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A NOVEL HETEROPOLYCYCLIC SYSTEM FROM N-METHYLQUINOXALINIUM IODIDE AND NITROETHANE

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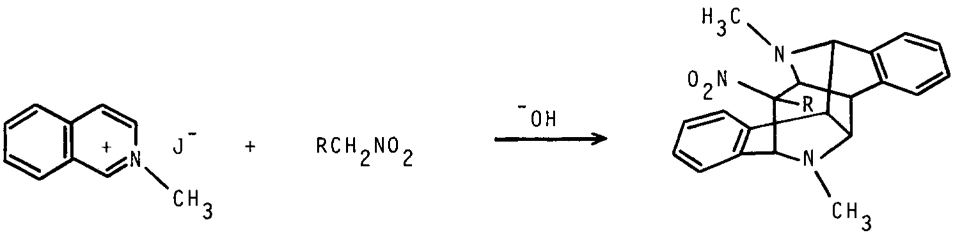
Summary: Reaction of N-methylquinoxalinium iodide with nitroethane results in either the 1:2 diadduct at C-2 and C-3 or the formation of substituted 1,3,6,10-tetraazatetracyclo$[7.3.1.0.^{2,7}0^{6,13}]$tridecane derivative.

It was previously found that nitroalkanes react with N-methylisoquinolinium iodide in the presence of a base to yield heteropolycyclic compounds to which the structure 1 was assinged.$^{1)}$



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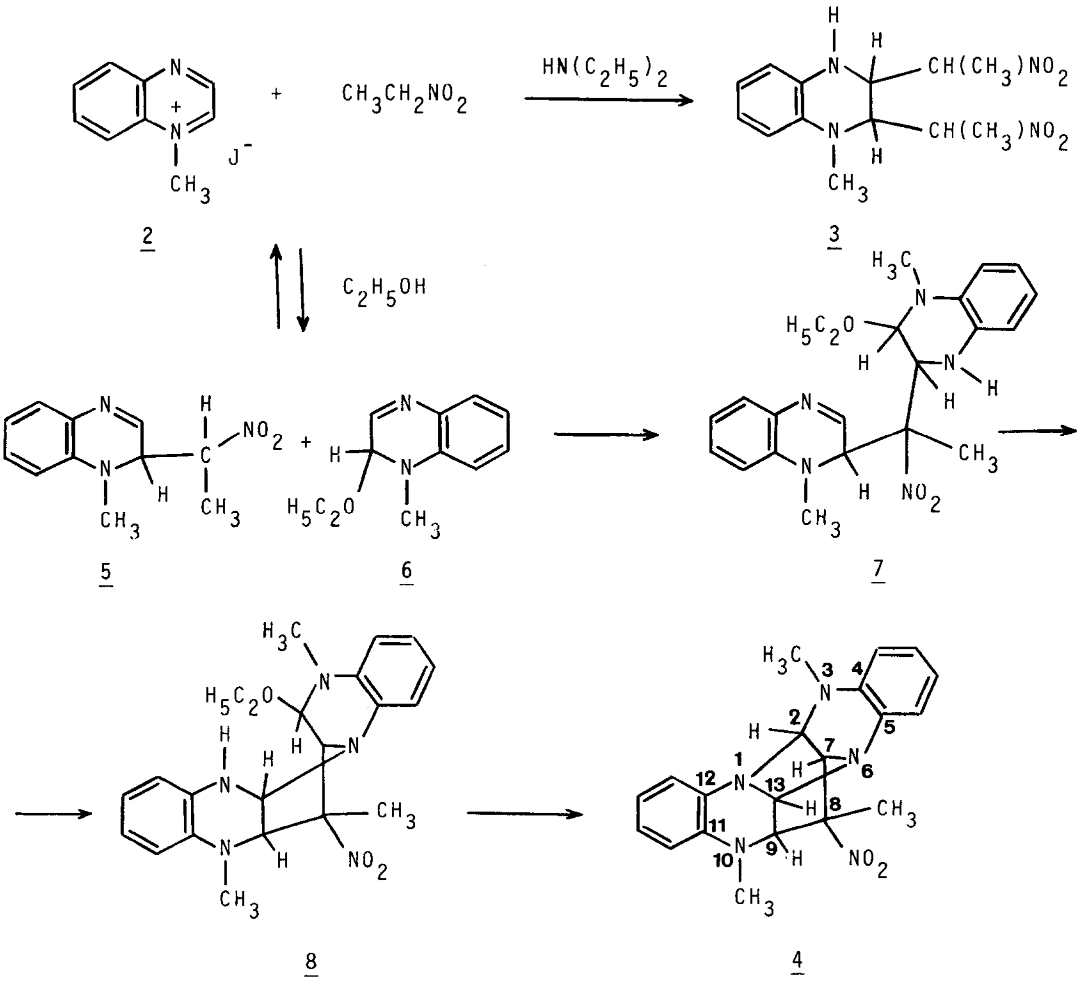
In this communication we wish to show another example of the unusual condensation of a N-methylazinium cation with a nitroalkane.

The ability of N-methylquinoxalinium iodide (2) to add two molecules of nucleophilic reagents is well established.$^{2)}$ In full agreement with this observation 2,3-di(1-nitroethyl)-1-methyl-1,2,3,4-terahydroquinoxaline (3) is formed in good yield (87 %) when the cation 2 reacts with an excess of nitroethane in the presence of diethylamine.$^{3)}$ Evidence for the structure 3 is provided by the ^1H NMR spectra of compound 3 and its 2,3-D_2-analogue.$^{4)}$

Alternatively, when nitroethane is allowed to react with a three fold excess of the quaternary salt 2 in an ethanolic solution containing diethylamine another product (4) is formed in yield 37 %. The ^1H and ^{13}C NMR and mass spectrometry data of the product obtained have shown that it has the formula $C_{20}H_{21}N_5O_2$ and consists of two tetrahydroquinoxaline fragments condensed with a nitroethane moiety.[5)] This product has been identified by means of X-ray crystallography (Figure) [6)] as 3,8,10-trimethyl-8-nitrodibenzo[d,k]-1,3,6,10-tetraazatetracyclo$[7.3.1.0^{2,7}0^{6,13}]$tridecane-4,11-diene (4).

On the basis of results obtained in earlier studies,[2)] we suggest that the formation of 4 occurs via the intermediacy of 5 - 8.



In accordance with the reactivity of N-methylquinoxalinium iodide (2) in nucleophilic addition reactions [2)] the σ-adducts 5 and 6 are expected to be formed initially under the conditions mentioned above. Sound evidence for the formation of 6 in an ethanolic solution of 2 in the presence of diethylamine has recently been obtained by ^{1}H NMR spectroscopy.2c) Also it seems highly probable that these σ-adducts 5 and 6 can interact to give the intermediate 7 followed by intramolecular cyclizations (Scheme 2). The mechanism suggested enables us to explain why CH-active nitroethane becomes attached to C-2 of one molecule of 2 and to C-3 of another one.

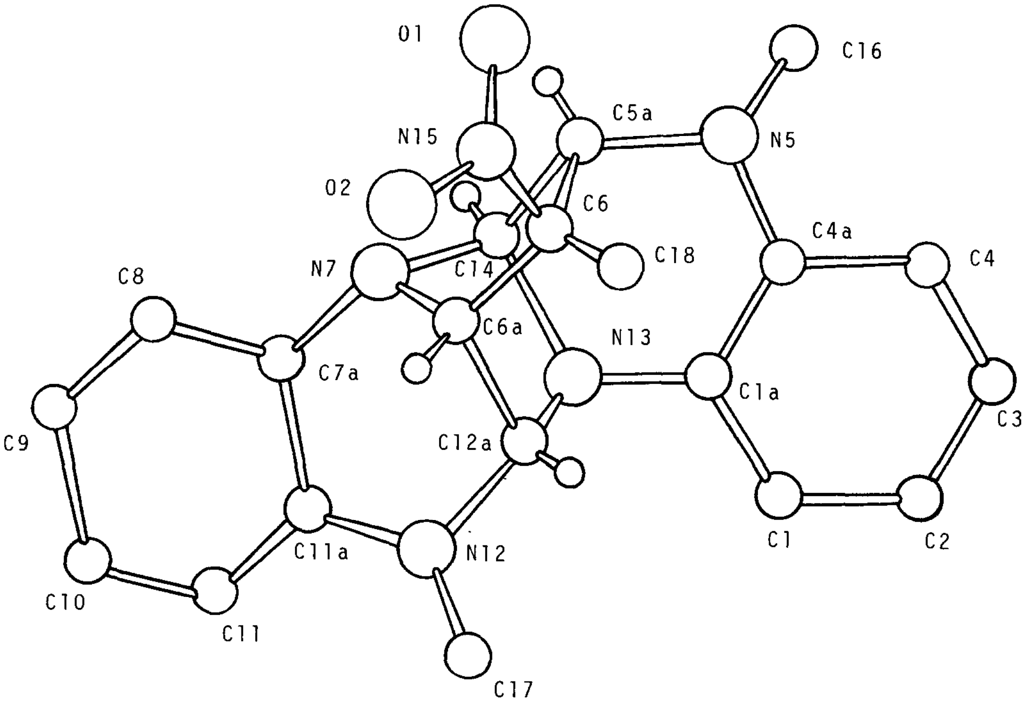


Figure. Three dimentional structure of 4

The reaction of N-methylquinoxalinium iodide (2) with nitroethane in ethanol is a simple one-step route to the tetraazatetracyclotridecane derivative 4. It seems to be a very attractive and promising method for the synthesis of related heteropolycyclic compounds. Investigation of the scope of this reaction is in full progress now.

References and Notes

1) W.R.Schleigh, Tetrahedron Lett., 1405 (1969).

2 a) J.W.Bunting, M.G.Meathrel, Can.J.Chem.,50, 919 (1972).

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3) All new compounds gave satisfactory elemental analyses.

4) Compound 3: m.p. 196-197^o, ^{1}H NMR ($CDCl_3$), δ = 1.53 (d, 3H, CH_3, J= 7 Hz), 1.57 (d, 3H, CH_3, J= 7 Hz), 2.90 (s, 3H, NCH_3), 3.4 - 4.8 (m, 4 CH, the multiplet is transformed into two quartets at 4.50 and 4.60 ppm in the spectrum of 2,3-D_2-analogue of 3), 5.82 (s, 1H, NH), 6.4 - 6.8 (m, 4H, arom. protons).

5) Compound 4: m.p. 217-218^o, ^{1}H NMR ($CDCl_3$), δ = 1.30 (s, 3H, CH_3), 3.14 (s, 3H, NCH_3), 3.24 (s, 3H, NCH_3), 4.10 (s, 1H,CH), 4.36 (m, 2H, CH), 4.64 (m, 1H, CH), 6.5 - 7.5 ppm (m, 8H, arom.protons), ^{13}C NMR ($CDCl_3$), δ = 18.0 (CH_3), 37.8 and 38.4 (two NCH_3 groups), 64.6, 66.0, 80.8 and 81.8 (4 CH), 96.2 (C-NO_2), 109.5, 113.4, 117.0, 118.3, 124.7, 125.3, 125.8, 127.3, 129.7, 132.4, 136.6 and 141.9 ppm (two benzene rings). M^+= 363.

6) The crystal analysis was carried out on a Synthex P1 diffractometer (graphite monochromated CuK_α radiation, $\theta/2\theta$ -scanning $2 \leq 2\theta \leq 120^o$). 2100 Reflections with $F^2 \geq 3\sigma$ were collected. The crystals are monoclinic with cell constants: a = 7.751(1), b = 17.159(4), c = 13.855(3) Å, β = 105.44(2)^o. V = 1776.3(6) Å^3, $d_{calc.}$= 1.31 g/cm^3. Space group is $P2_1/c$ with 4 molecules per unit cell. The structure was solved by a straightforward method and refined to a R value of 0.056. The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK. Any request should be accompanied by the full literature citation for this communication.

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