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CONFORMATIONAL EFFECTS IN ELECTRON IMPACT INDUCED ELIMINATION REACTIONS IN THE 1,2-DIPHENYLETHANOL SYSTEM.

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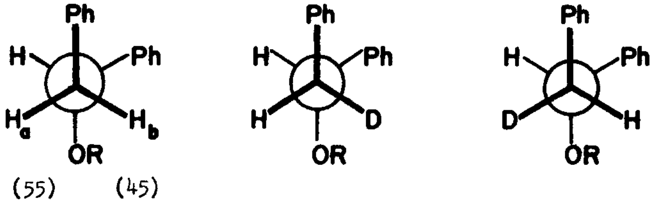
The varied effects of stereochemistry on the mass spectral fragmentation patterns of various isomeric sets of organic compounds have been reviewed critically recently (1), and it is obvious that most previous literature reports refer to epimers of cyclic compounds. Notable exceptions are the studies of Natalis et al. on cis- and trans-acyclic alkenes (2), of Audier et al. using erythro- and threo-allylic alcohols (3), and Green's elegant demonstration that diastereotopic hydrogens are distinguished in the 1,3-elimination of HCl from 2-chloropentane (4).

We report here our preliminary observations of stereoselective elimination process in conformationally mobile systems, in this case expulsion of H_2O and CH_3OH from 1,2-diphenylethanol (1) and its methyl ether (2) in the mass spectrometer.

Fig. 1



1 R=H dl-erythro - 3 R=H dl-threo - 4 R=H

2 R=CH_3 5 R=CH_3 6 R=CH_3

cis- and trans-Stilbene were converted separately to the corresponding oxides, and then by lithium aluminum deuteride reduction to dl-erythro-2-d_1-1,2-diphenylethanol (3) and dl-threo-2-d_1-1,2-diphenylethanol (4) respectively. The methyl ethers 5 and 6 were secured from 3 and 4 by Williamson ether synthesis. Mass spectra (5) were obtained at convenient electron energy intervals from 70 to 10 eV (nominal), and source temperature intervals from 60 to 250°. The relative proportions of water and methanol lost as ROH and ROD from each of the diastereomeric alcohols (3, 4) and methyl ethers (5, 6) respectively are recorded in Table I for 10 eV spectra (6). The expulsion of water from the diastereomeric alcohols was shown to be a clean β-elimination process, unsullied by H/D scrambling in the precursor molecular ions (7), by the exclusive expulsion

Table I: Loss of ROH and ROD from Molecular Ions 3, 4, 5 and 6.

Source Temp.	[M-ROD]:[M-ROH][a] at 10 eV			
	3	4	5	6
80°	36:64	48:52	31:69	35:65
250°	30:70	40:60	32:68	40:60

[a] Expressed as percent of total elimination.

of HOH, HOD and HOD respectively, noted in the 10 eV mass spectra (5) of 1-d_1-1,2-diphenylethanol, O-d_1-1,2-diphenylethanol and 2,2-d_2-1,2-diphenylethanol. No metastable ion peak has yet been observed for the reactions studied here. However, injection of 1 on a heated preparative g.l.c. column (8) gave no indication of any stilbenes generated pyrolytically.

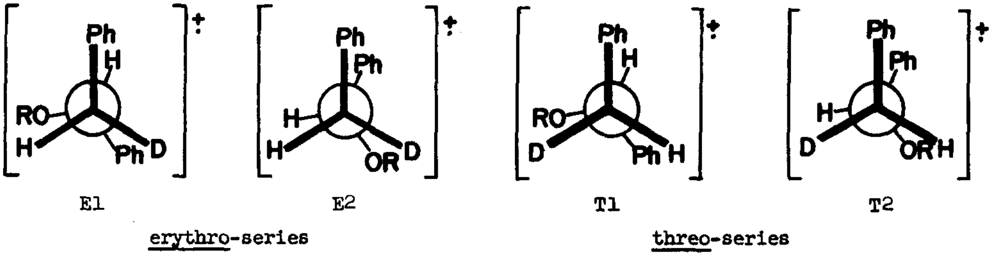
Since the [M-ROD]:[M-ROH] ratios are different for diastereomeric substrates (Table I), a degree of stereoselectivity must obtain. To separate conformational effects from isotope effects, calculations based on the original simple form of the quasi-equilibrium theory (9) of mass spectra were performed, which lead for example to a stereoselectivity of 55:45 for the diastereotopic hydrogen atoms H_a and H_b abstracted by water elimination from 1 at 10 eV and 80° source temperature (Table II), and to an isotope effect (10) of 1.87 under the same conditions. The magnitude of the stereoselectivity is expressed here (Table II) as the ratio of H_a to H_b lost [M-ROH_a]:[M-ROH_b] in the expulsion of water and methanol from 1 and 2 respectively, after correction for an isotope effect. The isotope effect is expressed here as the ratio of H to D lost ([M-ROH]:[M-ROD]) in each diastereomeric pair 3, 4 and 5, 6 after correction for conformational effects.

Table II: Stereoselectivity in Elimination of Diastereotopic Hydrogen Atoms in 1 and 2.

Source Temp.	1, R=H		2, R=CH_3	
	H_a	H_b	H_a	H_b
80°	55	45	54	46
250°	56	44	53	47

In applying the calculations, the activated complexes shown in Fig. 2 were considered, assuming a cis-stereoelectronic requirement for elimination (4,11), and relative transition state energies of E2 > T1 > T2 > E1 were assigned. If the non-bonded interactions between Ph/H and Ph/D, and between H/H and H/D, are taken as effectively the same magnitude, then the transition state

Fig. 2: Transition States for Electron Impact Induced *cis*-β-Elimination



pair E1 and T1 differ only in the energy associated with the isotope effect, to a first approximation. The same holds for E2 and T2. Similarly, transition states E1 and T2 differ only in the non-bonded interaction energies (Ph/H *vs*. Ph/Ph), and the same obtains for T1 and E2. Since in every instance, greater loss of ROH than ROD was observed (13) (Table 1), isotope effects are apparently the major factor to influence relative transition state energies. Thus, the overall energy difference between *erythro*-transition states E1 and E2 is the *sum* of isotope effect and conformational effects, whereas between *threo*-transition states T1 and T2 it is the *difference* between isotope effect and conformational effects.

The calculations further assumed the same ionization potentials, internal energies of molecular ions, and energy distributions (14) for diastereomeric pairs of compounds, and that product composition is dependent on relative activation energies for competing reactions (15).

In summary, the evidence presented suggests that the electron impact induced β-elimination of ROH in the 1,2-diphenylethanol system (**1**, **2**) at low electron energies is subject to conformational influences. A *cis*-elimination is visualized, proceeding *via* transition states that tend to minimize phenyl/phenyl interactions, and lead to the preferential formation of ionized *trans*-stilbene as the (apparent) immediate product of the reaction. These findings also suggest that the geometry of the ground state molecule is not drastically altered in the *reacting* molecular ions. Mechanisms are preferred (4) which invoke concerted elimination of ROH, or else prior abstraction of the diastereotopic hydrogens H_a/H_b by the hydroxyl (or methoxyl) group.

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3. H.E. Audier, H. Felkin, M. Fetizon, and W. Vetter, Bull. Soc. Chim. France, 3236 (1965).
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5. A Varian Atlas CH4B mass spectrometer was employed, with molecular beam inlet system (sample unheated externally), accelerating voltage 3 kV, trap current 2 to 5 μA, and resolution approximately 500. At least 12 scans of flattopped peaks were taken and averaged for each reported reading. Under these conditions, the [M-ROD]:[M-ROH] ratios were almost independent of source temperature in range 60-250°.
6. With increasing electron energy, the difference in [M-ROD]:[M-ROH] for diastereomers decreases, until at 20 eV the ratios are 51:49.
7. N.M.M. Nibbering and Th. J. deBoer, Org. Mass Spectrom., 1, 365 (1968).
8. A 6' x 1/4" column of 20% DC-550 on Anakrom ABS at 250° with an injection pot temperature of 300° was employed. Observed contact time (retention time) was 2 minutes.
9. H.M. Rosenstock, M.B. Wallenstein, A.L. Wahrhaftig and H. Eyring, Proc. Natl. Acad. Sci. U.S., 38, 667 (1952); H.M. Rosenstock and M. Krauss, in Mass Spectrometry of Organic Ions, Ed. F.W. McLafferty, Academic Press, New York, 1963, Chap. 1.
10. See J.K. MacLeod and C. Djerassi, J. Am. Chem. Soc., 89, 5182 (1967).
11. Rigorous isotope labelling experiments have also clearly demonstrated the cis- nature of 1,4-elimination of HCl from cyclohexyl chloride.[12] A consideration of relative transition state energies for a trans-elimination suggests greater [M-ROD]:[M-ROH] ratios for the erythro-series, rather than threo- as found in the present work.
12. M. M. Green and J. Schwab, Tet. Letts., 2955 (1968).
13. The very similar [M-ROD]:[M-ROH] ratios recorded (Table I) for both the alcohols and the methyl ethers suggests that the influence of any intramolecular hydrogen bonding effects can be discounted.
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15. At the nominal 10 eV electron energy, no further decomposition of the M-ROD or M-ROH ions could be detected.