MIGRATION OF AN ACETYL GROUP IN 1,3,4-OXADIAZOLIUM SALTS

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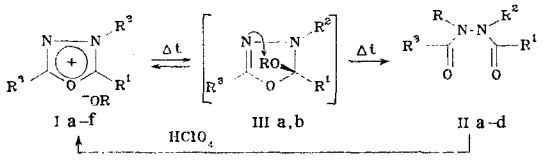
The acetyl group in 1,3,4-oxadiazolium salts Ia and Ib is capable of migrating to the β-nitrogen atom in the ring like a proton in the corresponding pseudobases Ic and Id.



I a–f III a,b II a–d

I, II a, b $R=CH_3CO$; a, b, c $R^1=R^2=R^3=C_6H_5$; b, d, f $R^1=C_6H_4OCH_3$-p; $R^2=R^3=C_6H_5$; c, d R=H; e, f $R=ClO_3$

Oxadiazolium acetates Ia and Ib are obtained from the corresponding perchlorates Ie and If under the action of potassium acetate in media in which potassium perchlorate precipitates. Oxadiazolium acetates Ia and Ib readily isomerize upon heating to triacylhydrazines IIa and IIb. The latter also form during heating for several minutes from diacylhydrazines IIc and IId under the action of acetic anhydride in the presence of catalytic amounts of potassium acetate (without a catalyst the process takes several hours). In all likelihood, the acylation is realized with the intermediate formation of crypto salts IIIa and IIIb, since under the same (and even more severe) conditions benzanilide, which is not capable of transfer to an intermediate cyclic state of type III, does not undergo N-acetylation.

Under the action of perchloric acid, N-acetylated diacylhydrazines IIa and IIb, like the N-unsubstituted analogs IIc and IId, form oxadiazolium perchlorates Ie and If. An acetyl group is eliminated in the process.

The composition and structure of compounds IIa and IIb were confirmed by the data from elemental analysis and the IR and PMR spectra and by back synthesis (in the case of compound IIa, from 1-phenyl-2-acetylhydrazine and benzoyl chloride in pyridine).

1-Phenyl-1,2-dibenzoyl-2-acetylhydrazine (IIa) was obtained with a 75% yield, mp 140–146°C (from methanol). IR spectrum (in Nujol): 1745 s, 1705 s, 1680 s cm^{-1}. PMR spectrum (Tesla BS-487, CCl_4, HMDS): 2.6 (s, 3H); 6.6–7.6 ppm (m, 15H, aromatic CH).

1-Phenyl-1-(4-methoxybenzoyl)-2-benzoyl-2-acetylhydrazine (IIb) was obtained with an 82% yield, mp 131–135°C (from methanol). IR spectrum (KBr): 1730 s, 1692 s, 1680 s cm^{-1}. PMR spectrum (CCl_4, HMDS): 2.5 (s, 3H), 3.7 (s, 3H) 6.5–7.6 ppm (m, 14H, aromatic CH). In both cases, acetic anhydride or acetonitrile served as the reaction medium.

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