thermometer and was found to be in the range of 23.5 ± 0.5 °C during all experimental runs.

Elimination Reactions. The apparatus consisted of a modified glass coldtrap in which the gas inlet tube was extended to below the level of the reaction solution.[13,22] Additional stirring was achieved by means of a glass-covered magnetic stirrer. Into the clean, dry lower section of this trap was weighed the alcohol (5.9 mmol); a solution of fresh potassium dimsyl (20 mL, 0.25 M) was added to the alcohol under argon. The upper section containing the gas inlet and outlet tubes was put in place, and the apparatus was lowered into an oil bath (50 °C). A nitrogen sweep gas (350 mL min^{-1}) was used. The N_2 outlet was connected to an overflow trap which in turn was connected by glass ball joints to a cold trap. This was immersed in a Dewar flask containing dry ice/2-propanol. The cold trap contained methanol (2 mL). The reaction vessel was allowed to equilibrate for 5–10 min, with the gas going through the reaction. The gas inlet line was modified so that the 2-iodobutane (2.0 mmol) was added via a septum, by means of a syringe down through the gas inlet tube, directly into the reaction. The reaction was stopped by disconnecting the cold trap at precise intervals (1–3 min). The methanol–butene solution was transferred to serum vials which were sealed. Duplicate GLC analyses were done on each sample by using a 24 ft × $^1/_8$ in. column packed with 20% Ukon 50 LB2000 and operated at room temperature. The yield of 1-butene was seen to decrease with reaction time, giving more *cis*-2-butene. This isomerization of the olefin was most pronounced with the strong alkoxides. To correct for this error, we extrapolated all measurements to zero time by linear-regression analysis.

Dimsyl stock solutions were prepared as follows. The alkali hydride was washed under N_2 four times with pentane. The flask and pressure-equalizing addition funnel containing Me_2SO were evacuated to remove the last traces of pentane. Me_2SO was added carefully before the hydride became completely dry.[39] The addition of the Me_2SO was controlled to prevent excessive bubbling when potassium hydride was used. The resulting dimsylate solutions were titrated and adjusted to 0.25 M. With sodium hydride the reaction with Me_2SO is slow, and the sonication procedure of Sjoberg was employed.[40] The dimsyl solutions are labile[26] and were maintained at 20 °C and used within a few hours. Identical results were obtained when resublimed *t*-BuOK was added to Me_2SO to generate the alkoxide solution.

Acknowledgment. The authors wish to thank D. A. Johnson for spectral interpretation and C. G. Cârdenas for helpful discussions.

Registry No. 1, 4948-28-1; 2, 4948-29-2; *tert*-butyl alcohol, 75-65-0; tricyclohexylmethanol, 17687-74-0; *trans*-2-butene, 624-64-6; *cis*-2-butene, 590-18-1; 2-iodobutane, 513-48-4; 1-butene, 106-98-9.

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[39] Extreme caution must be exercised when handling potassium hydride. Brown, C. A. *J. Org. Chem.* **1974**, *39*, 3913.

[40] Sjoberg, K. *Tetrahedron Lett.* **1966**, 6383.

Chemistry of the 2-Pinanols. 2.[1] Investigation of the Utility of the Enhanced Basicities of the Pinanoxide Bases

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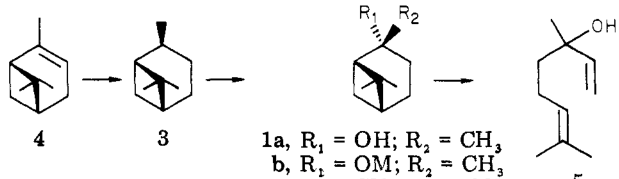
The utility of the alkoxides of *cis*- and *trans*-2-pinanol has been investigated. Yields comparable to and exceeding those obtained with *tert*-butoxide are reported for the alkylation of ethyl acetoacetate, for the conversion of α-pinene oxide to *trans*-pinocarveol and *cis*-3-pinen-2-ol, and for the isomerization of vinylnorbornene and limonene. Dehydrohalogenation was effected rapidly on bornyl chloride and 2,6-dichlorocamphane—compounds reported to be inert to potassium *tert*-butoxide in *tert*-butyl alcohol. Reactions with 1-octyl bromide and with benzyl chloride showed that the pinanoxides have nucleophilicities comparable to that of *tert*-butoxide.

Potassium *tert*-butoxide (*t*-BuOK) has occupied a unique position among alkoxide bases. First, it has been the strongest alkoxide of known pK_b, and second, it has been the most hindered base whose conjugate acid was available both in quantity and at reasonable cost.[2] The use of hydroboration–carbonylation techniques has recently made available more exotic, hindered, tertiary alcohols[3] which have not achieved widespread utility as hindered alkoxides.[4]

The *cis*- and *trans*-pinanols (**1a** and **2a**) are intermediates in the industrial synthesis[5] of linalool (**5**) which is a perfumery compound as well as an intermediate in the syntheses of vitamins A and E. The pinanols are prepared by hydrogenation of α-pinene (**4**) followed by autoxidation of the resultant pinanes (**3**; 4% *trans*, 96% *cis*). Hydrogenation of the pinane hydroperoxides yields *cis*-pinanol and *trans*-pinanol (3.5:1).[6] The chemistry of the pinanols has not been examined extensively although they have provided useful models for solvolysis studies.[7] *trans*-Pinanol has proven to be a strategic synthetic intermediate for the synthesis of grandisol,[8] α-bergamotene,[9] and other terpenes[10] since it provides access to functionalization at



4 3

1a, R_1 = OH; R_2 = CH_3
b, R_1 = OM; R_2 = CH_3
2a, R_1 = CH_3; R_2 = OH
b, R_1 = CH_3; R_2 = OM

5

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[1] Part 1: Kane, B. J.; Marcelin, G.; Traynor, S. G. *J. Org. Chem.*, preceding paper in this issue. *cis*- and *trans*-pinanol are available from PCR Research Inc.

[2] Pearson, D. E.; Buehler, C. A. *Chem. Rev.* **1974**, *74*, 45.

[3] Brown, H. C. *Acc. Chem. Res.* **1969**, *2*, 65.

[4] Bartsch, R. A.; Ingram, D. D. *J. Org. Chem.* **1975**, *40*, 3138.

[5] The formulae do not imply absolute stereochemistries. The synthesis of (+)- and (−)-**5** can be achieved from (−)-**1a**, (+)-**2a** and (+)-**1a**, (−)-**2a**, respectively. Ohloff, G.; Klein, E. *Tetrahedron*, **1962**, *18*, 37. For laboratory-scale preparations **1a** is more conveniently prepared by the reduction of β-pinene oxide while **2a** is prepared by the reaction of nopinone with methyl Grignard.

[6] The change in the cis to trans ratios from pinane to the pinanols is an example of the loss of stereochemical integrity observed in free-radical reactions.

[7] Salmon, J. R.; Whittaker, D. *J. Chem. Soc. B* **1971**, 1249. Indyk, H.; Whittaker, D. *J. Chem. Soc., Perkin Trans. 2* **1974**, 313. Abraham, A.; Vilkas, M. *Bull. Soc. Chim. Fr.* **1960**, 1450.

[8] Hobbs, P. D.; Magnus, P. D. *J. Am. Chem. Soc.* **1976**, *98*, 4594.

[9] Gibson, T. W.; Erman, W. F. *J. Am. Chem. Soc.* **1969**, *91*, 4771.

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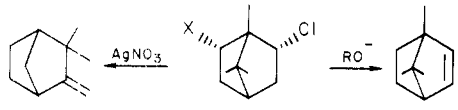
the *gem*-dimethyl bridge. Under solvolytic conditions, the *p*-nitrobenzoate ester of *cis*-pinanol has been found to be almost 2 orders of magnitude more reactive than the trans ester.[7] This reactivity difference has a parallel among the alcohols themselves in that *cis*-pinanol is much more susceptible to dehydration to pinenes than *trans*-pinanol. The simple alkanoic esters of **1a** and **2a** have not been described in the literature, and attempts to prepare them have yielded only the rearrangement products: bornyl, fenchyl, and terpinyl acetates.[11]

The proliferation of papers describing exotic amide, methide, phenoxide, and alkoxide bases exemplifies the continuing need to develop strong bases which are readily accessible. The *cis*- and *trans*-2-pinanoxides (**1b** and **2b**) fulfill this need and are the strongest alkoxide bases yet reported.[1] In order to determine the practical utility for these bases, we examined some of the common reactions which require alkoxide bases in dimethyl sulfoxide (Me_2SO) or in the alcohol itself: elimination, isomerizaiton, alkylation, and a nucleophilicity test.

Results and Discussion

Eliminations. Bornyl Chloride. The dehydrohalogenation of alkyl halides is a reaction of synthetic and commercial utility.[12] Although a large variety of alkyl halides is available for the study of elimination reactions, few provide sufficient difficulty of reaction to constitute good tests of base strength. Two notable exceptions are bornyl chloride (**7a**) and 2,6-dichlorocamphane (**7b**). The elimination of bornyl chloride has been examined under a variety of conditions,[13] yielding bornylene (**8**) in very low conversion (5%) with *t*-BuOK–*t*-BuOH at reflux and high conversion (95%) with the same base after prolonged refluxing in DMF or Me_2SO.[13a] Amyl alkoxide has also yielded bornylene at high temperature.[13b–d] A more selective reaction with high conversion was obtained by Hanack with the alkoxide from 2-*n*-butylcyclohexanol.[14] Silver nitrate in Me_2SO causes a change of mechanism from E_2 to E_1, giving camphene (**6**) as the only product.[15]



6 7a, X = H
b, X = Cl 8

The pinanoxides[16] were examined in the respective refluxing pinanol with **7a**. Potassium *trans*-pinanoxide (*trans*-PinOK, **2b**) was also examined in a refluxing DMF solution containing **7a**. The results clearly show that the combination of increased reaction temperature and basicity have a dramatic influence on the degree of conversion compared with the case of *t*-BuOK (see Table I). The conversions were almost quantitative in 1 h with the potassium pinanoxides in refluxing pinanol. The reactions with the pinanoxide bases were also carried out in Me_2SO at 70, 90, and 100 °C. At the latter two temperatures the reproducibility was extremely poor, with the percent conversion remaining static after a certain time period. Potassium dimsyl exhibited similar behavior. This lack of reactivity is due to the thermal instability of potassium dimsyl[1,17] which decomposes to less basic products. While this problem is not normally observed with *t*-BuOK–Me_2SO,[18] bases whose pK_b's approach that of dimsyl ion show substantial concentrations of dimsyl present in Me_2SO solution (eq 1).

Table I. Elimination of Bornyl Chloride (7a)

base	solvent	temp, °C	time, h	% conversion
t-BuOK	*t*-BuOH[a]	83	12	5
	DMF[a]	130	13	85
	Me_2SO[b]	70	1	14.8
			4	24.0
			24	40.5
cis-PinOK	*cis*-pinanol[c]	197	0.17	60.5
			0.5	87.3
			1.0	94.8
	Me_2SO[b]	70	1	13.3
			4	26.6
			24	59.7
trans-PinONa	*trans*-pinanol[c]	195	1.0	44.0
			5.0	92.4
trans-PinOK	*trans*-pinanol[c]	195	0.17	57.9
			0.5	85.9
			1.0	97.0
	DMF[b]	130	3.5	99.0
	Me_2SO[b]	70	1	15.9
			4	32.4
			24	61.2
dimsyl⁻ [e]	Me_2SO[b]	70	1	7.9
			4	14.0
			24	18.0
DBU[d]	Me_2SO[b]	70	1	1.3
			4	1.7
			24	7.1

[a] Reference 13a. [b] [R-Cl] = 0.5 M, [base] = 0.5 M. [c] [R-Cl] = 0.6 M, [base] = 0.8 M. [d] 1,5-Diazabicyclo[5.4.0]undec-5-ene. [e] K^+ as cation.

$$RO^- + CH_3SOCH_3 \rightleftarrows ROH + {}^-CH_2SOCH_3 \quad (1)$$

The percent conversion of **7a** with a variety of bases in Me_2SO at 70 °C is also given in Table I. The order of reactivity under these conditions is *trans*-PinOK > *cis*-PinOK *t*-BuOK > $K^+Me_2SO^-$ > DBU.

Even at 70 °C potassium dimsyl shows thermal instability. Significantly higher conversions were obtained when the dimsyl reaction was carried out at 60 °C (e.g., 14 h, 55.4%). Although dimsyl decomposition is a problem as far as reproducibility of results is concerned for solutions of neat dimsyl, there is evidence that reaction with strong alkoxide bases in Me_2SO can be carried out at higher temperatures. Thus, *trans*-pinanoxide in Me_2SO containing **7a** at 130 °C (560 mm) gave a 53% yield of bornylene overhead in 15 min. The use of DBU in Me_2SO to carry out eliminations with bromoalkanes has been reported,[19] but under the present conditions **7a** showed almost no reaction.

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[10] Bosworth, N.; Magnus, P. D. *J. Chem. Soc., Perkin Trans. 1* **1972**, 943.

[11] Burrows, W. D.; Eastman, R. *J. Am. Chem. Soc.* **1959**, *81*, 245. The acetates of **1a** and **2a** have now been prepared and isolated. Traynor, S. G.; Gorman, C. R.; Coleman, J. B., unpublished results.

[12] Campbell, J. B. U.S. Patents 3 639 492, 1972, and 3 981 937, 1976. Coley, S. U.S. Patent 3 898 294, 1975. Smith, L. A. U.S. Patent 3 965 203, 1976.

[13] (a) Borowiecki, L.; Bessiere, Y. C. *Bull. Soc. Chim. Fr.* **1967**, 2364. (b) Meerwin, H.; Joussen, J. *Ber. Dtsch. Chem. Ges. B* **1922**, *55*, 2529. (c) Kwart, H.; Null, G. *J. Am. Chem. Soc.* **1956**, *78*, 5943. (d) Avela, E. *Ann. Acad. Sci. Fenn., Ser. A11* **1956**, 84. (e) The elimination of bornyl bromide by *t*-BuOK–18-crown-6 has also been reported recently. Dehmlow, E. V.; Lissel, M. *Synthesis* **1979**, 372.

[14] Hanack, M.; Hahnle, R. *Ber. Dtsch. Chem. Ges.* **1962**, *95*, 191.

[15] Mehta, C. *Indian J. Chem.* **1971**, *9*, 559.

[16] The term potassium pinanoxide (PinOK) refers to the potassium alkoxide of **1a** or **2a** unless otherwise stated.

[17] Brown, C. A. *J. Org. Chem.* **1974**, *39*, 3913.

[18] A 1.0 M solution of alkoxide in Me_2SO contains the following approximate percentages of dimsyl species: 1.7% *t*-BuOK, 19% *cis*-PinOK, 23% *trans*-PinOK.

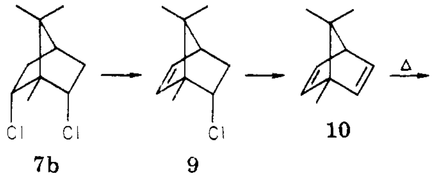
[19] Oediger, H.; Moller, F. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 76.

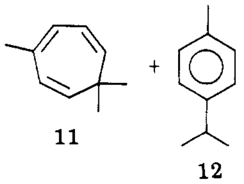
Table II. Elimination of 2,6-Dichlorocamphane (7b)

base	solvent	temp, °C	time	% conversion	k_{rel}
t-BuOK	*t*-BuOH[a]	230	6 h	0	
	Me_2SO[b]	70	1 h	19.3	
			4 h	48.8	
			10 h	76.8	
			24 h	83.0	1.0
cis-PinOK	*cis*-pinanol[c]	197	3 min	81.5	
			7 min	89.0	
			12 min	96.0	
	Me_2SO[b]	70	1 h	22.1	
			4 h	52.3	
			10 h	79.0	
			24 h	85.9	3.0
trans-PinOK	*trans*-pinanol[c]	195	3 min	92.6	
			7 min	98.0	
			12 min	99.0	
	Me_2SO[b]	70	1 h	26.3	
			4 h	59.8	
			10 h	81.0	
			24 h	89.8	9.0
trans-PinONa	*trans*-pinanol[c]	195	15 min	80.3	
			26 min	90.5	
			55 min	98.9	
DBU	Me_2SO[b]	70	24 h	4.0	
	toluene	110	24 h	7.0	

[a] Reference 13c. [b] [R-Cl] = 0.13 M, [base] = 0.26 M. [c] [R-Cl] = 0.33 M, [base] = 0.72 M.

2,6-Dichlorocamphane. Chlorination of α-pinene yields 2,6-dichlorocamphane (**7b**) which is reported to be extremely resistant to dehydrohalogenation.[13c] Sodium 2-*n*-butylcyclohexanoxide[20] as well as the alkoxide of 1-octanol[21] has been used successfully to carry out this elimination to bornadiene (**10**). However, the use of alkoxides of primary and secondary alcohols at high temperature is complicated by the formation of byproducts due to the Guerbet reaction.[22] *cis*- and *trans*-pinanoxides were reacted with **7b** in refluxing *cis*- and *trans*-pinanol, respectively, as well as Me_2SO. The reaction was also carried out with *t*-BuOK and DBU in Me_2SO at 70 °C (Table II). These results clearly show the facile dehydrohalogenation of **7b** by the pinanoxide bases in refluxing pinanol. Kwart and Null suggested that the decreased reactivity of **7b** compared with that of bornyl chloride (**7a**) was due to the deactivation by the second halogen.[13c] The rate of reaction of **7b** was faster with the pinanoxides than that of **7a** both in refluxing alcohol and in Me_2SO. The greater reactivity of **7b** compared to that of **7a** which was observed under our conditions was likely due to the relief of steric strain in the sterically crowded dichloride **7b**. The possibility that the faster reaction of **7b** is due to participation by a different mechanism is unlikely since the reaction was determined to be second order overall for the three bases in Me_2SO. 6-Chlorobornylene (**9**) was detected by GC/MS and was observed to react further to bornadiene. As with bornyl chloride the order of reactivity within the pinanoxides in refluxing pinanol is *trans*-PinOK > *cis*-PinOK > *trans*-PinONa.[23]



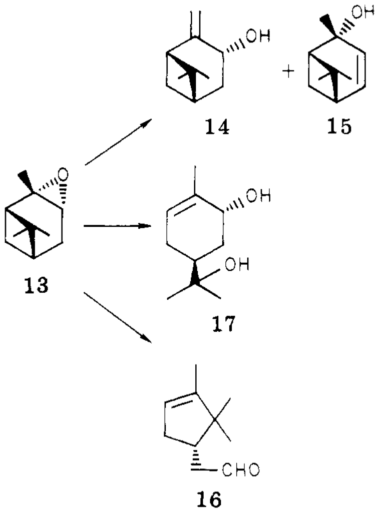


While the reaction of **7b** with *t*-BuOK–*t*-BuOH is reported to yield only starting material, we decided to examine the reactivity of **7b** with *t*-BuOK–Me_2SO. Under these aprotic,[24] dissociating conditions the reaction was observed to take place, giving a high conversion of **7b** (Table II), but the rate was slower than that measured with the pinanoxide bases.

The formation of traces of *p*-cymene (**12**) and 3,7,7-trimethyltropilidene (**11**) was observed on prolonged heating of the reaction product.[21]

Base Isomerizations. Base-catalyzed isomerizations constitute an important facet of synthetic methodology. Two areas were chosen to be examined with the pinanoxide bases: epoxide isomerization and alkene isomerization.

Epoxide Isomerizations. α-Pinene oxide (**13**) has been isomerized under a variety of conditions. Lithium in diethylamine[25] as well as aluminum alkyls[26] yield *trans*-pinocarveol (**14**), Lewis acids give campholenic aldehyde (**16**) as the major product,[26,27] active alumina gives a mixture of products,[28] and protic acid hydration[29] yields sobrerol (**17**).



The isomerization of **13** with *t*-BuOK–DMF[30,31] has been reported to yield *trans*-pinocarveol as the exclusive product of β-elimination. The reaction in DMF was repeated by using *t*-BuOK and *cis*- and *trans*-PinOK at 115 °C. Analysis of the reactions after 1 h by GLC on a glass

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[20] Hanack, M.; Eggensperger, R.; Hanle, R. *Justus Liebigs Ann. Chem.* **1962**, *652*, 96.

[21] Willcott, R. M.; Boriak, C. J. *J. Am. Chem. Soc.* **1968**, *90*, 3287.

[22] Klein, E.; Thomel, F.; Winkler, H. *Justus Liebigs Ann. Chem.* **1973**. Yates, J. E. U.S. Patent 3 860 664, 1975.

[23] A similar decrease in reactivity on changing the counterion to Na^+ has been previously observed in Me_2SO. Bank, S. *J. Org. Chem.* **1972**, *37*, 114.

[24] The term "aprotic solvent" for Me_2SO is misleading. While this is true to a large extent for bases weaker than *t*-BuOK, it does not hold for bases as strong as the pinanoxides.

[25] Crandall, J. K.; Crawley, L. C. *Org. Synth.* **1973**, *53*, 17.

[26] Lewis, J. B.; Hendrick, G. W. *J. Org. Chem.* **1965**, *30*, 4271. Hartshown, M. P.; Kirk, D. N.; Wallis, F. A. *J. Chem. Soc.* **1964**, 5494.

[27] Teisseire, P.; Galfre, A.; Plattier, M.; Corbier, B. *Recherches* **1966**, *15*, 52

[28] Joshi, V. S.; Damodaran, N. P.; Dev, S. *Tetrahedron* **1968**, *24*, 5817.

[29] Cocker, W.; Crowley, K. J.; Srinivasan, K. *J. Chem. Soc. Perkin Trans. 1*, **1972**, 1971.

[30] Rykowski, Z.; Burak, K.; Chabuzinski, Z. *Rocz. Chem.* **1974**, *48*, 1619.

[31] Montheard J. P.; Bessiere, Y. C. *Bull. Soc. Chim. Fr.* **1968**, 336.

Table III. Isomerization of α-Pinene Oxide (13)

base	solvent	temp, °C	time, h	% product 13	% product 14	% product 15	10^4k, s^{-1}	k_{rel}
t-BuOK	Me_2SO^a	70	1	40.1	44.0	15.9		
			2	14.7	63.4	21.9	2.75	1.0
		90^c	48		62.1	37.9		
	DMF^b	115	1		71.2	28.8		
cis-PinOK	Me_2SO^a	70	1	37.4	45.6	17.0		
			2	14.0	63.2	22.8	2.78	1.0
	DMF^b	115	1		72.1	27.9		
trans-PinOK	Me_2SO^a	70	1	24.6	49.2	26.2		
			2	6.4	62.5	31.1	3.67	1.3
	DMF^b	115	1		67.7	32.3		

[a] [epoxide] = 0.22 M, [base] = 1.1 M, average of duplicate runs. [b] [epoxide] = 0.23 M, [base] = 1.02 M, by procedure of ref 30. [c] [epoxide] = 0.77 M, [base] = 0.85 M, by procedure of ref 31.

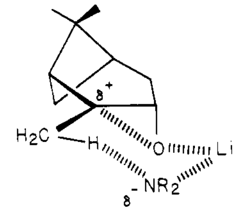
Table IV. Isomerization of Limonene (18) in Me_2SO^a at 60 °C

$base^b$	% product 18	% product 19	% product 20	% product 21	% product 22	% product 23	% product 12	10^6k, s^{-1}	k_{rel}
t-BuOK	46.6	0.5	24.7	8.3	16.1	2.1	1.7	4.2	1.0
cis-PinOK	37.6	0.9	29.0	9.6	19.1	2.5	1.3	5.6	1.3
trans-PinOK	9.1	1.0	42.6	13.6	27.9	3.0	2.8	14.0	3.3

[a] Product distribution after 48 h. [b] [Olefin] = 0.4 M, [base] = 0.6 M.

capillary SP-2100 column revealed two peaks, as reported,[30] the faster eluting of which was almost identical, by retention time, with the starting material. However, when the analysis was carried out on a Carbowax-20M GLC column, the first-eluting peak was cleanly removed from the starting epoxide **13**. GC/MS, coinjection, and isolation of both products by distillation revealed the unknown product to be *cis*-3-pinen-2-ol (**15**) and the longer retention time product to be *trans*-pinocarveol. Likewise, the reaction of **13** with *t*-BuOK–Me_2SO at 90 °C for 48 h[31] gave the same two products, which were identified by coinjection with authentic material. Having established the presence of the two anticipated products of β elimination, we reexamined the reaction with *cis*- and *trans*-PinOK and *t*-BuOK–Me_2SO at 70 °C. The complete results are given in Table III and again show the faster reaction obtained with the pinanoxides compared with that with *t*-BuOK. There is little difference between the bases in the ratio of **14** to **15**, indicating that the direction of elimination is not very sensitive to changes in base steric hindrance in this system. The pseudo-first-order rate constants for the isomerization of **13** show a closer similarity than anticipated on the basis of alkoxide pK_b alone. In contrast to the complete lack of reactivity observed with *t*-BuOK–*t*-BuOH,[30,31] *trans*-PinOK gave a 90.7% conversion of α-pinene oxide in 0.5 min in refluxing *trans*-pinanol. The products were *cis*-3-pinen-2-ol (17.6%) and *trans*-pinocarveol (68.6%).

The absence of the tertiary alcohol **15** from the reaction of **13** with lithium diethylamide in ether has been rationalized as being the result of the absence of a suitable anti proton which would allow β elimination.[32-34] Subsequently, the syn nature of β eliminations from epoxides under these conditions was discovered by Rickborn.[35] α-Pinene oxide contains a syn proton at C_4 with the correct orientation for β elimination but yields essentially no **15** with lithium diethylamide. There are two possible causes of the difference in product distribution between these reaction conditions. First, the contribution of an anti elimination mechanism under highly dissociating conditions cannot be ignored since the stereochemical constraints of a syn elimination have only been demonstrated under nonionizing conditions where associated base predominates. The second possibility is that a mechanistic continuum exists for these reactions similar to the variable E2 transtition-state theory observed in other β eliminations.[36] In the case of epoxides the continuum would cover the synchronous E2–E1B mechanisms. The higher than anticipated discrimination[37] of a C_{10} vs. a C_4 proton in **13** by lithium diethylamide can be rationalized by assuming the normal syn elimination mechanism. In this case reaction with associated base results in complexing the lithium ion with oxygen and a concurrent weakening of the C–O bond in the direction which results in greatest stabilization of the incipient partial positive charge, i.e., C_2–O. This increases the acidity of a proton at C_{10} and favors the formation of *trans*-pinocarveol. Furthermore, examination of Dreiding models of the transition states for the formation of **14** and **15** shows that the chair transition state leading to **14** is free of steric restraint in contrast to that for formation of **15** which experiences steric hindrance from the endo proton at C_7.



Under highly dissociating conditions such as alkoxide in Me_2SO, a more "E1cB-like" mechanism would impose less base discrimination by virtue of decreased directionality imposed by the counterion. Testing this explanation by isomerizing **13** in *t*-BuOK–Me_2SO while varying the

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(32) The near complete absence of **15** (>2%) under these conditions was confirmed by the present authors.

(33) Crandall, J. K.; Chang, L. H. *J. Org. Chem.* **1967**, *32*, 435.

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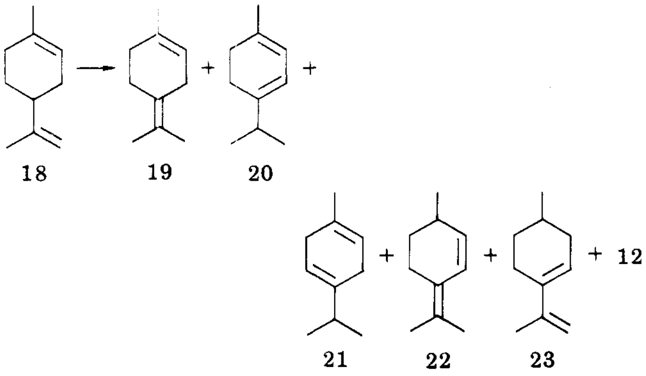
cation and, thus, the degree of dissociation gave results that are in agreement with but do not provide the dramatic difference in selectivity observed with lithium diethylamide in ether. Lithium, sodium, and potassium *tert*-butoxide provided **15** and **14** in the ratios of 3.9:1, 3.4:1, and 2.8:1, respectively.

Olefin Isomerization.[38] Limonene (**18**) is an olefin particularly well suited to study since it contains two differently substituted double bonds. The isomerization of the isopropenyl moiety of **18** has been shown by Schriesheim to be a relatively slow reaction with *t*-BuOK–Me$_2$SO at 55 °C. Under these same conditions equilibration of the other isomeric menthadienes is fast.[39] The equilibration of these dienes has also been examined[40] with *t*-BuOK–*t*-BuOH at 200 °C. The isomerization of limonene was carried out with the three alkoxide bases in Me$_2$SO at 60 °C. The results in Table IV show the pseudo-first-order rate constants as well as the product distribution after 48 h. As in previous examples the rate differences are in the expected order and are relatively small. Under these conditions terpinolene (**19**) was completely isomerized in 15 min to the same equilibrated mixture of dienes as obtained from **18**.



The isomerization of limonene with *trans*-PinOK in refluxing *trans*-pinanol did not give the same mixture of equilibrated dienes but instead gave mostly *p*-cymene. The complete absence of *p*-menthenes indicated that the dehydrogenation did not occur by simple disproportionation. After 21 h at reflux the conversion, determined by using an internal standard, was 98%. The product distribution was as follows: **18**, 2.3%; **20**, 12.6%; **22**, 4.9%; **23**, 8.1%; **12**, 72.0%. Surprisingly, the isomerization of **18** with *t*-BuOK–*t*-BuOH at 200 °C is reported to yield only 4% *p*-cymene after 30 h,[40] while *t*-BuOK–Me$_2$SO at 100 °C after 4 h yielded **12**, 84.3% with 97.7% conversion.[41] With the exception of the *t*-BuOH example, aromatization is generally facilitated by higher reaction temperatures. The formation of *p*-cymene occurs by disproportionation when **18** is treated with lithium dimethylamide in HMPA at room temperature.[39]

Treatment of 2-vinyl-5-norbornene in Me$_2$SO at 50 °C for 23 h gave the following conversions to 2-ethylidene-5-norbornene: *t*-BuOK, 81.8%; *cis*-PinOK, 83.6%; *trans*-PinOK, 91.3%. The latter olefin is commonly used as a polymerization crosslinker, and its formation has been the subject of several patents.[42]

Alkylations. Alkoxide bases are commonly used in the alkylation of active methylene groups. As a part of the overall evaluation of the pinanoxide bases, the alkylation of ethyl acetoacetate with *n*-butyl iodide in tetrahydrofuran was examined.[43] The pinanoxides gave comparably high yields of ethyl *n*-butylacetoacetate: *t*-BuOK, 96.6%; *cis*-PinOK, 93.5%; *trans*-PinOK, 93.8%.

Nucleophilicity. The standard procedure for the determination of nucleophilic character is the competition between the nucleophile of interest and methoxide ion in methanol.[44] However, for anionic species much more basic than methoxide this system is unsuitable. The pinanoxides were therefore evaluated in a qualitative manner along with *t*-BuOK by reaction with 1-octyl bromide in Me$_2$SO at 70 °C for 1 h.[45] The yields of the octenes (ca. 75%) and the octyl ethers (ca. 25%) were similar for the three bases. Reaction of the bases with benzyl chloride in THF[46] at 30 °C for 5 h gave the alkyl ethers in 72–94% of the theoretical yields at 56–62% conversion. Thus, the pinanoxides **1b** and **2b** appear to have a nucleophilic character similar to that of the *tert*-butoxide ion.

Conclusion

The present study has shown that the *cis*- and *trans*-2-pinanoxides are alkoxides which can be utilized with results that are generally superior to those of *t*-BuOK for a large variety of reactions that require strong bases. It is probable that the useful limit of alkoxide basicities in Me$_2$SO has been reached with these bases and without the large rate enhancements anticipated on the basis of pK_b. The plurality of species generated by these bases in Me$_2$SO places a degree of uncertainty on the rates and mechanisms under study. Under such circumstances both the kinetic and thermodynamic basicities of competing species must be considered. These features may be partly responsible for generally poorer results for *cis*-pinanoxide than for *trans*-pinanoxide which are of very similar basicities.[47]

A unique feature of these bases in the high boiling points (195–197 °C) of their conjugate acids. This allows for the generation of the alkoxides using alkali metal hydroxides followed by azeotropic removal of water and further permits higher reaction temperatures at atmospheric pressure. On the negative side, separation of the reaction product(s) from the pinanols may at times be problematic and will limit the utility of these bases.

A potentially useful feature of the pinanoxides is that they can be prepared optically active and are therefore potential chiral auxiliary reagents for organic synthesis.

Experimental Section

^{1}H NMR spectra were measured by using a 60-MHz Perkin-Elmer R-20B spectrometer. Chemical shifts are reported in ppm (δ) downfield from tetramethylsilane. Elemental analyses were carried out by Galbraith Laboratories Inc. GC/MS spectra were recorded on a Varian Mat 112 mass spectrometer and data system. Gas chromatographic analyses were carried out as follows: column 1, SP-2100, 30-m glass capillary, 0.22 mm i.d., 75–220 °C, 4 °C/min; column 2, Carbowax, 60-m glass capillary, 0.22 mm i.d., 75–160 °C, 4 °C/min; column 3, UCW-98 (10% on Chromosorb WHP), 6 ft × 2 mm i.d. glass; 75–230 °C, 4 °C/min. GLC chromatograms were automatically integrated by a General Au-

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tomation SPC-16/45 computer. For reactions in which internal standards were added, relative response factors were used to determine yields and conversions. All solvents were freshly distilled from calcium hydride. All results are the average of two or more runs. *cis*-Pinanol (**1a**), mp 50.3 °C, bp 85–87 °C (10 mm), was 98–100% pure (GLC). *trans*-Pinanol (**2a**), mp 46.9 °C, bp 80–82 °C (10 mm), was 99–100% pure. Spectral data have been reported previously.[1]

Alkoxide Preparation. The alkoxide–Me_2SO solutions were prepared on a vacuum line as follows. A three-necked 1-L flask containing a pressure-equalizing addition funnel, a magnetic stirrer, a vacuum outlet, and a septum was charged with potassium hydride (KH, 10.9 g, 22%, Pressure Chemical).[48] The KH was washed with pentane (4 × 25 mL) under nitrogen. After the pentane was removed, the vacuum was applied carefully with the cautious addition of Me_2SO (100 mL). The vacuum was maintained until the reaction was complete and the last traces of pentane were removed. Since potassium dimsyl solution was unstable, immersion of the reaction flask in a water bath at 20 °C prolonged the useful lifetime of the straw-colored solution. A sample of the dimsyl solution was titrated and the resultant solution adjusted to 0.5 M with Me_2SO.

The alkoxide–alcohol solutions were prepared by heating the alkali metal in the respective alcohol to reflux under nitrogen. With potassium metal the alkoxide formation was complete in 25 min and with sodium metal in 1 h.

Bornyl Chloride (7a) Eliminations. The alcohol (12.9 mmol) was added to a freshly prepared dimsyl solution (25 mL, 0.5 M) under nitrogen with stirring, and the flask was immersed in an oil bath at 70 °C. When equilibrium was reached, bornyl chloride (2.13 g, 12.5 mmol) was added. The reaction was sampled at intervals and analyzed by GLC (column 2). The conversion of starting material was calculated from the ratio of **7a** and α-fenchyl chloride (~5%) which is an inert impurity in most bornyl chloride samples.

Reactions in pinanol solvent (50 mL) were carried out by adding bornyl chloride (5.0 g, 29.8 mmol) and dodecane (5 g) as internal standard to the refluxing alcohol solution containing the alkoxide (40 mmol). In all cases the reactions were sampled at intervals, and the samples were worked up by quenching in brine followed by extraction with ether–pentane. The dried extracts ($MgSO_4$) were analyzed by GLC. The results are given in Table I.

To a solution of *trans*-PinOK in DMF (0.5 mL) was added bornyl chloride (12.5 mmol) at 130 °C. The reaction mixture turned black upon heating, and a solid material slowly formed in the reaction flask. The reaction was complete after 3.5 h. It is believed that the pinanoxides may react with DMF on prolonged heating.

2,6-Dichlorocamphane (7b) Eliminations. The alcohol (2.3 mmol) was weighed into a 10-mL glass vial containing dry Me_2SO (1.0 mL) under nitrogen. A freshly prepared dimsyl solution (4.1 mL, 0.53 M) was added to the vial which was sealed with a septum seal (Wheaton). The vial was placed in an oil bath at 70 °C. Diphenyl ether (0.15 g) was added via a syringe as the internal standard. After 20 min 2,6-dichlorocamphane (0.22 g, 1.06 mmol) in dry Me_2SO (3.3 mL) was added via a syringe to the vial, and the homogeneous solution was shaken. The reaction was also shaken when aliquots were removed for GLC analysis (column 3). The intermediate 6-chlorobornylene (**9**) was identified by GC/MS [*m/e* (relative intensity) 93 (100), 108 (78), 43 (39), 91 (31), 41 (23), 77 (22), 57 (21), 155 (2)] and was separated from **2a** by using a Carbowax-20M column.

A 100-mL flask was charged with **7b** (1.3 g, 6.3 mmol), dodecane (2.0 g) as internal standard, and dry toluene (30 mL). The reaction was brought to reflux, and DBU (1.92 g, 12.6 mmol, Aldrich) was added. The reaction was refluxed at 100 °C for 24 h, during which samples were removed and analyzed by GLC. When Me_2SO was used as the solvent, the reaction temperature was 70 °C.

A 100-mL flask was charged with pinanol (50 mL) and potassium metal (1.4 g, 0.036 mol) and brought to reflux (195–197 °C) with stirring under nitrogen. When alkoxide formation was complete, 2,6-dichlorocamphane (3.5 g, 16.7 mmol) was added to the reaction. Conversions were calculated with pinanol as the internal standard. The results are given in Table II.

The relative rate constants were determined by the average rate method (log $\Delta A/\Delta t$ vs. log $\bar{A}$).

To a dry 500-mL distillation flask fitted with a 6-in. Vigreux column and a condenser was added *trans*-pinanol (220 g) and potassium metal (20 g, 0.51 mol). The flask was heated slowly to 120 °C with a nitrogen purge until the potassium had dissolved. 2,6-Dichlorocamphane (43 g, 0.208 mol) was added and the reaction heated to 190 °C. The distillate (37 g) containing bornadiene (26.3 g, 94.4% conversion) was collected at atmospheric pressure for a 15-min period. Chromatography on silica and elution with pentane gave pure bornadiene (16.6 g, 59.6% of the theoretical yield), mp 100–102 °C (lit.[20] mp 103 °C).

α-Pinene Oxide (13) Isomerization. Potassium dimsyl solutions (6.3 mL, 1.1 M) were prepared as previously described and added to 10-mL vials containing the alcohol (0.71 mmol). After equilibration at 70 °C, α-pinene oxide (0.21 g, 1.4 mmol) was added via a syringe. The vial was then shaken thoroughly and also when samples were removed for GLC analysis (column 2).

α-Pinene oxide (1.0 g, 6.5 mmol) was added to a solution containing *t*-BuOK (3.2 g, 28.5 mmol) in DMF (28 mL) at 115 °C. After 1 h GLC analysis showed all the starting material had reacted, and two products were present, **14** (71.2%) and **15** (28.8%).

α-Pinene oxide (50 g, 0.33 mol) was added slowly to a solution of *t*-BuOK (0.33 mol) in DMF (280 mL) at 115 °C. The reaction was cooled after 75 min, water (500 mL) was added carefully, and the reaction mixture was extracted with ether. The dried ether extracts ($MgSO_4$) were filtered and evaporated, yielding the crude product mixture (37 g) which was fractionated on a spinning-band column. *cis*-3-Pinen-2-ol [**15**; 6.1 g, 97.8%, bp 72–74 °C (10 mm)] and *trans*-pinocarveol [**14**; 13.3 g, 96%, bp 78 °C (10 mm)] were the distillate components and were identified by NMR, IR, mass spectral, and GLC comparison with authentic samples.

Potassium pinanoxide reactions in DMF were carried out as follows. KH (5.8 g, 28.5 mmol) was washed with pentane (3 × 50 mL) under nitrogen. Pinanol (4.4 g, 28.8 mmol) was carefully added to the suspension, and after the addition was complete, the excess pentane was removed in vacuo. Dry DMF (28 mL) was added followed by **13** (1.0 g, 6.5 mmol) when the reaction reached 115 °C. The reaction was stopped and was analyzed by GLC after 1 h. The direct preparation of alkoxides with KH in DMF is not possible due to hydride reduction of the solvent.

trans-Pinanol (14 g) and potassium metal (0.0256 mol) were refluxed under nitrogen until the evolution of hydrogen had ceased. α-Pinene oxide (25.6 mmol) and dodecane (2.0 g) were added via a syringe to the reaction at 195 °C. After 0.25 min the conversion was 64.9%, and after 0.5 min it was 90.7%. The further reaction of *trans*-pinocarveol was observed and was 85% consumed within 2 min. Four products were formed in the latter reaction, the major components of which were identified by GC/MS as *trans*-pinocamphone and apopinocamphone (2:1).

Limonene (18) Isomerizations. The isomerizations in Me_2SO at 60 °C were carried out by the method of Schriesheim.[39] The concentrations of base and olefin were 0.6 and 0.4 M, respectively. The identities of the reaction products were confirmed by GLC retention time (column 2) and GC/MS comparison with authentic samples. The order of elution of the *p*-menthadienes on Carbowax is as follows: 2,4-*p*-menthadiene; α-phellandrene; 1(7),8-*p*-menthadiene; α-terpinene (**20**); limonene (**18**), β-phellandrene; γ-terpinene (**21**); 3,8-*p*-menthadiene (**23**); *p*-cymene (**12**); terpinolene (**19**), 2,4(8)-*p*-menthadiene (**22**).

The isomerization of **18** with *trans*-PinOK in refluxing *trans*-pinanol was carried out as follows. KH (9.1 g, 50 mmol) was washed with pentane (3 × 50 mL) under nitrogen. *trans*-Pinanol (2.5 g) was added carefully to the suspension, and after the addition was complete, the excess pentane was removed in vacuo. The reaction was heated to a gentle reflux, and limonene (4.7 g, 35 mmol) was added along with tetradecane (1.0 g) as internal standard. The conversion of **18** with respect to time was as follows: 1 h, 24.6%; 8 h, 85.7%; 14 h, 96.9%, 21 h 98.5%. The product distribution at 21 h is given in the text. Several minor menthadienes (<1% each) were also observed.

5-Vinyl-2-norbornene Isomerization. The reactions were carried out in 10-mL septum-sealed vials at 50 °C as described

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[48] The manipulation of potassium hydride requires great care.[17]

previously. GLC analysis (column 2) indicated that the cis and trans isomers of 5-ethylidene-2-norbornene were the sole reaction products. The identity of the latter was confirmed by GLC spiking with authentic material (Aldrich) and GC/MS. The concentrations of base and olefin were 0.6 and 0.4 M in Me$_2$SO, respectively. The starting material (Aldrich) is actually a mixture of 69.4% endo and 30.6% exo isomers which isomerize at different rates. The results are given in the text.

Alkylation of Ethyl Acetoacetate. To a dry 500-mL three-necked flask under nitrogen fitted with a condenser, an addition funnel, and a magnetic stirrer was added KH (22%, 14.5 g, 0.08 mol). The suspension was washed twice with pentane (50 mL) and once with THF. After removal of most of the solvent, fresh THF (100 mL) was added. Pinanol (12.6 g, 0.082 mol) was added carefully over a 10-min period. When the reaction ceased, ethyl acetoacetate (10.6 g, 0.082 mol) and *n*-decane (10 g) in THF (100 mL) were added dropwise with stirring. When the addition was complete, the reaction mixture was brought to reflux, and *n*-butyl iodide (15.0 g, 0.082 mol) was added. Aliquots were removed at intervals and titrated. GLC analysis (column 2) of the reaction mixture was used to calculate the product yield from the internal standard which was corrected for the difference in response factors. A similar procedure was carried out for *t*-BuOK (Ventron) which was freshly sublimed.

2-Pinanyl Ethers. The reactions of the alkoxides with *n*-octyl bromide were carried out in Me$_2$SO at 70 °C.[45] In each case a single long retention time product, the alkyl ether, was observed along with a mixture of octenes at shorter retention time (column 2). The ratio of octenes varied with reaction time and base. The octyl ethers were identified by GC/MS. *cis*-2-Pinanyl octyl ether: *m/e* (relative intensity) 71 (100), 43 (86), 41 (72), 93 (51), 81 (50), 99 (43), 57 (38), 266 (1, M$^+$). *trans*-2-Pinanyl octyl ether: *m/e* (relative intensity) 71 (100), 43 (85), 93 (82), 41 (71), 99 (41), 81 (40), 69 (39), 57 (38), 266 (2, M$^+$).

Benzyl chloride (27.3 mmol) was added to a solution of the alkoxide (27.3 mmol) in THF (25 mL) containing dodecane (2.0 g). The reaction was stirred at 30 °C for 5 h and analyzed by GLC (column 2). *t*-BuOK gave 94.4% of the theoretical yield of *tert*-butyl benzyl ether[46] at 58.8% conversion. *cis*-PinOK gave 72.2% of the theroetical yield at 56.2% conversion of *cis*-2-pinanyl benzyl ether: bp 170 °C (10 mm); NMR (CDCl$_3$) δ 0.94 (s, 3 H), 1.22 (s, 3 H), 1.28 (s, 3 H), 1.4–2.4 (m, 8 H), 4.24 (AB q, 2 H, J = 11 Hz $\nu_A - \nu_B$ = 0.11), 7.25 (s, 2 H); mass spectrum, *m/e* (relative intensity) 93 (100), 91 (98), 79 (69), 77 (52), 41 (42), 108 (40), 107 (39), 92 (31). Anal. Calcd for C$_{17}$H$_{24}$O: C, 83.55; H, 9.90. Found: C, 83.79; H, 10.03. *trans*-PinOK gave 89.3% of the theoretical yield at 61.5% conversion of *trans*-2-pinanyl ether: bp 170 °C (10 mm); NMR (CDCl$_3$) δ 1.1 (s, 3 H), 1.2 (s, 3 H), 1.26 (s, 3 H), 1.5–2.5 (m, 8 H), 4.32 (s, 2 H), 7.28 (s, 5 H); mass spectrum, *m/e* (relative intensity) 91 (100), 93 (33), 43 (30), 95 (19), 136 (19), 92 (18), 41 (17), 79 (15). Anal. Calcd for C$_{17}$H$_{24}$O: C, 83.55; H, 9.90. Found: C, 83.60; H, 9.88.

Isolation of the Alkoxides 1b and 2b. The physical properties of the pinanoxides have not yet been studied in detail. *cis*-PinOK yielded a pale yellow amorphous solid on isolation, while *trans*-PinOK was a pale brown waxy solid. A 1:1 solid THF complex was obtained from *trans*-PinOK but was not formed with *cis*-PinOK.

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Registry No. 1a, 4948-28-1; **1b** (M = K), 72611-32-6; **2a**, 4948-29-2; **2b** (M = K), 72611-33-7; **7a**, 464-41-5; **7b**, 54353-49-0; **9**, 72611-34-8; **12**, 99-87-6; **13**, 32162-27-9; **14**, 1674-08-4; **15**, 38211-97-1; **18**, 138-86-3; **19**, 586-62-9; **20**, 99-86-5; **21**, 99-85-4; **22**, 586-63-0; **23**, 586-67-4; *endo*-5-vinyl-2-norbornene, 25093-48-5; *exo*-5-vinyl-2-norbornene, 23890-32-6; *cis*-5-ethylidene-2-norbornene, 28304-66-7; *trans*-5-ethylidene-2-norbornene, 28304-67-8; *cis*-2-pinanyl octyl ether, 72611-35-9; *trans*-2-pinanyl octyl ether, 72611-36-0; *cis*-2-pinanyl benzyl ether, 72611-37-1; *trans*-2-pinanyl benzyl ether, 72611-38-2.

Brønsted Plots in the Reactions of 2,4-Dinitrophenyl Acetate and Methyl Phenyl Carbonate with Substituted Pyridines

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Rate constants are reported for nucleophilic attack of a series of 3- or 4-substituted pyridines on 2,4-dinitrophenyl acetate and methyl phenyl carbonate at 25 °C, and ionic strength 0.2 M. The Brønsted plot obtained is curved for the acetate and linear for the carbonate. The first shows two linear regions (at low and high pK_a values with slopes 0.85 and 0.2, respectively) and a curvature in between. The Brønsted slope for the carbonate is 1.3. The Brønsted curve can be accounted for in terms of a tetrahedral intermediate in the reaction path and a change in the rate-determining step from breakdown of the intermediate to its formation, as the substituted pyridine becomes more basic. A semiempirical equation based on these assumptions fits the experimental data. From the shape of the curved Brønsted plot, an equal leaving ability from the tetrahedral intermediate for 2,4-dinitrophenolate and a (hypothetical) pyridine of pK_a = 7.3 is deduced. The influence of the group that does not leave on the relative leaving abilities of phenolates and pyridines is discussed.

Curved Brønsted plots obtained in nucleophilic reactions of carbonyl compounds have often been interpreted in terms of a tetrahedral intermediate in the reaction path and a change in the rate-determining step from leaving-group expulsion to attack by the nucleophile as the nucleophile becomes more basic.[1-6] Quantitative evaluation of the relative leaving abilities of pyridines and chloride anion,[5] thiol and oxygen anions,[3] quinuclidines and phenolates,[4] and pyridines and phenolates[6] from a tetrahedral intermediate has been attempted from semiempirical equations based on the above assumptions.

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