

A New Entry to Triazoles from Carbohydrates

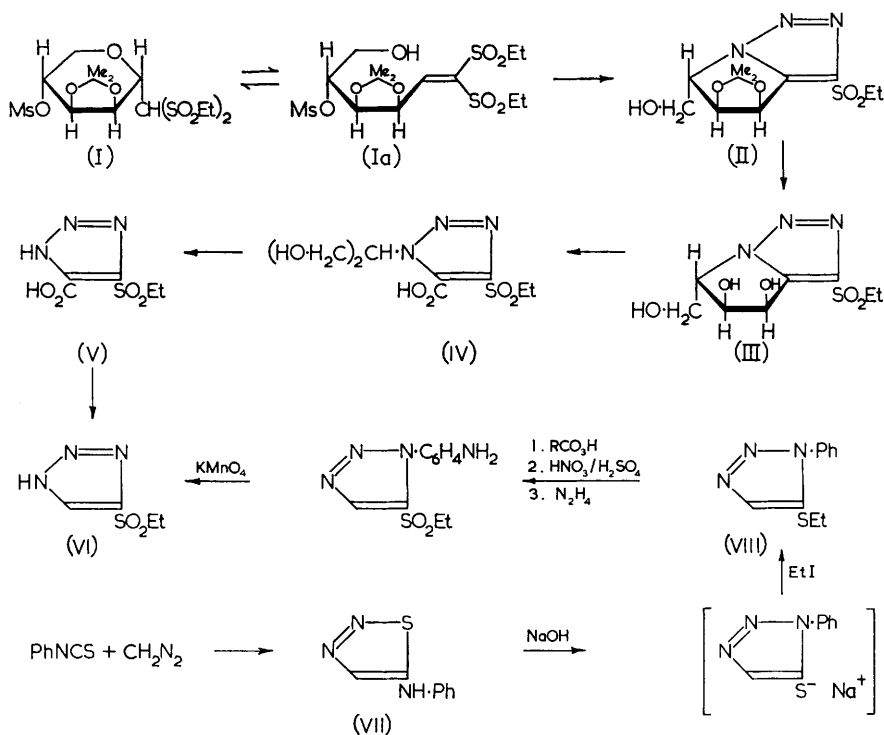
By A. FARRINGTON and L. HOUGH

(Department of Organic Chemistry, The University, Bristol)

REACTION of the 4-methanesulphonate of 1,1-diethylsulphonyl-2,3-*O*-isopropylidene- α -D-lyxo-pyranosylmethane¹ (I) with sodium azide in *NN*-dimethylformamide did not yield the expected 4-azido-derivative but gave, by more extensive reaction and rearrangement, a crystalline triazole

derivative (II), with m.p. 195° and $[\alpha]_D + 95^\circ$ (pyridine), in 70% yield.

Mass spectrometry, kindly carried out by Dr. W. A. Wolstenholme of A.E.I. Ltd., confirmed the molecular formula as $C_{11}H_{17}N_3O_5S$ and revealed that it readily forms an $(M + 1)^+$ ion and, as



¹L. Hough and A. C. Richardson, *J. Chem. Soc.*, 1962, 1024.

expected,² loses CH_3 . Clearly, two of the sulphonyl groups in (I) had been eliminated and n.m.r. showed that one ethylsulphonyl group had been retained. An infrared spectrum revealed the absence of an azido-group and the presence of sulphonyl and hydroxyl groups; benzylation afforded a mono-ester. No reaction was observed when the product was treated with Raney nickel under forcing conditions, suggesting the presence of a stable triazole ring. Acid hydrolysis gave a triol (III), $\text{C}_8\text{H}_{13}\text{N}_3\text{O}_5\text{S}$ $\{[\alpha]_D + 31^\circ (\text{H}_2\text{O})\}$, due to removal of the isopropylidene group and subsequent periodate oxidation and reduction with sodium borohydride gave an optically inactive triol (IV), $\text{C}_8\text{H}_{16}\text{N}_3\text{O}_5\text{S}$, without any loss of carbon. These results are consistent with the presence of a ring system containing an $\alpha\beta$ -diol and an exocyclic hydroxymethyl group. Further oxidation with

alkaline potassium permanganate gave the carboxylic acid (V), $\text{C}_8\text{H}_9\text{N}_3\text{O}_5\text{S}$, which on decarboxylation afforded 4-ethylsulphonyl-1,2,3-triazole (VI). The latter was identical with the product synthesised by the route outlined below in which the thiadiazole³ (VII) was converted into the triazole by the method of Kindt-Larsen and Pedersen.⁴

The n.m.r. spectrum of the monobenzoate of (II) was consistent with the structure assigned, namely (1*S*)-hydroxymethyl-(2*R*, 3*S*)-*O*-isopropylidenepyrrolido[1,2-*c*]-4-ethylsulphonyl[1,2,3]-triazole, and revealed that inversion of configuration had occurred at C-4 of (I) during the elimination of the mesyloxy-group. The triazole (II) probably arises by 1,3-dipolar addition to the hex-1-ene (Ia) followed by the elimination of the mesyloxy and ethylsulphonyl groups.

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² D. C. De Jongh and K. Biemann, *J. Amer. Chem. Soc.*, 1964, **97**, 67.

³ J. C. Sheehan and P. T. Izzo, *J. Amer. Chem. Soc.*, 1949, **71**, 4059.

⁴ T. Kindt-Larsen and C. Pedersen, *Acta Chem. Scand.*, 1962, **16**, 1800.