of water, dried ($MgSO_4$), and concentrated. The residue was distilled to yield 8.7 g of phenol, specific activity 0.336 μCi/mmol (calcd: 0.37 μCi/mmol for completed exchange of 2, 4, and 6 protons). Bromination of a sample of this phenol in water containing hydrobromic acid yielded 2,4,6-tribromophenol, mp 188.5–191.0°, specific activity $\leq 1 \times 10^{-4}$ μCi/mmol.

Reimer–Tiemann Synthesis with ^3H-Phenol.—The Reimer–Tiemann procedure given above was repeated by adding 0.81 g of the above phenol and 0.10 g of unlabled salicylaldehyde to a solution of 100.5 g (2.63 mol) of sodium hydroxide in 115 ml of water and treating the solution with 40 g of chloroform. After acidification and steam distillation, the distillate was extracted with fifteen 3-ml portions of dichloromethane which were pooled, dried, and evaporated. The resulting 0.4 g of crude salicylaldehyde was converted directly to benzisoxazole by treatment with 1 g of hydroxylammonium *O*-sulfonate in 2 ml of water, followed by extraction with dichloromethane to remove neutral impurities. The aqueous layer was brought to pH 7 with sodium bicarbonate and extracted with three 5-ml portions of dichloromethane, which were pooled and evaporated. The residue was distilled in a bulb-to-bulb apparatus at 1 mm to yield 0.12 g of benzisoxazole, identified by its infrared spectrum, specific activity 0.134 μCi/mmol. When 97.85 mg of this sample was treated with excess sodium methoxide in methanol and the methanol was recovered quantitatively by lyophilization, it was found to show 71.1 dpm/0.822 mmol or 3.9×10^{-5} μCi/mmol; *o*-cyanophenol recovered by acidification of the lyophilization residue was found to possess 99% of the activity of the benzisoxazole.

Registry No.—Salicyladehyde, 90-02-8; *O*-acetoxybenzal choride, 26693-22-1.

Electronegativity, Acids, and Bases. IV. Concerning the Inductive Effect of Alkyl Groups

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Although the inductive effects of alkyl groups have long been appreciated, there has been some confusion concerning the electron donating or withdrawing ability of alkyl groups relative to each other and to the hydrogen atom. Thus, there has been some uncertainty concerning the basicity of alkylamines based upon pK_b's in aqueous solution, but Condon[1] has shown clearly that, if hydration effects are accounted for, the basicity order is $R_3N > R_2NH > RNH_2 > NH_3$, in accord with increasing electron density on the nitrogen with increasing substitution. Furthermore, $(CH_3)_3C > (CH_3)_2CH > CH_3CH_2 > CH_3 > H$ in *electron donating* ability toward N, O, C_6H_5, etc. These results have been confirmed in gas phase studies by Munson[2] and by Brauman and Blair.[3]

Recently, Brauman and Blair[3] have measured gas-phase acidities of various aliphatic alcohols and have shown that acidity increases in the order $H_2O < CH_3OH < CH_3CH_2OH < (CH_3)_2CHOH < (CH_3)_3COH < (CH_3)_3CCH_2OH$ and $CH_3CH_2OH < CH_3CH_2CH_2OH < CH_3CH_2CH_2CH_2OH < CH_3CH_2CH_2CH_2CH_2OH < (CH)_3COH$. This indicates that in the alkoxide ions, $R'O^-$, *electron withdrawing* ability also decreases $R_3C > R_2CH > RCH_2 > CH_3 > H$. In terms of any concept of fixed electronegativity[4] the apparent reversal of electronegativity seems paradoxical. Recent molecular orbital calculations by the MINDO[5] and CNDO/2[6] methods have rationalized the experimental results of Brauman and Blair. Some of these "predictions" would have been more useful had they not appeared *a posteriori*. It is the purpose of this note to call attention to earlier, though neglected, work in this area and to interpret these results in terms of simple model.

Though the inductive effects of alkyl groups have been discussed almost exclusively in terms of electron donation, Ingold[7] pointed out that this common behavior was a result of the fact that these groups are generally attached to *more electronegative substituents*. More recently, Schubert and coworkers[8] have cogently argued the same point, alkyl groups can donate *or* accept electron density depending upon the nature of the substrate. Furthermore, the latter workers made an extremely important observation; larger alkyl groups tend to be better electron donors because they are more polarizable. Therefore, they should also *be better electron acceptors when bonded to less electronegative substrates.* Two parameters are thus involved in charge transfer: inherent electronegativity and capacity (polarizability).

In a previous paper,[9] the group electronegativities of alkyl groups were calculated using the principle of electronegativity equalization,[10,11] and it was shown that the inherent or neutral electronegativities of alkyl groups are (1) slightly higher than hydrogen, (2) very similar to each other, ranging from 2.27 to 2.29,[12] and (3) not sufficient to differentiate among the groups. It was also shown that the principal differences among them lie in their varying *charge coefficient*, *b*, the rate at which the electronegativity changes with gain or loss of electron density. The increased electron donor ability of more highly substituted groups (toward electronegative substrates such as N, O, C_6H_5, etc.) results from their relatively low values of *b*, where the electronegativity is expressed as

$$\chi = a + b\,\delta \tag{1}$$

Simply stated, other things being equal, the more atoms in a group, the more readily the group can donate electron density since the resulting charge can be spread over more atoms.

In the previous paper[9] it was suggested that the same effect should be operative in allowing a group to *absorb* electron density. At that time, no good examples were known to the author for alkyl groups since the most obvious compounds to consider, the metal alkyls, $M^{\delta+}$—$R^{\delta-}$, are polymeric and not amenable to treatment. It was pointed out, however, that the electron withdrawing ability of perfluoroalkyls should increase with increasing size and that for transfers of charge density greater than *ca.* 0.1 they will be better acceptors

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(1) F. E. Condon, *J. Amer. Chem. Soc.*, **87**, 4481, 4485, 4491, 4494 (1965).

(2) M. S. B. Munson, *ibid.*, **87**, 2332 (1965).

(3) J. I. Brauman and L. K. Blair, *ibid.*, **90**, 6561 (1968); **92**, 5986 (1970).

(4) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

(5) N. C. Baird, *Can. J. Chem.*, **47**, 2306 (1969).

(6) T. P. Lewis, *Tetrahedron*, **25**, 4117 (1969).

(7) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953 p 70.

(8) W. M. Schubert, R. B. Murphy, and J. Robins, *Tetrahedron*, **17**, 199 (1962).

(9) J. E. Huheey, *J. Phys. Chem.*, **69**, 3284 (1965).

(10) R. T. Sanderson, *J. Chem. Educ.*, **31**, 2 (1954); "Chemical Periodicity," Reinhold, New York, N. Y., 1969.

(11) J. Hinze and H. H. Jaffé, *J. Amer. Chem. Soc.*, **84**, 540 (1962); J. Hinze, M. A. Whitehead, and H. H. Jaffé, *ibid.*, **85**, 148 (1963).

(12) Based on electronegativities from ref 11: C_{te} = 2.46; H_s = 2.21; F_p = 3.90.

TABLE I

CALCULATED CHARGES IN ALKOXIDE IONS

	Present work				MINDO,[b]	CNDO/2,[c]
Anion, RO^- [a]	δ_O	δ_R	δ_C	δ_H	δ_O	δ_O
OH^-	−0.658	−0.342		−0.342	−1.08	
CH_3O^-	−0.526	−0.474	−0.161	−0.104	−0.91	−0.68
$C_2H_5O^-$	−0.492	−0.508	−0.114	−0.056	−0.85	−0.67
$C_3H_7O^-$	−0.477	−0.523	−0.093	−0.034	−0.81	−0.66
$C_4H_9O^-$	−0.469	−0.531	−0.081	−0.023		−0.66
$C_5H_{11}O^-$	−0.464	−0.536	−0.074	−0.015		−0.66

[a] The oxygen is assumed to be hybridized with 20% s character in the hydroxide ion and 26.4% s character in the alkoxides. These values are from the 104.5° bond angle in H_2O and the somewhat greater angle (~110°) in alcohols. Under the relaxed steric conditions of the anion, the s character probably changes somewhat. Small changes in s character do not change the results significantly. [b] Reference 5. [c] Reference 6.

than the fluorine atom itself. The results confirmed the earlier arguments of Schubert, *et al.*[8,13]

The experimental work of Brauman and Blair[3] provides striking confirmation of the expectation expressed above. In the negatively charged alkoxide anion (the conjugate base of the acidic alcohol), the negative charge resides predominantly on the oxygen but the ion will be stabilized (*i.e.*, its basicity will be reduced) to the extent that this charge can be delocalized[14] onto the alkyl groups. In this case the electronegativities of the alkyl groups (2.27–2.29) are all *greater* than that of an oxygen atom with a unit negative charge ($\chi_o \leq 0$)[15] and hence absorb electron density from the latter and the larger groups are capable of absorbing a greater amount before becoming saturated. This interpretation is thus essentially the same as that suggested earlier by Schubert, *et al.*,[8] the larger groups are more polarizable and can absorb charge more readily, but may be expressed in terms of electronegativity parameters derived from fundamental *atomic* properties rather than intuitive arguments. The results are given in Table I. It should be noted that these results were obtained using the simplifying assumption of electronegativity equalization.[9–11] The problems and errors inherent in this simplification have been discussed elsewhere[9,16] and attempts have been made to improve the calculations by various means,[17] but it may be said that the *qualitative* trends shown in Table I will not be altered by such attempts to improve the quantitative calculations with the possible exception of the very large groups (*n*-butyl, *tert*-butyl, *n*-pentyl). While the present values can hardly be interpreted as accurate estimates of the real charges, they are internally self-consistent and at least as reasonable as the estimates obtained by more elaborate methods. The very high values of the MINDO estimates (−0.8 to −1.0 on oxygen)[5] and CNDO/2 estimates (−0.67 on oxygen with almost no dependence upon the nature of R)[6,17a] result from the neglect of the effect of forcing large electron densities on a small oxygen atom.[18]

It is apparent that when discussing the inductive effect of groups it will be necessary to consider both inherent electronegativity and relative charge capacity. In some ways, this result is akin to Pearson's suggestions[19] that a hardness–softness factor (the HSAB principle) be considered in addition to inherent strength in acids and bases. However, even here the possibility of confusion can exist. Pearson and Songstad[20] have claimed that the *tert*-butyl group is "harder" than the methyl group and that it is a poorer electron donor (toward electronegative substrates) despite general opinion to the contrary. As can be seen from the above discussion, the *tert*-butyl group is both a better donor and a better acceptor (in appropriate situations) than methyl or hydrogen. If experimental criteria and applications of the HSAB rule indicate that *tert*-butyl is "harder" than methyl, it is apparent that factors other than polarizability must be responsible for "softness." This conclusion has been reached on the basis of other evidence elsewhere.[17,21]

Registry No.—OH^-, 14280-30-9; CH_3O^-, 3315-60-4; $C_2H_5O^-$, 16331-64-9; $C_3H_7O^-$, 26232-83-7; $C_4H_6O^-$, 26232-84-8; $C_5H_{11}O^-$, 26675-02-5.

Acknowledgment.—I should like to thank Professor W. M. Schubert for helpful criticism of this article.

(13) Unfortunately, ref 8 was unknown to the author in 1965. Although derived independently, Figure 1 of ref 9 provides a quantification of Figure 2 of ref 8 for the electron donating and withdrawing properties of alkyl groups with respect to the hydrogen atom.

(14) The term delocalization is used here to mean simply that all the atoms in the alkoxide ion acquire a negative charge through the inductive effect with no implications of conjugation or hyperconjugation.

(15) A *negative* electronegativity, like a negative pH, is an extremely unlikely, though possible situation. The meaning of this value is that oxygen *cannot* contain a total unit negative charge while coexisting in a covalent bond with *any* other atom or group of atoms.

(16) R. Ferreira, *J. Phys. Chem.*, **68**, 2240 (1964); G. Klopman, *J. Amer. Chem. Soc.*, **86**, 1463 (1964); J. E. Huheey, *J. Phys. Chem.*, **70**, 2086 (1966).

(17) J. E. Huheey, *J. Org. Chem.*, **31**, 2365 (1966); R. S. Evans and J. E. Huheey, *J. Inorg. Nucl. Chem.*, **32**, 777 (1970).

(17a) NOTE ADDED IN PROOF.—Similar results have recently been obtained by R. B. Hermann, *J. Amer. Chem. Soc.*, **92**, 5298 (1970)

(18) For discussions of the relation between effective charge and Coulomb integrals in terms of fixed (*i.e.*, ionization potential) electronegativity *vs.* variable orbital electronegativity, see G. Doggett, *Theor. Chim. Acta*, **15**, 344 (1969), and references therein.

(19) R. G. Pearson, *J. Amer. Chem. Soc.*, **85**, 3533 (1963); *J. Chem. Educ.*, **45**, 581, 643 (1968).

(20) R. G. Pearson and J. Songstad, *J. Amer. Chem. Soc.*, **89**, 1827 (1967).

(21) R. S. Evans and J. E. Huheey, *J. Inorg. Nucl. Chem.*, **32**, 373 (1970); J. E. Huheey and R. S. Evans, *ibid.*, **32**, 383 (1970).

Preparation of Bridgehead Alkyl Derivatives by Grignard Coupling

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We have developed a simple, high yield way to convert adamantane-type bridgehead bromides to the cor-

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