Stereochemistry of the Reactions of Oxetans with Rhodium(I) and Silver(I) Catalysts

By Howard A. J. Carless

(*Department of Chemistry, Birkbeck College, Malet Street, London* WC1E 7HX)

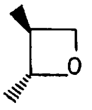
Summary Methyl-substituted oxetans (**1**)—(**4**) undergo a highly stereoselective ring-cleavage reaction on treatment with $[Rh(CO)_2Cl]_2$ or $AgBF_4$.

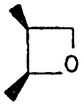
One of the problems of assigning stereochemistry to geometrical isomers of substituted oxetans is that proton vicinal coupling constants are similar in magnitude for both *cis*- and *trans*-oxetan isomers.[1] Generally, the *cis*-isomers have marginally larger vicinal coupling constants.† It is now reported that stereochemistry can be assigned to the methyl-substituted oxetans (**1**)—(**5**) by treatment with rhodium dicarbonyl chloride dimer or silver tetrafluoroborate (see Table). Grigg and co-workers[2] have previously noted the ring-cleavage of some oxetans catalysed by this Rh^I complex. Oxetans (**1**)—(**4**) undergo a highly stereoselective ring-cleavage reaction to give the alkene and a carbonyl compound. Oxetan (**5**) would then be expected to give a mixture of *cis*- and *trans*-alkene, as observed. This method confirms the structural assignments made by Yang[3] for oxetans (**3**)—(**5**), but reverses the assignment of the 2,3-dimethyloxetans (**1**)—(**2**) made on the basis of n.m.r. data by Russian workers.[4]

Table. But-2-ene product distributions (%) from metal-ion catalysed oxetan ring-cleavage

	$[Rh(CO)_2Cl]_2$[a]		$AgBF_4$[b]	
	trans	*cis*	*trans*	*cis*
(**1**)	96	4[c]	97	3
(**2**)	5·5	94·5[c]	6	94
(**3**)	96·5	3·5	98·5	1·5
(**4**)	3·5	96·5	4	96
(**5**)	28	72	28	72

[a] Typical experiments employed a 10:1 mole ratio of oxetan to catalyst, *ca.* 10% conversion to products, at 80° in CCl_4. [b] 70—80°, no added solvent. [c] <0·5% propene produced.


(1)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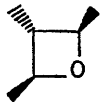
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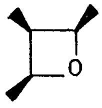
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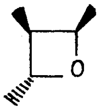
(5)

(*Received, 24th September* 1974; *Com.* 1202.)

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† *E.g.* oxetans (**2**), (**4**) and (**5**) have ${}^3J_{2,3}(cis)$ 7·6, 6·7 and 7·0 Hz; oxetans (**1**), (**3**) and (**5**) have ${}^3J_{2,3}(trans)$ 6·0, 6·1 and 6·0 Hz, respectively.

[1] See, *e.g.* N. J. Turro and P. A. Wriede, *J. Amer. Chem. Soc.*, 1968, **90**, 6863; J. A. Barltrop and H. A. J. Carless, *ibid.*, 1972, **94**, 1951; N. C. Yang, M. Kimura, and W. Eisenhardt, *ibid.*, 1973, **95**, 5058.

[2] G. Adames, C. Bibby, and R. Grigg, *J.C.S. Chem. Comm.*, 1972, 491.

[3] N. C. Yang and W. Eisenhardt, *J. Amer. Chem. Soc.*, 1971, **93**, 1277.

[4] Y. Y. Samitov, A. V. Bogatskii, and G. A. Filip, *Zhur. org. Khim.*, 1971, **7**, 585.