NITROSYLATION OF ETHYL ESTERS OF α-(3,3-DIMETHYL-1,2,3,4-TETRAHYDRO-1-ISOQUINOLYLIDENE)CARBOXYLIC ACIDS

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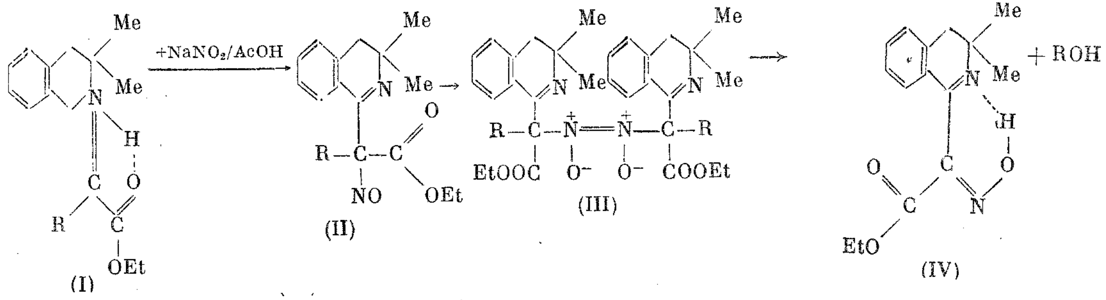
We have discovered an unusual transformation of the ethyl esters of α-(3,3-dimethyl-1,2,3,4-tetrahydro-1-isoquinolylidene)carboxylic acids (I) to the ethyl ester of (3,3-dimethyl-3,4-dihydro-1-isoquinolyl)hydroxyiminoacetic acid (IV), which is accompanied by cleavage of the $C_{alkyl}-C_{\alpha}$ bond in the case of (Ib-f).



R = H(a), CH_3(b), C_2H_5(c), n-C_3H_7(d), n-C_4H_9(e), i-C_5H_{11} (f).

Upon the action of the nitrosylating mixture, esters (Ib-f) apparently initially are converted to C-nitroso compounds (IIb-f) which are viscous blue oils. The UV spectrum for (IIb): λ_{max} 620 nm, ε 115. IR spectrum of (IIb) (ν, cm^{-1}): 1715 (C=O), 1615 (C=N), 1570 (N=O). PMR spectrum for (IIb) (δ, ppm): 0.88-1.62 m (9H, $OCH_2\underline{CH}_3$ and $>C(CH_3)_2$), 1.95 s (3H, $CH_3-\overset{|}{\underset{|}{C}}-$), 2.42-2.98 m (2H, $-C-CH_2-C-$), 4.18 q (2H, $OC\underline{H}_2CH^3$), 6.68-7.75 m (4H, aromatic protons).

Nitroso compounds (IIb-f) readily dissolve in excess acid, and they turn yellow after 2-3 h, indicating their dimerization to (IIIb-f). After neutralization of the acid solutions of (IIIb-f) by the action of NH_4OH or Na_2CO_3, oxime (VI) is obtained in 60-97% yield independently of the nature of R (the yield is dependent on the nature of R), mp 167-169°C (from acetone), hydrochloride salt, mp 218°C (dec.). PMR spectrum (δ, ppm): 1.24 t (3H, $OCH_2C\underline{H}_3$), 1.30 s (6H, $>C(CH_3)_2$), 2.67 s (2H, $-C-CH_2-C-$), 4.12 q (2H, $OC\underline{H}_2CH_3$), 7.00- 7.50 m (4H, aromatic protons), 12.35 s (1H, OH). IR spectrum (ν, cm^{-1}): 3450 (OH), 1725 (C=O), 1605 (C=N), 1565 (C=N). The structure of (IV) was indicated by elemental analysis and its identity to a sample obtained from (Ia).

Although the mechanism for the transformation of (Ib-f) to (IV) is not clear, we have established that the formation of (IV) occurs only after the addition of nucleophiles to the reaction mixture, and intermediate nitroso compounds (IIb-f) are not converted to oxime (IV) upon treatment by the same nucleophiles.

LITERATURE CITED

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