Table I. Solvent Dependence of Chemical Shifts and Coupling Constants (cps) for *cis*-1,2-Dichlorofluoroethylene

Solvent	$\delta_H^{a,b}$	$J_{C^{13}-H}^{a}$	ϕ_F^{c}	$J_{C^{13}-F^{19}}$
Cyclohexane	362.0	195.6	4763	300.0
Benzene	323.4	198.0	...	...
Carbon disulfide	369.8	195.5	4675	300.0
Isopropyl ether	389.4	199.6	...	...
Chloroform	372.9	199.6	4746	300.0
Acetone	405.5	199.6	...	...
Acetonitrile	390.4	198.0	4798	298.6
N,N-Dimethylformamide	424.4	202.5	4807	297.0
Dimethyl sulfoxide	428.8	201.0	4767	298.0

[a] The proton chemical shifts are accurate to ±0.2 cps and coupling constants to ±0.1 cps. The fluorine chemical shifts and coupling constants are accurate to ±1.0 cps and ±0.5 cps, respectively. [b] Proton chemical shifts are for 1% solutions and are relative to internal TMS. [c] Fluorine chemical shifts are for 50% solutions and are given relative to external Cl_3CF.

Table II. Solvent Dependence of Chemical Shifts and Coupling Constants (cps) for *trans*-1,2-Dichlorofluoroethylene

Solvent	δ_H^{a}	$J_{C^{13}-H}$	ϕ_F	$J_{C^{13}-F^{19}}$
Cyclohexane	325.2	201.7	4501	306.9
Benzene	286.3	204.0	...	...
Carbon disulfide	333.6	201.8	4468	306.6
Isopropyl ether	352.6	205.2	...	...
Chloroform	336.2	203.8	4491	306.2
Acetone	377.3	205.9	...	...
Acetonitrile	355.7	204.5	4558	304.5
N,N-Dimethylformamide	390.7	208.6	4565	302.9
Dimethyl sulfoxide	394.7	207.1	4518	304.2

[a] Experimental conditions are the same as for the *cis* isomer, Table I.

those observed in different solvents. The proton and fluorine chemical shifts for both isomers show a marked *decrease* in solvents of higher dielectric constant. In contrast the C^{13}–H coupling constants *increase* in magnitude while the C^{13}–F^{19} coupling constants *decrease* in the more polar solvents. Both the proton and fluorine chemical shifts vary linearly[7] with the respective $J_{C^{13}-H}$ and $J_{C^{13}-F^{19}}$ coupling constants in different solvents. A linear correlation is also noted between the directly bonded couplings and J_{H-F}, over the same range of solvents. These observations indicate that the medium effect acts to change the shieldings and coupling constants by a similar mechanism. Since the chemical shifts follow the trend expected if the reaction field of the solvent is the dominant influence,[8] it is likely that the changes in coupling constants are also largely due to this effect.[9]

The solvent-induced changes in magnitude of $J_{C^{13}-H}$ and $J_{C^{13}-F^{19}}$ can be rationalized in terms of the MO theory of Pople and Santry[10] for directly bonded coupling constants. Considering the C^{13}–H coupling constant, an increase in the magnitude of the reaction field acting in the region of the C–H bond will tend to increase the s character[11] of the C-hybrid bonding orbital and hence will lead to a more positive value for $J_{C^{13}-H}$; if the sign of $J_{C^{13}-H}$ is positive,[12] then $J_{C^{13}-H}$ will increase in more polar solvents as is observed. For the C^{13}–F^{19} coupling, the reaction field acting in the region of the C–F bond will tend to draw the bonding electrons closer to the F atom. The increased polarity of the bond results in a trend of the C^{13}–F^{19} coupling constant to more positive values; since the sign of $J_{C^{13}-F^{19}}$ is most likely negative,[13] the observed coupling constant decreases in magnitude.

The present results show the possibility of obtaining evidence about the signs of directly bonded coupling constants from their solvent dependence without recourse to double resonance techniques. A similar suggestion was made recently[2j] in connection with the solvent dependence of the geminal and vicinal couplings in styrene oxide. The usefulness of solvent effects for sign determination is limited, however, to simple systems in which solute–solute and solute–solvent interactions are easily characterized.

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(6) The high solute concentration (50%) required in order to observe the $J_{C^{13}-F^{19}}$ satellites precluded the observation of any concentration dependence for this coupling constant.

(7) The pronounced high-field shift in benzene is due to the anisotropic diamagnetic susceptibility of the solvent molecules.

(8) F. Hruska, E. Bock, and T. Schaefer, *Can. J. Chem.*, **41**, 3034 (1963).

(9) Watts and co-workers[2i] have suggested that the medium effect on $J_{C^{13}-H}$ in some dihaloethylenes is due in part to a specific interaction between a solvent molecule and the halogen substituent. Such a possibility cannot be completely ruled out in the present systems; however, it is not expected to be the predominant factor.

(10) J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964).

(11) Electrostatic repulsion between the bonding electron and the negatively charged reaction field will force the electron closer to the C atom; *cf.* Evans.[2a]

(12) P. C. Lauterbur and R. J. Kurland, *J. Am. Chem. Soc.*, **84**, 3406 (1962).

(13) G. V. D. Tiers, *ibid.*, **84**, 3972 (1962).

(14) Visiting summer scientist, 1965.

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An Explanation for the Predominance of *cis*-2-ene over *trans*-2-ene in *p*-Toluenesulfonate Eliminations

Sir:

A recent communication[1] reports that *cis*-2-ene is formed more rapidly than *trans*-2-ene when secondary tosylates undergo base-promoted eliminations with potassium *t*-butoxide in *t*-butyl alcohol. It was suggested[1] that these data could be rationalized in terms of a steric model involving the steric requirements of both the attacking base and the leaving group.

We have studied the products formed from 2-butyl and 2-pentyl tosylates using various solvents and two alkoxide bases and have also observed this unusual effect when reactions were carried out in *t*-butyl alcohol with both bases. The reaction conditions were the same as previously reported.[2] The data are summarized in Table I.

Examination of these and the previous[1,2] data suggests that: (1) the predominance of *cis*-2-ene over *trans*-2-ene is the result of a solvent effect since it is peculiar to *t*-butyl alcohol and not to the identity of the base, and (2) contrary to previous hypotheses[1,3] the steric requirements of alkoxide bases in general are relatively unimportant in tosylate eliminations.

Any consideration of the proposed steric requirements[1,3] of attacking base must take into account the degree of β-C–H bond stretching in the transition

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(1) H. C. Brown and R. L. Klimish, *J. Am. Chem. Soc.*, **87**, 5517 (1965).

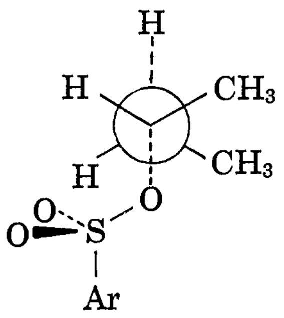
(2) D. H. Froemsdorf and M. E. McCain, *ibid.*, **87**, 3983 (1965).

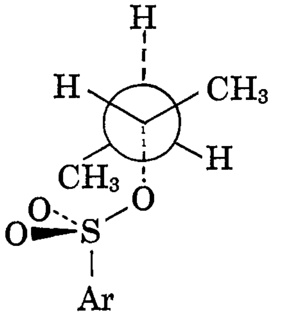
(3) H. C. Brown, I. Moritani, and Y. Okamoto, *ibid.*, **78**, 2193 (1956).

Table I. Products from the Elimination of Secondary Alkyl Tosylates at 55°

Expt	Alkyl group	Solvent	Base	% 1-ene	*trans*-2-ene/*cis*-2-ene
1	2-Butyl	EtOH	KOEt	35	1.95[a]
2	2-Butyl	*t*-BuOH	KOEt	54	0.80
3	2-Butyl	*t*-BuOH	KO-*t*-Bu	64	0.58
4	2-Pentyl	EtOH	KOEt	42	1.90[a]
5	2-Pentyl	*t*-BuOH	KOEt	62	0.57
6	2-Pentyl	*t*-BuOH	KO-*t*-Bu	73	0.38

[a] Data from ref 2.


I


II

state. The importance of this consideration is exemplified by the fact that in consideration of the steric requirements of halogen both the covalent bond radii and van der Waals radii must be considered.[4] The covalent bond radii appear to be the more important consideration since the steric requirement of chlorine is apparently greater than that of iodine.[5] Kinetic studies on tosylates[6] demonstrate that the E1cb character of the transition state is significantly greater in *t*-butyl alcohol than in ethanol. Product studies in DMSO,[2] when compared with the results in ethanol, reveal that with or without a factor for the effect of solvation[7] the steric requirement of the attacking base is relatively unimportant in related reactions.

That *t*-butyl alcohol inhibits C–X[8] stretching in the transition state in comparison with other solvents is demonstrated by the fact that the decrease in the *trans*-2-ene:*cis*-2-ene ratio reported here for tosylates parallels the effect observed in halide eliminations.[9,10]

Thus, we believe the evidence is strong that the transition state for tosylate eliminations in the *t*-butyl alcohol is basically one in which C–H stretching is of major importance with C–O stretching delegated to a minor role. Clearly this allows the elimination of the steric effect of base as a factor. However, this does allow the stereochemical requirements of the leaving group to assume a role in the transition state,[11] and the decision as to which transition state, I or II, is more energetically favorable then becomes much the same problem as determining the relative population in the ground state of the conformers from which structure I and II can be considered to be derived. Examination of Fisher–Hirschfelder–Taylor molecular models reveals that the C-1 as well as the C-4 methyl group interferes with free rotation of the tosylate group about the C–O bond. Thus, the preferred orientation of the tosylate would be to project to the side opposite C-1 as shown. From this, it is apparent that the C-4 methyl group will interfere with free rotation about the S–O bond in structure II whereas it will not in structure I. Thus, structure I allows more rotational freedom to the tosylate group. This effect apparently must be more important than the methyl–methyl interactions developed in structure I. Extension of this phenomenon to the 2-pentyl system predicts that the *trans*-2-ene:*cis*-2-ene ratio would decrease as observed (expt 5 and 6) since tosylate–alkyl interaction is considered more important than alkyl–alkyl. However, as C–O bond stretching increases, the alkyl–alkyl interaction increases and at the same time the tosylate–alkyl interaction decreases; thus structure II becomes more and more energetically favorable and the *trans*-2-ene:*cis*-2-ene ratio increases (expt 3, 2, and 1, or 6, 5, and 4).

The above results suggest that the stereochemical requirement of leaving groups may be a factor when the degree of C–X stretching is very small; this condition is most likely to exist when the transition state has a great deal of E1cb character. By analogy, the size of attacking bases may possibly be a factor when the degree of C–H stretching is very small; this condition is most likely to exist when the transition state has a great deal of E1 character and/or a weak base is used.

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(4) (a) H. C. Brown and O. H. Wheeler, *J. Am. Chem. Soc.*, **78**, 2199 (1956); (b) H. C. Brown and I. Moritani, *ibid.*, **78**, 2203 (1956).

(5) A. J. Berlin and F. R. Jensen, *Chem. Ind.* (London), 998 (1960).

(6) C. H. DePuy and C. A. Bishop, *J. Am. Chem. Soc.*, **82**, 2532 (1960).

(7) H. C. Brown and M. Nakagawa, *ibid.*, **78**, 2197 (1956).

(8) Where X designates the leaving group.

(9) D. H. Froensdorf, M. E. McCain, and W. Dowd, unpublished results.

(10) D. H. Froemsdorf, M. E. McCain, and W. W. Wilkison, *J. Am. Chem. Soc.*, **87**, 3984 (1965).

(11) A referee has suggested that the sulfone oxygens in the tosylate group are hydrogen bonded to alcohol, thus attributing the unique effect observed in *t*-butyl alcohol to the greater steric requirement of the solvated leaving group. Infrared studies of O–H and S–O stretching frequencies of carbon tetrachloride solutions containing both *t*-butyl alcohol and 2-butyl tosylate reveal that this is not an important consideration.

(12) National Science Foundation Undergraduate Research Participant.

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2-Decaprenyl-6-methoxyphenol, an Apparent Biosynthetic Precursor of Ubiquinone-10[1]

Sir:

A new phenolic substance, which is an apparent precursor of ubiquinone-10, has been isolated. Structural and synthetic data on this product are in agreement with structure V ($n = 10$), 2-decaprenyl-6-methoxyphenol[1] or 2-[3′-methyl-2-butenylenakis(3′-methyl-2′-butenylene)]-6-methoxyphenol. Four intermediates in the biosynthetic sequence from *p*-hydroxybenzoic acid (I) to ubiquinone-10 (VI, $n = 10$) are now evident.

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(1) (a) Coenzyme Q. LXXIII. (b) Nomenclature is based on a recommendation of an IUPAC–IUB Commission of Biochemical Nomenclature.