due in part to the salting-out effect of the ammonium bromide in solution. After separating this layer, the rest of the product and unreacted formamide were separated by vacuum distillation. Due to its extreme solubility in formamide (0.5 g of NH_4Br/1 of g formamide at 100°), the ammonium bromide did not precipitate out until about 95% of the formamide had distilled [100° (9 mm)]. This was filtered off and distillation was continued until all the liquid had distilled.

Combination of the composition of various parts of the separation gave the material balance in Table III.

TABLE III
MATERIAL BALANCE

					Products	Moles
$C_8H_{17}Br$	+ H_2O	+ $HCONH_2$	$\xrightarrow[3\text{ hr}]{135°}$		$C_8H_{17}OH$	0.13
mol 0.5	1.0	10.0			$HCO_2C_8H_{17}$	0.33
					NH_4Br	0.5
					H_2O	0.41
					$C_8H_{17}Br$	0
					$HCONH_2$	9.4

The amount of formamide recovered was 99% of theory for the reaction of 1 mol per mol of bromide. The analyses for ammonium bromide (determined by molecular weight and bromide determination) and octyl bromide (by gas chromatography) show that all of the octyl bromide had reacted. However, the octyl products as such account for only 92% of theory. Later work showed that *n*-octyl formamide was formed, thus accounting for this discrepancy. There was no evidence for the formation of an olefin[4] from octyl bromide in this reaction. The amount of water consumed can be seen from the distribution of ester–alcohol obtained. The total molar amount of octyl products, 0.46 mol, plus the moles of alcohol formed due to hydrolysis, 0.13 mol, agree exactly with the water balance, 0.59 mol consumed, to show that the stoichiometry of the reaction is as written in eq 1 and 2.

Ammonia in Formamide.—When ammonia reacted with a mixture of the halide and formamide, either anhydrous or aqueous (5–10%), the major product is the N-alkyl-substituted amide in 90% yield.

$$RX + HCONH_2 + NH_3 \xrightarrow[1\text{ nr}]{150°} HCONHR + NH_4X$$

There is about 5% dialkylformamide formed as well as 5% alcohol. In effect, the high selectivity of this reaction provides a new route to primary amines from primary alkyl halides.

Experimental Section

Gas chromatographic analyses of the reaction products were performed on an F & M Model 720 chromatograph using 10 ft × 1/8 in. columns packed with 15% Carbowax on 60–80 mesh HMDS-treated Chromosorb W. The C_8 alcohol, ester, and bromide were analyzed at 140° and the substituted amides at 200°. Product peaks were identified by comparison of retention time with authentic samples and by combined mass–glpc and ir–glpc analyses of the individual peaks.

Aqueous Formamide.—A mixture of 96.5 g (0.5 mol) of *n*-octyl bromide, 450 g (10 mol) of formamide, and 18 g (1 mol) of water was heated at 135° for 3 hr in a 1-l., three-neck flask equipped with stirrer, condenser, and thermometer. After heating, the solution was cooled to room temperature, and it separated into two layers. The upper layer and the 60–90° cut from the bottom layer, obtained by vacuum distillation at 9 mm, contained all the *n*-octyl formate and *n*-octyl alcohol. These two fractions were combined and distilled to produce 52 g (0.33 mol) of *n*-octyl formate and 17 g (0.13 mol) of *n*-octyl alcohol for an over-all yield of ester–alcohol of 92%.

Formamide and Ammonia.—Anhydrous ammonia (0.47 mol) was dissolved in 2.5 mol of formamide and 0.125 mol of *n*-octyl bromide in a stirred autoclave and heated to 150°. At the end of 1.5 hr, the solution was cooled down and analyzed; 97.6% of the bromide had been converted. The products were 91% *n*-octylformamide, 2.7% N,N-dioctylformamide, and 6.3% *n*-octyl alcohol.

Registry No.—*n*-Octyl formate, 112-32-3; *n*-octyl alcohol, 111-87-5.

(4) N. Kornblum and R. K. Blackwood, *J. Amer. Chem. Soc.*, **78**, 4037 (1956).

Benzene Shifts in the Nuclear Magnetic Resonance Spectra of Alcohols

PAUL V. DEMARCO AND L. A. SPANGLE

Department of Molecular Structure Research, The Lilly Research Laboratories, Eli Lilly and Company, Indianapolis, Indiana 46206

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In previous studies, solvent shifts induced by benzene in a wide variety of solutes containing different functional groups were examined.[1] On the basis of these studies, widely differing models have been proposed for the geometry of benzene–solute collision complexes. Recently, in an attempt to generalize the phenomena of benzene–polar solute associations, Ledaal[2] has proposed that the geometry of such interactions can be rationalized in terms of one model,[3] common to solutes containing any polar functional group, and has demonstrated considerable success in applying this model to a wide variety of examples.

This communication has two purposes: first, to demonstrate that aromatic solvent induced shifts, ASIS ($\Delta = \delta_{CDCl_3} - \delta_{C_6D_6}$), in compounds containing the hydroxyl function cannot be adequately rationalized in terms of the model proposed by Ledaal for solute–solvent associations; second, to emphasize that in systems where the solute dipole is free to assume a number of preferred conformations, as in hydroxyl-containing solutes, the magnitude of resultant solvent shifts will be dependent upon the population of each conformational species in solution, a fact not pointed out in previous studies, although of intrinsic importance to the interpretation of ASIS.

In accordance with the Ledaal model,[2] two solute–solvent geometrical relationships are possible for benzene association to hydroxyl-containing solutes. These are illustrated in Figure 1a and 1b.

Because of the nature of the screening environment associated with aromatic systems,[4] both models, a and b, predict increased shielding for *all solute protons* in benzene relative to chloroform. Analysis of the results

(1) J. Ronayne and D. H. Williams, *J. Chem. Soc., B*, 540 (1967), and references cited therein.

(2) T. Ledaal, *Tetrahedran Lett.*, No. 14, 1683 (1968).

(3) According to this model, benzene association takes place from the positive end of the solute dipole and in such a manner as to allow the solute dipole axis to be located along the sixfold axis of symmetry of the associated benzene nucleus.

(4) J. A. Pople, *J. Chem. Phys.*, **24**, 1111 (1956); J. A. Pople, W. G. Schneider, and H. J. Bernstein," High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., 1959, pp 180–183.

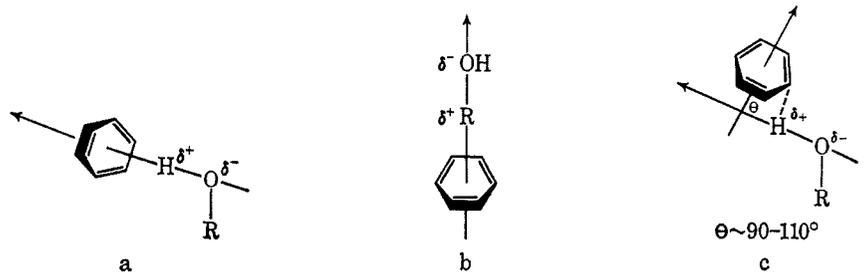

Figure 1.—Possible modes of benzene–hydroxyl function association.

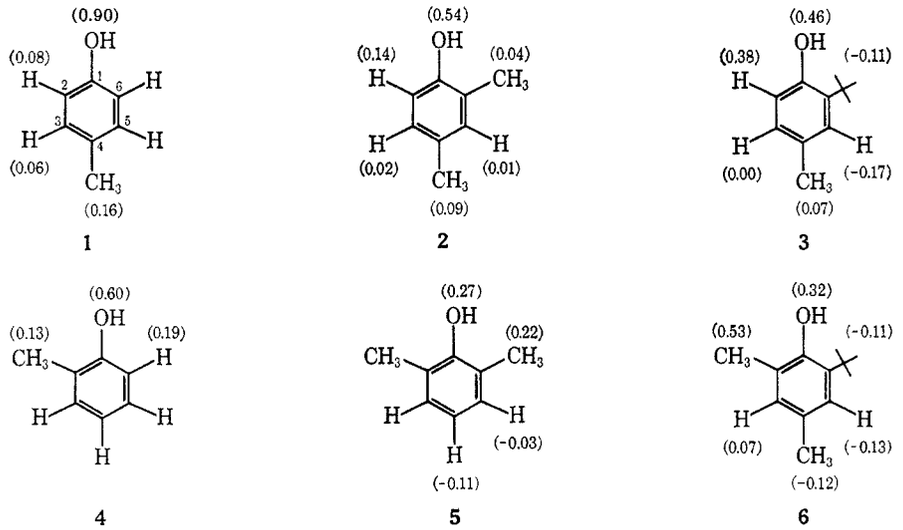

Figure 2.—Phenol Δ values (in parenthesis) beside corresponding protons (parts per million).

of solvent shift studies carried out on a number of phenol and androstanol derivatives, summarized in Figure 2 and Table I, indicate that both positive (increased shielding in benzene) and negative (decreased shielding in benzene) Δ values are recorded for the different solute protons in the systems under study. As a result, benzene–solute geometrical relationships a and b must be rejected on the grounds of incompatibility with the experiment data. We therefore propose an alternative model for benzene–alcohol association, depicted in Figure 1c, which is consistent with observed solvent shift results.

TABLE I

Δ VALUES[a] FOR H-18 AND H-19 PROTONS IN SOME HYDROXY STEROIDS

No.	Compd	Δ (H-19)	Δ (H-18)
7	5α-Androstan-1α-ol	0.10	
8	5α-Androstan-2α-ol	0.11	
9	5α-Androstan-2β-ol	−0.08	
10	5α-Androstan-3α-ol	0.08	
11	5α-Androstan-3β-ol	0.09	
12	5α-Androstan-4α-ol	0.10	
13	5α-Androstan-4β-ol	−0.11	
14	5α-Androstan-15α-ol		0.10
15	5α-Androstan-15β-ol		−0.11
16	5α-Androstan-16α-ol		0.08
17	5α-Androstan-16β-ol		−0.09
18	5α-Androstan-17α-ol		0.10
19	5α-Androstan-17β-ol		0.03

[a] $\Delta = \delta_{CDCl_3} - \delta_{C_6D_6}$ ppm.

Because of considerable upfield shifts recorded for solute hydroxyl protons (see Figure 2) in benzene relative to chloroform, benzene–alcohol association is presumed to originate through the formation of weak hydrogen bonds between solute hydroxyl protons and the solvent π electrons,[5] the geometry of the association being such as to allow the sixfold axis of symmetry of the benzene nucleus and the axis of symmetry of the OH bond to lie mutually perpendicular or very nearly so (see Figure 1c). The validity of the proposed model becomes increasingly evident during the rationalization of observed ASIS.

Phenolic Systems.—In *ortho*-unsubstituted phenols (R = H), two conformers, a and b (Figure 3), are equally probable, with the result that their corresponding benzene-associated complexes will be equally populated in solution. Δ values for protons in **1** are thus net shift values resulting from the algebraic sum of screening contributions from solvent benzene molecules associated *syn* and *anti* to these protons.[8] Since solute protons *syn* are proximal to and in the shielding region of the associated benzene nucleus while solute protons *anti* are remote from and in the deshielding region, the shielding component experienced by a given solute proton is expected to be larger than the deshielding

(5) OH· · · · · π hydrogen bonding has been amply demonstrated in previous infrared[6] and nmr[7] studies.

(6) P. von R. Schleyer, D. S. Trifan, and R. Bacskai, *J. Amer. Chem. Soc.*, **80**, 6691 (1958).

(7) M. Oki and H. Iwamura, *Bull. Chem. Soc. Jap.*, **35**, 1552 (1962); R. J. Ouellet, D. L. Mraks, and D. Miller, *J. Amer. Chem. Soc.*, **89**, 913 (1967); D. C. Kleinfelter, *ibid.*, **89**, 1734 (1967); L. W. Reeves and W. G. Schneider, *Can. J. Chem.*, **35**, 251 (1957).

(8) Solute protons are *syn* to associated benzene when they are on the same side of the solute as the direction of association (*e.g.*, H_2 and H_3 in a, Figure 3) and *anti* when they are on the opposite side (*e.g.*, R and H_5 in a, Figure 3).

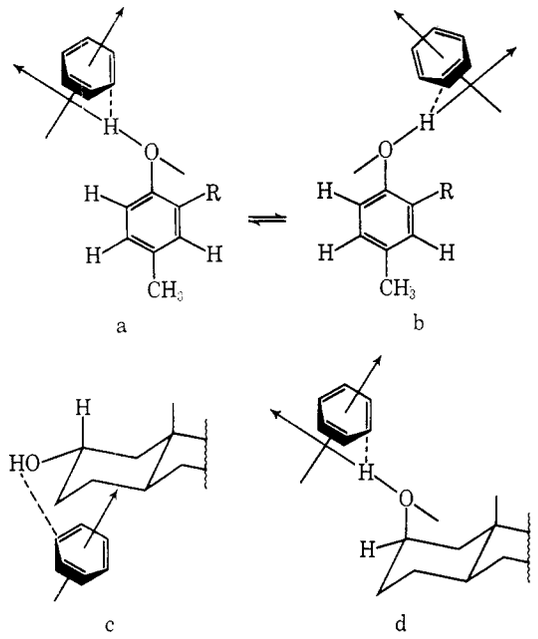

Figure 3.—Proposed model for stereochemical nature of benzene–alcohol association.

component. Thus, for compound **1** in benzene, the over-all net effect should be one of increased shielding for all solute protons. This is indeed observed to be the case, since $H_2(H_6)$, $H_3(H_5)$, and p-CH_3 illustrate increased shieldings of 0.08, 0.06, and 0.16 ppm, respectively.

Increase in the steric size of the *ortho* substituent in phenols will seriously disturb the population equilibrium between a and b such that, as R increases in size, the population of species b becomes smaller. Thus, progressive increases in the steric bulk of R from H, as in **1**, to $-CH_3$, as in **2**, to $-C(CH_3)_3$, as in **3**, should result in corresponding increases and decreases in the shielding of solute protons *syn* and *anti*, respectively, to the site of association. That this is observed to be the case is evidenced by the recorded Δ values for protons in **1**, **2**, and **3**. It is seen that H_2 becomes increasingly shielded [0.08 (**1**), 0.14 (**2**), and 0.38 (**3**)], while R [0.08 (**1**), 0.04 (**2**), and −0.11 (**3**)] and H_5 [0.06 (**1**), 0.01 (**2**) and −0.17 (**3**)] become increasingly deshielded. Parallel observations are observed for protons in **4**, **5**, and **6**, (see Figure 2) and add further support for the proposed model.

Hydroxy Steroids.—Small, but nevertheless significant, Δ values are recorded for the H-18 and H-19 protons in a number of monohydroxy steroids. Results, summarized in Table I, indicate that these protons experience increased shielding in benzene ($\Delta \cong 0.1$) except in those cases where hydroxyl and methyl groups are situated 1,3 diaxial (**9**, **13**, **15**, and **17**) to each other. In such cases, shifts to lower field are noted ($\Delta \cong -0.1$ ppm). The stereochemical nature of the benzene–solute complexes which rationalize these observations is shown in Figure 3c and 3d for solutes 5α-androstan-2α-ol, respectively, and demonstrate that in the former case benzene associates from the α face while in the latter case association takes place from the β face of the steroid molecule. The above findings indicate that, in addition to other solvent shift techniques,[9] benzene Δ values may be useful in establishing both the location and the stereochemical nature of protons situated in the vicinity of hydroxyl functions.

Although the model proposed above (Figure 1c) for benzene–hydroxyl function association is qualitatively in good agreement with observed solvent shift data, it is naive to presume that this model represents the total physical picture for such interactions. Indeed, it is possible that secondary association of benzene to solute phenol molecules, in a manner similar to that demonstrated for benzene association to toluene and *t*-butyl benzene,[2] could give rise to complexes of greater than 1:1 stoichiometry. Our interpretation of observed Δ values (Figure 2), however, if correct, suggests that the contribution to the total screening coefficient from such secondary associations is small.

(9) P. V. Demarco, E. Farkas, D. Doddrell, B. L. Mylari, and E. Wenkert, *J. Amer. Chem. Soc.*, **90**, 5480 (1968).

Experimental Section

Nmr spectra were recorded at 100 MHz at normal probe operating temperature (30 ± 1°) using TMS as internal lock and reference. Sample concentrations were maintained at less than 5% w/v. Peak positions were recorded by observing difference 1 on the frequency counter (*i.e.*, the difference between the manual and sweep oscillator frequencies) and phenolic proton resonance positions calculated from first-order analysis of their spectra.

Phenols 1–6 were commercially available compounds and were used without further purification. Hydroxy steroids (**7**–**19**), recorded in Table I, were synthetically prepared. Experimental details regarding their synthesis will be published elsewhere. These compounds display the requisite spectral properties and give correct elemental analyses.

Registry No.—**1**, 106-44-5; **2**, 105-67-9; **3**, 2409-55-4; **4**, 95-48-7; **5**, 576-26-1; **6**, 2311-05-9; **7**, 2287-84-5; **8**, 20707-85-1; **9**, 1225-47-4; **10**, 7657-50-3; **11**, 1224-92-6; **12**, 20707-77-1; **13**, 20707-78-2; **14**, 1090-01-3; **15**, 734-66-7; **16**, 1032-14-0; **17**, 1032-15-1; **18**, 19037-37-7; **19**, 1225-43-0.

Carbonium Ions. XXII. The Formation of Transient, Primary Carbonium Ions by Oxidation of Carboxylic Acids

N. C. Deno, W. E. Billups, John S. Bingman, Robert R. Lastomirsky, and Robert G. Whalen

Department of Chemistry, Pennsylvania State University, University Park, Pennsylvania 16802

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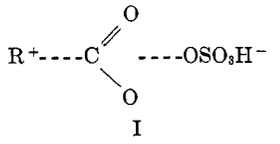
Solutions of $K_2S_2O_8$ in sulfuric acid or oleum oxidize carboxylic acids at 25°. The structures of the products are in accord with a mechanism involving formation of a mixed anhydride of the carboxylic acid and peroxymonosulfuric acid (Caro's acid) followed by exothermic decomposition of the mixed anhydride as shown.



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