The Cleavage of t-Adamantyloxy-radicals

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Summary Two-step reaction sequences to 4-substituted tricyclo[4,3,1,$0^{3,8}$]decanes and 3-substituted tricyclo[3,3,1,$0^{3,7}$]nonanes are reported: the key step in each case involves the scission of a t-adamantyloxy-radical.

INTEREST has been shown recently in the chemistry of tricyclo[3,3,1,$0^{3,7}$]nonanes†[1] and of tricyclo[4,3,1,$0^{3,8}$]decanes.†[2,3] In the second case, tricyclo[4,3,1,$0^{3,8}$]decan-4-one (X) was prepared using the adamantan-2-yl → tricyclo[4,3,1,$0^{3,8}$]decan-4-yl cation rearrangement.[3] The migration appears to proceed in a synthetically useful yield only if it is of the pinacol–pinacolone type (*i.e.* an adamantan-1-ol-2-yl cation was employed).[3b] Nevertheless, starting from commercially available materials (*i.e.* adamantane-1-carboxylic acid) the preparation of the tricyclic ketone requires a ten-stage sequence in which the overall yield is at best 8·5%. The routes available to 3-substituted tricyclo[3,3,1,$0^{3,7}$]nonanes are scarcely better. We report here on superior routes to both systems by way of the scission of the t-adamantyloxy-radicals (II, VII) which were conveniently generated from the corresponding hypohalites (I, VI).

(i) *Hypochlorites.* The following illustrates the procedure for compounds (I). A solution of 2-methyladamantan-2-ol hypochlorite (I; X = Cl, R = Me) in dry CCl_4 was prepared by the action of chlorine monoxide on the parent alcohol[4] at 0°. Thermolysis at the reflux temperature (8 h) or photolysis at 0° (30 min) yielded 3-chlorobicyclo[3,3,1]non-7-yl methyl ketone (IV; X = Cl, R = Me) in 75—80% yield, b.p. 110—116° (bath)/0·3 mm. The assigned structure follows from the analytical and spectral data: i.r. (film)

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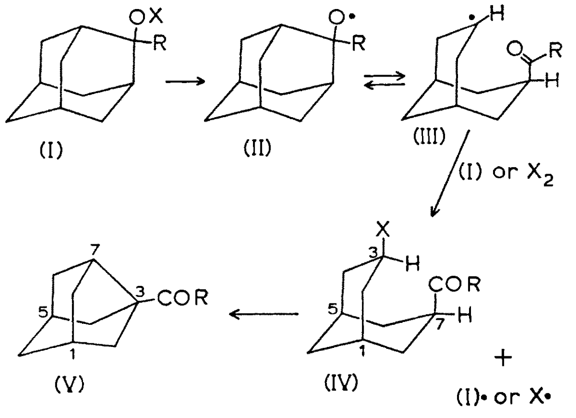
† Commonly (and ambiguously) referred to as noradamantanes and isoadamantanes (protoadamantanes), respectively.

1705, 1355, and 770 cm^{-1}; 100 MHz n.m.r. (CCl$_4$) τ 5·60 (1H, t of t, $J_{AX}+J_{BX}$ 36 Hz; 3-H), 7·35 (1H, t of t, $J'_{AX}+J'_{BX}$ 37 Hz; 7-H), 8·01 (3H, s; Me), and 7·70—8·70 (12H, m); *m/e* (M^+) 202, and 200.

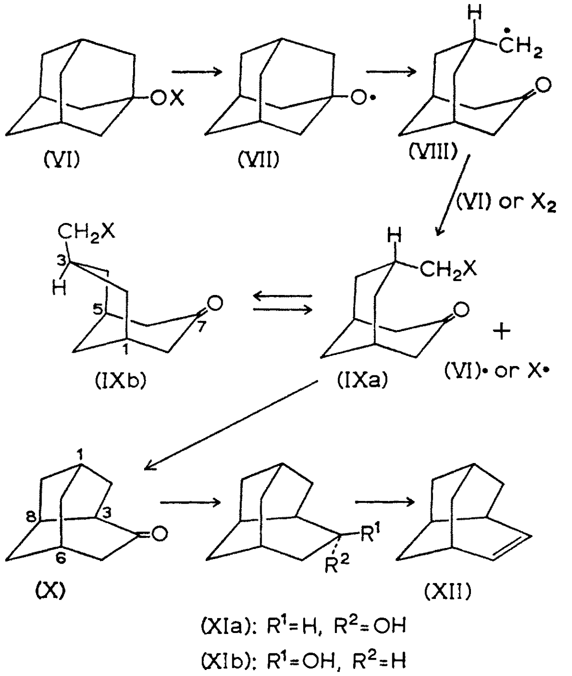


The thermolabile chloroketone was converted by base (*e.g.* KOH–MeOH) into methyl tricyclo[3,3,1,0^{3,7}]non-3-yl ketone (V; R = Me), b.p. 60—65° (bath)/0·7 mm. (80%); oxime m.p. 152—153° (mixture of isomers). The conversion (I) → (V) could be reduced to a single stage merely by eluting the crude reaction product (in benzene) over basic alumina (66% yield based on I; X = H, R = Me). The product was not tricyclo[4,3,1,1^{3,8}]undecan-4-one,[5] and the assigned structure follows from the physical data: i.r. (CCl$_4$) 1697, and 1355 cm^{-1}; 100 MHz n.m.r. (CCl$_4$) τ 7·42 (1H, t of t, $J_{AX}+J_{BX}$ 14 Hz; 7-H), 7·71br (2H, m; 1-H and 5-H), 7·96 (3H, s; Me), and 8·00—8·46 (10H, m); *m/e* (M^+) 164.

Haloform degradation (KOH–Br$_2$–aq. dioxan) of (V; R = Me) gave tricyclo[3,3,1,0^{3,7}]nonane-1-carboxylic acid (V; R = OH) in 88% yield, m.p. 108—109° (lit.[1a] m.p. 106—107°); i.r. (CCl$_4$) 3300—2600br, 1693, 1416, 1310, and 1293 cm^{-1}; 60 MHz n.m.r. (CCl$_4$) τ −1·65 (1H, s; CO$_2$$H$), 7·28 (1H, t of t, $J_{AX}+J_{BX}$ 14 Hz; 7-H), 7·70—8·55 (12H, m).

In contrast, only a very low yield of tricyclo[4,3,1,0^{3,8}]decan-4-one (X) was obtained in the analogous sequence from (VI; X = Cl).

(ii) *Hypoiodites.* The hypoiodite (VI; X = I) was prepared *in situ* in dry benzene by the action of lead tetra-acetate and iodine (in the presence of dry calcium carbonate)[6] on adamantan-1-ol. Thermolysis at 55—60° (higher temperatures decomposed the thermolabile product) for 1·5 h gave a colourless crystalline product (40—45%), m.p. 78—79° (from MeOH and then light petroleum at −78°), identified as *endo*-3-iodomethylbicyclo[3,3,1]nonan-7-one (IX; X = I); i.r. (CCl$_4$) 1708 cm^{-1}; 60 MHz n.m.r. (CCl$_4$) τ 7·05 (2H, d, J 6·3 Hz; CH_2I), 7·45–8·60 (11H, m), 9·14br (2H, t, separation between outer lines *ca.* 22Hz; boat axial 2-H and 4-H); *m/e* (M^+) 278. The data favour conformer (IXb).



The iodoketone was converted by base (*e.g.* KOH–MeOH, or pyridine) into tricyclo[4,3,1,0^{3,8}]decan-4-one (X; 70—75%), m.p. 212—214° (from aq. MeOH or sublimation; lit.[3b] m.p. 205—208°).

Reduction of (X) by lithium aluminium hydride gave a 2 : 1 mixture of the epimeric alcohols (XI; 90%), m.p. 232—234° (*cf.* ref. 3b). Pyrolysis of (XI) xanthate gave tricyclo[4,3,1,0^{3,8}]dec-4-ene (XII; 34%), m.p. 183—185°: i.r. (CCl$_4$) 3035, 1633, 870, and 696 cm^{-1}; 100 MHz n.m.r. (CCl$_4$) τ 3·89 (2H, m; 4-H and 5-H), 7·38 (2H, m; 3-H and 6-H), and 7·50—8·66 (10H, complex m). Attempted dehydration of mixture (XI) by the toluene-*p*-sulphonyl chloride–pyridine method[5] gave instead mainly adamantan-2-ol toluene-*p*-sulphonate (I; X = C$_7$H$_7$SO$_2$, R = H).

The analogous reactions of hypoiodites (I; X = I, R = Me, Et, or Ph) took an abnormal course; thus (I; X = I, R = Me) gave a yellow crystalline di-iodoether (C$_{11}$H$_{18}$I$_2$O).

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[6] For example see: von Ch. Meystre, K. Heusler, J. Kalvoda, P. Wieland, G. Anner, and A. Wettstein, *Helv. Chim. Acta*, 1962, **45**, 1317.