A New Reaction of Oximes

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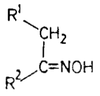
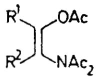
Summary Ketoximes, when heated with a mixture of acyl chloride, acetic anhydride and pyridine, at 100° C for 1—3 h give the α-*O*-acyl-*NN*-diacyl derivatives.

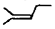
Cyclohexanone oxime on heating with a mixture of pyridine, acetic anhydride and acetyl chloride at 80 °C gave the compound (IIa) the structure of which has been assigned on the basis of its i.r., n.m.r. and mass spectra, and satisfactory elemental analyses. This transformation has been found to be a general reaction of ketoximes of the structural types (Ia)—(Ie). The reaction is also brought about by acetic anhydride and pyridine hydrochloride, or acetic anhydride and toluene-*p*-sulphonic acid.

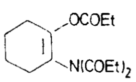


(I)

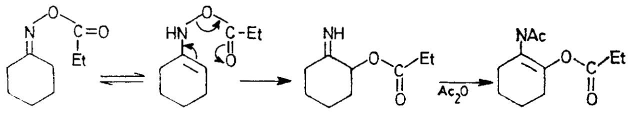


(II)

	R^1	R^2	Yield/%
(a);	-(CH$_2$)$_4$-		55
(b);	-(CH$_2$)$_3$-		17
(c);	Me	Me	30
(d);	Me		46
(e);	Me	Ph	58

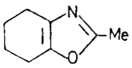


(III)

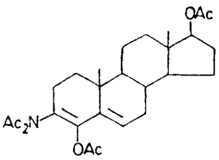


(IV)

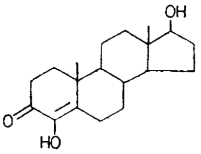
(V)



(VI)



(VII)



(VIII)

In a typical experiment a mixture of cyclohexanone oxime (15 g; 132 mmol) and pyridine (15 ml) was treated with acetic anhydride (15 ml; 148 mmol), with ice cooling. To the cooled mixture was added dropwise acetyl chloride (15 ml; 211 mmol). This mixture was heated on a steam-bath for 3 h, poured into water and extracted with chloroform. Removal of chloroform and distillation of the residue gave the triacetoxy compound (IIa) as a colourless, foul smelling liquid, b.p. 85–90 °C, 5 mmHg, n_{25}° 1·4875, which gave single spot on silica gel (chloroform) with an R_F value different from cyclohexanone, cyclohexanone oxime, or cyclohexanone oxime acetate [I.r. (smear)ν_{max} 1765 (enol acetate carbonyl), 1720 (diacetylamino carbonyl), 1660 (C=C) cm^{-1}; n.m.r. (CCl$_4$) δ 1·7 (4H, m), 1·9 {3H, s, -O-C(O)-Me} 2·3 {6H, s, N(COMe)$_2$}, 2·5 (4H, m); *m/e* 239].

Similarly the tripropionate (III) was obtained from cyclohexanone oxime, pyridine, propionic anhydride and propionyl chloride in 58% yield. When the cyclohexanone oxime propionate (IV) was treated with pyridine hydrochloride in acetic anhydride, *NN*-diacetyl-*O*-propionate (V) was obtained suggesting the intramolecular migration of the *O*-acyl group. The triacetate (IIa) undergoes hydrolysis under mild acid or basic conditions to give the corresponding 2-methyl oxazole (VI). The triacetate (VII) obtained from testosterone acetate oxime, on treatment with alcoholic hydrogen chloride gave the known diosphenol[1] (VIII) in 72% yield.

(*Received*, 20*th November* 1975; *Com.* 1298.)

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[1] C. Djerassi, G. Rosenkranz, J. Romo, St. Kauffmann, and J. Pataki, *J. Amer. Chem. Soc.*, 1950, **73**, 4534.