

Notes

Explanation of the Formation of Alkyl Nitrites in Dilute Solutions;
Butyl and Amyl Nitrites

BY WILLIAM A. NOYES

That nitrous acid is amphoteric, giving both hydrogen and hydroxyl ions in the same manner as hypochlorous acid,¹ is shown by the blue color of nitrous anhydride developed when a dilute acid is added to an ice cold solution of sodium nitrite. Ethyl alcohol is an acid, giving hydrogen ions, as is shown by the action of metallic sodium, by the conductivity of absolute alcohol, which is less than that of pure water, and by the probability of a trifling volatilization of calcium ethylate, $\text{Ca}(\text{OC}_2\text{H}_5)_2$, when absolute alcohol is distilled over calcium oxide.² That it is not amphoteric, giving hydroxyl ions, to any appreciable extent is shown by the fact that ethyl ether has never been found in absolute alcohol.

Many years ago Wallach and Otto³ described a method of preparing ethyl nitrite from dilute alcohol and nitrous acid but they made no remark on the surprising character of this reaction in comparison with those used for the preparation of esters of other weak acids. The explanation is apparent from the considerations given above. The alcohol reacts as an acid

and the nitrous acid as a base:

$$\begin{array}{c} \text{C}_2\text{H}_5 : \ddot{\text{O}} : \text{H}^+ \\ \ddot{\text{O}} : : \text{N}^+ \quad \left| \quad \ddot{\text{O}} : \text{H} \end{array}$$

The following method of preparing butyl and amyl nitrites, which is much simpler and quicker than those described in the literature,⁴ has been developed by careful experiments on the basis of the principles given.

Dilute 14.5 cc. of concd. sulfuric acid of 96% (one-fourth mole) with 10 cc. of water, cool to 0°, add 39 g. (one-half mole = 37 g.) of normal butyl alcohol or 46 g. of amyl alcohol and cool again. Introduce the resulting homogeneous mixture, during five to ten minutes, beneath the surface of 38 g. of sodium nitrite dissolved in 150 cc. of water. The nitrite solution is cooled in a dish containing ice and water and the contents kept thoroughly mixed by a rapid, whirling motion. Remove the flask from the ice water and allow it to stand for a few minutes until the contents separates in three layers, butyl nitrite above, a saturated solution of sodium sulfate and crystals of sodium sulfate below. Separate sharply in a separatory funnel and wash twice by shaking vigorously with 10 cc. of a solution of 25 g. of salt and 2 g. of acid sodium carbonate in 100 cc. of water.

(1) W. A. Noyes and T. A. Wilson, *THIS JOURNAL*, **44**, 1630 (1922). S. Goldschmidt, *Ber.*, **52**, 753 (1919), had previously shown the same fact by distilling a solution of hypochlorous acid at a very low temperature but he did not appreciate the theoretical importance of his experiment.

(2) Noyes, *THIS JOURNAL*, **45**, 861 (1923).

(3) Wallach and Otto, *Ann.*, **253**, 251 (1889). See also, Noyes, "Organic Chemistry for the Laboratory," fifth edition, p. 286.

(4) R. Adams and O. Kamm, *THIS JOURNAL*, **40**, 1285 (1918); last English translation of Gattermann-Wieland, p. 136.

If the nitrite is to be used for a purpose where a little water will do no harm, no further purification is required and the yield is 93 to 95% on the basis of the sulfuric acid used. After standing for a day or two with anhydrous sodium sulfate, the yield is about 90%. The nitrite retains a very small amount of the alcohol used. This is very rarely objectionable but it may be removed by careful distillation with a good column, under diminished pressure. Distillation under atmospheric pressure causes some decomposition.

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RECEIVED MAY 26, 1933
PUBLISHED SEPTEMBER 5, 1933

Aliphatic Hydrocarbons in "Lorol"¹

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Since "Lorol" has recently become available in large quantities, it is one of the best sources of higher aliphatic alcohols. In the course of the distillation of fifty pounds of this material, certain small intermediate fractions were obtained whose presence could not be immediately accounted for. Investigation showed them to be azeotropic mixtures of a paraffin hydrocarbon and an alcohol in the ratio of about 1 to 2.

One of the fractions, boiling at 187–188° (wt. 185 g.), was shaken with benzoyl chloride and sodium hydroxide solution and distilled. Octyl benzoate and a liquid insoluble in concentrated sulfuric acid were recovered. A fraction, boiling at 157–158° (100 mm.) (wt. 105 g.), when treated in a similar manner, yielded decyl benzoate and again an oil insoluble in sulfuric acid. The properties of these two substances, as given in Table I, indicate definitely that they were *n*-undecane and *n*-tridecane.

It seems very probable that, during the high-pressure reduction of the coconut oil, these hydrocarbons were also formed, by the hydrogenolysis

TABLE I
PHYSICAL CONSTANTS OF HYDROCARBONS ISOLATED FROM "LOROL"

	From fraction boiling at 187–188°	<i>n</i> -Undecane	From fraction boiling at 157–158° at 100 mm.	<i>n</i> -Tridecane
M. p., °C.	–28 ^a	–25.65 ^b	–6	–6.2 ^c
B. p., °C.	195–198	195.84 ^b	161–165 (100 mm.)	162.5 ^c (100 mm.)
d_4^{20}	0.7457	0.73667 ^b	0.7543	0.7534 ^d
n_D^{25}	1.4200	1.41727 ^b	1.4250	1.4250 ^e

^a The melting point was not depressed by the admixture of some authentic *n*-undecane. ^b Shepard, Henne and Midgley, *THIS JOURNAL*, 53, 1948 (1931). ^c Krafft, *Ber.*, 15, 1699 (1882). ^d Calculated from the data of Krafft. ^e Estimated from the data of Shepard, Henne and Midgley.

(1) Trade name of a commercial product consisting of a mixture of aliphatic alcohols formed by the high-pressure hydrogenation of coconut oil.

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