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Chemistry of the 2-Pinanols. 1. Pinanoxide Basicities

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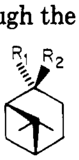
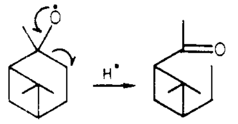
The basicities of the alkoxides of *cis*- and *trans*-2-pinanol were examined colorimetrically and conductimetrically. The colorimetric measurements gave the following pK_a values for the conjugate acids in dimethyl sulfoxide (Me_2SO): 30.4, *tert*-butoxide; 32.5, tricyclohexylmethoxide; 32.6, *cis*-pinanoxide; 32.8, *trans*-pinanoxide. The pinanoxides are the most basic alkoxides yet measured. Conductivity measurements of Me_2SO solutions containing these bases revealed that very complex equilibria processes were operative. A study of the elimination of 2-iodobutane in Me_2SO with the pinanoxide bases showed a good correlation with base strength. No steric effects such as those observed with tricyclohexylmethoxide were apparent for the pinanoxide bases.

The recent availability of large quantities of *cis*- and *trans*-pinanol (**1a** and **2a**) has made these compounds more accessible to study.[1] Although the pyrolysis of **1a** and **2a** to linalool[2] and solvolysis of these alcohols and their *p*-nitrobenzoate esters[3] have been studied extensively, no study has been made of these compounds as sources of hindered tertiary alkoxides.



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

Concurrent efforts in the analysis of base-promoted reactions with the pinanoxides **1b** and **2b** indicated[4] that these bases are significantly stronger than *tert*-butoxide and do not possess the undesirable fragmentation exhibited by other hindered bases such as tri-*tert*-butylmethoxide.[5] Although the pinanoxyl radical **3** obtained from pinane hydroperoxide can show substantial ring cleavage[6] to the cyclobutyl ketone **4**, the pinanoxide anion exhibits evidence of decomposition only after prolonged refluxing in the corresponding alcohol at 195–197 °C. The unique properties of high basicity and alkoxide stability as well as high boiling point [**1a**, 197 °C; **2a**, 195 °C (760 mm)] and easy availability of the alcohols prompted us to further examine the basicities of the alkoxides **1b** and **2b** in Me_2SO.



3 **4**

We have attempted to clarify the thermodynamic basicity of the pinanoxide anions **1b** and **2b** by measurement of their equilibrium constants with the weakly acidic Me_2SO, where Me_2SO^- denotes the dimsyl anion.

$$RO^- + Me_2SO \rightleftarrows ROH + Me_2SO^-$$

In addition, the degree of ionization, measured as the pK_a of the conjugate acid (i.e., the alcohol), was measured in a solution of Me_2SO. Measurements of the equilibrium constants were performed colorimetrically and conductimetrically, since both methods have been previously shown to yield reliable results.[7,8] The primary goal of these studies was to compare the base strength of the pinanoxides and the more commonly used potassium *tert*-butoxide. Tricyclohexylmethoxide has been reported to be considerably stronger than *tert*-butoxide in THF[9] and was also included in our studies.

The relationship between base strength and degree of Hofmann elimination from 2-haloalkanes has been established by Bartsch.[10] Of considerable interest is the behavior of highly ramified bases such as tricyclohexylmethoxide[11] and the compact, but hindered, bases such as the pinanoxides, whose basicities would be expected to exceed that of *tert*-butoxide.[4] While the amount of dimsyl anion present in a solution of *tert*-butoxide in Me_2SO is very low[12] and does not greatly interfere with the positional orientation of elimination reactions,[13] the effect on orientation of bases stronger than *tert*-butoxide, which have significant concentrations of dimsyl anion, is unknown. It was of interest, therefore, to examine the orientation vs. basicity correlation in solutions containing alkoxide and methide base species where kinetic and thermodynamic basicities may have a different influence.

Results and Discussion

Colorimetric Determination of Base Strengths. The method used for the colorimetric determination of the pK_a of the alcohols is similar to that described by Bordwell et al.[14] The method is based on the attainment of equilibrium between the acid of interest and a second acid, of known pK_a, containing a known concentration of its colored anion. The final equilibrium state is determined from the known extinction coefficient of the colored anion and the initial concentrations of all the species involved.

The pK_a's of the acids *tert*-butyl alcohol, *cis*-pinanol, *trans*-pinanol, and tricyclohexylmethanol were determined with this method at various concentrations by titrating solutions of the respective acids against solutions of the indicator acids. The indicator acids were chosen so that

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[1] The older literature refers to **1a** and **2a** as pinene hydrate and methyl nopinol, respectively. *cis*- and *trans*-pinanol are available from PCR Research Chemicals Inc.

[2] Ohloff, G.; Klein, E. *Tetrahedron* **1962**, *18*, 37.

[3] Indyk, H.; Whittaker, D. *J. Chem. Soc., Perkin Trans. 2* **1974**, 313. Salmon, J. R.; Whittaker, D. *J. Chem. Soc. B* **1971**, 1249.

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[7] Bordwell, F. G.; Matthews, W. S. *J. Am. Chem. Soc.* **1974**, *96*, 1214, 1216.

[8] Exner, J. H.; Steiner, E. C. *J. Am. Chem. Soc.*, **1974**, *96*, 1782.

[9] Brown, C. A. *J. Chem. Soc., Chem. Commun.* **1974**, 680.

[10] Bartsch, R. A.; Pruss, G. M.; Bushaw, B. A.; Wiegers, K. E. *J. Am. Chem. Soc.* **1973**, *95*, 3405. Bartsch, R. A.; Weigers, K. E.; Gruitz, D. M. *Ibid.* **1974**, *96*, 430.

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

[12] Ritchie, C. D.; Uschold, R. E. *J. Am. Chem. Soc.* **1967**, *89*, 2960.

[13] Bartsch, R. A. *J. Org. Chem.* **1970**, *35*, 1023, 1334.

[14] Mathews, W. S.; Bares, J. E.; Bartmess, J. E.; Bordwell, F. G.; Cornforth, F. J.; Drucker, G. E.; Margolin, Z.; McCallum, R. J.; McCollum, G. J.; Vanier, N. R. *J. Am. Chem. Soc.* **1975**, *97*, 7006. Bordwell, F. G. *Pure Appl. Chem.* **1977**, *49*, 963.

0022-3263/80/1945-0895$01.00/0

Table I. Measured pK_a using the Colorimetric Method

base	pK_a of conjugate acid	base	pK_a of conjugate acid
tert-butoxide	30.4	*cis*-pinanoxide (2)	32.6
tricyclohexylmethoxide	32.5	*trans*-pinanoxide (1)	32.8

their pK_a's differed by no more than two units from the acid of interest. Triphenylmethane was used as the indicator for determining the pK_a of *tert*-butyl alcohol in accordance with other experimenters.[12,14] The other three acids, because of their larger pK_a's, were measured by using diphenylmethane (DPM). The indicator method for estimating acidity has been used primarily to obtain pK_a values of carbon acids or stronger oxyacids.[14] In such cases the only equilibrium which needs to be considered is that between the indicator anion (In$^-$), generated by reaction with dimsyl and the acid of interest, ROH (eq 1).

$$ROH + In^- \rightleftarrows RO^- + HIn \quad (1)$$

$$RO^- + K^+ \rightleftarrows ROK \quad (2)$$

$$RO^- + Me_2SO \rightleftarrows Me_2SO^- + ROH \quad (3)$$

$$Me_2SO^- + K^+ \rightleftarrows Me_2SOK \quad (4)$$

$$Me_2SO + In^- \rightleftarrows Me_2SO^- + HIn \quad (5)$$

$$In^- + K^+ \rightleftarrows KIn \quad (6)$$

$$RO^- + ROH \rightleftarrows (RO)ROH^- \quad (7)$$

The colorimetric technique for evaluating pK_a is subject to serious interference from contaminants, and although extensive precautions were taken to protect the solutions from the atmosphere and other foreign matter, it is unlikely that all interferences were eliminated. Because of these interferences, most of which would tend to increase the acidity of the system, the pK_a's obtained should be regarded as lower limits.[15]

The average values of pK_a obtained in three experimental runs for each of the measured compounds are shown in Table I and reveal the anticipated increase in base strength with increased steric effects[16] in going from *tert*-butoxide to tricyclohexylmethoxide and the pinanoxides **1b** and **2b**. Brown determined the relative base strengths for a series of alkoxides in THF, including tricyclohexylmethoxide, and found it to be considerably stronger than *tert*-butoxide.[9] It is therefore significant that the pinanoxides are at least as basic as tricyclohexylmethoxide, although it is difficult to precisely measure base strengths in extreme systems such as those reported here. In addition to the ease of contamination previously discussed, other effects tend to obscure the true value of the pK_a's when these are measured colorimetrically. Ion pairing in potassium dimsyl and alkoxide solutions (eq 2, 4, and 6) would tend to introduce a significant error in colorimetrically determined pK_a's. In fact, ion pairing in potassium *tert*-butoxide and dimsyl solutions has been previously reported,[8,17] and we have no reason to believe that other alkoxides would behave differently. Using the value for the ion-pairing constant obtained by Exner and Steiner[8] for potassium dimsyl, we calculate that at a typical working concentration of 0.01 M, ca. 12% of the potassium dimsyl is associated in Me$_2$SO. Arnett has shown that because Me$_2$SO is a poor anion solvator, in the presence of alcohol, alkoxide ions resort to homohydrogen bonding for stabilization[18] (eq 7). This means that new species, mainly RO$^-$–ROH, are formed as the alkoxide reacts with Me$_2$SO, thus forming alcohol (eq 3), and compete with the color-producing reaction which we hoped to measure. An additional difficulty in establishing absolute values of pK_a is the fact that at very low acid strengths, such as were measured here, the indicator anion can enter into a competitive equilibrium with Me$_2$SO (eq 5). This would not be expected to cause difficulties when triphenylmethane, which is at least five orders of magnitude more acidic than Me$_2$SO, is used, but represents a real problem with measurements using DPM as indicator. Bordwell has studied the equilibrium between DPM and Me$_2$SO and found deviation from Beer's law in the behavior of the system.[19] The effect of this deviation was minimized by carrying out the experiments at a fairly high concentration of alcohol, within the linear portion of the absorbance curve. At the typical experimental concentration of 0.01 M, we calculated that the equilibrium constant would be in error by approximately ±0.4 pK units by making the assumption that the DPM anion absorption behaved according to Beer's law.

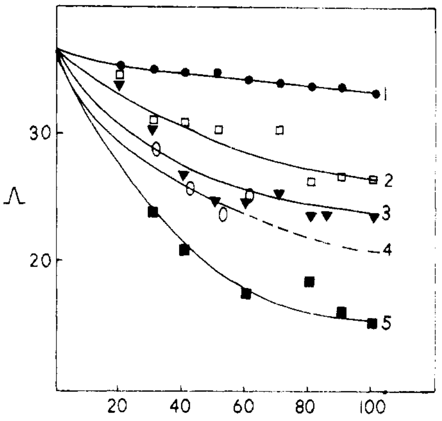

Figure 1. Limiting equivalent conductivities as a function of concentration for the potassium alkoxides in Me$_2$SO. Points are measured experimental values; lines are estimated: 1 = dimsyl, 2 = *trans*-pinanoxide, 3 = *cis*-pinanoxide, 4 = tricyclohexylmethoxide, 5 = *tert*-butoxide.

Conductimetric Determination of Base Strength. Due to the high basicity of the systems under study and the uncertainty of the pK_a's determined colorimetrically, an alternate method for the evaluation of equilibrium constants was used. Measurements of the conductivity of the potassium alkoxides in Me$_2$SO were carried out in the concentration range of 0.001–0.01 M. For a strong electrolyte, a plot of the apparent equivalent conductivity, Λ, vs. the square root of the concentration exhibited a linear relationship. The accuracy of the experimental procedure was checked by comparing the data obtained for potassium dimsyl with published data[8] and was found to be similar within experimental error. Extrapolation to infinite dilution[20] gave a limiting equivalent conductivity of 36.53. This compares favorably with the value of 37.30 obtained

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(15) From replicate experiments the standard deviation was found to be about 0.3 pK units. It should be noted, however, that errors due to impurities and oxygen contaminants would be reproducible in all runs and would introduce a constant error into the experiment.

(16) Acharya, S. P.; Brown, H. C. *J. Chem. Soc., Chem. Commun.* **1968**, 305.

(17) Schriesheim, A.; Rowe, C. A. *J. Am. Chem. Soc.* **1962**, *84*, 3160. Cram, D. J.; Kingsbury, C. A.; Rickborne, B. *Ibid.* **1961**, *83*, 3688.

(18) Arnett, E. M.; Small, L. E. *J. Am. Chem. Soc.* **1977**, *99*, 808.

(19) We thank Professor Bordwell for this information. The pK_a's of the alkoxides reported here must be regarded as relative and are likely to be subject to revision.

(20) Fuoss, R. M.; Krauss, C. A. *J. Am. Chem. Soc.* **1933**, *55*, 476.

Table II. Variation in Percentage of 1-Butene from 2-Iodobutane[a] at 50 °C

entry	base	pK_a of conj acid in Me_2SO	% 1-butene	trans/cis[i]	solvent
1	sodium benzoate	11.1[b]	6.1	2.68	Me_2SO
2	sodium acetate	12.6[b]	6.6	2.86	Me_2SO
3	sodium phenoxide	18.0[c]	9.9	3.79	Me_2SO
4	potassium methoxide	28.2,[d] 27.9[e]	18.5	3.24	Me_2SO
5	potassium *tert*-butoxide	30.4,[f] 30.6[g]	21.5	3.34	Me_2SO
		29.2[e]	20.6	3.11	DMF
	sodium *tert*-butoxide		20.2	3.22	Me_2SO
6	potassium tricyclohexylmethoxide	32.5[f]	26.7	2.90	Me_2SO
7	potassium *cis*-pinanoxide	32.6[f]	20.6	3.29	Me_2SO
			21.7	3.86	DMF
	sodium *cis*-pinanoxide		20.5	3.42	Me_2SO
8	potassium *trans*-pinanoxide	32.8[f]	20.8	3.45	Me_2SO
			21.2	3.75	DMF
	sodium *trans*-pinanoxide		20.0	3.11	Me_2SO
9	potassium dimsyl	35.1[h]	17.9	3.15	Me_2SO
10	sodium dimsyl		10.0	3.15	Me_2SO
11	potassium (methylsulfonyl)methide	31.1[h]	19.6	2.90	Me_2SO
12	sodium (methylsulfonyl)methoxide		11.3	3.14	Me_2SO

[a] [2-BuI] = 0.1 M, [base] = 0.25 M; the olefinic percentages are reproducible to ±1%. [b] Kolthoff, I. M.; Chantooni, M. K.; Bhowmik, S. *J. Am. Chem. Soc.* **1968**, *90*, 23. [c] Bordwell, F. G. "EUCHEM Conference on Mechanisms of Elimination Reactions"; Assisi, Italy, 1977. [d] Coetzee, J. F.; Ritchie, C. D. "Solute-Solvent Interactions"; Marcel Dekker: New York, **1969**; p 230. Value adjusted by using *t*-BuOK, pK_a = 30.4[f]. [e] Reference 18. [f] This work. [g] Value from ref 12 adjusted to pK_a = 35.1 for Me_2SO. [h] Reference 14. [i] Ratio of *trans*- to *cis*-2-butene.

by Exner and Steiner.[8] The apparent equivalent conductivities of the potassium alkoxides were determined by direct comparison of the measured resistance to that of an equimolar concentration of potassium dimsyl. These results are shown in Figure 1. As expected, the values of Λ for the alkoxides roughly parallel the order of basicities determined by the colorimetric method, since as the basicity of the alkoxide increases, the equilibrium will be further to the right.

$$RO^- + Me_2SO \rightleftarrows Me_2SO^- + ROH$$

It is difficult to precisely correlate the conductivity behavior of alkoxide–dimsyl systems with their basicity due to the lack of exact knowledge of the pertinent equilibria. In their work on the ion-pairing behavior of *tert*-butoxide, Exner and Steiner[8] developed a mathematical model which was fitted to the obtained conductivity data by using a scheme of seven equilibrium processes. These included the alkali–base ion-pairing processes (eq 2 and 4), the solution process of eq 7, and the proton-exchange reaction of eq 3. In addition eq 8–10 were

$$RO(ROH)^- + ROH \rightleftarrows RO(ROH)_2^- \tag{8}$$

$$RO(ROH)^- + K^+ \rightleftarrows KRO(ROH) \tag{9}$$

$$RO(ROH)_2^- + K^+ \rightleftarrows KOR(ROH)_2 \tag{10}$$

added in order to correctly fit the shape of the conductivity curve. Although this model fits the experimental data quite well, we have doubts as to its ability to yield reliable values for each of the equilibrium systems involved. Indeed, a discrepancy of nearly 2 orders of magnitude is observed between the values for the equilibrium constants obtained for eq 3 using the mathematical model and the values directly obtained by Ritchie[12] and by Bordwell[21] (1.3×10^{-3} vs. 3.3×10^{-5} and 1.7×10^{-5}, respectively). This discrepancy can only be explained by invoking a more complicated equilibrium scheme.

Our conductivity measurements empirically support the idea of an extremely complex system of equilibria. Attempts were made to calculate the conductivity vs. concentration curve for the alkoxides of interest by using the values of pK_a determined colorimetrically along with literature or estimated values for the other equilibria.[8] Limiting equivalent conductivities for the alkoxides and solvated anions were estimated from their ionic size. Although it was reasonably easy to calculate curves of the desired shape, we had no success in satisfactorily fitting our conductivity values. In all cases, the calculated results were larger than the experimental values. This pattern can be easily rationalized if one considers that any aggregation of ions, such as further solvation or ion pairing, would tend to decrease the observed value of the equivalent conductivity of the solution.

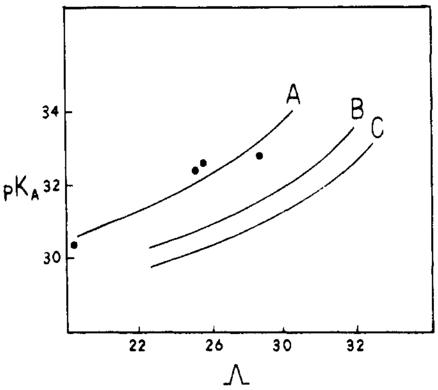

Figure 2. Plot of measured Λ at 0.05 M vs. calculated pK_a by using three equilibria (curve C) and four equilibria (curve B). Experimental results are shown with curve A drawn only for reference.

A comparison of the experimental results at a concentration of 0.05 M with results obtained by mathematical modeling of the system using only three (eq 2, 3, and 4) and four equilibria (eq 2, 3, 4, and 6) is shown in Figure 2. It can be easily seen that although inclusion of further equations will continue to bring the experimental and calculated values closer to one another, the pattern of basicity will remain the same, and complete correlation can only be regarded as fortuitous in light of the number of estimates involved in the calculations.

Elimination Reactions. 2-Iodobutane was subjected to reaction with the pinanoxide bases **1b** and **2b** at 50 °C

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[21] The value we attribute to Bordwell was calculated from the data of ref 12 by using a pK_a value of 30.6 for triphenylmethane.[14]

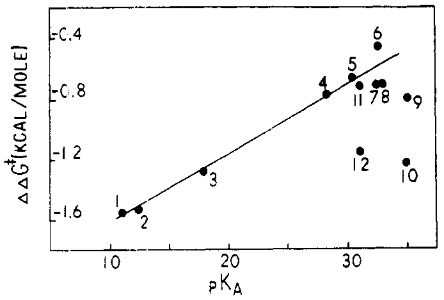

Figure 3. Plot of the free-energy difference for formation of 1-butene and *trans*-2-butene vs. the pK_a of the conjugate acid of the base.

in Me_2SO by using the sweep-gas technique developed by Bartsch.[10,22] To provide reference data, we also examined potassium methoxide and *tert*-butoxide and sodium benzoate, acetate, and phenoxide bases. These results (Table II) are within experimental error of the published data[10] and show a clear correlation between the differences in transition-state free energies for formation of positional isomers ($\Delta\Delta G^{\ddagger}$) and basicity[23] (Figure 3). A small deviation from this correlation is observed for the pinanoxide bases (entries 7 and 8) as well as for tricyclohexylmethoxide (entry 6), the former giving less and the latter giving more 1-butene than would be expected on the basis of basicity alone. The lower than expected terminal olefin yield observed with the pinanoxides was not a result of competing olefin isomerization which can occur under these conditions.[24]

Surprisingly, potassium dimsyl (entry 9) gave significantly more 1-butene than sodium dimsyl (entry 10). However, sodium *tert*-butoxide and the sodium pinanoxides gave relative proportion of 1-butene and $\Delta\Delta G^{\ddagger}$ values very close to those of the potassium alkoxides. To determine if a base-association phenomenon existed or if the potassium dimsyl solutions decomposed to other basic species,[26] we used dimethyl sulfone as its sodium (entry 12) and potassium (entry 11) methide bases. As in the dimsyl case a substantial difference in 1-butene formation was observed. In both methide bases examined the countercation change results in $\Delta\Delta G^{\ddagger}$ differences of ca. 0.4 kcal mol^{-1}. It is tempting to dismiss the cation influence as a result of differences arising from elimination by associated and dissociated methide anions.[27] However, the effect of associated base in hydroxylic solvents has been shown to increase the proportion of terminal olefin.[28] The reversal of this behavior in a polar nonhydroxylic solvent such as Me_2SO may be due to contributions from ion aggregation, solvation, or association changes.

For very strong bases such as the pinanoxides, in which substantial concentrations of dimsyl anion coexist, the possibility arises that the dimsyl anion could act as a competitive base and lower the proportion of terminal olefin. Indeed, the dimsyl anion has been claimed to be the exclusive agent for effecting the isomerization of 1-octene,[29] although the present data do not show this to be the case in elimination reactions. In each of these reactions, both the kinetic and thermodynamic basicities of the respective species must be considered.

To examine the kinetic basicity of the dimsyl anion compared with that of the strong basic alkoxides, we measured the rate of gas evolution from the reaction of 2-iodobutane with sodium dimsyl and found it to be comparable with that observed when sodium *tert*-butoxide, ethoxide, or pinanoxides were used. These results indicate that the rates of elimination by alkoxide and dimsyl bases are of the same order of magnitude and that one might expect to see some contribution of this competition to the amount of 1-butene formed from the pinanoxides.[30] In order to overcome this competition, we carried out the elimination reactions using potassium *tert*-butoxide and *cis*- and *trans*-pinanoxides in DMF. Bartsch has previously shown that *tert*-butoxide in DMF gives a product distribution very similar to that obtained in Me_2SO.[13] Suppression of the competition of dimsyl anion with the pinanoxides by conducting the reaction in DMF had no effect on the percent of 1-butene or $\Delta\Delta G^{\ddagger}$. This could also be the result of several factors such as solvation, dielectric constant, and the overall lack of sensitivity of the technique to detect small changes. However, the role of the dimsyl anion in this particular reaction is believed to be small for two reasons: first, because of the small deviation from expected behavior by the pinanoxides and second, because changing the cation in these bases exerted no change in terminal olefin percentage, unlike the methide bases.

The relationship between base strength and the degree of Hofmann elimination is seen to hold reasonably well for very strong bases such as the pinanoxides. It is surprising that these strong bases do not appear to exhibit steric effects in this elimination reaction.[31] Thus, there appears to be, for the first time, a clear differentiation between base-size and base-strength effects for bases stronger than *tert*-butoxide. It has been assumed in the past that increased alkoxide strength is a function of inductive effects and of solvation which is dependent upon steric hindrance. Perhaps a distinction should be drawn between two types of steric hindrance which affect the measurable basicity of an alkoxide. First, there is the hindrance which renders the alkoxide inaccessible for solvation by the solvent. Second is the hindrance or steric bulk which prevents the alkoxide from approaching a relatively inaccessible proton. For the most part, these two effects go hand in hand—a hindered ramified alkoxide will not be well solvated and, in the reaction with 2-iodobutane, for example, will abstract the more available proton and provide more Hofmann product. The pinanoxides may present an example where these two factors are differentiated. They are very resistant to solvation and therefore very basic. However, they are also extremely compact relative to such bases as tricyclohexylmethoxide and show no steric effect in the aforementioned elimination. The recent report of elimi-

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[22] The authors are grateful to Professor Bartsch for providing details of the apparatus and helpful discussions.

[23] A similar plot is obtained from the free-energy differences for the formation of 1-butene and *cis*-2-butene vs. pK_a for these bases.

[24] A small but significant amount of isomerization of 1-butene to *cis*-2-butene by the strong bases[25] was observed with time with this particular apparatus. All experimental results were corrected for this isomerization.

[25] Pines, H.; Stalick, W. M. "Base-Catalyzed Reactions of Hydrocarbons and Related Compounds"; Academic Press: New York, 1977; p 43.

[26] The thermal decomposition of sodium dimsyl has been observed. Price, C. C.; Yukuta, T. *J. Org. Chem.* **1969**, *34*, 2503. Photochemical reactions of carbanions in Me_2SO have also been observed. Tolbert, L. M. *J. Am. Chem. Soc.* **1978**, *100*, 3952. The experience of these authors has been that a potassium dimsyl solution is even more labile than a sodium dimsyl solution and deteriorates at room temperature within a few hours.

[27] The degree of dissociation of sodium and potassium dimsyl has been shown to differ significantly.[18]

[28] Bartsch, R. A.; Pruss, G. M.; Cook, D. M.; Buswell, R. L.; Bushaw, B. A.; Wiegers, K. E. *J. Am. Chem. Soc.* **1973**, *95*, 6745.

[29] Asinger, F.; Fell, B.; Krings, P. *Chem. Ber.* **1966**, *99*, 1737.

[30] On the basis of the relative pK_a's, we estimate the following percentages of dimsyl anion in an 0.25 M alkoxide/Me_2SO solution: ca. 41%, *trans*-pinanoxide; ca. 35%, *cis*-pinanoxide; ca. 31%, tricyclohexylmethoxide; ca. 3%, *tert*-butoxide.

[31] Bartsch, R. A.; Read, R. A.; Larsen, D. T.; Roberts, D. K.; Scott, K. J.; Cho, B. R. *J. Am. Chem. Soc.* **1979**, *101*, 1176.

Table III. ^{13}C Chemical Shifts of 1 and 2[a]

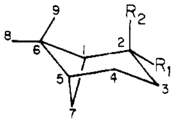
carbon	δ_{1a}	$\Delta\delta_{1b}$[b]	δ_{2a}	$\Delta\delta_{2b}$[b]	δ_{2a}[c]
1	54.4	2.6	53.6	3.0	53.7
2	72.9	−0.9	74.4	−0.6	76.0
3	32.0	4.2	31.95	4.6	32.1
4	27.3	0.8	28.2	1.5	28.5
5	40.6	0.6	41.1	0.4	40.8
6	37.8	0.3	38.5	0.1	38.4
7	25.0	0.7	24.5	0.8	24.4
8	27.9	0.7	27.9	0.6	27.6
9	23.4	0.7	23.8	0.5	23.6
10	31.6	3.3	32.0	3.3	31.7

[a] Spectra recorded in Me_2SO-d_6. The alcohols were recorded at 50 °C relative to tetramethylsilane as internal standard. The alkoxides were recorded at 60 °C relative to Me_2SO (δ 40.0). [b] $\Delta\delta = (\delta_{RONa} - \delta_{ROH})$. [c] $CDCl_3$, reassigned literature values.[34]

nations from 4-methyl-2-pentyl iodides and tosylates[31] suggests that these substrates may provide an even more sensitive probe to differentiate between steric-bulk and steric-hindrance effects for these and other strong bases.

Conformational Analysis of the *cis*- and *trans*-Pinanoxides. The similarity in base strengths of the pinanoxides is somewhat surprising if one considers steric hindrance to solvation to exert the major influence since the oxyanion is on the more accessible α face in *cis*-pinanoxide whereas in *trans*-pinanoxide it is nestled in the cavity formed on the β face by the cyclobutane ring and the C_9 methyl group. In an effort to understand more clearly the similar basicities of **1b** and **2b**, we turned to the conformational analysis of the alkoxides in Me_2SO solution.

The bicyclo[3.1.1] skeleton of the pinanols has a great deal of flexibility and can adopt the bridged chair (**5**), the planar Y (**6**), or the bridged boat (**7**) conformations.[32] While the pinanols can be readily distinguished by their ^1H NMR spectra due to the shielding of the C_{10} methyl (R_2 in **1a**) by the ring in *cis*-pinanol,[33] the conformations are more difficult to determine. Whittaker[34] has recently applied ^{13}C NMR analysis to determine the conformation of a variety of pinane derivatives. That analysis of *trans*-pinanol suggested that it existed in the Y conformation. This is surprising in that it is the only pinane not possessing a double bond (which locks the molecule in a Y conformation) to have this conformation. This planar conformation has severe eclipsing interactions. We have analyzed the ^{13}C spectra of *cis*- and *trans*-pinanol and their sodium alkoxides in Me_2SO-d_6 and have reassigned[35] the chemical shifts of C_7, C_8, and C_{10} in *trans*-pinanol. The significance of this reassignment lies in the use of the C_7 chemical shift to determine the conformation (Table III). The change of chemical shift of C_7 would result in the reassignment of the chair conformation to *trans*-pinanol due to the upfield shift[34] of C_7, resulting from steric interaction between C_3 and C_7. It is clear from Table III that the chair conformation would also be preferred by *cis*-pinanol and both alkoxides (**1b** and **2b**). However, Stevens has recently calculated that the skewed boat is the preferred conformation for *cis*-pinanol.[36] The apparent discrepancy with the ^{13}C data may be due to the upfield shift of C_7 resulting from steric interaction with the pseudoaxial hydroxyl group rather than with C_3. Thus, the difficulty of conformational determination in bicyclo[3.1.1] ring systems by this technique is exemplified.



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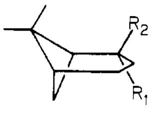

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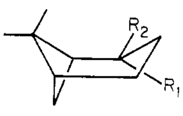

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Although *trans*-pinanoxide is more sterically hindered than the *cis* compound, in both cases the relative inaccessibility of the oxyanion apparently renders solvation difficult, thereby increasing the basicities and making the pinanoxides the most basic alkoxides yet measured.[37]

Experimental Section

cis- and *trans*-pinanol were distilled to at least 99.6% purity. Tricyclohexylmethanol (Aldrich) was used without further purification. Me_2SO was freshly distilled after at least 8 h of refluxing over calcium hydride. The first cuts were discarded. Sodium hydride and potassium hydride were obtained from Ventron and Parrish Chemical Co., respectively. ^{13}C NMR spectra were measured at 60.905 MHz on a Bruker HFX-270 Fourier transform spectrometer. Chemical shifts are reported in parts per million (δ) downfield from tetramethylsilane for the alcohols.

Colorimetric Measurements. The experimental technique for all the colorimetric work is similar to that described by Bordwell and co-workers.[14] Because of the ease of contamination of the compounds of interest with more acidic compounds, extreme care was taken in the handling and transferring of reagents. All glassware and reservoirs were thoroughly cleaned and dried in an oven at 120 °C, followed by storage in a vacuum desiccator for several hours prior to use. Solutions of the acids were made by adding the sample into a dried, tared container and capping it with a silicone-rubber septum. The container was weighed, and the desired volume of freshly distilled Me_2SO was added by means of a syringe, with the exact amount determined gravimetrically. All subsequent transfers were made by means of syringe.

Conductance Measurements. All conductivity measurements were made by employing a YSI conductivity bridge, Model 31. The conductivity cell was of the dipping type, and its constant was determined by calibration with a standard solution of potassium chloride.[38] Replicate measurements gave a value of 0.184 ± 0.001 cm^{-1} for the cell constant, and this value was used throughout the calculations.

A three-necked, 250-mL, round-bottomed flask was fitted with the conductivity cell by means of a standard-taper joint. To this vessel was added a measured amount of Me_2SO, typically 200 mL, enough to cover the Pt electrodes. A 50-mL equilibrated buret containing a standardized solution, approximately 0.05 M, of the alkoxide of interest in Me_2SO was connected to the flask. A side arm in the buret was connected to a dry-nitrogen line which continuously flushed the system at a flow of approximately 30 mL min^{-1}. The mixture was stirred gently with a magnetic bar.

Before the start of an experiment, the entire assembly was dried in a 120 °C oven overnight and allowed to cool in a vacuum desiccator. All transfers of solutions were made under nitrogen in a glovebag. Conductimetric measurements were taken of the pure Me_2SO and of the solution resulting from addition of a known volume of alkoxide solution from the buret. Readings stabilized in a matter of minutes and were stable for at least 8 h. Thermostating of the experimental assembly was deemed unnecessary as the laboratory temperature varied by less than 0.5 °C in the time required to perform an experiment (usually about 20 min). The laboratory temperature was measured by using a digital

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[32] The methylene group at C_7 is regarded as the bridging carbon.

[33] Coxon, J. M.; Dansted, E.; Hartshown, M. P.; Richards, K. E. *Tetrahedron Lett.* **1969**, 1149.

[34] Holden, C. M.; Whittaker, D. *Org. Magn. Reson.* **1975**, *7*, 125.

[35] The authors are grateful to Dr. Whittaker for confirmation of these observations.

[36] Texter, J.; Stevens, E. S. *J. Org. Chem.* **1979**, *44*, 3222.

[37] The interference of competing equilibria with more acidic alcohols has now been corrected. The pK_a values of MeOH, EtOH, and *i*-PrOH in Me_2SO have been determined as 29.0, 29.8, and 30.25, respectively. The value of *t*-BuOH has been calculated to be 32.2. Olmstead, W. N.; Margolin, Z.; Bordwell, F. G., submitted for publication in *J. Org. Chem.* We thank Professor Bordwell for these data.

[38] Daggett, H. M.; Bair, E. J.; Kraus, C. A. *J. Am. Chem. Soc.* **1951**, *73*, 799.

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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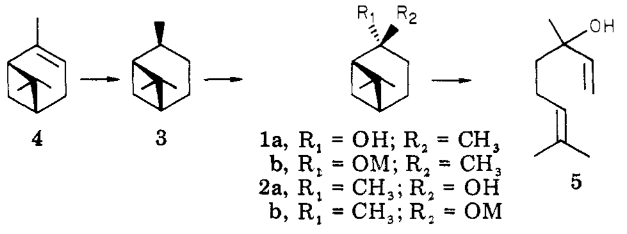
The utility of the alkoxides of *cis*- and *trans*-2-pinanol has been investigated. Yields comparable to and exceeding those obtained with *tert*-butoxide are reported for the alkylation of ethyl acetoacetate, for the conversion of α-pinene oxide to *trans*-pinocarveol and *cis*-3-pinen-2-ol, and for 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



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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

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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.

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[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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