PREPARATION OF PRIMARY β-HYDROXYLAMINO OXIMES

L. B. Volodarskii and A. Ya. Tikhonov

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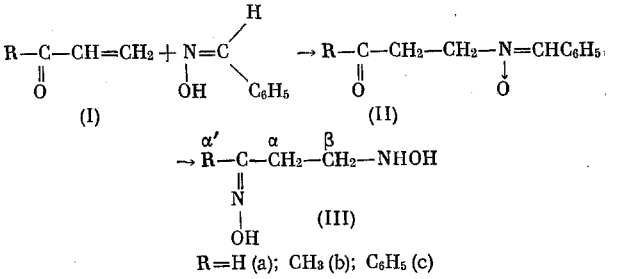
Continuing our study of hydroxylamine derivatives containing an oxime group [1], we undertook the preparation of some primary β-hydroxylamino oximes [2].

The reaction of acrolein (Ia), methyl vinyl ketone (Ib) and phenyl vinyl ketone (Ic) with anti-benzaldehyde oxime in alcohol (cf. [3]) gave the corresponding N-(3-oxo-1-alkyl)-α-phenylnitrones in quantitative yield [(IIa), oil; (IIb), mp 65-66°; (IIc), mp 113-114°]. Infrared spectra of (IIa-c): 1690-1730 (C=O), 1590-1595 (C=N), 1157-1169 cm^{-1} (N→O). Ultraviolet spectra of (IIa-c): λ_{max} 294-296 nm (lgε 4.14-4.24)



R=H (a); CH_3 (b); C_6H_5 (c)

The treatment of nitrones (IIa-c) with hydroxylamine gave in 70% yields respectively the N-(3-oximino-1-propyl)-, N-(3-oximino-1-butyl)- and N-(1-oximino-1-phenyl-3-propyl)hydroxylamines [(IIIa), mp. 106-108°; (IIIb·HCl), mp 117-119°, (IIIc·HCl), mp 159-161°]. NMR spectra, δ ppm: (IIIa) (CD_3OD), mixture of syn- and anti-isomers (1:1); syn-isomer, 2.57 (α-CH_2, dt, $J_{\alpha\alpha}$ 5.2 Hz, $J_{\alpha\beta}$ 6.2 Hz), 3.03 (β-CH_2, t, $J_{\beta\alpha}$ 6.2 Hz); anti-isomer, 2.39 (α-CH_2, dt, $J_{\alpha\alpha'}$ 5.8 Hz, $J_{\alpha\beta}$ 6.2 Hz), 3.03 (β-CH_2, t, $J_{\beta\alpha}$ 6.2 Hz); (IIIb ·HCl) (D_2O), 2.78 (α-CH_2, t, J 7.0 Hz), 3.60 (β-CH_2, t, J 7.0 Hz); (IIIc·HCl) (D_2O), 3.33, 3.61 (−CH_2 −CH_2−, A_2B_2, J 5.2 Hz) (t= triplet, dt= doublet of triplets).

LITERATURE CITED

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