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# Bicyclic Structures Prohibiting the Walden Inversion. The Synthesis of 1-Bromotriptycene

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This paper describes the synthesis of 1-bromotriptycene, the properties and reactions of which are the subject of the preceding paper. The reactions used in the synthesis are summarized in Fig. 1 and are closely parallel to the scheme used in the synthesis of triptycene[1] except for certain improved steps. The purification of 9-bromoanthracene was facilitated by the use of cuprous chloride or cuprous bromide instead of phenol in the dehydrobromination of anthracene dibromide. Cuprous bromide and cuprous chloride yielded identical products, but cuprous bromide was used to avoid all danger of halogen interchange. In the reduction of the dioxime to the diamine, sodium sulfide in ethyl alcohol solution was found to possess advantages over stannous chloride previously used. In the deamination of the diamine entrance of halogen into the nucleus was avoided by conducting the diazotization in the presence of 50% hypophosphorous acid at −3°. 1-Bromotriptycene was obtained in colorless rhomb-shaped tablets melting at 246–248°.

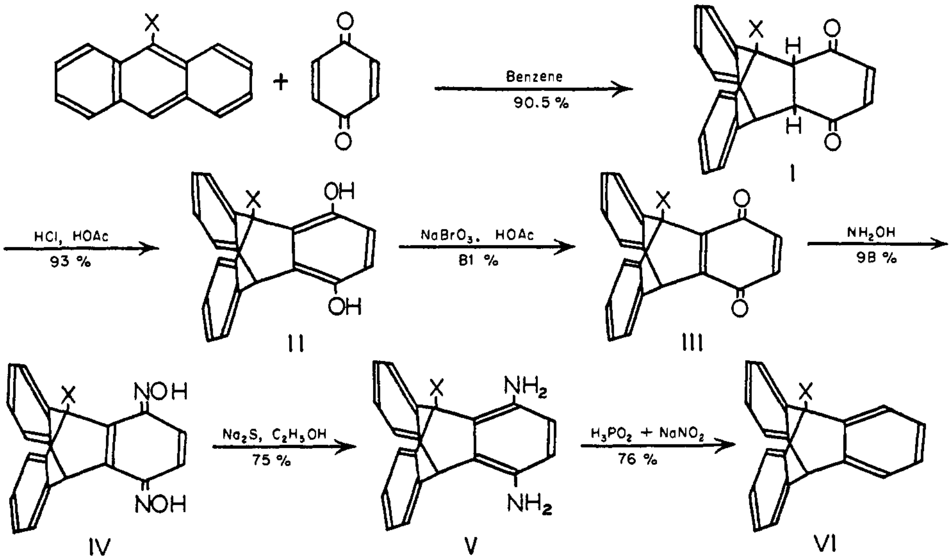

Fig. 1.

## Experimental Part

**Anthracene Dibromide.**—Anthracene, purified by distillation with ethylene glycol,[2] was brominated by the method of Barnett and Cook,[3] except that carbon tetrachloride was used as a solvent instead of carbon disulfide.

**9-Bromoanthracene.**—(A) Anthracene dibromide was warmed in toluene solution containing a trace of phenol by the method of Barnett and Cook.[3] Purification was accomplished following the directions of Bachmann and Kloetzel.[4]

(B) Anthracene dibromide, prepared from 36 g. of anthracene, was added to 300 cc. of toluene, then 54 g. of cuprous bromide[5] was added with vigorous stirring. After an hour the mixture was heated on the steam-bath for about four hours, then it was cooled and filtered. The solid was washed with benzene and these washings were combined with the toluene solution. The solvents were removed by steam distillation, and the resulting brown solid was dried and vacuum-distilled. The yellow distillate (b. p. 220–227° at 14 mm.) was extracted from the receiver with boiling hexane and the soluble portion crystallized from the hexane on cooling. This amounted to 24 g. of 9-bromoanthracene m. p. 99–102°, corresponding to a 48% yield from anthracene. The insoluble high-melting product was not identified.

**Keto Form of 1-Bromotriptycenehydroquinone (I, X = Br).**—A solution of 20 g. of 9-bromoanthracene and 40 g. of benzoquinone in 200 cc. of benzene was boiled under reflux for six hours (or more) on the steam-bath. The benzene was removed by steam distillation and the remaining bright red solid was washed with water until quinone was no longer removed. It was then dried and extracted with the smallest possible amount of chloroform in a Soxhlet extractor. Petroleum ether was added to the extract to precipitate the remainder of the adduct. This process gave 25.5 g. of yellowish tan crystals (90.5%) m. p. 193–195° to a dark red melt. Further recrystallization did not change the melting point or the color.

*Anal.* Calcd. for $C_{20}H_{13}BrO_2$: C, 65.78; H, 3.59. Found: C, 65.60; H, 3.84.

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[1] P. D. Bartlett, M. J. Ryan and S. G. Cohen, THIS JOURNAL, **64**, 2649 (1942).

[2] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, p. 345.

[3] E. de B. Barnett and J. W. Cook, *J. Chem. Soc.*, **125**, 1084 (1924).

[4] W. E. Bachmann and M. C. Kloetzel, *J. Org. Chem.*, **3**, 55 (1938–1939).

[5] J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., New York, N. Y., 1923, Vol. III, p. 192.

**1-Bromotriptycenehydroquinone** (II, X = Br).—A mixture of 43 g. of the addition product I and 700 cc. of glacial acetic acid was stirred on the steam-bath with a few cc. of concentrated hydrochloric acid. The material gradually dissolved, then the white hydroquinone started to crystallize from the solution. After several hours the stirring was stopped and the mixture was cooled. Filtration gave 40 g. (93%) of the hydroquinone, which did not melt but charred starting at 290°.

*Anal.* Calcd. for $C_{20}H_{13}O_2Br$: C, 65.78; H, 3.59. Found: C, 65.19; H, 3.81.

**1-Bromotriptycenequinone** (III, X = Br).—A mixture of 19.7 g. of the hydroquinone (II) and 450 cc. of glacial acetic acid was stirred at room temperature, and a solution of 7 g. of sodium bromate in 90 cc. of water was added gradually. The resulting orange mixture was cooled nearly to its freezing point and then filtered. This gave an orange powder, which on recrystallization from acetic acid gave 15.8 g. (81%) of small orange crystals m. p. 284.5–285.2°.

*Anal.* Calcd. for $C_{20}H_{11}BrO_2$: C, 66.3; H, 3.03. Found: C, 66.19; H, 3.03.

Other oxidizing agents were also tried for this reaction, but only vanadium pentoxide gave the desired product in good yield. Oxidation of II in acetic acid or alcohol solution with ferric chloride, iodine, sodium bromate in the presence of sodium acetate, or hydrogen peroxide in the presence of metallic silver gave a dark red easily crystallized substance which was shown to be quinhydrone by its formation from equal amounts of II and III.

The dioxime (IV) was prepared by boiling a solution of 7 g. of the quinone (III) and 14 g. of hydroxylamine hydrochloride in 600 cc. of ethanol overnight. Pouring this solution into water precipitated 7.5 g. (98%) of the dioxime as a yellow-brown powder, which gradually decomposed on heating.

*Anal.* Calcd. for $C_{20}H_{13}N_2O_2Br$: C, 60.83; H, 3.17; N, 7.03. Found: C, 61.07; H, 3.31; N, 7.10.

**2,5-Diamino-1-bromotriptycene** (V, X = Br).—Five grams of the dioxime (IV) was dissolved in 300 cc. of boiling ethanol, then 25 g. of sodium sulfide nonahydrate was added and boiling was continued for one-half hour. Then the solution was slowly added to a boiling dilute aqueous solution of sodium sulfide. The product, a mixture of a fine powder and a crystalline material, was washed with boiled water to remove traces of sulfide. The resulting nearly white diamine weighed 3.5 g. (75%) and melted with decomposition at 230–235°.

*Anal.* Calcd. for $C_{20}H_{15}N_2Br$: C, 66.2; H, 4.16. Found: C, 67.0; H, 4.64.

**1-Bromotriptycene** (VI, X = Br).—Five hundred cc. of 50% hypophosphorous acid in which was dissolved 2.5 g. of sodium nitrite was cooled in a 1-l. flask to about −3°, then 3 g. of 2,5-diamino-1-bromotriptycene dissolved in 150 cc. of glacial acetic acid was added slowly. After three hours at a temperature not greater than −3°, the flask was filled with ice and placed in the cold room overnight. The resulting yellowish suspension was then allowed to warm to room temperature and extracted with benzene. The benzene solution was washed with concentrated sulfuric acid, sodium hydroxide and water. The benzene was then replaced with alcohol by distillation with a large excess of alcohol, and this alcohol solution was then boiled with Nuchar. From the filtered and cooled solution 1.4 g. of white crystals deposited, and 0.7 g. was obtained from the mother liquor. The total yield was then 2.1 g. or 76% of this substance, m. p. 242–247°. Further purification can be accomplished by sublimation, by recrystallization from alcohol or by chromatography on alumina from petroleum ether solution. This last method is most effective in removing traces of yellow substances and gives a product melting 246–248° (sealed tube). No very sharply melting samples were ever obtained. The crystals were examined microscopically for characterization by G. De La Mater, who gave the following description. Bromotriptycene, crystallized from benzyl alcohol, consists of rhomb-shaped tablets having an acute terminal angle of about 74°. It is probably monoclinic with the plane of symmetry bisecting the obtuse terminal angle. This is in contrast to triptycene, which forms rectangular tablets with bevelled edges. The analysis was done on a sample melting at 246–248°.

*Anal.* Calcd. for $C_{20}H_{13}Br$: C, 72.09; H, 3.93. Found: C, 72.28; H, 4.04.

**Addition of 9-Anthraldehyde to Benzoquinone.**—The method of Fieser[6] was used to prepare 9-anthraldehyde. A solution of 6.8 g. of this aldehyde and 11.8 g. of quinone in 60 cc. of benzene was boiled for four hours. Evaporation of the solvent, washing with hot water, and crystallization from chloroform and petroleum ether gave 8.6 g. (82%) of the adduct (I, X = CHO) as small yellow crystals, m. p. 188–189°.

*Anal.* (by M. Racich) Calcd. for $C_{21}H_{14}O_3$: C, 80.24; H, 4.49. Found: C, 80.88; H, 5.02.

The hydroquinone (II, X = CHO) was produced by enolization of the adduct by the method used for the brominated compound. It melted at 300.5–302° with practically no decomposition.

**Aldehydotriptycenequinone** (III, X = CHO).—The oxidation was accomplished as before using sodium bromate in acetic acid solution, giving an orange powder, m. p. 299–301° with dec.

*Anal.* Calcd. for $C_{21}H_{12}O_3$: C, 80.75; H, 3.87. Found: C, 80.52, 81.01; H, 4.54, 4.30.

**Reaction of 9,9′-Dianthryl and Quinone.**—Dianthryl was prepared by the method of Eckert and Hofmann.[7] The method of Liebermann and Gimbel[8] gave exclusively anthrone, and it is interesting that this preparation is practically identical with that given for anthrone by Meyer.[9] A solution of 2.3 g. of 9,9′-dianthryl and 5 g. of quinone in 40 cc. of benzene was boiled under reflux for four hours. The benzene was evaporated and the residue was boiled with water to remove the quinone. The resulting brown powder was heated with acetic acid and a few drops of hydrochloric acid to rearrange any addition product. After several hours the mixture was filtered and short, pale yellow needles crystallized from the filtrate. This substance melted at 312–313° and was of different appearance from dianthryl, but analysis showed that this was not the desired product, $C_{40}H_{26}O_4$, although it might have been the addition product of two molecules of dianthryl and one of quinone, $C_{62}H_{40}O_2$.

*Anal.* (by M. Racich) Calcd. for $C_{40}H_{26}O_4$: C, 88.42; H, 4.6. Calcd. for $C_{62}H_{40}O_2$: C, 91.15; H, 4.93. Found: C, 92.88; H, 5.48.

## Summary

The synthesis of 1-bromotriptycene has been carried out using the sequence of reactions shown in Fig. 1.

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[7] A. Eckert and A. Hofmann, *Monatsh.*, **36**, 497 (1915).

[8] C. Liebermann and A. Gimbel, *Ber.*, **20**, 1855 (1887).

[9] K. H. Meyer, *Org. Syntheses*, Coll. Vol. I, p. 60 (1941).