

factor $\log(1 - \nu)$ is 2.2×10^{-3} compared to $\log(1 - \nu) = 0$ under conditions of no fatigue.

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Appendix

The rate appearance of L is given in eq A1a

$$\frac{d[L]}{dt} = \frac{I_a \Phi}{NV} - k_d[L] \quad (\text{A1a})$$

$$I_a = I_0(1 - e^{-\epsilon_D[D]t}) \quad (\text{A1b})$$

where I_a is the light absorbed and is defined in eq A1b. Taking into account the inner filter effect and that $d[L]/dt = 0$ at the photostationary state, we obtain eq A2. The symbols are defined in the text.

$$L_s = \left\{ \left(\frac{I_0 \Phi}{NVk_d} \right) \times \frac{[1 - \exp(-2.303)(\epsilon_D D_s + \epsilon_L L_s)l](\epsilon_D D_s)}{(\epsilon_D D_s + \epsilon_L L_s)} \right\}^{1/n} \quad (\text{A2})$$

In general the steady state concentration of the dark form, D_s , is given in eq A3 where n is the stoichiometric number of moles of product per mole of reactant and D_0 is the initial concentration of the dark form.

$$D_s = D_0 - \frac{1}{n} L_s \quad (\text{A3})$$

Substituting eq A3 into eq A2 results in the general expression in eq 3 in the Experimental Section. If the absorption spectra of D and L do not overlap and the light reaction can be driven at a wavelength at which L does not absorb, eq 3 reduces to

$$L_s = \left\{ \left(\frac{I_0 \Phi}{NVk_d} \right) \times \left[1 - \exp(-2.303)(\epsilon_D) \left(D_0 + \frac{1}{n} L_s \right) l \right] \right\}^{1/n}$$

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Reaction of 1-Halonaphthalenes with Nucleophiles by the SRN1 Mechanism of Aromatic Substitution¹

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Abstract: 1-Halonaphthalenes react in liquid ammonia with several nucleophiles under light or potassium metal stimulation. With acetate or cyanomethyl anions as nucleophiles, a mixture of the substitution products and products derived from reduction of the naphthalene ring is obtained under potassium metal stimulation. Photostimulated reactions with the same nucleophiles and with alkyl mercaptide ions give the substitution products in high yields. These reactions probably proceed by the SRN1 mechanism. We suggest that the product distribution can be used to determine the structure of the radical anion intermediate formed.

Aryl radicals are intermediates in the recently recognized SRN1 mechanism of aromatic nucleophilic substitution.² Supply of an electron to an aromatic compound bearing a suitable leaving group forms a radical anion which then ejects the nucleofugic substituent, emerging as an aryl radical.³ The radical combines with a nucleophile to form a new radical anion. This radical anion must dispose of the extra electron or otherwise react to form a stable product. It may take another electron, giving reduced products (ketonate anions^{4,5} and hydrocarbon derived carbanions⁵), or it may

suffer fragmentation (cyanomethyl⁶ and ethyl mercaptide anions⁷).

The solvated electron in solutions of alkali metals in liquid ammonia is very effective as an electron source.⁸ In other studies, SRN1 reactions stimulated by solvated electrons have afforded fair to good yields of substitution products.^{2-6,9} Alternatively, an initiating electron-transfer process can be stimulated photochemically¹⁰ or from electrodes.¹¹

Among the aromatic compounds studied, phenyl deriva-

Table I. Reactions of 1-Halonaphthalenes with Acetonate Anion in Liquid Ammonia^a

| 1-X-Naph | | | Yield, % ^b | | | | |
|----------|--------------------|---------------------------------|-----------------------|-----------------|-------------------|----------------------|----------------------|
| X | M | Promoter | 1-X-Naph | Naph | 1-NA ^c | DH-1-NA ^d | TH-1-NA ^e |
| Cl | 0.050 | <i>hν</i> , ^f 90 min | | 2 | 88 ^g | | |
| Cl | 0.033 | 60 min ^h | 100 | | | | |
| Cl | 0.050 ⁱ | K, 0.037 M | 55 | 4 | 14 | 13 | 14 |
| | | K, 0.076 M | 24 | 7 | 22 | 25 | 20 |
| | | K, 0.120 M | 2 | 9 | 22 | 36 | 32 |
| Cl | 0.050 | K, 0.145 M | | 8 ^j | 23 | 33 | 36 |
| I | 0.043 ⁱ | K, 0.013 M | 68 | 3 | 11 | 8 | 10 |
| | | K, 0.031 M | 47 | 5 | 17 | 16 | 15 |
| | | K, 0.052 M | 26 | 7 | 19 | 24 | 23 |
| I | 0.040 | K, 0.120 M | | 10 ^j | 6 | 44 | 40 |
| Cl | 0.044 | K, 0.045 M ^k | 39 | 7 | 13 | 15 | 15 |
| | | K, 0.098 M ^k | 13 | 17 | 16 | 19 | 24 |

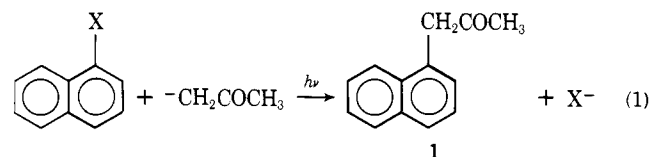
^a Acetonate anion was always present in ca. twice the amount of substrate. K metal was added bit by bit unless otherwise stated. ^b Yields determined by combined GLC and NMR methods unless otherwise quoted. Products were column chromatographically isolated and their structures determined by ir, NMR, and mass spectra. ^c 1-Naphthylacetone. ^d 1,2- and 1,4-dihydro-1-naphthylacetone. ^e 1,2,3,4-tetrahydro-1-naphthylacetone. ^f See ref 16. ^g 1,1-Bis(1-naphthyl)acetone was also present but not quantified. ^h Dark. ⁱ Samples (ca. 2 ml) were taken after each addition of K metal and added to ca. 9 ml of water and extracted with ether. The ether layer was examined by GLC and after elimination of the solvent by NMR. ^j Together with 1,4-dihydronaphthalene (about 50%). ^k Potassium metal added in one piece.

tives are the most common, although some reactions involving 1-naphthyl,¹² 2-quinolyl,¹³ and 4-isoquinolyl¹⁴ radicals have been reported. Recently it has been reported that certain bromine or iodine derivatives of naphthalene, biphenyl, anthracene, and phenanthrene react with acetone enolate anion in liquid ammonia under photostimulation by the SRN1 mechanism.¹⁵

We now report that under experimental conditions similar to those used for reactions of phenyl radicals with cyanomethyl, alkyl mercaptide, and ketone enolate anions, 1-halonaphthalenes react with these nucleophiles giving good yields of substitution products probably by the SRN1 mechanism.

Results and Discussion

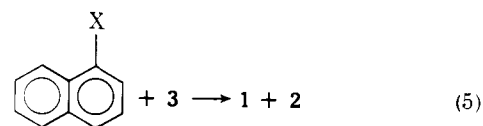
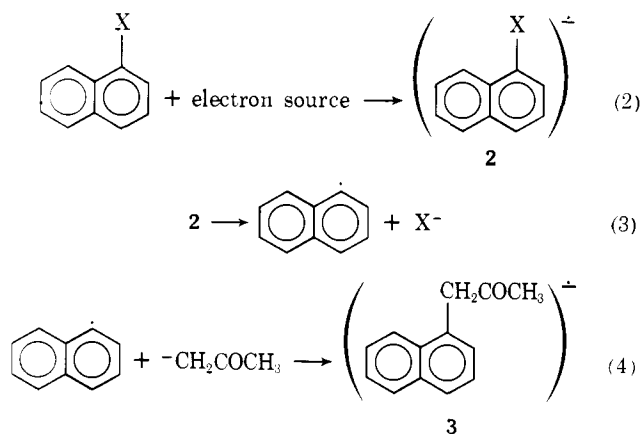
Ketone Enolate Anions. When solutions of 1-halonaphthalenes and acetone anion in refluxing liquid ammonia are irradiated with Pyrex-filtered uv lamps,¹⁶ reaction occurs according to eq 1.



A control run carried out in the dark under the same reaction conditions gave no reaction (Table I).

The presumed reaction mechanism is sketched in Scheme I. This is the standard SRN1 mechanism of aromatic substi-

Scheme I

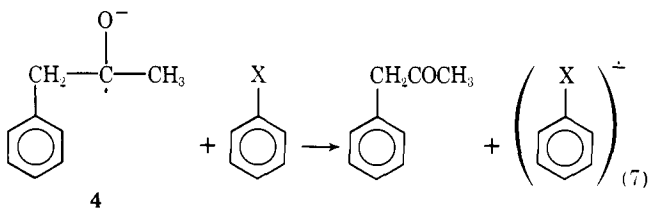


termination steps (6)

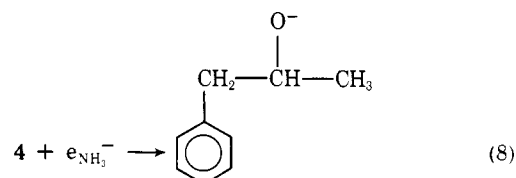
tution,² adapted to the immediate case.

The reaction stimulated by potassium metal gives a mixture of naphthalene, 1-naphthylacetone, 1,2- and 1,4-dihydro-1-naphthylacetone, and 1,2,3,4-tetrahydro-1-naphthylacetone (Table I).

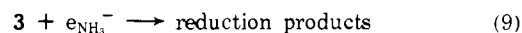
The reaction of phenyl radical with acetone anion under solvated electron stimulation gives a mixture of phenylacetone and 1-phenyl-2-propanol.⁴ It was suggested that the radical anion formed when phenyl radical couples with acetone anion is ketyl-like radical anion 4, which becomes involved in two competing reactions, electron transfer to the



substrate (eq 7) and electron capture to form, ultimately, alkoxide ion (eq 8).⁴



This general mechanism can equally well explain our data; we call attention particularly to the competition between reaction 5 and 9.



In order to see whether the reduction products are formed by the reaction of eq 9 or by reaction of the 1-naphthylacetone 1 product with solvated electrons in excess, we carried out an experiment with potassium metal added in deficiency. We added small amounts of potassium metal, and we took a sample of the reaction mixture after each addition. GLC and NMR analysis of the samples showed that products representing reduction in the naphthalene moiety

Table II. Reaction of 1-Chloronaphthalene with Acetophenone Enolate Anion in Liquid Ammonia

| 1-Cl-Naph, M | PhCOCH ₂ ⁻ K ⁺ , ^a M | K metal, ^b M | Yield, % ^d | | |
|--------------------|---|----------------------------|-----------------------|-----------------|--------------------|
| | | | 1-Cl-Naph | Naph. | 1-NAP ^c |
| 0.030 | 0.070 | 0.046 | 49 | 23 | 25 |
| 0.025 | 0.070 | 0.045 | 11 | 33 | 57 |
| 0.018 ^e | 0.056 | 0.026 | 77 | 9 | 12 |
| | | 0.047 | 47 | 25 | 22 |
| | | 0.107 | 0 | 35 ^f | 23 ^g |

^a Acetophenone enolate anion was prepared from acid-base reaction with *t*-BuOK. ^b K metal was added bit by bit. ^c 1-NAP = α -(1-naphthyl)acetophenone. ^d Yield determined by GLC. ^e Samples were taken as indicated in the footnote *i* (Table I). ^f About 14% correspond to 1,4-dihydronaphthalene; ^g Two new substances appeared with similar retention times as α -(1-naphthyl)acetophenone, but it was not possible to isolate them (GLC, column chromatography, and TLC); NMR analysis of the mixture showed that they were not reduced in the naphthalene ring.

are formed even when 60% of the 1-halonaphthalene remains unchanged (Table I).

Unless 1-naphthylacetone is extraordinarily reactive toward solvated electrons, these results indicate that the reduction products come from the radical anion intermediate **3**.

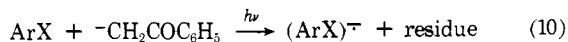
The former possibility seems unlikely considering that halobenzenes of very different reactivity, as determined in photostimulated reactions,¹⁰ have shown to be unselective toward solvated electrons.¹⁷ In a separate experiment, we also found no selectivity between chlorobenzene and 1-chloronaphthalene toward solvated electrons.¹⁸ Therefore we conclude that the radical anion **3** is reduced in the sense of eq 9, giving rise to the observed products.

Changing the leaving group from chlorine to iodine gave no change in the product distribution. Again, formation of the reduced naphthalene ring is observed, even with potassium metal in deficiency (Table I).

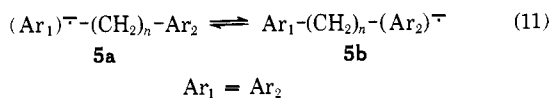
It is noteworthy that we did not find any product derived from reduction of the carbonyl group in the sense of eq 8. We shall comment later on these results.

The reaction of 1-chloronaphthalene with acetophenone anion promoted by solvated electrons leads mainly to α -(1-naphthyl)acetophenone with *no formation* of products derived from reduction of the naphthalene ring, even with an excess of potassium metal (Table II).

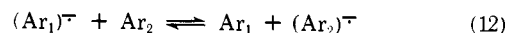
The photostimulated reaction of 1-chloronaphthalene with acetophenone enolate anion gave only ca. 8% yield of α -(1-naphthyl)acetophenone after 3 h irradiation.¹⁶ The analogous reaction with halobenzenes failed to form α -phenylacetophenone.¹⁹ However, 2-chloroquinoline reacted with the lithium salt of acetophenone when irradiated in liquid ammonia to give 82% of 2-phenacylquinoline by an SRN1 mechanism.^{13b} We have no good explanation for this behavior of acetophenone enolate anion, except that quinoline is a better electron acceptor than naphthalene and much better than benzene;²⁰ that might facilitate electron transfer in the probable initiation step of the photostimulated reaction



When an aryl radical reacts with a nucleophile of the type $^-\text{CH}_2\text{-Z}$ (for the present case $\text{Z} = -\text{COCH}_3$ or $-\text{COC}_6\text{H}_5$), a radical anion intermediate is formed. The extra electron can be located either in Z or in the aryl moiety. It is known that when a radical anion of a molecule that has two unsaturated moieties separate by other atoms such as **5** is formed, a fast intramolecular electron transfer between both moieties occurs (eq 11).²²

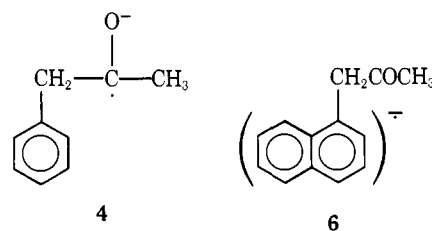


It is expected that when $\text{Ar}_1 \neq \text{Ar}_2$, the equilibrium **11** will be shifted toward the more stable radical anion. In intermolecular electron transfer reactions, the equilibrium depicted in eq 12 favors the most stable radical anion.²³

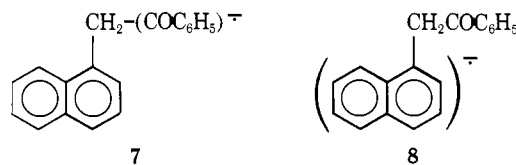


In a radical anion of the type $(\text{ArCH}_2\text{Z})^\cdot$, the principal location of the extra electron is suggested by the reduction products obtained in reactions stimulated by solvated electrons.

As was pointed out, phenyl radical and acetone anion give the radical anion **4**. The reduction of the naphthalene ring in the reaction with 1-naphthyl radical leads us to suggest that the radical anion formed is best represented as **6**.



The fact that no reduction of the naphthalene ring occurs during reaction of 1-chloronaphthalene with the acetophenone enolate anion might indicate that **7** is the predominant form of the radical anion intermediate or that the radical anion intermediate is best represented as **8**, but that **8** is so much more stable than **6**, that there is time for the competing bimolecular reaction of eq 5 to occur.

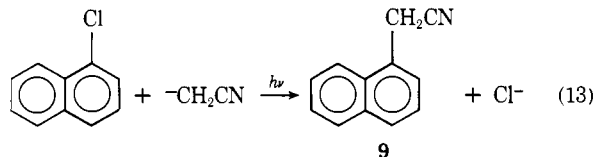


However, **8** would not be expected to be much more stable than **6** since there is no direct conjugation between the $-\text{COC}_6\text{H}_5$ moiety and the naphthalene ring, and the substrate which would accept the extra electron in the transfer step 5 is the same. For that reason, we suggest that **7** is the predominant form of the radical anion intermediate.

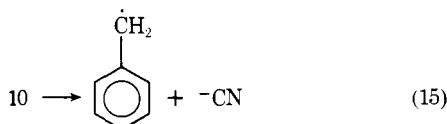
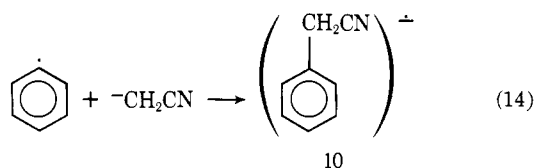
Comparing the energy of the lowest unoccupied molecular orbital (LUMO) of the Z and Ar moieties which can accept the extra electron in radical anions **4**, **6**, and **7**, one finds the order: benzene > $-\text{COCH}_3$ > naphthalene > $-\text{COC}_6\text{H}_5$, which is in good agreement with the postulated structures.²⁰

These results might suggest that when an aromatic radical $(\text{Ar}\cdot)$ couples with a carbanion of type $^-\text{CH}_2\text{-Z}$, the extra electron in the radical anion intermediate will go mainly to the lower LUMO, either in Z or Ar .

Cyanomethyl Anion. When solutions of 1-chloronaphthalene and cyanomethyl anion are irradiated¹⁶ in refluxing liquid ammonia, reaction occurs according to eq 13.

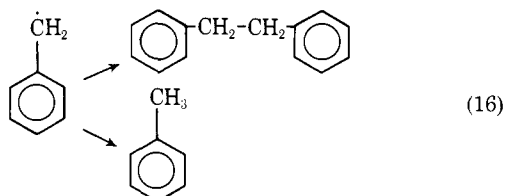


Under similar experimental conditions, bromobenzene and cyanomethyl anion afforded a mixture of benzene (1%), toluene (2%), phenylacetonitrile (8%), diphenylmethane (1%), and 1,2-diphenylethane (18%).⁶ These results were explained by a photostimulated SRN1 mechanism as sketched in Scheme I with $\text{-CH}_2\text{CN}$ as nucleophile for the present case. Some additional steps were suggested to explain the formation of the various products.⁶ The radical anion **10**, formed by reaction of phenyl radical with cyanomethyl anion (eq 14), may either transfer the surplus



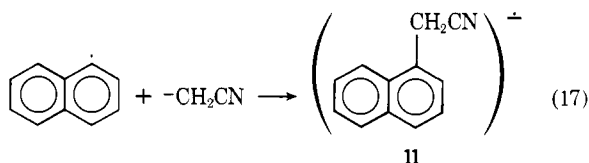
electron to another molecule of the aromatic substrate, forming phenylacetonitrile in the sense of eq 5, or eject cyanide ion thereby forming a benzylic radical (eq 15).

The benzylic radical can then dimerize to give 1,2-diphenylethane or abstract a hydrogen atom to give toluene (eq 16).⁶ The reaction of 1-chloronaphthalene with cyano-



nomethyl anion under photostimulation can also be explained by a SRN1 mechanism as sketched in Scheme I; however, there are interesting differences in the product distribution.

1-Naphthylacetonitrile radical anion **11** formed in the coupling of 1-naphthyl radical with cyanomethyl anion (eq 17) does not undergo fission since the only product formed



was **9** (except some bis(1-naphthyl)acetonitrile, that represents double arylation) (Table III).

This difference in behavior might be explained by a difference in stability of the radical anion **10** compared with **11**, which would make more effective the bimolecular electron transfer step 5 than C-CN bond rupture in the sense of eq 15. However, we believe that there are more fundamental differences between radical anions **10** and **11**.

As was argued above, when a carbanionic nucleophile of the type $\text{-CH}_2\text{-Z}$ couples with an aromatic radical, the extra electron must go either to Z or to the aromatic moi-

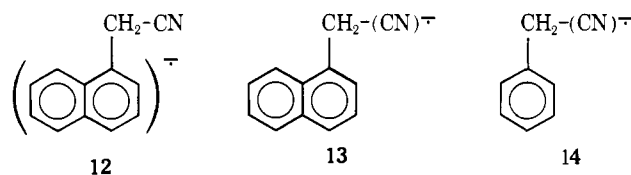
Table III. Reaction of 1-Chloronaphthalene with Cyanomethyl Anion in Liquid Ammonia^a

| 1-X-Naph | | Promoter | Yield, % ^d | | |
|-------------------------|-------|-------------------------------|-----------------------|--------------------|-------------------|
| X | M | | Naph | 1-NAN ^b | DNAN ^c |
| Cl | 0.050 | $h\nu$, ^e 100 min | 4 | 89 | 7 |
| Cl | 0.039 | K, 0.092 M | 23 | 60 ^f | 13 |
| $\text{-CH}_2\text{CN}$ | 0.035 | K, 0.072 M | | 100 ^f | |

^a Cyanomethyl anion was prepared from KNH_2 obtained in situ and was present in ca. twice the amount of substrate. K metal was added bit by bit. ^b 1-Naphthylacetonitrile. ^c Bis(1-naphthyl)acetonitrile. ^d Yields determined by GLC. ^e See ref 16. ^f Quantified together with 1,2- and 1,4-dihydro-1-naphthylacetonitrile due to partial overlap of the peaks. The presence of 1,2- and 1,4-dihydro derivatives were confirmed by NMR analysis.

ety, and where it goes will depend on the energy of the LUMO.

Since in the present case the energy of the LUMO of naphthalene is $-0.618 \beta^{21,24}$ and the LUMO of Z (Z = -CN) is $-0.820 \beta^{24,25}$ (compare with the LUMO of benzene = $-1.000 \beta^{21,24}$), the structure of the radical anion is expected to be **12**.



Radical anion **13** would be expected to undergo C-CN bond cleavage as the phenylacetonitrile radical anion **14** does. It would be hard to explain greater stability for **13** than **14** because there is no direct conjugation between the CN moiety and the naphthalene ring. Moreover, the order of the LUMO energies, benzene > CN > naphthalene, agrees with the formation of **12** and **14** and *not* **13**.

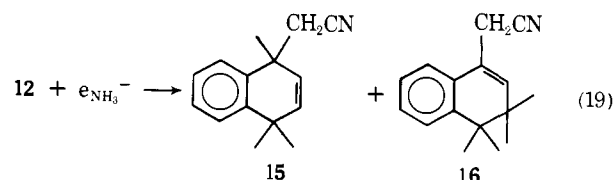
We can not say from our results whether radical anion **13** is initially formed by eq 4, and then forms **12** by an intramolecular electron transfer (eq 18), which is known to be



very fast,²² or whether **12** is formed directly from the coupling of 1-naphthyl radical with cyanomethyl anion.

Disregarding the question of the structure of the radical anion initially formed in step 4, the equilibrium shown in eq 18 should be established very fast,²² and it will favor the more stable radical anion.²³ The state of equilibrium in turn depends on the energy level of the LUMO of the group that accepts the electron.

In order to demonstrate more definitively which is the intermediate involved in this reaction, we investigated the reaction of 1-chloronaphthalene with cyanomethyl anion stimulated by potassium metal as electron source. As expected, there was no C-CN bond cleavage, but rather reduction of the naphthalene ring (Table III). Reduction of the naphthalene ring can be explained if the radical anion **12** is involved in competing reactions, namely, electron transfer in the sense of eq 5 or reduction (eq 19).



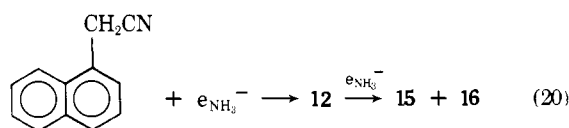
It is expected that the radical anion formed from the coupling of 1-naphthyl radical with an anion gives the same

Table IV. Photostimulated Reactions of 1-Halonaphthalenes with Mercaptide Ions in Liquid Ammonia^a

| 1-X-Naph | RSH | | Time, min | Yield, % ^c | | | |
|----------|-------|---|-----------|-----------------------|----|----------|------------------|
| | X | M | | R | M | 1-X-Naph | NSR ^b |
| Cl | 0.056 | <i>n</i> -BuSH | 0.112 | 190 | 58 | 31 | 10 |
| Cl | 0.056 | <i>n</i> -BuSNa ^d | 0.080 | 170 | 1 | 18 | 81 |
| Cl | 0.056 | HOCH ₂ CH ₂ SH | 0.184 | 165 | 5 | 19 | 71 |
| I | 0.050 | HOCH ₂ CH ₂ SK ^d | 0.148 | 150 | 16 | 8 | 74 |

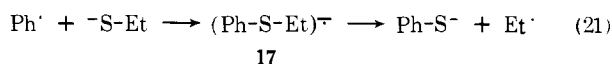
^a See ref 16. ^b 1-naphthyl alkyl sulfide. ^c Determined by GLC. The products were isolated by column chromatography and characterized by ir and NMR analysis. ^d The RS⁻M⁺ were prepared in situ by the reaction of RSH and the M in equivalent amount.

radical anion as when the product of substitution adds an electron.²⁵ Accordingly, we investigated the reaction of 1-naphthylacetonitrile with solvated electrons in liquid ammonia. In this reaction, there was no C-CN cleavage either, instead, reduced 1-naphthylacetonitrile was formed; this again suggests the formation of the radical anion **12** (eq 20).



Phenylacetonitrile and solvated electrons gave C-CN bond rupture, affording toluene in almost quantitative yields,⁶ which in turn suggest the formation of radical anion **14** as intermediate and ejection of cyanide in the sense of eq 16.

Alkyl Mercaptide Anions. Ethyl mercaptide had been shown to react with phenyl radicals to give a modest yield of the substitution product, ethyl phenyl sulfide, together with a substantial amount of thiophenol. These results were explained by an SRN1 reaction where the radical anion intermediate **17**, formed by reaction of phenyl radical with ethyl mercaptide, decomposes to thiophenoxide ion and ethyl radical (eq 21).⁷



When 1-chloronaphthalene and ammonium *n*-butyl mercaptide dissolved in liquid ammonia were irradiated by Pyrex-filtered light,¹⁶ naphthalene (31%) and *n*-butyl 1-naphthyl sulfide (10%) were obtained. However, the sodium salt of *n*-butyl mercaptide under similar conditions gave naphthalene (18%) and *n*-butyl 1-naphthyl sulfide (81%) (Table IV).

The photostimulated reaction of 1-chloronaphthalene with 2-mercaptoethanol in liquid ammonia affords 71% of 1-naphthyl 2-hydroxyethyl sulfide together with 19% of naphthalene.

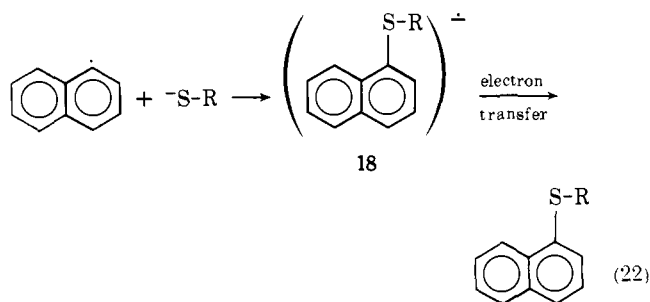
The potassium salt of 2-mercaptoethanol gave almost the same result in reaction with 1-iodonaphthalene. No products derived from reaction with the alkoxide ion function were obtained.

These results can easily be explained by a SRN1 mechanism as in Scheme I with ⁻S-R as nucleophile.

The contrasting behavior of 1-naphthyl radical compared with phenyl radical is probably to be attributed to greater stability of the radical anion **18** derived from 1-naphthyl radical (eq 22) than for the corresponding intermediate **17** from phenyl radical (eq 21).

Inasmuch as the radical anion of naphthalene is more stable than that of benzene,²¹ **18** would be expected to be

more stable than **17**. Greater stability of **18** would enable it to survive long enough to transfer an electron in a bimolecu-



lar step (eq 5) and thereby give the substitution product without fragmentation.

Experimental Section

General. Reagents were all commercially available materials and were purified by standard procedures, except for *n*-butyl mercaptan which was prepared according to standard procedures.²⁷

NMR spectra were recorded on a Varian T-60 nuclear magnetic resonance spectrometer with Cl₄C as solvent, and all spectra are recorded in parts per million relative to Me₄Si (δ). Thin layer chromatography was performed on silica gel plates. Column chromatography was performed on neutral aluminum oxide (Merck). Mass spectral measurements were obtained with a Hitachi Perkin-Elmer Model RMV-6 E mass spectrophotometer. Gas chromatographic analyses were performed on a Varian Aerograph Series 2400, with flame ionization detector, and yields were determined by peak area corrected for the detector response. The column was 5 ft \times 1/8 in., packed with 1.5% of OV-101 on 100-120 Chromosorb G.

Ketone anions were prepared from *t*-BuOK obtained in situ by the iron catalyzed reaction.²⁸ Cyanomethyl anion was prepared in situ from the acid-base reaction with KNH₂, formed previously from potassium metal and little FeCl₃ as catalyst. Alkyl mercaptide anions were prepared from reaction of the alkali metal with the alkyl mercaptan in liquid ammonia.

Reactions Stimulated by Alkali Metal. A procedure for arylation of acetone anion is representative. The reaction was carried out in a three-neck, round-bottom flask fitted with a solid CO₂-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 200 ml was distilled into the reaction flask in a current of dry nitrogen. After the addition of *tert*-butyl alcohol (0.024 mol), potassium metal (0.024 mol) was added, and after about 10 min, a small amount of ferric chloride was added to catalyze the formation of *t*-BuOK.²⁸ After the metal had all reacted, acetone (0.024 mol) was added dropwise. After a few minutes, 0.011 mol of 1-chloronaphthalene was added and then potassium metal (0.029 mol) was added in small pieces. When samples were taken during runs, a piece of 8-mm glass tubing, J-shaped at the lower end, was used to scoop out portions of the reacting solution. This allowed taking samples of approximately 2 ml of ammonia solution, each of which was added carefully to ca. 10 ml of water.

To quench the reaction, excess ammonium chloride was added to the brownish-red solution, turning it light yellow. Diethyl ether (100 ml) was 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 GLC.

Photostimulated Reactions. The reaction mixtures were prepared as described above. The reaction flask was then placed into a reactor equipped with uv lamps,¹⁶ and the reaction mixture was irradiated for the time periods indicated in the tables. Care was taken to rinse the outside wall with isopropyl alcohol frequently to avoid the formation of ice. To quench the reaction, excess ammonium chloride was added, and the work-up was similar to the other reactions.

Reaction of 1-Naphthylacetonitrile with Potassium Metal. To 200 ml of dry liquid ammonia under slow current of dry nitrogen in a three-neck round-bottom flask, 1-naphthylacetonitrile (0.0070 mol) was added and then potassium metal (0.0145 mol) was added, bit by bit. The reaction was quenched with ammonium chloride, and ether (100 ml) was added. After evaporation of the ammonia, water was added, and the ether and water extracts were separated. GLC analysis of the ether extracts showed three peaks with retention time similar to 1-naphthylacetonitrile, but due to partial overlap it was not possible to quantify them. NMR analysis showed the peaks characteristic of 1,4-dihydronaphthalene derivatives (δ 5.85 and singlets in the aromatic region around δ 7.0).

Identification of Products. Analysis was performed and samples were collected by column chromatography on neutral alumina. Unreacted starting material and naphthalene were identified by comparison of their retention times and NMR spectra with authentic samples. Evidence for the identity of the other products is presented: 1,2,3,4-tetrahydro-1-naphthylacetone, NMR δ 1.7 (m, 4 H), 2.03 (s, 3 H), 2.6 (m, 2 H), 2.70 (s, 2 H), 3.17 (m, 1 H), 7.00 (s, 4 H), the mass spectrum showed a molecular ion peak at m/e 188 and peaks at 159, 145, 130, 129, 128, 117, and 115; 1,4-dihydro-1-naphthylacetone, NMR δ 2.00 (s, 3 H), 3.4 (m, 3 H), 3.53 (s, 2 H), 5.83 (m, 2 H), 6.96 (s, 4 H); the mass spectrum showed a molecular ion peak at m/e 186 and peaks at m/e 143, 129, 117, and 115; 1-naphthylacetone, NMR δ 1.83 (s, 3 H), 3.82 (s, 2 H), 7.2–8.0 (m, 7 H), the mass spectrum has a molecular ion peak at m/e 184 and peaks at 141, 115; 1-naphthylacetophenone, NMR δ 4.72 (s, 2 H), 7.2–8.2 (m, 12 H), the mass spectrum showed a molecular ion peak at m/e 246 and peaks at 215, 202, 141, 115, 105; 1-naphthylacetonitrile, NMR δ 3.86 (s, 2 H), 7.25–7.8 (m, 7 H), identical with an authentic sample,²⁹ the mass spectrum showed a molecular ion peak at m/e 167; bis(1-naphthyl)acetonitrile, NMR δ 6.31 (s, 1 H), 7.2–7.8 (m, 14 H), the mass spectrum showed a molecular ion peak at m/e 293; *n*-butyl 1-naphthyl sulfide, NMR δ 0.90 (t, 3 H), 1.47 (s, 4 H), 2.82 (t, 2 H), 7.2–7.8 (m, 6 H) and 8.2–8.4 (m, 1 H); 2-hydroxyethyl 1-naphthyl sulfide, NMR δ 2.97 (t, 2 H), 3.50 (t, 2 H), 4.1 (s, 1 H), this peak disappears after shaking the solution with D₂O, 7.2–7.8 (m, 6 H) and 8.3–8.5 (m, 1 H).

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