Vacuum distillation using a 20-cm. Vigreux column gave 15 g. of thiophenol, 3 g. of product, b.p. 120–125° (3 mm.) and 5 g. of high boiling residue. The 3,5-dinitrobenzoate of the product had a m.p. 92–100°, indicating a mixture of the phenylthiopropanols. The reaction was repeated a third time using 85% phosphoric acid. Distillation gave 15 g. of thiophenol, 4 g. of product, b.p. 110–125° (1–2 mm.) and 5 g. of residue. The 3,5-dinitrobenzoate of the product had a m.p. 90–98°, again indicating a mixture of the phenylthiopropanols.

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Carbon-alkylation Reactions of Nitroalkanes. The Reaction of *p*-Nitrobenzyltrimethylammonium Iodide and Sodium 2-Propanenitronate

BY HAROLD SHECHTER AND RALPH B. KAPLAN

p-Nitrobenzyl halides react with sodium salts of nitro compounds to yield carbon-alkylated derivatives, whereas benzyl halides substituted in the para position with other groups, either electronegative or electropositive, give oxygen-alkylated products.[1] Recently Hamlin[2] reported that reaction of aqueous benzyldimethylphenylammonium chloride with the sodium salt of 1- or 2-nitropropane yields benzaldehyde and dimethylaniline. It has now been found that *p*-nitrobenzyltrimethylammonium iodide reacts rapidly with sodium 2-propanenitronate, in refluxing ethanol, to yield 2-methyl-2-nitro-*p*-nitrophenylpropane, trimethylamine and sodium iodide (Equation 1), whereas reaction of benzyltrimethylammonium iodide and sodium 2-propanenitronate occurs slowly in diethylene glycol at 150° to give benzaldehyde in low yields. It appears, therefore, that alkylation reactions of salts of nitroalkanes with benzyl halides or quaternary benzylammonium compounds follow similar courses and that alkylation of nitroparaffins by amines does not always proceed through an elimination–addition mechanism.[3]

$$p\text{-}NO_2C_6H_4CH_2N(CH_3)_3I + (CH_3)_2CNO_2Na \longrightarrow$$
$$p\text{-}NO_2C_6H_4CH_2C(CH_3)_2NO_2 + (CH_3)_3N + NaI \quad (1)$$

Experimental

2-Methyl-2-nitro-*p*-nitrophenylpropane.—*p*-Nitrobenzyltrimethylammonium iodide (30 g., 0.093 mole), m.p. 195°, lit. 198°,[4] was added to a mixture of sodium (2.2 g., 0.096 mole) and 2-nitropropane (65 g., 0.75 mole) in absolute ethanol (400 ml.) and the solution was then refluxed for 30 hours. As the solution was heated, the odor of trimethylamine became apparent, and trimethylamine was evolved continuously throughout the reaction. The brown mixture was then distilled until much of the alcohol had been removed. The residue, upon being cooled slowly, crystallized first to yield *p*-nitrobenzyltrimethylammonium iodide (5.3 g., 0.0165 mole, 17.7%), m.p. 194–195°, and then a crude mixture of the quaternary ammonium salt and 2-methyl-2-nitro-*p*-nitrophenylpropane. Decolorization and fractional recrystallization of the crude product from mixtures of ethanol and water yielded pure 2-methyl-2-nitro-*p*-nitrophenylpropane (12.4 g., 0.585 mole) in 63% yield; m.p. 64–65°, lit.[1c] 65°. The melting point of the product was not depressed by an authentic sample which was prepared from *p*-nitrobenzyl chloride and sodium 2-propanenitronate.[1c]

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[1] (a) T. Posner, *Ber.*, **31**, 657 (1898); (b) L. Weisler and R. W. Helmkamp, THIS JOURNAL, **67**, 1167 (1945); (c) H. B. Hass and M. L. Bender, *ibid.*, **71**, 1767 (1949); (d) H. B. Hass, E. J. Berry and M. L. Bender, *ibid.*, **71**, 2290 (1949); (e) H. B. Hass and M. L. Bender, *ibid.*, **71**, 3482 (1949).

[2] W. E. Hamlin, Abstract, Ph.D. Thesis, University of Illinois, 1949.

[3] H. R. Snyder and W. E. Hamlin, THIS JOURNAL, **72**, 5082 (1950).

[4] E. Stedman, *J. Chem. Soc.*, 1902 (1927).

The Clemmensen Reduction of Butyroin

BY WALTER T. SMITH, JR.

It was surprising to find that reduction of butyroin with amalgamated zinc and hydrochloric acid gave not octanol-4, as might be expected, but instead gave a ketone, octanone-4. This is unusual in two respects; first, in that a ketone is formed under conditions which usually result in the reduction of ketones to hydrocarbons and, second, in that it appears to involve the reduction of a hydroxyl group while leaving a carbonyl group untouched.

Under the conditions used for the reduction, the octanone as well as the butyroin are essentially insoluble in the reaction mixture. It seemed likely that if the reaction mixture was homogeneous the octanone might be more easily reduced to octane. However, when runs were made in which the water was replaced by sufficient ethyl alcohol or acetic acid to make a completely homogeneous reaction mixture, the main product was still octanone-4.

Although the yield of octanone-4 is 36% when the reduction is carried out for only two hours, the amount of octanone formed is not decreased by its reduction to octane when the time of the reaction is extended. Thus, in runs of four, ten and twenty-seven hours the yield of ketone is 50–60%.

The amount of octane formed in any of the reactions, even those running for as long as twenty-seven hours, must be very small. The boiling point of the small foreruns rose steadily to that of octanone-4, with no leveling off near the boiling point of octane. In order to exclude the possibility that any octane which might be formed was escaping through the condenser, a twenty-hour run was made in which any vapors which escaped through the condenser were collected in a trap cooled in Dry Ice and isopropyl alcohol. Only a trace of liquid was collected in the trap and its refractive index was not that of octane. It appears that octanone-4 is resistant to reduction under the conditions employed here. When a sample of octanone-4 was refluxed with amalgamated zinc and hydrochloric acid for five days the forerun was not appreciably larger than in other runs on butyroin, although the recovered octanone-4 had a wider boiling range than originally.

The possibility that 4,5-octanediol might be an intermediate in the reaction was suggested by the fact that this glycol has been reported to yield octanone-4 when heated with dilute sulfuric acid in a sealed tube.[1] To test this possibility *meso*-4,5-octanediol was refluxed with hydrochloric acid of the same concentration used in the reductions. Although some ketone is formed in this way, the amount is so small that the glycol cannot be considered as an intermediate. The presence of amal-

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[1] L. Bouveault and R. Locquin, *Compt. rend.*, **140**, 1699 (1905).