0.1 *M* NaCl-D_2O was maintained at 54.8° and integrated with the others. After 2 months no sign of exchange was observed—the nmr peaks were still sharp and unsplit,[10,11] and the integral values were unchanged from the original. We were, therefore, unable to obtain rate constants for the uncatalyzed reaction. This contrasts with Rappe's findings,[4,5] which were that, after "several months" at 30°, exchange could be observed. After 2 months at nearly double this temperature we could observe none. This finding is in accord with our previous estimate[1] that the uncatalyzed reaction would contribute 1% or less to the total reaction at 60°, with acetate concentrations in D_2O of 0.1 *M* or more. In support also is Hine's recent estimate[8] that the uncatalyzed deuteration of methoxyacetone would contribute a maximum value of 0.2% of the total to base-catalyzed reaction rates, under a wide variety of conditions. It is likely that a high rate of "uncatalyzed exchange," where observed, is really the result of catalysis by unrecognized impurities.

We believe that this work firmly establishes the dependence of relative catalytic constants (k_{CH_2}/k_{CH_3}), for deuterium exchange into 2-butanone, on the nature of the catalyzing base. Such dependence was to be expected, since enolization is closely analogous to bimolecular elimination, in which product ratios depend on the base employed.[12] The relative importance of the steric requirements of the base and of its strength is not completely understood at this time.[12]

Experimental Section

Reagent grade chemicals were used; acetic acid and 2-butanone being redistilled before use. Sodium acetate was dried at 160° to obtain the anhydrous material. D_2O was used as supplied by the Columbia Organic Chemicals Co. Stock reagent solutions, made up gravimetrically, were two sodium acetate-acetic acid buffer solutions in D_2O, with buffer ratios of 0.0936 and 0.0469; the acetate concentration in each case being about 1.1 *M*. Aliquots of these solutions were then diluted with a solution of sodium chloride in D_2O of equivalent molarity. By this procedure ten solutions with acetate concentrations varying between about 1.1 and 0.11 *M*, at a constant buffer ratio of 0.0936 and a constant ionic strength of about 1, were obtained, as well as ten similar solutions at a buffer ratio of 0.0469. Addition of 0.1 ml of 2-butanone to 1 ml of the above solutions resulted in a 2-butanone concentration of 1.18 *M*, an ionic strength of 1.04, and the acetate concentrations shown in Table I. After mixing, the solutions were sealed into standard nmr tubes which had been cleaned with chromic acid, thoroughly rinsed, and dried.

Samples were immersed in a thermostat at 54.8°, together with a sample containing 2-butanone and 1.04 *M* sodium chloride, but no acetate. Integrations were performed every 1 or 2 days as necessary, after quenching exchange by chilling the tube with ice. Reaction outside the bath was negligible, and time outside the bath was not counted.

Exchange was followed to at least one half-life by integrating the signals from the 1 and 3 positions, using the β-methyl group as internal standard, on a Varian A-60 instrument.[1,11] Each sample was integrated six times and an average was taken.

The integral from the β-methyl group was taken as internal standard and the areas for the 1 and 3 positions were converted into the average number of hydrogen atoms per molecule remaining at these positions. On plotting the logarithms of these numbers against time, good straight lines were obtained even for exchanges followed to over two half-lives. Each graph contained at least 15 points. A linear least-squares program for the IBM 7040 computer was used to obtain pseudo-first-order rate constants and their standard deviations, and, from these figures, acetate catalysis constants.

For the study of deuterioxide catalysis at 54.8°, a deuterioxide concentration of 1.962×10^{-3} *M* was used. The probe temperature was set, using the variable-temperature controller, at 54.8 ± 0.5°, and the deuterioxide solution was equilibrated to that temperature by leaving it in the probe for a few minutes. Butanone at the same temperature was then added, after which the tube was shaken and replaced in the probe. Integrations were performed every 150 sec over a 90-min period, which was about one half-life under the reaction conditions. The signal from the nonexchanging β-methyl group was used to normalize integrals (I_t) as described above, and best fits to the equation $\log I_t = k^{\text{obsd}}t/2.303$ were computed.

Registry No.—2-Butanone, 78-93-3.

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[10] Splitting of the nmr peaks was taken to be a more reliable indication of initial deuterium substitution than change in the integral values. See ref 11 for splitting patterns resulting from varying amounts of substitution.

[11] O. S. Tee and J. Warkentin, *Can. J. Chem.*, **43**, 2424 (1965).

[12] H. C. Brown and R. L. Klimisch, *J. Amer. Chem. Soc.*, **88**, 1425 (1966), and references contained therein.

Conformational Analysis of the Carbon–Oxygen Bond of Alcohols Using J_{HCOH}

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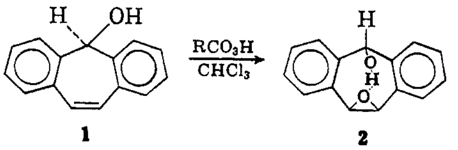
Since the report that J_{HCOH}[1] can often be determined in DMSO solution[2], several papers[3-6] have appeared in which a conformational dependence is invoked for J_{HCOH} similar *in qualitative form* to that observed for J_{HCCH}.[7,8] Unfortunately, it is difficult to restrict rotation about the C–O bond of an alcohol, so that values of J^{trans}_{HCOH} and J^{cis}_{HCOH} have not been available, thus precluding corroboration and quantitative application of this potentially useful conformational probe. We have, quite fortuitously,[9] synthesized an alcohol in which the pertinent rotation is restricted by strong internal hydrogen bond formation and from which a value can be obtained for J^{trans}_{HCOH}.

Epoxidation of **1** by *m*-chloroperbenzoic acid yields **2**; the nmr ($CDCl_3$) spectrum showed signals at τ



1 **2**

2.75 (m, 8 H, aromatics), 4.65 (d, 1 H, *J* = 12.5 cps, carbinol methine), 5.20 (d, 1 H, *J* = 12.5 cps, hydroxyl), 5.59 (s, 2 H, methines adjacent to epoxide function). The infrared spectrum has a single,

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[1] *I.e.*, the nmr coupling constant of a hydroxyl proton with a vicinal carbinol proton.

[2] O. L. Chapman and R. W. King, *J. Amer. Chem. Soc.*, **86**, 1256 (1964).

[3] C. R. Rader, *ibid.*, **88**, 1713 (1966).

[4] J. J. Uebel and H. W. Goodwin, *J. Org. Chem.*, **31**, 2040 (1966).

[5] R. J. Ouelette, *J. Amer. Chem. Soc.*, **86**, 4378 (1964).

[6] R. J. Ouelette, D. L. Marks and D. Miller *ibid.*, **89**, 913 (1967).

[7] M. Karplus *ibid.*, **85**, 2870 (1963).

[8] Similar conformational dependencies have been found for J_{HCCCH} (G. J. Karabatsos, C. E. Orzech, Jr., and N. Hsi, *ibid.*, **88**, 1817 (1966)) and J_{HCCF} (K. L. Williamson, Y. Li, F. H. Hall, and S. Swager, *ibid.*, **88**, 5679 (1966)).

[9] N. L. Bauld and Y. S. Rim, *ibid.*, **89**, 179 (1967).

somewhat broad, hydroxyl stretch at ν ($CHCl_3$) 3440 cm^{-1} which is unaffected by dilution (no free −OH from 15–1%). Clearly, **2** is exclusively internally hydrogen bonded and must have the assigned *cis* structure. The strength of the hydrogen bond is such that it resists rapid proton exchange in $CDCl_3$, so that J_{HCOH} is observable (12.5 cps). This value is also obtained in CCl_4 and is unaffected by dilution (15–5% $CDCl_3$) or temperature (−60° to ambient). Even DMSO only slightly disrupts the bond. In this solvent J_{HCOH} = 10.7 cps. The addition of several drops of water still does not affect the hydroxyl doublet, but addition of a few drops of acid does eliminate it.

The coupling constants obtained here are more than twice as large as any we have noted in the literature (3.5–5.7 cps[3–6]). It is therefore suggested, and models support this suggestion, that the internal hydrogen bond of **2** effectively locks the O–H bond into a conformation *trans* (ϕ = 180°) to the carbinol methine C–H bond and that, accordingly, $J_{\mathrm{HCOH}}^{trans}$ = 12–13 cps.

In contrast to **2**, **1** has J_{HCOH} (DMSO) = 4 cps (no splitting observed in $CDCl_3$). This is a typical HCOH splitting and indicates that the large splitting found for **2** is unrelated to the electronegativity of the adjacent phenyl rings.

The value of $J_{\mathrm{HCOH}}^{trans}$ found here is in the range observed for $J_{\mathrm{HCCH}}^{trans}$ (sp^3 carbon) (10.5–12.4 cps[10]). The "free rotation" value of J_{HCOH} (3.5–5.7 cps) is apparently a little smaller than that of J_{HCCH} (6–8 cps). It therefore appears that J_{HCOH} (ϕ) and J_{HCCH} (ϕ) are quantitatively comparable.

Registry No.—**1**, 15591-50-1; **2**, 15591-51-2.

Acknowledgment.—We thank the National Science Foundation and the Welch Foundation for support of this work.

[10] A. A. Bothner-by, "Advances in Magnetic Resonances," Vol. I, Academic Press Inc., New York, N. Y., 1965, p 203.

The Preparation and Reactions of Some Stable Dibenzotropylium and Dihydrodibenzotropylium Ions

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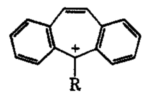
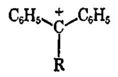
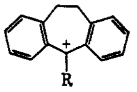
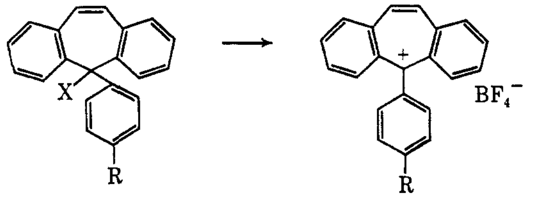
The stability of the dibenzotropylium and some 5-aryldibenzotropylium ions has been determined by measurement of their pK_{R^+} values[1–3] (Table I). These results are noteworthy because the phenyl- and *p*-methoxyphenyl-substituted compounds were less stable than the unsubstituted one. Examination of the pK_{R^+} values of the di- and triphenylmethyl series (Table I) would have predicted the order of stability to be *p*-methoxyphenyl > phenyl > unsubstituted in the dibenzotropylium series. These unexpected results were attributed to steric inhibition of resonance. The dihydrodibenzotropylium ions exhibited the expected order of stability (Table I), the only discrepancy being the large difference in pK_{R^+} between the unsubstituted ion and the diphenylmethyl ion. The values reported in Table I for the dibenzo- and dihydrodibenzotropylium ions have been confirmed in our work.

Table I[a]
pK_{A^+} Values

R			
H	−3.7	−13.3	−8.0
C_6H_5	−5.8	−6.6	−7.0
	−5.7[b]		−6.7[b]
p-$MeOC_6H_4$	−6.1	−3.4	−4.5

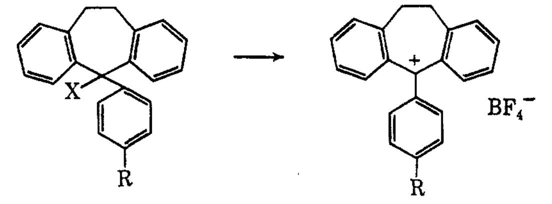
[a] See ref 1. [b] See ref 3.

The purpose of this investigation was to examine the possibility of preparing stable ions of the dibenzotropylium (**2**) and dihydrodibenzotropylium (**4**) types, and study their chemical properties. The ions chosen for examination were those having the *p*-methoxyphenyl (**2a** and **4a**) and *p*-dialkylaminophenyl group (**2b**, **2c**, and **4b**).



1a, R = OMe; X = OH
b, R = NMe_2; X = OH
c, R = OMe; X = H
d, R = OH; X = H
e, R = NMe_2; X = H

2a, R = OMe
b, R = NMe_2
c, R = NEt_2



3a, R = OMe; X = OH
b, R = NMe_2; X = OH
c, R = OMe; X = H
d, R = OH; X = H
e, R = NMe_2; X = H

4a, R = OMe
b, R = NMe_2

The *p*-methoxyphenyldibenzotropylium ion **2a** was isolated as the black fluoroborate in good yield from the corresponding alcohol **1a**, upon treatment with fluoroboric acid. Although it can be stored unchanged in the cold, it is rapidly converted back into the alcohol by atomospheric moisture. Sodium borohydride reduction of **2a** gave ether **1c**, which was identical with material prepared from the *p*-hydroxy compound **1d**. When treated with cycloheptatriene, compound **2a** abstracted a hydride ion and gave the tropylium ion (86%), as would be predicted from the pK_{R^+} values (Table I) of the two ions (tropylium ion pK_{R^+} = +9.9).[4]

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[1] G. Berti and A. DaSettimo, *Ann. Chim.*, **49**, 1237 (1959).

[2] G. Berti, *J. Org. Chem.*, **22**, 230 (1957).

[3] P. Rumpf and R. Reynaud, *Bull. Soc. Chim. Fr.*, **1964**, 558.

[4] A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 365.