

a sample melting at 79–81°. Comparison of this material with an authentic sample¹¹ confirmed this structure.

α-Benzoyl-9-anthranilacetonitrile. To a mixture of 9-anthraldehyde¹² (4.6 g.) and benzoyl chloride (3.5 g.) in 30 ml. of dioxane at 0–5°, sodium cyanide (2.5 g.) in water (40 ml.) was added dropwise with stirring during the course of 1 hr. The resulting solution after stirring for an additional 2 hr. and standing at room temperature overnight was poured into water. The resulting oil solidified on standing and was taken up in ether. Partial removal of the solvent gave crystals melting at 146–150°; yield 1.8 g. Two successive crystallizations from benzene and from ethyl acetate, respectively, gave a sample melting at 148.5–150°.

(11) L. Fieser and J. L. Hartwell, *J. Am. Chem. Soc.*, **60**, 2555 (1938).

(12) L. F. Fieser, J. L. Hartwell, and J. E. Jones, *Org. Syntheses, Coll. Vol. III*, 98 (1955).

Anal. Calcd. for C₂₃H₁₅O₂N: C, 81.90; H, 4.45. Found: C, 81.63; H, 4.44.

Further concentration of the ether gave 2.0 g. of anthraldehyde.

9-Methyl-10-cyanoanthracene. 9-Methyl-10-anthraldehyde oxime¹³ (0.94 g.) was refluxed with 20 ml. of acetic anhydride for 15 min. The solution after cooling was poured into water and gave 0.80 g. of 9-methyl-10-cyanoanthracene melting at 208–210°. One recrystallization from a mixture of benzene and 60–68° petroleum ether melted at 208–210°. A mixture with the above oxime melted at 170–178°.

Anal. Calcd. for C₁₆H₁₁N: C, 88.48; H, 5.07. Found: C, 87.76; H, 5.02.

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(13) L. F. Fieser and J. E. Jones, *J. Am. Chem. Soc.*, **64**, 1666 (1942).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

Acenaphthene Chemistry. V.¹ 1,2-Diketopyracene²

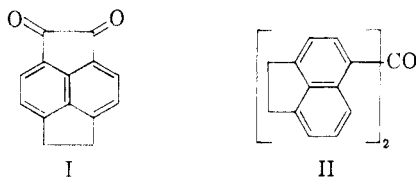
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1,2-Diketopyracene was prepared by the reaction of oxalyl bromide and acenaphthene with aluminum bromide as the catalyst. Reduction of the diketone formed pyracene. The reaction of 1,2-diketopyracene with phenylmagnesium bromide formed 1,2-diphenyl-1, 2-dihydroxypyracene which was oxidized to 5,6-dibenzoylacenaphthene.

The older literature describing attempts to synthesize compounds containing two five-membered rings fused to the opposite *peri* positions of naphthalene has been reviewed by Kloetzel and Chubb.³ These authors prepared 1,2-benzopyracene. Anderson and Wade⁴ synthesized the unsubstituted hydrocarbon, pyracene.

In one of the early attempts to prepare a compound with the pyracene ring system, Fleischer and Wolff⁵ treated acenaphthene with oxalyl bromide in the presence of aluminum chloride and obtained an impure compound which was described as pyracene hemiquinone (1,2-diketopyracene, I). The analysis did not confirm this suggested structure. We repeated their experiment and obtained



(1) Previous paper: H. J. Richter and F. B. Stocker, *J. Org. Chem.*, **24**, 214 (1959).

(2) This work was supported by the National Institute of Health, Grant Cy-2997-Cy; taken from a portion of the thesis submitted by F.B.S. to the University of Colorado, in partial fulfillment of the requirements for the Ph.D. degree, 1958.

(3) M. C. Kloetzel and F. L. Chubb, *J. Am. Chem. Soc.*, **72**, 150 (1950).

(4) A. G. Anderson, Jr., and R. H. Wade, *J. Am. Chem. Soc.*, **74**, 2274 (1952).

(5) K. Fleischer and P. Wolff, *Ber.*, **53**, 925 (1920).

in low yield the yellow product which they described as pyracene hemiquinone. It was purified chromatographically and shown to correspond to di-5-acenaphthyl ketone (II) described by Dziewonski and co-workers.⁶ This product was not totally unexpected since it is known that oxalyl halides decompose to carbon monoxide and carbonyl halide.⁷ Liebermann⁸ obtained 5-acenaphthoic acid from acenaphthene and oxalyl chloride with aluminum chloride catalyst and in our experiment, also, some of the acid was obtained.

With aluminum bromide as the catalyst we obtained yellow needles, m.p. 305–306°. This new substance formed a bisulfite addition compound and a quinoxaline derivative indicating 1,2-diketopyracene (I). A Clemmensen reduction of the 1,2-diketone formed pyracene which was confirmed by a mixed melting point determination with an authentic sample.⁹

In previous work¹ it was shown that the dibenzoylation of acenaphthene with aluminum chloride as catalyst formed 3,6-dibenzoylacenaphthene m.p. 149–150°. The 5,6-dibenzoyl derivative, m.p. 207–208°, was obtained from 1,2-diketopyracene by reaction with phenylmagnesium bromide and oxidizing the resulting 1,2-diphenyl-1,2-pyra-

(6) K. Dziewonski, W. Kahl, W. Koezoroska, and A. Wulffsohn, *Bull. intern. acad. polon.*, **A**, 194 (1933).

(7) R. C. Fuson, *Advanced Organic Chemistry*, John Wiley and Sons, Inc., New York, N. Y., 1950, p. 335.

(8) C. Liebermann and M. Zsuffa, *Ber.*, **44**, 202 (1911).

(9) We are indebted to Prof. Anderson⁴ for supplying us with a sample of pyracene.

enediol with lead tetraacetate. A study of the glycols prepared from I is currently in progress.

EXPERIMENTAL

The reaction of oxalyl bromide and acenaphthene with aluminum chloride as the catalyst. Di-5-acenaphthyl ketone. This reaction was carried out as described by Fleischer and Wolff.⁵ The crude product obtained from the reaction of 0.2 mole acenaphthene and 0.2 mole oxalyl bromide was extracted with 2 l. of boiling benzene. The benzene solution was in turn extracted with 10% aqueous sodium carbonate solution, which on acidification gave 4.56 g. of a cream colored solid, m.p. 212–214°, which was shown to be 5-acenaphthoic acid. The benzene solution was evaporated to dryness and the resulting yellow-brown residue was chromatographed on an alumina column. Elution with benzene gave a small amount of bright yellow crystals, m.p. 220–226°. Four recrystallizations from benzene raised the melting point to 237–238° (lit. 234–235°).⁶ This was reported as 1,2-diketopyracene, m.p. 226°.⁵

Anal. Calcd. for C₂₅H₁₈O: C, 89.79; H, 5.42. Found: C, 90.23; H, 5.42.

1,2-Diketopyracene. Anhydrous aluminum bromide (62.5 g., 0.2 mole) was added in portions to a stirred solution of 0.1 mole (17.6 g.) of acenaphthene and 0.1 mole (25 g.) of oxalyl bromide in 1400 ml. of dry carbon disulfide maintained at 0°. After warming to room temperature overnight the mixture was maintained at 35° for 30 min. The carbon disulfide was decanted from the dark residue which was then hydrolyzed with cold dilute hydrochloric acid. Steam was passed through the hydrolyzed mixture to remove residual carbon disulfide. The carbon disulfide decanted from the reaction mixture did not contain any reaction product. The brown residue (20.0 g.) was extracted with hot toluene. This toluene solution was extracted with 10% aqueous sodium carbonate and then extracted exhaustively with saturated sodium bisulfite solution. A precipitate of the bisulfite addition compound formed in the aqueous layer. This was removed by filtration and treated with dilute sodium hydroxide to liberate the diketone which was combined with the precipitate obtained by treating the sodium bisulfite extract with solid sodium carbonate. There was obtained 3.85 g. (16.2%) of product m.p. 303–304°. The yields in subsequent preparations were very inconsistent. It was crystallized from methyl ethyl ketone and then from acetone to yield orange-yellow needles, m.p. 305–306°. It was found advantageous to extract with aqueous sodium bisulfite at 80° as outlined for the isolation of acenaphthenequinone.¹⁰

Anal. Calcd. for C₁₄H₈O₂: C, 80.76; H, 3.87. Found: C, 81.01; H, 3.87.

In the first preparation of this compound, oxalyl bromide (44.0 g., 0.204 mole) in 100 ml. of carbon disulfide was added dropwise during the course of 1.5 hr. to a solution of 112.0 g. (0.420 mole) of anhydrous aluminum bromide and 31.0 g. (0.201 mole) of acenaphthene in 250 ml. of dry carbon disulfide. The mixture was kept at 0° during the addition and for 6 hr. after the addition. A brown sticky mass separated which made stirring difficult. The carbon disulfide was decanted and the brown solid remaining (54.0 g.) was extracted with hot toluene. The product was isolated by bisulfite extraction. This preparation gave only 0.50 g. (1.2%) 1,2-diketopyracene, m.p. 303–304°. Evaporation of the toluene left a brown residue from which di-5-acenaphthyl ketone was obtained.

When acenaphthene dissolved in carbon disulfide was added dropwise to a solution of aluminum bromide and oxalyl bromide in the same solvent at 0° a brown solid was produced from which no di-5-acenaphthyl ketone or 1,2-diketopyracene could be isolated. At high dilution this in-

verse addition gave the same brown product. This substance could not be crystallized and was not investigated further.

The reaction of 1,2-diketopyracene with o-phenylenediamine. A mixture was prepared from 0.0893 g. of 1,2-diketopyracene, 0.0464 g. of o-phenylenediamine, and 10 ml. of glacial acetic acid. Warming for 15 min. produced a clear yellow solution. The cooled solution was poured into 200 ml. of cold water. A pale yellow precipitate formed which was removed by filtration and dried, m.p. 274–276°. The yield was quantitative. Crystallization from benzene-petroleum ether, b.p. 60–70°, gave pale yellow micro needles, m.p. 275–276°.

Anal. Calcd. for C₂₀H₁₂N₂: N, 10.00. Found: N, 9.76.

Pyracene. Amalgamated zinc (10 g.) was added to a mixture of 8 ml. of water, 20 ml. of concentrated hydrochloric acid, 25 ml. of toluene, and 0.50 g. of 1,2-diketopyracene. The mixture was boiled vigorously under reflux for 30 hr. Additions of 5 ml. of concentrated hydrochloric acid were made every 6 hr. The color in the toluene layer gradually changed from pale orange to yellow. The toluene layer was separated and the solvent was removed. The solid that remained was sublimed yielding very pale yellow prisms, m.p. 212–215° (sealed capillary). The sublimed solid (0.09 g., 21%) was recrystallized from cyclohexane and petroleum ether, b.p. 60–70°, to yield colorless prisms, m.p. 218–220° (sealed capillary) (lit.² 214.5–217.5°). The infrared spectra of an authentic sample of pyracene⁹ and the compound obtained above are identical.

1,2-Diphenyl-1,2-pyracenediol. To a suspension of 1.0 g. (0.0048 mole) of 1,2-diketopyracene in 50 ml. of dry benzene was added 15 ml. of an ether solution of phenylmagnesium bromide (3.0 molar). The mixture became warm and the diketone dissolved giving an orange solution. This solution was refluxed for 29 hr. and hydrolyzed with dilute acetic acid. The benzene layer was subjected to steam distillation which left a brown oily residue. The water was decanted and the oil was dried. Attempts to crystallize the crude product were unsuccessful. An alumina column was prepared in dry petroleum ether, b.p. 60–70°, and to it was added 1.47 g. of the oil dissolved in 10 ml. of dry benzene. Elution with petroleum ether, b.p. 60–70°, removed a low melting solid (probably biphenyl). Equal portions of petroleum ether (b.p. 60–70°)-diethyl ether removed a product which separated as white needles during evaporation of the solvent. This product, m.p. 179–181° (0.67 g. 38%), was recrystallized from ethanol-water to yield white needles, m.p. 180–181°.

Anal. Calcd. for C₂₆H₂₀O₂: C, 85.69; H, 5.53. Found: C, 85.98; H, 5.81.

4,5-Dibenzoylnaphthalic anhydride. To a solution of 0.42 g. (0.0012 mole) of 1,2-diphenyl-1,2-pyracenediol in 20 ml. of glacial acetic acid was added 1.0 g. (0.010 mole) of chromium trioxide dissolved in a minimum of water. The mixture was heated at reflux for 2 hr. During this time a white solid separated. The cooled solution was filtered and the solid was washed with acetic acid and dried. There was obtained 0.35 g. (75%) of product, m.p. 279–283°. Crystallization from dilute acetic acid with decolorizing charcoal gave colorless prisms, m.p. 283–284°.

Anal. Calcd. for C₂₆H₁₆O₃: C, 76.84; H, 3.47. Found: C, 76.96; H, 3.52.

5,6-Dibenzoylacenaphthene. To a solution of 0.12 g. (0.33 mmole) of 1,2-diphenyl-1,2-pyracenediol in 7 ml. of cold glacial acetic acid was added 0.15 g. (0.34 mmole) of lead tetraacetate and the mixture was shaken until the solid dissolved (2 to 5 min.). Colorless crystals began to separate. The mixture was allowed to stand overnight and the product was separated by filtration. The yield of crystals, m.p. 205–207°, was quantitative. One recrystallization from an alcohol-water mixture gave colorless needles, m.p. 207–208°.

Anal. Calcd. for C₂₆H₁₈O₂: C, 86.17; H, 5.01. Found: C, 86.32; H, 4.86.

(10) C. F. H. Allen and J. A. Van Allen, *Organic Synthesis*, Coll. Vol. III, 1 (1955).