4-alkyl-, and 5-alkyl-1-alkynes were used as substrates. The inspection of Table I show that the yields in the diene (**5**) are very improved, while the formation of trialkylbenzenes is substantially hindered, when the alkyne has the substituent alkyl group in the α position with respect to the triple bond. Thus, the reaction of 3-methyl-1-pentyne with $(i\text{-}C_4H_9)_3Al$ under the reported experimental conditions (Table I, entry 4), followed by successive hydrolysis, give a 45% isolated yield of (*E*)-3,7-dimethyl-4-methylene-5-nonene (**5**), having a satisfactory chemical purity (>90%). Unfortunately, the yields in the dimer drop when the substituent alkyl group of the alkyne is in the β or γ position with respect to the triple bond.

It is noteworthy that the increasing size of the alkyl group attached to the 3 position of the 1-alkyne results in a progressive decreasing of the yields of the aromatic products (Table I, entries 3–6). This result seems to indicate that the competitive aromatizing reaction has greater steric requirements than the dimerization reaction. The improved yields in the trialkylbenzenes when 4-methyl-1-hexyne and 5-methyl-1-heptyne are used are consistent with this consideration. Reasonably steric factors may be responsible for the prevailing formation of the symmetrical over the unsymmetrical trialkylbenzene too.[7]

In exploring more widely the influence of some variables on the reaction, we have found that the molar ratio 1-alkyne to $(i\text{-}C_4H_9)_3Al$ is important to determine the direction of the reaction toward dimerization or cyclotrimerization of the terminal acetylenes (Table II). In fact, while increasing the molar ratio 1-hexyne to $(i\text{-}C_4H_9)_3Al$ from 1.0 to 3.0 has little effect on the product yields, probably because of the intervention of the other two isobutyl groups of the organoaluminum compound,[8] the excess of $(i\text{-}C_4H_9)_3Al$ with respect to the acetylenic substrate results in an increase of the diene (**5**) yields with respect to those of the aromatic products (entry 9).[9] At molar ratio 1-alkyne to $(i\text{-}C_4H_9)_3Al$ higher than 3.0, the yields of the aromatic products are strongly improved, even if the rate of the reaction decreases appreciably and tetramerization may occur as a side reaction (Table II). The reaction rate is increased and comparable results are obtained when the reaction is carried out in refluxing benzene; thus, 3-methyl-1-pentyne may be converted into 1,3,5-tri-*sec*-butylbenzene (48% GLC yield) (Table II, entry 17).

The preparative possibilities of these nickel-catalyzed reactions should be borne in mind. In fact 2,4-dialkyl-1,3-butadienes of trans configuration, not otherwise available, can be prepared in satisfactory or excellent yields in relation to the structure of the 1-alkyne. Moreover, the highly selective cyclotrimerization of the monoalkylacetylenes we observed suggests the use of these reactions as an alternative method for the synthesis of benzene derivatives having bulk alkyl substituents in the 1,3,5 positions of the aromatic ring.[7,10]

Experimental Section[11]

Triisobutylaluminum and 1-hexyne were commercial products (Fluka A. G. Co., Buchs) which were carefully distilled before use. The other 1-alkynes (**1**) employed were prepared through the corresponding α olefins by published methods.[12] Bis(*N*-methylsalicylaldimine)nickel was prepared and purified as reported elsewhere.[3] All the reaction products were recovered by preparative GLC and were identified by analysis of NMR, IR, and mass spectra.

General Procedure. In a typical run (Table I, entry 4) a weighed amount of $(i\text{-}C_4H_9)_3Al$ (5.94 g, 30 mmol) was transferred from a sealed capillary glass vial to a two-necked flask (100 ml), equipped with a magnetic stirrer, a Versilic silicone cap, and a glass stopcock, containing the nickel complex (0.163 g, 0.5 mmol) cooled at 0 °C. 3-Methyl-1-pentyne (**1**, 2.46 g, 30 mmol) was injected by hypodermic syringe through the cap and then the flask was placed in a thermostated bath at 25 ± 0.3 °C. After 40 h and removal of the volatile products (isobutane, isobutene, and unreacted **1**), the residual reaction mixture was cautiously hydrolyzed with dilute sulfuric acid, extracted with ether, and analyzed by GLC (silicone SE 301, 50–190 °C). Removal of the solvent and careful distillation gave (*E*)-3,7-dimethyl-4-methylene-5-nonene (**5**, 1.12 g, 45% yield) in addition to a high-boiling fraction. By preparative GLC (butanediol succinate LAC 6R-860, 100–170 °C) pure **5**, bp 81 °C(17 mmHg), $n^{25}{}_D$ 1.4575, IR (neat) 3090, 880 ($C{=}CH_2$), 1610, and 965 cm^{-1} (trans $-CH{=}CH-$), and pure 1,3,5-tri-*sec*-butylbenzene (**6**,[13] 0.09 g) were recovered.

Registry No.—$(i\text{-}C_4H_9)_3Al$, 100-99-2; $Ni(mesal)_2$, 14322-02-2.

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(11) Distillation and handling of all the reactants were performed under dry, purified nitrogen. All reaction were carried out at least in duplicate under a nitrogen atmosphere. GLC analyses were performed on a Perkin-Elmer F 30 instrument with flame ionization detectors and nitrogen as carrier gas, while preparative GLC was carried out on a Perkin-Elmer F 21 chromatograph. Spectral measurements were determined with the following instruments: IR, Perkin-Elmer Model 225; NMR, Jeol JMN PS-100; mass spectra, Varian MAT CH 7.
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Correlation of the Gas Phase Basicities of Primary Amines with the New Gas Phase Alkyl Inductive Substituent Constants

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Received June 2, 1976

Precise measurements of the intrinsic base strengths of an extended series of amines have recently become available from ion cyclotron resonance spectroscopic equilibrium constants.[1] Brauman and Blair[2] interpreted their striking observation that alkyl groups increase both acidity and basicity in the gas phase as due primarily to the polarization of R by a nearby ionic center. That is, polarizable alkyl groups stabilize both positive and negative charge centers which are in close proximity. This polarizability effect, in the simple electrostatic model, falls off very rapidly (r^{-4}) with distance between the centers of polarizability and of charge.[2,3] Distant alkyl groups,

Table I. Relative Proton Affinities, ΔPA, of RNH_2, and the Corresponding σ_I (R) and $\Delta\sigma_I$ (R) Values

Registry no.	R	ΔPA,[a] kcal/mol	$-\sigma_I$[c]	$-10^2\ \Delta\sigma_I$	ΔE_I,[e] kcal/mol
74-89-5	Me	0.0[b]	0.046	0.0	0.0
75-04-7	Et	2.7	0.057	1.1	4.4
107-10-8	*n*-Pr	3.9	0.061	1.5	6.0
109-73-9	*n*-Bu	4.4	0.063	1.7	7.9[f]
75-31-0	*i*-Pr	5.0	0.065	1.9	7.9
78-81-9	*i*-Bu	4.9	0.065	1.9	8.3
13952-84-6	*sec*-Bu	6.1	0.069	2.3	8.3
5813-64-9	neo-Pt	5.8	0.069	2.3	9.5
75-64-9	*t*-Bu	7.0	0.074	2.8	9.4
110-58-7	*t*-Am	8.3	0.078[d]	3.2	10.6

[a] ±0.2 kcal, cf. ref 11. [b] $PA(MeNH_2) = 210 \pm 2$ kcal (ref 17); $\Delta PA = PA(RNH_2) - PA(MeNH_2)$; still more recent PA values (ref 5) yield ΔPA's consistently higher by around 0.4 kcal/mol than those given in the table, but a plot of these values vs. σ_I is not quite as good as the plot in Figure 1. [c] Reference 10. [d] L. S. Levitt and B. W. Levitt, *Tetrahedron*, **29**, 941 (1973); also ref 10. [e] Reference 5. [f] Reference 14 gives this as 7.6; $\Delta E_I = E_I(MeNH_2) - E_I(RNH_2)$; $E_I(MeNH_2) = 222.8$ kcal/mol (ref 5).

however, have been found[4] to destabilize rather than stabilize negative charge, i.e., gas-phase *acidities* are decreased in phenols, acetylenes, and carboxylic acids.[4] These destabilizing effects can be interpreted as a result of dipoles between R groups and sp^2 or sp hybridized C atoms.[4]

Aue, Webb, and Bowers[5] have recently shown that the orders of magnitude of the observed effects of alkyl groups on the gas-phase base strengths of amines are consistent with the simple electrostatic model. However, assumptions regarding polarizabilities of alkyl groups and uncertain distance factors (extended conformations were taken) were both necessary.[5]

An alternative approach to treating these data involves the use of substituent constants. Polar substituent constants, σ^*, for alkyl groups were originally obtained by the Ingold–Taft relationship,[6] from the rates of the acid- and base-catalyzed hydrolysis of esters. Although the polar and the directly related inductive (σ_I) substituent constants for alkyl groups have been strongly questioned,[7] applications to numerous series of ionization potential data, for both organic[8] and organometallic compounds,[9] have been quite successful. Very recently a review of the σ_I values for alkyl groups has been made,[10] and results from several different approaches, both empirical and theoretical, were found to give a consistent and precise set of inductive substituent parameters. Since both alkyl amines and their conjugate acids are formally saturated, and both involve very similar (approximately) sp^3 tetrahedral geometries at the nitrogen atom, the gas-phase base strengths appear ideally suited for testing the applicability of the σ_I values. The new σ_I values themselves are claimed[10] to be *intrinsic* measures of alkyl induction and polarizability, having been obtained both from statistical analysis of gas-phase ionization potential data and polarizability "models", neither of which involve any solvation effects.

Figure 1 shows a plot of the gas-phase basicities (relative proton affinities) for an extended series[11] of primary alkyl amines vs. the corresponding σ_I (R) values (data from Table I). That is, the standard free energy (or enthalpy) changes for the following gas-phase proton transfer reactions are plotted in Figure 1:

$$RCH_2NH_2 + CH_3NH_3^+ \rightleftharpoons RCH_2NH_3^+ + CH_3NH_2$$

The remarkable linear relationship shown in Figure 1 clearly demonstrates the applicability of the σ_I parameter to equilibria of this kind. The equation for the regression is

$$\Delta PA = -258\Delta\sigma_I \text{ kcal/mol} \qquad (1a)$$

which has s.d. = 0.1 kcal and $r = 0.999$. Equation 1a can also be written (with the limitations noted in reference 17).

$$PA(RNH_2) = 198 - 258\sigma_I\,(R)\ (\text{kcal}) \qquad (1b)$$

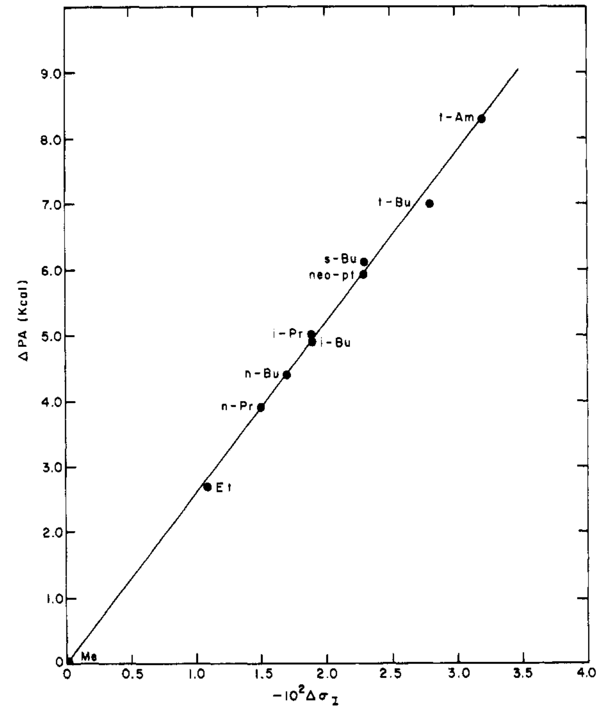

Figure 1. Correlation of the proton affinities of primary aliphatic amines, RNH_2, by the substituent parameter, σ_I (R). Abscissa: $-10^2\Delta\sigma_I = -[\sigma_{I(R)} - \sigma_{I(CH_3)}]10^2$. Ordinate: $\Delta PA = PA_{(RNH_2)} - PA_{(CH_3NH_2)}$.

Two alternative interpretations may be made of the excellent correlation found in Figure 1. First, the observed alkyl substituent effect on gas-phase base strengths and the σ_I parameters are both determined to quantitative approximation by polarizability effects, involving no internal inductive effects.[2,3] Second, the σ_I parameters are a measure of internal inductive effects of alkyl groups, but the observed alkyl substituent effects are a combination of polarizability and internal inductive effects, both having very nearly the same structural dependencies, i.e., on chain lengthening and branching. We cannot at the present time distinguish with certainty between these two interpretations. However, a recent comparison[12] of the quantitative effects of alkyl groups on the gas-phase acidity of alcohols with the corresponding gas-phase basicities of the amines does suggest that the second interpretation[12] is the correct one.

Since the ionization potentials, E_I, of the three classes of amines are also a linear function[13] of $\Sigma\sigma_I$, it necessarily follows that the ΔPA values for the primary amines are likewise a linear function of their E_I's. The equation for the E_I–σ_I correlation was found to be[13]

$$E_I = 9.62 + 13.8\sum\sigma_I\,(R)\ (eV) \qquad (2)$$

Using, however, IP data very recently obtained[5] by the PES method (which yields vertical rather than the adiabatic E_I's by the PI method[14]), one obtains an excellent correlation with the new gas-phase σ_I values (with $r = 0.991$) for the complete series of primary amines discussed here. The new E_I–σ_I correlation equation is given by

$$E_I(RNH_2) = E_I(NH_3) + a_I\sigma_I = 10.19 + 11.49\sigma_I\,(R)\ (eV) \qquad (2a)$$

Eliminating σ_I (R) from eq 1b and 2a leads to

$$PA(RNH_2) = 18.44 - 0.966E_I\ (eV) \qquad (3)$$

from which good estimates of proton affinities can be made directly from the experimental ionization potentials, or vice versa. (The correct chronology of the relationships given above is, of course, ref 13, 1b, and 5 and eq 1a and 1b of the present paper.)

Good linear plots of PA vs. E_I for primary amines have previously been published.[1b,5] In accord with eq 3, as has already been demonstrated for the alcohols[15] and ethers,[16] the greater the basicity at the atom with a lone pair of electrons, the lower is the ionization potential at that atom.

In view of the fact that Figure 1 represents a nearly perfect correlation, it is tempting to actually *define* the σ_I (R) values in terms of the gas-phase proton affinities of primary amines. If this is done from the relation

$$-\sigma_I\,(R) = \Delta PA/258 + 0.046 \qquad (4)$$

the results for the alkyl groups in the order they appear in Table I are 0.046, 0.056, 0.061, 0.063, 0.066, 0.065, 0.070, 0.069, 0.074, and 0.079, almost precisely the same as the σ_I values obtained by detailed statistical analysis of ionization potential data.[10]

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A General Procedure for the Base-Promoted Hydrolysis of Hindered Esters at Ambient Temperatures

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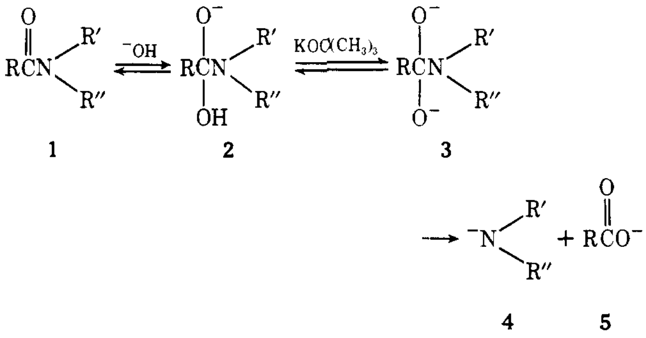
Received June 7, 1976

Recently, we reported that essentially "anhydrous hydroxide" was an excellent reagent for the hydrolysis of tertiary amides at ambient temperatures.[1] This reagent was generated via the reaction of 2 equiv of potassium *tert*-butoxide with 1 equiv of water.[2] Mechanistically, it appeared that the relatively unsolvated hydroxide added to the tertiary amide, **1**, to produce **2**. Removal of a hydroxylic proton from **2** would then produce the dianion, **3**. Fragmentation of **3** then produced the most stable pair of anions, which in this case was **4** and **5**. Utilizing this concept, a series of tertiary amides was hydrolyzed in yields ranging from 65 to 100% in relatively short reaction times at room temperature. The facility of this process suggested to us that similar reaction conditions might permit the base-catalyzed hydrolysis of hindered esters at room temperature. This report provides the details of our study of the base-promoted hydrolysis of esters at ambient temperatures.



In any study of the saponification of hindered esters, the classes of esters which must be considered include esters of pivalic acid, mesitoic acid, and *tert*-butyl alcohol. Table I lists the yields obtained in the room temperature hydrolysis of these and other esters. In a typical procedure, approximately 1 equiv of ester, 2 equiv of water, and 8 equiv of potassium *tert*-butoxide were stirred as a slurry for 2–48 h at room temperature. As shown in Table I, close to quantitative yields could be obtained from most of the simple esters in relatively short times at room temperature. For highly hindered esters, longer reaction times were required, but hydrolysis could still be accomplished at room temperature.

While the heterogeneous nature of the reaction mixture made accurate kinetic data virtually unattainable, qualitative studies could be made. As shown in Table I, time vs. yield determinations were made for the hindered esters *tert*-butyl benzoate and methyl mesitoate. It would appear from this data that given sufficient time (5–6 days) even a very hindered ester such as methyl mesitoate could be saponified in close to quantitative yield at room temperature.

The mechanistic aspects of this ester hydrolysis are of interest. The mechanism of hydrolysis of hindered esters has been studied in detail[3-7] both in acid and in base. Although the vast majority of esters are saponified via a $B_{AC}2$ mechanism,[4,5,7] evidence has been presented that in special cases a $B_{AL}2$ mechanism can predominate.[5,6] In the normal hydrolysis of methyl mesitoate, acyl–oxygen cleavage has been shown to occur in aqueous media.[4,5] However, methoxide has been shown to react with methyl mesitoate to yield the mesitoate anion via alkyl–oxygen cleavage. Since little is known about