



Table I. Photostimulated Arylation of Cyanomethyl Anion in Liquid Ammonia

No.	ArX	Registry No.	M	KCH <sub>2</sub> CN M	Time, min	Yield, % <sup>b</sup>		
						ArX <sup>a</sup>	ArH	ArCH <sub>2</sub> CN
1 <sup>c</sup>	Bromobenzene	108-86-1	0.011	0.075	120		<i>d</i>	25 <sup>e</sup>
2 <sup>f</sup>	1-Chloronaphthalene	90-13-1	0.050	0.123	100 <sup>g</sup>		4	89 <sup>h</sup>
3	2-Chloronaphthalene	91-58-7	0.013	0.074	45		2	98 (93) <sup>i</sup>
4	9-Bromophenanthrene <sup>j</sup>	573-17-1	0.019	0.095	60	31	7	60
5	9-Bromophenanthrene <sup>k</sup>		0.009	0.060	120	14	16	70
6	1-Bromo-2-naphthoxide	59907-41-4	0.022	0.118	60	0 <sup>l</sup>	(98) <sup>i</sup>	0 <sup>l</sup>
7	Ethyl <i>p</i> -chlorobenzoate	7335-27-5	0.013	0.050	60	<i>d</i>		
8	<i>p</i> -Bromonitrobenzene	586-78-7	0.008	0.041	60	<i>d</i>		
9	4-Chlorobiphenyl	2051-62-9	0.016	0.077	20		4	96 (94) <sup>i</sup>
10	4-Chlorobiphenyl <sup>m</sup>		0.007	0.093	5	5	3	92
					15	3	3	94
					35			97 (90) <sup>i</sup>
11	4-Chlorobenzophenone	134-85-0	0.019	0.059	60		<i>d</i>	(97) <sup>i</sup>
12	2-Chloropyridine <sup>m</sup>	109-09-1	0.053	0.208	5	5	1	94
					30		1	98 (56) <sup>i</sup>

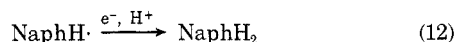
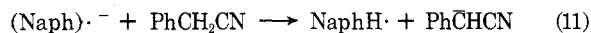
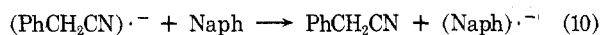
<sup>a</sup> Starting material recovered. <sup>b</sup> Yields determined by GLC, unless otherwise quoted. <sup>c</sup> Run carried out by A. B. Pierini. <sup>d</sup> Not quantified. <sup>e</sup> 1,2-Diphenylethane was obtained in 53% yield. This is a reaction similar to that reported in ref 2. <sup>f</sup> See ref 4. <sup>g</sup> In another similar experiment, 1-chloronaphthalene reacted quantitatively in less than 15 min. <sup>h</sup> Bis(1-naphthyl)acetonitrile was obtained in 7% yield. <sup>i</sup> Isolated crude product from which pure samples were obtained. <sup>j</sup> Slightly soluble in ammonia. <sup>k</sup> Starting material dissolved in ca. 5 ml of anhydrous diethyl ether. <sup>l</sup> Determined by TLC. <sup>m</sup> Samples were taken after the time indicated.

cyanomethyl anion stimulated by light in liquid ammonia to establish the scope and limitations of these reactions as a synthetic method and to demonstrate to what extent the products may be anticipated provided that the LUMO's of the aromatic and the CN moiety are known.

### Results and Discussion

We repeated the reaction of bromobenzene and cyanomethyl anion in liquid ammonia, reported by Bunnett and Gloor,<sup>2</sup> using a different light source (see Experimental Section) and wished to see if this caused any differences in the product composition. Although we obtained better yield (all the bromobenzene reacted in 120 min of irradiation whereas in the paper cited there was as much as 62% of unreacted bromobenzene after 120 min irradiation) the ratio of 1,2-diphenylethane (53%) to phenylacetonitrile (25%) was 2.12, similar to the value of 2.25 found previously.<sup>2</sup>

In an attempt to change the product composition we added catalytic amounts of naphthalene or biphenyl (5–10 mol %) with the expectation that these better electron acceptors would increase the rate of step 4, thereby decreasing the ratio of 1,2-diphenylethane/phenylacetonitrile. However, the reaction was strongly inhibited under these conditions. Inhibition of radical anion chain mechanism as Scheme I is precluded.<sup>6</sup> This inhibition may be also due to an acid–base reaction between phenylacetonitrile and naphthalene radical anion (eq 10–12).



A study of the reaction of phenylacetonitrile with naphthalene radical anion in various ether solvents has been reported.<sup>7</sup> It was found that proton abstraction (eq 11) was usually the major reaction pathway.<sup>8</sup>

In the small amounts of products formed, the ratio of 1,2-diphenylethane/phenylacetonitrile had not changed. This phenomenon is not fully understood and more work is being done along this line.

The photostimulated reactions of 2-chloronaphthalene and 9-bromophenanthrene with cyanomethyl anion in liquid ammonia lead to the acetonitrile derivatives **5** in high yields

(Table I). No products derived from C–CN bond cleavage were detected by NMR.

With 1-bromo-2-naphthoxide and cyanomethyl anion, we obtained only 2-naphthol, the reduction product (Table I). This result implies that there is a photostimulated electron transfer from the nucleophile to the substrate (step 1) but the radical **3** formed in step 2 does not couple with the cyanomethyl anion (step 3); instead it is reduced to give ultimately 2-naphthoxide. Similarly in the photostimulated reaction of *p*-bromophenoxide with acetone enolate anion in liquid ammonia only the dehalogenation product was obtained.<sup>9</sup> The lack of reactivity can be attributed to the low electrophilicity of an aromatic  $\sigma$  radical bearing an electron-releasing group.

Dehalogenation of haloaromatic compounds by thermal electron transfer from nucleophiles such as methoxide anion has been reported.<sup>10,11</sup>

All the polycyclic condensed hydrocarbons have lower LUMO values than the CN moiety, so we expected that all the halo derivatives would give the  $\alpha$ -acetonitrile derivatives in the photostimulated reaction with cyanomethyl anion in liquid ammonia. On the other hand, the benzene ring has a LUMO value higher than the CN moiety as mentioned before, but an appropriate substituent attached to the ring may decrease its LUMO to a value lower than that of the CN moiety, and different reaction products might well be obtained (no C–CN bond cleavage).

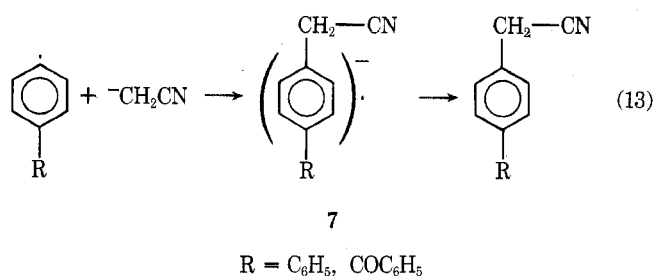
In order to probe our hypothesis, we studied halobenzenes with substituents attached to the ring that decrease the LUMO value of the aromatic moiety. Substituents such as nitro, CO<sub>2</sub>Et, C<sub>6</sub>H<sub>5</sub>, and COC<sub>6</sub>H<sub>5</sub> fulfill this requirement.

Unfortunately the photostimulated reaction of *p*-bromonitrobenzene and ethyl *p*-chlorobenzoate with cyanomethyl anion in ammonia did not give substitution or reduction products. Apparently other reactions took place. Nitro-substituted compounds also fail to give photostimulated reaction with acetone enolate anion in ammonia.<sup>9</sup>

The photostimulated reaction of *p*-chlorobiphenyl and *p*-chlorobenzophenone with cyanomethyl anion in ammonia gives the  $\alpha$ -acetonitrile derivatives in high yields, and no products derived from C–CN bond cleavage were observed (Table I).

It is remarkable that the presence of a substituent such as C<sub>6</sub>H<sub>5</sub> and COC<sub>6</sub>H<sub>5</sub> can change the product composition so

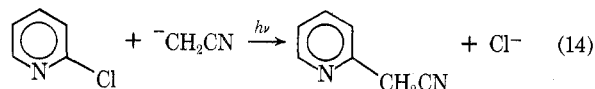
dramatically in the reaction of para-substituted phenyl radical with cyanomethyl anion (eq 13).



These results are in agreement with our predictions based on the LUMO's of the aromatic moiety.

Not only may a substituent attached to the benzene ring bring about a lower LUMO value than the CN moiety, but so may replacement of one of the ring carbons by an electronegative heteroatom such as nitrogen, as in the case of pyridine.

Accordingly, we found that the photostimulated reaction of 2-chloropyridine with cyanomethyl anion in ammonia gave 2-pyridylacetonitrile in high yields also without C-CN bond cleavage (eq 14).

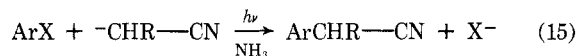


**Rate of the Reaction.** The photostimulated reaction of bromobenzene with cyanomethyl anion in liquid ammonia is remarkably slower than the reaction with acetone enolate anion.<sup>2,12</sup> The differences in rates were attributed to the important steps (6-8) that interrupt the chain mechanism lowering the overall rate of the reaction.

In a few experiments with 1-chloronaphthalene, 4-chlorobiphenyl, and 2-chloropyridine (Table I), which are substrates where steps 6-8 do not take place, samples were taken after different periods of reaction in order to measure qualitatively the rate of reaction. All of them reacted quantitatively in less than 15 min.

Competition experiments between acetone enolate anion and cyanomethyl anion with 1-chloronaphthalene give no reproducible results (reactivity ratio between 0.5 and 3), but it is evident from these experiments that the reactivities of both anions are very similar. These results indicate that it is not the intrinsic reactivity of acetonitrile which makes the reaction of bromobenzene with acetonitrile anion slower than that of acetone enolate anion, but rather the important steps that interrupt the chain mechanism in the former case.

**Synthetic Applications.** In view of the results reported here, we conclude that this is an important synthetic method for obtaining  $\alpha$ -aryl or hetaryl acetonitrile derivatives (eq 15).



The general conditions necessary to obtain good yields of arylation product are that the aromatic moiety must have a lower LUMO than the CN moiety and must not have an electron-releasing substituent such as O<sup>-</sup> or NMe<sub>2</sub> or a sub-

stituent that reacts with cyanomethyl anion. Benzene derivatives, polycyclic aromatic hydrocarbons, and heteroaromatic hydrocarbons are suitable substrates.

### Experimental Section

**General.** Melting points have not been corrected. NMR spectra were recorded on a Varian T-60 nuclear magnetic resonance spectrophotometer using CCl<sub>4</sub> as solvent, unless otherwise quoted, and all the spectra are reported in parts per million relative to Me<sub>4</sub>Si ( $\delta$ ). Thin layer chromatography was performed on silica gel plates. Gas chromatographic analyses were performed on a Varian Aerograph Series 2400 with flame ionization detector, using a column packed with 3% Silicon Rubber SE-30 on Chromosorb P 80-100, 6 ft  $\times$  0.125 in.

**Materials.** Acetonitrile (BPC Erba) was dried over anhydrous K<sub>2</sub>CO<sub>3</sub>, refluxed with P<sub>2</sub>O<sub>5</sub>, and distilled as needed. All the haloaromatic compounds were commercially available and were used as received, except 9-bromophenanthrene<sup>13</sup> and 1-bromo-2-naphthol,<sup>14</sup> which were prepared according to the method described. Liquid ammonia was dried with Na metal and distilled under nitrogen into the reaction flask. Cyanomethyl anion was prepared as described.<sup>2,4</sup>

**Photostimulated Reactions.** The photostimulated reactions were carried out in a photochemical reactor equipped with two 250-W uv lamps, Philips, Model HTP, emitting maximally at ca. 360 nm, with water jacket refrigeration. The method used was as described.<sup>4</sup> Products were isolated and identified by standard procedures.

**Identification of Products.** Analyses were performed on pure samples obtained from the crude products. Unreacted starting materials and dehalogenation products were identified and quantified by comparison of their GLC retention time and/or by TLC. Evidence for the identity of other products is now presented.

$\beta$ -Naphthylacetonitrile was recrystallized from petroleum ether, NMR spectrum identical with that of an authentic sample;<sup>15</sup> 9-phenanthrylacetonitrile recrystallized from petroleum ether, mp 96-97 °C (lit.<sup>16</sup> mp 96.5-97 °C), NMR 3.90 (s, 2 H), 7.38-7.88 (m, 7 H), and 8.28-8.72 ppm (m, 2 H); 4-biphenylacetonitrile, NMR identical with that of an authentic sample;<sup>17</sup> 4-benzoylphenylacetonitrile, recrystallized from petroleum ether, mp 63-64 °C (lit.<sup>18</sup> mp 64 °C), NMR (solvent acetone-*d*<sub>6</sub>) 3.60 (s, 2 H), 7.22-7.90 ppm (m, 9 H); 2-naphthol, TLC (benzene as solvent) *R*<sub>f</sub> 0.29 (1-bromo-2-naphthol has *R*<sub>f</sub> 0.64), NMR identical with that of authentic sample. 2-Pyridylacetonitrile, NMR identical with that described in the literature.<sup>19</sup>

**Registry No.**—Cyanomethyl, 2932-82-3

### References and Notes

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