the precise conditions of each reaction. Levy and Scaife have found that dinitrogen trioxide adds to simple olefines to form nitro-nitroso-adducts, in which the nitro-group again attaches itself to the carbon atom carrying the greater number of hydrogen atoms. This shows that the trioxide is also an electrophilic addendum, and that it adds in the successive parts nitronium ion and 'monomeric hyponitrite' ion. The structure of dinitrogen trioxide, and its polarization in additions, are therefore as shown in formula VI; and the direction of polarization need cause no surprise, since LeFèvre⁹ has pointed out that the tautomeric electron-attraction of the nitroso-group is greater than that of the nitro-group. Formula VI clearly accords with the blue colour of the trioxide, and, since N—N links in general are weak, with its ready dissociability. Finally, taking account of the auto-oxidation of dinitrogen trioxide to dinitrogen tetroxide at -100° , and of the reduction of the latter by nitric oxide back to the trioxide at -150° ¹⁰, one may conclude that dinitrogen tetroxide is correctly represented by formula V (= I).

V

VI

Thus, having regard to both the physical and chemical evidence, we feel that the long-debated question of the structures of the stable forms of these oxides may be regarded as settled.

C. K. INGOLD

E. HILDA INGOLD

Sir William Ramsay and Ralph Forster
Laboratories,
University College, London, W.C.1.
March 28.

¹ Schaarschmidt, *Z. angew. Chem.*, **31**, 933 (1924).

² Longuet-Higgins, *Nature*, **153**, 408 (1944).

³ Riebsomer, *Chem. Rev.*, **36**, 157 (1945).

⁴ *J. Chem. Soc.*, 1093 *et seq.* (1946).

⁵ *Proc. Roy. Soc., A*, **141**, 342 (1933).

⁶ *J. Chem. Phys.*, **6**, 40 (1938).

⁷ *Z. Phys.*, **70**, 699 (1931).

⁸ *Z. Phys.*, **68**, 184 (1931).

⁹ *Nature*, **130**, 400 (1932).

¹⁰ Francesconi and Sciacci, *Gaz. Chim. Ital.*, **34**, i, 447 (1904).

Retinene₂ and Vitamin A₂

RETINENE₁, first noted by Wald in his work on the visual-purple cycle, is the aldehyde of vitamin A₁, from which it has been prepared in high purity². Retinene₂, the corresponding aldehyde of vitamin A₂, enters into the porphyropsin cycle of freshwater fish retinas. It has been obtained by fractionation of the aldehydes prepared from a mixture of vitamins A₁ and A₂ derived from ling-cod liver oil³. As described by Wald, retinene₂ shows $\lambda_{\max}$ 405 m μ in chloroform and 705 m μ in the antimony trichloride colour test. The preparation obtained by oxidation of vitamin A₂ by means of manganese dioxide shows $\lambda_{\max}$ 405 m μ (chloroform), 385 m μ (cyclohexane), and 720 m μ (antimony trichloride test) fading to 705 m μ .

If vitamin A is oxidized by means of aluminium tertiary butoxide (Oppenauer reaction) using benzene as solvent and diethyl ketone as hydrogen acceptor, a C₂₀ aldehyde is obtained^{4,5}. This aldehyde cannot be distinguished from retinene₂. When fed to vitamin A-deficient rats, it gives rise in the lining of the

small intestine and in the liver to a product showing the properties of vitamin A₂ ($\lambda_{\max}$ 345 m μ , 284 m μ ; 693 m μ , antimony trichloride colour test). When retinene₂ is similarly treated with aluminium tertiary butoxide, the C₂₀ aldehyde is obtained in better yield.

Retinene₂, prepared from ling-cod liver oil (that is, from vitamin A₂) by oxidation with manganese dioxide, gives a crystalline 2,4-dinitrophenylhydrazone, m.p. 160–161°. The C₂₀ aldehyde prepared from vitamin A or retinene₁ gives the same compound (no depression in mixed melting point).

These experiments indicate that vitamin A₂ differs from vitamin A by one additional conjugated double bond situated in the ring. This agrees with the structure attributed to the C₂₀ aldehyde by Heilbron and his colleagues⁴. The aldehyde⁶ corresponding in structure with Karrer's alternative formulation for vitamin A₂ is very different from retinene₂.

R. A. MORTON

M. K. SALAH

A. L. STUBBS

University of Liverpool.

April 1.

¹ Morton, R. A., and Goodwin, T. W., *Nature*, **153**, 405 (1944).

² Ball, S., Goodwin, T. W., and Morton, R. A., *Biochem. J.*, **40**, *Proc. lix* (1946).

³ Morton, R. A., Salah, M. K., and Stubbs, A. L., *Biochem. J.*, **40**, *Proc. lix* (1946).

⁴ Howarth, E., Heilbron, I. M., Jones, W. E., Morrison, A. L., and Polya, J. B., *J. Chem. Soc.*, **123** (1939).

⁵ Hawkins, E. G. E., and Hunter, R. F., *Biochem. J.*, **38**, 34 (1944).

⁶ Karrer, P., Geiger, A., and Bretscher, E., *Helv. Chim. Acta*, **24**, 161E (1941).

Conversion of 2-Aceto-furan to Hexen-2-dion-4,5-acetal-I and Pyrocatechol

SEVERAL workers have already tried unsuccessfully to synthesize 2-amino-furan¹, probably because this compound decomposes very readily. Nevertheless, it was thought that the substance might be produced by a milder procedure. Therefore, we have tried to apply to furan derivatives the reaction discovered by P. W. Neber² on *p*-toluenesulphonyl derivatives of certain aromatic ketoximes, according to the following scheme.

However, on shaking *p*-toluenesulphonyl 2-aceto-furan-oxime (I) with ethanol, not the expected 2-amino-furan or rather its toluenesulphonic acid salt (II) was formed; but, in addition to toluenesulphonic acid ammonium, a yellowish-green, strongly