1; compare Dziewonski and Trzesinski, *Chem. Abs.*, **32**, 4978 (1938).

hours, saponification took place. The solvent was evaporated, the potassium salt acidified and **β-(3-pyrenyl)-crotonic acid** recrystallized from ethyl malonate; m. p. 233°. *Anal.* Found: C, 83.5; H, 5.2. Calcd. for $C_{20}H_{14}O_2$: C, 83.9; H, 4.9.

Pyrene and β-Chlorobutyryl Chloride.—At room temperature and under constant stirring, β-chlorobutyryl chloride (14 g.) was added slowly to a mixture of pyrene (20 g.), carbon disulfide (75 cc.) and aluminum chloride (30 g.). The mass was stirred for two more hours, and decomposed with ice and concentrated hydrochloric acid. The carbon disulfide solution was washed with sodium carbonate solution, dried and distilled. The *ketone* (VI?) formed distilled at 170° under 0.02 mm. pressure, and after trituration with methyl alcohol was recrystallized from the same solvent and from low-boiling light petroleum; m. p. 101°. *Anal.* Found: C, 88.4; H, 5.4. Calcd. for $C_{20}H_{14}O$: C, 88.9; H, 5.2.

Summary

Pyrene adds two atoms of lithium, C_4 and C_9 or C_3 and C_{10} being the most likely positions. Carbonation gave a dihydro-pyrene-dicarboxylic acid.

Some reactions of β-(3-pyrenyl)-acrylic acid have been studied. With diazomethane, besides esterification, methylation occurs at the β-carbon atom.

With β-chlorobutyryl chloride and aluminum chloride, pyrene gives a keto-cyclopenteno derivative, probably of formula (VI). The analogous reaction of anthracene leads to two isomeric ketones $C_{18}H_{14}O$.

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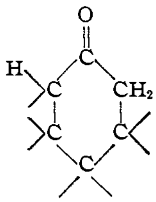
Cerin and Friedelin. VI. Surface Films of Cerin, Friedelin and Some Related Substances

BY NATHAN L. DRAKE AND JOHN K. WOLFE[1]

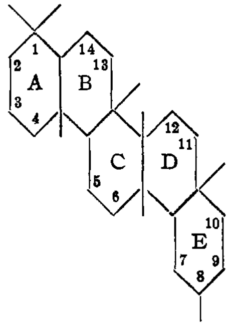
Previous work[2] has shown that friedelin is a polycyclic triterpenoid ketone, $C_{30}H_{50}O$, containing the unit of structure, I.



I

Dehydrogenation of friedelinol, the carbinol corresponding to friedelin, has not yielded isolable oxygen-containing fragments from which the location of I in the polymethylperhydropicene nucleus might be inferred. It is the purpose of the present paper to describe studies of surface films of certain relatives of friedelin. From these investigations we have been able to draw certain general conclusions regarding the position of the carbonyl group in friedelin.

Dehydrogenation of friedelinol yields: 1,2,7-trimethylnaphthalene, 1,2,5-trimethylnaphthalene, 1,2,5,6-tetramethylnaphthalene (in small quantity), 1,2,8-trimethylphenanthrene and 1,8-dimethylpicene.[3] The carbon skeleton, II, proposed by Ruzicka for oleanolic acid[4] explains the formation of these dehydrogenation products fairly satisfactorily.



II

The unit, I, might be located in II with its carbonyl at one of the three positions 14, 5, or 9. Position 14, 5, or 9 (cpd. III) is most satisfactory in the light of the surface film studies described below, but the carbonyl of friedelin cannot be here because friedonic acid, the keto acid obtained from friedelin by oxidation, has a hydrogen atom on the carbon adjacent to its carbonyl group.[2b] Position 5 (cpd. IV) is an unsatisfactory location for the

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[1] From the Ph.D. dissertation of John K. Wolfe, University of Maryland, 1939.

[2] Drake and Campbell, (a) THIS JOURNAL, **58**, 1681 (1936); (b) Drake and Wolfe, *ibid.*, **61**, 3074 (1939).

[3] Drake and Haskins, *ibid.*, **58**, 1684 (1936); Houston, Dissertation, University of Maryland, 1938.

[4] Ruzicka, Goldberg and Hofmann, *Helv. Chim. Acta*, **20**, 325 (1937).