The Triamide of Methane-tricarboxylic Acid

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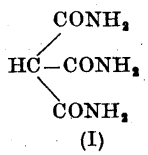
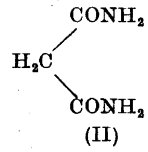
In connection with work on compounds with adamantoid structure (urotropine structure), we were interested in preparing the triamide I. Earlier attempts to obtain this substance had failed. Philippi *et al.*[1], who treated ethyl methane-tricarboxylate with dry liquid ammonia in sealed tubes at room temperature, could only isolate malonamide (II) and urethane (III). This indicates a direct cleavage of the molecule, effected by ammonia.

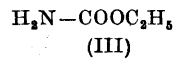
The present authors attempted to perform the reaction in aqueous or alcoholic ammonia at various concentrations, but malonamide was in every case obtained. On treatment with gaseous ammonia in nonpolar solvents, the ammonium salt of the ester separated. The desired compound was at last obtained in moderate yield by converting the ester into the ammonium salt, which was left to stand in an ammonia atmosphere for several days. The product was then treated with concentrated aqueous ammonia as described in the experimental part.



(I)



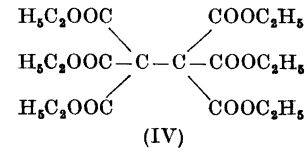
(II)



(III)

Once formed, the compound is fairly stable and can be recrystallised from hot water. It melts with decomposition at about 203°.

Attempts to prepare compounds of adamantoid structure from the triamide have so far been unsuccessful. Substitution of the "acid" hydrogen by a more or less bulky alkyl group might perhaps favour the ring closure and we plan to extend the work in this direction. Experiments with a triester without "acid" hydrogen might also throw some light on the mechanism of the formation of the triamide and the cleavage of the ester molecule. It should be mentioned, however, that the ethyl ethane-hexacarboxylate (IV), investigated by Philippi *et al.*[1], seems quite inert towards ammonia. Even after long treatment with dry liquid or concentrated aqueous ammonia, the ester was recovered unchanged.



(IV)

Experimental. A 50 ml two-necked flask is filled with gaseous ammonia, taken from a bomb and dried with solid potassium hydroxide. 20 ml (22.2 g) of ethyl methane-tricarboxylate [2] are introduced into the flask and a slow current of dry ammonia is passed through the apparatus. When all the ester has been converted into the dry ammonium salt (which requires about 30 min.), the flask is closed with rubber stoppers and left to stand for at least three days. 15 ml of concentrated aqueous ammonia are then added and the flask is shaken from time to time until a homogeneous solution is obtained. On further standing, the triamide gradually separates; after three days it is filtered off, washed with water, alcohol and ether and recrystallised from hot water. In some cases, the crude product was contaminated by the lower-melting malonamide, which could be removed by extraction with cold water. The triamide is much less soluble.

The triamide forms needles with m.p. 203° (decomp.). Yield 1–2 g (7–14 %). (Found: C 33.03; H 4.76; N 28.85. Calc. for $C_4H_7O_3N_3$: C 33.10; H 4.86; N 28.96.)

The ester may be diluted with 5–10 ml of dry ether during the reaction, but this modification has no favourable effect on the yield.

The triamide can also be prepared from methyl methane-tricarboxylate. In this case, addition of ether is appropriate since the methyl ester melts at 43°.

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1. Philippi, E., Hanusch, J. and von Wacek, H. *Ber.* **54** (1921) 901.
2. Lund, H. and Voigt, A. *Org. Syntheses, Coll. volume II*, New York 1946, p. 594.

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