Tetrahedron Letters No.24, pp. 2059-2060, 1970. Pergamon Press. Printed in Great Britain.

SYNTHESIS AND NMR SPECTRUM ANALYSIS OF 4,6-DIAZADIHOMOADAMANTAN-5-ONE (4,6-DIAZATRICYCLO[5.3.1.1^{3,9}]DODECAN-5-ONE)[1]

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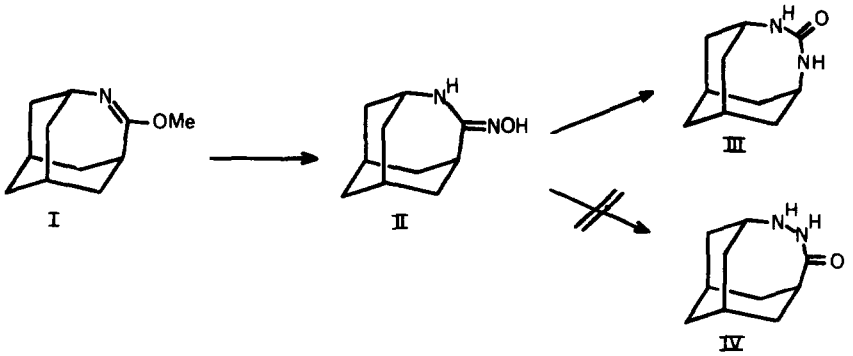
(Received in UK 14 April 1970; accepted for publication 23 April 1970)

Ring expansion of an adamantane to an azahomoadamantane was recently described[2]. We now wish to report the ring enlargement of an azahomoadamantane to a diazadihomoadamantane.

A reaction of 5-methoxy-4-azahomoadamant-4-ene[3] (I) with H_2NOH in boiling MeOH for 3 hours gave 4-azahomoadamantan-5-one oxime (II) in 71% yield[4]; mp. 212-217°C(dec.); IR (KBr): 3400 (NH), 3230, 3130 (broad, OH), 1665 (C=N), 920 (N-O) cm^{-1}; NMR ($CDCl_3$): δ 8.38 (broad, OH), 5.95 (broad, NH), 3.50 (m, 1H, HC-N), 2.62 (m, 1H, HC-C=N), 2.16-1.62 (m, 12H, remaining protons). Treatment of II with polyphosphoric acid at 125°C for 30 minutes afforded 4,6-diazadihomoadamantan-5-one[4] (III) in 56% yield; mp 327-329°C (dec.); IR (KBr):3210, 3060 (NH), 1680 (N-C=O) cm^{-1}. The NMR spectrum in TFA (Fig.1) shows two equivalent NH protons (δ 7.3) and two equivalent bridgehead protons α to the NH-C=O group (δ 4.03, J_{A-NH} = 7 Hz). This is consistent with the symmetrical structure III and excludes the unsymmetrical structure IV. Due to the symmetry of the molecule the proton signal between δ 1.5 and δ 2.5 can be interpreted quite easily after spin decoupling (Fig.1): four equivalent protons B at δ 1.83, four equivalent protons C at δ 2.33, J_{BC} = 15 Hz (J gem), two equivalent protons D at δ 2.00 and two equivalent protons E at δ 1.60. The assignment of D and E is based on the apparent bandwith (D is broader, having more vicinal couplings).



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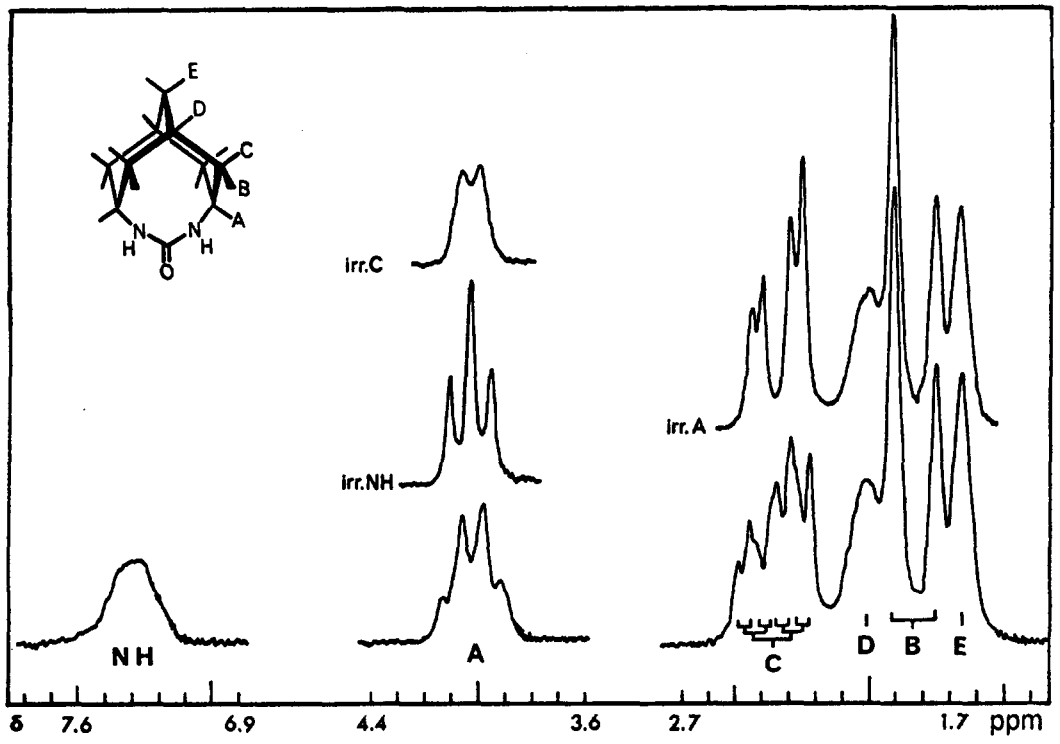

Fig. 1

An interesting feature is the difference between the vicinal coupling constants, measured in the spin-decoupled spectra, of the protons A, B, C and D: $J_{AB} \simeq 0$ Hz, $J_{BD} \simeq 0$ Hz, $J_{AC} = 7.5$ Hz, $J_{CD} = 4.0$ Hz. J_{AB} must be very close to zero, because the signals of proton B are not sharpened on irradiation of proton A. The difference between the vicinal coupling constants clearly indicates a difference between the dihedral angles of the C-H bonds, which are about 90° for AB and about 20° for AC according to the Karplus relation. This difference between the dihedral angles clearly demonstrates a partially flattened chair conformation of the two six membered rings in this strained molecule.

The assignment of the protons B and C was based on the observed coupling constants and the apparent dihedral angles in a Dreiding model.

References and Footnotes

1. We prefer the name 4,6-diazadihomoadamantan-5-one
2. J.G.Korsloot, V.G.Keizer and J.L.M.A.Schlatmann, Rec.Trav.Chim. 88, 447 (1969).
3. The synthesis of this compound will be published elsewhere.
4. A satisfactory elemental analysis and a mass spectrum consistent with the assigned structure were obtained.