$K \leqslant 10^{-5}$ *M*. Hence the affinity of the diazines for amide ions is very high.

No nmr evidence was found for the formation of an adduct between pyridine and amide ion in ammonia, although the solution gradually discolored at room temperature.

Other complexes will be reported shortly.

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A Principle for Establishing a Carbon Chain on an Aromatic Ring in Place of Nitrogen, Oxygen, Fluorine, Sulfur, Chlorine, Bromine, or Iodine Functionality[1]

Sir:

Methods for attaching a carbon chain to an aromatic ring are few and subject to severe limitations. Thus, Friedel–Crafts reactions, SNAr arylation of carbon nucleophiles,[2] and arylation of carbanions *via* arynes[3] afford mixtures of isomers or require the presence of special activating groups. Organometallic methods suffer from other disadvantages.

The recently recognized affinity of aryl radicals for certain nucleophiles[4,5] and the fact that aryl radicals can be generated through the action of solvated electrons upon aromatic compounds carrying nucleofugic[6a] substituents[4,6b] suggest a new and general principle of synthesis. A carbon moiety, provided as a suitable carbanion, is caused to attach to an aromatic ring by exposing it and an aromatic system carrying a suitably nucleofugic substituent to stimulation by solvated electrons; the electrons provoke formation of an aryl radical which coordinates with the nucleophile, and finally an excess electron is relinquished. The mechanism is in part as sketched in Scheme I.

Scheme I

$$e^- + ArX \longrightarrow [ArX]\cdot^- \tag{1}$$

$$[ArX]\cdot^- \longrightarrow Ar\cdot + X^- \tag{2}$$

$$Ar\cdot + R{:}^- \longrightarrow [ArR]\cdot^- \tag{3}$$

$$[ArR]\cdot^- + ArX \longrightarrow ArR + [ArX]\cdot^- \tag{4}$$

We now report that the acetone enolate ion is a suitable carbanion, that liquid ammonia is a suitable solvent, and that sodium or potassium metal is a suitable source of electrons for synthesis according to this principle. Moreover, we find that several substituents in which the first atom is variously nitrogen, oxygen, fluorine, sulfur, chlorine, bromine, or iodine are sufficiently nucleofugic to allow substantial yields of arylation products to be obtained. Details on a number of reactions are set forth in Table I.

The products obtained are in part arylacetones, $ArCH_2COCH_3$, in part 1-aryl-2-propanols, $ArCH_2CH(OH)CH_3$, and in part 1,1-diarylacetones which represent double arylation. The sum of arylacetone and 1-aryl-2-propanol yields is as high as 89% as analyzed by glpc or as high as 71% as isolated and weighed. Little effort has been made to optimize yields. For isolation purposes, the mixture of arylacetone and 1-aryl-2-propanol formed was sometimes treated with an oxidizing reagent[7] so that both could be isolated as the ketone.

Table I. Reactions with Potassium Acetonate in Ammonia at −78°, Provoked by Potassium Metal

Substrate	[Substrate], *M*	$[CH_3COCH_2^-K^+]$, *M*	[K],[a] *M*	Method[b]	Yields, %[c] $C_6H_5CH_2COCH_3$	 $C_6H_5CH_2CH(OH)CH_3$	 Other
C_6H_5F	0.064	0.27	0.10	B	3	46	$(C_6H_5)_2CHCOCH_3$, 2
C_6H_5Cl	0.30	0.80	0.46	B	68[d]		
C_6H_5Br	0.38	0.94	0.35	B	52[d]		
C_6H_5Br	0.12	0.33	0.044	A	67	10	$(C_6H_5)_2CHCOCH_3$, 14 C_6H_5Br, 3
C_6H_5I	0.18	0.60	0.18	B	71[d]		
C_6H_5I	0.18	0.68[e]	0.17[e]	B	52[d]		
$(C_6H_5)_2O$	0.024	0.25	0.018	A		4.5	$(C_6H_5)_2O$, 93
$C_6H_5OP(O)(OEt)_2$	0.040	0.27	0.068	B	4	42	
$(C_6H_5)_2S$	0.030	0.14	0.045	A	18	71	C_6H_5SH, 84
$C_6H_5NMe_3^+I^-$	0.024	0.20	0.022	A	46	18	$(C_6H_5)_2CHCOCH_3$, 7
$C_6H_5NMe_3^+I^-$	0.12	0.68[e]	0.18[e]	B	56[d]		
$p\text{-}CH_3C_6H_4Br$	0.053	0.28	0.060	A	57[f]	17[g]	$C_6H_5CH_3$, 26
$p\text{-}CH_3C_6H_4NMe_3^+I^-$	0.045	0.43	0.064	A	30[f]	42[g]	$C_6H_5CH_3$, 6
$p\text{-}CH_3OC_6H_4Br$	0.061	0.21	0.043	A	36[h]	10[i]	$C_6H_5OCH_3$, 44
$p\text{-}CH_3OC_6H_4NMe_3^+I^-$	0.016	0.56	0.024	A	20[h]	39[i]	$C_6H_5OCH_3$, 40

[a] Concentration of K (or Na) if no reaction had occurred. [b] Method A, substrate added to $CH_3COCH_2^-K^+$ and K in NH_3; method B, K added to substrate and $CH_3COCH_2^-K^+$ in NH_3 until blue color persisted. [c] Yields are based on substrate introduced; unless otherwise specified, they are by glpc, with nmr and ir confirmation of product identities. [d] Yield of isolated product, after oxidation of product mixture;[7] no 1-phenyl-2-propanol isolable by this procedure. [e] Na instead of K. [f] *p*-Tolylacetone. [g] 1-(*p*-Tolyl)-2-propanol. [h] *p*-Anisylacetone. [i] 1-(*p*-Anisyl)-2-propanol.

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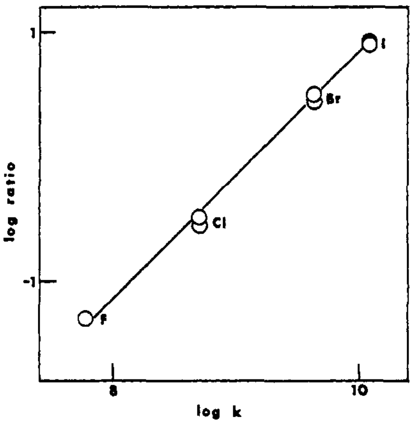


Figure 1. Correlation of log (phenylacetone/1-phenyl-2-propanol product ratio) with log *k* for reactions with the hydrated electron in water,[9] for the four halobenzenes. Most of the data are from experiments not listed in Table I. The alkali metal was K except that it was Na for one of the two points for iodobenzene.

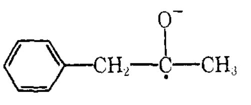
Arylation occurs without isomerization in the aryl group. When arylation was effected with *p*-bromotoluene, *p*-bromoanisole, or *p*-tolyl- or *p*-anisyltrimethylammonium iodide, the arylacetones obtained were in all cases para isomers uncontaminated by ortho or meta isomers, as shown by comparison of properties with those of authentic samples.

To date, only one other ketone enolate ion has been investigated, namely, that from cyclopentanone. It was para tolylated with *p*-tolyltrimethylammonium iodide in ammonia at −33°. By glpc, the yields of 2-(*p*-tolyl)cyclopentanone and 2-(*p*-tolyl)cyclopentanol were 28 and 37%, respectively; after oxidation[7] and work-up, the isolated yield of ketone was 34%.

The fact that aryltrimethylammonium ions and aryl diethyl phosphates may be employed is of special significance because of the ease with which these can be obtained from aromatic amines and phenols,[8] respectively.

We suspect this principle of synthesis to have much wider validity than actually demonstrated in our experiments. We anticipate that yet other aromatic substituents may have sufficient nucleofugicity to be useful, that the method is applicable to ketone enolate ions and carbanions from nitriles[4] in general, and that other types of carbanions as well as other solvents and other sources of electrons may be employed.

In our experiments, the proportions of arylacetone and 1-aryl-2-propanol obtained varied according to the identity of X in ArX. The naive view that the alcohol product is derived simply by reduction of the ketone in an electron-rich environment is refuted by the fact that phenylacetone is not reduced to 1-phenyl-2-propanol by potassium in liquid ammonia under the conditions of our experiments. It is converted to an enolate ion instead.



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The ratios of phenylacetone to 1-phenyl-2-propanol, as obtained from the four halobenzenes, correlate linearly (in log–log fashion) with their rates of reaction with the hydrated electron;[9] see Figure 1. The slope is 1.01 and the correlation coefficient is 0.998. We suggest that the immediate product of combination of phenyl radical with acetonate ion is ketyl-like radical anion **1** which is then involved in competing reactions: electron transfer to ArX as in eq 4 or reduction to the alcohol. The mechanism of the latter is uncertain, but presumably its rate is independent of the identity of the halogen atom of the original halobenzene. On the other hand, the rate of electron transfer according to eq 4 depends on the identity of the halogen much the same as when the halobenzene reacts with the hydrated electron.

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Molecular Magnetic Moments, Magnetic Susceptibility Anisotropy, Molecular Quadrupole Moment, and Sign of the Electric Dipole Moment in Methylsilane

Sir:

We report here the molecular Zeeman effect in CH_3SiH_3 and CH_3SiD_3. The results give the magnitudes and relative signs of the molecular *g* values, the magnetic susceptibility anisotropy, and the molecular quadrupole moments of the molecule.

The microwave spectra of both $H_3{}^{28}SiCH_3$ and $D_3{}^{28}SiCH_3$ have been studied previously and a substitutional structure is also available.[1] The equations describing the linear and quadratic Zeeman effect in a symmetric top have been developed in detail[2–4] and the experimental apparatus involving the high-field electromagnet has been described previously.[5] $J = 0 \rightarrow 1$ transitions in both H_3SiCH_3 and D_3SiCH_3 were observed with $\Delta M = \pm 1$ selection rules. The $J = 0 \rightarrow 1$ transition of CH_3SiH_3 was split by 962 ± 3 kHz at a field of 17,603 ± 20 G, and the center frequency of the doublet was shifted by −14 ± 5 kHz from the zero field frequency of 21,937.93 MHz. The $J = 0 \rightarrow 1$ transition of CH_3SiD_3 was split by 830 ± 5 kHz at a field of 17,602 ± 20 G, and the center frequency of the doublet was shifted by −12 ± 5 kHz from the zero field frequency of 19,245.46 MHz. From eq 1 of ref 3 the splitting of the doublet is given by $2\mu_0 g_\perp H/h$ and the shift is given by $-H^2(\chi_\perp - \chi_\parallel)/15h$. Thus we obtain the following values for $g_\perp$

$$\begin{array}{ll} CH_3SiH_3 & |g_\perp| = 0.03583 \pm 0.00012 \\ CH_3SiD_3 & |g_\perp| = 0.03092 \pm 0.00019 \end{array} \qquad (1)$$

Notice that the sign of $g_\perp$ cannot be determined from this analysis. From the center frequency shifts a value

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