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THE REACTION OF 1-NITROPROPANE WITH FORMALDEHYDE AND AMMONIA.
1,3-DI-(2-NITROBUTYL)-5-ETHYL-5-NITROHEXAHYDROPYRIMIDINE

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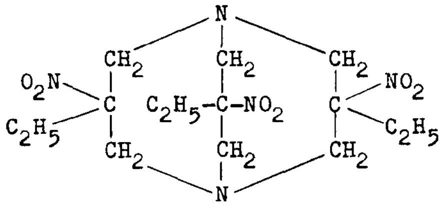
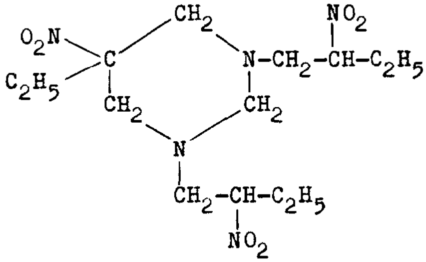
It was formerly found[1,2,3] that 1-nitropropane reacting with formaldehyde and an excess of ammonia could yield compound I, to which the structure of 3,7,10-triethyl-3,7,10-trinitro-1,5-diazabicyclo (3,3,3) undecane (Ia) was assigned.



Ia



Ib

Now, we have reinvestigated the reaction of nitroparaffins with formaldehyde and ammonia as well as the structure of the products.

We have found that the NMR spectrum of compound I (m.p. 107-108°) prepared according to the known method[2] does not agree with previously suggested structure Ia.

The NMR spectrum of compound I (Fig.1.) shows a multiplet with the chemical shift value τ=5.45 ppm, characteristic of protons in the methine group bonded to the nitro group[4] and intensity corresponding to two protons. This indicates that there are two $>CH-NO_2$ groups in the molecule. The signals in the range of τ=6.2 - 7.6 ppm and integral intensity of ten proton units correspond to five methylene groups. The multiplets at about 8.2 ppm and 9.1 ppm and intensities of six and nine protons, respectively, correspond to three ethyl groups. We therefore suggest that only the structure of the 1,3-di-(2-nitrobutyl)-5-ethyl-5-nitrohexahydropyrimidine (Ib) is in agreement with the NMR spectrum.

The signals in the range of 6.2 - 7.6 ppm correspond to the three methylene groups from the hexahydropyrimidine ring and the two side-chain methylene groups adjacent to the nitrogen atoms of the hexahydropyrimidine ring. The

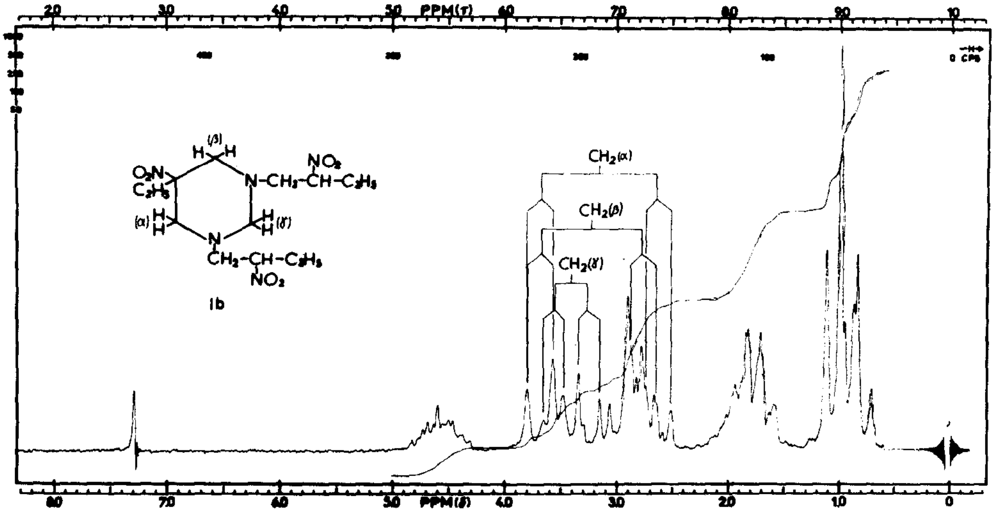


Fig. 1.

frequency sweep double resonance technique, with the irradiation frequency at the methine multiplet ($>CH-NO_2$), allowed us to distinguish three quartets corresponding to the AB systems of three methylene groups from the hexahydropyrimidine ring, as shown on the spectrum (Fig.1.). The chemical shift differences between axial and equatorial protons within each methylene group of the ring may suggest$^{5)}$ the chair conformation of hexahydropyrimidine ring with an axial nitro group at 5-position.

We have confirmed structure Ib for compound I by mass spectrometry. The parent peak M^+ is at value of m/e =361.

Analysis of the NMR and the mass spectra of products obtained from the reaction of nitroparaffins with formaldehyde and ammonia and investigation of its stereochemistry will be published later.

The NMR spectrum was measured at 60 Mc/sec with a Varian HA-60-IL apparatus using a 10% solution in $CDCl_3$ of substance I with TMS as standard.

The mass spectrum was measured in a Hitachi 6A apparatus.

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