The pH at half-neutralization (pK_a) was 2.9, and the neutralization equivalent was 396 (calcd, 400.6). Purple solutions of Va prepared from IVa by base and kept under nitrogen slowly faded in a month at room temperature.

1-*t*-Butyl-2-thio-3-chromene (IIb) was prepared by treating 30 g of I in 500 ml of ether with 100 ml of 1.48 *M* *t*-butylmagnesium chloride.[7] When the ether layer was quenched with aqueous ammonium chloride, 2.1 g (12%) of white crystalline dimer of I, mp 230–231°, precipitated. The ethe layer was stripped of solvent by distillation; the distillate was found to have glpc peaks corresponding to isobutylene and 2,2,4-trimethylpentane. Addition of a small amount of acetone to the residue gave the isomeric dimer of I, mp 199–200°.[8] The acetone mother liquor was evaporated and vacuum distilled to give a main fraction, bp 120–133° (0.07 mm). Vacuum sublimation of this oil at 0.3 mm at room temperature gave 4.0 g (22%) of liquid 2-thio-3-chromene, and, when the sublimation temperature was raised to 40°, 5.5 g (22%) of IIb, mp 63–64°.

Anal. Calcd for $C_{13}H_{16}S$: C, 76.41; H, 7.89; S, 15.63. Found: C, 76.29; H, 7.75; S, 15.86.

1-*t*-Butylnaphthalenium perchlorate (IIIb) was prepared from IIb by treatment with sulfuryl chloride at −78° (as for IIa). Recrystallization from glacial acetic acid gave light yellow leaflets, mp 196–197°.

Anal. Calcd for $C_{13}H_{15}SClO_4$: C, 51.56; H, 4.99; S, 10.59; Cl, 11.71. Found: C, 51.82; H, 5.00; S, 10.37; Cl, 11.80.

The uv absorbance (methanol) showed λ_{max} (log ϵ) at 205 (4.41), 240 (3.90), 290 (3.57), 302 (3.67) and 320 mμ (3.72), and the nmr (trifluoroacetic acid) showed bands at τ 0.80 (3 H), 1.30–1.83 (3 H), and 7.87 (9 H).

1-*t*-Butyl-2-phenyl-2-thio-3-chromenium perchlorate (Vb) was prepared by treating a slurry of 1 g of IIIb in 50 ml of ether with 5 ml of 2.46 *M* phenylmagnesium bromide in THF. The purple solution was quenched with cold aqueous ammonium fluoride, precipitating 1.11 g (88%) of IVb. Recrystallization from glacial acetic acid gave 0.88 g (70%), mp 169–170°.

Anal. Calcd for $C_{19}H_{21}SClO_4$: C, 59.91; H, 5.56; S, 8.42; O, 16.80; Cl, 9.31. Found: C, 60.03; H, 5.41; S, 8.57; O, 16.84; Cl, 9.26.

The same compound was obtained in 36% yield with phenyllithium. The uv absorbance showed λ_{max} (log ϵ) at 232 (5.34), 275 (3.70), and 297 mμ (3.87), and nmr bands at τ 1.52 (doublet, 1 H, J = 10 cps), 1.90–2.53 (multiplet, 9 H), 2.78 (double doublet, 1 H, J = 10 and 2 cps), 4.93 (doublet, 1 H, J = 2 cps), and 8.73 (9 H).

Efforts to convert IVb to Vb were unsuccessful with potassium hydroxide in ethanol; the pH jumped from 6 to 12 on addition of less than 10% of 1 equiv of base. By reaction with potassium ethoxide or *t*-butoxide in DMSO, however, a port-wine color developed, perhaps due to Va. The color faded in a day or so, as did that of a phenyllithium reaction mixture.

Registry No.—IIa, 20707-97-5; IIb 20707-98-6; IIIa, 20728-45-4; IIIb, 20707-99-7; IVa, 20708-00-3; Vb, 20708-01-4; Va, 20708-02-5.

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(7) "Organic Syntheses," Coll. Vol. I, John Wiley & Sons, Inc., New York, N. Y., 1941, p 524.

(8) Structure proof, properties, and other methods of preparation of these *meso-* and *dl*-1,1 dimers of I are described in theses by M. Siskin and C. K. Miao, Department of Chemistry, University of Pennsylvania.

Reactions of Alkyl Halides in Amides Containing Water or Ammonia

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The reaction of alkyl halides with anhydrous acetamide has been reported by Erickson[1] to yield the substituted amide and by Joyce[2] to yield esters. Bredereck[3] and coworkers reported that the reactions of anhydrous formamide with alkyl halides yield formates or substituted formamides depending on the structure of the halide. In all of the above reactions, at least 2 mol equiv of anhydrous amide are required and only primary amides react.

Aqueous Amides.—We wish to report that, in the presence of water, all types of amides react with halides to yield a mixture of the corresponding ester and alcohol (Table I). In addition, only 1 mol of amide is consumed per mol of halide. All types of halides react (Table II) except fluorides, vinylic halides, and halogenated aromatics. The over-all reaction is as follows

$$RX + R'CONR_2'' + H_2O \longrightarrow R'CO_2R + NR_1''H_2X \quad (1)$$

$$R'CO_2R + H_2O \rightleftharpoons ROH + R'CO_2H \quad (2)$$

where R is alkyl or aralkyl, and R′ and R″ are organic or hydrogen.

TABLE I

REACTION OF AQUEOUS AMIDES WITH *n*-OCTYL BROMIDE

Amide	Bromide conversion, %[a]	Products, %[b]		Temp, °C	Time, hr	A/W/H[c]
		Alcohol	Ester			
$HCONH_2$	100	17.9	80.6	160	1	20:2:1
$HCON(CH_3)_2$	94.8	24.3	70.5	135	2	28:5:1
$CH_3CON(CH_3)_2$	74	49	25	130	3	9:6:1
$C_6H_5CONH_2$	99.4	18.0	79.4	170	3	20:3:1
$HCONHC_6H_5$[d]	99	19.4	79.6	160	2	20:3:1

[a] Based on unreacted bromide recovered. [b] The difference, if any, between % products and % conversion is due to formation of N-alkyl-substituted amides. [c] Molar ratios of amide/water/halide. [d] There was appreciable (5–10%) hydrolysis to aniline also.

TABLE II

REACTIONS OF VARIOUS HALIDES WITH AQUEOUS FORMAMIDE[a]

Halide	Halide conversion, %[b]	Temp, °C	Time, hr
$C_8H_{17}Cl$	63	140	3
$C_8H_{17}Br$	100	140	3
$C_8H_{17}I$	100	140	3
$C_6H_{13}CHBrCH_3$	97	140	3

[a] Molar ratio of amide/water/halide, 22:6:1. [b] Products are the corresponding formate–alcohol mixture.

By contrast, less than 2% ester–alcohol formed when anhydrous dimethylformamide was refluxed (152°) with *n*-octyl bromide for 3 hr.

For purposes of determining the stoichiometry of the reaction of octyl bromide with aqueous formamide, the distribution of alcohol in the product was determined by acetylation; excess (unreacted) water was determined by Karl Fischer titration; ammonium bromide was determined by titration with standard silver nitrate solution; and the excess formamide was determined by distilling and weighing. No determination of free formic acid, if any, was made. The recovery procedure for the material balance takes advantage of the fact that at room temperature, about 90% of the alcohol–ester product separates as a top layer. This may be

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(1) J. L. E. Erickson, *Chem. Ber.*, **59B**, 2665 (1926).

(2) R. M. Joyce (to Du Pont Co.), U. S. Patent 2,375,301 (1945).

(3) H. Bredereck, R. Gomper, and G. Theilig, *Chem. Ber.*, **87**, 537 (1954).

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.

$$RX + HCONH_2 + NH_3 \xrightarrow[1\ \text{hr}]{150°} HCONHR + NH_3X$$

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.

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

Benzene Shifts in the Nuclear Magnetic Resonance Spectra of Alcohols

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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

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[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.