

## SYNTHESIS OF 9-SUBSTITUTED HOMOADAMANTANES

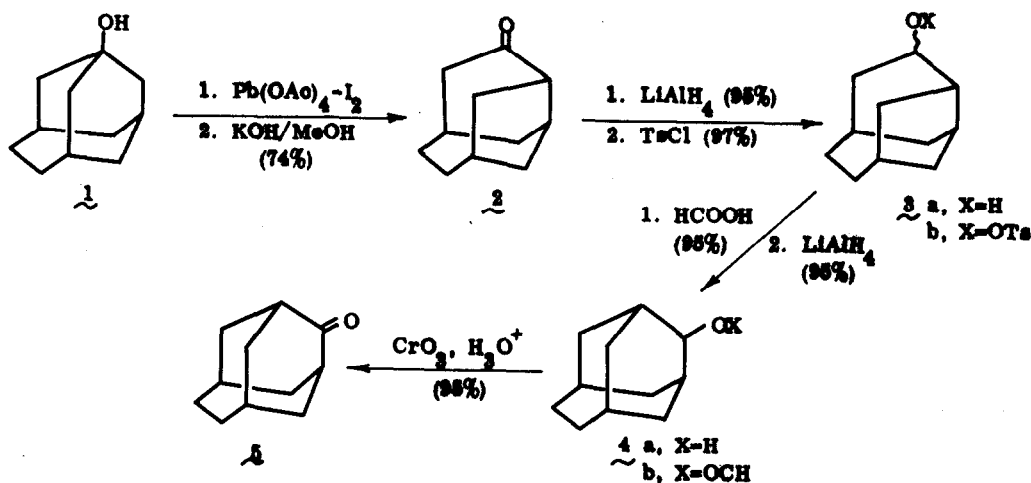
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**Summary:** 9-Homoadamantanone was prepared conveniently from 1-homoadamantanol via 10-homoprotoadamantan-4-one in 58% overall yield.

Although the homoadamantane system has been extensively studied,<sup>1,2</sup> no 9-substituted homoadamantane derivative has been previously prepared. 9-Substituted homoadamantanes are interesting compounds which resemble structurally the 2-substituted adamantanes, but which should rearrange more readily.

In this work we report a convenient, 79% overall yield synthesis of 9-homoadamantanone (5) from 10-homoprotoadamantan-4-one (2, tricyclo[4.3.2.0<sup>3,8</sup>]undecan-4-one). This ketone is readily available by thermolysis of 1-homoadamantyl hypoiodite (prepared in situ from 1-homoadamantanol, 1) followed by the base promoted intramolecular cyclization of the resulting iodo ketone.<sup>3</sup>



Thus,  $\text{LiAlH}_4$  reduction of ketone 2 (1.0 g, 6.1 mmol) yielded 95% of a 4.5 : 1 mixture of 10-homoprotoadamantan-4-ols (3a), which was converted (97%) into the corresponding tosylates (3b) by the usual procedure.<sup>4</sup> Formolysis of the tosylate mixture (1.8 g, 5.6 mmol) at 55 °C for 3 hrs produced oily 9-homoadamantyl formate<sup>5</sup> (4b) in 95% yield. (Solvolysis in 75% aqueous acetone in the presence of excess  $\text{Na}_2\text{CO}_3$  (reflux, 24 hrs) yielded 90% of a 1 : 1 mixture of 3a and 4a, in addition to 10% of 10-homoprotoadamant-4-ene.) Crude formate 4b was reduced by  $\text{LiAlH}_4$  to yield 95% of 9-homoadamantanol (4a) which was readily converted into 9-homoadamantanone (5) by Jones

oxidation. Pure ketone 5 ( $\geq 97\%$  by GLC; 0.79 g, 95% based on 4a) was obtained by column chromatography (neutral  $\text{Al}_2\text{O}_3$  activity III, eluent: pentane  $\rightarrow$  ether). Wolff-Kishner reduction of ketone 5 produced the parent hydrocarbon, whose  $^1\text{H}$  NMR, IR, and mass spectra were identical to those of an authentic sample of homoadamantane.

The physical and spectral properties of 9-homoadamantanol (4a) and 9-homoadamantanone (5) are given below: 4a mp 271-273  $^\circ\text{C}$ ;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  30.71, 30.79, 31.13, 33.54, 33.76, 34.03, 38.11, and 73.85 ppm;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.0-2.5 (17H, m), 3.6 ( $\alpha$ -H, t, J 3Hz) ppm; IR (KBr) 3280(s), 2900(s), 2845, 1445, 1060, 1035, 945  $\text{cm}^{-1}$ ; MS m/e 166(3%), 148(100), 119(52), 93(63), 79(58), 67(31); 5 mp 263-265  $^\circ\text{C}$ ;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  30.88, 33.39, 40.77, 47.12, 203.74 ppm;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.5-2.6 (m) ppm; IR (KBr) 2920(s), 2850, 1720(s), 1450, 1045, 970  $\text{cm}^{-1}$ ; MS m/e 164(100%), 146(5), 93(35), 79(40), 67(37).

Studies of the chemistry of 9-substituted homoadamantanes in general and with respect to the synthesis of 1,9- and 2,9-disubstituted homoadamantanes are currently in progress.

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#### References and Notes

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5.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.0-2.5 (16H, m), 4.8 ( $\alpha$ -H), 8.0 (OOCH) ppm; IR (film) 2910(s), 2850, 1725(s), 1450, 1180(s), 1150  $\text{cm}^{-1}$ ; MS m/e 148(100%), 105(40), 102(74), 79(32), 67(21).

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