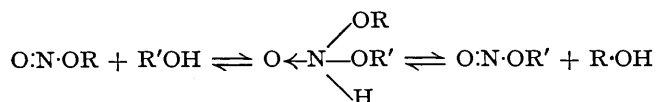


## NOTES

*The Interaction of l-β-Octyl Nitrite and dl-β-Butanol.* By J. KENYON and D. P. YOUNG.

It is well known that the alkyl group of a nitrous ester is exchanged with very great ease and rapidity for that of an alcohol in which it is dissolved, and the suggestion has been made (*vide* "The Organic Chemistry of Nitrogen," Sidgwick, 1937) that the ready exchange may be due to complex formation according to the equation :



In an attempt to obtain evidence bearing on this suggestion, *l*-β-octyl nitrite was gently heated with two molecular proportions of *dl*-β-butanol, as it was thought possible that the optically active ester might combine preferentially with the *d*- or the *l*-form of the alcohol, in which case both the β-butyl nitrite produced and the uncombined butanol would be optically active. Although the reaction proceeded smoothly and completely, both the resulting β-butyl nitrite and the recovered β-butanol were devoid of optical activity; the other product of the reaction, *l*-β-octanol, was isolated in a state of optical purity.

The interesting hypothesis mentioned above remains, therefore, still unproven.

*l*-β-Octyl nitrite was prepared by passing nitrosyl chloride into a well-cooled solution of *l*-β-octanol in four times its weight of pyridine (cf. Pickard and Hunter, J., 1923, **123**, 441). Next day the mixture was shaken with water, and the ester extracted with ether, washed with dilute acid, dried, and distilled (yield, 80%). It was a pale yellow, mobile liquid of pleasant odour, b. p. 63—65°/15 mm.,  $n_D^{18.5}$  1.4202,  $d_4^{18}$  0.861,  $\alpha_{5461}^{18}$  - 1.13° (*l*, 0.25), whence  $[\alpha]_{5461} - 5.28^\circ$  (Shriner and Young, *J. Amer. Chem. Soc.*, 1930, **52**, 3332, who obtained this compound as a by-product from the interaction of β-octyl bromide and silver nitrite, give  $n_D^{20}$  1.4218,  $d_{20}^{20}$  0.857,  $[\alpha]_D - 6.85^\circ$  in alcoholic solution).

When a mixture of *l*- $\beta$ -octyl nitrite (7.9 g.) and *dl*- $\beta$ -butanol (7.4 g.; 2 mols.) was slowly distilled through a short fractionating column, *dl*- $\beta$ -butyl nitrite, b. p. 70—75°, readily came over, followed by unchanged *dl*- $\beta$ -butanol, b. p. 98—105°. The residual *l*- $\beta$ -octanol, b. p. 83—85°/20 mm., was of unchanged rotatory power.

The experiment was repeated, the mixture of octyl nitrite and butanol being kept at room temperature for 3 days before distillation: the result, however, was the same.—BATTERSEA POLYTECHNIC, LONDON, S.W. 11. [Received, April 28th, 1938.]

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*Manganese Perchlorate and Per-rhenate.* By J. GERALD F. DRUCE.

MANGANESE perchlorate was prepared by Serullas (*Ann. Chim. Phys.*, 1831, **46**, 297) by the interaction of barium perchlorate and manganese sulphate. It has also been prepared by the action of perchloric acid upon manganese chloride (private communication from Prof. G. Frederick Smith of Urbana, Ill.). A more convenient method was to dissolve manganese carbonate in perchloric acid, filter off any undissolved carbonate, and allow the filtrate to concentrate in a vacuum over anhydrous magnesium perchlorate. Pale pink, deliquescent needle prisms separated [Found:  $\text{ClO}_4'$ , 53.8; Cl, 18.9.  $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  requires  $\text{ClO}_4$ , 55.0; Cl, 19.4%]. The crystals melted at 155°, and began to decompose at 165° with evolution of water vapour, oxygen (glowing splint rekindled), and oxides of chlorine (colourless gas which bleached litmus). Decomposition was rapid at 230°, and the black residue, after complete decomposition, was found to be manganese dioxide, free from chlorine. Anhydrous manganese perchlorate could not be isolated in a pure state.

*Manganese per-rhenate* was obtained in deliquescent, pink, prismatic needle crystals by dissolving manganese carbonate in per-rhenic acid and concentrating the solution in a vacuum desiccator over magnesium perchlorate. The crystals were dried on porous plate in a desiccator [Found:  $\text{H}_2\text{O}$ , 9.0.  $\text{Mn}(\text{ReO}_4)_2 \cdot 3\text{H}_2\text{O}$  requires  $\text{H}_2\text{O}$ , 8.9%]. The anhydrous salt [Found: Re, as nitron per-rhenate, 66.5; Mn, as  $\text{Mn}_3\text{O}_4$ , 9.63.  $\text{Mn}(\text{ReO}_4)_2$  requires Re, 67.5; Mn, 10.0%] was pink and readily absorbed water to form a solution of the per-rhenate. The anhydrous salt did not melt below 300°. At somewhat higher temperatures rhenium heptoxide volatilised and a dark residue, finally  $\text{Mn}_3\text{O}_4$ , remained.

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