Keten Imine–Dimethyl Sulphoxide Oxidation of 2′,3′-*O*-Isopropylideneadenosine

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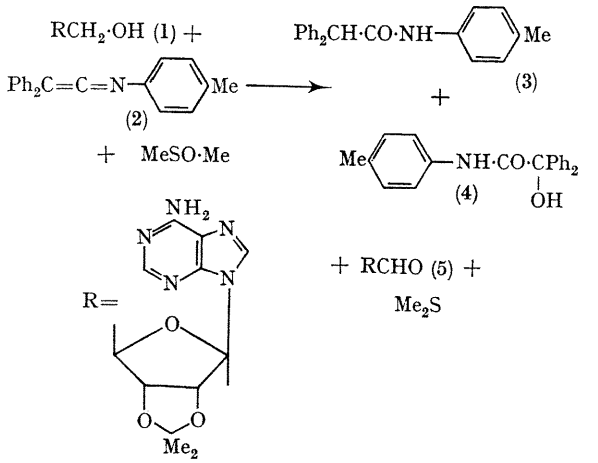
INTEREST in the use of dimethyl sulphoxide in a variety of oxidation reactions has considerably increased in recent years. The Me_2SO–carbodi-imide oxidation of alcohols to the corresponding aldehydes and ketones has been reported by Pfitzner and Moffatt.[1] Our studies on the acid-catalysed reactions of keten imines with methyl sulphoxide have indicated the possible usefulness of this reagent in effecting the ready oxidation of the 5′-hydroxy-group in 2′,3′-*O*-isopropylideneadenosine (1).[2]

A mixture of diphenylketen *p*-tolylimine (2) (30 mmoles), 100% phosphoric acid (2·5 ml.), anhydrous dimethyl sulphoxide (5 ml.) and (1) (5 mmoles) was stirred for 24 hr. at room temperature. When the mixture was poured into water *N*-(*p*-tolyl)diphenylacetamide (3) and *N*-(*p*-tolyl)-α-hydroxydiphenylacetamide (4)[3] were precipitated, and filtered off. 2′,3′-*O*-Isopropylideneadenosine-5′-aldehyde (5) was isolated from the filtrate as its crystalline 2,4-dinitrophenylhydrazone in 60% yield; m.p. 130—131°, $[\alpha]_D^{25}$ + 49·25° (*c* 0·2, ethanol), λ_{max} (EtOH) 355 and 260 nm. (ε 26,750 and 19,000); the n.m.r. spectrum and elemental analysis were consistent with the structure suggested.



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