

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

Sodium in Liquid Ammonia as a Dehydrohalogenation Agent and its Use in the Synthesis of Acetylenes

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The action of solutions of sodium in liquid ammonia on organic halides has received considerable attention. It has been shown¹ that the halogen is removed quantitatively by such solutions from all types of organic halides. The fate of the organic residue, however, has been determined in only a relatively small number of cases. An examination of the reported work reveals that although sodium in liquid ammonia usually acts as a dehalogenation and/or hydrogenation agent there are a few cases in which dehydrohalogenation results. For example Chablay² observed that alkyl halides gave varying amounts of the alkenes, Kirrmann³ found that 1-bromoheptene gave traces of pentyne and Dean and Berchet⁴ have recently reported a 1.4% yield of styrene from phenethyl bromide.

Several years ago we found that vinyl chloride was dehydrohalogenated by sodium in ammonia to give acetylene. In an effort to evaluate this reagent as a possible tool in acetylene synthesis its action on a number of halogeno compounds which give acetylenes when desaturated by the standard dehydrohalogenation agents has been investigated. The results are tabulated below.

TABLE I

Organic halide	Moles of Na used	Principal product identified ^a	Yield, %
β -Bromostyrene	2	Phenylacetylene	96
α -Chlorostyrene	2	Phenylethane	15
<i>p</i> -Methyl- α -chlorostyrene	2	Tolylacetylene	63
Stilbene dibromide	15	Dibenzyl	73
Styrene dibromide	3	Phenylacetylene	66
2-Bromodecene-1	2	Decene-1	56

^a The acetylenes were identified as the mercury derivative. Phenylethane, dibenzyl and decene-1 were identified by their physical properties and were shown to be free from any trace of α -acetylenic material.

Of the compounds used β -bromostyrene, *p*-methyl- α -chlorostyrene and styrene dibromide gave acetylenes. The remaining substances all gave compounds in which the halogen atom or atoms were replaced by hydrogen. In no case

were the acetylenes entirely free from hydrogenation products. Since these impurities are very difficult to remove by physical means and chemical purification is expensive with regard to both time and materials, sodium in ammonia, despite the ease of manipulation and the high yields obtained, does not appear to be a suitable tool for the preparation of *pure* acetylenes.

It is interesting to note that α -chlorostyrene gave no acetylenes while β -bromostyrene gave an excellent yield. This is in agreement with the work of Nef⁵ who reports a similar behavior of α - and β -bromostyrenes with sodium in ether.

Experimental Part

The procedure employed will be illustrated by β -bromostyrene and 2-bromodecene-1.

β -Bromostyrene.—A solution of 90 g. of β -bromostyrene in 200 ml. of anhydrous ether and 600 ml. of ammonia was prepared in a 2-liter 3-necked flask fitted with a mechanical stirrer, dropping funnel and a gas outlet. A solution of 34 g. of sodium in 300 ml. of ammonia was slowly added through the dropping funnel with vigorous stirring. When the addition was complete, the volume was reduced to 500 ml. and 600 ml. of water was cautiously added in such a manner that it ran down the side of the flask, thus minimizing losses due to spattering. An oil usually separated. In some cases, however, it was necessary to add a few millimeters of 1:1 hydrochloric acid to completely clear up the water layer. The oil was washed with 10% hydrochloric acid to remove ammonia, and dried over potassium hydroxide. On distillation 49 g. of material was collected at 138–140° (96% yield assuming the material to be phenylacetylene).

Two hundred grams of this material was carefully fractionated and the portion boiling at 138.4–138.8° was retained. This fraction had the following properties: d_{25}^0 0.9005; n_D^{25} 1.5333; γ_{25} 30.75 dynes/cm. Phenylacetylene prepared by Hessler's method⁶ has the following properties: b. p. 141.70–141.75°; d_{25}^0 0.9246; n_D^{25} 1.5517; γ_{25} 33.26 dynes/cm.

The material prepared in ammonia gave a white precipitate with ammoniacal silver nitrate and reacted with iodine in liquid ammonia⁷ forming phenyliodoacetylene. On treatment with alkaline mercuric cyanide solution⁸ it gave a high yield of diphenylethynyl mercury, m. p. 124.2–124.6°. When iodinated by iodine in alcohol, diiodostyrene, m. p. 75.4–75.8°, was produced in excellent yield.⁹

(5) Nef, *Ann.*, **308**, 267 (1899).(6) Hessler, *This Journal*, **44**, 425 (1922): "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, New York, 1932, p. 428.(7) Vaughn and Nieuwland, *This Journal*, **55**, 2150 (1933).(8) Vaughn, *ibid.*, **55**, 3453 (1933).(9) Peratoner, *Gazz. chim. ital.*, **11**, **22**, 69 (1892).(1) Chablay, *Ann. chim.*, [9] **1**, 510 (1914); Vaughn and Nieuwland, *Ind. Eng. Chem., Anal. Ed.*, **3**, 247 (1931).(2) Chablay, *Ann. chim.*, [9] **1**, 469 (1914).(3) Kirrmann, *Compt. rend.*, **181**, 671 (1925).(4) Dean and Berchet, *This Journal*, **52**, 2823 (1930).

2-Bromodecene-1.—A mixture of 45 g. of 2-bromodecene, 400 ml. of ammonia, and 200 ml. of ether was vigorously agitated and treated with a solution of 12 g. of sodium in 200 ml. of ammonia. On working up the product two fractions were obtained: Fraction I, 16 g., b. p. 75–78° at 30 mm., n_D^{25} 1.4215, d_{25} 0.743; Fraction II, 10 g., b. p. 138–146° at 23 mm., n_D^{24} 1.4296. Fraction I was soluble and Fraction II insoluble in ethanol. Fraction I is undoubtedly decene-1 as indicated by the following values recently reported¹⁰ for this compound: b. p. 171–173°, d_{20} 0.7447, n_D^{20} 1.4259. Fraction I did not give even the slightest opalescence with alkaline mercuric cyanide solution. On bromination the decene took the calculated quantity of bromine and gave 27 g. of material: b. p. 145–160° at 18 mm., d_{25} 1.324, n_D^{24} 1.4891. On treatment with sodamide¹¹ in liquid ammonia the bromide gave a good yield of decyne-1.

(10) Waterman, van't Spijker and von Westen, *Rec. trav. chim.* **48**, 1097 (1929).

(11) Vaughn, Vogt and Nieuwland, to be published.

Fraction II was refractionated and gave 7 g. of material: b. p. 142.5° at 28 mm., n_D^{23} 1.4308, d_{25} 0.7636, γ_{25} 26.46 dynes/cm. The material was insoluble in ethanol, water and hydrochloric acid and reacted very slowly or not at all with bromine in carbon tetrachloride. It gave no precipitate with alkaline mercuric cyanide solution.

Summary

1. Six organic halides which give acetylenes when dehydrohalogenated have been treated with sodium in liquid ammonia. In some cases the halogen was replaced by hydrogen and in others acetylenes were obtained.

2. Acetylenes prepared by dehydrohalogenation with sodium in ammonia are contaminated by hydrogenation products.

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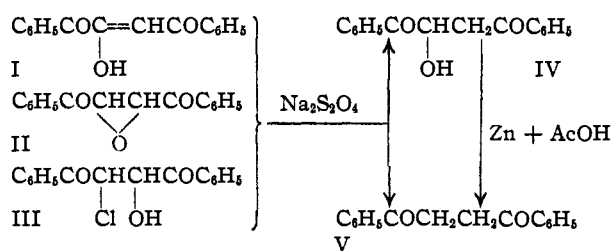
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The Reduction of Dibenzoyl ethenol and of Dibenzoyl ethylene Oxide and Chlorohydrin

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The reduction of dibenzoyl ethenol (I) and dibenzoyl ethylene oxide II and chlorohydrin III with zinc and glacial acetic acid gives largely dibenzoyl ethane V. With sodium hydrosulfite, however, there are obtained mixtures of dibenzoyl ethane and dibenzoyl hydroxyethane IV; the latter is stable under these conditions and is therefore an independent end-product of the reaction, but it is reduced further to dibenzoyl ethane by means of zinc and glacial acetic acid.



Dibenzoyl ethenol in some instances appears to function in the sense of the tautomeric enol form, $\text{C}_6\text{H}_5\text{COCOCH}=\text{C}(\text{OH})\text{C}_6\text{H}_5$.¹ On the basis of this formulation reduction to dibenzoyl hydroxyethane would be expected, but the loss of the oxygen during the sodium hydrosulfite reduction would be difficult to account for. The

(1) Lutz, Wilder and Parrish, *THIS JOURNAL*, **56**, 1980 (1934).

ease of reduction of dibenzoyl ethenol is comparable with that of its alkyl ethers, $\text{C}_6\text{H}_5\text{COC}(\text{OCH}_3)=\text{CHCOC}_6\text{H}_5$, whereas the isomeric methyl and ethyl ethers, $\text{C}_6\text{H}_5\text{COCOCH}=\text{C}(\text{OR})\text{C}_6\text{H}_5$, are attacked by these same reducing agents only under considerably more drastic conditions and are not affected by sodium hydrosulfite or by zinc and glacial acetic acid under the usual conditions. It is evident, therefore, that only the enol form I, dibenzoyl ethenol, is involved.

Dibenzoyl hydroxyethane was shown to have the structure IV by the various transformations which are illustrated in (2). It is converted into an acetyl derivative (VII) by the action of cold acetyl chloride or acetic anhydride at 70°. When heated with acetyl chloride, however, it behaves like a tertiary alcohol, the hydroxyl group being replaced by chlorine giving dibenzoyl chloroethane VIII. The latter reaction is accomplished easily, also using benzoyl chloride or thionyl chloride. The methoxyl group in dibenzoyl methoxyethane, $\text{C}_6\text{H}_5\text{COCH}(\text{OCH}_3)\text{CH}_2\text{COC}_6\text{H}_5$, is similarly replaced by chlorine with phosphorus pentachloride (a reaction which confirms this structure²). Pyrolysis, or the action of boiling acetic anhy-

(2) Cf. Lutz, *ibid.*, **51**, 3008 (1929).