

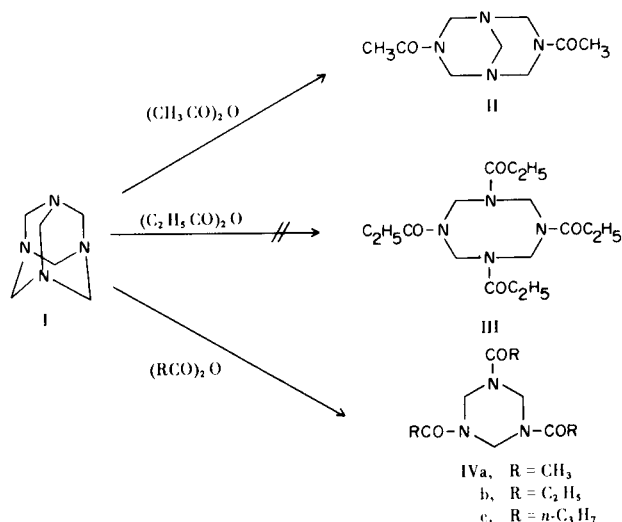
## The Reaction of Alkanoic Anhydrides with Hexamethylenetetramine

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A recent paper by Hodge (1) on the reaction of hexamethylenetetramine (I) with acetic and propionic anhydrides, prompts us to report some of our observations on this subject.



The only product isolated from mixing I with acetic anhydride in work reported to date is 3,7-diacetyl-1,3,5,7-tetraazabicyclo[3.3.1]nonane (II). Aristoff and coworkers (2) obtained a 6% yield of II; Hodge (1) cites 9 to 45%. Our maximum yield was 34%, obtained at 0-4° in a two-hour reaction period. However, using modified conditions (to be reported later) we were able to obtain over 90% yields of II.

We have also made the novel observation that heating I for ca. 2 hours at 90-100° with three alkanoic anhydrides (acetic, propionic, and *n*-butyric) yields the corresponding triacylhexahydro-*s*-triazines (IV) in fair yields. Attempts to prepare an analogous triazine from isobutyric anhydride were unsuccessful.

It has been stated (1) that III is formed by heating I with propionic anhydride. We have repeated this preparation, and have obtained a compound in the same yield and with the same melting point and nmr spectrum as those reported. However, it was found to be IVb, and

not III as claimed. It is noted that the characterization data cited (1) (nmr spectrum and elemental analysis) would not distinguish between III and IVb.

It therefore appears that the reaction of I with alkanoic anhydrides follows the pattern shown by it (3) in reaction with nitrous and nitric acids and with sulfonyl halides, in that compounds of basic structures II or IV result, depending upon the conditions used.

## EXPERIMENTAL (4)

1,3,5-Triacetylhexahydro-*s*-triazine (IVa).

Compound I (10 g., 72 mmoles) was added at room temperature with stirring to acetic anhydride (41 g., 0.4 mole). A mild exotherm raised the temperature to 35°, after which the mixture was heated for 2 hours at 98°. The solution was cooled to 5°, 200 ml. water was added, and the mixture was stirred for 30 minutes. The solution was then reduced to a viscous yellow liquid by vacuum distillation. Water (25 ml.) was added, and the mixture was cooled and stirred to induce precipitation. The solid product was filtered and dried *in vacuo* over sodium hydroxide pellets. It weighed 8.8 g., m.p. 93-96°; a second crop, 0.7 g., was obtained with the same m.p., corresponding to a total yield of 63% based on I. The m.p. and ir and nmr spectra were identical with those of a sample of IVa prepared from acetonitrile and trioxane by a published procedure (5); the ir spectrum agrees with that reported (5); nmr (deuteriochloroform):  $\delta$  2.25 (s, 9, CH<sub>3</sub>),  $\delta$  5.30 (s, 6, CH<sub>2</sub>).

1,3,5-Tripropionylhexahydro-*s*-triazine (IVb).

The crude product obtained by following the above procedure was recrystallized from 2-propanol. The yield was 8.6 g. (47% based on I); m.p. 151°; mol. wt. (osmometric) calcd. 255; found 246, 250. The m.p., ir, and nmr spectra were identical with those of samples of IVb prepared by published procedures from propionitrile and trioxane (5,6,7), and from propionamide and paraformaldehyde (6). Published melting points for IVb vary widely. In our hands, the same m.p. (151°) was noted for samples made by the three methods; it agrees fairly well with that cited by Hodge (152-154°) (1). Our nmr and ir spectra agree with those reported (1,5) and with the assigned structure.

1,3,5-Tri-*n*-butyrylhexahydro-*s*-triazine (IVc).

The above procedure was followed. Vacuum distillation of the hydrolyzed reaction mixture gave 9.8 g. (46%) of crude product, m.p. 50-55°, raised to 79.5° by recrystallization from water-acetone (60:40). A product of identical m.p., ir and nmr spectra was obtained from trioxane and *n*-butyronitrile. This compound is

reported in the literature (8), but without the citation of m.p. or other characterizing data. Ir (potassium bromide), 2960, 2880, 1650, 1420, 1370, 1350, 1245, 1190, 1155, 1105, 1070, 1010, 950, 860, 765, 715, and  $520\text{ cm}^{-1}$ ; nmr (deuteriochloroform):  $\delta$  0.97 (t, 9,  $J \cong 7\text{ Hz}$ ,  $\text{CH}_3$ ),  $\delta$  1.67 (m, 6,  $J \cong 7\text{ Hz}$ ,  $\text{CH}_3\text{CH}_2$ ),  $\delta$  2.50 (t, 6,  $J \cong 7\text{ Hz}$ ,  $\text{COCH}_3$ ),  $\delta$  5.30 (s, 6,  $\text{N-CH}_2$ ).

*Anal.* Calcd. for  $\text{C}_{15}\text{H}_{27}\text{N}_3\text{O}_3$ : C, 60.6; H, 9.2. Found: C, 60.8; H, 9.3. Mol. wt. (osmometric): Calcd.: 297. Found: 296, 295.

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