

There was 8 g. of an intermediate fraction between 85–155°, then 91 g. of cyclohexanone was collected at 155–156.5°. The residue weighed 30 g. The yield was 60% of the theoretical. The cyclohexanone was identified as the semicarbazone, m. p. 165°.

Pyrolysis

By Refluxing.—Twenty-four grams of cyclohexanone was refluxed for one hundred and fifteen hours. The solution became orange-colored. On vacuum distillation, 20 g. of the ketone was recovered at 60–64° (30 mm.), and 2.5 g. of cyclohexylidencyclohexanone was collected at 158–162° (30 mm.). The oxime of the latter melted at 147–152°.

Through Hot Tube.—During one hour, 24 g. of cyclohexanone was passed through a Pyrex combustion tube heated to 700–725°. The tube was 120 × 2 cm. and was filled with pieces of porcelain. Condensables were removed from the gas stream by a coil condenser, then the gas was passed through aniline. The condensate, on distillation at 85–100°, yielded 1 g. of a mixture of water (droplets visible) and cyclohexadiene. At 150–160°

there was collected 2.5 g. of cyclohexanone (oxime, m. p. 87°). The cyclohexadiene was converted into 1,2,3,4-tetrabromocyclohexane, m. p. 140°, on treatment with bromine in carbon tetrachloride.

No acetanilide was found in the aniline trap; hence, no ketene was formed.

With Ketene Lamp.—Ninety grams of cyclohexanone was placed in the ketene lamp³ and decomposed during one hour. The effluent gas was conducted through aniline. The volume of unabsorbed gas (S. T. P.) was 6.8 liters. No acetanilide was obtained from the aniline trap.

Summary

Cyclohexanone is formed in good yields by dehydrogenation of cyclohexanol. The cyclohexanone yielded no ketene on pyrolysis at 700° but some cyclohexadiene was identified. Prolonged refluxing gave rise to small amounts of cyclohexylidencyclohexanone.

(3) Hurd and Williams, *THIS JOURNAL*, **58**, 962 (1936).

EVANSTON, ILLINOIS

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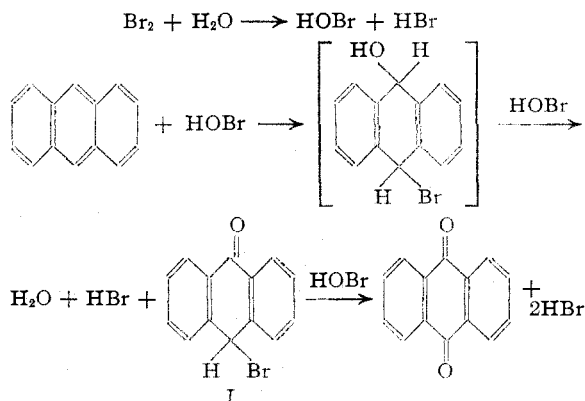
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Reaction of Bromine with Anthracene in Dioxane

BY CHARLES C. PRICE AND CLAY WEAVER

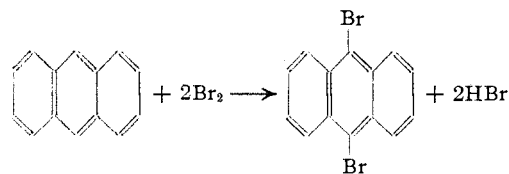
In experiments on the reaction of anthracene with bromine using dioxane as a solvent,¹ it was noted that more hydrogen bromide was evolved than could be accounted for on the basis of bromination of the hydrocarbon, since two-thirds to three-fourths of the bromine consumed appeared as hydrobromic acid after addition of water to the reaction mixture.

As a tentative explanation, it was assumed that the bromination of a mole of anthracene induced the bromination of one or two moles of dioxane by an ionic mechanism. It has been discovered,



(1) Price, *THIS JOURNAL*, **58**, 1834 (1936).

however, that the anomalous formation of hydrobromic acid in dioxane, even with material which had been distilled from sodium, was due to the presence of traces of water. In the presence of the basic solvent, the water and bromine react with the anthracene as hypobromous acid, leading to the formation of 9-bromoanthrone (I) and anthraquinone, thus accounting for the high percentage of acid formed. When precautions were taken to exclude atmospheric moisture from freshly dried dioxane, the normal reaction took place.

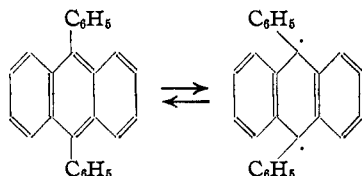


Since this eliminates the evidence for the ionic mechanism suggested by Price and Thorpe² for the *cis-trans* isomerization of diethylmaleate in the presence of bromine and anthracene, the alternative atomic-free radical mechanism they suggested is therefore to be preferred, not only from analogy with the photochemical reaction,³

(2) Price and Thorpe, *ibid.*, **60**, 2839 (1938).

(3) Wachholtz, *Z. physik. Chem.*, **125**, 1 (1929); Schmidt, *ibid.*, **B1**, 205 (1930).

but on the basis of the structure of anthracene (particularly its *meso*-diaryl derivatives). Dufraisse⁴ has recently suggested that the reactivity of these compounds, especially their ability to form peroxides on exposure to oxygen, is analogous to the behavior of triarylmethyl radicals, and that these molecules actually exist to some extent as di-radicals.



Experimental

Reagents.—Anthrone, prepared from anthraquinone,⁵ was reduced to anthracene according to Martin's directions.⁶ The anthracene crystallized as plates which melted at 216–216.5° (corr.) and which showed a deep purple fluorescence. Commercial dioxane was purified according to the directions of Scatchard and Benedict,⁷ b. p. 100.5–101° (corr.). Bromine was purified as before.¹ The purified dioxane did not react with this bromine, even up to 75°.

Procedure.—Standard bromine and anthracene solutions (ca. 1%) in dry dioxane (protected from atmospheric moisture) were mixed. Canary yellow needles separated in one minute. At the end of fifteen minutes the reaction mixture was poured into water containing potassium iodide. The bromine consumed by one sample was 0.0496 mole and

(4) Dufraisse, *Bull. soc. chim.*, [5] 6, 422 (1939).

(5) "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1931, p. 52.

(6) Martin, *THIS JOURNAL*, 58, 1438 (1936).

(7) Scatchard and Benedict, *ibid.*, 58, 837 (1936).

the hydrogen bromide evolved 0.0494 mole, by another 0.0472 and 0.0463 mole, respectively, the required values for the equation of the formation of 9,10-dibromoanthracene. This substance was isolated by filtration after the titrations. It formed canary yellow needles from acetic acid, m. p. 221° (corr.). From a 0.50-g. sample, 0.93 g. (99%) was obtained.

If precautions to exclude atmospheric moisture were not observed, 9-bromoanthrone and anthraquinone were isolated as well. In a particular experiment, 5 cc. of water and 1.2 g. each of bromine and anthracene were added to 95 cc. of dioxane. A sample of this mixture showed a ratio of 0.0566 mole of bromine consumed to 0.0996 mole of hydrogen bromide evolved. After thirty minutes the reaction mixture was poured into 100 cc. of water. The precipitate (0.6 g.) was recrystallized from benzene-petroleum ether to give thick square plates of 9-bromoanthrone (I), m. p. 142–144° (corr.), with decomposition.⁸

Anal. Calcd. for C₁₄H₉OBr: Br, 29.30. Found: Br, 29.35.

Extraction of the aqueous filtrate with ether, followed by evaporation of the solvent, yielded 0.6 g. of pale yellow needles of anthraquinone, m. p. 280–282° (corr.).

When a higher percentage of water was added, all the bromine consumed appeared as hydrogen bromide and the sole product was anthraquinone.

Summary

Unless moisture is excluded rigorously, the reaction of bromine with anthracene in dioxane leads to the formation of 9-bromoanthrone and anthraquinone, as well as the normal product, 9,10-dibromoanthracene.

(8) Goldman (*Ber.*, 20, 2437 (1887)) and Meyer (*Ann.*, 379, 62 (1911)) each report a melting point of 148°.

URBANA, ILLINOIS

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[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

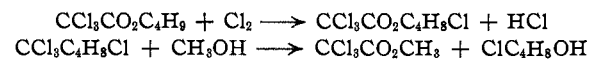
Chlorination of Butyl Trichloroacetates

By HOWARD M. WADDLE AND HOMER ADKINS

The direct chlorination of *n*-butyl, *i*-butyl and *s*-butyl trichloroacetates seemed to offer a method for the preparation of chlorobutanols and of ascertaining the relative reactivity toward chlorine of hydrogens on primary, secondary and tertiary carbon atoms.¹

Buffet found that *n*-butyl trichloroacetate could be rather rapidly chlorinated at 110–120° under the light from a 150-watt tungsten electric light bulb. Various monochlorobutyl trichloroacetates were formed which could be methanolized to the corresponding chlorobutanols.

(1) Geo. M. Buffet, Ph.D. Thesis, University of Wisconsin, Madison, 1933.



Later experience showed that it was preferable to separate carefully the chloro-esters by fractional distillation and to saponify the pure esters, rather than to attempt to separate the alcohols obtained by methanolysis or hydrolysis of a mixture of esters.

n-Butyl, *i*-butyl and *s*-butyl trichloroacetates were prepared in 82 to 89% yields by refluxing two moles of trichloroacetic acid and four moles of the alcohol for six to eight hours. The excess alcohol and water were removed by distillation through a Vigreux column, 35 cm. in length. Emulsions are likely to be formed if the alcohol is not rather completely removed before the crude esters are