trans:*cis* Olefin Ratios in the Elimination Reactions of 1-Benzylethyl Halides and Toluene-*p*-sulphonate in Different Base–Solvent Systems

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trans:*cis* Olefin ratios have been determined for the elimination reactions of 1-benzylethyl halides and tosylate $PhCH_2CHXMe$ (X = Br, I, or OTs) in different base–solvent systems. The *trans* : *cis* ratio is substantially the same for X = Br and I, whereas a lower value is observed for X = OTs. The basicity of the nucleophile does not appear significantly to affect the *trans* : *cis* ratio. However, an increase in this ratio is observed in going from a protic to a dipolar aprotic solvent and from EtONa–EtOH to Bu^{t}OK–Bu^{t}OH. Ion association increases the *trans* : *cis* ratio when X = I and Br, whereas it has practically no effect on the geometrical orientation when X = OTs. The present results are discussed by comparison with those obtained in the corresponding reactions of non-activated substrates.

RECENT studies [1,2] have shown that in elimination from β-phenyl-activated compounds the geometrical orientation is influenced in a different manner by structural changes in the substrate and in the base–solvent system than in elimination from non-activated substrates. Thus, it has been found that in elimination from 1-benzylethyl halides in EtONa–EtOH the highest *trans* : *cis* ratio is observed when the leaving group is fluoride; in contrast fluoride exhibits the smallest *trans* : *cis* ratio in the corresponding eliminations from 1-methylpentyl [3] and 1-methylbutyl halides.[4] Moreover when the base–solvent system is changed from EtONa–EtOH to Bu^{t}OK–Bu^{t}OH the *trans* : *cis* ratio increases in elimination from 1-benzylethyl chloride, but decreases [5] in the corresponding reactions of non-activated alkyl halides.

Further insight into this phenomenon is required. Accordingly, we have determined the *trans* : *cis* olefin ratios for the elimination reactions of 1-benzylethyl tosylate and halides $PhCH_2CHXMe$ (X = OTs, Br, or I) in different base–solvent systems.

RESULTS

In all cases examined the *trans* : *cis* 1-phenylpropene ratio was measured by g.l.c. Allylbenzene was also produced but in very small amounts (<1% for X = Br and I and 1—4% for X = OTs).

Reaction times and base concentrations were selected in each case in order to render negligible the influence of the isomerization reactions of allylbenzene and of *trans*- and *cis*-1-phenylpropene on the *trans* : *cis* ratios. Reactions with sodium phenoxide and 4-nitrophenoxide in EtOH were carried out in the presence of equimolar amounts of phenol and 4-nitrophenol, respectively. Control experiments showed that in the absence of base no solvolysis of the substrates examined occurred under the reaction conditions.

Results are reported in the Table.

DISCUSSION

anti-Stereochemistry for elimination from 1-benzylethyl chloride has been recently shown for a variety of conditions.[6] It seems reasonable to assume the same stereochemistry for the reactions of the present substrates.

Leaving Group Effects.—The *trans* : *cis* ratio in elimination from 1-benzylethyl bromide and iodide in Bu^{t}OK–Bu^{t}OH is practically identical with that observed for the corresponding chloride.[2] Thus, in this base–solvent system the change in leaving group from chloride to bromide to iodide has no significant effect on the value of the *trans* : *cis* ratio. This result parallels that previously obtained [1] for elimination from 1-benzylethyl halides (X = I, Br, and Cl) promoted by EtONa in EtOH. In EtONa–EtOH, however, a *trans* : *cis* ratio very different from that of the other halides was obtained when the fluoride was the substrate. Unfortunately, it has not been possible to confirm this finding in Bu^{t}OK–Bu^{t}OH since the elimination from the fluoride in this base–solvent system was found to occur at a rate comparable with that of isomerization of the olefins produced.

trans : *cis* Olefin ratios obtained in the eliminations from $PhCH_2CHXMe$ (X = I, Br, or OTs) in different base–solvent systems

Base–solvent	*t*/°C	X I	 Br	 OTs
EtONa–EtOH	60	28.3 [a]	24.7 [a]	9.7
PhONa–EtOH [c]	60		17.0	
$4-NO_2C_6H_4ONaC_6H_4$–EtOH [d]	60		18.0	
PhONa–DMF [e]	30		48.0	
$4-NO_2C_6H_4ONa$–DMF [f]	30		52.0	
$4-NO_2C_6H_4ONa$–DMSO [g]	30			15.0
PhONa–DMSO [h]	30		70.0	23.0
2,6-$Bu^t_2C_6H_3ONa$–DMSO [i]	30		106.0	23.5
Bu^{t}OK–Bu^{t}OH [l]	60	74.5	78.5	21.0
Bu^{t}OK–crown ether–Bu^{t}OH [m]	60	28.5	30.0	22.5

[a] Data from ref. 1. [b] [EtONa] = 0.21M; reaction time (r.t.) 24—34 h. [c] [PhONa] = [PhOH] = 0.2M; r.t. 4—5 h. [d] $[4-NO_2C_6H_4ONa] = [4-NO_2C_6H_4OH]$ = 0.2M; r.t. 24 h. [e] [PhONa] = 0.1M; r.t. 15—30 min. [f] $[4-NO_2C_6H_4ONa]$ = 0.5—0.8M; r.t. 15—60 h. [g] $[4-NO_2C_6H_4ONa]$ = 0.2M; r.t. 5—24 h. [h] [PhONa] = 0.05—0.07M; r.t. 10—30 min. [i] [2,6-$Bu^t_2C_6H_3ONa$] = 0.15—0.3M; r.t. 30—60 min. [l] [Bu^{t}OK] = 0.2—0.8M; r.t. 15—120 min. [m] [Bu^{t}OK] = [dicyclohexyl-18-crown-6-ether] = 0.2M; r.t. 30—180 s.

In eliminations from phenyl-activated substrates the values of the *trans* : *cis* olefin ratio also derive from differences in the extent of conjugation of the phenyl group with the partial negative charge which develops on

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[2] S. Alunni, E. Baciocchi, R. Ruzziconi, and M. Tingoli, *J. Org. Chem.*, 1974, **39**, 3299.

[3] R. A. Bartsch and J. F. Bunnett, *J. Amer. Chem. Soc.*, 1968, **90**, 408.

[4] W. H. Saunders, jun., S. R. Fahrenholtz, E. A. Caress, J. P. Lowe, and M. Schreiber, *J. Amer. Chem. Soc.*, 1965, **87**, 3401.

[5] R. A. Bartsch, G. M. Pruss, D. M. Cook, R. L. Buswell, B. A. Bushau, and K. E. Weigers, *J. Amer. Chem. Soc.*, 1973, **95**, 6745.

[6] S. Alunni, E. Baciocchi, R. Nicoletti, and M. Tingoli, *J.C.S. Perkin II*, 1975, 1669.

C_β in the transition state,* as well as from differences in the extent of conjugation with the developing double bond, and from non-bonded interactions of the substituents at C_α and C_β. Thus, in the reactions of these systems an increase of the *trans* : *cis* ratio may result from an increase of the carbanion character and/or of the extent of the double bond formation in the transition state. Since, according to the theory of the variable transition state,[7] an increase of the carbanion character of the transition state is accompanied by a decrease of the degree of double bond formation,† it follows that in elimination from phenyl-activated substrates geometrical orientation may exhibit a reduced sensitivity to changes in the transition state structure. Therefore, the near constancy of the *trans*: *cis* ratio observed for chloride, bromide, and iodide leaving groups can be rationalized by assuming that the effect of the increase of carbanion character, in going from the iodide to the chloride, is more or less compensated for by the simultaneous decrease in the extent of double bond formation.

Changes in the carbanion character of the transition state with the nature of the leaving group could become more important for elimination promoted by crown ether-complexed Bu^{t}OK which is a much more basic nucleophile than uncomplexed Bu^{t}OK. With this nucleophile, iodide and bromide give a similar *trans* : *cis* ratio but smaller than that previously observed with the chloride.[2] According to a recent investigation,[9] the transition state for a *syn*-elimination promoted by crown ether-complexed Bu^{t}OK in Bu^{t}OH is significantly more carbanionic than that for the corresponding reaction promoted by Bu^{t}OK in Bu^{t}OH.

The eliminations from 1-benzylethyl tosylate in EtONa–EtOH, Bu^{t}OK–Bu^{t}OH, and PhONa–DMSO show a *trans* : *cis* ratio which is much smaller than that observed in the elimination from the halides. This result is expected since in the transition state leading to the *trans*-olefin the large tosylate group must necessarily interact with the substituents at both C_α and C_β.[10] Interestingly, the difference in the *trans* : *cis* ratio between halide and tosylate leaving groups becomes substantially smaller when the nucleophile is crown ether-complexed Bu^{t}OK.

Base–Solvent Effects.—The effect of the nucleophile basicity on the *trans* : *cis* ratio can be determined by considering the results obtained in the elimination from 1-benzylethyl bromide in EtOH and DMF and from 1-benzylethyl tosylate in DMSO.

With the former substrate in EtOH a slightly larger *trans* : *cis* ratio is observed with EtONa than with PhONa. The same trend is also found for the reactions of 1-benzylethyl tosylate in DMSO. However, in elimination from 1-benzylethyl bromide in DMF and in EtOH the *trans* : *cis* ratio has practically the same value with both sodium phenoxide and sodium 4-nitrophenoxide.

Thus, it appears that the basicity of nucleophile exerts little or no influence on the geometrical orientation of elimination from phenyl-activated substrates. Interestingly, in the reactions of non-activated substrates also, basicity does not significantly influence the geometrical orientation.[11]

Coming to the solvent effect we find that in elimination from 1-benzylethyl bromide promoted by sodium phenoxide there is a significant increase in the *trans* : *cis* ratio, too large to be ascribed only to a temperature effect, in passing from a protic (EtOH) to a dipolar aprotic solvent (DMF, DMSO). Moreover, the *trans* : *cis* ratio is slightly larger in DMSO than in DMF.

Higher *trans* : *cis* ratios in dipolar aprotic than in protic solvents have also been observed for elimination from non-activated substrates;[5,‡] this was related to less ion-pairing of the base in the dipolar aprotic solvent. This explanation, however, cannot be applied to elimination from activated substrates where reduced ion-pairing produces a decrease of the *trans* : *cis* ratio (see below).

Finally a significantly larger *trans* : *cis* ratio in Bu^{t}OK–Bu^{t}OH than in EtONa–EtOH is observed, with all the substrates investigated. With crown ether-complexed Bu^{t}OK in Bu^{t}OH the *trans* : *cis* ratio decreases with both 1-benzylethyl bromide and iodide, but remains unchanged with 1-benzylethyl tosylate. The results obtained previously for elimination from 1-benzylethyl chloride are, therefore, substantially confirmed. In contrast, with non-activated substrates the opposite trend is observed.

The results obtained in the reactions of non-activated substrates have been explained on the basis of the larger steric requirements of Bu^{t}OK in Bu^{t}OH (where it exists as ion pairs or aggregates of ion pairs) than of EtONa in EtOH and crown ether-complexed Bu^{t}OK in Bu^{t}OH.

Probably the changes in geometrical orientation found with 1-benzylethyl halides are also determined by steric effects, an increase of the steric requirements of the base producing, however, an increase of the *trans* : *cis* ratio. This conclusion is supported by the fact that the reaction of 1-benzylethyl bromide with sodium 2,6-di-t-butylphenoxide exhibits a higher *trans* : *cis* ratio than that with phenoxide, and, tentatively, may be rationalized as

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* Examination of molecular models shows that this conjugation is more feasible for the conformation leading to the *trans*- than for that leading to the *cis*-olefin.

† According to a different view [8] an increase of the carbanion character of the transition state could be accompanied by an increase of the degree of double bond formation. However, in this case, a regular increase in the *trans* : *cis* ratio in going from the iodide to the chloride should have been observed.

‡ There is an exception, however, as in elimination from 2-iodobutane promoted by sodium phenoxide no change in the *trans* : *cis* ratio is observed when the solvent is varied from EtOH to DMSO.[11]

[7] J. F. Bunnett, *Angew. Chem.*, 1962, **74**, 731.

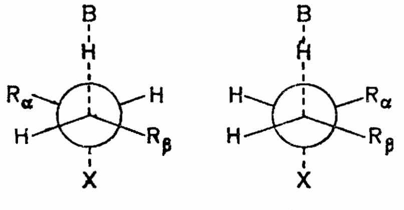
[8] L. J. Steffa and E. R. Thornton, *J. Amer. Chem. Soc.*, 1967, **89**, 6149.

[9] R. A. Bartsch, E. A. Mintz, and R. M. Parlman, *J. Amer. Chem. Soc.*, 1974, **96**, 4249. However unpublished results from this laboratory indicate that this effect is less evident for an *anti*-elimination.

[10] H. C. Brown and R. L. Klimisch, *J. Amer. Chem. Soc.*, 1965, **87**, 5517; D. H. Froemsdorf, W. Dowd, and K. E. Leimer, *ibid.*, 1966, **88**, 2345.

[11] R. A. Bartsch, C. F. Kelly, and G. M. Pruss, *J. Org. Chem.*, 1971, **36**, 662.

follows. When R_β (the substituent at C_β) is a phenyl group the extent of conjugation in the transition state with both the incipient double bond and the partial negative charge at C_β is certainly larger in the transition state leading to the *trans*-olefin (I) than in that leading to the *cis*-olefin (II). Thus it is possible that in this case the interactions of a large base with R_α and R_β [even if less in (II) than in (I), as suggested] exert a larger destabilizing effect on (II), by determining a further decrease of the conjugative effect of R_β, than on (I), where, in contrast, such interactions could not lead to a substantial decrease of the conjugative effect of R_β. As a consequence an increase of the *trans* : *cis* ratio should be observed.



(I) (II)

When the leaving group is the *p*-tosylate group [X = OTs in (I) and (II)], no increase of the *trans* : *cis* ratio is observed when the base is changed from sodium phenoxide to sodium 2,6-di-t-butylphenoxide in DMSO and from dissociated to associated Bu^tOK in Bu^tOH. These results are difficult to reconcile with the increase of the *trans* : *cis* ratio observed for the reaction of 1-benzylethyl tosylate when the base–solvent system is changed from EtONa–EtOH to Bu^tOK–Bu^tOH.

EXPERIMENTAL

Materials.—1-Benzylethyl tosylate was prepared according to the procedure described by Tipson.[12] 1-Benzylethyl iodide,[13] b.p. 75° at 1 mmHg, and bromide,[13] b.p. 62° at 1 mmHg, were prepared by the reactions in acetone of 1-benzylethyl tosylate with NaI and LiBr, respectively. Dicyclohexyl-18-crown-6 ether was prepared by following the procedure described by Pedersen.[14] Dimethylformamide was stored over molecular sieves then distilled under nitrogen. Dimethyl sulphoxide was used directly from freshly opened bottles.

Base–Solvent Solutions.—Solutions of potassium alkoxide in the corresponding alcohol were prepared as previously described.[2] Sodium phenoxide was prepared by the reaction of phenol with an equimolar amount of NaOH in water. Water was removed under reduced pressure and the residue recrystallized from dry acetone. Sodium *p*-nitrophenoxide was obtained from *p*-nitrophenol and sodium methoxide in methanol. After evaporation of the alcohol, the residue was recrystallized from water. Before use both phenoxides were kept at 100° and 1 mmHg for 90 min. Solutions of these phenoxides were prepared by dissolving weighed amounts of salts in the various solvents. Sodium 2,6-di-t-butylphenoxide in DMSO was prepared according to the procedure described by Bartsch *et al.*[15]

Procedure.—The experimental procedure and g.l.c. analytical technique were described previously.[2] The average error in the *trans* : *cis* ratio is *ca.* ±5%.

Control Experiment.—No solvolysis of the substrates was observed under the reaction conditions used for elimination. Blank experiments also showed that for the reaction times and base concentrations used the *trans* : *cis* ratio was not affected by isomerization of allylbenzene and *trans*- and *cis*-1-phenylpropene.

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