Eliminations promoted by Weak Bases. Part 7.[1] *E*2C and *E*2H Reactions of Cyclohexyl Toluene-*p*-sulphonate with Triphenylphosphine and Other Neutral Bases

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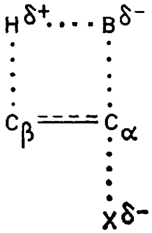
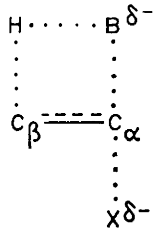
The competitive elimination (*E*2) and substitution (S_N2) reactions of cyclohexyl tosylate with triphenylphosphine are examined. Triphenylphosphine is taken to be representative of neutral weak bases which have good nucleophilic affinity for carbon. But it is a poor reagent for elimination when compared with anionic weak bases which are also good carbon nucleophiles. The stronger neutral bases triethylamine and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) are more effective than the anions in inducing elimination. It is concluded that whilst an interaction between the base and C_α is an important structural component of the *E*2C transition state, the interaction is primarily electrostatic rather than covalent (S_N2-like) as has been previously supposed. The reaction of Ph_3P with cyclohexyl bromide, a more *E*2H-like substrate, is almost completely substitution, indicating that neutral weak bases are also ineffective when more *E*2H-like transition states are involved, as is to be expected.

AGREEMENT has not yet been reached as to the nature of the transition stage involved in the second-order *E*2 elimination reactions of substrates leading to ' loose ' transition states (ones with good leaving groups, secondary or tertiary C_α, and no activation of the proton on C_β) with weak bases which are also strong carbon nucleophiles.[2] One suggestion is that the weak bases interact more strongly with C_α of the substrate in the transition state than with the β-bound proton, making these so-called *E*2C transition states (I) or (II) somewhat S_N2-like as far as the bonding situation at C_α is concerned.[2a] One of the items of evidence offered in support of this contention [3] is the fact that log k_E for the elimination reactivities of anionic bases of the category in question (halides, thiolates, *etc.*) with cyclohexyl tosylate, in acetone, dimethylformamide (DMF), Bu^tOH, EtOH, and MeOH correlates linearly with log k_s for the concomitant S_N2 reactions, as shown by the open circles in the Figure. The Brönsted plot of log k_E against the pK_a values of the bases in DMF is a scatter diagram [3] suggesting that proton basicity has little influence on elimination reactivity, as is required by transition states (I) and (II). Likewise a plot of log k_E pertaining to $C_6H_{11}OTs$ against log k_s for the S_N2 reactions of Bu^nBr, an S_N2 substrate giving a tighter transition state,[4] with the



(I)



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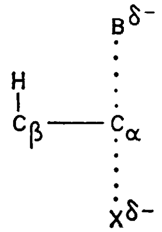

(S_N2)

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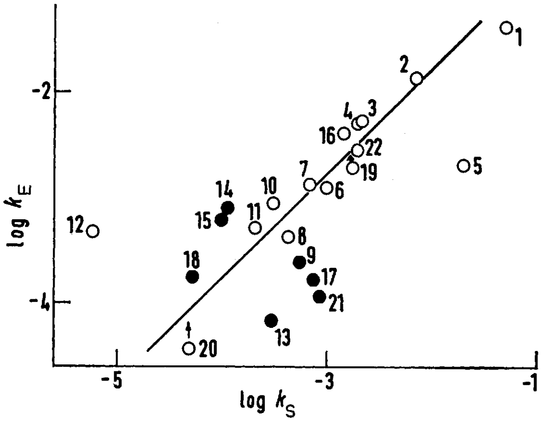
[1] Part 6, D. J. McLennan and R. J. Wong, *J.C.S. Perkin II*, 1974, 1818.

[2] (*a*) A. J. Parker, *Chem. Tech.*, 1971, **1**, 297; (*b*) W. T. Ford, *Accounts Chem. Res.*, 1973, **6**, 410; (*c*) W. H. Saunders and A. F. Cockerill, ' Mechanisms of Elimination Reactions,' Wiley, New York, 1973, pp. 53, 69, 194; (*d*) J. F. Bunnett and D. L. Eck, *J. Amer. Chem. Soc.*, 1973, **95**, 1897, 1900; (*e*) D. J. McLennan, *Tetrahedron*, 1975, **31**, 2999.

[3] (*a*) A. J. Parker, M. Ruane, G. Biale, and S. Winstein, *Tetrahedron Letters*, 1968, 2113; (*b*) P. Beltrame, G. Biale, D. J. Lloyd, A. J. Parker, M. Ruane, and S. Winstein, *J. Amer. Chem. Soc.*, 1972, **94**, 2240.

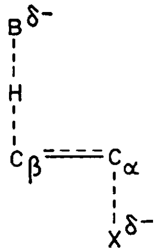
[4] A. J. Parker, *Chem. Rev.*, 1969, **69**, 1.

same anions is random,[3,5d] indicating that *E*2C transition states are loose, with B and X being weakly held to the remainder of the transition state and largely sharing the negative charge originally on B$^-$.

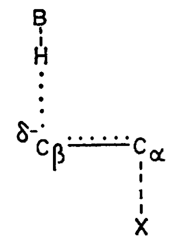


Plot of log k_E against log k_s for reactions of bases with cyclohexyl toluene-*p*-sulphonate at 75°. Open circles: anionic bases; closed circles: neutral bases. Base–solvent systems are: 1, PhS$^-$; 2, OAc$^-$; 3, Cl$^-$; 4, PhO$^-$; 5, N_3^-; 6, *p*-$NO_2C_6H_4S^-$; 7, Br$^-$; 8, *p*-$NO_2C_6H_4O^-$; 9, Ph_3P (all in Me_2CO); 10, Cl$^-$; 11, Br$^-$; 12, Bu^tO^-; 13, Ph_3P; 14, DBN; 15, Et_3N (all in Bu^tOH); 16, Cl$^-$; 17, Ph_3P; 18, DBN (all in DMF); 19, PhS$^-$; 20, *p*-$NO_2C_6H_4S^-$; 21, Ph_3P (all in EtOH); 22, *p*-$NO_2C_6H_4S^-$ in MeOH

On the other hand the log k_E — log k_s plots for substrates leading to tighter transition states, *e.g.* cyclohexyl bromide and *cis*-1,2-dibromocyclohexane are scatter plots, whilst the corresponding Brönsted relationships are reasonably good.[3] Parker and his co-workers argue that an increase in substrate tightness induces a shift in transition state character in the *E*2H direction, towards (III) or (IV), where proton basicity rather than carbon nucleophilicity is expected to be the more important determinant of *E*2 reactivity. It is also to be expected that a change to a stronger base would induce an *E*2C ⟶ *E*2H shift,[3] and the positive deviation of the Bu^tO^-–Bu^tOH point from the linear plot in the Figure is evidence for this.



(III)



(IV)

If loose *E*2C transition states (I) or (II), and loose S_N2 transition states are a requirement for conformity with the linear relationship, it follows that points for neutral weak bases which are also reasonably good carbon nucleophiles should lie close to the line, for nothing in the various arguments put forward in favour of (I) or (II) demands that bases be anionic.[3,5] Triphenylphosphine comes to mind as a base of this type. It is highly reactive towards MeI and MeOTs in MeOH, and is a weak base in water.[6] It may thus be classed alongside RS$^-$ as a soft base[7] and should be an effective *E*2C base, as are thiolate ions.*

We now describe a study of the behaviour of Ph_3P and more strongly basic neutral reagents towards $C_6H_{11}OTs$. Triphenylphosphine has previously been used in olefin-forming eliminations,[8] but no kinetic results are available.

RESULTS

The reactions of $C_6H_{11}OTs$ (*ca.* 0.015M) with the bases Ph_3P, Et_3N, and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) were kinetically examined in various solvents. Since olefin-forming solvolysis competes to a small extent, pseudo-first-order conditions were employed, with $[\text{base}]_0$ being at least seven times greater than $[C_6H_{11}OTs]_0$. Plots of k_ψ, the observed first-order rate coefficient against [base] are linear. The small intercepts correspond to k_ψ^0, the solvolysis rate constants of $C_6H_{11}OTs$ in the various solvents, values for which are available in the literature. Values of k_E and k_s, the respective second-order rate constants for elimination and substitution, were calculated for each run from equations (1) and (2), in which f_E is the olefin fraction observed at the given base concentration and f_E^0 is the fraction of olefin resulting from solvolysis.[9] Equation (3) allows calculation of f_{2E}, the fraction of olefin arising from second-order reactions.

$$k_E = (f_E k_\psi - f_E^0 k_\psi^0)/[\text{base}] \tag{1}$$

$$k_s = [(1 - f_E)k_\psi - (1 - f_E^0)k_\psi^0]/[\text{base}] \tag{2}$$

$$f_{2E} = k_E/(k_E + k_s) \tag{3}$$

In this kinetic analysis it is assumed that k_ψ^0 is independent of [base], since there is no way of experimentally checking whether or not this is so. If any dependence is viewed as a non-electrolyte 'salt effect,' the Winstein–Fainberg equation[10] could be used to estimate corrections to k_ψ^0. A theoretical analysis of salt-induced accelerations (*b* values) in solvolysis[10b] has shown that *b* is a function of the dipole moment of salt ion-pairs, and the same procedure might be appropriate for non-electrolytes. The relatively small *b* value of 45 (Me_2CO) pertains to the effect of thiourea (μ 4.89 D in dioxan)[11] on $C_6H_{11}OTs$ solvolysis, whilst

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* Note that Ph_3P is an effective debrominating reagent in the olefin-forming *E*2Hal reactions[2a] of *vic*-dibromides. See I. J. Borowitz, D. Weiss, and R. K. Crouch, *J. Org. Chem.*, 1971, **36**, 2377 and references therein.

[5] (*a*) G. Biale, A. J. Parker, S. G. Smith, I. D. R. Stevens, and S. Winstein, *J. Amer. Chem. Soc.*, 1972, **94**, 115; (*b*) G. Biale, D. Cook, D. J. Lloyd, A. J. Parker, I. D. R. Stevens, J. Takahashi, and S. Winstein, *ibid.*, 1971, **93**, 4735; (*c*) G. Biale, A. J. Parker, I. D. R. Stevens, J. Takahashi, and S. Winstein, *ibid.*, 1972, **94**, 2235; (*d*) A. J. Parker, M. Ruane, D. C. Palmer, and S. Winstein, *ibid.*, p. 2228.

[6] R. G. Pearson, H. Sobel, and J. Songstad, *J. Amer. Chem. Soc.*, 1968, **90**, 319; R. G. Pearson and J. Songstad, *J. Org. Chem.*, 1967, **32**, 2899.

[7] R. G. Pearson, *Chem. in Britain*, 1967, **3**, 103; R. G. Pearson and J. Songstad, *J. Amer. Chem. Soc.*, 1967, **89**, 1827.

[8] I. J. Borowitz, K. C. Kirby, P. E. Rusek, and R. Virkhaus, *J. Org. Chem.*, 1968, **33**, 3686 and references therein,.

[9] D. J. McLennan, *J.C.S. Perkin II*, 1972, 1577.

[10] (*a*) S. Winstein and A. H. Fainberg, *J. Amer. Chem. Soc.*, 1956, **78**, 2763; (*b*) C. L. Perrin and J. Pressing, *ibid.*, 1971, **93**, 5705.

[11] W. D. Kumler and G. M. Fohlen, *J. Amer. Chem. Soc.*, 1942, **64**, 1944.

$b = 3.0$ for the effect of urea in EtOH.[12] Triphenylphosphine is much less polar (μ 1.39 D in benzene) [13] and so should exhibit an even smaller kinetic effect. This is therefore neglected.

Experimental results are shown in the Table. Dissection of rate constants and olefin fractions into the second-order components *via* equations (1)—(3) is also presented. It is clear that over the range of concentrations employed, k_E and k_S are indeed constant. Values of f_E were invariant between 10 and 14 half-lives, where checked.

A less extensive investigation of the reactions of cyclohexyl bromide in acetone was carried out. Solvolysis was negligibly slow, and results are also displayed in the Table.

Rate constants and olefin fractions for the reactions of cyclohexyl tosylate [a] with neutral bases in various solvents at 75°

Base	Solvent	$[\text{Base}]_0/\text{M}$	$10^5 k\psi/\text{s}^{-1}$	f_E	$10^5 k_E/\text{l mol}^{-1}\,\text{s}^{-1}$	$10^5 k_s/\text{l mol}^{-1}\,\text{s}^{-1}$	f_{2E}
	Me_2CO [b]		0.017 [c]	1.00 [c,d]			
Ph_3P	Me_2CO [b]	0.074 0	5.62	0.320	24.1	51.6	0.318
Ph_3P	Me_2CO [b]	0.103	7.58	0.309	22.6	50.8	0.307
Ph_3P	Me_2CO [b]	0.130	10.7	0.298	24.4	50.8	0.304
	Bu^tOH [b]		0.12 [c]	0.830			
Ph_3P	Bu^tOH [b]	0.089 6	3.66	0.209	6.75	29.1	0.188
Ph_3P	Bu^tOH [b]	0.151	5.42	0.211	6.91	28.2	0.197
	DMF		0.59 [e]	0.47 [e]			
Ph_3P	DMF	0.100	9.6	0.192	15.6	74.4	0.173
Ph_3P	DMF	0.200	18.3	0.202	17.1	71.4	0.193
Ph_3P	DMF	0.250	22.9	0.190	16.3	72.9	0.183
	EtOH [b]		2.64 [f]	0.717 [g]			
Ph_3P	EtOH [b]	0.091 2	11.5	0.254 [h]	11.3	85.9	0.116
Ph_3P	EtOH [b]	0.121	14.4	0.231 [i]	11.9	85.3	0.122
DBN	Bu^tOH	0.073 4	6.96	0.822	82.3	10.9	0.883
DBN	Bu^tOH	0.121	11.3	0.874	80.8	11.6	0.874
Et_3N	Bu^tOH	0.101	7.30	0.861	61.2	9.8	0.862
Et_3N	Bu^tOH	0.198	14.1	0.866	61.2	9.4	0.867
Ph_3P	Me_2CO [b,j]	0.092 4	0.540	0.038	0.22	5.62	0.038
Ph_3P	Me_2CO [b,j]	0.124	0.582	0.040	0.23	5.69	0.039
DBN	DMF	Various [e]			18.0	5.2	0.776
DBN	DMF [j]	Various [e]			61.8	0.6	0.990

[a] $[C_6H_{11}OTs]_0$ *ca.* 0.015M. [b] Contains 2,6-lutidine *ca.* 0.015M. Values of k_ψ and f_E were independent of 2,6-lutidine concentration in the 0.01—0.03M range. [c] From ref. 3. [d] Assumed. [e] Extrapolated from results at other temperatures in ref. 16. [f] From S. Winstein and N. J. Holness, *J. Amer. Chem. Soc.*, 1955, **77**, 5562. [g] From W. Hückel, R. Bross, O. Fechtig, H. Feltkamp, S. Geiger, M. Hanack, M. Heinzel, A. Hubels, J. Kurz, M. Maier, D. Maucher, G. Naher, R. Neidlein, and R. B. Rashingkar, *Annalen*, 1959, **624**, 142. [h] Also *ca.* 5% of product assumed to be cyclohexyl ethyl ether. [i] Also *ca.* 3% cyclohexyl ethyl ether. [j] Substrate is cyclohexyl bromide.

DISCUSSION

Deviant Bases.—The $\log k_E$ against $\log k_S$ plot for anionic bases is shown (open circles) in the Figure. This line is established using the solvents acetone, Bu^tOH, DMF, MeOH, and EtOH. Some points pertain to temperatures below 75°, and as olefin fractions generally increase with increasing temperature,[3,14] the points represent minima as far as $\log k_E$ is concerned, and this is indicated by arrows. Regression analysis establishes equation (4) for these points (excluding Bu^tO^- and N_3^-, see later). The relationship gives a correlation coefficient of 0.989, a standard deviation of fit of the $\log k_E$ values of 0.20, and linearity is significant at the 99.9% confidence level.

$$\log k_E = (0.99 \pm 0.08)\log k_S + (0.17 \pm 0.25) \quad (4)$$

One implication of this linear free energy relationship is that the elimination and substitution transition states are structurally similar as suggested by Winstein and Parker.[3] But there are pitfalls in making such assumptions.[15] At this stage it would be safer simply to state that all the elimination transition states are similar in structure, as are the substitution transition states, and that since both sets are loose their energies respond similarly to changes in nucleophilicity irrespective of differences in intimate structural details. Deviations from this linear free energy relationship may then be discussed in terms of changes in the character of the elimination or substitution transition states (or both).

It is instructive to consider the positive deviations, significant to at least a 95% confidence level, of the stronger bases Bu^tO^-, Et_3N, and DBN first. Undoubtedly such bulky species will be somewhat hindered in their approach to C_α in the S_N2 mode, although Et_3N and DBN have S_N2 reactivities comparable to Cl^- and Br^- in Bu^tOH. Were (I) or (II) the elimination transition state, one might expect a similar retardation in elimination rate and hence adherence to equation (4). The lack of correlation thus implies that the strong base $E2$ transition states are different from those utilized by the weakly basic anions, and a shift in the $E2$H direction is clearly responsible. The high Brönsted β parameter (0.9) for reaction of cyclohexyl bromide (a substrate giving tighter transition states than $C_6H_{11}OTs$) with amidine bases in DMF [16] is evidence for this, and may be contrasted with $\beta = 0.27$ ($C_6H_{11}OTs$) and 0.36 ($C_6H_{11}Br$) for eliminations induced by thiolate ions in EtOH.[17]

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[12] D. J. McLennan, following paper.

[13] G. M. Phillips, J. S. Hunter, and L. E. Sutton, *J. Chem. Soc.*, 1945, 146.

[14] C. K. Ingold, 'Structure and Mechanism in Organic Chemistry,' Bell, London, 1969, 2nd edn., p. 686.

[15] W. A. Pryor and K. Smith, *J. Amer. Chem. Soc.*, 1970, **92**, 2731.

[16] G. E. Reinert, Ph.D. Thesis, University of Delaware, 1972.

[17] D. J. McLennan, *J. Chem. Soc. (B)*, 1966, 705.

Now that it is established that neutral bases, *per se*, are not abnormally unreactive in the $E2$ mode, we now consider the negative deviations of the Ph_3P points from the linear free energy relationship; negative deviations which are apparently associated with *weak* neutral bases which would not be expected to react through $E2$H-like transition states with ease.

The Ph_3P points deviate in a negative sense by between 3.5 and 5 standard deviations, so the probability is greater than 99.9% that they do not lie on the anion-generated line.[18] The Dixon nearest-neighbour test [19] gives the result that they lie off the line at the 99% confidence level, at least.

We must consider the question of whether the Ph_3P deviations are a result of enhanced k_S values relative to the anionic bases, depressed k_E values, or a combination of both. Central to this problem is the question of whether or not Ph_3P can be classed, along with the anionic bases with which it is being contrasted, as a good carbon nucleophile. As far as the observed k_S values are concerned, it is amongst the poorer carbon nucleophiles towards $C_6H_{11}OTs$ of those being considered. In acetone its reactivity places it between OAr^- and Br^-, whilst in Bu^tOH it lies between Br^- and Cl^-. But neither is it grossly unreactive when the (small) spread of anion reactivities is taken into account.

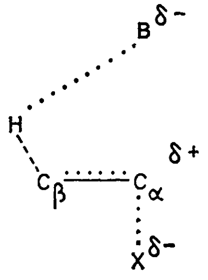
Solvent effects and the essential looseness of transition state structures contribute to the relative poorness of Ph_3P in the present S_N2 reactions as can be illustrated by the work of Pearson and Songstad on MeI and MeOTs in MeOH and MeCN.[6,20]

From the practical viewpoint, the question posed earlier can be simply answered. The anions that conform to the linear plot do so in a variety of solvents, and there is no reason to suspect that solvent anomalies apply to Ph_3P. And the latter, while not a strong S_N2 nucleophile towards $C_6H_{11}OTs$ for reasons which are reasonably well understood, is nonetheless no worse than the worst of the conforming anions. It would thus be better to look elsewhere for the sources of the Ph_3P deviations.

Although it is established that thermodynamic basicity has little influence on $E2$ reactivity as far as the anions are concerned,[3] it is conceivable that the basicity of Ph_3P in the relevant solvents is so low compared with the anions that a diminution in k_E is occasioned.* Relevant pK_a values with which to test this possibility are not available, but an argument may be advanced which suggests that neutral base pK_a values are about numerically the same for water or DMF as solvent. The argument is based on solvent effects on nitrogen base pK_a values,[6,21-23] and holds true for aniline, ammonia, and tetramethylguanidine for which direct comparison is available.[22,24] Thus Ph_3P could be a stronger base than Br^- in acetone, and yet the latter is (marginally) a better $E2$ reagent towards $C_6H_{11}OTs$. Basicity factors concerning Ph_3P are thus unimportant in understanding the negative deviations.

We are left with the conclusion that the negative deviations are a consequence of the structure of the $E2$C transition state. For reasons mentioned earlier, we must reject transition states (I) and (II) since these do not serve to differentiate the behaviour of anionic *versus* neutral bases. An alternative $E2$C transition state, which is constitutionally suitable when the weak base is anionic, but which is energetically unfavourable when the weak base is neutral, must be considered.

The $E2$C *Transition State*.—We have recently proposed the structure (V) for the $E2$C transition state for an anionic base, and have shown that existing results can best be interpreted in terms of such a model.[2e] The distinguishing feature of this species is the predominantly electrostatic interaction between the hardly neutralized anionic base and a reasonably well developed partial positive charge at C_α. Parker and his co-workers have stated that they know of no experimental results that allow distinction between (I) and (II) on one hand and (V) on the other.[25] † The present work provides the distinction.



(V)

The source of stabilization for anionic bases in tran-

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* Note that although DBN is 9.5 pK units more basic than Cl^- in DMF (refs. 16 and 21) the latter is *ca.* 20 times more reactive in that solvent in the $E2$ mode towards $C_6H_{11}OTs$. Such a comparison is, however, meaningless in view of the different transition state structures involved.

† *Note added in proof:* D. Cook, *J. Org. Chem.*, 1976, **41**, 2173, has recently reported substantial secondary hydrogen isotope effects associated with the hydrogens bonded to C_γ in $E2$C reactions of cyclohexyl toluene-*p*-sulphonate, and claims that these are compatible only with (I) or (II), in which double bond formation is substantial. However, Cook has neglected the fact that the 1,3-diaxial repulsive interaction between one of these hydrogens and the leaving group is relieved on proceeding from initial to transition state whatever the mechanism, and that the changes in associated vibrational frequencies will induce an isotope effect of the type observed.

[18] O. L. Davies and P. L. Goldsmith, ' Statistical Methods in Research and Production,' Oliver and Boyd, Edinburgh, 1972.

[19] J. D. Hinchen, ' Practical Statistics for Chemical Research,' Methuen, London, 1969, p. 27.

[20] L. B. Engemyr and J. Songstad, *Acta Chem. Scand.*, 1972, **26**, 4179.

[21] B. W. Clare, D. Cook, E. C. F. Ko, Y. C. Mac, and A. J. Parker, *J. Amer. Chem. Soc.*, 1966, **88**, 1911.

[22] I. M. Kolthoff, M. K. Chantooni, and H. Smagowski, *Analyt. Chem.*, 1970, **42**, 1622.

[23] C. D. Ritchie and P. D. Heffley, *J. Amer. Chem. Soc.*, 1965, **87**, 5402; C. D. Ritchie and G. H. Megerle, *ibid.*, 1967, **89**, 1447.

[24] D. D. Perrin, ' Dissociation Constants of Organic Bases in Aqueous Solution,' Butterworths, London, 1965.

[25] D. Cook, R. E. J. Hutchinson, J. K. McLeod, and A. J. Parker, *J. Org. Chem.*, 1974, **39**, 534; D. Cook, R. E. J. Hutchinson, and A. J. Parker, *ibid.*, p. 3029.

sition state (V) is not available to neutral weak bases and if (V) is involved in the latter's reactions they will exhibit low elimination reactivity. The system may eschew loose transition states altogether and pass through a more *E*2H-like species such as (III). It is clear that stronger neutral bases react to advantage with $C_6H_{11}OTs$ in the elimination mode in this way. But for a weaker neutral base like Ph_3P, transition state (III) demands a strong B · · · H partial bond.

The present work allows no distinction between the above alternatives. What is clear, however, is that weak neutral bases are expected to be poor elimination reagents when compared with weak anionic bases. In other words, k_E should be depressed relative to k_S for the former when compared with the latter, and this is found.

Why then is the anionic log k_E *versus* log k_S plot linear, now that it has been established that the *E*2C transition state (V) does *not* resemble an S_N2 transition state? An answer is given by our empirical analysis of nucleophilic reactivity in *E*2 and S_N2 reactions wherein it is shown that log k_E for even purely *E*2H eliminations should correlate linearly with log k_S for S_N2 reactions of the same substrate so long as the respective transition states are loose.[2e]

Finally we consider the *E*2 and S_N2 reactivities of Ph_3P towards cyclohexyl bromide. The respective transition states are expected to be tighter by virtue of bromide being a poorer and more electronegative leaving group than OTs.* In particular the *E*2 transition state should be more *E*2H-like, and in view of earlier remarks concerning the lack of efficiency of weak bases (whether neutral or anionic) in such situations, it is not surprising that only a small proportion of olefin is found (Table). On the other hand, stronger neutral bases such as DBN are remarkably good eliminating agents towards cyclohexyl bromide.[16,26] In the *E*2 modes the rate ratio $k_E(Cl^-)/k_E(Ph_3P)$ is 23 for $C_6H_{11}OTs$ and 250 for $C_6H_{11}Br$, whilst for substitution the respective $k_S(Cl^-)/k_S(Ph_3P)$ ratios are 4 and 6 (solvent acetone). It can thus be seen that k_E for the Ph_3P–$C_6H_{11}Br$ reaction is depressed relative to the other rate constants, and this suggests that *E*2H transition states are particularly inappropriate for such a base.

The behaviour of another neutral base (thiourea) in reactions with cyclohexyl tosylate and bromide is considered in the following paper.

EXPERIMENTAL

Substrates, bases, and solvents were prepared and/or purified conventionally. Cyclohexyltriphenylphosphonium bromide was prepared as described [27] and was recrystallised from EtOAc–$CHCl_3$, and water, m.p. 272—273° (lit.,[27] 255—259°) (Found: C, 66.5; H, 6.4; Br, 18.7. Calc. for $C_{24}H_{26}BrP$: C, 66.8; H, 6.2; Br, 18.8%). Zerolit FFIP anion exchange resin (B.D.H., 52—100 mesh) was converted to the tosylate form by treatment with aqueous HOTs. Cyclohexyltriphenylphosphonium bromide (3 g) in H_2O (50 ml) was stirred with resin (25 g) for 2 h at room temperature. After filtration the aqueous solution was concentrated to yield crystals of cyclohexyltriphenylphosphonium tosylate which, after recrystallization from H_2O and dilute aqueous HOTs, had m.p. 219—221° (Found: C, 71.9; H, 6.6. Calc. for $C_{31}H_{33}O_3PS$: C, 72.0; H, 6.4%).

Reaction Products.—The substitution product from the $C_6H_{11}OTs$–Ph_3P reaction in acetone containing 2,6-lutidine was isolated by pouring the product mixture into a dilute aqueous NaOH solution and repeatedly extracting with CCl_4 and pentane. The crystals collected after concentration of the aqueous extract were identical with those described above.

The amount of cyclohexene formed in kinetic runs was assayed by g.l.c. (OV-17 column at 60°; toluene internal standard) after extraction of infinity samples into n-pentane. A mock infinity solution containing known amounts of cyclohexene, Ph_3P, cyclohexyltriphenylphosphonium tosylate, 2,6-lutidine, toluene, and HOTs,H_2O in acetone was subjected to n-pentane extraction from dilute aqueous HCl, and the g.l.c. assay gave results no more than 1% low. The mock infinity solution was found to be stable with respect to the cyclohexene and total cation concentrations for a period of one month at 75°.

Kinetics.—Standard solutions containing substrate, base, 2,6-lutidine (where appropriate), and toluene were made up in the solvent of choice and portions (6 ml) were sealed in ampoules, which were placed in a constant temperature bath. At various times, ampoules were withdrawn, cooled, and portions (5 ml) were run into H_2O (10 ml) contained in a separating funnel. The aqueous layer was washed three times with CCl_4 or $CHCl_3$, and with pentane, transferred quantitatively to a column containing Zeocarb 225 cation exchange resin (10 g; H^+ form), and was washed through using the minimum quantity of water. Titration with NaOH yielded the total cation concentration.[28] Values of k_ψ were reckoned from the slopes of accurately linear plots of log $(V_\infty - V_t)$ against time (the *V* terms are the NaOH titres). Standard deviations corresponded to no more than a 3% uncertainty in k_ψ. The aforementioned mock infinity solution was treated in a like fashion and the NaOH titre was within 0.2% of the known total cation concentration.

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* For this reason we consider invalid the use of k_{OTs}/k_{Br} as an index of transition state character in (especially) bimolecular reactions, since, with a given base in a given solvent, RBr and ROTs must react through transition states of markedly different character.

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