SRN1 Phenylation 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-diphenylethane when the cyanomethyl 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 SRN1 mechanism of aromatic nucleophilic 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 nucleophilic substitution 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 SRN1 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]

Heretofore, aromatic SRN1 reactions involving α-cyanocarbanion nucleophiles have received only preliminary attention. Kim and Bunnett[6] observed chlorobenzene to react with the cyanomethyl anion and potassium metal in liquid ammonia to form phenylacetonitrile, toluene, benzene, and aniline. Rossi[11] conducted a similar experiment, with iodobenzene instead of chlorobenzene, and obtained a substantial amount of 1,2-diphenylethane (DPE)[12] as well as the other products mentioned.

We now report a study of several reactions of this general type, involving six monosubstituted benzenes and the carbanions from seven aliphatic nitriles. The results are of interest to preparative chemistry. Also, they illuminate significant features of the reaction mechanism.

Most of our observations conform to the generalized scheme of eq 1.

$$\mathrm{PhX} + \mathrm{RCH^-\,K^+} \xrightarrow[\mathrm{NH_3}]{\mathrm{K}} \mathrm{PhCHR} + \mathrm{PhCH_2R} + \mathrm{Ph_2CHR} + \mathrm{PhCH(R)\text{—}CH(R)Ph} + \mathrm{C_6H_6} + \mathrm{C_6H_5NH_2} \quad (1)$$

(CN on the RCH⁻ K⁺ and on PhCHR)

Results

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

Table I concerns several experiments involving the cyanomethyl anion, from reaction of acetonitrile with an equimolar amount of KNH_2. 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[5]) 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 cyanomethyl anion (eq 1, R = H) are those described by earlier workers, as mentioned, plus a small amount of diphenylmethane (DPM).[12] Toluene is prominently formed, in yields ranging from 14 to 49%. 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

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(4) J. K. Kim and J. F. Bunnett, *J. Amer. Chem. Soc.*, **92**, 7463 (1970).

(5) J. L. Dye, *Accounts Chem. Res.*, **1**, 306 (1968).

(6) J. K. Kim and J. F. Bunnett, *J. Amer. Chem. Soc.*, **92**, 7464 (1970).

(7) R. A. Rossi and J. F. Bunnett, *J. Org. Chem.*, **37**, 3570 (1972).

(8) R. A. Rossi and J. F. Bunnett, *J. Amer. Chem. Soc.*, **94**, 683 (1972).

(9) R. A. Rossi and J. F. Bunnett, *J. Org. Chem.*, **38**, 1407 (1973).

(10) R. A. Rossi and J. F. Bunnett, *J. Org. Chem.*, **38**, 3020 (1973).

(11) R. A. Rossi, unpublished work.

(12) Glossary of acronyms: BME, benzyl methyl ether; DPE, 1,2-diphenylethane; DPM, diphenylmethane; MPAN, 3-methylphenylacetonitrile; MPAN⁻, anion of MPAN; PAN, phenylacetonitrile; PBN, α-phenylbutyronitrile.

TABLE I

REACTIONS OF MONOSUBSTITUTED BENZENES WITH CYANOMETHYL ANIONS, PROVOKED BY POTASSIUM METAL IN LIQUID AMMONIA

Run no.	Registry no.	Substituent	PhX, mmol	CH_2CNK, mmol	K, mmol	NH_3, ml	Temp, °C	Method[a]	Ether, ml	Yield, % Toluene	PAN[b]	DPM[c,e]	DPE[d,e]	C_6H_6	Aniline
1	462-06-6	F	25	115	63	150	−33	A[f]	80	44	2	Trace	8	31	~1
2		F	14	76	40	110	−33	A[g]	65	30	3	0.7	3	44	*h*
3		F	40	123	107	250[i]	−78	AB[j]		49	3	4	23	10	2
4	108-90-7	Cl	22	87	55	130	−33	A[k]	70	40	7	2	12	20	~2
5		Cl	60	150	69	50	−33	A[l]		18	31	~2	5	17	*m*
6		Cl	64	160	95	50	−33	B		24	24	~3	9	17	*m*
7		Cl	63	75	110	50	−33	B		16	19	5	3	27	*m*
8		Cl	165	165	330	50	−78	B		14	19	3	5	30	
9		Cl	67	80	81	50	−78	B		31	18	5	14	26	*m*
10		Cl	30	88	37 (15)[n]	60	−78	B		27	12	2	40	8	
11		Cl	64	80	87 (34)[o]	60 (150)	−78	AB		35	22	7	12	18	
12		Cl	146	49	254 (85)[p]	50 (250)	−33	AB		46	3	3	7	22[q]	10[q]
13	108-86-1	Br	27	106	69	150	−33	B	70	26	5	3	14	43	~1
14	591-50-4	I	25	95	64	150	−33	B	70	14	5	4	25	32	*m*
15	2510-86-3	$OPO(OEt)_2$	50	80	90 (25)[r]	50	−78	AB		43	3	1	7	11	~3[s]
16	98-04-4	$N(CH_3)_3^+I^-$	63	78	85	50	−78	AB[t]		26	5	4	19	21	~7

[a] Methods: A, the monosubstituted benzene, neat or in solution, was slowly added to a solution of CH_2CNK and K metal; AB, the monosubstituted benzene, neat or in solution, was slowly added to a solution of CH_2CNK, and K metal was added slowly in small portions so as to keep K metal in more or less constant excess; B, to a solution of CH_2CNK and the monosubstituted benzene, a small piece of K metal was added and then, after the blue color had vanished, another small piece, etc. [b] PAN = phenylacetonitrile. [c] DPM = diphenylmethane. [d] DPE = 1,2-diphenylethane. [e] The yield calculation takes account of the fact that 2 mol of C_6H_5X are required to form 1 mol of DPM or DPE. [f] C_6H_5F in ether (5 ml) added during 30 min; quenched with C_6H_5COONa, then NH_4Cl. [g] C_6H_5F in ether (40 ml) added. [h] Not sought. [i] Not distilled before use. [j] C_6H_5F in NH_3 (150 ml) added during 90 min; quenched with C_6H_5COONa, then NH_4Cl. [k] C_6H_5Cl in ether (5 ml) added during 40 min. [l] C_6H_5Cl added as fast as possible (during 5 min); vigorous refluxing. [m] A tiny peak at the retention time for aniline. [n] After addition of 37 mmol of K in especially small pieces, ice was added until the orange color faded, and then a further 15 mmol of K. [o] Half the C_6H_5Cl was added, then about 44 mmol of K, then the rest of the C_6H_5Cl, then about 43 mmol of K, then 390 mmol of ice (causing the orange color to fade), then 34 mmol of K. [p] After addition of 254 mmol of K, 670 mmol of ice and 200 ml of ammonia were added, and then 85 mmol of K (with shaking of the thick slurry). [q] Based on C_6H_5Cl. [r] After addition of 90 mmol of K, ice was added and then 25 mmol of K. [s] 4% of phenol also obtained. [t] K added in two portions, each followed by half the substrate.

TABLE II

REACTIONS OF MONOSUBSTITUTED BENZENES WITH ANIONS FROM NITRILES OF STRUCTURE RCH_2CN, PROVOKED BY POTASSIUM METAL IN LIQUID AMMONIA

Run no.	R	X of C_6H_5X	Registry no.	[RCH-CN^-], *M*	[C_6H_5X], *M*	K, *M*[b]	Temp, °C	Method[a]	Yield, % Ph-CH_2R	PhCH-RCN	Ph_2-CHR	Ph-CHCRHRPh[c] Meso	Rac	C_6H_6	Aniline
17	CH_3	Cl	42117-12-4	1.38	0.87	2.0 (0.65)	−78	AB	22	*d*	*d*	5	5	34	5
18	CH_3	Cl		1.40	2.80	3.98	−33	AB	34	6	7	6	6	38[e]	10[e,f]
19	CH_3	$OPO(OEt)_2$		1.16	0.73	1.7 (0.1)[g]	−78	AB	14	*d*	*d*	7	7	35	5[h]
20	CH_3	$N(CH_3)_3^+I^-$		1.07	0.67	1.26	−78	AB[i]	8	*d*	*d*	8	8	36	3
21	C_2H_5	F	42117-13-5	1.28	0.43	1.09	−78	AB[j]	28	4	*d*	13	13	35	13
22	C_2H_5	Cl		1.37	4.1	6.04	−33	AB[k]	37	0.5	13			27[e]	3[e]
23	C_2H_5	I		0.30	0.16	0.20	−33	A	6	29	2	12	12	27	*l*
24	C_2H_5	$OPO(OEt)_2$		1.04	0.15	0.30	−33	B	28	4	0.2	1	1	20	*n*
25	$(CH_3)_2$[o]	Br	42117-14-6	0.98	2.94	5.3	−33	AB	27					31	7
26	*n*-C_3H_7	Cl	42117-15-7	1.09	3.30	6.3 (1.7)	−33	AB	56	*d*	*m*	*m*	*m*	38[e]	14[e]
27	*n*-C_3H_7	$OPO(OEt)_2$		1.58	0.60	1.45 (0.2)	−33	BA[p]	38	10	*d*	*d*	*d*	27	*q*
28	$(CH_3)_2CH$	Cl	42117-16-8	1.64	3.2	4.9	−33	AB	37[r]	19[r]	12	*d*	*d*	31[e]	~5[e]
29	$(CH_3)_2CH$	$OPO(OEt)_2$		1.80	0.72	1.48	−78	B	20	7				36	~2[s]
30	$(CH_3)_2CH$	$OPO(OEt)_2$		1.30	0.52	0.85 (0.23)	−33	BA[p]	31	10	*d*	*d*	*d*	32	*d*
31	$(CH_3)_2CH$	$OPO(OEt)_2$		0.63	0.20	0.70	−78	AB[j]	22	15	*d*	*d*	*d*	41	2
32	C_6H_5	$OPO(OEt)_2$	18802-89-6	1.44	1.12	1.47	−78	AB	12	3[t]	6			25	1[u]
33	C_6H_5	$N(CH_3)_3^+I^-$		1.50	1.19	2.08	−78	AB	17		12			43	1[v]

[a] 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. [c] The glpc peaks for racemic and meso stereoisomers were not fully resolved, but were approximately equal in area; the sum of the two could be measured accurately, and was arbitrarily allocated in equal parts to meso and racemic. [d] A tiny peak at the expected retention time. [e] Based on C_6H_5Cl. [f] 4% of C_6H_5Cl recovered. [g] The K indicated in parentheses was added after ice and 150 ml of ether. [h] Phenol (2%) also formed. [i] Excess K present at the end was destroyed by addition of ice. [j] The C_6F_5X, in 150 ml of NH_3, was added during 90 min. [k] After reaction, NH_3 was added to increase the volume from *ca.* 50 ml to 200 ml, followed by 10 g of ice and 75 mmol of K. [l] 12% of C_6H_5I recovered. [m] Detected qualitatively. [n] Phenol (29%) and some 4-amino-3-cyano-3-heptene also formed. [o] Isobutyronitrile. [p] Method BA: the C_6H_5X and K metal were both added in portions, but so as always to keep C_6H_5X in excess. [q] Phenol (8%) also formed. [r] After decyanation of the isolated product mixture, 50% of isobutylbenzene and a mere trace of 2-phenyl-3-methylbutanonitrile were obtained. [s] Phenol (6%) also formed. [t] Identification solely by glpc retention time. [u] Phenol (12%) also formed; 80% of PAN recovered. [v] 76% of PAN recovered.

the variation is often difficult to correlate with differences in reaction participants or conditions. Alkylbenzenes, $PhCH_2R$, corresponding to toluene 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, Ph_2CHR, appear to a significant extent in only a few runs, most of which involve the aromatic substrate in excess. Dimeric products, meso and racemic PhCHRCHRPh, are formed in amounts totalling as high as 26% in reactions of the anions from propio- and butyronitrile, but only in minor amounts in the other runs. The yields of aniline are variable, but never large.

Photostimulated Reactions.—Inasmuch as SRN1 reactions of halobenzenes with acetone enolate ion

TABLE III

REACTIONS OF BROMOBENZENE WITH CYANOMETHYL ANION, AND REACTIONS WITH MIXED CYANOMETHYL AND ACETONE ENOLATE IONS, IN LIQUID AMMONIA AT −33°

Run no.	$[C_6H_5Br]$, M	$[KNH_2]$, M[a]	$[CH_3CN]$, M[a]	[Acetone], M[a]	Reaction time, min	Promoter	Yield, %: C_6H_5Br[b]	C_6H_6	Toluene	PAN	DPM	DPE	Phenylacetone
34	0.08	0.46	0.46		120	Dark	98	1					
35	0.08	0.52	0.54		120	$h\nu$	62	1	2	8	1	18	
36	0.07	0.74	0.68	0.07	125	$h\nu$	44	3	2	14	1	36	<0.3
37	0.07	0.92	0.46	0.46	120	$h\nu$	55	2	3	8	0.6	19	<2[c]
38	0.07	0.90	0.46	0.46	~5[d]	K[d]		4	22	12	1	32	<2[c,e]

[a] Concentration that would have prevailed had there been no reaction of CH_3CN or acetone with KNH_2. [b] Recovered. [c] Precise glpc yield determination difficult because of partial overlap with other peaks. [d] Potassium metal (0.15 mol) added bit by bit. [e] 1-Phenyl-2-propanol (*ca.* 5%) also obtained.

TABLE IV

ATTEMPTS TO OBSERVE REACTIONS OF BENZYL RADICALS WITH THE ANION OF 3-METHYLPHENYLACETONITRILE IN REFLUXING AMMONIA

Run no.	Radical source: Identity	Radical source: Concn, M	[MPAN$^-$],[a] M	[K], M[b]	Method[c]	Yield, %: Toluene	PAN	DPE	Other products
40	BME[d]	0.30		0.78	B	71		29	
41	BME[d]	0.32	0.32	0.60	B	70	*e*	26	*f*
42	C_6H_5Cl / CH_2CN^-	0.45 / 1.35	0.45	0.79	B	42	5[g]	29	*h*

[a] MPAN$^-$ = anion of 3-methylphenylacetonitrile. [b] Concentration that would have prevailed had there been no reaction. [c] See footnote *a*, Table I. [d] BME = benzyl methyl ether. [e] 3-Methylphenylacetonitrile (73%) recovered. [f] Benzyl methyl ether (1%) recovered. [g] 3-Methylphenylacetonitrile (93%) recovered. [h] Also obtained were C_6H_5Cl (8%) and C_6H_6 (15%).

occur not only as provoked by solvated electrons,[8] but also with great facility under stimulation by near-ultraviolet light,[9] 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.[9] The product pattern resembles that from potassium metal stimulated reactions of the cyanomethyl anion with bromobenzene, with the important exception that the benzene and toluene yields are quite small relative to those of PAN and DPE.[12]

It was thought that photochemical reaction of bromobenzene with mixtures of the cyanomethyl and acetone enolate ions might occur more readily than with the cyanomethyl anion alone. There was found to be a somewhat greater consumption of bromobenzene in reaction with mixtures of the carbanions (runs 36 and 37) than with the cyanomethyl anion alone (run 35), but the increase was slight. Remarkably, the photochemical reactivity of bromobenzene with acetone enolate ion is severely depressed by admixture of cyanomethyl anions; compare run 37 with typical runs reported by Rossi and Bunnett.[9]

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[8] 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 phenylacetonitrile anion. In order to check this possibility, the experiments outlined in Table IV were performed.

Run 40 concerns the action of potassium metal on benzyl methyl ether. The formation of DPE in 29% yield indicates that benzyl radicals are, at least in part, intermediates in this reaction.[13]

The objective of runs 41 and 42 was to see whether benzyl radicals are able to combine with the anion of 3-methylphenylacetonitrile (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,

(13) Schorigin and Skoblinskaya[14a] obtained DPE from the action of sodium in ammonia on benzyl phenyl ether. They, and later Burwell,[14b] attributed this result to two-electron cleavage of the ether to phenoxide and benzyl anions, followed by SN2 reaction of benzyl anion with the ether, displacing phenoxide ion. However, that explanation would require the SN2 reaction to be faster than proton capture by benzyl anion from the ammonia solvent, which is unlikely. Waters[15] perceived years ago that one-electron cleavage of benzyl ethers, to generate benzyl radicals, can occur. The sodium–ammonia cleavage of benzyltrimethylammonium ion to form bibenzyl in yield as high as 70% has been interpreted preferentially in terms of a radical mechanism.[16]

(14) (a) P. Schorigin and S. A. Skoblinskaya, *C. R. (Dokl.) Acad. Sci. URSS*, **14**, 505 (1937); *Chem. Zentralbl.*, **108**, II, 1993 (1937). (b) R. L. Burwell, Jr., *Chem. Rev.*, **54**, 675 (1954).

(15) W. A. Waters, "The Chemistry of Free Radicals," 2nd ed, Oxford University Press, London, 1948, p 171.

(16) J. T. Wrobel, A. S. Bien, and K. M. Pazdro, *Chem. Ind. (London)*, 1569 (1968).

TABLE V
REACTIONS OF PHENYLACETONITRILE (PAN) AND α-PHENYLBUTYRONITIRLE (PBN) WITH ALKALI METALS IN LIQUID AMMONIA AT −33°

Run no.	Substrate	[Substrate], M	Alkali metal	[K] or [Na], M[a]	Other substance: Identity	Other substance: Concn, M	Method[b]	Quench	Yield, %: Educt[c]	Yield, %: Toluene
43	PAN	0.10	K	0.11			B	NH_4Cl	46	52[d]
44		0.22	Na	0.45			A	C_6H_5COONa[e]	51	52[d]
45		0.21	Na	0.43			A	Ice	9	91[d]
46		0.25[f]	K	0.63	KNH_2	0.5[f]	B	*g*	100	0.4
47		0.30[f]	K	0.85	KNH_2	0.65[f]	*h*	Ice	49	49
48		0.20	Na	0.44	H_2O	2.0	B			98
49		0.20	Na	~0.87	H_2O	2.0	B			36[i]
50	PBN	0.20	K	0.25			B	NH_4Cl	48	45[j]
51		0.10	K	0.20	$(NH_4)_2SO_4$	0.025[k]	B		36	53[j]
52		0.10	K	0.22	$(NH_4)_2SO_4$	0.17[k]	B		6	67[j]
53		0.10	K	0.23	CH_3OH	*l*	B[l]	*l*		73[j]

[a] Concentration that would have prevailed had there been no reaction. [b] See footnote *a*, Table I. [c] PAN or PBN. [d] 1-2% of DPE also formed. [e] Followed by NH_4Cl. [f] Concentration that would have prevailed at start had there been no reaction of PAN with KNH_2. [g] After 45 min, the blue color had vanished, and NH_4Cl was added to neutralize. [h] To PAN and KNH_2 in NH_3, K metal was added all at once, followed quickly by ice. [i] *Ca.* 56% of another product, probably 2,5-dihydrotoluene,[21] was obtained. [j] 1-Phenylpropane. [k] $(NH_4)_2SO_4$ is insoluble; the concentration that would have prevailed had it dissolved is given. [l] Enough K metal to give a persistent blue color was added, then enough CH_3OH to discharge the color, then more K metal, etc.; total CH_3OH about 5 ml.

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-phenylethane 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 MPAN.

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,[17] 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.*,[18b] 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,[21,22] and then neutralized with NH_4Cl. Run 45 was quenched directly with ice, while the reaction mixture was still blue owing to solvated electrons; Arapakos, *et al.*,[18b] 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

$$2RCH_2CN + 2Na \longrightarrow RCH_3 + RCHCN^-Na^+ + NaCN \quad (2)$$

afforded 91% of toluene, 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 KNH_2 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 KNH_2 under catalysis by the iron present in the medium; iron had been used to catalyze formation of KNH_2 in the beginning of the experiment. When the blue color had vanished, the mixture was neutralized with NH_4Cl 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 KNH_2 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 KNH_2. 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-

(17) M. M. Rising and E. W. Lowe, *J. Amer. Chem. Soc.*, **52**, 2524 (1930); L. A. Walter and S. M. McElvain, *ibid.*, **56**, 1614 (1934); L. I. Smith and L. J. Spillane, *ibid.*, **65**, 202 (1943).

(18) (a) P. G. Arapakos, *J. Amer. Chem. Soc.*, **89**, 6794 (1967); (b) P. G. Arapakos, M. K. Scott, and F. E. Huber, Jr., *ibid.*, **91**, 2059 (1969).

(19) S. Bank and S. P. Thomas, *Tetrahedron Lett.*, 305 (1972).

(20) C. Fabre and Z. Welvart, *Bull. Soc. Chim. Fr.*, 2620 (1965); *C. R. Acad. Sci., Ser. C*, **270**, 1887 (1970); H. Thies, H. Schoenenberger, and P. K. Qasba, *Arch. Pharm. (Weinheim)*, **302**, 897 (1969); T. Cuvigny, M. Larcheveque, and H. Normant, *C. R. Acad. Sci.*, **274**, 797 (1972); A. R. Doumaux, Jr., *J. Org. Chem.*, **37**, 508 (1972).

(21) A. P. Krapcho and A. A. Bothner-By, *J. Amer. Chem. Soc.*, **81**, 3658 (1959).

(22) S. S. Hall, S. D. Lipsky, F. J. McEnroe, and A. P. Bartels, *J. Org. Chem.*, **36**, 2588 (1971).

phenylethane, 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 PBN 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 about 50% decyanation, 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 SRN1 mechanism,[4] adapted to the present situation, is sketched in eq 3–6. First (eq 3) an elec-

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

$$[\mathrm{PhX}]\cdot^- \longrightarrow \mathrm{Ph}\cdot + \mathrm{X}^- \quad (4)$$

$$\mathrm{Ph}\cdot + \mathrm{RCHCN}^- \longrightarrow \left[\mathrm{PhCHCN}\right]\cdot^- \quad (5)$$

$$\left[\mathrm{PhCHCN}\right]\cdot^- + \mathrm{PhX} \longrightarrow \mathrm{PhCHCN} + [\mathrm{PhX}]\cdot^- \quad (6)$$

tron 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-cyanoalkyl 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.

$$\mathrm{PhCHCN} + \mathrm{RCHCN}^- \rightleftharpoons \mathrm{PhC{=}CN}^- + \mathrm{RCH_2CN} \quad (7)$$

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

$$\left[\mathrm{PhCHCN}\right]\cdot^- \longrightarrow \mathrm{PhCH}\cdot + \mathrm{CN}^- \quad (8)$$

$$\mathrm{PhCH}\cdot + \mathrm{PhCH}\cdot \longrightarrow \mathrm{PhCH{-}CHPh} \quad (9)$$

$$\mathrm{PhCH}\cdot + \mathrm{e^-_{sol}} \longrightarrow \mathrm{PhCH}:^- \quad (10)$$

$$\mathrm{PhCH}:^- + \mathrm{NH_3} \longrightarrow \mathrm{PhCH_2R} + \mathrm{NH_2}^- \quad (11)$$

$$\mathrm{Ph}\cdot + \mathrm{e^-_{sol}} \longrightarrow \mathrm{Ph}:^- \quad (12)$$

$$\mathrm{Ph}:^- + \mathrm{NH_3} \longrightarrow \mathrm{C_6H_6} + \mathrm{NH_2}^- \quad (13)$$

$$\mathrm{PhCH}\cdot + \mathrm{Ph}\cdot \longrightarrow \mathrm{Ph_2CHR} \quad (14)$$

$$\mathrm{PhC{=}CN}^- + \mathrm{Ph}\cdot \longrightarrow \left[\mathrm{Ph_2CCN}\right]\cdot^- \quad (15)$$

$$\left[\mathrm{Ph_2CCN}\right]\cdot^- \longrightarrow \mathrm{Ph_2C}\cdot + \mathrm{CN}^- \quad (16)$$

$$\mathrm{Ph_2C}\cdot + \mathrm{e^-_{sol}} \longrightarrow \mathrm{Ph_2C}:^- \quad (17)$$

$$\mathrm{Ph_2C}:^- + \mathrm{NH_3} \longrightarrow \mathrm{Ph_2CHR} + \mathrm{NH_2}^- \quad (18)$$

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[23] that disproportionation of α-alkylbenzyl radicals occurs only about one tenth as fast as combination.

The formation of toluene and other products of type $\mathrm{PhCH_2R}$ 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.[24]

Two routes to DPM and other products of type $\mathrm{Ph_2CHR}$ are postulated. One route is combination of 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 finally reduction (in steps 17 and 18) of the benzhydrylic 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

$$\mathrm{PhCH}\cdot + \mathrm{R'H} \longrightarrow \mathrm{PhCH_2R} + \mathrm{R}\cdot' \quad (19)$$

$$\mathrm{Ph}\cdot + \mathrm{R'H} \longrightarrow \mathrm{C_6H_6} + \mathrm{R}\cdot' \quad (20)$$

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 phenyl radical with amide ion followed by disposal of a surplus electron. That aromatic primary amines are readily formed in SRN1 reactions is reported elsewhere.[6,7]

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 SRN1 reactions of bromobenzene with acetone enolate ion in liquid ammonia afford phenylacetone in high yield without appreciable formation of benzene as a by-product, unless a good hydrogen atom donor (such as isoprop-

(23) M. J. Gibian and R. C. Corley, *J. Amer. Chem. Soc.*, **94**, 4178 (1972).
(24) J. F. Garst, *Accounts Chem. Res.*, **4**, 400 (1971); G. D. Sargent, *Tetrahedron Lett.*, 3279 (1971).

$$Ph\cdot + NH_3 \not\rightarrow C_6H_6 + H_2N\cdot \quad (21)$$

$$Ph\cdot + Ph\cdot \not\rightarrow Ph\text{–}Ph \quad (22)$$

$$PhC(R)=CN^- + PhCH(R)\cdot \not\rightarrow \left[PhCH(R)\text{–}C(CN)Ph\right]^{\cdot -} \quad (23)$$

oxide ion) is also present.[9] That phenyl radical dimerization (step 22) plays no substantial role is shown by the undetectability of biphenyl as a product. The possibility that DPE and other benzylic radical dimers are formed by alkylation of an α-phenyl nitrile anion (step 23) followed by cyanide ion loss, etc., is discarded because of the unreactivity of benzyl radical with the anion (MPAN$^-$) of 3-methylphenylacetonitrile, as shown by runs 41 and 42, Table IV.

Relationship of Product Distribution to Nucleofugic Group.—The chief products of potassium metal stimulated reaction of halobenzenes with acetone enolate ion are phenylacetone and 1-phenyl-2-propanol.[8] There is a remarkable relationship between the phenylacetone–1-phenyl-2-propanol product ratio and the nucleofugic substituent, in the sense that mainly the ketone is obtained from iodobenzene and mainly the secondary alcohol from fluorobenzene, with the others falling between. This has been attributed to competition between two reaction pathways available to the radical anion formed by addition of phenyl radical to the enolate ion: it may be reduced to alkoxide ion, or it may transfer an electron to another halobenzene molecule (in a step analogous to eq 6) and appear as ketone.[8] The latter pathway is more rapidly traversed the larger the halogen,[25] and that accounts for the predominance of the ketone product from iodobenzene.

One might anticipate a similar competition in the present series of reactions, specifically, between steps 6 and 8. Accordingly, one might expect, in reactions of halobenzenes with the cyanomethyl anion (Table I), to get relatively more phenylacetonitrile with larger halogens and relatively more of products derived from benzyl radical (toluene and DPE)[12] with smaller halogens. (Since DPM might be formed either from benzyl radical or from the anion of PAN and is a minor product anyhow, let us for the moment ignore it.) Very crudely the observed yields conform to these expectations: the lowest yields of PAN and relatively high yields of toluene and DPE are obtained from fluorobenzene. However, there is no clear trend in the product patterns from chloro-, bromo-, and iodobenzenes. Evidently other factors, perhaps details of reagent addition technique, exert a greater influence on product proportions.

Decyanation of Nitriles.—The action of solvated electrons on nitriles to effect decyanation is accounted for by an initial step in which the nitrile accepts an electron to become a radical anion analogous to that formed in step 5, followed by scission to radical and cyanide ion (step 8) and reduction of the radical to hydrocarbon (steps 10 and 11). The amide ion formed in step 11 undergoes an acid–base reaction with the nitrile, converting it to its anion which is resistant to 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_4Cl), 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 SRN1 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,[9] its reaction with the cyanomethyl anion responds only sluggishly to illumination; see Table III. Responsible for the difference is the proclivity of the $[PhCH_2CN]\cdot^-$ 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,[9] 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 35 (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

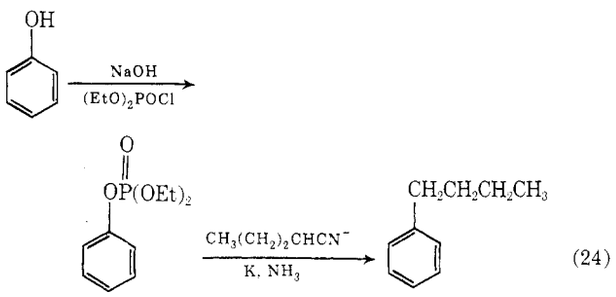
The reactions we describe constitute a method for installing an alkyl group on a benzene ring in place of a nucleofugic substituent. Examples that we report (in Table II) concern the introduction of ethyl, propyl, isopropyl, butyl, isobutyl, and benzyl groups, as well as the methyl group (Table I).

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

(25) M. Anbar and E. J. Hart, *J. Amer. Chem. Soc.*, **86**, 5633 (1964), report that rates of reactions of the hydrated electron with monohalobenzenes increase with the size of the halogen.

50%, the method may nevertheless be useful in synthesis. First, the alkyl group is introduced specifically at the site vacated by the nucleofugic substituent.[26] In contrast, introduction of an alkyl group by Friedel–Crafts alkylation or acylation (followed by reduction) is at the mercy of the orienting effects of other nuclear substituents. Second, the alkyl group is installed without rearrangement, whereas the introduction of straight-chain or β-branched alkyl groups by the Friedel–Crafts method is severely complicated by isomerization within the alkyl group.[27]

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.[7] The sequence of two operational steps depicted in eq 24 effects, for example,



(24)

the transformation of phenol to *n*-butylbenzene in an overall yield of 33%; the yield is 87% in the esterification step[7] 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, and 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 $PhCH_2R$ 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 $PhCH_2R$ 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 alkylbenzene. 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 $PhCH_2R$ 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, SRN1 phenylation appears to be inferior to benzyne phenylation of the nitrile anion.[28] Benzyne phenylation followed by decyanation would furnish an alkylbenzene, but synthetically such a method would suffer some disadvantages: benzyne 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 benzynes sometimes gives mixtures of positional isomers.

Our experiments, especially run 48, Table V, support other indications[18b,20] 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 CO_2–isopropyl 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 KNH_2. 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.[29] 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 NH_4Cl, which caused the color to fade. Diethyl ether (50 ml) and internal standards (ethylbenzene and biphenyl) were added, and the ammonia 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 glpc on a column of 10% Carbowax 20M on Chromosorb P.

Identification of Products.—Analysis was performed on samples collected by preparative glpc on columns of either 10% silicone rubber SE-54 or 10% Carbowax 20M on Chromosorb P.

Unreacted starting material, benzene, alkylbenzenes, α-phenyl nitriles, diphenylmethane, triphenylmethane, 1,2-diphenylethane, 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-Phenylvaleronitrile had ir (CCl_4) 2250 cm^{-1}; mass spectrum[30] *m/e* (rel intensity) 159 (molecular ion, 17), 133 (10), 117 (100), 116 (20), 91 (50), 77 (10).

α-Phenylisovaleronitrile had ir (CCl_4) 2250, 1390, 1365 cm^{-1};

(26) The absence of cine substitution in reactions by the SRN1 mechanism has been demonstrated in other studies.[6,8] In the present work, a run with *p*-bromotoluene and the cyanomethyl anion under conditions similar to those of run 13, Table I, afforded *p*-xylene (17%) uncontaminated by ortho or meta isomers.

(27) R. O. C. Norman and R. Taylor, "Electrophilic Substitution in Benzenoid Compounds," Elsevier, Amsterdam, 1965, pp 157–173.

(28) V. Dryanska, K. Ivanov, and V. Lachkova, *God. Sofii. Univ., Khim. Fak.*, **64**, 445 (1969–1970); *Chem. Abstr.*, **78**, 135,838 (1973).

(29) For reactions at −78°, the flask was immersed in a solid CO_2–isopropyl alcohol bath, and, for reactions at −33°, there was no cooling.

(30) The mass spectra were obtained on a Hitachi RMU-GE spectrometer at an ionization potential of 80 eV.

TABLE VI
NMR DATA OF DIPHENYLALKANES[a]

Compd	Methyl protons: Pattern	Methyl protons: δ, ppm	Methyl protons: J_{A_3-B}, Hz	Aromatic protons: Pattern	Aromatic protons: δ, ppm
meso-2,3-Diphenylbutane	"d"	1.02	6.5	"s"	7.17
rac-2,3-Diphenylbutane	d	1.21	6.5	"s"	6.93
Mixture of *meso*- and *rac*-3,4-diphenylhexane[b,c]	t	0.51	6.5[d]	m	~7
	t	0.72	6.5[d]	"s"	7.2
Mixture of *meso*- and *rac*-4,5-diphenyloctane[c]	"t"	~0.7		m	~6.9
	"t"	~0.85		"s"	~7.13

[a] All nmr spectra were run on a Varian A56/60 spectrometer. [b] Although small amounts of *meso*- and *rac*-3,4-diphenylhexane sufficient for ir and mass spectral analysis could be isolated by glpc, it was practicable to isolate the larger amount needed for nmr only as a mixture of isomers. [c] Each line refers to a different isomer. [d] Refers to CH_2–CH_3 splitting in the ethyl groups.

mass spectrum *m/e* (rel intensity) 159 (molecular ion, 3), 118 (10), 117 (100), 116 (9), 91 (5), 90 (16), 89 (12), 77 (4).

1,1-Diphenylethane had ir (CCl_4) 3100–2880, 1590, 1480, 1440, 1350, 695 cm^{-1}; mass spectrum *m/e* (rel intensity) 182 (molecular ion, 25), 167 (100), 166 (11), 165 (28), 152 (16), 105 (7), 103 (10), 91 (9), 77 (22), m* 138.3 (167 → 152).

1,1-Diphenylpropane had ir (CCl_4) 3100–2870, 1600, 1490, 1450, 1375, 695 cm^{-1}; mass spectrum *m/e* (rel intensity) 196 (molecular ion, 7), 167 (100), 165 (38), 152 (20), 115 (10), 91 (16), 77 (9), m* 142.3 (196 → 167), m* 138.3 (167 → 152).

1,1-Diphenylbutane had ir ($CHCl_3$) 3100–2870, 1600, 1490, 1450, 695 cm^{-1}; mass spectrum *m/e* (rel intensity) 210 (molecular ion, 9), 167 (100), 165 (20), 152 (12), 115 (4), 91 (6), 77 (4), m* 138.3 (167 → 152), m* 132.8 (210 → 167).

1,1-Diphenyl-2-methylpropane had ir (CCl_4) 3100–2880, 1595, 1490, 1450, 1375, 1360, 695 cm^{-1}; mass spectrum *m/e* (rel intensity) 210 (molecular ion, 3), 167 (100), 165 (25), 152 (13), 115 (7), 91 (8), 77 (6), m* 138.3 (167 → 152), m* 132.8 (210 → 167).

***meso*-2,3-Diphenylbutane.**—The product crystallized after evaporation of the ether from run 19: mp 125–126° (lit.[31] mp 128°); ir (CCl_4) 3120–2880, 1600, 1490, 1450, 1370, 695 cm^{-1}; nmr, see Table VI; mass spectrum *m/e* (rel intensity) 210 (molecular ion, 0.4), 115 (2), 106 (57), 105 (100), 104 (29), 91 (8), 79 (19), 77 (22), m* ~101 (131 → 115), m* 59.5 (105 → 79).

***rac*-2,3-Diphenylbutane** had an ir (CCl_4) differing slightly from the spectrum of the meso form between 1300 and 800 cm^{-1}; nmr, see Table VI; mass spectrum virtually identical with the spectrum of the meso compound.

***meso*-3,4-Diphenylhexane** had ir ($CHCl_3$) 3110–2870, 1600, 1490, 1450, 1375 cm^{-1}; nmr, see Table VI; mass spectrum *m/e* (rel intensity) 238 (molecular peak, not detected), 119 (100), 118 (41), 115 (12), 91 (87), 77 (20), m* 69.6 (119 → 91), m* 46.5 (91 → 65).

***rac*-3,4-Diphenylhexane** had an ir ($CHCl_3$) fingerprint region slightly different from the spectrum of the meso compound; nmr, see Table VI; mass spectrum virtually identical with the spectrum of the meso form.

***meso*- and *rac*-4,5-Diphenyloctane.**—The compounds were not separated under the conditions of our glpc sampling: ir ($CHCl_3$) 3110–2870, 1600, 1490, 1450, 1370, 695 cm^{-1}; nmr, see Table VI; mass spectrum *m/e* (rel intensity) 266 (molecular peak, <0.01), 167 (8), 133 (88), 132 (70), 117 (10), 115 (8), 104 (9), 92 (29), 91 (100), 77 (10), m* 62.2 (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. Phenylacetone was identified by comparison of its glpc retention time and mass spectrum with those of an authentic sample. 1-Phenyl-2-propanol was identified by ir ($CHCl_3$), 3600, 3450, 3110–2850, 1600, 1490, 1450, 1370, 690 cm^{-1}, and nmr (CCl_4), δ 1.08 (d, J = 6.5 Hz, 3 H), 2.6 (d, J = 6.5 Hz, 1 H), 2.64 (d, J = 6.5 Hz, 1 H), 3.7 (s, 1 H, exchanged with D_2O), ~3.85 (m, J = 6.5 Hz, 1 H), 7.12 (s, 5 H).

Aldol-type condensation products were also found. 4-Hydroxy-4-methyl-2-pentanone and 3-hydroxy-3-methylbutanonitrile were formed in all competitive reactions and were identified by their nmr, ir, and mass spectrum. In the photoreaction 37, about 4% of 3-hydroxy-3-methyl-4-phenylbutanonitrile was also formed, by condensation of phenylacetone and cyanomethyl anion: nmr (CCl_4) 1.23 (s, 3 H), 2.29 (s, 2 H), 2.78 (s, 2 H), 3.14 (s, 1 H), 7.18 (s, 5 H); ir (neat) 3460, 3090–2930, 2250, 1600, 1500, 1450, 1380, 700 cm^{-1}; mass spectrum *m/e* (rel intensity) 175 (molecular peak, ~0.2), 160 (0.8), 159 (1.2), 135 (7), 117 (4), 115 (3), 92 (100), 91 (83), 77 (3), m* 101.3 (135 → 117), m* 46.5 (91 → 65).

From the potassium-stimulated reaction 38, *ca.* 2% of 1,3-diphenyl-2-methyl-2-propanol was isolated. It was probably formed by condensation of phenylacetone with the anion of phenylacetonitrile, followed by decyanation: nmr (CCl_4) δ 0.96 (s, 3 H), 1.67 (s, 1 H), 2.7 (s, 4 H), 7.16 (s, 10 H); ir ($CHCl_3$) 3585, 3460, 3080–2850, 1600, 1490, 1445, 1370 cm^{-1}; mass spectrum *m/e* (rel intensity) 226 (molecular peak, not detected), 211 (1), 208 (6.5), 193 (67), 136 (11), 135 (100), 134 (22), 117 (30), 115 (14), 92 (50), 91 (85), 77 (11), m* 101.3 (135 → 117), m* 46.5 (91 → 65), m* 24 (77 → 43).

Reactions of Benzyl Radicals (Table IV).—The runs designed to find reaction of benzyl radical with anions were performed in the same way as the phenylations of nitrile anions. An authentic sample of 1-(3′-methylphenyl)-2-phenylethane was prepared by our new decyanation method: 3.5 g of 2-(3′-methylphenyl)-3-phenylpropanonitrile, obtained by the method of Ganellin and Stolz,[32] was added to a mixture of ammonia (100 ml) and diethyl ether (50 ml); 3.6 g of ice was added, followed by sodium (0.89 g) in small bits. Ammonium chloride was added and the ammonia was evaporated. After the usual work-up the ether was removed. From the residue 2.4 g (78%) of the product was obtained by distillation: bp 91–94° (0.2 Torr); nmr (CCl_4) δ 2.25 (s, 3 H), 2.80 (s, 4 H), ~6.8 (m, 4 H), 7.06 (s, 5 H); mass spectrum *m/e* (rel intensity) 196 (molecular peak, 31), 106 (16), 105 (100), 91 (74), 79 (16), 77 (30), m* 59.5 (105 → 79), m* 56.3 (196 → 105), m* 46.5 (91 → 65).

Decyanation Reactions of Table V.—These reactions were conducted similarly to the phenylations of nitrile anions. The ammonia, however, was not distilled and air was not excluded.

Registry No.—CH_2CNK anion, 2932-82-3; BME, 538-86-3; MPAN⁻, 42117-18-0; PAN, 140-29-4; PBN, 769-68-6; K, 7440-09-7; Na, 7440-23-5; α-phenylvaleronitrile, 5558-78-1; α-phenylisovaleronitrile, 5558-29-2; 1,1-diphenylethane, 612-00-0; 1,1-diphenylpropane, 1530-03-6; 1,1-diphenylbutane, 719-79-9; 1,1-diphenyl-2-methylpropane, 1634-11-3; *meso*-2,3-diphenylbutane, 4613-11-0; *rac*-2,3-diphenylbutane, 2726-21-8; *meso*-3,4-diphenylhexane, 39952-67-5; *rac*-3,4-diphenylhexane, 42087-02-5; 4,5-diphenyloctane, 42117-21-5; 1-phenyl-2-propanol, 698-87-3; 3-hydroxy-3-methyl-4-phenylbutanonitrile, 42117-22-6; 1,3-diphenyl-2-methyl-2-propanol, 42117-23-7; 1-(3′-methylphenyl)-2-phenylethane, 34403-06-0.

(31) F. v. Wessely and H. Welleba, *Chem. Ber.*, **74**, 777 (1941).

(32) C. R. Ganellin and J. C. S. Stolz, *J. Chem. Soc. C*, 2132 (1969).