Pyrano-sultone: A Novel Binuclear Heterocyclic System

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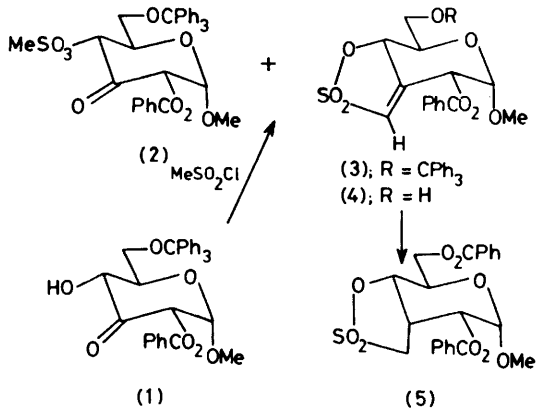
Summary Reaction of the α-keto alcohol (**1**) with $MeSO_2Cl$–Et_3N–CH_2Cl_2 gives, in addition to the keto sulphonate (**2**), the unsaturated sultone (**3**) the relative amounts of which vary with temperature; when pyridine is the proton acceptor, the sultone is not formed, and hydrogenation gives the saturated sultone (**5**) exclusively.

WE report herein the formation of a novel binuclear heterocyclic system comprised of fused pyranose and sultone rings.

In connection with other work we wished to prepare a sulphonate ester of the protected α-keto alcohol (**1**). Reaction of (**1**) with toluene-*p*-sulphonyl chloride in pyridine proceeded in very low yield, and so the procedure utilising methanesulphonyl chloride and triethylamine in methylene chloride prescribed for hindered alcohols[1] was tried. The desired methanesulphonate (**2**) was indeed formed (Scheme 1) but it was accompanied by an unexpected side product



SCHEME 1

which was isolated by fractionation on a silica column to give a crystalline compound of composition $C_{34}H_{30}O_8S$,† m.p. 217—217·5 °C; $[\alpha]_D^{23}$ + 79·2 (*c*, 2·41 $CHCl_3$); *m/e* 598 (M^+); δ (60 MHz, $CDCl_3$, rel. to Me_4Si) 5·33 (1H, d, $J_{1,2}$ 4 Hz, H-1); 5·83 (1H, dd, $J_{2,7}$ 2 Hz, H-2); 5·3 (1H, dd, $J_{4,5}$ 10 Hz, H-4); 3·9 (1H, m, H-5); 3·5 (2H, m, H-6); 6·75 (1H, t, H-7); and 7·4 and 8·1 (20H, m, $PhCO_2$ and Ph_3CO). The n.m.r. spectrum did not show signal due to the $MeSO_2$ protons. Double irradiation of H-2 caused the triplet at δ 6·75 to collapse to a doublet. The foregoing data suggested that the side-product was the sultone (**3**).

Detritylation ($CHCl_3$, HCl, 0 °C) of (**3**) gave a syrupy product (**4**), ν ($CHCl_3$) 3400 (OH), 1600 and 1665 (olefinic), and 1025, 1170, and 1345 (sulphonate) cm^{-1}, *m/e* 325 (M^+ — OMe), whose n.m.r. spectrum [δ (60 MHz) 5·33 (1H, d, H-1), 5·82 (1H, dd, $J_{1,2}$ 4, $J_{2,7}$ 2 Hz, H-2), 5·3 (1H, hidden m, H-4), 3·95 (3H, m, H-5, H-6, and H-6′), 6·86 (1H, t, $J_{4,7}$ 2 Hz, H-7), 3·42 (3H, s, OMe), and 7·6 and 8·1 (5H, m, $PhCO_2$)] showed good correspondence with that of (**3**) indicating that there had been no gross structural changes.

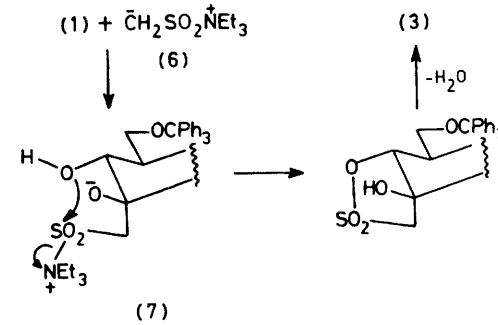
Compound (**4**) was hydrogenated smoothly (EtOH, 10% Pd–C, atmospheric pressure) and the product was benzoylated to give crystals of (**5**),† m.p. 74—74·5 °C (decomp.), $[\alpha]_D^{23}$ + 62·3° (*c*, 0·97 $CHCl_3$); *m/e* 431 (M^+ — OMe), δ (220 MHz) 5·09 (1H, d, $J_{1,2}$ 4·0 Hz, H-1), 5·30 (1H, dd, $J_{2,3}$ 6·3 Hz, H-2), 3·80 (1H, dddd, H-3), 4·85 (1H, dd, $J_{3,4}$ 6·8, $J_{4,5}$ 10·0 Hz, H-4), 4·37 (1H, ddd, $J_{5,6}$ 5·0, $J_{5,6'}$ 2·5 Hz H-5), 4·58 (1H, dd, $J_{6,6'}$ 12·5 Hz, H-6,H-6′ form an AB), 4·68 (1H, dd, H-6′), 4·12 (1H, t, $J_{3,7a}$ 13·0, $J_{7a,7e}$ 12·75, Hz, H-7a), 3·57 (1H, dd, $J_{3,7e}$ 7·3 Hz, H-7e), 3·45 (3H, s, OMe), and 7·45, 7·58, and 8·04 (5H, m, $PhCO_2$). The quintet assigned to H-3 collapsed when either of the quartets for H-2 or H-4 was irradiated. The relevant couplings showed that H-3 was in the equatorial orientation indicating that, as expected, hydrogenation had occurred from the upper face of (**4**).

TABLE. Percentages[a] of compounds (**2**) and (**3**) formed from (**1**)[b] at various temperatures.

Temp./°C	(2)/%	(3)/%
−75	100	0
−30	90	10
0	85	15
40	65—70	30—35
−10[c]	100	0

[a] Determined by integrating of the $MeSO_3$-signal of (**2**) and the vinylic proton signal of (**3**). [b] Compound (**1**) was treated with 1·1 equiv. of methanesulphonyl chloride and triethylamine (5 equiv.). [c] In this experiment sulphonylation was carried out using pyridine and the sulphonyl chloride in the usual way.

In an effort to optimise the yield of (**3**) a study was made of the effect of temperature on the relative amounts of (**2**) and (**3**) formed (Table). Unfortunately conditions could not be found which gave (**3**) as the exclusive, or even the major product. Interestingly, with the conventional sulphonylating medium of methanesulphonyl chloride and pyridine, the ester (**2**) was the exclusive product.



SCHEME 2

Resubjecting (**2**) to the reaction medium, or treatment with NaH–tetrahydrofuran did not afford (**3**) indicating that the latter is not a secondary product of the former. An alternative rationalisation for the formation of (**3**) involves an aldol-type condensation of the zwitterion (**6**) (formed from the reaction of sulphene with triethylamine[3]) giving the ammonium betaine (**7**). Formally this condensation resembles the first step of Wittig olefination.[4] The two remaining steps, cyclisation and dehydration may occur either in the order shown in Scheme 2 or the reverse, since our data do not provide pertinent evidence.

No significant biological activity has been detected in any of these sultones.

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† These compounds gave satisfactory elemental analyses.

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