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Evidence from Crystal Structures for an Incipient Fragmentation Reaction

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Bond length changes in a series of 7 equatorial tetrahydropyranyl acetals appear to map out the early stages of a fragmentation process.

We have shown[1] that there is a simple correlation between reactivity towards hydrolysis and the length of the C–O bond (*x*) being broken in the series of axial tetrahydropyranyl acetals (**1**). Compounds with good leaving groups ArO^- (derived from strongly acidic phenols) show a marked lengthening of this bond, coupled with a significant shortening of the endocyclic acetal C–O bond (*n*). These changes are consistent with increasingly efficient overlap between the non-bonding electron pair on oxygen and the antibonding σ^*_{C-OAr} orbital[2] (which is lowered in energy by electron-withdrawing Ar groups) and may be regarded, since the same n–σ^* interaction is involved in breaking this bond, as marking progress along the reaction co-ordinate for C–O cleavage.[1]

We now have data for a series of 7 equatorial acetals containing structure (**2**), which have no lone pair *antiperiplanar* to the C–OR bond. Bond lengths in the C*–O–C–OR fragment are listed in Table 1, in increasing order of electronegativity of the OR group. All three bonds show significant trends. The largest effect is the lengthening of the C–OR bond, as it is also in the axial series. The length of the central C–O bond changes very little, though significant shortening is apparent when the full range of leaving group is taken into account. But the most remarkable effect is the substantial increase in length of the remote C*–O bond, which over the series of 7 compounds is about half that observed for the exocylic C–OR bond. (No such effect is observed in the axial series.)†

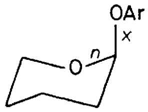
Table 1. C–O Bond lengths around the acetal centre of the tetrahydropyranyl acetals (**2**)—(**4**).

Compound	pK_a of ROH	Bond length (Å)[a] C*	—O	—C	—OR	Ref.
(**2**), R = *N*-Phthalimidomethyl	*ca.* 12.5[b]	1.418(4)		1.419(4)	1.392(4)	4
(**3**), R = Ph	9.95[c]	1.437(3)		1.411(3)	1.415(3)	5
(**3**), R = 4-$O_2NC_6H_4$	7.14[c]	1.448(4)		1.412(4)	1.424(4)	6
(**4**), R = 2,4-$(O_2N)_2C_6H_3$	4.11[c]	1.449(4)		1.411(4)	1.448(5)	7
(**4**), R = 3,5-$(O_2N)_2C_6H_3CO$	2.80[c]	1.447(3)		1.416(3)	1.468(3)	8
(**4**), R = $(PhO)_2P{=}O$	*ca.* 1.4[d]	1.461(3) 1.465(3)		1.413(3) 1.408(3)	1.456(2)[e] 1.457(2)[e]	4
(**4**), R = $MeSO_2$	−0.6[c]	1.458(3)		1.403(3)	1.478(3)	4

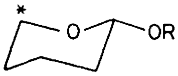
[a] Numbers in brackets are standard errors in the last figure quoted. [b] pK_a estimated by the method of J. P. Fox and W. P. Jencks, *J. Am. Chem. Soc.*, 1974, **96**, 1436. [c] W. P. Jencks and J. Regenstein in 'Handbook of Biochemistry,' ed. H. A. Sober, Chemical Rubber Publishing Co., Cleveland, Ohio, 1968, p. J150. [d] V. A. Baranskii and B. I. Istomin, *Org. Reactivity, Tartu*, 1978, **15**, 230, quote pK_a 1.45 for the *p*-tolyl derivative in water. [e] Two molecules in the asymmetric unit.

In the equatorial acetals (**2**) this bond is *antiperiplanar* to C–OR, just as is the axial lone pair on the ring oxygen in the axial compounds (**1**). So the likely explanation is that the observed pattern of bond length changes represents the effects of σ-conjugation.[3] σ–σ^* Overlap, between the σ-bonding orbital of the C*–O bond and the antibonding σ^*_{C-OR} orbital, also becomes more efficient as the σ^* level is lowered by increasing electron-withdrawal. (The effects are expected to be smaller than those caused by n–σ^* overlap in the axial series, because a non-bonding electron pair is a better donor than a σ-bonding orbital.[3])

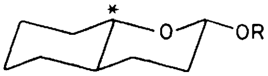
The canonical forms [*e.g.* (**4**)$\longleftrightarrow$(**5**)] for σ-conjugation represent ground and intermediate states in a fragmentation reaction, with the contribution from structure (**5**) increasing for compounds with better leaving groups RO^-. In fact the compound (**4**, R = SO_2Me) with the best leaving group, and



(**1**)



(**2**)



(**3**)

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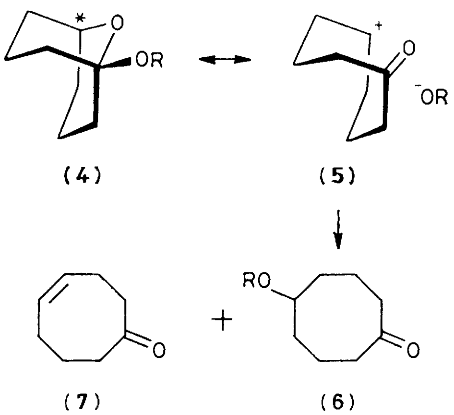
† We have so far measured crystal structures for six axial tetrahydropyranyl acetal systems. For the phenyl,[9] *p*-chlorophenyl,[10] *p*-nitrophenyl,[11] 2,5-dinitrophenyl,[12] 2,4-dinitrophenyl,[13] and 3,5-dinitrobenzoyl[14] compounds the lengths of the remote C*–O bond are 1.448(3), 1.430(3), 1.436(5), 1.445(4), 1.433(5), and 1.414(6) Å, respectively.



(4) (5) (7) (6)

the longest C–OR bond, is known to break down to the products (**6**) and (**7**) expected from the ion pair (**5**). So the bond length changes induced by making OR a better leaving group in the series of tetrahydropyranyl acetals shown (Table 1) may be regarded as marking progress along the reaction co-ordinate for the fragmentation reaction (**4**) → (**5**).

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References

1 P. G. Jones and A. J. Kirby, *J. Chem. Soc., Chem. Commun.*, 1979, 288.

2 A. J. Kirby, 'The Anomeric Effect and Related Stereoelectronic Effects at Oxygen,' Springer-Verlag, Heidelberg, in the press; 'The Anomeric Effect: Origin and Consequences,' eds. W. A. Szarek and D. Horton, A.C.S. Symposium Series, No. 87, Am. Chem. Soc., Washington D.C., 1979.

3 N. D. Epiotis, R. L. Yates, J. R. Larson, C. R. Kirmaier, and F. Bernardi, *J. Am. Chem. Soc.*, 1977, **99**, 8379.

4 P. G. Jones, G. M. Sheldrick, A. J. Kirby, and A. J. Briggs, unpublished work.

5 P. G. Jones, O. Kennard, S. Chandrasekhar, and A. J. Kirby, *Acta Crystallogr., Sect. B*, 1978, **34**, 3835.

6 P. G. Jones, O. Kennard, S. Chandrasekhar, and A. J. Kirby, *Acta Crystallogr., Sect. B*, 1979, **35**, 239.

7 P. G. Jones, G. M. Sheldrick, A. J. Kirby, C. M. Evans, R. Glenn, and J. Stegemann, *Z. Kristallogr.*, 1982, **160**, 45.

8 P. G. Jones, G. M. Sheldrick, A. J. Kirby, R. Glenn, and M. Halstenberg, unpublished work.

9 P. G. Jones, O. Kennard, S. Chandrasekhar, and A. J. Kirby, *Acta. Crystallogr., Sect. B*, 1978, **34**, 2947.

10 P. G. Jones, G. M. Sheldrick, A. J. Kirby, R. Glenn, P. Ramaswamy, and M. Halstenberg, *Z. Kristallogr.*, in the press.

11 P. G. Jones, O. Kennard, A. J. Kirby, and R. J. Martin, *Acta. Crystallogr., Sect. B*, 1979, **35**, 242.

12 P. G. Jones, G. M. Sheldrick, A. J. Kirby, and R. Glenn, *Z. Kristallogr.*, submitted for publication.

13 P. G. Jones, O. Kennard, A. J. Kirby, and R. J. Martin, *Acta. Crystallogr., Sect. B*, 1979, **35**, 755.

14 P. G. Jones, G. M. Sheldrick, A. J. Kirby, R. Glenn, and P. Ramaswamy, *Z. Kristallogr.*, submitted for publication.