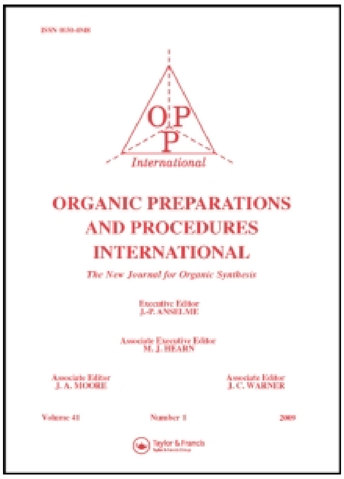

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THE PREPARATION OF A FORMALDEHYDE ADDUCT OF 3-DIMETHYLAMINO-2,2-DIMETHYLPROPIONALDEHYDE

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THE PREPARATION OF A FORMALDEHYDE ADDUCT OF 3-DIMETHYLAMINO-2,2-DIMETHYLPROPIONALDEHYDE

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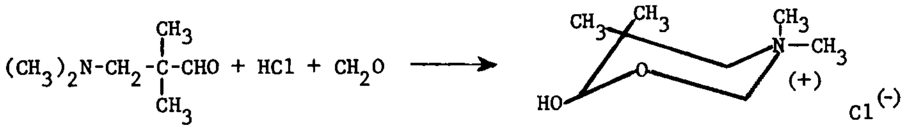
We have found that a reaction occurs between 3-dimethylamino-2,2-dimethylpropionaldehyde hydrochloride and formaldehyde in aqueous solution, resulting in the formation of an adduct. When a less polar solvent such as acetone is added to the solution of reactants, the adduct separates as a crystalline solid which is quite stable. The infrared spectrum exhibits no carbonyl absorption which is consistent with the postulated structure, I.

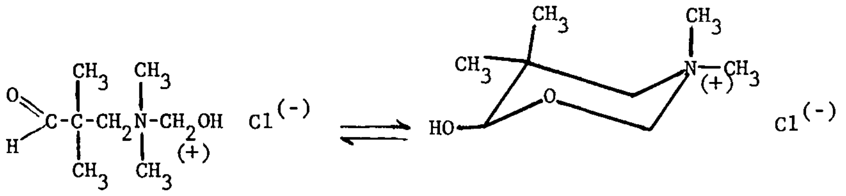


$(CH_3)_2N\text{-}CH_2\text{-}C(CH_3)_2\text{-}CHO + HCl + CH_2O \longrightarrow$

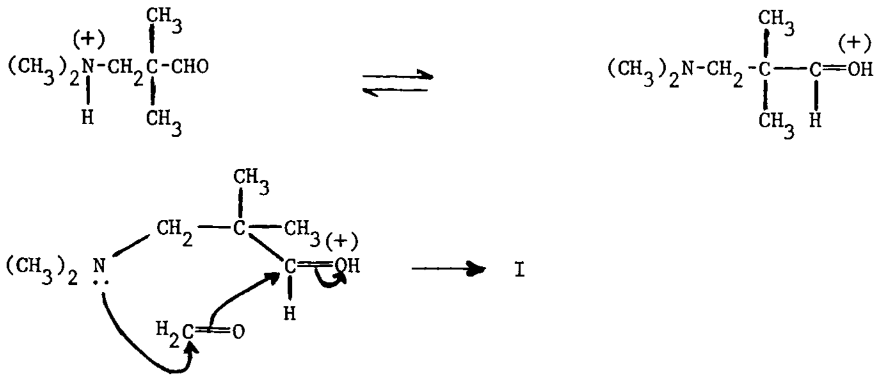
I

Thus far only mono-and dialkylamines have been shown to react with formaldehyde(1), with the exception of a patent describing a synthesis of alkoxymethylene quaternary ammonium salts from the condensation of tertiary amine hydrochlorides, alcohols and paraformaldehyde under anhydrous conditions(2).

We believe that in general tertiary amine hydrochlorides and formaldehyde in water are in equilibrium with the corresponding N-methylol quaternary ammonium salts(3). In the case of 3-dimethylamino-2,2-dimethylpropionaldehyde, we believe that the equilibrium position is displaced to favor the production of the adduct due to ring-closure of the N-methylol group with the aldehyde function in a manner similar to that well known for the cyclic hemiacetal forms of sugars.



The fact that the NMR spectrum in water shows a detectable equilibrium only with starting materials is also consistent with a referee's proposal of a different mechanism not involving a methylol intermediate.



The NMR spectrum of I in DMSO-d_6 supports the postulated structure. The NMR spectrum in D_2O however, indicates a mixture of starting materials and compound I in approximately equimolar amounts at room temperature. At elevated temperatures the concentration of I decreases but returns to its former value as the temperature is lowered.

Compound I is an active formaldehyde donor and as such is a protein hardener. The methone derivative of formaldehyde is easily prepared by mixing I with methone and dilute base. Compound I is destroyed with alkali yielding formaldehyde and free 3-dimethylamino-2,2-dimethylpropionaldehyde.

Experimental

Adduct of formaldehyde and 3-dimethylamino-2,2-dimethylpropionaldehyde (6-hydroxy-3, 3, 5, 5-tetramethyltetrahydro-1, 3-oxazinium chloride, I)

Into a 250 ml. beaker were placed 16.6 g. (0.1 mole) 3-dimethylamino-2,2-dimethylpropionaldehyde hydrochloride. This salt is prepared by neutralization of the free aminoaldehyde (Eastman Distillation Products) with gaseous hydrogen chloride in ether. The salt was dissolved in 25 ml. of water and 8.1 g. (0.1 mole) of 37% formaldehyde aqueous solution was added. The contents were allowed to stand for one hour and then poured into 2 liters of acetone with agitation. Compound I which separated out as large crystals, was filtered and dried to give 13 g. (66%) of product, m.p. 174°C. The compound may be recrystallized from ethanol-ether, although in most cases analytical samples are obtained directly from the reaction.

Anal. Calcd. for $C_8H_{18}ClNO_2$: C, 49.1; H, 9.2; N, 7.2; Cl, 18.2 Found: C, 49.1; H, 9.2; N, 7.2; Cl, 18.4.

NMR (DMSO-d_6) δ 1.02 (s,3), 1.05 (s,3), 3.10 (s,3), 3.14 (s,3)

3.48 (s,2), 4.92 (s,2), 4.82, 4.92 (s_1,s_2,1, hydroxyl), 7.65, 7.74 (s_1,s_2,1, methine).

When an aqueous solution of I is mixed with an equivalent of methone in the presence of a trace of base, a white solid is obtained, m.p. 191°C. Its melting point and infrared spectrum(4) are identical to that of the product obtained from methone and formaldehyde. When I is added to a warm gelatin solution, the presence of alkali promotes instantaneous tanning as with formaldehyde itself. Compound I thus behaves chemically as a formaldehyde donor similar to compounds such as N-methylolpyrrolidone.

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