Aprotic Diazotization of *endo*-7-Aminomethylbicyclo[3,3,1]nonan-3-one

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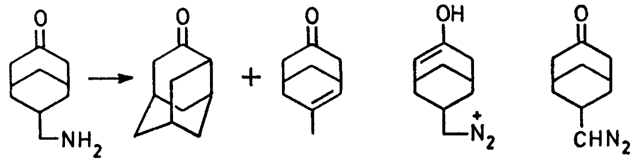
Summary Aprotic diazotization of *endo*-7-aminomethylbicyclo[3,3,1]nonan-3-one yields protoadamantan-4-one and 3-methylbicyclo[3,3,1]non-2-en-7-one; the latter was converted into adamantan-1-ol on catalytic hydrogenation with Pd–C.

There has been much interest[1] in diazotization of aliphatic amines recently. We report here the deamination of *endo*-7-aminomethylbicyclo[3,3,1]nonan-3-one[2] (**1**), as well as the behaviour of one of the products on catalytic hydrogenation. Under aprotic conditions (isopentyl nitrite–acetic acid–benzene),[3] (**1**) gave principally (**2**) (67%) (characterized by comparison with authentic material[4]) and (**3**) (20%). (**2**) could possibly be formed *via* a diazonium enol[5] (**4**) or diazoalkane[6] (**5**) intermediate.



(1) (2) (3) (4) (5)

The liquid product (**3**) was identified by microanalysis, its n.m.r. [δ ($CDCl_3$): 1·58 (3H, s), 1·8–2·9 (10H, m), and 5·5 (1H, indefinite d) p.p.m.]; and i.r. spectrum (neat) [ν_{max} 3030, 2940, 2870, 1710, 1430, 1370, 1230, 1170, 1070, 915, and 848 cm^{-1}], and its conversion into the known[7] 3-methylbicyclo[3,3,1]non-2-ene, by Wolff–Kishner reduction.

Catalytic hydrogenation of (**3**) in absolute alcohol with Pd–C in a Parr apparatus furnished adamantan-1-ol in very good yield. Examples in which these conditions lead to thermodynamically stable products have been presented, and mechanistic aspects have been discussed.[8] Related transformations have also been observed involving suitably substituted bicyclo[3,3,1]nonanes in other systems.[9]

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[1] R. A. Moss, *Chem. Eng. News*, 1971, **49**, 28, and references therein.

[2] P. Kovacic, J.-H. Liu, E. M. Levi, and P. D. Roskos, *J. Amer. Chem. Soc.*, 1971, **93**, 5801.

[3] L. Friedman and J. H. Bayless, *J. Amer. Chem. Soc.*, 1969, **91**, 1790.

[4] R. M. Black and G. B. Gill, *Chem. Comm.*, 1970, 972; W. H. W. Lunn, *J. Chem. Soc.* (*C*), 1970, 2124.

[5] M. Miyano and C. R. Dorn, *J. Org. Chem.*, 1972, **37**, 268.

[6] D. M. Bailey, J. E. Bowers, and C. D. Gutsche, *J. Org. Chem.*, 1963, **28**, 610; J. R. Alford and M. A. McKervey, *Chem. Comm.*, 1970, 615.

[7] R. A. Appleton and S. H. Graham, *Chem. Comm.*, 1965, 297.

[8] S. Siegel and G. V. Smith, *J. Amer. Chem. Soc.*, 1960, **82**, 6087; S. Siegel and B. Dmuchovsky, *ibid.*, 1964, **86**, 2192.

[9] M. Eakin, J. Martin, and W. Parker, *Chem. Comm.*, 1965, 206.