Transannular Reactions in the Bicyclo[3,3,1]nonane System

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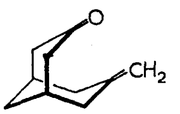
THE report by Stetter *et al.*[1] of bridging reactions of 7-*exo*-methylenebicyclo[3,3,1]nonan-3-one (I) prompts us to describe some of our recent findings.

Lithium aluminium hydride reduction of (I)[2] gave the corresponding alcohols (IIa) and (IIIa) in the ratio of 1 to 5, configurational assignments being based on p.m.r., and high-dilution infrared spectra, and g.l.c. behaviour. Sodium–moist ether reduction of (I) furnished (IV) as the sole product; the structure for this alcohol m.p. 165—166° follows from its p.m.r. spectrum in $D_2O/CDCl_3$ solution which showed a sharp unsplit methyl signal at τ9·0 (3-H), and no signal in the region τ4—6·5. An analogous reductive cyclisation has recently been described by Stork.[3]

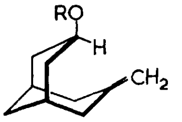
The treatment of (IIa) and (IIIa) respectively with toluene-*p*-sulphonyl chloride in pyridine gave the corresponding tosylates (IIb), m.p. 74—75° and (IIIb) m.p. 88—89°. Shaking a solution of the tosylate (IIb) in ether with 6N-sulphuric acid at room temperature for three hours produced a smooth conversion into adamantan-1-ol (identified by mixed m.p., comparative high-resolution infrared spectra, and g.l.c. analysis). The epimeric tosylate (IIIb) was unaffected by this treatment, although prolonged shaking with 6N-hydrochloric acid yielded a mixture of (IIIb) and the isomer (V). The conversion of (IIb) into adamantan-1-ol constitutes a π-route[4] to the 1-adamantyl cation.[5]

The ease with which suitably substituted bicyclo[3,3,1]nonane compounds undergo transannular cyclisation to yield adamantane derivatives[6] is further illustrated by the conversion of the tosylate (IIIb) into a mixture of adamantane and 3-*exo*-methylenebicyclo[3,3,1]nonane in the ratio of 3·75 to 1 by treatment with lithium aluminium hydride. In addition, Wolff–Kishner reduction of (I) gave adamantane as the only isolated product.

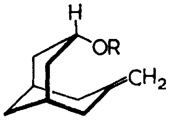
Solvolytic rate measurements on (IIb) and (IIIb) and conformational studies in this series are under active investigation.



(I)

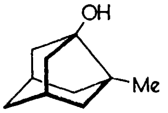


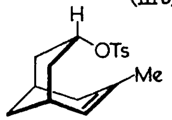
(IIa) R=H
(IIb) R=Ts



(IIIa) R=H
(IIIb) R=Ts

(IV)





(V)

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[1] H. Stetter, J. Gärtner, and P. Tacke, *Angew. Chem.*, **1965**, **4**, **153**.

[2] H. Stetter and P. Tacke, *Chem. Ber.*, **1963**, **96**, **694**.

[3] G. Stork, S. Malhotra, H. Thompson, and M. Uchibayashi, *J. Amer. Chem. Soc.*, 1965, **87**, 1148.

[4] B. Capon, *Quart. Rev.*, 1964, **18**, 45, and references cited there.

[5] R. C. Fort and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1964, **86**, 4194. R. C. Fort, P. von R. Schleyer, W. E. Watts, M. B. Comisarow, and G. A. Olah, *ibid.*, 1964, **86**, 4195.

[6] R. C. Fort and P. von R. Schleyer, *Chem. Rev.*, 1964, **64**, 277.