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LETTERS TO THE EDITOR

Synthesis of Diacylals of Amino-Substituted Aldehydes

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It is known that the reaction of aldehydes and carboxylic acid anhydrides affording diacylals (1,1-dialkanoates) occurs only in the presence of acid catalysts BF_3 and PCl_3 [1].

We first found that dialkylamino-substituted aldehydes **I** react with carboxylic acids anhydrides **II** under mild conditions without any catalyst.

$$\underset{\mathbf{I}}{R^1_2NCH_2CMe_2CHO} + \underset{\mathbf{II}}{(R^2CO)_2O} \rightarrow \underset{\mathbf{III}}{R^1_2NCH_2CMe_2CH(OCOR^2)_2}$$

III, $R^1 = R^2 = Me$ (**a**), $R^1 = Me$, $R^2 = Et$ (**b**), $R^1 = Me$, $R^2 = Ph$ (**c**), $R^1 = Et$, $R^2 = Me$ (**d**).

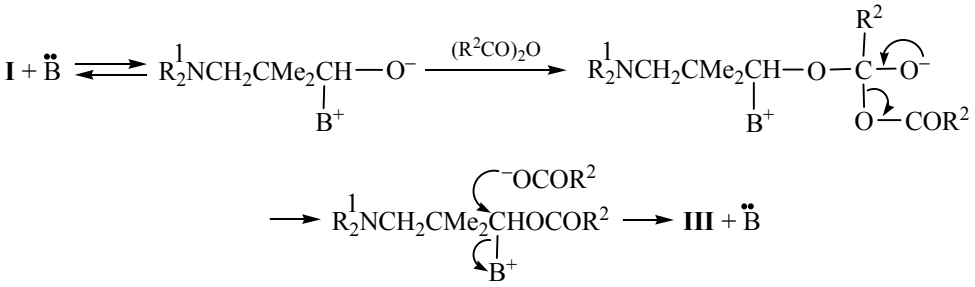
Obviously, the starting aldehyde **I** with tertiary amine moiety acts as a nucleophilic catalyst B (Scheme 1).

An equimolar mixture of compounds **I** and **II** was kept at room temperature for two weeks till the disappearance of the aldehyde proton signal at δ 10 ppm in the ^1H NMR spectrum of the reaction mixture. After the removal of volatile substances the residue was distilled to give diacylals **IIIa**–**IIIb** as individual compounds. Product **IIIc** is a thick liquid non-distillable in a vacuum. It was identified as a quaternary ammonium salt **IV** (Scheme 2).

To a solution of the compound **IIIc** in acetonitrile was added dropwise a slight excess of methyl iodide at room temperature under stirring. After 6 h the solvent and volatiles were removed, the residue was recrystallized from ethanol.

3-(Dimethylamino)-2,2-dimethylpropane-1,1-diethanoate (IIIa). A mixture of 5 g (0.038 mol) of 3-(dimethylamino)-2,2-dimethylpropanal **Ia** and 3.95 g (0.038 mol) of acetic anhydride was kept in a sealed ampule for 14 days and then distilled in vacuum. Yield 8 g (54%), bp 51–52ºC (0.065 mm Hg), n_D^{20} 1.4336. ^1H NMR spectrum (acetone-d_6), δ, ppm: 0.8 s (6H, CMe_2), 1.93 s (6H, COMe), 2.07 s (2H, CH_2N), 2.17 s

Scheme 1.



Scheme 2.

$$Me_2NCH_2CMe_2CH(OCOPh)_2 + MeI \rightarrow I^- \; \underset{\mathbf{IV}}{Me_3N^+CH_2CMe_2CH(OCOPh)_2}$$

(6H, NMe_2), 6.5 s (1H, CH). Found N, %: 6.17. $C_{11}H_{21}NO_4$. Calculated N, %: 6.06.

3-(Dimethylamino)-2,2-dimethylpropane-1,1-dipropanoate (IIIb) was obtained from 5 g (0.038 mol) of **Ia** and 5.04 g (0.038 mol) of propionic anhydride. Yield 6.3 g (62.7%), bp 73–74°C (0.082 mm Hg), n_D^{20} 1.4352. ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 6.55 s (1H, CH), 2.15 s (2H, CH_2N), 2.70 s (6H, NMe_2), 2.10 q (4H, $COCH_2$, $^3J_{HH}$ 7 Hz), 0.90 t (6H, $COCH_2CH_3$, $^3J_{HH}$ 7 Hz), 0.80 s (6H, CMe_2). Found N, %: 6.02. $C_{13}H_{25}NO_4$. Calculated N, %: 5.93.

3-(Dimethylamino)-2,2-dimethylpropane-1,1-dibenzoate (IIIc) was obtained from 5 g (0.038 mol) of **Ia** and 8.76 g (0.038 mol) of benzoic anhydride. Yield 12.66 g (92%). Ammonium salt of **IIIc** was obtained as follows. To a solution of 12.36 g (0.035 mol) of compound **IIIc** in 35 ml of anhydrous acetonitrile was added dropwise 5.93 g (0.042 mol) of methyl iodide at room temperature. The mixture was stirred at 25ºC for 6 h. Yield 17.1 g (93.5%), mp 124–125ºC (ethanol). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.5 s (6H, CMe_2), 3.7 s (9H, NMe_3), 4.08 s (2H, CH_2N), 7.41 s (1H, CH), 7.15–8.1 m (10H, Ph). Found N, %: 6.22. $C_{13}H_{25}NO_4$. Calculated N, %: 5.93.

3-(Diethylamino)-2,2-dimethylpropane-1,1-diethanoate (IIId) was obtained from 5 g (0.032 mol) of **Ib** and 3.25 g (0.032 mol) of acetic anhydride. Yield 4.7 g (57%), bp 72–73ºC (0.01 mm Hg), n_D^{20} 1.4368. ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 0.8 s (6H, CMe_2), 0.91 t (6H, NCH_2Me, $^3J_{HH}$ 6.75 Hz), 1.93 s (6H, COMe), 2.07 s (2H, CH_2N), 2.5 q (4H, NCH_2Me, $^3J_{HH}$ 6.75 Hz), 6.5 s (1H, CH). Found N, %: 6.22. $C_{13}H_{25}NO_4$. Calculated N, %: 5.93.

The ^{1}H NMR spectra were registered on a Tesla BS-567A spectrometer operating at 100 MHz, internal reference TMS. The ^{31}P NMR spectra were recorded on a RYa-2303 instrument (21 MHz) relative to 85% H_3PO_4.

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