

Anal. Calcd. for $C_{17}H_{11}O_8N \cdot C_8H_5N$: C, 65.32; H, 3.99. Found: C, 65.22; H, 4.01.

Saponification of the above oxidation product yielded **5,6-benzoquinoline-2,4,7-tricarboxylic acid (XIV)**, which melted at 285–286° with decomposition.

Anal. Calcd. for $C_{16}H_9O_6N$: C, 61.72; H, 2.92. Found: C, 61.81; H, 3.19.

3' - Amino - 5,6 - benzoquinaldine - 4,7 - dicarboxylic Acid Lactam (XV).—Three and sixty-eight hundredths grams of 3-aminonaphthostyryl, 0.88 g. of acetaldehyde, and 0.88 g. of pyruvic acid dissolved in 200 cc. of alcohol were refluxed for four hours. After concentration a yellow crystalline precipitate was obtained, which was purified from non-acidic material and was finally obtained in a yield of 0.5 g. It melted at 340–342° with decomposition.

Anal. Calcd. for $C_{16}H_{10}O_3N_2$: C, 69.04; H, 3.62. Found: C, 69.04; H, 3.40.

3-Hydroxy-1,2,3,4-tetrahydro-5,6-benzoquinoline (XVI).— β -Naphthylamine was condensed with an equimolecular amount of epichlorohydrin by the method recently developed for α -naphthylamine derivatives,¹¹ and the resulting product was purified as the hydrochloride, from dilute hydrochloric acid.

Anal. Calcd. for $C_{13}H_{14}ONCl$: C, 66.22; H, 5.99. Found: C, 66.41; H, 5.95.

The free base after recrystallization melted at 82–83°.

Anal. Calcd. for $C_{13}H_{14}ON$: C, 78.35; H, 6.58. Found: C, 78.65; H, 6.95.

Summary

1. A convenient method of synthesis of certain 4-hydroxyquinoline and 4-hydroxy-5,6-benzoquinoline derivatives has been found in the condensation of aniline and β -naphthylamine derivatives with acetylmaleic ester or ethoxymethylenemaleic ester followed by cyclization at 250°.

2. The method of Conrad and Limpach for the synthesis of 4-hydroxyquinoline from acetoacetic ester and aniline has been extended to include certain substituted β -naphthylamines.

3. The introduction of a carboxyl group in position 3 of 4-hydroxy-5,6-benzoquinoline-7-carboxylic acid was accomplished by means of the Reimer-Tiemann reaction.

4. Epichlorohydrin on condensation with β -naphthylamine gave 3-hydroxy-1,2,3,4-tetrahydro-5,6-benzoquinoline.

NEW YORK, N. Y.

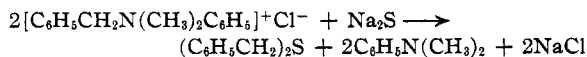
RECEIVED JUNE 28, 1939

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

Cleavage of Quaternary Ammonium Salts by Sodium Sulfide. II

BY H. R. SNYDER AND J. C. SPECK

In an earlier communication¹ it was shown that benzyldimethylphenylammonium chloride (I) is cleaved readily by aqueous sodium sulfide to yield benzyl sulfide and dimethylaniline. A number of other salts containing sulfur in its lower valences were also found to be effective cleaving agents. The reaction is of the same type as that observed in the splitting of thiamin² (vitamin B₁) with sodium bisulfite, in which a group similar to benzyl is detached from a quaternary nitrogen atom.



It now has been found that the groups other than benzyl attached to the nitrogen atom play an important part in the cleavage. For instance, benzyltrimethylammonium chloride was completely unaffected under conditions which brought

about rapid decomposition of benzyldimethylphenylammonium chloride. That this difference is not due merely to the weight of the phenyl group was shown by the fact that benzyldicyclohexyldiethylammonium chloride also resisted the action of aqueous sodium sulfide. Phenyltrimethylammonium iodide, and tetra-*n*-butylammonium iodide also failed to undergo cleavage. Even the presence of two benzyl groups on the nitrogen atom does not produce an activation similar to that in benzyldimethylphenylammonium chloride, since dibenzyldiethylammonium iodide was only very slightly cleaved. Benzyldimethylpyridinium chloride, on the other hand, underwent rapid scission to pyridine and benzyl sulfide. It appears, therefore, that the linkage between an alkyl group and the nitrogen atom of a quaternary salt is labile when the nitrogen is attached to or is part of an aromatic system.

It might be predicted that the allyl group would display a mobility similar to that of

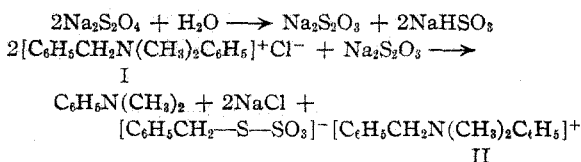
(1) For the first paper in this series see Snyder and Speck, *This Journal*, **61**, 668 (1939).

(2) Williams, Waterman, Keresztesy and Buchman, *ibid.*, **57**, 536 (1935).

benzyl. This prediction was confirmed by the rapid cleavage of allyldimethylphenylammonium bromide by aqueous sodium sulfide.

It seemed likely that the less reactive quaternary salts might undergo the cleavage if more vigorous conditions were employed. This was accomplished by the use of the high-boiling solvent, diethylene glycol. Benzyltrimethylammonium bromide, which was unaffected by boiling aqueous sodium sulfide, gave more than 50% of cleavage products when the reaction was carried out at 135–150°. Tetra-*n*-butylammonium iodide, which would be expected to fall among the most stable quaternary salts, underwent cleavage to the extent of at least 70% at 175°.

Since sodium hydrosulfite has been used for the reduction of certain quaternary ammonium compounds,³ it was desirable to test its action on an easily cleaved salt such as benzyldimethylphenylammonium chloride.⁴ Rapid cleavage occurred when an aqueous solution of these reagents was heated. The products were dimethylaniline and a neutral salt which proved to be benzyldimethylphenylammonium-S-benzylthiosulfate (II), identical with the product from the action of sodium thiosulfate on the quaternary salt.¹ Meyer⁵ has shown that sodium hydrosulfite undergoes hydrolysis to sodium thiosulfate and sodium bisulfite. This may account for the formation of a thiosulfate derivative in the present case, although the possibility of benzylation prior to conversion to thiosulfate is not excluded.



Experimental

Benzylcyclohexyldiethylammonium chloride was prepared by heating benzyl chloride and *N,N*-diethylcyclohexylamine in absolute alcohol; m. p. 179° (dec.).

Anal. Calcd. for $\text{C}_{17}\text{H}_{28}\text{NCl}$: Cl, 12.6. Found: Cl, 12.7.

Allyldimethylphenylammonium bromide was prepared from allyl bromide and dimethylaniline in anhydrous ether

(3) Karrer, Ishii, Kahnt and van Bergen, *Helv. Chim. Acta*, **21**, 1174 (1938).

(4) Although this quaternary salt and sodium hydrosulfite have been used as ingredients of mixtures employed in dyeing [German Patents 184,381 and 231,543; *Friedlaender*, **8**, 881; **10**, 439], a search of the literature failed to reveal any statement of their interaction.

(5) Meyer, *Z. anorg. Chem.*, **34**, 43 (1903).

at room temperature. Because of the extreme hygroscopicity of this salt, its melting point was not determined.

Anal. Calcd. for $\text{C}_{11}\text{H}_{16}\text{NBr}$: Br, 33.0. Found: Br, 32.6.

Cleavage with Aqueous Sodium Sulfide.—The procedure employed was that previously described.¹ No evidence of cleavage was observed with benzyltrimethylammonium bromide, phenyltrimethylammonium iodide or tetra-*n*-butylammonium iodide. Benzylcyclohexyldiethylammonium chloride underwent some cleavage, as shown by the formation of a small amount of a water-insoluble oil. Dibenzyl-diethylammonium iodide, heated with aqueous sodium sulfide for three hours, gave about 3% of benzyl sulfide. Benzylpyridinium chloride gave 65% of pyridine and 69% of benzyl sulfide. Allyldimethylphenylammonium bromide gave 41% of dimethylaniline and 44% of allyl sulfide.

Cleavage with Sodium Sulfide in Aqueous Diethylene Glycol.—To a solution of 12.0 g. of sodium sulfide hydrate in 80 cc. of diethylene glycol was added 23.0 g. of phenyltrimethylammonium bromide. The solution was heated to reflux for one hour at 135°, read on a thermometer immersed in the solution. Additional diethylene glycol was added until the boiling point rose to 150°, and refluxing was continued one-half hour. The trimethylamine liberated during the heating was absorbed in standard acid; yield 54%. Benzyl sulfide was extracted from the cold reaction mixture with benzene and crystallized from ether; yield 47%.

Fourteen grams of sodium sulfide hydrate was dissolved in 50 cc. of diethylene glycol and the solution was boiled in an open vessel until the temperature was 175°. To the cooled solution was added 22.0 g. of tetra-*n*-butylammonium iodide. The solution was heated under reflux for fifteen minutes. The cooled solution was extracted with petroleum ether. The tri-*n*-butylamine was separated from the solvent by extraction with dilute acid and treatment with alkali. The yield of tri-*n*-butylamine boiling at 205° was 7.5 g. (70%).

Cleavage with Sodium Hydrosulfite.—To 100 cc. of water was added 24.8 g. of benzyldimethylphenylammonium chloride and 17.4 g. of sodium hydrosulfite. The solution was heated under reflux for fifteen minutes. After cooling it was shaken with ether, which caused crystallization of the heavy oil that had formed during the heating. From the ether extraction of the solid and mother liquor there was obtained 3.5 g. (58%) of dimethylaniline. The dry solid weighed 12.4 g. (60%). A sample crystallized from alcohol and ether melted at 104°; this melting point was not depressed by admixture of authentic benzyldimethylphenylammonium-S-benzylthiosulfate.¹

Anal. Calcd. for $\text{C}_{22}\text{H}_{28}\text{O}_3\text{NS}_2$: C, 63.7; H, 6.03; N, 3.38. Found: C, 63.77; H, 6.26; N, 3.20.

Summary

Quaternary ammonium salts containing both an aromatic group and a benzyl or allyl group attached to the nitrogen atom are readily cleaved by boiling aqueous sodium sulfide, yielding benzyl

or allyl sulfide and a tertiary amine. Other quaternary salts undergo similar cleavage at higher temperatures in diethylene glycol solution.

Benzyltrimethylphenylammonium chloride is

rapidly cleaved by sodium hydrosulfite, yielding dimethylaniline and benzyltrimethylphenylammonium-S-benzylthiosulfate.

URBANA, ILLINOIS

RECEIVED AUGUST 21, 1939

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Hydrogenation of Substituted Acetylenes with Raney Nickel¹

BY KENNETH N. CAMPBELL AND MICHAEL J. O'CONNOR

Other workers have shown that the course of the catalytic hydrogenation of substituted acetylenes is profoundly influenced both by the nature of the substituents and by the catalyst employed. With platinum catalysts,² in general, there is no change in the velocity of hydrogenation when two atoms of hydrogen have been absorbed, while with the less active palladium catalysts,^{2,3} there is frequently a great diminution in velocity, and it is possible to isolate the intermediate olefin in a pure state.

In this connection, it seemed of interest to study the catalytic hydrogenation of substituted acetylenes, using Raney nickel as the catalyst. Dupont⁴ has made a similar study, which was, however, limited to 1-heptyne, phenylacetylene, 2-octyne and 1-methoxy-2-nonyne. He reported that the two monosubstituted acetylenes showed little or no change in velocity of reduction when one molar equivalent of hydrogen had been absorbed, but that the disubstituted ones did.

We have extended the investigation to include mono- and dialkylacetylenes, mono- and diphenylacetylenes, and phenylmethylacetylene, in order to determine the effect of substitution on the course of the reaction. We have found that all the acetylenes studied are readily reduced at room temperature, and pressures of three to four atmospheres, and that at the beginning, at least, the reaction is markedly exothermic.

Our results show a relation between the symmetry of the acetylene molecule and the course of the reduction. The reduction curves for the monoalkylacetylenes showed a slight change in

slope at half reduction, while the dialkylacetylenes showed a more pronounced change in slope, which was particularly noticeable in the case of the symmetrical dialkylacetylenes. Phenylacetylene and phenylmethylacetylene, which are electronically the least symmetrical of the acetylenes studied, showed no change in slope in the reduction curve at half reduction. Diphenylacetylene, on the other hand, readily absorbed one molar equivalent of hydrogen, and the reaction stopped at this point, yielding isostilbene.

By stopping the reduction when one molar equivalent of hydrogen had been absorbed, it was possible to isolate the corresponding olefin in most cases. Raney nickel seems, therefore, to act catalytically similarly to palladium, and is easier to use. This appears to be a good method for preparing many pure olefins, with the double bond in a definite position, which are not readily obtainable by other methods. When the reduction is carried to completion, pure saturated hydrocarbons are obtained. Analyses made on the crude half-reduction products from the monoalkylacetylenes showed that less than 0.5% of acetylene remained. Since the acetylene used up accounts for practically all of the hydrogen absorbed, it is evident that very little saturated hydrocarbon was present. The physical constants of the 1-hexene and 1-heptene obtained by us compare favorably with those recorded in the literature. The method of analysis was not applicable to the products from the dialkylacetylenes, but since these showed a more pronounced change in slope in the reduction curve than did the monoalkylacetylenes, it is justifiable to assume that the olefins obtained are not appreciably contaminated by acetylenes or paraffins. Dupont⁴ showed by means of Raman spectra that the olefins obtained by the half-reduction of 2-octyne and 1-methoxy-2-nonyne contained little or no unreduced acetylene.

(1) Paper No. XXXV on the chemistry of substituted acetylenes; previous paper, *THIS JOURNAL*, **61**, 1462 (1939).

(2) Zalkind, *Z. physik. Chem.*, **104**, 177 (1923); Zalkind and Mokhnach, *J. Russ. Phys.-Chem. Soc.*, **62**, 1643 (1930); Ott and Schroeter, *Ber.*, **60**, 624 (1927).

(3) Bourguet, *Compt. rend.*, **180**, 1753 (1925); Gredy, *Bull. soc. chim.*, [5] **2**, 1029 (1935); Sherrill, *THIS JOURNAL*, **60**, 2562 (1938); Stoll and Rouve, *Helv. Chim. Acta*, **21**, 1542 (1938).

(4) Dupont, *Bull. soc. chim.*, [5] **3**, 1030 (1936).