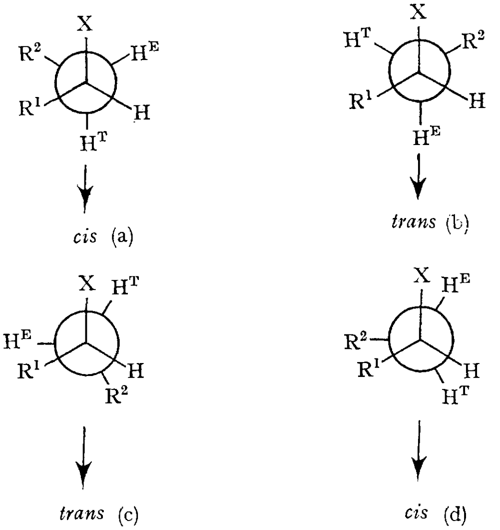
The Interpretation of *trans*- to *cis*-Olefin Ratios in Bimolecular Elimination Processes

By J. SICHER,* J. ZÁVADA, and M. PÁNKOVÁ

(*Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Science, Prague*)

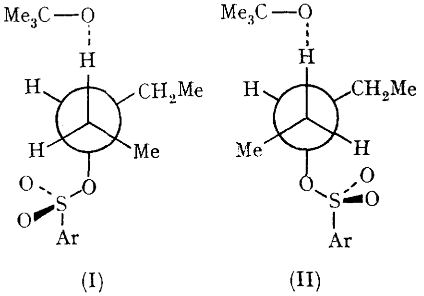
THE ratios in which *trans*- and *cis*-olefins are formed in elimination processes are frequently used as a criterion of "double-bond development" in the transition state.[1] The customary analysis of $E2$ eliminations of the type $R^1CH_2{\cdot}CHXR^2 + B^- \rightarrow$ (*cis*- and *trans*-) $R^1CH{=}CHR^2 + BH + X^-$ ($X = \overset{+}{N}Me_3$, OTs, Br, *etc.*), conducted in terms of repulsive interactions between the groups R^1 and R^2 (Scheme 1a and b), leads to the prediction that the ratio of *trans*- to *cis*-olefin produced will be greater than unity. Such an analysis is invariably carried out assuming an *anti*-elimination mechanism;[1] obviously a corresponding analysis in terms of a *syn*-elimination process (Scheme 1c and d) also leads to this conclusion.



cis (a)
trans (b)
trans (c)
cis (d)

SCHEME 1

Cases of preferred *cis*-olefin formation in $E2$ eliminations though not numerous are, nevertheless, known.[2] Different interpretations have been proposed for such results. The arguments suggested by Brown and Klimisch[1] for the preferred formation of *cis*-pent-2-ene from the reaction of 1-methylbutyl toluene-*p*-sulphonate with potassium t-butoxide in t-butyl alcohol may be given as an example because they are the most recent, as well as the most explicit. These authors believe this outcome to be "a consequence of the fact that the large steric requirements of both the leaving arene sulphonate group and the solvated t-butoxide base cause transition state (I) to be more favourable than transition state (II)" (Scheme 2). This interpretation has, with minor modification, been accepted by Froemsdorf and Robbins.[2]



SCHEME 2

Our discovery that *anti*-elimination is by no means the sole reaction path in simple bimolecular eliminations[3] places the problem of the *trans–cis* olefin ratios in an entirely new light; in particular, it shows that its discussion requires a complete re-allocation of the contributions of the *syn* and *anti* reaction paths (*syn* → *trans*, *syn* → *cis*, *anti* → *trans*, and *anti* → *cis*). Such an allocation has been made (in the preceding Communications) for the formation of dec-5-ene, under a variety of reaction conditions, from 1-butylhexyltrimethylammonium base and from 1-butylhexyl toluene-*p*-sulphonate.

The Table shows that, of the eight elimination reactions examined, three give the *cis*-olefin preferentially. However, considering the *anti*-elimination component alone, we see that this route leads to the *cis*-olefin preferentially in six cases out of eight! Hence preferred *cis*-olefin formation in *anti*-elimination cannot result simply from special steric characteristics,† such as a bulky

---

† Obviously, neither hydroxide nor methoxide is a "bulky" base (reactions 1 and 4); the 'onium group is "bulky" but not branched (reactions 1—5), bromine is neither "bulky" nor branched (the reaction of 1-butylpentyl bromide with Bu^{t}OK–benzene gives 56% of *cis*-non-4-ene[4]); finally t-butoxide in benzene or dimethyl sulphoxide is not solvated (reactions 3, 2, and 6).

trans-*to*-cis *Dec-5-ene ratios in the* syn- *and* anti-*components of the elimination of* 1-*butylhexyltrimethylammonium base and* 1-*butylhexyl toluene*-p-*sulphonate*[2]

Run	X	Base/solvent	Overall *trans/cis* ratio	*syn*-Route			*anti*-Route		
				$k_{s \to t}$	$k_{s \to c}$	$k_{s \to t}/k_{s \to c}$	$k_{a \to t}$	$k_{a \to c}$	$k_{a \to t}/k_{a \to c}$
1	$-NMe_3$	pyrolysis	2·4	67·4	1·4	48	3·6	27·6	0·13
2	$-NMe_3$	Bu^{t}OK/DMSO	4·0	72·9	1·6	46	7·1	18·4	0·39
3	$-NMe_3$	Bu^{t}OK/benzene	10	82·4	2·3	36	8·6	6·7	1·3
4	$-NMe_3$	Bu^{t}OK/Bu^{t}OH	2·4	61·8	1·7	36	9·2	26·3	0·35
5	$-NMe_3$	MeOK/MeOH	0·27	6·7	5·8	1·2	14·3	73·2	0·20
6	–OTs	Bu^{t}OK/benzene	0·85	15·1	4·3	3·5	30·9	49·7	0·62
7	–OTs	Bu^{t}OK/Bu^{t}OH	0·41	4·7	4·1	0·87	24·3	65·6	0·37
8	–OTs	Bu^{t}OK/DMF	3·2	3·4	1·8	1·9	72·6	22·2	3·3

[a] For reaction conditions see preceding Communications.

and solvated base and bulky and branched leaving groups, as visualized by Brown and Klimisch,[1] if for no other reason than because it represents the usual rather than an exceptional reaction outcome.

We must therefore come back to the question of the role played by $R^1 - R^2$ repulsive interactions in determining the *trans–cis* ratios in the two alternative elimination modes. For a simple unbranched open-chain system such as the one now studied a consideration of the $R^1 - R^2$ interactions leads to the crude estimate that in *anti*-elimination the *trans*-olefin will predominate by a factor of say 3—5; in *syn*-elimination by a somewaht greater factor, say about 5—10. Actually, the value of the ratio $k_{s \to t}/k_{s \to c}$ (*syn*-route) for reaction 1—4 is 35—50 and hence much greater than simple consideration of $R^1 - R^2$ eclipsing effects would lead one to expect. For the *anti*-route there is even less agreement with the above prediction; with the exception of reactions 3 and 8 the values of $k_{a \to t}/k_{a \to c}$ found fall short of the estimate by a factor of 10 or even more.

Neither simple considerations of the steric characteristics of base or leaving group nor the magnitude of $R^1 - R^2$ repulsive interactions alone can thus account for the observed results. The operation of some effect which so far has escaped notice must therefore be considered, at least for those processes in which *syn*- and *anti*-elimination proceed side by side. It is tentatively suggested that the observed results can be rationalized by assuming that the two hydrogens on C-β (C-2 in our system) differ intrinsically in their reactivity: an inspection of the four alternative conformations (Scheme 1) shows that both the conformers a and c, through which the greatest part of *anti*- and *syn*-elimination, respectively, have been shown to proceed, involve reaction of the hydrogen H^T, whereas both the "unreactive" conformers (b and d) involve reaction of the hydrogen H^E. The hydrogens H^T and H^E are diastereotopic[5] and the postulate that they differ in reactivity therefore seems reasonable.[6] We propose to discuss possible origins of the reactivity differences between H^T and H^E on a subsequent occasion.

(*Received, June* 11*th*, 1968; *Com.* 766.)

---

[1] D. J. Cram, F. D. Greene, and C. H. DePuy, *J. Amer. Chem. Soc.*, 1958, **78**, 790; W. B. Smith and W. H. Watson, *ibid.*, 1962, **84**, 3174; M. R. Sayhun and D. J. Cram, *ibid.*, 1963, **85**, 1263; H. C. Brown and R. L. Klimisch, *ibid.*, 1965, **87**, 5517; A. K. Colter and D. R. McKelvey, *Canad. J. Chem.*, 1965, **43**, 1282; W. H. Saunders, S. R. Fahrenholtz, E. A. Caress, J. P. Lowe, and M. Schreiber, *J. Amer. Chem. Soc.*, 1965, **87**, 3401; H. C. Brown and O. H. Wheeler, *ibid.*, 1956, **78**, 2199; D. H. Froemsdorf, W. Dowd, and K. E. Leimer, *ibid.*, 1966, **88**, 2345.

[2] A. C. Cope, N. A. LeBel, and W. R. Moore, *J. Amer. Chem. Soc.*, 1957, **79**, 4720; D. H. Froemsdorf and M. D. Robbins, *ibid.*, 1967, **89**, 1737; J. N. Feit and W. H. Saunders, *Chem. Comm.*, 1967, **610**; J. L. H. Allan and M. C. Whiting, *J. Chem. Soc.*, 1953, 3314; J. Závada and J. Sicher, *Coll. Czech. Chem. Comm.*, 1965, **30**, 438.

[3] *Cf.* preceding Communications.

[4] J. Závada, J. Krupička, and J. Sicher, *Coll. Czech. Chem. Comm.*, 1968, **33**, 1393.

[5] K. Mislow and M. Raban, "Topics in Stereochemistry", Interscience, New York, 1967, vol. I, ch. 1.

[6] A. Rauk, E. Buncel, R. Y. Moir, and S. Wolfe, *J. Amer. Chem. Soc.*, 1965, **87**, 5498; S. Wolfe and A. Rauk, *Chem. Comm.*, 1966, 778.