Synthesis and Solvolysis of Tricyclo[3.2.1.0^{3,6}]octan-1-ylmethyl Toluene-*p*-sulphonate

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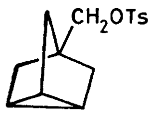
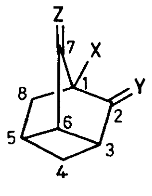
Summary The convenient synthesis and acetolysis of tricyclo [3.2.1.0^{3,6}]octan-1-ylmethyl toluene-*p*-sulphonate are described.

A recent report on the solvolysis of the nortricyclylmethyl system (**1**)[1] prompted us to study the four-membered ring analogue (**2a**). Several syntheses of this tricyclic skeleton have been described.[2] However, none of these procedures would lead to compounds with a substituent at the bridgehead position. We report here for the first time the synthesis and acetolysis of tricyclo[3.2.1.0^{3,6}]octan-1-ylmethyl toluene-*p*-sulphonate (**2a**).



(1)



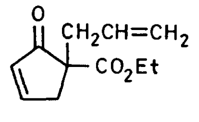
(2)

a; X = CH_2OTs, Y = Z = H_2
b; X = CO_2Et, Y = Z = H_2
c; X = CH_2OH, Y = Z = H_2
d; X = CO_2Et, Y = O, Z = H_2
e; X = CO_2Et, Y = H_2, Z = O
f; X = CO_2Et, Y = $(MeS)_2$, Z = H_2
g; X = CO_2Et, Y = H_2, Z = $(MeS)_2$
h; X = CH_2OAc, Y = Z = H_2

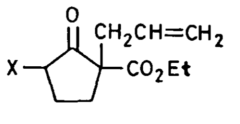
The cyclopentenone (**3**) (b.p. 90—92 °C at 6 mmHg)† was obtained in 36% yield by hydrogen peroxide oxidation of the selenide (**4b**) which was prepared from (**4a**) by treatment with lithium di-isopropylamide followed by benzeneselenenyl bromide at −78 °C.[3] The cyclopentenone (**3**) was irradiated at 0 °C to afford a mixture of (**2d**) and (**2e**) (71%, *ca.* 10 : 1; b.p. 83—85 °C at 0·06 mmHg). Without separation of the isomers, the mixture was treated with methanethiol in ether with boron trifluoride–ether as catalyst to give a mixture of

† All new compounds exhibited satisfactory spectroscopic and analytical data consistent with the proposed structures.

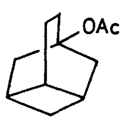
(**2f**) and (**2g**) (b.p. 105—110 °C at 0·05 mmHg) in essentially quantitative yield. The thioacetals (**2f**) and (**2g**) were then refluxed with W-2 Raney-nickel in ethanol to yield (**2b**) (91%, b.p. 120—124 °C at 20 mmHg). The structure of (**2b**) was unambiguously proved, particularly, by its ^{13}C n.m.r. spectrum which exhibits only nine signals, at δ 14·2 (CH$_3$), 34·6 (C-3 and C-5), 35·9 (C-4), 41·0 (C-2 and C-8), 43·2 (C-6), 44·0 (C-7), 53·1 (C-1), 59·9 (CH$_2$O), and 175·3 (CO) p.p.m. Lithium aluminium hydride reduction of (**2b**) afforded (**2c**) (89%, b.p. 112—114 °C at 20 mmHg) which was then transformed to (**2a**) by the usual manner.



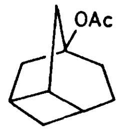
(3)



(4)a; X = H
b; X = SePh



(5)



(6)

The rates of acetolysis of (**2a**) were measured at three different temperatures in glacial acetic acid with 1% acetic anhydride. The first-order rate constants are (1·05±0·01) × 10^{-5} s^{-1} at 99·2 °C, (2·33±0·12) × 10^{-5} s^{-1} at 111 °C, and (3·71±0·29) × 10^{-5} s^{-1} at 119 °C, and the activation parameters are calculated to be $\Delta H^{\ddagger} = 17{\cdot}8 \pm 1{\cdot}5$ kcal mol^{-1} and $\Delta S^{\ddagger} = -34{\cdot}0 \pm 3{\cdot}9$ cal K^{-1} mol^{-1}.‡ We have also studied the solvolysis of bicyclo[2.2.1]heptan-1-ylmethyl toluene-*p*-sulphonate under the same conditions for comparison. The rate constant (1·13 × 10^{-5} s^{-1} at 99·2 °C) is in good agreement with the literature data.[4] The rate constant for the acetolysis of (**2a**) is about six times greater than that for neopentyl derivative,[5] slightly smaller than that for bicyclo[2.2.1]heptan-1-yl system, and much larger (20-fold) than that for nortricyclic compound (**1**).[1] It is noteworthy that the more strained (**2a**) even reacts slightly more slowly than the less strained norbornyl derivative. Moreover, the discrepancy in rate constants between (**1**) and (**2a**) suggests that, unlike the cycloproprane moiety in (**1**), the cyclobutane ring has little effect on the solvolytic reactivity of (**2a**).

The large negative $\Delta S^{\ddagger}$ and smaller $\Delta H^{\ddagger}$ are of interest. The results tend to favour an S_N2-like mechanism, and this seems also to be supported by our work on the product distribution. Thus, (**2a**) was refluxed with anhydrous acetic acid to give (**2h**), (**5**), and (**6**) in 34, 47, and 10% yield, respectively, in addition to two minor rearranged products (9%) whose structures are not clear yet. No internal return product was obtained. The yield of the unrearranged product (**2h**) was unusually high in comparison with results for the related bridgehead neopentyl systems.[1,4,5] This discrepancy is striking. The driving force in the Wagner–Meerwein rearrangement of the neopentyl system is the relief of steric strain. It is interesting that the difference between the calculated strain energies[6] for the skeletons (**2a**) and (**5**) or (**6**) are small (⩽ 2 kcal mol^{-1}). Consequently, the rearrangement process may not be favourable in the solvolysis of (**2a**) and nucleophilic solvent attack may become dominant.

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‡ 1 cal = 4·184 J.

[1] P. J. Chenier, J. R. McClure, and D. J. Golembeski, *J. Org. Chem.*, 1978, **43**, 4306.

[2] R. R. Sauers, C. A. Weston, and B. I. Dentz, *J. Org. Chem.*, 1980, **45**, 2813 and references therein.

[3] H. J. Reich, J. M. Renga, and I. L. Reich, *J. Am. Chem. Soc.*, 1975, **97**, 5434.

[4] R. L. Bixler and C. Niemann, *J. Org. Chem.*, 1958, **23**, 742; J. W. Wilt, H. F. Dabek, Jr., J. P. Berliner, and C. A. Schneider, *ibid.*, 1970, **35**, 2402.

[5] K. B. Wiberg and B. R. Lowry, *J. Am. Chem. Soc.*, 1963, **85**, 3188; J. E. Nordlander, S. P. Jindal, P. v. R. Schleyer, R. C. Fort, Jr., J. J. Harper, and R. D. Nicholas, *ibid.*, 1966, **88**, 4475.

[6] E. M. Engler, J. D. Andose, and P. v. R. Schleyer, *ibid.*, 1973, **95** ,8005; M. R. Smith and J. M. Harris, *J. Org. Chem.*, 1978, **43**, 3588.