

cooled to -20° . The crystalline material obtained was pale tan in color and melted at 137° with decomposition.

p-Benzoquinonedioxime was prepared by the method of J. H. Trepagnier.¹¹ Decomposition of our samples began in the range 230° to 240° .

p-Benzoquinonedioxime to *p*-Nitroaniline. Three g. (0.0217 mole) of the dioxime and 170 g. of polyphosphoric acid (Victor Chemical Works, 115% ortho equivalent) in a 200 ml., 3-necked flask were heated by an oil bath to $133-137^{\circ}$ for 90 min. with rapid stirring. The reaction mixture was poured over a 400-500 ml. volume of crushed ice. The purple, aqueous solution was filtered by suction to remove a small amount of black, gummy material and then extracted 12-14 times with 50 ml. portions of ether.

The combined ether extracts were washed with two portions of 10% sodium hydroxide, dried over anhydrous magnesium sulfate, and distilled. The residue, after removing the last trace of solvent i.v., weighed 1.26 g. (42%) and melted only one degree lower than pure *p*-nitroaniline. Identification was made by conversion to the acetyl and benzenesulfonyl derivatives and determination of mixed melting points with authentic samples.

The sodium hydroxide wash solution was neutralized to pH 7.5-8 and extracted four times with ether, yielding 0.1 g. of the dioxime.

p-Benzoquinonemonoxime benzenesulfonate. A modification of previously published procedures was used.^{3,5,12} To 6.0 g. (0.049 mole) of nitrosophenol dissolved in 70 ml. of pyridine was added slowly 8.6 g. (0.049 mole) of benzenesulfonyl chloride, keeping the temperature of the reaction mixture under 25° . After the reaction mixture had been

allowed to stand for 5 min., water was added slowly, with cooling, to precipitate the benzenesulfonate. The product was filtered, washed with 3*N* HCl and water until the odor of pyridine had been removed, and dried in a vacuum desiccator. The yield was 11.2 g. (94%) of fine, yellow needles, m.p. $130-131^{\circ}$, sufficiently pure for the subsequent steps. Pure material can be obtained by recrystallization from ether, m.p. $132.5-133^{\circ}$.

p-Benzoquinonedioxime bis(benzenesulfonate)s. To 4 g. (0.029 mole) of *p*-benzoquinonedioxime dissolved in 45 ml. of pyridine was slowly added 14.8 g. (0.87 mole) of benzenesulfonyl chloride keeping the temperature of the reaction mixture under 55° . After 5 minutes of shaking, the reaction mixture was diluted with 150 ml. of water. The resulting precipitate was filtered, washed with 3*N* HCl and water, and dried in a vacuum desiccator. The yield was 11.95 g. (95%) of tan product which decomposed and sintered over the range $160-170^{\circ}$.

This product was recrystallized, with decolorization, from acetone to effect the primary separation of the high and low melting forms. The granules which formed, consisting mainly of the higher melting form, were filtered and dried, and purified by repeated crystallization from dry acetone. Sparkling, chunky crystals, m.p. $196-197^{\circ}$ (dec.), or $203-204^{\circ}$ (dec.) in a preheated bath.

Anal. Calcd. for $C_{18}H_{14}O_6N_2S_2$: C, 51.66; H, 3.37; N, 6.70; S, 15.33. Found: C, 52.15; H, 3.65; N, 6.85; S, 16.01.

To the filtrate from the primary separation was added enough water to precipitate the remainder of the derivative. By recrystallization of this product from carbon tetrachloride, the pure low melting form was obtained. Small white needles, m.p. $157-158^{\circ}$ (dec.).

Anal. Calcd. for $C_{18}H_{14}O_6N_2S_2$: C, 51.66; H, 3.37; N, 6.70; S, 15.33. Found: C, 51.38; H, 3.43; N, 6.21; S, 15.43.

(11) U. S. Patent 2,446,165, *Chem. Abstr.*, **42**, 8213d (1948).

(12) E. Bornstein, *Ber.*, **29**, 1484 (1896).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY STATE UNIVERSITY OF IOWA]

Abnormal Beckmann Rearrangement of 9,10-Dihydro-9,10-(11-ketoethano)anthracene Oxime¹

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9,10-Dihydro-9,10-(11-ketoethano)anthracene oxime undergoes an abnormal Beckmann rearrangement when treated with either phosphorus pentachloride, benzenesulfonyl chloride and alkali, polyphosphoric acid, boron trifluoride, or hydrogen chloride. The first two reagents formed 9-anthranylacetone nitrile while the last three gave 9-anthranylacetamide. The structures of these two products were demonstrated by synthesis.

In previous work on the determination of the importance of three dimensional structures in the analgetic behavior of compounds, 9,10-dihydro-9,10-(11-aminoethano)anthracenes were synthesized and found to be inactive as analgetics.³

Attempts to modify this three dimensional structural feature by including the nitrogen in the bridge is described in the present work. A Beckmann rearrangement of 9,10-dihydro-9,10-(11-ketoethano)-

anthracene oxime (I) was tried with phosphorus pentachloride and found to yield 9-anthranylacetone nitrile (II). This reaction is analogous to the second order Beckmann rearrangement observed with the oximes of aldehydes, pivalophenone⁴ and other tertiary ketones⁵ under similar conditions.

Since benzenesulfonyl chloride and alkali and hydrogen chloride in acetic acid often give a normal rearrangement with some of these examples,⁴ these reagents were also tried on the oxime I. The first of these gave the nitrile II while the

(1) Abstracted in part from the Ph.D. thesis of J. V. Hallum, August 1952.

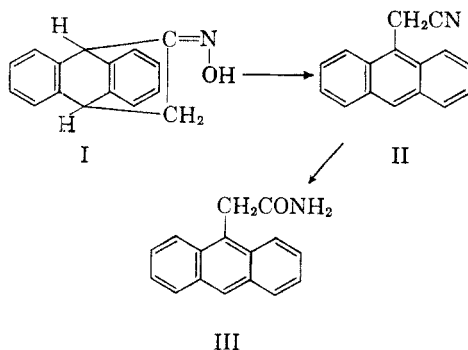
(2) Public Health Research Fellow of the National Institutes of Health, 1951-52.

(3) S. Wawzonek and J. V. Hallum, *J. Org. Chem.*, **18**, 288 (1953).

(4) R. F. Brown, N. M. van Gulick, and G. H. Schmid, *J. Am. Chem. Soc.*, **77**, 1094 (1955).

(5) R. E. Lyle and G. G. Lyle, *J. Org. Chem.*, **18**, 1058 (1953).

second one produced a mixture of the amide III and the nitrile II in which the former predominated. The newer Beckmann reagents, polyphosphoric acid⁶ and boron trifluoride,⁷ behaved similarly and



caused a rearrangement to 9-anthranylacetamide (III). Abnormal Beckmann rearrangements have already been reported for polyphosphoric acid.⁸ The present example is the first observed using boron trifluoride.

The structure of the nitrile was demonstrated by synthesis from 9-chloromethylantracene using sodium cyanide and by the catalytic reduction of α -benzoxy-9-anthranylacetonitrile. The other compound possible from the Beckmann reaction, 9-methyl-10-cyanoanthracene, was also synthesized from 10-methyl-9-anthraldehyde oxime and was found to be different from the Beckmann rearrangement product (II).

The identity of 9-anthranylacetamide (III) was demonstrated by its formation in the hydrolysis of the acetonitrile (II) with boron trifluoride in acetic acid and water. The use of sulfuric acid in this reaction gave mainly a mixture of 9-anthranylacetic acid and its decarboxylated product, 9-methylantracene.

The observed abnormal Beckmann rearrangement is unique in that no tertiary groups are attached to the ketone moiety in the molecule. The tendency to form an aromatic system by the loss of a proton in the group involved, seems to be the driving force in this example.

EXPERIMENTAL⁹

9-Anthranylacetonitrile (II). (a) 9,10-Dihydro-9,10-(11-ketoethano)anthracene oxime³ (25 g.) was dissolved in 300 g. of phosphorus oxychloride at 0° and phosphorus pentachloride (30 g.) was added slowly keeping the temperature below 10°. The resulting solution was heated to reflux and poured onto ice. The pale green solid (21.8 g.) was filtered and after crystallization twice from petroleum ether (b.p. 86–100°) and once from acetic acid, melted at 161–3°.

(6) E. C. Horning and V. L. Stromberg, *J. Am. Chem. Soc.*, **74**, 2680 (1952).

(7) C. R. Hauser and D. S. Hoffenberg, *J. Org. Chem.*, **20**, 1482 (1955).

(8) R. K. Hill and R. T. Conley, *Chem. & Ind. (London)*, 1314 (1956).

(9) Melting points are not corrected.

Anal. Calcd. for $C_{16}H_{10}N$: C, 88.48; H, 5.07; N, 6.45. Found: C, 88.03; H, 4.89; N, 6.96.

(b) The oxime (II) (1.17 g.) was mixed with benzenesulfonyl chloride (0.9 g.), and sodium hydroxide (0.5 g.) in 20 ml. of acetone containing 5 ml. of water and refluxed for 2 hr. The resulting dark red solution upon pouring into water gave 0.85 g. of the nitrile melting at 159–162° after one recrystallization from acetic acid.

(c) 9-Chloromethylantracene¹⁰ (0.4 g.) in 20 ml. of 95% ethanol was refluxed with sodium cyanide (0.1 g.) in 1 ml. of water for 1 hr. Concentration of the solution gave the nitrile (II) (0.1 g.) melting at 159–163° after one crystallization from acetic acid.

(d) α -Benzoxy-9-anthranylacetonitrile (1 g.) was refluxed in 10 ml. of tetralin with palladium black (0.2 g.) for 19 hr. Removal of the tetralin and naphthalene by steam distillation gave the nitrile (II) (0.25 g.) melting at 162–164° after crystallization from petroleum ether (86–100°) and acetic acid respectively.

9-Anthranylacetamide (III). (a) 9,10-Dihydro-9,10-(ketoethano)anthracene oxime (2.35 g.) was heated with stirring with polyphosphoric acid (64 g.) at 100–130° for 5 min. and at 130° for an additional 5 min. The resultant dark green solution was cooled and poured into water. The gray solid (2.05 g.) obtained after successive crystallizations from ethyl acetate and ethanol gave yellow needles melting at 253–6° (dec.).

Anal. Calcd. for $C_{16}H_{13}ON$: C, 81.70; H, 5.53. Found: C, 81.31; H, 5.31.

(b) 9,10-Dihydro-9,10-(11-ketoethano)anthracene oxime (I) (2.0 g.) in 20 ml. of acetic acid was treated with gaseous boron trifluoride until the solid went into solution. Addition of water and dilute sodium hydroxide precipitated 1.8 g. of 9-anthranylacetamide (III).

(c) The oxime I (5.0 g.) in acetic acid (110 ml.) was treated with gaseous hydrogen chloride for 30 min. and the resulting solution was allowed to stand for 24 days. The solution was resaturated with hydrogen chloride several times during this period. The solid (2.3 g.) was filtered off and melted at 250–255° (dec.). The filtrate was poured into water and extracted with methylene chloride. The extract after washing with sodium carbonate solution was concentrated and gave an additional 0.92 g. of the amide (III). Further concentration gave a mixture (0.25 g.) of the amide (III) and the oxime (I). Evaporation to dryness gave a mixture (1.5 g.) consisting of the nitrile (II), amide (III), and the oxime (I).

(d) 9-Anthranylacetonitrile (II) (0.5 g.) in a mixture of acetic acid (20 ml.) and water (2 ml.) was treated with gaseous BF_3 until the temperature reached 140°. The resulting solution was cooled and treated with 6*N* sodium hydroxide (130 ml.). The solid formed was filtered; yield, 0.51 g. Crystallization from ethyl acetate gave 9-anthranylacetamide melting at 253–255° (dec.).

9-Anthranylacetic Acid. 9-Anthranylacetonitrile (III) (3.0 g.) was refluxed in acetic acid (75 ml.) with 50% sulfuric acid (25 ml.) for 3 hr. The resulting solution was poured into water and extracted with ether. Extraction of the ether with sodium carbonate followed by acidification gave 9-anthranylacetic acid (1.61 g.) melting at 212–220° (dec.). Two recrystallizations from benzene gave a sample melting at 215–226° (dec.). The actual melting point varied with the rate of heating.

Anal. Calcd. for $C_{16}H_{12}O_2$: C, 81.36; H, 5.09. Found: C, 81.42; H, 5.04.

The ether layer on concentration gave impure 9-anthranylacetamide (0.25 g.) melting at 240° and 9-methylanthracene which after one crystallization from methanol melted at 75–78°; yield 0.5 g. A second crystallization gave

(10) W. T. Hunter, J. S. Buck, F. W. Gubitz, and C. H. Bolen, *J. Org. Chem.*, **21**, 1512 (1956).

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

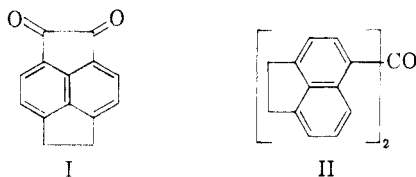
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1,2-Diketopyracene was prepared by the reaction of oxalyl bromide and acenaphthene with aluminum bromide as the catalyst. Reduction of the diketone formed pyracene. The reaction of 1,2-diketopyracene with phenylmagnesium bromide formed 1,2-diphenyl-1,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