nored) at 160°, these compounds are "locked in structures with the neopentyl groups in trans positions". They further conclude that since for **10** "collapse" of the two methylene doublets (actually two methylene quartets when phosphorus coupling is considered) occurs at 60°, the rotational barrier about the phosphorus–carbon bond in **10** is ca. 16 kcal/mol.

Simple symmetry arguments[2] demand the observed nonequivalence for **2**, **4**, **12**, and **10** without recourse to conformational arguments, and similarly these same arguments demand that **5**, **1**, and **11** not exhibit nonequivalence. Compounds **2**, **4**, **12**, and **10** lack the plane of symmetry in any conformation that **5**, **1**, and **11** possess in a single (noneclipsing) conformation. The methylene protons of **2**, **4**, **12**, and **10** are diastereotopic and observably anisochronous, while those of **5**, **1**, and **11** are enantiotopic and, expectedly under achiral conditions, isochronous. Further, it can be categorically stated that the observed "collapse" of the methylene signals of **10** is accidental, i.e., an artifact of temperature-dependent chemical shifts, and is in no manner an indicator of the phosphorus–carbon rotational barrier. Lastly, for **9**, the

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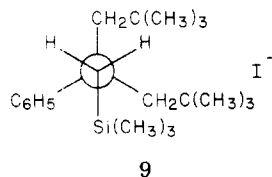
observation that the CH_2Si signal is a singlet while that of the $CH_2C(CH_3)_3$ groups is an AB quartet is a priori predictable; the CH_2Si groups are enantiotopic while the $CH_2C(CH_3)_3$ groups are diastereotopic.

In conclusion, no information relative to the conformations of compounds **1**, **2**, **4**, **5**, **9**, **10**, **11**, or **12** can be deduced from this study other than that the phosphorus–carbon rotational barriers of **1**, **5**, and **11** are, as expected, low.

(2) (a) K. Mislow and M. Raban, *Top. Stereochem.*, 1, 1 (1967); (b) J. Jacobus and M. Raban, *J. Chem. Educ.*, 46, 351 (1969).

Reactivity of Free and Associated Phenoxides in Syn and Anti Elimination Reactions in Dimethyl Sulfoxide

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It is now well recognized that in an E2 elimination the competition between anti and syn pathways can be strongly influenced by the base association.[1] Namely, the relative proportion of the syn process generally increases when the reaction is carried out under experimental conditions favoring the formation of contact pairs or larger aggregates. It has been suggested that syn eliminations promoted by an associated base take place via the transition state **1**, where a presumably advantageous inter-

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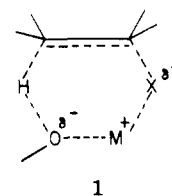
action between the leaving group and the positive counterion is possible.

In order to get more quantitative information on this problem it seemed of interest to look for systems where the contributions of free ions and contact pairs to the overall rate can be separately evaluated with reasonable precision. This separation appeared possible for reactions promoted by phenoxides in dimethyl sulfoxide (Me_2SO). Thus, we have kinetically investigated the eliminations from *trans*-2,3-dihydro-2,3-dichlorobenzofuran (**2**), its 3-deuterated counterpart (**3**) (syn processes), and 2-phenyl-

2   3
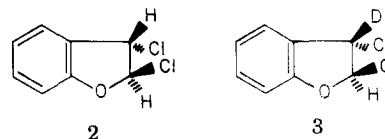
ethyl chloride (**4**) (anti process), in this base–solvent system. For comparison purpose also the substitution reactions of *n*-butyl bromide (**5**) have been studied. Even though the extent of base association is not very high in Me_2SO, recent studies have shown that it is sufficient to significantly change the relative proportion of syn and anti elimination from 3-hexyl tosylate.[2]

Results and Discussion

The reactions of **2**–**5** have been carried out in 99% Me_2SO[3] using tetraethylammonium phenoxide as the base in the absence and in the presence of LiBr (0.015–0.15 M). From **2** and **3**, 3-chlorobenzofuran is the exclusive reaction product (see Experimental Section). The quantitative formation of styrene from **4** and *n*-butyl phenyl ether from **5** has been shown by previous work.[4,5]

Kinetics have been followed spectrophotometrically measuring the rate of disappearance of the base at 310–330 nm. The phenoxide concentration has been kept at ca 4 $\times 10^{-4}$ M, that of the substrate being 15–100 fold higher. Excellent first-order plots have been obtained in each case and the second-order rate constants (k_{obsd}) calculated as usual. All kinetic data are collected in Table I.

In consideration of the nature of the salt and its low concentration, it is reasonable to assume that k_{obsd} values obtained in the reactions promoted by tetraethylammonium phenoxide represent the rate constants (k_i) of nonassociated phenoxide ions. The absence of association of tetraethylammonium phenoxide is also clearly shown by the fact that in the presence of tetraethylammonium bromide (up to 0.1 M) there is practically no change in k_{obsd} for the reactions of **2**, **4**, and **5**.

In contrast, k_{obsd} decreases drastically when the reactions are carried out in the presence of LiBr. This is certainly

(1) Sicher, J. *Angew. Chem. Int. Ed. Engl.* 1972, *11*, 200; Pánková, M.; Svoboda, M.; Závada, J. *Tetrahedron Lett.* 1972, 2465 and references cited therein. Bartsch, R. A.; Wiegers, K. E. *Ibid.* 1972, 3819.

(2) Borchardt, J. L.; Swanson, J. C.; Saunders, W. H., Jr., *J. Am. Chem. Soc.* 1974, *96*, 3918.

(3) The solution of tetraethylammonium hydroxide in Me_2SO used to convert phenol into phenoxide ions was slightly aqueous (see Experimental Section). Since different amounts of this solution were necessary in the various experiments the use of 99% Me_2SO was considered opportune in order to avoid changes in the water content of the solvent that could significantly influence the reaction rate.

(4) Alunni, S.; Baciocchi, E.; Perucci, P.; Ruzziconi, R. *J. Org. Chem.* 1978, *43*, 2414.

(5) Berge, A.; Ugelstad, J. *Acta Chem. Scand.* 1965, *19*, 742. Ugelstad, J.; Ellingsen, T.; Berge, A. *Acta Chem. Scand.* 1966, *20*, 1593.

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Table I. Kinetic Effect of Added Salts on the Reaction
Rates of 2–5 with Tetraethylammonium Phenoxides
in 99% Me$_2$SO at 30 °C

substate	[LiBr], M	[Et$_4$NBr], M	k_{obsd} M^{-1} s^{-1a}
trans-2,3-dichloro-2,3-			1.79
dihydrobenzofuran (2)	0.0156		0.581
	0.0176		0.595
	0.0323		0.379
	0.0436		0.317
	0.0487		0.282
	0.0679		0.228
	0.0889		0.189
	0.0913		0.194
	0.108		0.168
		0.0375	1.75
		0.0587	1.78
		0.0939	1.78
trans-2,3-dichloro-2,3-			0.720
dihydro-3-deuteriobenzo-	0.0400		0.131
furan (3)	0.0548		0.110
	0.0782		0.0859
	0.0884		0.0780
	0.111		0.0680
2-phenylethyl chloride (4)			0.0410
	0.0176		0.0114
	0.0411		0.00624
	0.0723		0.00373
	0.0915		0.00313
	0.0979		0.00287
		0.0375	0.0418
		0.0587	0.0394
		0.0939	0.0400
n-butyl bromide (5)			0.260
	0.0236		0.0634
	0.0548		0.0323
	0.0781		0.0244
	0.0979		0.0202
	0.102		0.0190
	0.139		0.0147
	0.145		0.0138
		0.0888	0.256

^{a} The average error is ± 1.1%.

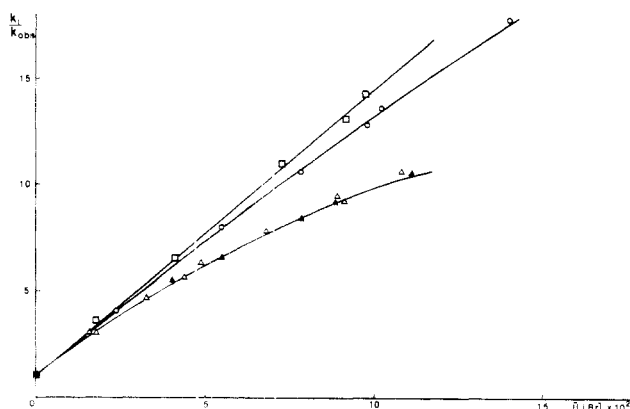**Figure 1.** k_i/k_{obsd} (see text) vs. [LiBr], M, for the syn eliminations from **2** (△) and **3** (▲), the anti elimination from **4** (□), and the substitution reactions of **5** (○).

due to the formation of C$_6$H$_5$O$^-$Li$^+$ contact pairs which exhibit much less reactivity than solvated C$_6$H$_5$O$^-$ ions. Even though the qualitative trend is the same for all substrates, when k_i/k_{obsd} values are plotted against LiBr concentration (Figure 1) a straight line is obtained in the case of the reactions of **4** (anti eliminations), whereas a significantly downward curved line is obtained in the syn eliminations from **2** and **3**. These plots already suggest that as the concentration of contact pairs increases the negative effect on the overall elimination rate is much less important in the syn than in the anti process. An in-

termediate behavior appears to pertain to the substitution reactions of **5**.

For reactions which are simultaneously promoted from solvated C$_6$H$_5$O$^-$ ions and contact pairs C$_6$H$_5$O$^-$Li$^+$, eq 1 holds, where k_{ip} is the rate constant of the contact pair. From eq 1, eq 2 can be obtained, where K is the equilibrium constant for the formation of the contact pair from the solvated phenoxide ion and Li$^+$.[6]

$$k_{obsd}([C_6H_5O^-] + [C_6H_5O^-Li^+]) = k_i[C_6H_5O^-] + k_{ip}[C_6H_5O^-Li^+] \quad (1)$$

$$k_{obsd} = (k_i + k_{ip}K[Li^+])/(1 + K[Li^+]) \quad (2)$$

Since eq 2 can be easily converted into

$$(k_i - k_{obsd})/[Li^+] = k_{obsd}K - k_{ip}K \quad (3)$$

a straight line, with K as the slope and $k_{ip}K$ as the intercept, should be obtained by plotting $(k_i - k_{obsd})/[Li^+]$ against k_{obsd}. Actually, with the kinetic data of the reactions investigated such plots have turned out to exhibit an excellent linearity ($r > 0.99$ in each case). K values of 138, 138, 135, and 133 have been calculated from the data of the reactions of **2, 3, 4,** and **5,** respectively, so satisfactory agreement indicating that the application of eq 2 is warranted and that secondary ionic strength effects have to be insignificant probably owing to nearly constant activity coefficients of the species involved in the range of LiBr concentrations used.[9]

From the intercept of the plots for the syn eliminations from **2** and **3**, k_{ip} values of 6.0×10^{-2} and 2.6×10^{-2} M^{-1} s^{-1} respectively have been calculated. Thus, the reactivity of the C$_6$H$_5$O$^-$Li$^+$ contact pairs in the syn elimination is small, but significant, being ca. 30-fold lower than that of solvated C$_6$H$_5$O$^-$. In contrast, in the reactions of **4** the intercept of the plot $(k_i - k_{obsd})/[Li^+]$ vs. k_{obsd} is practically zero, thus suggesting a negligible reactivity of the C$_6$H$_5$O$^-$Li$^+$ contact pairs in the anti elimination reaction. This conclusion is also supported by the fact that when k_{ip} is very small, the term $k_{ip}K[Li^+]$ in eq 2 can be neglected with respect to k_i and a linear dependence of k_i/k_{obsd} on [Li$^+$] and therefore on [LiBr] is predicted, a behavior which we had already noted for the reactions of **4** (Figure 1).[10]

These results are in line with the observed phenomenon that the increase in the ion association leads to an increase in the relative proportion of the syn process in an elim-

(6) In Me$_2$SO LiBr exists as solvent-separated ions as clearly shown by IR[7] and NMR[8] measurements.

(7) Maxey, B. W.; Popov, A. I. *J. Am. Chem. Soc.* **1969**, *91*, 20.

(8) Cahen, Y. M.; Handy, P. R.; Roach, E. T.; Popov, A. I. *J. Phys. Chem.* **1975**, *79*, 80.

(9) Therefore the K values obtained from eq 2 are actually conditional equilibrium constants, since they also include the activity coefficients of C$_6$H$_5$O$^-$ and Li$^+$. It must be noted, however, that the above suggested constancy of activity coefficients would not be predicted by the Debye–Huckel equation in its extended form, using the A and B parameters for dry Me$_2$SO and an a value of 6×10^{-8} cm (Kolthoff, I. M.; Chantooni, M. K., Jr.; Bhowmik, S. *J. Am. Chem. Soc.* **1968**, *90*, 23).

(10) If k_{ip} for the anti elimination (k_{ip}^{anti}) is, as seems to be the case, very close to zero, the k_{ip} value for the syn elimination (k_{ip}^{syn}) is also given by the equation

$$k_{obsd}^{syn}/k_{obsd}^{anti} - (k_i^{syn} - k_{obsd}^{syn})/(k_i^{anti} - k_{obsd}^{anti}) = k_{ip}^{syn}/k_{obsd}^{anti}$$

where no term containing Li$^+$ concentration is present. Using k_{obsd} for syn and anti eliminations at the same LiBr concentration (interpolated from experimental plots of k_{obsd} vs. LiBr) a linear plot of $k_{obsd}^{syn}/k_{obsd}^{anti} - (k_i^{syn} - k_{obsd}^{syn})/(k_i^{anti} - k_{obsd}^{anti})$ against $1/k_{obsd}^{anti}$ is obtained. From the slope a k_{ip} value of 6.2×10^{-2} for the syn elimination is calculated, in very good agreement with that derived from the straightforward application of eq 2. This agreement supports the previous suggestion that secondary ionic strength effects are negligible in the range of LiBr concentration used.

ination reaction.[1,2] However, they also indicate that the frequently reported statement that syn elimination reactions are favored by base association should be more appropriately replaced by the statement that base association disfavors syn eliminations much less than anti eliminations.

A point of interest is that in the syn elimination practically identical values of deuterium kinetic isotope effects are found for the reactions promoted by solvated $C_6H_5O^-$ ($k_i^H/k_i^D = 2.5$) and by $C_6H_5O^-Li^+$ pairs ($k_{ip}^H/k_{ip}^D = 2.4$). This finding is also confirmed by the observation that the values of k_i/k_{obsd} for 2 and 3 fit exactly the same plot, k_i/k_{obsd} vs. [LiBr] (Figure 1), thus indicating that the two reactions are similarly affected by the increase in LiBr concentration. Similar k^H/k^D values for syn eliminations promoted by associated and nonassociated base are not entirely expected, owing to the possible nonlinearity of the proton transfer in the former case. However, this factor might play a minor role when the proton transfer to the base has progressed to a large degree in the transition state,[11] which should be the case for the reactions of 2, exhibiting quite small values of deuterium kinetic isotope effect.

In the substitution reactions of 5 an approximate k_{ip} value of 1.5×10^{-3} M^{-1} s^{-1} can be calculated, ca. 170-fold smaller than k_i for the same reaction. Even though the error in this case is certainly very large since the intercept of the plot is not far from zero, it seems possible to conclude that the difference in reactivity between solvated $C_6H_5O^-$ ions and $C_6H_5O^-Li^+$ pairs is less in the substitution reaction that in the anti elimination. This conclusion is also supported by the fact that the plots of k_i/k_{obsd} vs. [LiBr] for the reactions of 4 and 5 fit different lines (Figure 1).

Thus, on the basis of the above results, it would seem that the reactivity ratio k_{ip}/k_i for the reactions of phenoxides in Me_2SO decreases in the order syn elimination > substitution > anti elimination.

Even though extention of this study to other substrates[12] is necessary in order to establish if this conclusion can be generalized and to which extent, it is interesting to note that the above order is that which, according to a recent suggestion,[13] should be expected on the basis of the probable geometrical arrangement of the transition states of these three processes when an associated base is the reacting species. An additional role could be also played by the degree of C-leaving group bond breaking in the transition state which determines the fraction of negative charge on the leaving group and consequently the strength of the interaction with the cation in the transition state. However, this factor is certainly less important than the geometrical one when syn and anti eliminations are compared. Accordingly, there is no doubt that the transition state of the syn eliminations from 2 is more carbanionic (and therefore with less C-Cl bond breaking) than the transition state of the anti eliminations from 4.

Experimental Section

Materials. *trans*-2,3-Dichloro-2,3-dihydrobenzofuran (2) and *trans*-2,3-dichloro-2,3-dihydro-3-deuteriobenzofuran (3) were prepared by chlorine addition in Et_2O at -5-0 °C on the cor-

responding benzofuran;[14] the NMR spectrum (CCl_4) of 3 exhibited peaks at δ 6.40 (1 H, s, 2-H) and 6.88-7.55 (4 H, m, ArH). 2-Phenethyl chloride (4) (Fluka) was purified by distillation [bp 84-85 °C (15 mm)]. *n*-Butyl bromide (5) (Erba RPE) was distilled in the presence of anhydrous K_2CO_3 at atmospheric pressure (bp 101 °C). Phenol (Erba RPE) was used without further purification. Lithium bromide (Hoescht), a commercial sample, was dried at 120 °C before use. Tetraethylammonium bromide (Erba RS) was used without further purification.

Solvent and Base. Me_2SO (99%, v/v) was prepared by placing exactly 10 mL of water into a 1-L volumetric flask that was then made up to the mark with Me_2SO (Erba RPE) previously degassed with dry N_2. Tetraethylammonium phenoxide was prepared by adding, under nitrogen, a 0.0116 M solution of tetraethylammonium hydroxide in 99% Me_2SO to a solution of phenol in the same solvent. The former solution was obtained by placing 250 μL of tetraethylammonium hydroxide (Fluka, 20% in water) into a 25-mL volumetric flask, which was then made up to the mark with 99% Me_2SO.

Kinetic Study. Kinetic experiments were carried out by following spectrophotometrically the disappearance of the phenoxide ion in the range 310-330 nm depending on the concentration of the lithium bromide. At this wavelength no appreciable absorbance is exhibited by the reaction products. The reactions were brought about in a stoppered two-limb silica cell. In one limb was placed the substrate solution (1 mL) and in the other at first the phenol-LiBr solution (1 mL) and successively, under nitrogen, an amount of 0.0116 M tetraethylammonium hydroxide solution calculated on the basis of previous spectrophotometric titration of the phenol solution as described in the literature[15] (100-200 μL). The cell was placed in the thermostated compartment of a Beckmann DB-GT spectrophotometer. After 20 min the solutions were mixed throughly and the cell was rapidly placed again in the cell compartment of the spectrophotometer. The final product of the reaction from 2 and 3 with phenoxide ion was the expected 3-chlorobenzofuran, as shown by comparison (GPC analysis[14] at 120 °C) with an authentic specimen.[14]

(11) Saunders, W. H., Jr. *Chem. Scr.* 1975, 8, 27.
(12) Since k_i/k_{ip} values depend on the nature of the leaving group, only systems with the same leaving group should be compared. This requirement is substantially fulfilled by our substrates since chlorine and bromine have very similar electronegativity (for instance σ* is 1.05 for $-CH_2Cl$ and 1.00 for $-CH_2Br$).
(13) Závada, J.; Pánková, M. *Collect. Czech. Chem. Commun.* 1978, 43, 1080.

(14) Baciocchi, E.; Ruzziconi, R.; Sebastiani, G. V. *J. Org. Chem.* 1979, 44, 28.
(15) Mandolini, L.; Masci, B.; Roelens, S. *J. Org. Chem.* 1977, 42, 3733.

Rearrangement of 6-Substituted 2,7-Dioxabicyclo[3.2.0]hept-3-enes to Furans

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Photochemical cycloaddition of aldehydes to furan leads to 6-substituted 2,7-dioxabicyclo[3.2.0]hept-3-enes (1) in good yields.[1,2] It has been shown that protic acids induce the conversion of 1 to the furan system; this opens a simple and practical route to 3-furylmethanols[2,3] (2).
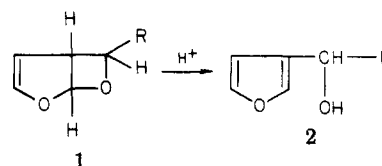
(1) S. Toki, K. Shima, and H. Sakurai, *Bull. Chem. Soc. Jpn.*, 38, 760 (1965); K. Shima and H. Sakurai, *ibid.*, 39, 1806 (1966).
(2) A. Zamojski and T. Kozluk, *J. Org. Chem.*, 42, 1089 (1977).