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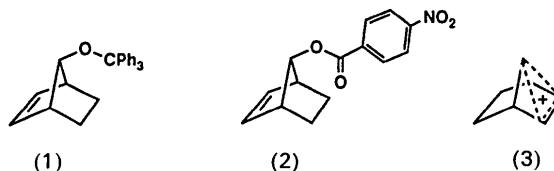
Experimental. We prepared a range of derivatives of the parent alcohol, *anti*-bicyclo[2.2.1]hept-2-en-7-ol. Some were too reactive to be crystallized – the solid 4-nitrobenzenesulfonate, for example, rapidly

decomposed even *in vacuo* – and most gave crystals unsuitable for single-crystal analysis. The two title compounds were prepared by conventional methods.

7-*anti*-Norbornenyl triphenylmethyl ether (1). *anti*-Bicyclo[2.2.1]hept-2-en-7-ol was alkylated with trityl chloride in refluxing CH_2Cl_2, in the presence of one equivalent of pyridine and a catalytic quantity of 4-dimethylaminopyridine, over 24 h. Colourless prisms, m.p. 378–380 K, were grown from diisopropyl ether–CH_2Cl_2.

7-*anti*-Norbornenyl 4-nitrobenzoate (2). The parent alcohol was esterified with 4-nitrobenzoyl chloride in CH_2Cl_2, in the presence of one equivalent of pyridine, to give a solid, m.p. 397–400 K. Colourless irregular crystals were grown by the liquid diffusion method from CH_2Cl_2–pentane.

Data in the following section refer to compound (1), and in most cases apply to (2) also. Where values for (2) are different, they are given in square brackets.

A crystal 0.6 × 0.5 × 0.5 [0.7 × 0.6 × 0.5] mm was mounted in a glass capillary. 4854 [5472] reflections ($\pm h + k \pm l$ and some $-l$ equivalents [$\pm h + k \pm l$]) were collected on a Stoe–Siemens diffractometer using monochromated Mo $K\alpha$ radiation ($2\theta_{max}$ 55°). Three check reflections showed no significant intensity change. No absorption or extinction correction was applied. Merging equivalents gave 4480 [2869] unique (R_{int} 0.009 [0.012]), index ranges after merging h 0 to 18 [0 to 12], k 0 to 11 [0 to 13], l -20 to 20 [-16 to 16], of which 3127 [2347] 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 52 [48] reflections in the 2θ range 20–23°. The structures were solved by routine direct methods and subjected to anisotropic full-matrix least-squares refinement on F. H atoms of the norbornenyl moiety were refined freely, other H were included using a riding model. The final R was 0.052 [0.063], with wR 0.052 [0.079]. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0002F^2$. 280 [208] parameters; S 2.0 [3.7]; max. Δ/σ 0.002 [0.004]; max. $\Delta\rho$ $+0.14$, -0.19 [$+0.29$, -0.32] e Å^{-3}.

Discussion. Final atomic coordinates for (1) and (2) are given in Tables 1 and 3, and derived parameters in Tables 2 and 4. Plots of (1) and (2), showing atom-numbering scheme, appear as Figs. 1 and 2.*

* Lists of structure factors, H-atom parameters and anisotropic thermal parameters, together with complete tables of bond lengths, bond angles and torsion angles, and packing diagrams have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54750 (40 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA0050]

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

	x	y	z	U_{eq}*
O(1)	4888 (1)	1155 (1)	2563 (1)	51 (1)
C(1)	5038 (1)	−265 (2)	1225 (1)	60 (1)
C(2)	5050 (1)	−1921 (2)	1112 (1)	77 (1)
C(3)	4584 (1)	−2518 (2)	1568 (2)	81 (1)
C(4)	4244 (1)	−1289 (2)	2007 (1)	66 (1)
C(5)	3470 (1)	−437 (2)	1184 (1)	74 (1)
C(6)	4012 (1)	252 (2)	649 (1)	70 (1)
C(7)	5091 (1)	−232 (2)	2238 (1)	52 (1)
C(10)	5684 (1)	2073 (2)	3134 (1)	47 (1)
C(11)	6238 (1)	2466 (2)	2538 (1)	47 (1)
C(12)	7065 (1)	1749 (2)	2632 (1)	60 (1)
C(13)	7483 (1)	2049 (2)	2010 (1)	72 (1)
C(14)	7081 (1)	3038 (2)	1282 (1)	70 (1)
C(15)	6256 (1)	3752 (2)	1175 (1)	63 (1)
C(16)	5841 (1)	3478 (2)	1799 (1)	54 (1)
C(21)	6270 (1)	1311 (2)	4091 (1)	49 (1)
C(22)	7181 (1)	1782 (2)	4682 (1)	67 (1)
C(23)	7666 (1)	1145 (2)	5569 (1)	81 (1)
C(24)	7255 (1)	38 (2)	5881 (1)	77 (1)
C(25)	6354 (1)	−429 (2)	5309 (1)	68 (1)
C(26)	5863 (1)	206 (2)	4425 (1)	57 (1)
C(31)	5242 (1)	3465 (2)	3364 (1)	51 (1)
C(32)	5809 (1)	4697 (2)	3761 (1)	68 (1)
C(33)	5453 (2)	5930 (2)	4020 (1)	87 (1)
C(34)	4528 (2)	5970 (2)	3899 (1)	93 (1)
C(35)	3950 (1)	4773 (2)	3502 (1)	84 (1)
C(36)	4303 (1)	3503 (2)	3228 (1)	64 (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* (1)

O(1)—C(7)	1.428 (2)	O(1)—C(10)	1.441 (1)
C(1)—C(2)	1.502 (2)	C(1)—C(6)	1.533 (2)
C(1)—C(7)	1.533 (3)	C(2)—C(3)	1.311 (3)
C(3)—C(4)	1.501 (3)	C(4)—C(5)	1.544 (2)
C(4)—C(7)	1.534 (2)	C(5)—C(6)	1.528 (3)
C(10)—C(11)	1.532 (2)	C(10)—C(21)	1.542 (2)
C(10)—C(31)	1.536 (2)		

C(10)—O(1)—C(7)	117.5 (1)	C(6)—C(1)—C(2)	107.0 (1)
C(7)—C(1)—C(2)	98.0 (1)	C(7)—C(1)—C(6)	101.2 (1)
C(3)—C(2)—C(1)	108.0 (2)	C(4)—C(3)—C(2)	108.1 (2)
C(5)—C(4)—C(3)	106.8 (2)	C(7)—C(4)—C(3)	98.1 (1)
C(7)—C(4)—C(5)	100.3 (1)	C(6)—C(5)—C(4)	103.8 (1)
C(5)—C(6)—C(1)	103.1 (1)	C(1)—C(7)—O(1)	116.7 (1)
C(4)—C(7)—O(1)	109.6 (1)	C(4)—C(7)—C(1)	93.9 (1)
C(11)—C(10)—O(1)	108.0 (1)	C(21)—C(10)—O(1)	110.3 (1)
C(21)—C(10)—C(11)	115.3 (1)	C(31)—C(10)—O(1)	105.2 (1)
C(31)—C(10)—C(11)	111.2 (1)	C(31)—C(10)—C(21)	106.4 (1)
C(12)—C(11)—C(10)	123.2 (1)	C(16)—C(11)—C(10)	118.6 (1)

The packing is unexceptional for (1), with the closest non-bonded C⋯C distance > 3.56 Å. The ester group of (2) adopts the usual Z conformation, with torsion angles C(7)—O(1)—C(10)—C(11) 177.6 (2) and O(1)—C(10)—C(11)—C(12) -174.1 (2)°. The molecules pack with the aromatic rings facing across centres of symmetry. Shortest non-bonded contacts between non-H atoms: O(3)⋯C(4) 3.41, O(3)⋯C(16) 3.32 Å (second atoms at $1 - x$, $1 - y$, $1 - z$; x, $1.5 - y$, $-0.5 + z$).

The original aim of this work was to compare a series of structures of derivatives of *anti*-bicyclo[2.2.1]hept-2-en-7-ol, to define the expected

Table 3. *Atomic coordinates* (× 10⁴) *and equivalent isotropic displacement parameters* ($\mathring{A}^2 \times 10^3$) *for* (2)

	x	*y*	*z*	U_{eq}*
C(1)	−221 (2)	5399 (2)	7784 (2)	64 (1)
C(2)	−876 (3)	4407 (2)	8442 (2)	72 (1)
C(3)	33 (2)	3459 (2)	8581 (2)	68 (1)
C(4)	1326 (2)	3791 (2)	8018 (2)	67 (1)
C(5)	2094 (2)	4893 (3)	8631 (2)	79 (1)
C(6)	1033 (3)	6002 (2)	8475 (2)	74 (1)
C(7)	571 (2)	4512 (2)	7108 (2)	63 (1)
O(1)	1538 (2)	5242 (1)	6504 (1)	75 (1)
O(2)	1690 (2)	3691 (2)	5356 (1)	115 (1)
C(10)	1981 (2)	4734 (2)	5649 (1)	61 (1)
C(11)	2911 (2)	5636 (2)	5106 (1)	51 (1)
C(12)	3352 (2)	5279 (2)	4141 (1)	60 (1)
C(13)	4190 (2)	6096 (2)	3605 (1)	62 (1)
C(14)	4590 (2)	7243 (2)	4056 (1)	54 (1)
C(15)	4193 (2)	7616 (2)	5019 (1)	60 (1)
C(16)	3331 (2)	6803 (2)	5542 (1)	57 (1)
N(1)	5450 (2)	8142 (2)	3477 (1)	70 (1)
O(3)	5712 (2)	7840 (2)	2594 (1)	97 (1)
O(4)	5831 (2)	9140 (2)	3896 (2)	101 (1)

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

Table 4. *Selected bond lengths* ($\mathring{A}$) *and angles* (°) *for* (2)

C(1)—C(2)	1.502 (3)	C(1)—C(6)	1.545 (3)
C(1)—C(7)	1.508 (3)	C(2)—C(3)	1.310 (3)
C(3)—C(4)	1.502 (3)	C(4)—C(5)	1.540 (3)
C(4)—C(7)	1.514 (3)	C(5)—C(6)	1.530 (4)
C(7)—O(1)	1.458 (3)	O(1)—C(10)	1.317 (2)
O(2)—C(10)	1.179 (3)	C(10)—C(11)	1.496 (3)

C(2)—C(1)—C(6)	106.6 (2)	C(2)—C(1)—C(7)	98.1 (2)
C(6)—C(1)—C(7)	101.2 (2)	C(1)—C(2)—C(3)	108.0 (2)
C(2)—C(3)—C(4)	107.5 (2)	C(3)—C(4)—C(5)	106.8 (2)
C(3)—C(4)—C(7)	98.3 (2)	C(5)—C(4)—C(7)	100.8 (2)
C(4)—C(5)—C(6)	103.4 (2)	C(1)—C(6)—C(5)	102.6 (2)
C(1)—C(7)—C(4)	94.8 (2)	C(1)—C(7)—O(1)	109.9 (2)
C(4)—C(7)—O(1)	113.7 (2)	C(7)—O(1)—C(10)	119.0 (2)
O(1)—C(10)—O(2)	124.0 (2)	O(1)—C(10)—C(11)	111.7 (2)
O(2)—C(10)—C(11)	124.3 (2)	C(10)—C(11)—C(12)	118.3 (2)
C(10)—C(11)—C(16)	121.6 (2)		

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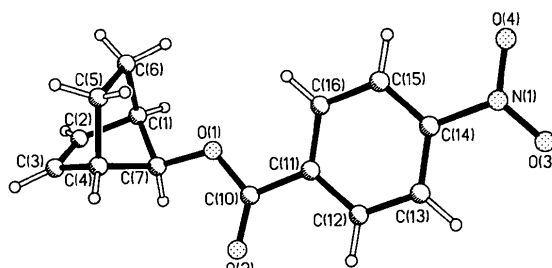
Fig. 2. Molecular structure of (2), showing the atom-numbering scheme.

linear relationship between the length of the C—O*X* bond and the pK_a of the conjugate acid, HO*X*, of the leaving group. This should allow a very sensitive measure of any interaction in the ground state between the π system and the developing positive charge at C(7). In the event, it proved impossible to grow satisfactory crystals of more than the two title compounds. So we are not able to carry out a detailed analysis of structure–reactivity correlations in this system. [The data of Macdonald & Trotter (1965, *R* factor 0.18) for the *anti-p*-bromobenzoate of 7-norbornenol are not accurate enough to be useful for this purpose.] However, the evidence we have from these two structures allows a rather firm negative conclusion.

The C—O*X* bond lengths of (1) and (2) are normal for an ether and an ester, respectively, of a secondary alcohol. Allen, Kennard, Watson, Brammer, Orpen & Taylor (1987) quote 1.429 and 1.460 Å, respectively, as mean values for such C—O bonds, and we
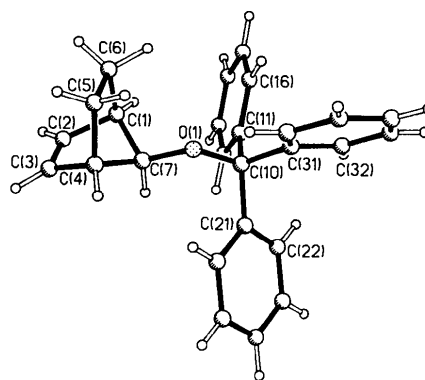
find 1.428 (2) and 1.458 (3) Å for this bond in (1) and (2). Furthermore, the geometry of the cyclohexene ring is almost identical in the ester and the ether, as also are the bond angles at the bridgehead. Angles C(2)—C(1)—C(7) and C(3)—C(4)—C(7), for example, are 98.0 (1) and 98.1 (1)° for (1), and 98.1 (2) and 98.3 (2)° for (2). Thus it is evident that there is no increased interaction between the π system and the more electron-deficient C(7) of (2), and thus no significant interaction of this sort in the ground state.

From the limited range of data available it begins to appear that in systems like (2), which react with substantial heavy-atom reorganization, this reorganization is not a gradual process, but occurs late on the reaction coordinate, and so rather suddenly. Bond breaking and rearrangement, at least in the early stages, are thus only weakly coupled. These ideas will be developed further elsewhere.

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Bond Length and Reactivity. Structure of 2-Phenylethyl p-Toluenesulfonate

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Abstract. $C_{15}H_{16}O_3S$, $M_r = 276.35$, triclinic, $P\bar{1}$, $a = 7.353$ (1), $b = 8.136$ (1), $c = 24.307$ (4) Å, $\alpha = 94.44$ (1), $\beta = 89.81$ (1), $\gamma = 105.51$ (1)°, $V = 1396.8$ (4) Å³, $Z = 4$, $D_x = 1.314$ Mg m⁻³, λ(Cu $K\alpha$) $= 1.54178$ Å, $\mu = 2.02$ mm⁻¹, $F(000) = 584$, $T = 293$ K. Final $R = 0.059$ for 3401 observed reflections $[F > 4\sigma(F)]$ and 355 parameters. The aymmetric unit contains two independent but structurally similar molecules. Each molecule adopts a folded conformation in which the two aromatic rings lie over each other, with a centroid-to-centroid distance of 4.05 Å in molecule (1) and 3.87 Å in molecule (2). The bond parameters within each molecule do not deviate significantly from expected values, but the torsion angles about the PhCH₂—CH₂ bond (C_{ar}—C—C—O) of 71.7 (3) and 68.4 (3)° for the two molecules show that the *gauche* conformation is preferred. A best value of 1.462 (4) Å is suggested for the length of the C—OX bond in a primary aliphatic tosylate.

Introduction. We are interested in the effects of substituents on the length of the C—OX bond in series of derivatives of alcohols, ROH. We have demonstrated simple correlations with reactivity in reactions in which this bond is broken ionically (Jones & Kirby, 1979, 1984; Edwards, Jones & Kirby, 1986), and are extending this investigation to examine the effects of β-substituents, in systems based on the general structure Y—CH₂—CH₂—OX. Of primary interest is the sensitivity of the C—OX bond length to changes in X, and how this depends on the substituent, Y; this change in C—OX bond length is found from the crystal structures of a series of derivatives of a parent alcohol. In the following series of papers we describe an investigation for compounds with Y = F. The variation found in C—OX distance then has to be compared with the

variation in the parent series, which in the general case will have Y = H. There are large numbers of crystal structures in the literature for simple derivatives of alcohols, such as ethers and esters, and a compilation of mean bond lengths in such systems is available (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). But for specific systems it is necessary to obtain new data. We describe here the structure of the p-toluenesulfonate ester of 2-phenylethanol, a key compound for one of our correlations.
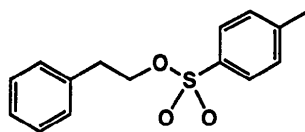
Experimental. The title compound was prepared by a general method for arenesulfonate esters. The alcohol (4 mmol) was added slowly to a stirred solution of the sulfonyl chloride (4.5 mmol) in pyridine (2 ml) at 273 K, and the solution stirred for 4 h more. Water (10 ml) was added, and the organic layer, together with diethyl ether extracts, collected and dried over MgSO₄.

2-Phenylethyl p-toluenesulfonate was purified by flash column chromatography from Merck Kieselgel 60 (eluant CH₂Cl₂) and recrystallized from CH₂Cl₂–hexane at 268 K to give the title compound as prisms, m.p. 311–312 K [lit. 308.5–309.6 K (Winstein, Lindegren, Marshall & Ingraham, 1953)]. Crystals were grown by the liquid diffusion technique, from CH₂Cl₂–hexane.

Crystal 0.06 × 0.40 × 0.40 mm; Nicolet $R3m\mu$ diffractometer, graphite-monochromated Cu $K\alpha$ radiation; cell parameters refined from diffractometer angles for 25 centred reflections ($50 < 2\theta < 55°$).