SYNTHESIS OF 4-ACYLMETHYL-4-PHENYL-2-DIETHYLAMINO-1,3-DITHIETANIUM PERCHLORATES

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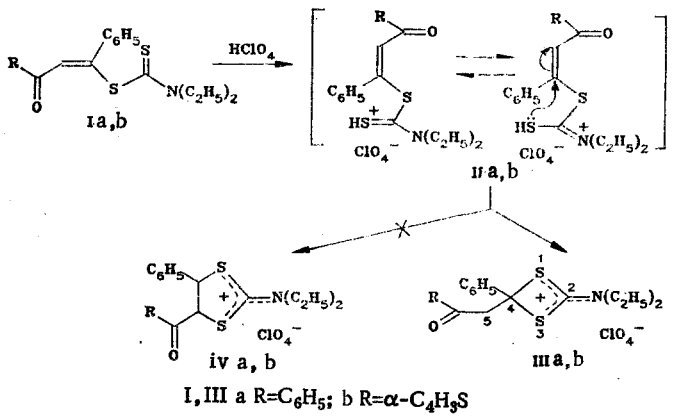
It is well known that the reaction of mineral acids ($HClO_4$, H_2SO_4) with β-ketodithioethers forms 2-substituted 1,3-dithiolium salts in good yield [1-3]. When these acids react with S-acylmethyl dithiocarbamates (Ia, b) the only products isolated are 2-dialkylamino-1,3-dithiolium salts [4, 5].

We have found that the action of 60% perchloric acid on S-acylvinyl-N,N-diethyldithiocarbamates (Ia, b), obtained by the reaction of N,N-diethyldithiocarbamic acid with α-acetylene ketones, causes intramolecular cyclization of the intermediate compounds IIa, b to form the previously unknown 4-acylmethyl-4-phenyl-2-diethylamino-1,3-dithietanium perchlorates (IIIa, b), instead of the possible 5-acyl-4-phenyl-2-diethylamino-1,3-ditholium salts



I, III a R=C_6H_5; b R=α-C_4H_3S

$HClO_4$ causes protonation of the thione sulfur, which is followed by nucleophilic addition of the mercapto group to the conjugated C=C bond; in this case the thiolate anion attacks the electron-deficient α-carbon. Indeed the only products of the reaction of S-(1,3-diphenyl-3-oxopropen-1-yl)- (Ia) and S-[3-thienyl-3)-1-phenyl-3-oxopropen-1-yl]-N,N-diethyldithiocarbamate (Ib) with excess perchlorate acid (about 3 ml per 9 mmoles of dithiocarbamate) at room temperature (or with slight warming in a water bath) are the 1,3-dithietanium perchlorates IIIa, b, and no 1,3-dithiolium salts IVa, b were detected. Perchlorates IIIa, b, which precipitate from the reaction mixture spontaneously or upon addition of a small amount of water, were filtered off and reprecipitated from alcohol by ether: IIIa, mp 173-175°; yield 97%; IIIb, mp 159-160°; yield 92%. In the PMR spectra of IIIa, b the proton signals of $COCH_2$ (about 5 ppm), and in the ^{13}C NMR spectrum the signals of $C_{(2)}$ (181.06); $C_{(4)}$ (52.64); and $C_{(5)}$ (49.45 ppm) confirm the proposed structure. IR spectrum (KBr): 1055-1120 (ClO_4^-), 1425 (CH_2), 1620 (C=N), 1675 cm^{-1} (C=O). Elemental analysis for C, H, N, and S of IIIa, b agrees with the calculated values.

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MECHANISM OF FORMATION OF 1,2-DIHYDRO-4H-3,1,-BENZOXAZINE FROM o-AMINOPHENYLDIPHENYLCARBINOL

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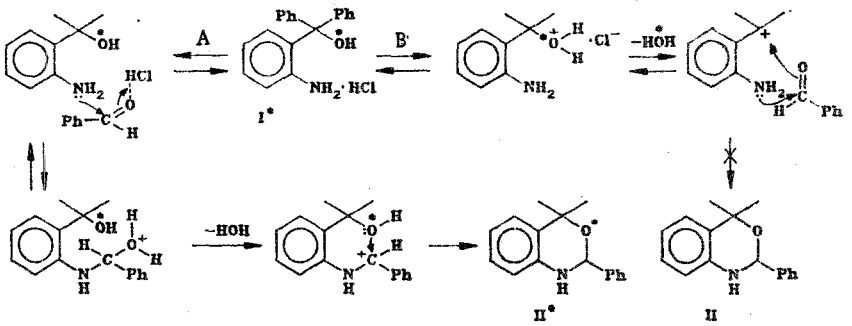
In the reaction of o-aminophenyldiphenylcarbinol with benzaldehyde in the presence of acid the 3,1-oxazine ring can form by two routes: by the electrophilic addition of the carbocation (that forms by dehydration of the alcohol) to the benzaldehyde oxygen (route B), or by initial nucleophilic addition of nitrogen to the benzaldehyde carbonyl oxygen, followed by detachment of a water molecule containing the carbonyl oxygen and heterocyclization to 1,2-dihydro-4H-3,1-benzoxazine (route A).



To determine the route by which the 3,1-oxazine ring is formed we studied the distribution of an isotopic tracer in two benzoxazines. The latter were obtained by the reaction of aminoalcohol hydrochloride I*, containing $O_{(18)}$ in the hydroxyl, with benzaldehyde in boiling absolute benzene (benzoxazine II*), and by the reaction of benzaldehyde enriched in $O_{(18)}$ with untagged aminoalcohol hydrochloride.

The ^{17}O NMR spectrum of II* shows the appropriate signal whereas in the second case this signal is absent. Mass spectrometric data showed that the $O_{(18)}$ of aminoalcohol hydrochloride I* goes entirely into compound II*, whereas in the other variant of the reaction no $O_{(18)}$ of benzaldehyde was observed in the benzoxazine.

According to ^{17}O NMR and mass spectrometry, alcohol oxygen takes part in heterocycle formation under these conditions, but benzaldehyde does not. In this reaction acid catalysis apparently takes place in the dissociation of the ammonium salt, which causes the introduction of the aldehyde. The liberated amino group attacks the carbon of the oxo group; this causes the equilibrium to shift and carries out route A.

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