$C_{19}H_{15}Cl_2O_4P$

Fig. 1. Molecular structure of (2), showing the atom-numbering scheme.

C(10)—O(10), is identical, within experimental error, with that for the 3,5-dinitrobenzoate ester already reported. This is to be expected, since the pK_a's of diphenyl phosphoric and 3,5-dinitrobenzoic acids differ by less than one unit, and the slope of the plot of bond length vs pK_a of the leaving group is only 0.003 Å/pK_a unit.

This plot was one of the original objectives of the work with these 2,6-disubstituted benzyl compounds (1). We had found earlier (Jones & Kirby, 1979, 1984) that there is a good linear relationship between

these parameters for many different series of compounds. But for derivatives of 1-phenylethanol, where the conformation about the benzylic C_α—Ar bond varies, the relationship was clearly not linear. This was ascribed to the variation with this dihedral angle of the ring-π–$\sigma^*_{C—OX}$ interaction, which was found to be the single most important factor affecting the length of the C—OX bond (Edwards, Jones & Kirby, 1986). The (best-least-squares) line drawn through the augmented data set has a correlation coefficient $r = 0.94$, clearly not very strong evidence for a linear relationship. Unfortunately the data are too few to support firm conclusions.

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Bond Length and Reactivity. Structure of 2-*endo*-Bornyl *p*-Toluenesulfonate

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Abstract. $C_{17}H_{24}O_3S$, $M_r = 308.45$, triclinic, $P\bar{1}$, $a = 7.9995$ (14), $b = 9.870$ (2), $c = 11.975$ (2) Å, $\alpha = 112.84$ (2), $\beta = 105.10$ (2), $\gamma = 93.56$ (2)°, $V = 826.9$ Å^3, $Z = 2$, $D_x = 1.238$ Mg m^{-3}, λ(Mo Kα) = 0.71069 Å, $\mu = 0.19$ mm^{-1}, $F(000) = 332$, $T = 293$ K. Final $R = 0.049$ for 2445 unique observed reflections. The C—OX bond length is normal for an ester at a secondary centre.

Introduction. We have suggested two rules that relate the length of a bond to the rate at which it is broken in ionic reactions in solution (Edwards, Jones &

Kirby, 1986): (i) the longer the bond in a given system, the faster it breaks; and (ii) the more reactive the system, the more sensitive is the length of the bond to structural variation. Our data refer specifically to C—OX bonds, but the principles should have broader application.

The basis of these effects is a contribution to the ground-state structure of systems R—OX from the valence-bond tautomeric form R^+ $^-$OX, which is greater the more stable is either of the two ions involved. This raises the intriguing possibility that by measuring accurate structures of series of such compounds, with R constant and varying leaving groups $^-$OX, it may be possible to identify structural changes in R associated with the need to accommodate the developing positive charge. Nowhere would a positive result of this sort be more interesting than in the series of structures which give rise to the so-called 'non-classical' carbonium ions [for a useful recent summary and list of references see Lenoir, Apeloig, Arad & von Schleyer (1988)], so we have attempted to apply our 'variable oxygen probe' to several such systems. We report results with derivatives of bicyclo[2.2.1]heptan-2-ol, and the structure of the p-toluenesulfonate (2) of $endo$-borneol.
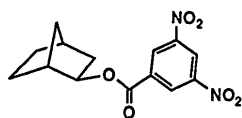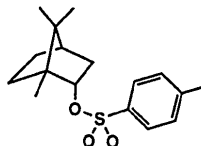
(1)   (2)

Experimental. We crystallized the parent alcohols, and many derivatives of exo- and $endo$-borneol and norborneol. Crystals of ten compounds were examined, but of these only two formed useful single crystals.

2-exo-Norbornyl 3,5-dinitrobenzoate (1) was prepared from the alcohol as described previously (Jones, Edwards & Kirby, 1986). Purification by preparative thin-layer chromatography (silica, eluant 40% hexane in CH$_2$Cl$_2$) gave the ester (96%), m.p. (from CH$_2$Cl$_2$–petroleum ether, b.p. 313–333 K) 377–379 K [lit. 377–378 K (Winstein & Trifan, 1949)]. Colourless, weakly diffracting needles were obtained by diffusion of petroleum ether (b.p. 313–333 K) into a solution in dichloromethane. Although the structure was solved, R (0.090) and some U values were very high, with strong suggestions of disorder (particularly some gross discrepancies in length between corresponding bonds in the two molecules in the asymmetric unit). The data are not of publishable quality.

2-$endo$-Bornyl p-toluenesulfonate (2). To p-toluenesulfonyl chloride (2.97 g, 15.6 mmol) dis-

solved in dry pyridine (2 ml) was added borneol (3 g, 13 mmol) dissolved in 3 ml of the same solvent, and the solution stirred under nitrogen for 24 h at room temperature. Then water was added and the solution extracted with CH$_2$Cl$_2$ (3 × 30 ml). The combined organic layers were washed with 1N HCl (3 × 30 ml), saturated sodium bicarbonate solution (3 × 30 ml) and then water (30 ml), and dried over anhydrous Na$_2$SO$_4$. Evaporation of the solvent under reduced pressure gave an oil, which was purified by preparative thin-layer chromotography on silica (eluant 1:1 ether–hexane) to yield the tosylate (75%), m.p. (from pentane) 343–348 K (dec.) [lit. 340 K (Tipson, 1944); 353.5 K (Hückel & Pietrzok, 1940)]. Irregular colourless blocks were obtained by evaporation from pentane.

A crystal 0.5 × 0.35 × 0.25 mm was mounted in a glass capillary. 4000 reflections ($-h\pm k\pm l$ and some $+h$ equivalents) were collected on a Stoe–Siemens diffractometer using monochromated Mo $K\alpha$ radiation ($2\theta_{max}$ 50°). Three check reflections showed no significant intensity change. No absorption or extinction correction was applied. Merging equivalents gave 2914 unique reflections (R_{int} 0.032, index ranges after merging h 0 to 9, k -11 to 11, l -14 to 14), of which 2445 with $F > 4\sigma(F)$ were used for all calculations (program system Siemens *SHELXTL-Plus*; Sheldrick, 1990). Cell constants were refined from $\pm\omega$ values of 38 reflections in the 2θ range 20–23°.

The structure was solved by routine direct methods and subjected to anisotropic cascade least-squares refinement on F. H atoms were included using a riding model. The final R was 0.049, with wR 0.063. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.00025F^2$. 202 parameters; S 2.5; max. Δ/σ 0.075; max. $\Delta\rho$ +0.31, -0.22 e Å^{-3}.

Discussion. Final atom coordinates for (2) are given in Table 1,* and derived parameters in Table 2. A plot of (2), showing the atom-numbering scheme, appears in Fig. 1.

The original aim of this work was to compare the structures of a series of derivatives of the exo and $endo$ alcohols. Points of special interest are differences between exo and $endo$ systems, and particularly the sensitivity of the length of the bond to the changing leaving group. In the event, it was possible to grow satisfactory crystals of only one compound. [Previous authors have found similar problems with

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Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement factors* ($\text{Å}^2 \times 10^3$) *for* (2)

	x	y	z	U_{eq}*
S	4141 (1)	6229 (1)	3308 (1)	55 (1)
C(1)	6172 (3)	3138 (2)	1379 (2)	48 (1)
C(2)	6453 (3)	4699 (2)	2458 (2)	47 (1)
C(3)	8269 (3)	4886 (2)	3419 (2)	58 (1)
C(4)	8846 (3)	3417 (3)	2763 (2)	65 (1)
C(5)	7702 (4)	2197 (3)	2887 (3)	78 (2)
C(6)	5890 (4)	1999 (3)	1935 (3)	73 (1)
C(7)	8096 (3)	3073 (2)	1333 (2)	54 (1)
C(8)	8855 (4)	4240 (3)	972 (2)	66 (1)
C(9)	8314 (4)	1537 (3)	434 (3)	81 (2)
C(10)	4750 (4)	2894 (3)	184 (2)	75 (1)
O(1)	5042 (2)	4813 (2)	3048 (1)	56 (1)
O(2)	3592 (2)	6485 (2)	2192 (2)	77 (1)
O(3)	2863 (2)	5940 (2)	3864 (2)	76 (1)
C(11)	5819 (3)	7721 (2)	4463 (2)	45 (1)
C(12)	6499 (3)	7754 (2)	5656 (2)	52 (1)
C(13)	7767 (3)	8939 (2)	6585 (2)	55 (1)
C(14)	8394 (3)	10113 (2)	6346 (2)	54 (1)
C(15)	7695 (3)	10042 (3)	5136 (3)	64 (1)
C(16)	6418 (3)	8873 (3)	4203 (2)	57 (1)
C(17)	9779 (4)	11399 (3)	7365 (3)	78 (1)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. *Selected bond lengths* (Å) *and angles* (°) *for* (2)

C(1)—C(2)	1.535 (4)	C(1)—C(6)	1.545 (5)	
C(1)—C(7)	1.558 (5)	C(1)—C(10)	1.500 (4)	
C(2)—C(3)	1.549 (4)	C(2)—O(1)	1.468 (4)	
C(3)—C(4)	1.524 (5)	C(4)—C(5)	1.543 (6)	
C(4)—C(7)	1.548 (5)	C(5)—C(6)	1.539 (5)	
C(7)—C(8)	1.523 (5)	C(7)—C(9)	1.533 (4)	
O(1)—S	1.573 (3)	O(2)—S	1.419 (3)	
O(3)—S	1.427 (3)	C(11)—S	1.757 (3)	

|			
O(1)—S—O(2)	110.5 (2)	O(1)—S—O(3)	103.0 (2)
O(2)—S—O(3)	119.5 (2)	O(1)—S—C(11)	104.5 (2)
O(2)—S—C(11)	108.5 (2)	O(3)—S—C(11)	109.7 (2)
C(2)—C(1)—C(6)	106.7 (3)	C(2)—C(1)—C(7)	100.1 (3)
C(6)—C(1)—C(7)	101.6 (3)	C(2)—C(1)—C(10)	113.6 (3)
C(6)—C(1)—C(10)	114.4 (3)	C(7)—C(1)—C(10)	118.7 (3)
C(1)—C(2)—C(3)	105.1 (3)	C(1)—C(2)—O(1)	110.8 (3)
C(3)—C(2)—O(1)	111.5 (3)	C(2)—C(3)—C(4)	101.9 (3)
C(3)—C(4)—C(5)	106.6 (3)	C(3)—C(4)—C(7)	103.0 (3)
C(5)—C(4)—C(7)	102.7 (3)	C(4)—C(5)—C(6)	103.0 (4)
C(1)—C(6)—C(5)	104.1 (3)	C(1)—C(7)—C(4)	93.5 (3)
C(1)—C(7)—C(8)	114.2 (3)	C(4)—C(7)—C(8)	113.8 (3)
C(1)—C(7)—C(9)	113.3 (3)	C(4)—C(7)—C(9)	113.9 (3)
C(8)—C(7)—C(9)	107.8 (3)	S—O(1)—C(2)	119.0 (3)
S—C(11)—C(12)	119.0 (3)	S—C(11)—C(16)	121.3 (3)
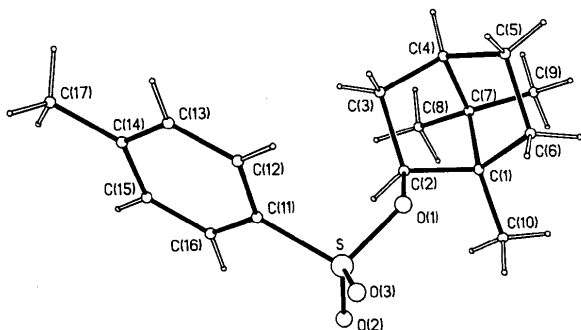
Fig. 1. Molecular structure of (2), showing the atom-numbering scheme.

this series: see, for example, Altona & Sundara-lingam (1972).] So we are not able to address the detailed questions of interest.

The C—OTs bond length in the *endo*-tosylate (2), 1.468 (4) Å, appears to be normal. It is identical, within experimental error, with the published mean value for C*—OSO$_2$C (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987), and with the length of the corresponding bond [also 1.468 (4) Å] in the related tosylate (3), measured by Apeloig *et al.* (Apeloig, Arad, Kapon & Kaftory, 1985; Apeloig, personal communication). The symmetry of the ring is also not significantly perturbed by the substituent: the interatomic distances C(2)—C(5) and C(6)—C(2), and the in-ring angles at C(1) and C(4) do not differ significantly. Thus there is no evidence for unusual behaviour for the structure of (2).

(3)

(4)
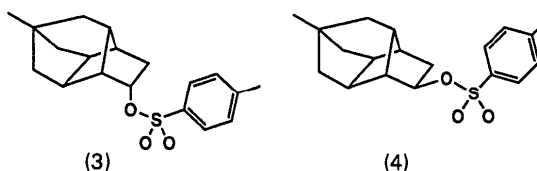
This is not to say that no effect on structure exists. Apeloig *et al.* (Apeloig, Arad, Kapon & Kaftory, 1985; Apeloig, personal communication) find a C—OTs bond length of 1.490 (6) Å for the *exo*-tosylate (4), which is indeed significantly longer than that in the *endo* isomer (3). And structures have recently become available for two 2-substituted-2-bornyl cations, the 2-methoxy derivative [methylated camphor, Montgomery, Grendze & Huffman (1987), counterion BF$_4^-$], and the 1,2,4,7-*anti*-tetramethyl-norbornyl derivative [Laube (1987), counterion Sb$_2$F$_{11}^-$]. Although these stabilized species are both closer to classical structures than the 2-unsubstituted cation is expected to be, both show clear evidence for partial bridging between C(2) and C(6), with pronounced shortening of C(1)—C(2) and concomitant lengthening of C(2)—C(6). Our experience, and that of others, suggests that the crystal structure correlation approach we have tried fails in this system for simple practical reasons. The parent bicyclo[2.2.1]heptyl system generally packs poorly. Good crystals are difficult to obtain, and the few accurate structures available containing this substructure carry significant substituent groups which improve packing. Also, as always in this sort of work, the most interesting compounds are those with the best leaving groups, which are by definition the most reactive, and thus the most difficult to handle.

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Bond Length and Reactivity. Structures of the Triphenylmethyl Ether and the 4-Nitrobenzoate Ester of anti-7-Norbornenol

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Abstract. 7-anti-Norbornenyl triphenylmethyl ether, (1), $C_{26}H_{24}O$, $M_r = 352.48$, monoclinic, $P2_1/n$, $a = 15.415$ (3), $b = 9.003$ (2), $c = 15.454$ (3) Å, $\beta = 114.32$ (2)°, $V = 1954.5$ Å^3, $Z = 4$, $D_x = 1.197$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.07$ mm^{-1}, $F(000) = 752$, $T = 293$ K. Final $R = 0.052$ for 3127 unique observed reflections. 7-anti-Norbornenyl 4-nitrobenzoate, (2), $C_{14}H_{13}NO_4$, $M_r = 259.26$, monoclinic, $P2_1/c$, $a = 9.3638$ (12), $b = 10.4685$ (10), $c = 12.827$ (2) Å, $\beta = 94.875$ (12)°, $V = 1252.8$ Å^3, $Z = 4$, $D_x = 1.374$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.10$ mm^{-1}, $F(000) = 544$, $T = 293$ K, $R = 0.063$ for 2347 unique observed reflections. The C—OX bond lengths [C(1)—O(1) of 1.428 (2) and 1.458 (3) Å in (1) and (2), respectively] are normal for an ether and an ester at a secondary centre.

Introduction. We have described in the previous paper (Jones, Schmidt-Bäse, Edwards & Kirby, 1992) why we are interested in examining structures known to give rise under solvolytic conditions to 'non-classical' carbonium ions [for a useful recent summary and list of references see Lenoir, Apeloig, Arad & von Schleyer (1988)]. We have attempted to apply our 'variable oxygen probe' to several such systems. In this paper we describe the structures of

two derivatives [(1) and (2)] of anti-bicyclo-[2.2.1]hept-2-en-7-ol. This system is of interest because of the extraordinary enhancement of solvolytic reactivity, of eleven orders of magnitude in rate, of the anti tosylate compared with the syn epimer (Winstein, Shatavsky, Norton & Woodward, 1955; Winstein & Stafford, 1957) or the saturated system (Woods, Carboni & Roberts, 1956). The effect was explained in terms of an intermediate non-classical ion (3), stabilized by overlap of the vacant orbital at C(7) with the π electrons of the 2,3 double bond. On the basis of an early study of the p-bromobenzoate corresponding to (2), Macdonald & Trotter (1965) concluded that the exceptional reactivity is not related to the small bridgehead angle (ca 97°).

(1)   (2)   (3)
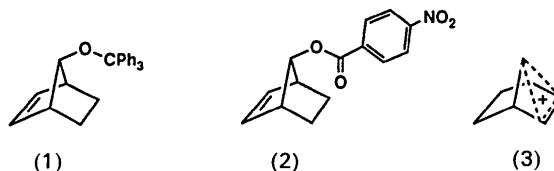
Experimental. We prepared a range of derivatives of the parent alcohol, anti-bicyclo[2.2.1]hept-2-en-7-ol. Some were too reactive to be crystallized – the solid 4-nitrobenzenesulfonate, for example, rapidly