

REACTION OF NITROPARAFFINS WITH FORMALDEHYDE AND AMMONIA.  
NEW 5-NITROHEXAHYDROPYRIMIDINE DERIVATIVES

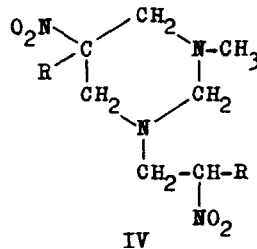
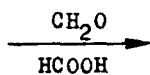
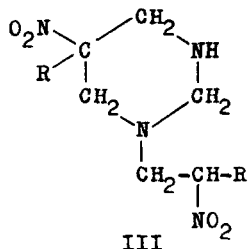
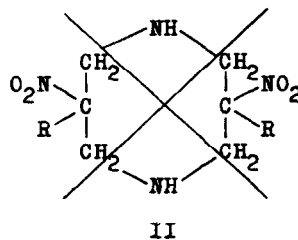
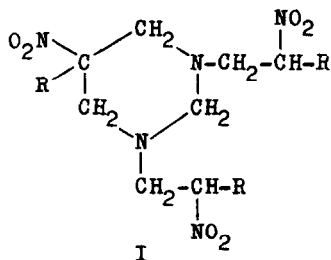
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In our previous paper<sup>1)</sup> it had been shown, that the product of the reaction of 1-nitropropane with formaldehyde and excess of ammonia, to which the structure of 3,7,10-triethyl-3,7,10-trinitro-1,5-diazabicyclo[3.3.3]undecane was initially assigned<sup>2)</sup>, has in fact the structure of 1,3-di-(2-nitrobutyl)-5-ethyl-5-nitrohexahydropyrimidine (Ib).



R = CH<sub>3</sub>- : Ia(114-5°), ~~Ia~~=IIIa(141-2°), IVa(117-8°)  
 R = C<sub>2</sub>H<sub>5</sub>- : Ib(107-8°), ~~Ib~~=IIIb(63-4°), IVb(88-9°)  
 R = n-C<sub>3</sub>H<sub>7</sub>- : Ic(109-10°), ~~Ic~~=IIIc(77-8°), IVc(73-4°)  
 Melting points are given in parentheses.

Presently we found that the correct structure for another compound obtained in this reaction and described originally<sup>2)</sup> as 3,7-diethyl-3,7-dinitro-1,5-diazacyclooctane(IIb) is really 1-(2-nitrobutyl)-5-ethyl-5-nitrohexahydropyrimidine (IIIb).

Furthermore, we have noted that compound Ib appears earlier than IIIb in the reacting mixture and that the latter is formed most probably by the decomposition of the former. This allowed us to obtain unknown compounds Ia and Ic from analogous reactions with nitroethane and 1-nitrobutane, respectively.

We have also found that the correct structures of known compounds IIa<sup>3)</sup> and IIc<sup>4)</sup> are IIIa and IIIc.

Methylation of compounds IIIa, b and c with formaldehyde in formic acid solution (Leuckart's method) gave their methyl derivatives IVa, b and c.

The new structures presented here are given on the basis of the NMR spectra as was shown previously<sup>1)</sup> for structure Ib. Each spectrum shows a multiplet with the chemical shift value  $\tau=5.45 \pm 0.1$  ppm, characteristic of protons in the methine group bounded to the nitro group<sup>5)</sup> and intensities corresponding to two protons for compounds Ia, b and c and to one proton for compounds IIIa, b, c, IVa, b and c. The signals in the range of  $\tau=6.1 - 7.9$  ppm have integral intensity corresponding to five methylene groups for compounds Ia, b and c and to four methylene groups for compounds IIIa, b, c, IVa, b and c. The frequency sweep double resonance technique, with the irradiation frequency at the methine multiplet ( $>CH-NO_2$ ), allowed us to distinguish among these signals the three quartets corresponding to the AB systems of three methylene groups from the hexahydropyrimidine rings of each compound. For compounds IIIa, b, c, IVa, b and c it was also possible to find a pattern of eight peaks for the side-chain methylene groups adjacent to the nitrogen atoms of the hexahydropyrimidine rings. In the spectra of compounds IIIa, b and c there are signals of NH protons at about 7.9 ppm and for compounds IVa, b and c there are singlets of N-methyl groups at 7.75 ppm. The spectra also show the signals of three or two appropriate R groups in agreement with the suggested structures.

Structures Ia,b,IIIa,b and IVa,b were confirmed by mass spectrometry. The parent peaks  $M^+$  are at value of  $m/e=319$  for compound Ia,  $m/e=361$  for Ib,  $m/e=232$  for IIIa,  $m/e=260$  for IIIb,  $m/e=246$  for IVa and  $m/e=274$  for IVb.

Since the molecules discussed have centers of asymmetry there is a possibility of diastereomerism. The problem is under investigation, and the results as well as preparative details will be published later.

The NMR spectra were measured in  $CDCl_3$  solutions at 60 Mc/sec with Varian HA-60-IL spectrometer. The mass spectra were measured in Hitachi 6A apparatus.

#### References

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