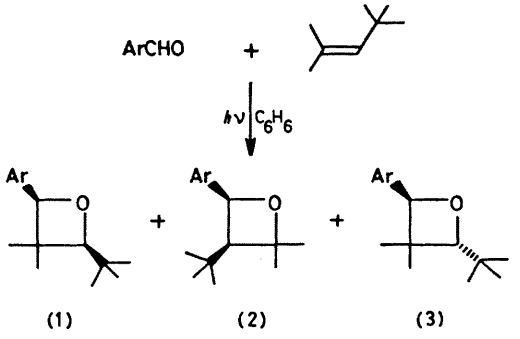
New Ring Expansion Reaction of 2-t-Butyloxetans

By HOWARD A. J. CARLESS* and HARISH S. TRIVEDI
(*Department of Chemistry, Birkbeck College, Malet Street, London* WC1E 7HX)

Summary The action of Lewis acids on aryl-t-butyloxetans (**1**) yields substituted tetrahydrofurans (**4**) or oxetan ring cleavage products; both are believed to be formed *via* carbocationic intermediates.

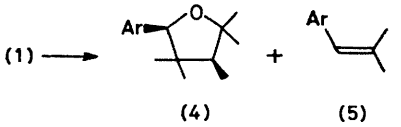
THE action of protic acids or Lewis acids on the oxetan ring often leads to ring cleavage[1] or polymerisation.[2] We now report the ring expansion of 2-t-butyloxetans to tetrahydrofurans [(**1**) → (**4**)] in the presence of Lewis acid catalysts. This rearrangement throws light on the mechanism of reaction of oxetans with Lewis acids.



(**1**) (**2**) (**3**)

SCHEME 1. Ar = Ph, 2-FC_6H_4, 4-ClC_6H_4, 4-CNC_6H_4, 4-PhC_6H_4, 2-MeC_6H_4, 4-MeC_6H_4, 4-$MeOC_6H_4$, 2,3-$(MeO)_2C_6H_3$, 1-naphthyl, or 2-naphthyl.

Photochemical cycloaddition of substituted benzaldehydes to 2,4,4-trimethylpent-2-ene yields the oxetans (**1**)—(**3**), as shown in Scheme 1.[3] The *cis* stereochemistry of the major isomer (**1**) can be assigned on the basis of ^1H and ^{13}C n.m.r. data. Treatment of the oxetans (**1**) with boron trifluoride etherate in diethyl ether or aluminium trichloride in benzene at room temperature leads to the ring-expanded products (**4**)† in the isolated yields shown in the Table. For entries 1—5, n.m.r. spectroscopy of the crude reaction mixture suggests that product (**4**) is formed in quantitative yield. In some cases, the arylalkene product (**5**) is formed from oxetan ring fission in a competitive process (entries 6—9) or in an exclusive process (entries 10—13). No reversion to aromatic aldehyde and 2,4,4-trimethylpent-2-ene was detected.



(**4**) (**5**)

† Structures are fully supported by i.r., mass, and n.m.r. (^1H and ^{13}C) spectral evidence. The only uncertainty we have is the stereochemistry of the single isomer of (**4**) produced, to which we assign the *cis* structure.

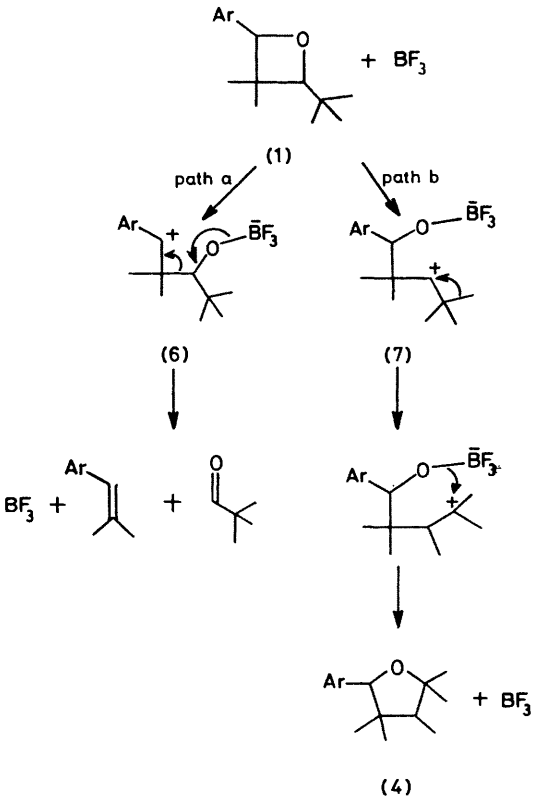
TABLE

Entry	Oxetan (1) Ar	Lewis acid	Time /h	Yield of (4)[a]/%	Yield of (5)[a]/%
1	Ph	$BF_3{\cdot}OEt_2$	30	73	0
2	Ph	$AlCl_3$	18	76	0
3	2-FC_6H_4	$BF_3{\cdot}OEt_2$	30	79	0
4	4-ClC_6H_4	$AlCl_3$	0·5	69	0
5	4-CNC_6H_4	$BF_3{\cdot}OEt_2$	30	46	0
6	4-PhC_6H_4	$BF_3{\cdot}OEt_2$	24	20	70
7	4-PhC_6H_4	$AlCl_3$	0·5	25	71
8	2-MeC_6H_4	$BF_3{\cdot}OEt_2$	30	39	17
9	4-MeC_6H_4	$BF_3{\cdot}OEt_2$	30	32	15
10	4-$MeOC_6H_4$	$BF_3{\cdot}OEt_2$	8	0	90
11	2,3-$(MeO)_2$-C_6H_3	$AlCl_3$	0·5	0	70
12	1-Naphthyl	$BF_3{\cdot}OEt_2$	48	0	20
13	2-Naphthyl	$BF_3{\cdot}OEt_2$	52	0	25

[a] Yields of isolated compounds. Products were isolated by addition of water to the reaction product, diethyl ether extraction, evaporation of the ether, and preparative t.l.c. on the residue.

The formation of a ring-expanded product suggests a reaction mechanism involving an intermediate with carbonium ion character, as outlined in Scheme 2. This scheme can also explain how substituents control the occurrence of ring expansion *vs.* ring fission. Co-ordination of the Lewis acid to the oxetan is followed by cleavage of either of the oxetan C_α bonds (paths a and b). Breaking of the carbon(aryl)–oxygen bond leads on to ring cleavage *via* a carbonium ion (**6**) (path a), whereas breaking of the carbon(t-butyl)–oxygen bond allows for a 1,2-methyl shift in the resulting carbonium ion (**7**) (path b).‡ The failure to detect aromatic aldehydes from the reaction suggests that the 1,2-shift is fast in comparison with ring fission. Subsequent ring closure gives the tetrahydrofuran (**4**). An electron-withdrawing substituent on the aryl ring reduces the stability of the ion (**6**) from path a, and ensures that ring expansion occurs. In contrast, electron-donating substituents on the aryl ring increasingly favour the path (a) leading to ring cleavage. The strongly electron-donating methoxy substituent leads exclusively to ring-cleavage. In fact, the sensitivity of methoxyaryloxetans to acid-catalysed ring cleavage has been recorded, and it occasionally precludes their isolation.[4]

Reports of the ring-expansion reactions of oxetans are rare, being restricted to carbene ring-insertion,[5] boron trifluoride-catalysed addition of carbonyl compounds to steroidal oxetans to yield 1,3-dioxans,[6] and boron trifluoride-catalysed ring expansion in the presence of t-butyl isocyanide.[7] The present work represents an example of intramolecular trapping of a rearranged carbonium ion, and it lends support to the idea that interaction of protic and Lewis acids with oxetans leads to intermediates with carbocationic character.[8]



SCHEME 2

(*Received, 18th January* 1979; *Com.* 052.)

‡ In terms of carbocation stability, path a (leading to the benzylic-type cation) would be expected to be preferred when Ar = Ph, although it is not found. It is likely that the aryl group adopts a conformation in which the aryl π-electrons are orthogonal to the developing *p*-orbital of the carbocation, and are thus unable to assist C–O bond breaking by path a. N.m.r. spectra of (**1**) do show a highly shielded *cis*-methyl group at C-3, in agreement with this suggested conformation. In contrast, C–O bond breaking by path b could be assisted by methyl migration from the t-butyl group to the developing carbocation; such a mechanism would avoid the need to invoke ion (**7**) in the ring expansion.

[1] S. Searles, in 'Heterocyclic Compounds with Three- and Four-Membered Rings,' pt. 2, ed. A. Weissberger, Interscience, New York, 1965, p. 983.
[2] G. Dittus, in Houben-Weyl 'Methoden der organischen Chemie,' Bd. VI/3, G. Thieme Verlag, Stuttgart, 1964, p. 493.
[3] H. A. J. Carless and H. S. Trivedi, unpublished results.
[4] D. R. Arnold, *Adv. Photochem.*, 1968, **6**, 301.
[5] H. Nozaki, H. Takaya, and R. Noyori, *Tetrahedron*, 1966, **22**, 3393.
[6] G. Schneider, I. Weisz-Vincze, A. Vass, and K. Kovács, *J.C.S. Chem. Comm.*, 1972, 713.
[7] T. Saegusa, N. Taka-Ishi, and Y. Ito, *Synthesis*, 1970, 475.
[8] A. Balsamo, P. Crotti, M. Ferretti, and F. Macchia, *J. Org. Chem.*, 1975, **40**, 2870.