# ATTEMPTS AT DETECTION OF 9, 10-DEHYDROANTHRACENE*

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Experiments directed towards the syntheses of suitable precursors for 9-10-dehydro-anthracene are described. Pyrolysis of a mercury derivative of anthracene and the reaction of lithium with 9-10-dibromoanthracene are discussed.

The pioneering studies of Wittig,[1] Roberts[2,3] and Huisgen[4] culminated in the recognition that certain benzene derivatives under suitable conditions undergo a 1,2-elimination to give benzyne as the reactive intermediate. These developments posed the question as to whether dehydroaromatic structures whose unsaturation involved other than adjacent positions were capable of existence. Subsequent investigations,[5-7] were therefore directed towards obtaining experimental evidence for a 1, 4-elimination, which in the case of benzene would lead to $p$-phenylene(A) and/or its mesomeric form 1,4-cyclohexadiene-dicarbene (B).
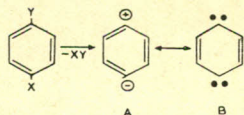


9, 10-Dehydroanthracene (I) was first discussed by Richardson, Browner and Amstutz[8] in 1956. These workers studied the kinetics of halide elimination from aryl halides with piperidine at *ca.* 200°. The energy of activation for these reactions was found to be around 25 kcal/mole. In the case of 9-chloro-and 9-bromoanthracene, however, a reduction in the energy of activation by about 5−9 kcal/mole was observed. It seems likely that the lower energies of activation are to be attributed to the resonance stabilisation of the transition state for the additive nucleophilic substitution rather than to a $p$-elimination mechanism leading to (I)
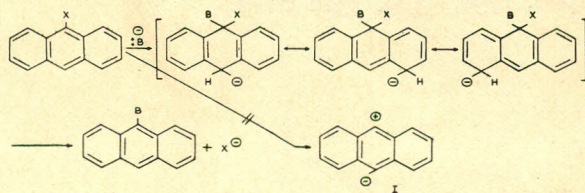


In an attempt to detect I, Hauser[9] investigated the reaction of 9-chloro-10-bromoanthracene (II) with phenyllithium. Mikhaliov and V. Bronovitskaya[10] had already shown the product of this reaction to be 9-chloro-10-lithioanthracene (III), stable in refluxing diethyl ether. Heating II with excess phenyllithium in tetrahydrofuran for 20 hr followed by carboxylation did not give the expected acid. 9-Phenylanthracene (IV) and anthracene were the only products isolated.
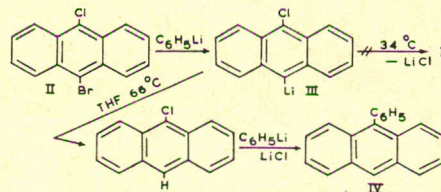


The author's work was directed at trapping I with olefins. It did not seem improbable that I might have the anthracene-9,10-dicarbene (1a) structure, since 1a, unlike anthracene, profits from the complete aromatisation of the outer benzene rings. Further, Ia should add to olefins in the manner of carbenes[11] to give the stable cyclopropane derivatives.

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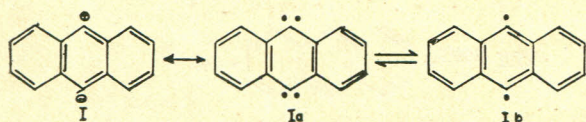
The oxidation of the unknown anthraquinone-9,10-bishydrazone (V) appeared a suitable method for the generation of I $a$. Attempts to prepare V by treating anthraquinone with hydrazine under a variety of conditions failed. Addition of Lewis acids $BF_3$ and $ZnCl_2$ failed to give the desired results.

A plausible route to V was envisaged in the reaction of anthraquinonedioxime bistosylate (VI) with $KNH_2$ in liquid ammonia:
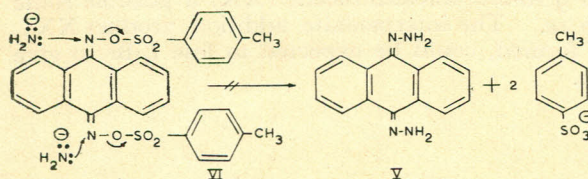
VI was prepared in 77% yield by treating anthraquinonedioxime [12] with tosyl chloride in pyridine. The reaction of VI with $KNH_2$ in liquid ammonia lead mainly to a complex mixture in which V could not be detected. It is conceivable that the electrostatic repulsion between the attacking nucleophile and the lone pair of electrons on the nitrogen atom to be attacked render such a displacement energetically unfavourable. The author is unaware of any case which involves a nucleophilic attack on nitrogen by a nitrogen anion.

Another potential precursor to I is betaine VII which we planned to derive from the amino acid VIII as follows :
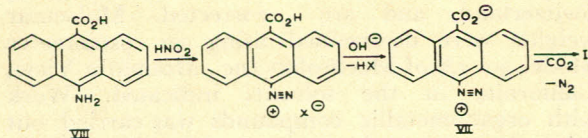
VIII was to be prepared following the general reaction sequence :
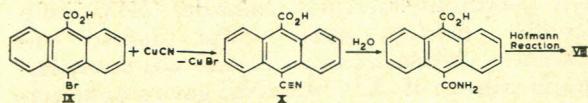
The first step, however, took an unforseen course. Refluxing IX with CuCN in quinoline gave 9-cyanoanthracene XI in 65 % yield. In order to prevent decarboxylation IX was transformed into the methyl ester XII with diazomethane. Refluxing XII with CuCN in quinoline surprisingly gave 14 % of XI. Careful chromatography of the reaction mixture gave a second product. Microanalytical data and the molecular weight determination showed it to be a quinolylanthracene. The product probably has the structure XIII (yield 10%.) We rationalize these changes via the reaction sequence :
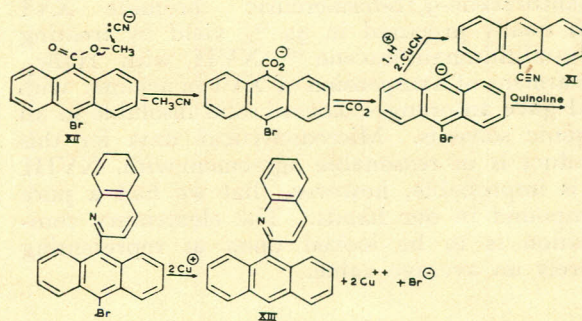
During the course of this work Norman and Ralph [13] reported that the reaction of XII with CuCN gave only XI. Their failure to isolate XIII is to be attributed to their method of work-up. The isolation of XIII in our work lends support to their proposed mechanism involving the anthracene anion which adds to solvent quinoline in a Tschitschibabin reaction. A reductive cleavage of bromide by the $Cu^+$ ion would lead to the isolated XIII. Examples of similar reactions are found in the work of Edwards and Stewart [14] who observed that cupric acetate in pyridine smoothly reduces aryl halides to their parent aromatic hydrocarbons.

We next looked for a suitable mercury derivative of anthracene as a starting material for the generation of I. The mercuration of anthracene has not been documented and it was therefore investigated. Following Huhn,[15] treatment of anthracene with HgO and trichloroacetic acid in $CCl_4$ and subsequent treatment with NaCl

gave 9-anthranylmercuric chloride (XIV) m.p 266–268° in 31% yield. The desired anthracene-9,10-bismercuric chloride was not isolated. Treatment of XIV with NaI gave a quantitative yield of 9,9′-dianthranylmercury (XV). In an attempt to further mercurate XV the undesired cleavage to XIV occurred.
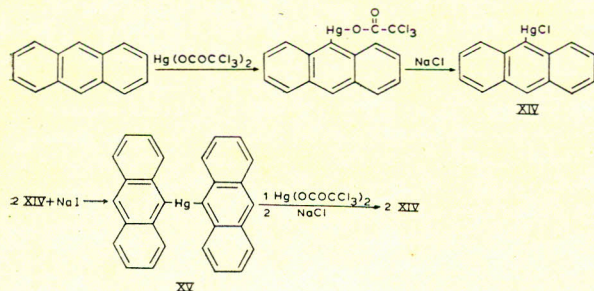


Anthracene-9,10-bismercuric bromide XVI was finally prepared in 42 % yield by treating 9,10-dilithiumanthracene [16] (XVII) with HgBr$_2$. Treatment of a suspension of XVI in acetone with NaI gave an orange-coloured solid insoluble in all organic solvents. Microanalytical data for this product is in reasonable agreement with XVIII. It is improbable, however, that we had a pure compound in our hands. The elementary composition is to be looked upon as representing merely an average value.
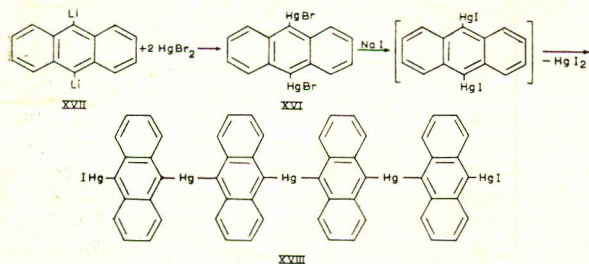


At 400° XVIII decomposed to give metallic mercury and anthracene along with unidentifiable polymeric material. Pyrolysis of XVIII in the presence of acenaphthylene again gave mercury and anthracene (40%). The expected adduct of Ia with acenaphthylene (XIX) could not be detected. Anthracene is most probably formed via free radical intermediates which abstract hydrogen atoms from other anthracene or acenaphthylene nuclei. It is not clear if and to what extent 1b is the precursor of anthracene.
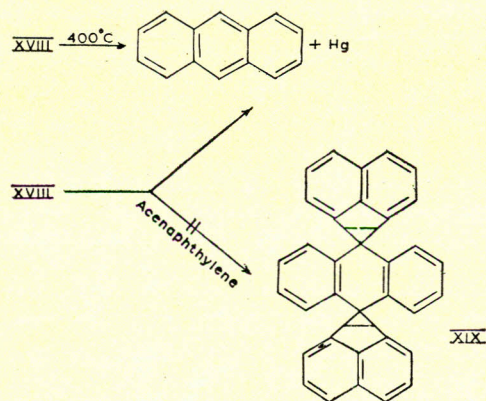


The addition of lithium or sodium metal to the meso positions of anthracene is well known.[17] We envisaged in the analogous addition of lithium to 9,10-dibromoanthracene (XX) a possible route to 1a. The intermediate addition product XXI, if formed, could be expected to lose LiBr to give 1a.
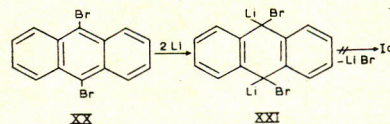


In the event however, anthracene, 9,10-dihydroanthracene (4%) and tetrahydrodianthranyl (10%) were obtained. The product composition suggests halogen –metal exchange reactions followed by condensation and reduction. In order to suppress halogen metal exchange, the reaction was repeated with 9,10-dichloroanthracene, in which case an intractable product mixture was obtained.

### Experimental

All m. ps were determined on an apparatus designed by Dr. Tottoli of W. Buchi, Flawil, Switzerland, and are corrected. Molecular weights were determined using an osmometer Model 30 1A of Mechrolab Inc., Mountain View, California, in the solvents indicated. Work with organometallic compounds was carried out using dry solvents in an inert atmosphere of dry and oxygen-free nitrogen. Alumina used for chromatography was of Merck grade. Microanalyses were carried out by Dr. A. Schoeller, Kronach, Oberfranken, W. Germany.

1. *Anthraquinoedioximebistosylate* (VI).—2.28 g (10 mmole) anthraquinonedioxime[12] was dissolved in the minimum amount of freshly dried and distilled pyridine at room temperature and stirred with 3.8 g (20 mmole) tosyl chloride. After 3 hr the pyridine solution was diluted with ethanol under ice-cooling until crystals began to seperate. The reaction mixture was allowed to crystallise overnight in the refrigerator. White crystals of VI were obtained, 4.1 g (77%), m.p. 180-184°(decomp). The product was recrystallised by dissolving in the minimum amount of pyridine and diluting with ethanol. Pure VI, m.p. 192° (decomp), was obtained ($C_{28}H_{22}N_2S_2O_6$ mol. wt. 546.6 requires : C, 61.52 ; H, 4.05; N, 5.11; S, 11.71, Found: C, 61.40; H, 4.16; N. 5.23; S, 11.70).

2. *Reaction of 9-bromoanthracene-10-carboxylic acid* IX[13] *with CuCN.*—4.62 g (15 mmole) IX and 2g (22 mmole) CuCN were refluxed in 100 ml freshly distilled quinoline for 2 hr. After removal of quinoline by steam distillation the copper salts were extracted with conc $NH_4OH$ and the residue washed with water and dried. Recrystallization from EtOH gave 2 g (65.5%) 9-cyanoanthracene (XI), m. p. 174-(N)176°. Another recrystallization from EtOH gave XI m.p. 177–178° (Found : C, 88.79; H, 4.55; N, 6.93. Calc for $C_{15}H_9N$; C, 88.67; H, 4.43; N, 6.89).

3. *Reaction of Methyl 9-bromoanthracene-10-carboxylate* (XII) [13] *with CuCN.*—3 g (9.5 mmole) XII and 1.2 g (13.4 mmole) CuCN were refluxed in freshly distilled quinoline for 2 hr. The residue obtained after the removal of quinoline and copper salts was chromatographed on 250 g basic $Al_2O_3$. Benzene eluted 0.3 g (15%) XI which on recrystallization from EtOH had m.p. 178-180° (mixed m.p.). Further elution with benzene gave a product which after two recrystallizations from cyclohexanebenzene gave pure 9-[quinolyl-(2)]-anthracene (XIII) m.p. 165-167° (9.6%) (Found: C, 90.58; H, 4.84; N, 4.66; mol. wt. 309.4 in acetone. $C_{23}H_{15}N$ (mol. wt. 305.4) requires: C, 90.46; H, 4.95; N, 4.59. Elution with EtOH gave oily mixtures.

4. *9-Anthranyl mercuric chloride* (XIV).—2.7 g (16.5 mmole) trichloroacetic acid and 0.55 g (3.1 mmole) anthrancene were dissolved in 100 ml $CCl_4$ and stirred with 1.88 g (8.7 mmole) HgO. After 3 hr the $CCl_4$ suspension was decanted from unreacted HgO and the liquid filtered to collect the $CCl_4$-insoluble product. A suspension of this product in MeOH on addition of a saturated solution of NaCl in water was stirred for 1 hr and the resulting precipitate was washed with water and the dried product extracted with 100 ml refluxing $CHCl_3$. On concentrating the $CHCl_3$ solution and allowing to stand 0.4 g (31%) XIV, m.p. 266–268°, was obtained as yellow needles. Recrystallization from $CHCl_3$–$CCl_4$ gave pure XIV, m.p. 270–271° (Found: C, 40.74; H, 2.25; Cl, 7.18. $C_{14}HgCl$ requires: C, 40.64; H, 2.13; Cl, 8.57). The $CCl_4$-insoluble product melting above 310° could not be crystallised.

5. *9,9′-Dianthranylmercury* (XV).—A solution of 0.54 g (3.6 mmole) NaI in 60 ml acetone was added dropwise while stirring to a suspension of 0.73 g (1.77 mmole) XIV in 100 ml acetone. After 2 hr the yellow product was filtered and extracted with hot acetone. 0.48 g (yield quantitative) XV, decomposition above 300°, were obtained. 220 mg of XV when recrystallized from 200 ml dimethyl formamide yielded 154 mg pure XV as orange crystals (Found: C, 60.55; H, 3.43. $C_{28}H_{18}Hg$ required: C, 60.60; H, 3.24).

6. *Reaction of* XV *with Trichloromercuric Acetate.*—A solution of 0.28 g (1.7 mmole) trichloroacetic acid in 20 ml $CCl_4$ and 0.17 g (0.8 mmole) HgO were added while stirring to a suspension of XV in 100 ml $CCl_4$. The reaction mixture was stirred for 24 hr at room temperature. The resulting yellow precipitate was suspended in 100 mlEtOH and the suspension treated with aqueous 0.2 g NaCl. The precipitate was dried and recrystallized from $CHCl_3$–$CCl_4$. 180 mg (50%) XIV, m.p. 269–270° (mixed m.p.), was obtained.

7. *Anthracene-9,10-bismercuric bromide* XVI.— To a solution of 20 g (60 mmole) 9,10-dibromoanthracene[18] in 350 ml. absolute ether under $N_2$ at room temperature was added 90 ml 1.31N n-butyllithium (120 mmole) solution. After 30 min 64.8 g (180 mmole) solid $HgBr_2$ was added to the reaction mixture. After the reaction had slackened, the yellow precipitate was collected, washed with three 300 ml portions of hot MeOH and dried. 18.5 g (42%) XVI was obtained as a yellow powder. Recrystallization from dimethyl sulfoxide gave 6 g (13%) XVI as yellow crystals which decomposed at 310–360° (Found: C, 23.44; H, 1.20; Br, 19.46. $C_{14}H_8Br_2Hg_2$ requires: C, 22.80; H, 1.09; Br, 21.68).

8. *Reaction of* XVI *with NaI.*—A solution of 1.35 g (9 mmole) NaI in 20 ml acetone was added dropwise while stirring to a suspension of 0.9 g (1.2 mmole) XVI in 100 ml acetone. After 3 hr the reaction mixture was centrifuged and the orange-yellow precipitate was washed with a hot aqueous solution of 1 g NaI and then with water till the filtrate was free of halogen. After washing the precipitate with hot acetone and drying at 90°, 0.53 g (90%) of XVIII was obtained as an orange powder. A Beilstein test of this product was weakly positive. It was insoluble in all common solvents. (Found: C, 34.31; H, 1.70; I, 12.06.[19] $C_{56}H_{32}Hg_5I_2$ requires: C, 34.27; H, 1.63; I, 12.94).

9. *Pyrolysis of* XVIII *in the Presence of Acenaphthylene.*— 1.96 g (1 mmole) XVIII were well mixed with 5.4 g.(35 mmole) acenaphthylene and 0.68 g (8 mmole) silver powder. The mixture was heated in a sealed tube at 210–220° for 2 hr. A part that had sublimed to the upper part of the tube (1.6 g) was seperated and chromatographed on 200 g basic $Al_2O_3$. Cyclohexane eluted 0.99 g acenaphthene, m.p. 96–97° (mixed m.p.). $CCl_4$ eluted 0.12 g anthracene, m.p., 215–216° (mixed m.p.). Benzene, $CHCl_3$ and MeOH eluted only tarry material.

Material at the bottom of the tube consisted of metallic mercury and a dark brown reaction mixture which was chromatographed on neutral $Al_2O_3$. Cyclohexane eluted 0.35 g acenaphthene, m.p. 95–96° (mixed m.p.). $CCl_4$ eluted 0.38 g. anthracene, m.p. 215–216° (mixed m.p.). No other products could be isolated. Anthracene was isolated in a total yield of 40%.

10. *Reaction of* 9,10-*dibromoanthracene*[18] XX *with lithium.*—A brown solution was obtained on shaking 5 g (15 mmole) XX with 1 g (145 mmole) lithium shavings in 100 ml absolute ether under $N_2$ in a sealed tube. On shaking the mixture for 2 days a blood-red solution was obtained. After 15 days the mixture was hydrolysed with MeOH, the solvents were removed and the residue extracted with water. Titration of the aqueous extract with $AgNO_3$ (Volhardt) gave 96% free bromide. The organic residue was chromatographed on 300 g neutral $Al_2O_3$. Cyclohexane eluted 265 mg of an impure crystalline product which was rechromatographed on 20 g neutral $Al_2O_3$. Petroleum ether (b.p. 60–70°) eluted light yellow crystals which on recrystallization from MeOH yielded 0.1 g. (4%) 9-10-dihydroanthracene, m.p. 110–111° (mixed

m.p.). Cyclohexane eluted 37 mg anthracene (1.4%) m.p. 215–216° (mixed m. p.). $CCl_4$ finally eluted a colourless product which on recrystallization from cyclohexane gave 0.2 g 9,9′-10,10′-tetrahydro-9, 9′-dianthranyl, m. p. 242–244°(decomp). (Found: C, 93.70; H, 6.54. $C_{28}H_{22}$ requires: C, 93.81; H, 6.18).

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