SR1 Phenolation of Nitrile Carbanions, and Ensuing Reactions.
A New Route to Alkylbenzenes$^{1,2}$

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Under stimulation by solvated electrons, the anions of aliphatic nitriles react with halobenzenes, phenyl diethyl phosphate, or phenyltrimethylammonium ion to form the α-phenyl derivative of the nitrile, the alkylbenzene that would result from decyanation thereof, and a benzylic radical dimer (e.g., 1,2-diphenylethylene when the cyanoamethyl anion is used), as well as minor products.

In the postulated mechanism, a phenyl radical combines with the nitrile anion to form the radical anion of an α-phenyl nitrile. The latter may lose an electron to appear as the nitrile, or it may expel cyanide ion forming a benzylic radical which dimerizes or is reduced to an alkylbenzene. The reaction has potential value in synthesis for the purpose of installing an alkyl group on an aromatic ring in place of a nucleofugic substituent or an amino or hydroxy group.

Aryl radicals are intermediates in the recently recognized SR1 mechanism of aromatic nucleophile substitution.$^{4}$ Supply of an electron to a substituted benzene, in which the substituent is a halogen or other suitable leaving group, forms a radical anion which then ejects the nucleofugic substituent, emerging as an aryl radical. The radical combines with a nucleophile to form a new radical anion which, upon getting rid of a surplus electron, becomes a stable nucleophile substituent product.

An alkali metal dissolved in liquid ammonia exists for the most part as alkali metal cations and solvated electrons,$^{5}$ and is effective in provoking SR1 reactions. Among the nucleophiles successfully involved in substitutions by this mechanism are the amide ion,$^{6,7}$ ketone enolate ions,$^{8,9}$ and hydrocarbon-derived carbanions such as the fluorenide ion.$^{10}$

Hereinafter, aromatic SR1 reactions involving α-cyanocarbanion nucleophiles have received only preliminary attention. Kim and Bunnett$^{11}$ observed chlorobenzene to react with the cyanoamethyl anion and potassium metal in liquid ammonia to form phenylacetonitrile, toluene, benzene, and aniline. Rossi,$^{12}$ in a similar experiment, with iodobenzene in place of chlorobenzene, and obtained a substantial amount of l,2-diphenylethane (DPE)$^{12}$ as m11 as the minor products. In the postulated mechanism, a phenyl radical combines with the nitrile anion to form the radical anion of an α-phenyl nitrile. The latter may lose an electron to appear as the nitrile, or it may expel cyanide ion forming a benzylic radical which dimerizes or is reduced to an alkylbenzene. The reaction has potential value in synthesis for the purpose of installing an alkyl group on an aromatic ring in place of a nucleofugic substituent or an amino or hydroxy group.

\[
\text{PhX} + \text{RCH}^- + \text{K}^+ \rightarrow \text{PhCHR}^- + \text{PhCHR}^- + \text{CN} + \text{H}^+ \]

PhCHR + PhCHR + PhCH-CHPh + C4H8 + C6H5NH2

Results

Our two principal series of experiments are summarized in Tables I and II.

Table I concerns several reactions involving the cyanoamethyl anion, from reaction of acetonitrile with an equimolar amount of KNH2. The several runs differ in the identity of the monosubstituted benzene employed, in the temperature, in the proportions of reactants, and in the method for conducting the experiment. In some runs, solvated electrons (from the dissolved potassium metal$^2$) were constantly in large excess over the aromatic substrate, while in others the concentration of solvated electrons was kept quite low. The products obtained from reactions with cyanoamethyl anion (eq 1, R = H) are those described by earlier workers, as mentioned, plus a small amount of diphenylmethane (DPM).$^{13}$ Toluene is prominently formed, in yields ranging from 14 to 40%. Benzene is also prominent, in yields from 8 to 44%. DPE is formed in considerable amount in some runs but to a minor extent in others; yields vary from 3 to 40%. The same can be said for phenylacetonitrile (PAN), the yields of which are from 2 to 31%. The highest yield of DPM encountered was 7%, and in some runs only trace amounts were formed. Aniline yields are also very small.

Despite the considerable differences in conditions and in results among the several runs of Table I, it is difficult to correlate product patterns with experimental variables. It should be noted that our procedures for the addition of potassium metal and/or aromatic substrate during the course of a run were not such as to provide close control of addition rates or of solvated electron concentration in the reaction mixture. In consequence, there may have been substantial variation of the concentration of solvated electrons and/or of reaction intermediates, even between runs ostensibly conducted by the same technique. For exceedingly fast reactions, as these are, such variation plausibly would have a significant effect on product proportions.

The experiments of Table II concern carbanions derived from other nitriles. Again there is substantial variation of product patterns between runs, and again...
the variation is often difficult to correlate with differences in reaction participants or conditions. Alkylbenzines, PhCH₂R, corresponding to tolune in Table I, are prominent products of most runs, as is benzene. Phenyl derivatives of the starting nitriles are formed in significant amounts in some runs but only in trace amounts in others. 1,1-Diphenylalkanes, Ph₂CHR, appear to a significant extent in only a few runs, most of which involve the aromatic substrate in excess. Dimetric products, meso and racemic PhCH₂CHRPh, are formed in amounts totaling as high as 26% in reactions of the anions from proprio- and butyronitrile, but only in minor amounts in the other runs. The yields of aniline are variable, but never large.

**Photostimulated Reactions.**—Inasmuch as Srnl reactions of halobenzenes with acetone enolate ion are formed in amounts totalling as high as 26% of the aromatic substrate in excess.

**TABLE I**

<table>
<thead>
<tr>
<th>Run no.</th>
<th>Registry no.</th>
<th>Substituent</th>
<th>Ph:X CH₂CNK</th>
<th>Temp (°C)</th>
<th>Ether</th>
<th>Method</th>
<th>Yield (%)</th>
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<td>45</td>
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</table>

See footnote a, Table I. b Concentration that would have prevailed had there been no reaction; the K indicated in parentheses was added after ice and 150 ml of ether. c Phenol (2%) also formed. d Detected qualitatively.
occur not only as provoked by solvated electrons, but also with great facility under stimulation by near-ultraviolet light; the action of light on mixtures of bromobenzene and cyanomethyl anion was investigated. Table III provides an overview of the results.

Negligible reaction occurs in the dark (run 34). However (run 35), there is appreciable reaction during 2 hr of exposure to near-ultraviolet radiation in the photochemical reactor. The reaction is sluggish, though, for only 38% of the bromobenzene reacts under those conditions. In contrast, the reaction of bromobenzene with acetone enolate ion under similar conditions is complete within 50 min or less. The product pattern resembles the benzene and toluene yields are quite small relative to those of PAN and DPE.12

The objective of runs 41 and 42 was to see whether benzyl radicals are able to combine with the anion of 3-methylphenylacetanilide (MPAN) rapidly enough to compete with other processes. As discussed below, such combination would be expected to lead ultimately to 1-(3'-methylphenyl)-2-phenylethane. In run 41, the formation of DPE in 29% yield indicates that benzyl radicals are, at least in part, intermediates in this reaction.13

Comparison of Reactivity toward Phenyl Radical.—The products obtained from photochemical reaction of bromobenzene with an equimolar mixture of the cyanomethyl and acetone enolate ions are mainly those attributable to reaction with the former of these species. The same qualitative result was obtained from potassium metal stimulated reaction of bromobenzene with a mixture of these nucleophiles (run 38). The reactivity of the cyanomethyl anion toward the phenyl radical is thus demonstrated to be much greater than that of acetone enolate ion. It is noteworthy that the phenylacetone-1-phenyl-2-propanol product ratio from potassium metal stimulated reaction of bromobenzene with this mixture of nucleophiles (run 38) was ca. 0.4, much lower than observed in reaction with acetone enolate ion uncontaminated with cyanomethyl anion.

Attempts to Observe Reactions of Benzyl Radicals with a Carbanion.—Conceivably (vide infra), DPE might have been formed by a reaction pathway involving combination of benzyl radical with the phenylacetanilide anion. In order to check this possibility, the experiments outlined in Table IV were performed.

The objective of runs 41 and 42 was to see whether benzyl radicals are able to combine with the anion of 3-methylphenylacetanilide (MPAN) rapidly enough to compete with other processes. As discussed below, such combination would be expected to lead ultimately to 1-(3'-methylphenyl)-2-phenylethane. In run 41,
the benzyl radical was generated by reaction of potassium metal with benzyl methyl ether and, in run 42, by the action of potassium metal on a mixture of chlorobenzene and cyanomethyl anion (see the discussion below). Although DPE was a prominent product of both reactions, no 1-(3'-methylphenyl)-2-phenylethylene was detectable as a product in run 41 or 42. We established that as little as 0.1% of this product would have been detectable. We conclude that benzyl radical is unreactive with the anion of MANP.

Decyanation of Nitriles.—We found it necessary to give some experimental attention to this topic, which is relevant both to experimental procedures for our reactions and to theoretical interpretation. Although instances of the decyanation of nitriles (RCN → RH) through the action of alkali metals were recorded decades ago,

only in recent years has the reaction received much forthright attention.18–20

We investigated the decyanation of phenylacetonitrile (PAN) and α-phenylbutyronitrile (PBN) in liquid ammonia medium. Results are summarized in Table V.

Runs 44 and 45 are especially illuminating. The conditions for these runs closely resemble those for an experiment of Arapakos, et al.,28 but they differ in the manner of quenching the reaction mixture at the end of the experiment. Run 44 was treated first with excess sodium benzoate, which destroys solvated electrons,31,32 and then neutralized with NH₄Cl. Run 45 was quenched directly with ice, while the reaction mixture was still blue owing to solvated electrons; Arapakos, et al.,28 also quenched with ice. The sodium benzoate quenched reaction gave a 52% yield of decyanation product (toluene), in nearly perfect accord with the balanced equation (eq 2). The ice-quenched reaction

2RCHCN + 2Na → RCH + RCHCN-Na⁺ + NaCN (2)

afforded 91% of tolune, in agreement with the 90% reported by Arapakos, et al.

These experiments imply, first, that the conjugate base of the nitrile resists decyanation by solvated electrons in ammonia. This implication is confirmed by run 46, in which a twofold excess of KNH₂ with respect to PAN was present. Such an excess converted the PAN entirely to its conjugate base. An excess of potassium metal was employed, but the reaction mixture was allowed to stand until the metal had all reacted to form KNH₂ under catalysis by the iron present in the medium; iron had been used to catalyze formation of KNH₂ in the beginning of the experiment. When the blue color had vanished, the mixture was neutralized with NH₄Cl and it was possible to recover nearly all the PAN originally introduced. A mere trace of toluene was formed.

A further implication of runs 44 and 45 is that a substantial amount of decyanation of the nitrile conjugate base occurs during quenching with ice if solvated electrons are still present. Substantiation is provided by the results of run 47 which, like run 46, had excess KNH₂ present at the time the potassium metal was introduced, but which was quenched by ice before there had been time for much of the metal to be converted to KNH₂. In run 47, half of the PAN was decyanated and half was recovered.

Run 48 was organized so that excess water was present during addition of alkali metal. It gave a superb yield (98%) of toluene. However, when decyanation is conducted in wet ammonia with use of more than 2 mol of alkali metal per mole of nitrile, a complication of Birch reduction of an unsaturated decyanation product can become serious, as demonstrated by run 49.

These experiments indicate that decyanation in liquid ammonia is optimally conducted by dissolving the nitrile in ammonia containing water and adding just 2 mol of alkali metal per mole of nitrile. We had occasion to employ approximately these conditions of decyanation in our synthesis of 1-(3'-methylphenyl)-2-

![Table V](image)

<table>
<thead>
<tr>
<th>Table V</th>
<th>Reactions of Phenylacetonitrile (PAN) and α-Phenylbutyronitrile (PBN) with Alkali Metals in Liquid Ammonia at −33°C</th>
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<tr>
<td>52</td>
<td>PBN</td>
</tr>
<tr>
<td>53</td>
<td>PBN</td>
</tr>
</tbody>
</table>

* Concentration that would have prevailed had there been no reaction. * Concentration that would have prevailed at start had there been no reaction of PAX with KNH₂. * After 45 min, the blue color had vanished, and NH₄Cl was added to neutralize. * To PAN and KNH₂ in NH₃, K metal was added all at once, followed quickly by ice. * Ca. 36% of another product, probably 2,5-dihydroto1uenel was obtained. * 1-Phenylpropane. * (NH₄)₂SO₄ is insoluble; the concentration that would have prevailed had it dissolved is given. * Enough K metal to give a persistent blue color was added, then enough CH₃OH to discharge the color, then more K metal, etc.; total CH₃OH about 5 ml.

phenylethene, described in the Experimental Section; this product was obtained in 78% yield by decyanation of 2-(3'-methylphenyl)-3-phenylpropanonitrile.

As for the experiments with PBX in Table V, run 50 resembles run 43 in that only a little more than 1 mol of alkali metal was used per mole of nitrile; both runs gave about 50% decayation, in accordance with eq 2. Runs 51–53 test the efficacy of decyanation when proton donors other than water are present during addition of the alkali metal; they suggest that ammonium sulfate and methanol are inferior to water for that purpose.

Discussion of Reaction Mechanisms

The SAm1 mechanism, adapted to the present situation, is sketched in eq 3–6. First (eq 3) an electron source, which is the solvated electron in most of our experiments, furnishes an electron to the aromatic substrate. The resulting radical anion (eq 4) undergoes scission, ejecting the nucleofugic group and appearing as an aryl radical. Then (eq 5) the radical combines with an α-arynoalkyl anion. The new radical anion thereby formed is metastable, and may transfer a surplus electron to another molecule of the aromatic substrate (eq 6), forming an α-phenyl nitrile, an observed product, as well as the same radical anion generated in eq 3. Because it is relatively acidic, the nitrile will then undergo the acid–base reaction of eq 7 rather completely.

\[
\text{PhX} + \text{electron source} \rightarrow [\text{PhX}^\cdot -] + \text{residue} \quad (3)
\]

\[
\text{Ph}^\cdot + \text{RCHCN}^- \rightarrow [\text{PhCHCN}^-]^\cdot \quad (4)
\]

\[
[\text{PhCHCN}^-]^\cdot + \text{PhX} \rightarrow \text{PhCHCN}^- + [\text{PhX}^\cdot -] \quad (5)
\]

Further steps are required in order to account for the other products actually formed (cf. eq 1). The steps of eq 8–18 are postulated. The key step (eq 8) is one

\[
[\text{PhCHCN}^-]^\cdot \rightarrow \text{PhCH}^- + \text{CN}^- \quad (8)
\]

\[
\text{PhCH}^- + \text{PhCH}^- \rightarrow \text{PhCH}^- - \text{CPhH} \quad (9)
\]

\[
\text{PhCH}^- + e^-_{\text{sol}} \rightarrow \text{PhCH}^- \quad (10)
\]

\[
\text{PhCH}^- + \text{NH}_3 \rightarrow \text{PhCH}_2\text{R} + \text{NH}_3^- \quad (11)
\]

\[
\text{Ph}^- + e^-_{\text{sol}} \rightarrow \text{Ph}^- \quad (12)
\]

\[
\text{Ph}^- + \text{NH}_3 \rightarrow \text{CPhH} + \text{NH}_3^- \quad (13)
\]

\[
\text{PhCH}^- + \text{Ph}^- \rightarrow \text{PhCH}_2\text{R} \quad (14)
\]

\[
\text{PhCH}^- + \text{Ph}^- \rightarrow [\text{Ph}_{\text{CCN}^-}]^\cdot - \quad (15)
\]

in which the nitrile radical anion which was formed in step 5 ejects cyanide ion and thereby is transformed into a benzylic radical. In steps 9 and 14, the benzylic radical dimerizes or combines with phenyl radical to form products such as reported in Tables I and II.

No doubt the scheme should be expanded to include a step, parallel to eq 9, in which the two benzylic radicals (except when R = H) react by disproportionation, but it is known that disproportionation of α-alkylbenzyl radicals occurs only about one tenth as fast as combination.

The formation of toluene and other products of type PhCH$_2$R is attributed to acquisition of an electron by the benzylic radical (eq 10) to form an anion, which then takes (eq 11) a proton from the ammonia solvent. Likewise, the genesis of benzene is ascribed to the sequence of steps 12 and 13. Steps analogous to eq 10 and 12 have been proposed in other studies.

Two routes to DPM and other products of type PhCH$_2$R are postulated. One route is combination of the phenyl radical with a benzylic radical (step 14). The other involves phenylation (in step 15) of the anion of the α-phenylated nitrile produced in steps 3–6, spontaneous scission (in step 16) of the radical anion thus formed, and final reduction (in steps 17 and 18) of the benzylic radical so generated. The feasibility of the second route is indicated by runs 32 and 33 of Table II in which the starting nitrile has an α-phenyl substituent. However, we see no grounds to exclude the first route.

Two further steps (19 and 20) likely play some part

\[
\text{PhCH}^- + \text{R}^\cdot \rightarrow \text{PhCH}_2\text{R} + \text{R}'^- \quad (19)
\]

\[
\text{Ph}^- + \text{R}^\cdot \rightarrow \text{CPh} + \text{R}'^- \quad (20)
\]

when diethyl ether or other good hydrogen atom donor is a component of the system. These are plausible, but we cannot assert that our experiments provide evidence for them because the same products (e.g., benzene and toluene) are formed in comparable yield when ether is absent.

The production of aniline is ascribed to combination of the phenyl radical with amide ion following by disposal of a surplus electron. That aromatic primary amines are readily formed in SAm1 reactions is reported elsewhere.

It is possible to exclude some conceivable steps. The possibility that phenyl radical abstracts a hydrogen atom from ammonia to form benzene (step 21) is rejected because photostimulated SAm1 reactions of bromobenzene with acetone enolate ion in liquid ammonia afford phenylacetonitrile in high yield without appreciable formation of benzene as a by-product, unless a good hydrogen atom donor (such as isopropylamine) is present.

\section{Discussion of Reaction Mechanisms}
solvated electrons (cf. run 46, Table V). Therefore the stoichiometry of eq 2 prevails.

However, during quenching with water the anion can be reconverted to the molecular nitrile which can accept solvated electrons, etc., enabling overall decyanation yields to exceed the 50% called for by eq 2. It should be noted that run 44, in which sodium benzoate was added to absorb electrons before acidification (with NH/Cl), conforms closely to the specifications of eq 2. Also, if an acid (e.g., water) is present during reaction of the nitrile with the alkali metal, it prevents the nitrile from being tied up as its conjugate base, and decyanation is facilitated.

It is remarkable that very little DPE appeared as a product of decyanation of PAN (Table V), in contrast to the substantial amounts formed in the SNN1 phenylation of cyanomethyl anion (Table I). At most, 2% of DPE was obtained in the decyanation experiments, and DPE was not detectable as a product of the decyanations which occurred in the presence of water. Presumably both phenylation of cyanomethyl anion and decyanation of PAN occur via PAN radical anions. If two reactions involve the same intermediate, they ought to give the same products under the same conditions. We are puzzled.

**Photostimulated Reactions.**— Whereas bromobenzene reacts rapidly and efficiently with acetone enolate ion under photostimulation,

8 its reaction with the cyanomethyl anion responds only sluggishly to illumination; see Table III. Responsible for the difference is the proclivity of the [PhCH₂CN⁻] radical anion to expel cyanide ion and form benzyl radical (eq 8). In this system, the benzyl radical is rather ineffective in propagating a reaction chain. It is not very reactive with nucleophiles, as we have shown in other studies, and tends to accumulate until it dimerizes (eq 9) or takes an electron and is reduced (eq 10); both are termination steps.

Thus while the photochemical reaction of bromobenzene with acetone enolate ion has a long propagating chain, as shown by its sensitivity to radical trapping agents, its reaction with cyanomethyl anion leads largely to radicals of low reactivity which engage mainly in termination steps. Moreover, because the cyanomethyl anion is more reactive than acetone enolate ion toward the phenyl radical, its net effect is that of a radical scavenger when present during reaction of the enolate ion with bromobenzene.

That little benzene or toluene was formed in photochemical run 33 (Table III) is consistent with the interpretation offered above for the genesis of these products. In a system providing few if any solvated electrons, steps 10 and 12 would necessarily be insignificant.

**Discussion of Potentialities in Synthesis**

The reactions we describe constitute a method for installing an allyl group on a benzene ring in place of a nucleofugic substituent. Examples that we report (in Table II) concern the introduction of ethyl, propyl, isopropyl, butyl, isobutyl, and benzyl groups, as well as the methyl group (Table I).

Although in our experience the yields of alkylbenzenes (reckoned on the basis of substituted benzene, with the nitrile anion in excess) were always less than

nitrile by-product is not utterly lost because it can be occur in the same pot by quenching the reaction mixture with ice and then adding more potassium metal. Of a nucleofugic aromatic substituent, the a-phenyl result was only partially as desired. There was some of Table II were conducted in that way, but the reaction improvement in the yield of toluene or other product of type phenyl nitrile nevertheless survived. Phenols are readily converted in high yield to their diethyl phosphate esters. The sequence of two operational steps depicted in eq 24 effects, for example, the transformation of phenol to n-butylibenzene in an overall yield of 33%; the yield is 87% in the esterification step and 38% in the alkylation step (run 27, Table II). As for aromatic primary amines, they are easily quaternized, and the trimethylammonio group is suitably nucleofugic (cf. run 16, Table I).

A third attractive feature is that the alkyl group can, with the interposition of one additional step, be introduced in place of a phenolic hydroxy group or an amino group. Phenols are readily converted in high yield to their diethyl phosphate esters. The sequence of two operational steps depicted in eq 24 effects, for example, the transformation of phenol to n-butylibenzene in an overall yield of 33%; the yield is 87% in the esterification step and 38% in the alkylation step (run 27, Table II). As for aromatic primary amines, they are easily quaternized, and the trimethylammonio group is suitably nucleofugic (cf. run 16, Table I).

For the purpose of installing an alkyl group in place of a nucleofugic aromatic substituent, the α-phenyl nitrile by-product is not utterly lost because it can be converted to the desired product by decyanation. It struck us that such decyanation might be caused to occur in the same pot by quenching the reaction mixture with ice and then adding more potassium metal. Runs 10, 11, 12, and 15 of Table I and runs 26, 27, 30 of Table II were conducted in that way, but the result was only partially as desired. There was some improvement in the yield of toluene or other product of type PhCH₂R but, except in run 25, a significant amount of the α-phenyl nitrile nevertheless survived.

Consideration of the postulated reaction mechanism, with particular attention to steps 9 and 10, suggests that the yield of toluene or other PhCH₂R product should be improved, relative to that of DPE or other benzylic radical dimer, by having a rich supply of solvated electrons constantly available. However, if solvated electrons are freely available, step 12, which (with step 13) produces benzene, should also be favored with consequent reduction of the yield of toluene/benzene. These concepts notwithstanding, we find in our experiments little relationship of the product pattern to the technique used for mixing reactants. Nevertheless, we have faith that, with effort, conditions could be defined that would afford reproducibly higher yields of alkylbenzene products than we actually got.

If the synthetic objective were to replace a cyano group in a precious nitrile by a phenyl group, the phenylating reagent (e.g., chlorobenzene) would be used in excess and losses of phenyl radicals to benzene would be of little consequence. Runs 22, 26, and 28 (Table II) were conducted with chlorobenzene in excess and they did give products of type PhCH₂R in somewhat higher yields than when the nitrile anion was in excess.

For the purpose of installing an α-phenyl group in the α position of an aliphatic nitrile, Sm3 α-phenylnitrilation appears to be inferior to benzene phenylation of the nitrile anion. Benzene phenylation followed by decyanation would furnish an alkylbenzene, but synthetically such a method would suffer some disadvantages: benzene is not readily generated from monosubstituted benzenes in the presence of carbanions when the substituent has oxygen or nitrogen as first atom, and arylation by substituted benzenes sometimes gives mixtures of positional isomers.

Our experiments, especially run 48, Table V, support other indications that nitrile decyanation through the action of solvated electrons is a useful synthetic transformation.

Experimental Section

Phenylation of Nitrile Anions, Stimulated by Alkali Metal.—A procedure for phenylation of cyanomethyl anion is representative. The reaction was carried out in a three-neck, round-bottom flask fitted with a solid CO₂-isopropanol alcohol condenser, stirred by a magnetic stirrer and constantly swept by a slow stream of dry nitrogen. Ammonia from a commercial cylinder was dried with potassium and 50 ml was distilled into the reaction flask in a current of dry nitrogen. Potassium (0.080 mol) and a little ferric nitrate were added to catalyze the formation of KN₃H. After the metal had all reacted (care was taken to rinse back into the solution the amide splashed up and deposited on the walls of the flask), the solution was cooled to –78° and acetonitrile (0.080 mol) was added dropwise. After a few minutes, 0.067 mol of chlorobenzene was added, and then potassium metal (0.081 mol) in small pieces. Some sodium benzoate was added and then the brownish-red mixture was neutralized by adding excess NH₃Cl, which caused the color to fade. Diethyl ether (50 ml) and internal standards (ethylbenzene and biphenyl) were added, and the ammonium was allowed to evaporate. Water was added, the two layers were separated, the aqueous phase was extracted with ether, and the combined ether fractions were washed neutral and dried over anhydrous sodium sulfate. The solution was analyzed by gpc on a column of 10% Carbosax 20M on Chromosorb P.

Identification of Products.—Analysis was performed on samples collected by preparative gpc on columns of either 10% silicone rubber SE-54 or 10% Carbosax 20M on Chromosorb P. Unreacted starting material, benzene, alkylbenzenes, α-phenyl nitriles, diphenylmethane, triphenylmethane, 1,2-diphenylethene, aniline, and phenol were identified by comparison of their glpc retention times and ir spectra with those of authentic samples, unless otherwise stated. Evidence for the identity of other products is now presented.

α-Phenylnorvaleronitrile had ir (CCl₄) 2250 cm⁻¹; mass spectrum at (m/e (rel intensity) 159 (molecular ion, 17), 133 (10), 117 (100), 110 (20), 91 (50), 77 (10), α-Phenylviloveronitrile had ir (CCl₄) 2250, 1390, 1355 cm⁻¹;
m/e (rel intensity) 266 (molecul ar peak, <0.01), 167 (s), 133 (88), 132 (70), 115 (10), 115 (8), 104 (9), 92 (29), 91 (100), 77 (10), *m* 69.2 (133 91), m* 46.5 (91 65).

Reactions of Table III.—For photostimulated reactions, the reaction mixtures were prepared as described above. The reaction flask was then placed into a Rayonet photochemical reactor and the mixture was irradiated by >350-nm lamps. For run 38, the experimental procedure was the same as for the phenylation of nitrile anions. Phenylation was identified by comparison of its gpc retention time and mass spectrum with those of an authentic sample. 1-Phenyl-2-propanol was identified by ir (CHCl₃), 3600, 3450, 3110-2870, 1600, 1450, 1350, 680 cm⁻¹; mass spectrum m/e (rel intensity) 266 (molecular peak, <0.01), 167 (s), 133 (88), 132 (70), 115 (10), 115 (8), 104 (9), 92 (29), 91 (100), 77 (10), *m* 69.2 (133 91), m* 46.5 (91 65).

Reactions of Table III.—For photostimulated reactions, the reaction mixtures were prepared as described above. The reaction flask was then placed into a Rayonet photochemical reactor and the mixture was irradiated by >350-nm lamps. For run 38, the experimental procedure was the same as for the phenylation of nitrile anions. Phenylation was identified by comparison of its gpc retention time and mass spectrum with those of an authentic sample. 1-Phenyl-2-propanol was identified by ir (CHCl₃), 3600, 3450, 3110-2870, 1600, 1450, 1350, 680 cm⁻¹; mass spectrum m/e (rel intensity) 266 (molecular peak, <0.01), 167 (s), 133 (88), 132 (70), 115 (10), 115 (8), 104 (9), 92 (29), 91 (100), 77 (10), *m* 69.2 (133 91), m* 46.5 (91 65).

Reactions of Table III.—For photostimulated reactions, the reaction mixtures were prepared as described above. The reaction flask was then placed into a Rayonet photochemical reactor and the mixture was irradiated by >350-nm lamps. For run 38, the experimental procedure was the same as for the phenylation of nitrile anions. Phenylation was identified by comparison of its gpc retention time and mass spectrum with those of an authentic sample. 1-Phenyl-2-propanol was identified by ir (CHCl₃), 3600, 3450, 3110-2870, 1600, 1450, 1350, 680 cm⁻¹; mass spectrum m/e (rel intensity) 266 (molecular peak, <0.01), 167 (s), 133 (88), 132 (70), 115 (10), 115 (8), 104 (9), 92 (29), 91 (100), 77 (10), *m* 69.2 (133 91), m* 46.5 (91 65).

Reactions of Table III.—For photostimulated reactions, the reaction mixtures were prepared as described above. The reaction flask was then placed into a Rayonet photochemical reactor and the mixture was irradiated by >350-nm lamps. For run 38, the experimental procedure was the same as for the phenylation of nitrile anions. Phenylation was identified by comparison of its gpc retention time and mass spectrum with those of an authentic sample. 1-Phenyl-2-propanol was identified by ir (CHCl₃), 3600, 3450, 3110-2870, 1600, 1450, 1350, 680 cm⁻¹; mass spectrum m/e (rel intensity) 266 (molecular peak, <0.01), 167 (s), 133 (88), 132 (70), 115 (10), 115 (8), 104 (9), 92 (29), 91 (100), 77 (10), *m* 69.2 (133 91), m* 46.5 (91 65).

Reactions of Table III.—For photostimulated reactions, the reaction mixtures were prepared as described above. The reaction flask was then placed into a Rayonet photochemical reactor and the mixture was irradiated by >350-nm lamps. For run 38, the experimental procedure was the same as for the phenylation of nitrile anions. Phenylation was identified by comparison of its gpc retention time and mass spectrum with those of an authentic sample. 1-Phenyl-2-propanol was identified by ir (CHCl₃), 3600, 3450, 3110-2870, 1600, 1450, 1350, 680 cm⁻¹; mass spectrum m/e (rel intensity) 266 (molecular peak, <0.01), 167 (s), 133 (88), 132 (70), 115 (10), 115 (8), 104 (9), 92 (29), 91 (100), 77 (10), *m* 69.2 (133 91), m* 46.5 (91 65).

Reactions of Table III.—For photostimulated reactions, the reaction mixtures were prepared as described above. The reaction flask was then placed into a Rayonet photochemical reactor and the mixture was irradiated by >350-nm lamps. For run 38, the experimental procedure was the same as for the phenylation of nitrile anions. Phenylation was identified by comparison of its gpc retention time and mass spectrum with those of an authentic sample. 1-Phenyl-2-propanol was identified by ir (CHCl₃), 3600, 3450, 3110-2870, 1600, 1450, 1350, 680 cm⁻¹; mass spectrum m/e (rel intensity) 266 (molecular peak, <0.01), 167 (s), 133 (88), 132 (70), 115 (10), 115 (8), 104 (9), 92 (29), 91 (100), 77 (10), *m* 69.2 (133 91), m* 46.5 (91 65).