[Contribution from the Department of Chemistry, Duke University]

The Cyclization of Nitriles. II. Formation of Anthracene Derivatives.[1,2,3]

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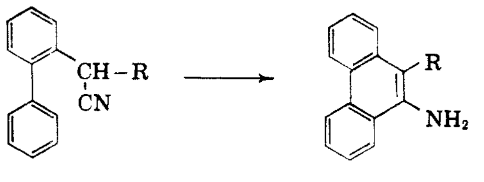
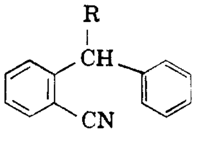
The recently described cyclization of 2-biphenylylacetonitriles I to yield 9-phenanthrylamines (II) has been extended to the cyclization of *o*-benzylbenzonitriles (III). Since the 9-aminoanthracenes are as a class very susceptible to air oxidation, the products isolated in a pure condition were in general hydroperoxides V or transformation products of hydroperoxides.

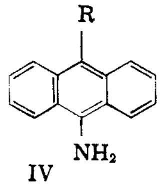
In an earlier communication[3] it was shown that 2-biphenylylacetonitriles I may be cyclized by the action of sulfuric acid to yield the isomeric 9-phenanthrylamines II. It seemed of interest to determine whether the cyclization of *o*-benzylbenzonitriles (III) might be effected to yield 9-aminoanthracenes IV or transformation products thereof.



I II

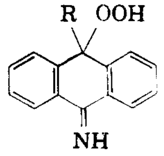


III

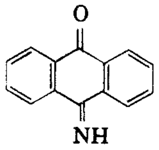


IV

Recently[4] it has been shown that the observed[5,6,7] instability of 9-aminoanthracene (IV, $R = H$) is due to the great ease with which it undergoes autoxidation. If oxygen is bubbled through an ether solution of the amine the product is anthraquinone monoimine (VI) while if the experiment is carried out at 0° it is possible to isolate the unstable intermediate 9-imino-10-hydroperoxy-9,10-dihydroanthracene (V, $R = H$).



V



VI

When *o*-benzylbenzonitrile (III, $R = H$)[8,9] was stirred at 0° with concentrated sulfuric acid, sulfonation appeared to be the chief reaction, but the basic fraction was a yellow solid which turned reddish-brown when exposed to the air. The product thus obtained may have been largely the expected amine as judged from the melting point, but it was not isolated in a pure condition. Recrystallization of the mixture of red-brown and yellow needles from benzene or ethanol led to a gradual color change to uniform red-brown color and a sharpening of the melting point at 218–219°.[10] Further recrystallization led to a broadening of the melting point and the appearance of yellow crystals until after many recrystallizations the silky pale yellow needles of anthraquinone monoimine[4] (VI) were obtained in over-all yields of 13–19%.

It might be expected that cyclization of *o*-cyanotriphenylmethane (III,[11] $R = C_6H_5$) might be accompanied by less sulfonation since the remaining *meso* position of the expected product (IV, $R = C_6H_5$) would be blocked. Actually it was found that cyclization afforded a 65% yield of an amine having the properties of 9-phenyl-10-aminoanthracene (IV, $R = C_6H_5$) as recently described by Rigaudy and Izoret,[4] and which in the presence of air was transformed to the known[4] hydroperoxide (V, $R = C_6H_5$).[12]

Cyclization of the related 1-(*o*-cyanophenyl)-1-phenylethane (III) ($R = CH_3$)[13] afforded the new 9-imino-10-hydroperoxy-10-methyl-9,10-dihydroanthracene (V, $R = CH_3$) in 49% yield. The new hydroperoxide (V, $R = CH_3$) is sufficiently stable to permit the formation of a hydrochloride salt.

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[2] Abstracted from a thesis submitted by D. J. B. in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1955.

[3] For the preceding communication of this series see Bradsher, Little, and Beavers, *J. Am. Chem. Soc.*, **78**, 2153 (1956).

[4] Rigaudy and Izoret, *Compt. rend.*, **238**, 824 (1954).

[5] Goldmann, *Ber.*, **23**, 2522 (1890).

[6] Meisenheimer and Connerade, *Ann.*, **330**, 165 (1904).

[7] Bartlett and Cohen, *J. Am. Chem. Soc.*, **62**, 1183 (1940).

[8] Bergmann, *J. Org. Chem.*, **4**, 1 (1939).

[9] Bradsher, *J. Am. Chem. Soc.*, **62**, 486 (1940).

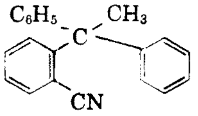
[10] This may be the unidentified product (m.p. 216–217°) obtained by Bartlett and Cohen (Ref. 7) when crystalline 9-aminoanthracene or its benzene solution was allowed to stand for several months.

[11] Bradsher and Smith, *J. Am. Chem. Soc.*, **65**, 451 (1943).

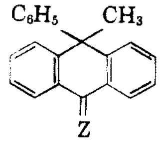
[12] Analytical results obtained with the hydroperoxide (dried at room temperature) showed a low value for carbon possibly due to the incomplete removal of the methanol used as a solvent.

[13] Berliner, *J. Am. Chem. Soc.*, **66**, 533 (1944).

The cyclization of 1-(*o*-cyanophenyl)-1,1-diphenylethane (VII)[14] was of particular interest in



VII



VIII

that the imine expected (VIII, Z = NH) as the first reaction product could not tautomerize to an aromatic amine and no hydroperoxide formation would be expected. Actually the product first obtained appeared to undergo hydrolysis to yield 9-keto-10-methyl-10-phenyl-9,10-dihydroanthracene (VIII, Z = O).

EXPERIMENTAL

Anthraquinone monoimine (VI) *by cyclization of o-benzylbenzophenone* (III), *R = H*). *o*-Benzylbenzonitrile[9] (5 g.) was shaken with 50 ml. of concentrated sulfuric acid at 0° and the mixture was allowed to stand for three hours. The deep red solution was next poured into 100 ml. of ice-water and sodium carbonate added until the solution was basic. The solution was extracted with ether, leaving a considerable amount of ether-insoluble material (probably sulfonate salts) in the aqueous phase. The ethereal extract was evaporated leaving a yellow solid which started turning red-brown as soon as it was exposed to the air. The mixture of yellow and red needles (1–1.2 g.) melted at 120–147°, mostly at 147° and may have been mostly 9-aminoanthracene (lit.[6] softens 135°, m.p. 145–150°).

When the crystals were allowed to stand in air the mixture of yellow and red-brown needles began to become uniformly red-brown. A yellow benzene or ethanol solution turned red on heating or standing for long periods. In one experiment a solution was allowed to stand for two or three days and allowed to crystallize. It yielded 1 g. of long red-brown needles m.p. 218–219°. Upon standing in air or upon repeated recrystallization the melting point became less sharp and then higher and finally melted sharply again at 223–225° at which time it was essentially pure anthraquinone monoimine (VI). Repeated experiments gave yields of 0.7–1.0 g. (13–19%) of the monoimine (VI) by this long process of crystallization.

An analytical sample of the monomine (VI) was obtained from ethanol as long pale yellow silken needles, m.p. 225–226.5° (Lit.[4] m.p. 224–226°.)

Anal.[15] Calc'd for $C_{14}H_9NO$: C, 81.14; H, 4.38. Found: C, 81.24; H, 4.17.

Conversion of the anthraquinone monoimine VI *to anthraquinone.* As further proof of the structure of the monoimine it (100 mg.) was hydrolyzed by refluxing for five hours with a mixture containing hydrochloric acid (20 ml.), water (10 ml.), and ethanol (10 ml.). The product collected and recrystallized from acetic acid melted at 282–284° alone or when mixed with an authentic sample of anthraquinone.

9-Imino-10-hydroperoxy-10-phenyl-9,10-dihydroanthracene (V, R = C_6H_5). One gram of *o*-cyanotriphenylmethane[11] dissolved slowly in 10 ml. of ice-cold concentrated sulfuric acid to yield a yellow solution which turned red on standing. The solution was poured into ice-water yielding a yellow solid which was stirred with sodium carbonate solution. The mixture was extracted with ether and the green fluorescent ethereal solution was evaporated under a vacuum at room temperature to yield 0.65 g. of yellow crystalline material, m.p. 160–163°, which was presumably 10-phenyl-9-aminoanthracene (lit.[4] m.p. 163–164°, golden prisms).

The crystalline material was dissolved in methanol, the yellow solution turning red upon heating or exposure to air. After standing for several days the solution gave colorless crystals which decomposed instantly on the block at 175°.

An analytical sample of the hydroperoxide (V, R = C_6H_5) prepared by recrystallization from methanol-petroleum ether decomposed instantly at 177–178° (Lit.[4] decomposes instantly at 175°).

Anal. Calc'd for $C_{20}H_{15}NO_2$: C, 79.71; H, 5.02. Found: C, 79.07; H, 5.23.

9-Imino-10-hydroperoxy-10-methyl-9,10-dihydroanthracene (V, R = CH_3). 1-(*o*-Cyanophenyl)-1-phenylethane[13] (5 g.) was dissolved in 50 ml. of sulfuric acid, cyclized, and worked up in the usual way. Evaporation of the ether solution at room temperature in an open evaporating dish afforded 2.86 g. (49%) of a yellow solid, m.p. 169–172°.

The analytical sample crystallized from ethanol as pale yellow prisms, m.p. 170–171°.

Anal. Calc'd for $C_{15}H_{13}NO_2$: C, 75.30; H, 5.48. Found: C, 75.15; H, 5.50.

The *hydrochloride* was obtained by precipitation from an ether-ethanol solution by the action of hydrogen chloride.

Anal. Calc'd for $C_{15}H_{14}ClNO_2$: C, 65.34; H, 5.12. Found: C, 65.50; H, 5.25.

With benzoyl chloride in pyridine the imino hydroperoxide (V, R = CH_3) gave a derivative of unknown structure, m.p. 149.5–150.5°.

Anal. Found: C, 78.45; H, 5.00; N, 3.53.

10-Methyl-10-phenyl-9-keto-9,10-dihydroanthracene (VIII, Z = O). One gram of 1-(*o*-cyanophenyl)-1,1-diphenylethane dissolved slowly in 10 ml. of ice-cold concentrated sulfuric acid giving a turbid yellow solution. After three hours it was worked up in the usual way yielding, upon evaporation of the ethereal solution 0.60 g. of pale yellow crystals m.p. 100–103°. After eight recrystallizations from ethanol 9-keto-10-methyl-10-phenyl-9,10-dihydroanthracene (VIII, Z = O) was obtained as white clusters of rectangular prisms, m.p. 161.5–162.5°.

Anal. Calc'd for $C_{21}H_{16}O$: C, 88.70; H, 5.67. Found: C, 88.78; H, 6.10.

A sodium fusion test for nitrogen gave negative results. The infrared absorption spectrum showed a strong absorption at 5.97 μ and no peak in the 2.94–3.03 μ region.

DURHAM, NORTH CAROLINA

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(14) Bradsher and Smith, *J. Am. Chem. Soc.*, **65**, 854 (1943).

(15) Analyses by Galbraith Laboratories, Knoxville, Tennessee.