the formation of three products as 16, 49, and 35% of volatile reaction product. The products were isolated by preparative glpc.

The first product was identified as ketone **7** and the second product as ketone **6**. The third component was a new compound whose structure is assigned as 2,5-dimethyl-4-isopropenyl-2,3-hexadien-5-ol (**13**), mp 35–36°. This material shows infrared absorption at 2.8, 5.15 (weak), 6.20, and 11.1 μ. The nmr spectrum displays a six-proton singlet at τ 8.66 ($C(CH_3)_2OH$), a six-proton singlet at 8.28 ($C{=}C{=}C(CH_3)_2$), a broad three-proton singlet at 8.22 ($C{=}CCH_3$), a one-proton signal at 7.7 (OH), and two one-proton multiplets at 5.05 and 4.72 ($C{=}CH_2$). The ultraviolet spectrum exhibits λ_{max}^{EtOH} 222 mμ (ϵ 13,600) and λ_{max}^{hexane} 218 mμ (ϵ 9000). The mass spectrum of **13** shows a parent ion at 166.1355 (calcd for $C_{11}H_{18}O$: 166.1358).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.35; H, 10.87.

Acid-Catalyzed Rearrangement of 13.—A small sample of allene **13** was stirred with 15 ml of glacial acetic acid containing 10 drops of concentrated sulfuric acid for 4 hr and the mixture was poured into water and extracted with several portions of pentane. After the combined extracts were dried, the solvent was removed to give a crude product containing **7** as the major component along with a small amount of enol acetate **12** as established by glpc isolation and comparison with authentic samples.

Rearrangement of 4 by Lithium Iodide.—A mixture of 26 mg of **4** and 0.5 g of anhydrous lithium iodide was heated to reflux in 30 ml of anhydrous ether for 56 hr. Glpc analysis indicated the formation of one major product (80%) which was collected by glpc and identified as ketone **6**.

Pyrolysis of 4.—A 102-mg sample of **4** was pyrolyzed in the flow system at 400° and 0.25 mm. This gave an 80% yield of two products in an 80:20 ratio. Isolation by glpc and comparison with authentic samples demonstrated that these materials were ketones **6** and **7**, respectively. In other runs the amount of **7** in the mixture varied from a trace to 20%.

Pyrolysis of 4 over Florisil.—A sample of epoxide **4** was pyrolyzed over Florisil (which had been dried at 200° and 0.25 mm for 4 hr) at 200° in the flow system at 0.25 mm. Glpc analysis indicated formation of 50% of **7** and 5% of **6** which were collected by preparative glpc and compared with authentic samples.

Hydrogenation of 13 in Acidic Methanol.—A 100-mg sample of **13** was dissolved in 10 ml of reagent grade methanol to which 10 drops of concentrated sulfuric acid had been added. This solution was hydrogenated at atmospheric pressure using 30% palladium on charcoal as catalyst. After the uptake of 2 mol of hydrogen, the resulting mixture was filtered to remove the catalyst, the filtrate was poured into 25 ml of water, and extracted several times with 25-ml portions of pentane. The pentane extracts were combined, washed with 25 ml of saturated sodium bicarbonate, and dried. After removal of the solvent by flash evaporation, the major product was isolated by preparative glpc and found to be ketone **11**.

Registry No.—**3**, 13303-30-5; **4**, 15448-69-8; **6**, 4868-12-6; **7**, 15448-71-2; **9**, 15448-72-3; **11**, 15448-73-4; **12**, 15448-74-5; **13**, 15448-75-6.

Acknowledgments.—Support of this research by the National Science Foundation in the form of a research grant (GP-6610) and an instrument grant (GP-5234) for purchase of the mass spectrometer used in this work is gratefully recorded. A Public Health Service Predoctoral Fellowship to D. R. P. is also acknowledged. Finally, the assistance of Mr. A. C. Clark in obtaining the mass spectral data is greatly appreciated.

Solvent Shifts of Proton Resonances Induced by Benzene and Pyridine in Epoxides and Ethers. An Aid to Structure Elucidation

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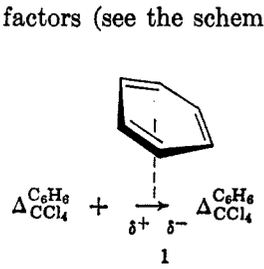
The solvent shifts of proton resonances induced by pyridine and benzene in some epoxides and ethers are reported. In the absence of severe steric effects or of effects due to additional functional groups, the benzene-induced shifts may be useful in differentiating an epoxide from a four-, five-, or six-membered cyclic ether. Different benzene-induced shifts are also observed for α- and β-methyl substituents in tetrahydrofuran derivatives. A preferred conformation for diisopropyl ether in which nonbonded interactions are minimal is also suggested by the solvent shifts. From a study of steric effects upon the shifts caused by the aromatic solvents in epoxyquinones, it is concluded that steric inhibition to the approach of bulk aromatic solvent to an epoxide proton flanked by a *t*-butyl group causes a deshielding contribution to the observed shift.

The solvent shifts of proton resonances induced by benzene relative to an "inert" solvent (solvent shift, $\Delta_{CCl_4}^{C_6H_6} = \delta_{CCl_4} - \delta_{C_6H_6}$ ppm) have proved to be of potential use in the elucidation of structural, stereochemical, and conformation problems; the empirical rules which have been deduced for ketones[1-6] may be cited as an example.

In general, it appears that benzene solvent molecules are transiently orientated by molecular or local solute dipoles, so that the benzene molecules solvate the positive end of the dipole while avoiding the negative end in a collision complex which may deviate from planarity due to steric factors (see the schematic representation **1**).[7]



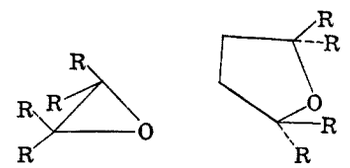
1

It appeared probable that useful correlations might be made for solvent shifts in epoxides and ethers and representative members of these classes have therefore been studied. In this paper the solvent shifts induced by both benzene ($\Delta_{CCl_4}^{C_6H_6}$) and pyridine ($\Delta_{CCl_4}^{C_6H_5N}$) are reported. The $\Delta_{CCl_4}^{C_6H_6}$ values are given first for the appropriate proton with each structure, followed by the

(1) D. H. Williams and N. S. Bhacca, *Tetrahedron*, **21**, 2021 (1965).
(2) G. D. Connolly and R. McCrindle, *Chem. Ind.* (London), 379 (1965).
(3) P. Laszlo and D. H. Williams, *J. Amer. Chem. Soc.*, **88**, 2799 (1966).
(4) C. Timmons, *Chem. Comm.*, 576 (1965).
(5) J. Ronayne, M. V. Sargent, and D. H. Williams, *J. Amer. Chem. Soc.*, **88**, 5288 (1966).
(6) D. H. Williams and N. S. Bhacca, *Tetrahedron*, **21**, 1651 (1965).
(7) J. Ronayne and D. H. Williams, *J. Chem. Soc., Sect. B*, 541 (1967).

corresponding $\Delta_{CCl_4}^{C_5H_5N}$ values in parentheses. All values refer to approximately 5% w/v solutions and normal probe temperature (37.5°). In those cases where the solvent shifts are approximate, the values could not be determined with the desired accuracy; *e.g.*, the resonances were very broad with poor signal to noise ratios.

Various types of cylic ethers (**2–10**) were studied and the values of $\Delta_{CCl_4}^{C_6H_6}$ seem to be quite useful in indicating both the ring size and location of alkyl substituents. Protons directly attached to the epoxide rings undergo a moderately large upfield shift (0.13–0.38 ppm) in benzene relative to carbon tetrachloride. This shift decreases with increasing ring size (compare **2, 6, 7, 10**). Such characteristic differences are to be anticipated since the α protons in a five- and six-membered cyclic ether lie nearer the negative end of the molecular dipole, *i.e.*, nearer the ether oxygen, than they do in trimethylene oxide which in turn has its α protons closer to the oxygen than those in ethylene oxide (contrast **11** and **12**, R = H). The type of association depicted in **1** will thus result in a relatively larger shielding of epoxide protons by benzene due to the anisotropy of the aromatic solvent and a gradual decrease in $\Delta_{CCl_4}^{C_6H_6}$ with increasing ring size.

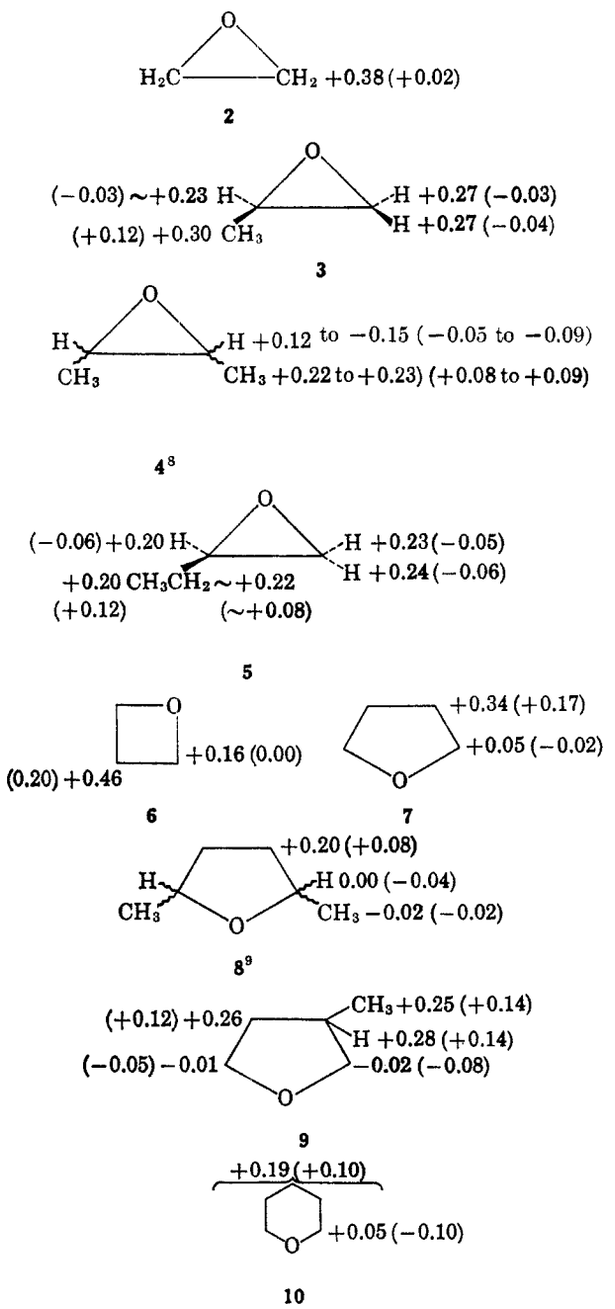


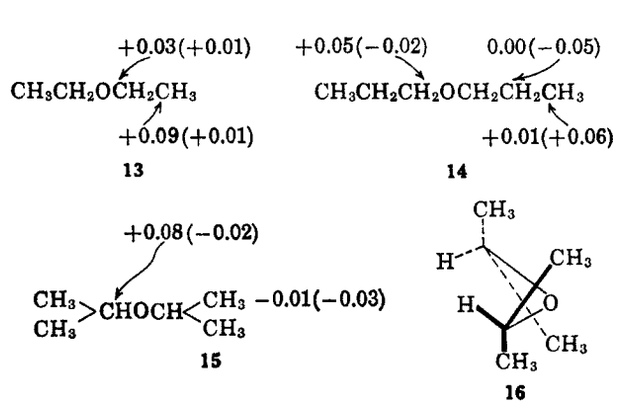
11 **12**

A similar generalization holds for α-alkyl substituents. The appropriate $\Delta_{CCl_4}^{C_6H_6}$ values for methylene or methyl protons directly attached to the epoxide rings in **3–5** are in the range +0.22 to +0.30 ppm, but in **8** the methyl resonance is shifted to slightly *lower* field in benzene. In the last case, the methyl group again lies nearer the negative end of the molecular dipole (contrast **11** and **12**, R = CH_3).

An additional consequence of the stereochemistry of association of benzene with five- and six-membered cyclic ethers is that, whereas α protons or α-alkyl substituents have small positive or negative $\Delta_{CCl_4}^{C_6H_6}$ values, β protons and β-alkyl substituents have larger positive values (see data for **7–10**). The differences in $\Delta_{CCl_4}^{C_6H_6}$ for α- and β-methyl groups are potentially the most useful since α and β protons are in any event differentiated by a large difference in chemical shift in any one solvent.

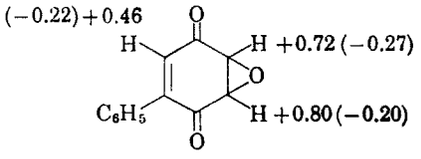
Three acyclic ethers (**13–15**) have also been examined. The most striking feature of these data is the small downfield shift of the methyl resonance of the diisopropyl ether (**15**) in benzene in contrast to the upfield shift of the α proton. In diisopropyl ether (**15**) the conformation (**16**) should be more highly populated than other possible conformations, because in **16** the nonbonded interactions are minimal. Hence the methyl groups would be expected on the average to spend more time near the negative end of the ether dipole (note the similarity between the positions and $\Delta_{CCl_4}^{C_6H_6}$ values of the methyl groups in 2,5-dimethyltetrahydrofuran (**6**) and **16**). The observed benzene solvent shifts support a preference for conformation **16** in diisopropyl ether.





(8) Quoted range of values covers shifts in both *cis* and *trans* isomers.
(9) Shifts the same within 0.01 ppm for both *cis* and *trans* isomers.

Solvent shifts induced by pyridine have also been correlated with structural features in some cases.[10-14] The $\Delta_{CCl_4}^{C_5H_5N}$ values are given in parentheses for the ethers discussed so far. The values for protons adjacent to the ether linkage (α position) are usually negative and if positive are very small ($\leq \pm 0.02$ ppm). Diagnostic differences for various ring sizes are not observed. However, the differences in $\Delta_{CCl_4}^{C_6H_6}$ and $\Delta_{CCl_4}^{C_5H_5N}$ values for α protons in the epoxides **3–5** are quite striking, the values being positive and negative, respectively. This trend (*vis.*, positive $\Delta_{CCl_4}^{C_6H_6}$ values *vs.* negative $\Delta_{CCl_4}^{C_5H_5N}$ values) for epoxide protons is greatly accentuated in some mono- and diepoxyquinones (**17–22** and **23–28**, respectively) which have been examined (the solvent shifts are summarized with the structural



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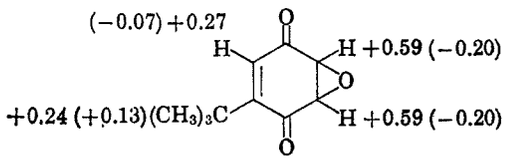

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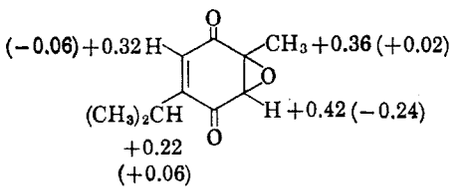

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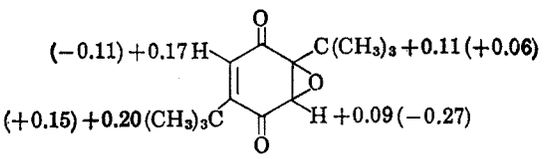

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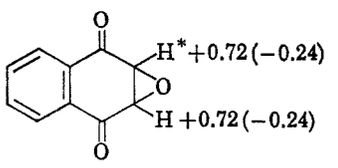

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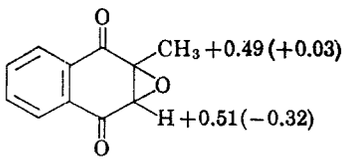

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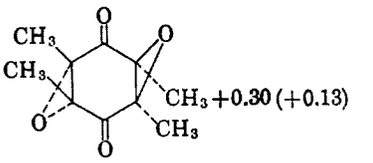

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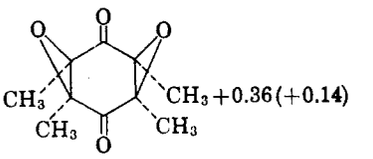

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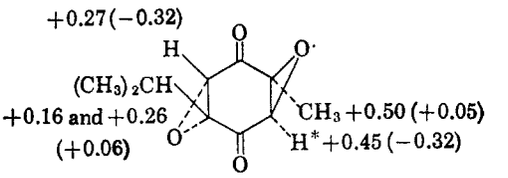

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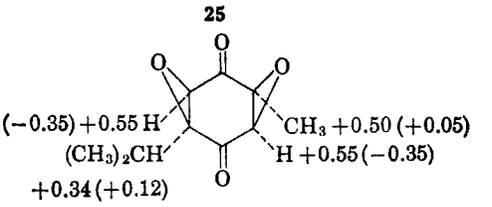

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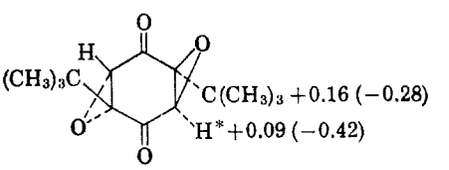

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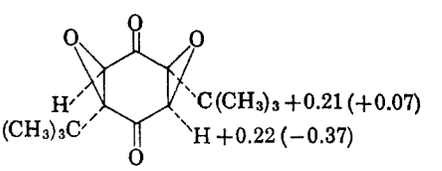

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formulae as before).[15] The effect is strikingly illustrated, for example, by the occurrence of the epoxide proton resonances of **17** at lower field in pyridine by no less than 1 ppm relative to a benzene solution.

By the introduction onto the epoxide ring of substituents of moderate (methyl and isopropyl) and large (*t*-butyl) steric bulk, it has been possible to evaluate the effect of steric factors on the solvent shifts observed for epoxide protons. The relevant data are summarized in Table I for compounds of partial structure **29**.

The large upfield shifts of the epoxide protons in benzene solution when R is hydrogen are considerably reduced when R is methyl. A similar effect is seen on comparing the $\Delta_{CCl_4}^{C_6H_6}$ values for ethylene oxide (**2**), propylene epoxide (**3**), and 2-butene epoxide (**4**). A very large reduction in the upfield shift in benzene solution is observed when R is changed from hydrogen to a *t*-butyl group (Table I). These large changes in

(10) G. Slomp and F. Mackellar, *J. Amer. Chem. Soc.*, **82**, 999 (1960).
(11) R. M. Moriarty, *J. Org. Chem.*, **28**, 1296 (1963).
(12) F. Johnson, N. A. Starkovsky, and W. D. Gurowitz, *J. Amer. Chem. Soc.*, **87**, 3492 (1965).
(13) D. H. Williams, *Tetrahedron Lett.*, 2305 (1965).
(14) D. H. Williams and D. A. Wilson, *J. Chem. Soc., Sect. B*, 144 (1965).

(15) The solvent shifts for the mono- and diepoxyquinones refer to deuteriochloroform as reference solvent ($\Delta_{CDCl_3}^{C_6H_6}$ and $\Delta_{CDCl_3}^{C_5H_5N}$). The change of reference solvent was dictated by the solubility of the compounds, but, since the solvent shifts observed in the quinones are usually large (this is especially true for the differences induced by benzene and pyridine), the change does not adversely affect the conclusions.

TABLE I
THE VARIATION OF SOLVENT SHIFTS OF EPOXIDE PROTONS (H*) WITH STERIC FACTORS

R	$\Delta^{C_6H_6}_{CDCl_3}$	$\Delta^{C_6H_5N}_{CDCl_3}$
H	+0.59 to +0.80	−0.20 to −0.27
CH_3	+0.34 to +0.55	−0.24 to −0.35
$(CH_3)_3C$	+0.09 to +0.22	−0.27 to −0.42

29

solvent shifts may *a priori* be associated largely with (i) steric inhibition of association of benzene at a polar site and (ii) steric inhibition to the approach of bulk solvent to the proton (H*) in question. The latter factor is independent of specific solute–solvent interaction, but must be considered since the exposed protons of a "spherical" solute (in this case the internal tetramethylsilane reference) are shifted upfield in benzene (relative to an external reference, even after a bulk susceptibility correction) because of the preferential orientation of disklike benzene molecules with respect to the "spherical" reference as indicated in **30**.[16] Therefore, a proton in the solute which is less exposed to the shielding effect associated with bulk benzene solvent than the protons of the reference will, in the absence of specific solvent–solute interactions, be deshielded relative to the internal reference. The factors considered under i and ii above should also be dominant in determining the pyridine-induced shifts. If steric inhibition of specific solvation is dominant in determining the differences in solvent shifts, then the shifts of H* in **29** should decrease in magnitude for *both* benzene and pyridine solution as R is changed from hydrogen to methyl to *t*-butyl. In contrast, if steric inhibition to the approach of bulk solvent is dominant, then both the $\Delta^{C_6H_6}_{CDCl_3}$ and $\Delta^{C_6H_5N}_{CDCl_3}$ values should become more negative as R is changed from hydrogen to methyl to *t*-butyl. In fact the $\Delta^{C_6H_5N}_{CDCl_3}$ values do become slightly larger (*i.e.*, more negative) as the bulk of R is increased, thus indicating the importance of steric inhibition to the approach of bulk solvent in these cases. This conclusion is supported by an examination of Dreiding models.

TMS

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It should also be possible to demonstrate the contribution to a solvent shift of steric inhibition to the approach of bulk solvent by means of variable temperature experiments. Such a contribution to the solvent shift will be temperature independent,[16] whereas that due to specific solute–solvent association will be temperature dependent (the shift increasing in magnitude at lower temperatures). Therefore **21, 25,** and **27** were selected for a variable-temperature study in d_8-toluene solution (as benzene is unsuitable for variable-temperature work) and pyridine solution. Since one is here trying to demonstrate a mechanistic aspect of solvent shifts (rather than formulating an empirical correlation), it was thought desirable to choose the most truly "inert" solvent which is available as reference solvent (in place of CCl_4 or $CDCl_3$) and accordingly hexane was employed.[16] The epoxide **25** was relatively insoluble in hexane at normal probe temperatures and therefore the spectrum was obtained at 40, 60, and 80°. The chemical shift of the epoxide proton resonances were temperature independent within experimental error (±1 cps). The solvent shifts $\Delta^{C_7D_8}_{C_6H_{14}}$ and $\Delta^{C_6H_5N}_{C_6H_{14}}$ observed for the epoxide protons indicated by asterisks in the temperature range −40 to +100° (pyridine solutions) and −80 to +100° (d_8-toluene solutions) are summarized in Figure 1.

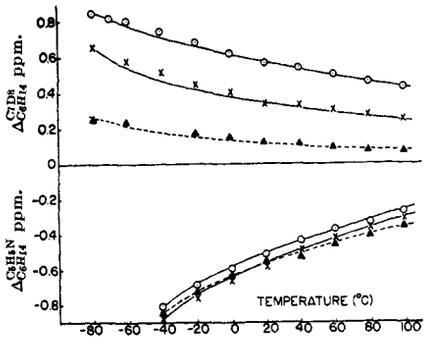

Figure 1.—Plot of solvent shift for epoxide protons in compounds **21** (○), **25** (×), and **27** (▲) against temperature.

Steric inhibition of complexing (*i.e.*, of specific solvent–solute interaction) will cause a decrease in the temperature dependence of that part of the solvent shift arising because of complexing. This temperature dependence of the solvent shift can be measured in terms of $\nu_{t_1} - \nu_0/\nu_{t_2} - \nu_0$ where ν_{t_1} and ν_{t_2} are the observed resonance frequencies of a proton at temperatures t_1 and t_2 in a complexing solvent and ν_0 is the resonance frequency of the proton in the absence of complexing.[17] If ν_0 for the epoxide protons of **21, 25,** and **27** is taken as the chemical shift in hexane solution, then the calculated values of $\nu_{-80} - \nu_0/\nu_{+100} - \nu_0$ for solutions in d_8-toluene are 0.85/0.42, 0.65/0.23, and 0.26/0.07 (taken from Figure 1), *i.e.*, 2.0, 2.8, and 3.7, respectively. On the basis of this analysis, the greatest temperature dependence of the solvent shift is observed when the steric inhibition toward association of d_8-toluene at the polar sites is greatest. This situation is obviously impossible, and it must therefore be concluded that, in the absence of complexing, the epoxide protons of **25** and **27** would resonate at lower field in d_8-toluene solution than they do in hexane solution. This situation would arise if the epoxide protons of **25** and **27** are less accessible to shielding by bulk d_8-toluene solvent than the protons of the internal TMS reference. The same conclusion must also be reached from a consideration of the variable temperature study in pyridine solution (Figure 1). Although the solvent shift $\Delta^{C_6H_5N}_{C_6H_{14}}$ at 40° is greatest for the most sterically hindered epoxide proton of **27**, the temperature dependence of its resonance position (measured in terms of $\nu_{-40} - \nu_0/\nu_{+100}$

(16) A. D. Buckingham, T. Schaefer, and W. G. Schneider, *J. Chem. Phys.*, **32**, 1227 (1960); see also J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., 1959, pp 424–426.

(17) For a theoretical discussion which relates the temperature dependent solvent shifts ($\Delta^{C_6H_6}_{CCl_4}$) to thermodynamic properties based upon an equilibrium between solute and solvent complexed solute, see ref 3.

$-\nu_0$ for pyridine and ν_0 taken from the hexane data) is least (2.9, 2.7, and 2.4 for **21**, **25**, and **27**, respectively). This observation may be interpreted in terms of a negative contribution to the solvent shift of the epoxide proton of **27** which is temperature independent. It is apparent that if the dotted lines of Figure 1 (curves for the di-*t*-butyl diepoxide) were extrapolated to high temperatures (approximating complex free solutions), they would approach each other at a resonance frequency for the epoxide proton *lower* than that observed for a hexane solution.

The stereochemistry assigned to the stereoisomeric pairs of diepoxides **23–24**, **25–26**, and **27–28** is only tentative[18] and unimportant for the present arguments. The assignments are based on the solvent-shift data and upon the conclusion that the less soluble higher melting isomer has the *trans* configuration.[18] In a *cis* diepoxide, the proton attached to one epoxide ring is further away from the negative end of the local dipole of the other epoxide ring relative to the situation in a *trans* diepoxide. Hence the compounds having the epoxide protons with the larger upfield solvent shifts in benzene are assigned the *cis* stereochemistry.

Experimental Section

Nmr Measurements.—The variable-temperature experiments were carried out using a Varian HA-100 nmr spectrometer with 2% w/v solutions. All other measurements were carried out on a Varian A-56/60 nmr spectrometer with 5% w/v solutions.

Epoxyquinones.—The epoxyquinones reported here were all synthesized by the direct oxidation of the corresponding quinone as reported in an earlier publication.[18]

Registry No.—Benzene, 71-43-2; pyridine, 110-86-1; **2**, 75-21-8; **3**, 15448-47-2; **4** (*cis*), 1758-33-4; **4** (*trans*), 15493-88-6; **5**, 15448-50-7; **6**, 503-30-0; **7**, 109-99-9; **8** (*cis*), 2144-41-4; **8** (*trans*), 15493-89-7; **9**, 13423-15-9; **10**, 142-68-7; **13**, 60-29-7; **14**, 111-43-3; **15**, 108-20-3; **17**, 10476-74-1; **18**, 10476-73-0; **19**, 10476-70-7; **20**, 10476-71-8; **21**, 15448-58-5; **22**, 15448-59-6; **23**, 15448-60-9; **24**, 10476-79-6; **25**, 10476-76-3; **26**, 10476-75-2; **27**, 10476-78-5; **28**, 10476-77-4; **29** (R = H), 15448-65-4; **29** (R = CH_3), 15448-66-5; **29** (R = $(CH_3)_3C$), 15448-67-6.

Acknowledgment.—Two of us (H. W. Moore and H. Raymond Shelden) are indebted to the National Science Foundation for partial support of this project from Grant GP. 5945.

(18) H. W. Moore, *J. Org. Chem.*, **32**, 1996 (1967).

Fluoroalkylamines

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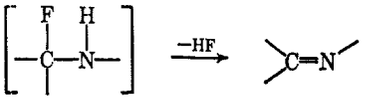
Lewis acids were used to activate fluorimines toward reactions with carbon nucleophiles. A wide variety of fluoroalkylamines was prepared and the chemistry of these very stable compounds was explored. A correlation between F^{19} nmr chemical shifts and the Hammett σ values is discussed.

Primary or secondary amines which contain fluorine atoms attached directly to their α-carbon atoms are known to be relatively unstable.[1] The base-catalyzed loss of the elements of hydrofluoric acid occurs readily (eq 1). The remarkable physical and chemical



(1)

properties of the fluoro alcohols[2a] derived from fluoro ketones[2b,c] and carbon nucleophiles prompted a study of the fluoroalkylamines which might be derived from fluorimines[3] and carbon nucleophiles (eq 2). Fluoro

$$RH + (R_f)_2C{=}NH \longrightarrow RC(R_f)_2NH_2 \qquad (2)$$

ketones and fluorimines differ, however, in reactivity toward nucleophiles, the latter being less electrophilic. Only one case of a reaction of a fluorimine with a carbon nucleophile (the very electron-rich isobutylene) has been reported.[4] We have found that Lewis acids activate fluorimines so that they undergo many of the reactions shown by fluoro ketones. This method has proved to be an excellent route to a wide variety of fluoroalkylamines. Several fluoroalkylamines were also prepared by alternate, less general routes.

Preparation of Fluoroalkylamines.—α,α-Bis(fluoroalkyl)benzylamines were prepared from fluorimines[3] and aromatic hydrocarbons under vigorous Friedel–Crafts conditions (Table I). The reaction usually was carried out at elevated temperatures in a "Hastelloy"-lined autoclave at autogenous pressure (eq 3). Reac-

(3)

tivity closely paralleled normal electrophilic substitution, with electron-donating groups activating and electron-withdrawing groups deactivating the ring. Yields varied from high to low depending on the aromatic hydrocarbon. Disubstitution was observed with phenol and 2 equiv of hexafluoroisopropylidenimine[3] (HFAI), but the hexafluoroisopropylamino group was sufficiently ring deactivating to prevent disubstitution in unactivated aromatic hydrocarbons. *para,para'* disubstitution was observed when compounds containing two benzene rings separated by a heteroatom or carbon chain were employed. 3,5-Dimethyl-4-

(1) F. S. Fawcett, C. W. Tullock, and D. D. Coffman [*J. Chem. Eng. Data*, **10**, 398 (1965)] describe the properties of N,N-bis(trifluoromethyl)amine; W. J. Middleton and C. G. Krespan [*J. Org. Chem.*, **30**, 1398 (1965)] describe the properties of heptafluoroisopropylamine.

(2) (a) W. J. Middleton and R. V. Lindsey, *J. Amer. Chem. Soc.*, **86**, 4948 (1964); (b) C. G. Krespan and W. J. Middleton, in "Reviews in Fluorine Chemistry," P. Tarrant, Ed., in press; (c) N. P. Gambaryan, E. M. Rokhlin, Yu. A. Zeifman, C. Ching-Yun, and I. L. Knunyants, *Angew. Chem.*, **78**, 1008 (1966).

(3) W. J. Middleton and C. G. Krespan, *J. Org. Chem.*, **30**, 1398 (1965).

(4) Y. V. Zeifman, N. P. Gambaryan, and I. L. Knunyants, *Izv. Akad. SSSR Ser. Khim.*, **1965** (8), 1472 (1965).