The Schmidt Reaction of Adamantanone

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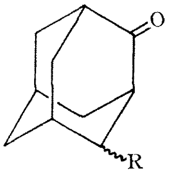
Summary The Schmidt reaction of adamantanone in glacial acetic acid–toluene-*p*-sulphonate gives the normal product (III).

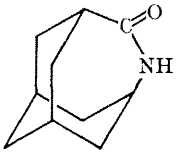
THE occurrence of an abnormal Schmidt reaction of adamantanone (I) in methanesulphonic acid to give 4-methylsulphonoxyadamantanone (II) has been reported.[1] Two recent reports[2,3] on the Beckmann rearrangement of (I)-oxime prompt us to publish our further results of the Schmidt reaction of (I).

The Schmidt reaction of (I) in glacial acetic acid catalysed with toluene-*p*-sulphonic acid gave the normal product, 4-azatricyclo[4,3,1,$1^{3,8}$]undecane-5-one (III)† [31%: m.p. >300°; *m/e* 165 (M^+), 150 ($M^+ - \mathrm{NH}$), 137 ($M^+ - \mathrm{CO}$), and 122 ($M^+ - \mathrm{CHNO}$); $\nu_{\max}$ (KBr) 3200, 3080, and 1650 cm.$^{-1}$; τ ($CDCl_3$) 2·80 (1H, s), 6·48 (s, 1H), 7·16 (s, 1H), 7·75 (s, 2H), and 7·80—8·20 (m, 10H). The highly strained lactam (III) was sufficiently basic to give a hydrochloride [m.p. >300°; $\nu_{\max}$ (KBr) 2600—2000 and 1655 cm^{-1}; *m/e* 165 ($M^+ - \mathrm{HCl}$)]. The Schmidt reaction of (I) in methanesulphonic acid gave (III) as a minor product (10%) in addition to the main product (II) (90%); the Schmidt reaction in trifluoroacetic acid and trichloroacetic acid gave only the starting material. The Beckmann rearrangement of (I)-oxime and its toluene-*p*-sulphonate also gave (III).

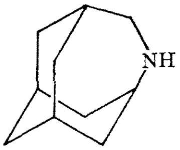
Reduction of (III) ($LiAlH_4$) gave 4-azahomoadamantane (IV): m.p. 198—200°; $\nu_{\max}$ (KBr) 3300 cm.$^{-1}$; *m/e* 151 (M^+), 136 ($M^+ - \mathrm{NH}$), and 122 ($M^+ - \mathrm{CH_2NH}$); τ ($CDCl_3$) 6·42 (1 H, m), 6·60 (1 H, s), 6·98 (2 H, d, *J* 3·0 Hz.), and 7·40—8·70 (13 H, m), picrate m.p. 283—285°.



(I) R = H
(II) R = O·SO_2Me



(III)



(IV)

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† All new compounds gave satisfactory elemental analyses.

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[3] V. L. Narayanan and L. Setescak, *J. Heterocyclic Chem.*, 1969, **6**, 445.