was extracted three times with 25-mL portions of methlene chloride and the combined extracts were washed twice with 5% NaOH, H_2O, dried over anhydrous Na_2SO_4, and concentrated under vacuum. Distillation through a short column under high vacuum yielded 80–85% of the corresponding sulfide. Molecular weights of all sulfides, as determined by mass spectroscopy, agreed with calculated values. The deuterated sulfides contained a minimum of 96% deuterium as determined by both proton NMR and mass spectroscopy.

Rearrangement of Allyl-*3,3-d*$_2$ Phenyl Sulfide in the Presence of Diphenyl Disulfide (1 ⇌ 1a). The deuterated allyl phenyl sulfide (0.954 *m*) and diphenyl disulfide (0.071–0.972 *m*) were dissolved in *o*-dichlorobenzene, syringed into an NMR tube, degassed, and sealed under vacuum. The tubes were heated to 160 °C in an oil bath for various time intervals, quenched in cold water, and analyzed by NMR. The disappearance of the S–CH_2 absorption (δ 3.30) and the appearance of the C=CH_2 absorption (δ 4.90) were monitored, and integration of the corresponding peak areas enabled calculation of the concentration of 1 at any time *t*. Triplicate runs were made for each concentration of diphenyl disulfide.

Analysis of Crossed Product Compositions. In general, a solution of the sulfide and disulfide dissolved in equimolar concentrations in *o*-dichlorobenzene (1.0 M) was syringed into Pyrex tubes. These were completely degassed and sealed under high vacuum before immersion in a 160 °C thermostated bath for given lengths of time. The product composition was analyzed on a polar ⅛ in. × 12 ft DEGA column and also on a ⅛ in. × 10 ft SE-30 column (10% liquid phase on 80/100 mesh Chromosorb WAW at 160 °C). The products of reaction were identified mainly by analytical comparison with authentic samples after isolation, as well as by retention times on the gas chromatograph.

Reaction tried	Disulfide reagent	Hours at 160 °C
2 ⇌ 2a	Diphenyl	6
4 ⇌ 4a	Diphenyl	16
3 ⇌ 3a	Di-*p*-tolyl	6

Registry No.—1, 61614-40-2; 1a, 62698-33-3; PhSSPh, 882-33-7.

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Reactions of Aromatic Radical Anions.[1] 13. Contributing Factors for the Partitioning Reaction of Sodium Naphthalene with Phenylacetonitrile

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The products, stoichiometry, and lack of reversibility of the partitioning reaction of sodium naphthalene and phenylacetonitrile have been studied. While the reaction has both reduction and hydrogen transfer pathways the latter dominate. The kinetic and product deuterium effect confirm this and indicate that the nitrile is the sole source of hydrogen. Structure variation of the nitrile indicates that only when the nitrile is not enolizable is reduction complete or even the predominant reaction. Solvent changes bring about a moderate change in reduction leading to a dampened ion-pairing effect. A proposal involving the intermediacy of the phenylacetonitrile radical anion is discussed. Additionally from competition experiments an extended scale of relative reactivities of many diverse reactions has been constructed.

Aromatic radical anions have an intrinsic duality of nature, and perhaps not surprisingly exhibit complex chemical behavior.[3] One widely exploited reaction is the ability to transfer electrons to another substrate, thus functioning as reducing agents. Examples of this mode of reaction include the reaction with metal halides,[4a] alkyl[1a,b,3c,4b] and aryl halides,[4c] alkyl and aryl tosylates,[4d] oxygen,[4e] sulfur dioxide,[4f] hydrogen,[4g] and nitrogen.[4h] Radical anions can also react as nucleophiles, abstracting a proton from a suitable acid or adding in a nucleophilic manner to a reactive center. Examples of these reactions include the reactions with water,[5a] alcohols,[5b] ethylene oxide,[5c] and trimethylsilyl chloride.[5d] In addition to these two primary reactions, radical anions exhibit some radical reactions such as radical–radical coupling. This reaction has been observed as a secondary process in the reactions of naphthalene radical anion with alkyl halides where the initially formed alkyl radical couples with a radical anion to yield an alkyl dihydronaphthyl anion.[6] Additionally hydrogen atoms are thought to couple with the naphthalene radical anion to give the dihydronaphthyl anion.[7]

Table I. Reaction of Sodium Naphthalene with Phenylacetonitrile in THF at 25 °C

Compd	Product yield, % Mode of addition: Direct	Inverse
3a[a]	91.2	82.1
4[b]	48.1	52.9
5[b]	36.5	40.2
6[a]	4.2	2.6
7[a]	4.0	2.3
8[b]	1.8	1.8
9[b]	0.4	0.4
10[b]	8.1	0.0
11[a]	0	7.8

[a] Yields of products are based on initial concentration of phenylacetonitrile. [b] Yields of products are based on initial sodium naphthalene concentration.

In select cases both primary reactions are seen. Aromatic radical anions can react with a molecule containing electron-withdrawing functionalities with α hydrogens by competitive reduction and abstraction processes. Such a competition is reported for the reaction of aromatic radical anions with *N*-*p*-tolyl-*p*-toluenesulfonamide.[8] Similarly, the reaction of aromatic radical anions with α-(diethylamino)phenylacetonitrile results in competitive abstraction of the α hydrogen forming the anion,[9] and electron transfer resulting in decyanation and eventual formation of diethylbenzylamine.[9]

The factors affecting reaction path or partitioning have been in some cases identified, but in the main are largely undefined. Understanding and control of the bifunctional reactivity of radical anions, while useful in itself for synthetic purposes, bears on related questions concerning other bifunctional reagents, notably anions. Accordingly this study was undertaken with the purpose of identifying and defining those factors which contribute significantly to the determination of the relative importance of electron transfer and nucleophilic reaction pathways in the reaction of an aromatic radical anion with a substrate capable of reacting via both pathways.

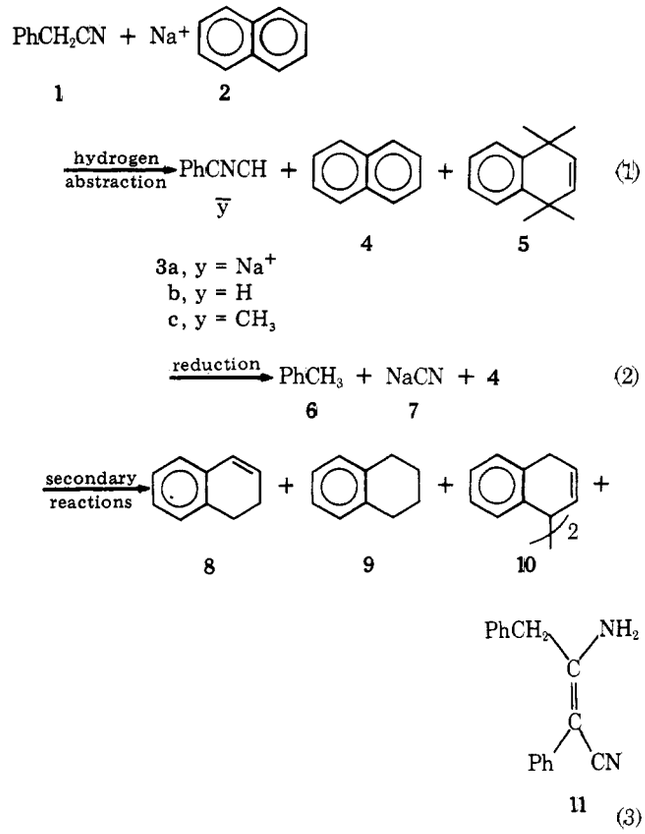
The compound selected for study is phenylacetonitrile. The hydrogens are known to be acidic with reported pK_a values of 20.8[10a] and 21.9.[10b] Additionally reductive decyanation should lead to resonance stabilized benzyl species. Moreover much is known about the corresponding halide and comparisons are facilitated. The subsequent sections of this paper describe experiments designed to probe the stoichiometry, material balance, reversibility, kinetic and product deuterium effect, competition with benzyl chloride, effect of reaction variables upon competition of hydrogen abstraction and reduction, and finally the effect of structural variations upon the nitrile.

Products

Stoichiometry and Material Balance. The reaction of phenylacetonitrile with sodium naphthalene in tetrahydrofuran (THF) yields (Scheme I and Table I) products derived from hydrogen abstraction and reduction as well as products of secondary reactions. Quenching the reaction mixture in H_2O led to **3b** and quenching in methyl iodide led to **3c**.

Product identification of compounds **4, 5, 6, 8,** and **9** was accomplished via gas chromatography retention times with authentic compounds. Additionally samples were trapped and analyzed by mass spectrometry. The phenylacetonitrile dimer (**11**) was shown to be identical with the authentic material prepared by an unambiguous synthesis[11] and shown spectroscopically to be β-amino-α,γ-diphenylcrotonitrile. The

Scheme I



structure of the naphthalene dimer (**10**) was not rigorously proved. Its identification rests upon the fact that it has the same gas chromatographic retention time as the known dimer produced when sodium naphthalene reacts with water.[12]

By quantitative gas chromatographic analysis of the reaction products employing an internal standard, 95 ± 7% of the initial naphthalene could be accounted for as recovered naphthalene, dihydronaphthalene, tetralin, and naphthalene dimer. Moreover 89 ± 6% of the initial phenylacetonitrile was accounted for as recovered phenylacetonitrile, toluene, and nitrile dimer. Material balances are thus acceptable and indicate that the major reactions are indeed being monitored. The mole ratio of the reactants required for complete reaction was determined with the use of internal standards in both the nitrile (**1**) and radical anion (**2**) solutions and titration to decolorization. The experimentally determined stoichiometry was found to be 1.0–1.1 which is close to the value of 1.0 required by Scheme I.

The absence of three possible products (phenethylamine, bibenzyl, and benzylated dihydronaphthalenes) was confirmed by adding small amounts of these materials to the reaction mixture and assaying their presence. Thus the analytical procedures would have detected 0.5% of these products had they been formed. These compounds are unreactive to the reaction conditions.

Reversibility. The potential reversibility of intermediate steps in product formation was demonstrated to be unimportant. For the product toluene, a likely intermediate is the phenylacetonitrile radical anion formed by electron transfer from sodium naphthalene (eq 4). That this electron transfer is not reversible was established by monitoring the yield of toluene as a function of added neutral naphthalene.

$$\text{Naph}^{-}\cdot + \text{PhCH}_2\text{CN} \rightarrow \text{Naph} + \text{PhCH}_2^{-}\cdot\text{CN} \quad (4)$$

Application of mass action to eq 4 predicts a decrease in electron transfer with increasing naphthalene. Addition of 100 mol % excess naphthalene to a solution 0.38 M in sodium

Table II. Isotopic Composition of Products of the Reaction of Sodium Naphthalene with Phenylacetonitrile-d_2

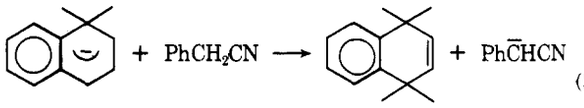
Compd	% d_0	% d_1	% d_2	% d_3
$PhCD_2CN$[a]	7.7	25.0	27.3	
$PhCH_3$	0.1	0.1	25.0	74.7
Dihydro	6.2	35.0	57.8	1.8

[a] Initial isotopic composition. The composition of the nitrile recovered after quenching the reaction mixture with saturated aqueous ammonium chloride was 97.5% d_0 and 2.5% d_1. Control experiments showed that phenylacetonitrile-d_2 underwent similar exchange under the workup conditions. There is substantial analogy for this observation.

naphthalene brought about an increase in the yield of toluene from 9 to 15%. A further doubling of the concentration of naphthalene led to a toluene yield of 17%. Whatever the reasons for the modest increase in yield of toluene may be, clearly toluene is not formed by a reversible electron transfer from naphthalene radical anion.

The reversibility of initial proton or hydrogen abstraction was probed by isolating naphthalene after reaction of sodium naphthalene with phenylacetonitrile-d_2. The recovered naphthalene was analyzed by high-resolution mass spectrometry and contained less than 0.5% deuterium. These results preclude reversibility of the initial proton or hydrogen transfer.

Finally, the reversibility shown in eq 5 of the dihydro-



(5)

naphthalene formation was investigated. Dihydronaphthalene exposed to a THF-d_8 solution of the phenylacetonitrile-d_1 anion (prepared by the reaction of sodium hydride with phenylacetonitrile-d_2) in an evacuated and sealed NMR tube exhibited no deuterium incorporation over a period of 5 h. Thus the phenylacetonitrile anion is insufficiently basic to remove a proton from dihydronaphthalene and hence the protonation of the dihydronaphthyl anion by phenylacetonitrile is irreversible.

Deuterium Isotope Effect. The deuterium isotope effect upon the competition between reduction and hydrogen abstraction and upon the products was examined. The reaction of sodium naphthalene with phenylacetonitrile-d_2 led to 11.1% toluene under conditions where the proton analogue gave 8.1%. Thus a small increase in the relative amount of reduction is observed. The kinetic isotope effect for the hydrogen abstraction is therefore small and can be estimated to be ~1.6 ± 0.3. This value is quite similar to the value of 1.4 ± 0.4 obtained for the reaction of sodium naphthalene with water.[13] (See Experimental Section, Table VIII, for calculations.)

The products of reaction of sodium naphthalene with phenylacetonitrile-d_2 were isolated and analyzed by mass spectrometry to determine the isotopic compositions. The results are presented in Table II. Examination of the table reveals several interesting observations. Recovered toluene is predominantly d_3 and recovered dihydronaphthalene is predominantly d_2. For this to be true, protonation of the intermediate benzyl-d_2 and dihydronaphthyl-d_1 anions must occur through reaction of the respective anions with phenylacetonitrile-d_2. If solvent molecules were providing protons the expected products would have been toluene-d_2 and/or dihydronaphthalene-d_1.

Competition Studies. Competition studies with a substrate which reacts exclusively via reduction with sodium naphthalene were performed. The reaction of benzyl chloride with sodium naphthalene in THF yields 83% bibenzyl, 12% toluene, and 5% benzylated dihydronaphthalene. Additionally there is ample evidence that this reaction proceeds via initial electron transfer.[14] When an equimolar mixture of benzyl chloride and phenylacetonitrile was reacted with a deficiency of sodium naphthalene the major product was bibenzyl and >90% of reaction involved benzyl chloride. Two facts emerge from these experiments. First, reaction of sodium naphthalene with benzyl chloride is considerably faster than reaction with phenylacetonitrile. Second, bibenzyl production is not affected by the presence of the acidic protons on phenylacetonitrile as it is when *tert*-butyl alcohol is present.[15]

Table III. Comparison of Reduction Determinations

Reaction	Temp, °C	Mode of addn	% redn Organic[a]	% redn Inorganic[b]
IV-15-3	25	Dir	10.1 ± 1.2	8.7
IV-15-4	25	Inv	7.0 ± 1.0	7.6
IV-15-5	0	Dir	9.7 ± 0.7	8.5
IV-31-10	0	Inv	8.1 ± 0.6	7.0
IV-31-22	−23	Dir	4.5 ± 0.4	5.0
IV-31-23	−23	Inv	6.6 ± 0.6	6.5

[a] Determined by the equation $2[PhCH_3]_{obsd}/[naph^{-}\cdot]_{initial}$, where $PhCH_3$ was analyzed by quantitative gas chromatography with internal standards and the factor of 2 is in analogy with the reduction of organic halides where 2 mol of radical anion is required to produce 1 mol of hydrocarbon. [b] Determined by the equation 2[NaCN]/([NaCN] + [NaOH]) where the concentrations of NaCN and NaOH were determined by titration (see Experimental Section) and the factor of 2 is in analogy with reductions of organic halides.

Table IV. Effect of Temperature and Mode of Addition on the Partitioning between Reduction and Hydrogen Abstraction

Mode of addn[a]	% redn 25 °C	% redn 0 °C	% redn −23 °C
Direct	8.9 ± 0.7	8.1 ± 0.5	2.9 ± 0.4
Inverse	5.5 ± 0.4	7.2 ± 0.8	8.6 ± 0.7

[a] Direct addition refers to addition of the nitrile to the radical anion and inverse addition refers to the addition of the radical anion to the nitrile solution.

Effect of Reaction Variables. Quantitative determination of the relative amounts of reduction and hydrogen abstraction in the reaction of sodium naphthalene with phenylacetonitrile utilized analyses of the products of reaction. Since toluene was shown to be the sole reduced organic product from phenylacetonitrile, the yield of toluene is simply related to the fraction of radical anion molecules that react via reduction. Moreover, since sodium cyanide is the sole inorganic product of reduction there should be a correspondence between the amount of reduction calculated by analysis of the inorganic products. Accordingly, Table III records the analyses calculated by the independent methods and reveals good agreement. In sum the competition between reduction and hydrogen abstraction can be conveniently and quantitatively assayed by monitoring the yields of toluene.

Initially attention was focused on the effect of temperature and mode of addition on the partitioning. These data are recorded in Table IV. The effects of temperature changes and mode of addition upon the competition are modest to nil. Accordingly the molecularity and activation energies of the processes giving rise to the two sets of products are similar. The possibility that they are in fact identical is precluded by the following solvent variation studies.

Table V. Effect of Solvent Variation on the Competition between Reduction and Proton Abstraction

Solvent system[a]	Ion pairing state[b]	% redn
THF-DEE	Tight[d]	6.4 ± 0.5
THF-THF	Tight[e]	8.8 ± 0.9
THF-DME	Mixture[e]	32.5 ± 2.0
THF-tetraglyme[c]	Glymated[f]	48.2 ± 3.2
THF-tetraglyme	Glymated[f]	19.6 ± 1.9
DME-DEE	Tight[d]	22.1 ± 1.2
DME-THF	Mixture[e]	36.0 ± 2.4
DME-DME	Loose[e]	44.5 ± 3.8
DME-tetraglyme[c]	Glymated[f]	47.8 ± 3.1
DME-tetraglyme	Glymated[f]	33.8 ± 2.7

[a] Radical anion (ca. 0.75 M) was prepared in the solvent listed first and diluted with an equal volume of the second solvent, unless otherwise noted. [b] States of iron pairing as listed were determined by others for dilute solutions, and are listed here as indicative of the strength of solvent-cation interactions. [c] Solutions were ca. 0.38 M in tetraglyme and 0.38 M in radical anion. [d] This solvent system provides tighter ion pairs than in pure THF or DME alone: N. Hirota, R. Carraway, and W. Schook, *J. Am. Chem. Soc.*, **90**, 3611 (1968). [e] P. Chang, R. U. Slates, and M. Szwarc, *J. Phys. Chem.*, **70**, 3180 (1966). [f] K. Hofelman, J. Jogur-Grodzinski, and M. Szwarc, *J. Am. Chem. Soc.*, **91**, 4645 (1969).

Table V records the effect of solvent variation on the competition reaction. Thus reduction can be varied from a minor process (~6%) to a major process (~50%) by solvent variation; however, we were unable to find conditions that would completely eliminate reduction or provide 100% reduction with this nitrile.

Structural Effects. The generality of the competition for other nitriles with acid hydrogens and the effect of nitrile structure were investigated by reacting a variety of nitrile compounds with sodium naphthalene in THF solution under comparable conditions. For those compounds recorded in Table VI, the sole reduced product was the hydrocarbon. There were no dimers, alkylated dihydronaphthalenes, or amines, and dihydronaphthalene accounted for the major portion of the hydrogen abstraction reaction. The reactions of *p*-chlorophenylacetonitrile and isobutyronitrile with sodium naphthalene led to complexities in the reaction mixtures which preclude analyses of the amounts of reduction occurring in these reactions. In the reaction with *p*-chlorophenylacetonitrile, the principal reaction was reduction of the carbon-chlorine bond. The major low-boiling product was phenylacetonitrile and a small amount of toluene. Additionally no *p*-chlorotoluene was formed and significant quantities of *p*-chlorophenylacetonitrile were recovered. Evidently hydrogen transfer still occurs, and since the reduction of the carbon-chlorine bond in chlorobenzene by sodium naphthalene in THF has a rate constant of 6.0×10^2 $[M]^{-1}$ s^{-1},[1a,16] an estimate of 10^2 $[M]^{-1}$ s^{-1} can be made for this reaction. The reaction of sodium naphthalene with isobutyronitrile is unusual as well. Addition of 1 equiv of the nitrile to the radical anion results in an intense red reaction mixture. Aqueous workup yields nearly equal quantities of 1,2- and 1,4-dihydronaphthalene and significant quantities of a naphthalene dimer. The yield of these products does not correspond to the theoretical yield for complete hydrogen transfer. Clearly there is hydrogen transfer, but important differences in products and yields from those observed with the other nitriles prevent meaningful comparison.

Discussion

While the effect of many of the reaction parameters can be rationalized by a competitive scheme with independent and precedented mechanisms, taken as a whole there is more evidence for a common genesis of the products. Critical among these factors are the absence of some expected products and the similarity of product yield with marked changes in reaction condition and structure.

Table VI. Effect of Nitrile Structure on the Competition between Reduction and Hydrogen Transfer

Registry no.	Nitrile	% redn[a]
140-29-4	$PhCH_2CN$	9
1823-91-2	$PhCH(CH_3)CN$	23
1195-98-8	$PhC(CH_3)_2CN$	100
86-29-3	Ph_2CHCN	48
2947-61-7	p-$MePhCH_2CN$	7
140-53-4	p-$ClPhCH_2CN$	*b*
78-82-0	$(CH_3)_2CHCN$	*b*

[a] Determined from the amount of reduced hydrocarbon toluene, ethylbenzene, cumene, etc., and a treatment similar to that in Table III. [b] Could not be determined; see text.

The products of the hydrogen transfer reaction of sodium naphthalene with phenylacetonitrile are unexceptional and bear strong similarity to the products of proton transfer with water[5a] and alcohols.[5b] This includes the small amounts of secondary products, 1,2-dihydronaphthalene, tetralin, and the naphthalene dimer. The fact that this dimer is found only when the radical anion is in excess is consistent with the proposed mechanism for dimer formation with small quantities of water. On the other hand, in spite of the product similarities, there are strong indications that the mechanism in this instance involves hydrogen atom transfer rather than proton transfer. Further discussion follows. The production of the phenylacetonitrile dimer when nitrile is in excess (inverse addition) is not unexpected considering the ability of α-cyano anions to add nucleophilically to the nitrile carbon of a second nitrile (Thorpe reaction).[11]

The reduction products merit some note. The absence of amine products contrasts with the reduction using sodium in ethanol.[17] The mechanism of both amine formation and reductive elimination of cyanide are thought to proceed via a nitrile radical anion.

$$RCN + \text{electron} \longrightarrow RCN^{-\cdot} \quad (6)$$

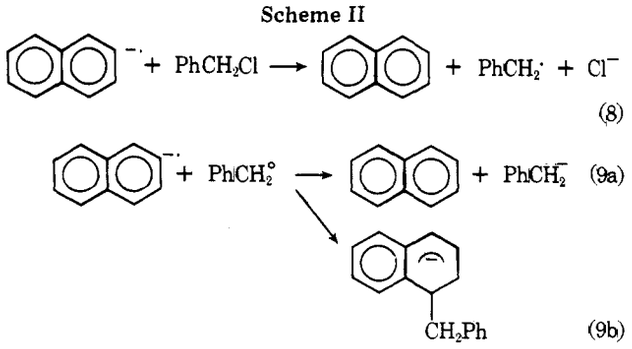
$$RCN^{-\cdot} \longrightarrow RCH_2NH_2 \quad (7a)$$

$$RCN^{-\cdot} \longrightarrow RH + NaCN \quad (7b)$$

However, proton transfer steps are required for reaction 7a and it is likely that in the absence of strong proton donors bond cleavage predominates.

The absence of benzylated dihydronaphthalenes and bibenzyl is more surprising, since the reaction of sodium naphthalene and benzyl chloride, known to be electron transfer, gives rise to significant quantities of bibenzyl and small amounts of benzyldihydronaphthalene. The mechanism for this reaction is considered to be that shown in Scheme II.

Scheme II



$$PhCH_2^- + PhCH_2Cl \longrightarrow PhCH_2CH_2Ph \quad (10)$$

$$PhCH_2^- + \text{proton source} \longrightarrow PhCH_3 \quad (11)$$

The absence of bibenzyl from the nitrile reaction could arise from the fact that the corresponding reaction with cyanides is much slower.

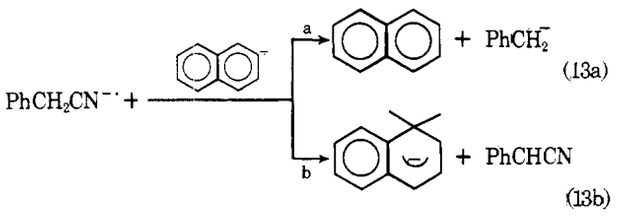
$$PhCH_2^- + PhCH_2CN \rightarrow PhCH_2CH_2Ph \quad (12)$$

However, since the product-determining step (eq 9) is leaving group independent, formation of benzylated dihydronaphthalene should be observed, unless the nitrile radical anion could react with sodium naphthalene to go directly to anion, thus bypassing the radical stage.

$$PhCH_2^-{\cdot}CN + Naph^-{\cdot} \rightarrow PhCH_2^- + \bar{C}N + Naph \quad (13a)$$

There is analogy from electrochemistry both for the existence of the radical anion of a nitrile and for subsequent reductive cleavage at higher potentials.[18] Therefore reduction of the nitrile radical anion would lead to the observed reduction products (eq 13a). Moreover, hydrogen abstraction from this species would lead to the remaining observed products (eq 13b, Scheme III), the nitrile radical anion thus being a com-

$$Naph^{-\cdot} + PhCH_2CN \longrightarrow Naph + PhCH_2CN^{-\cdot} \quad (4)$$



mon intermediate for both processes. While hydrogen atom abstraction is unusual, it has important analogy. The reaction is related to a known, rapid disproportionation reaction of neutral radicals. Radical–radical anion and radical anion–radical anion coupling reactions are similarly known to be fast reactions.[3c,19] Accordingly, it is reasonable that the radical anion–radical anion disproportionation by hydrogen atom transfer to give two resonance stabilized anions would be similarly rapid. Moreover, the electrochemical reduction of 4-nitrobenzyl cyanide gives rise to hydrogen gas and the α-cyano anion.[18b] Importantly Scheme III accommodates the following seemingly disparate findings.

As seen in Table I, the yield of $Ph\bar{C}HCN$ is far greater than that of $PhCH_3$. To have proton transfer products dominate over reduction products is surprising since activation energies for electron transfer are normally lower than those for proton transfer.[20] Additionally, the initial electron transfer appears to be irreversible, and therefore exothermic, as evidenced by the effect of added neutral naphthalene. Accordingly it is more likely that there is a rapid electron transfer in line with the favorable thermodynamics followed by competing steps. The similar temperature dependencies and molecularities of the processes agree with this scheme. Moreover, the dampened effect of ion pairing is understood better accordingly. The importance of solvation and ion pairing in radical anion chemistry is well documented.[21] Of particular importance to the current study, contrasting reactivities have been observed for electron transfer[22] and proton transfer with sodium naphthalene.[23] Interestingly, in each case the range of the effect is approximately two orders of magnitude. It is clear from Table V that the trend of product distribution with solvent variation is in the direction anticipated by kinetic studies of ion-pairing effect. Thus solvent systems that favor loosening of ion pairs give rise to more reduction. Nevertheless the magnitude of the effect is significantly dampened. The opposing order of reactivities from kinetic studies lead to an expected rate difference of 10^4 between electron transfer and proton transfer at the extremes of ion-pairing states used in this study. The observed difference of ~8 is sufficiently low to raise serious concerns. In contrast the common intermediate in Scheme III more easily accommodates these results.

Additionally, the effect of nitrile structure (Table VI) upon the competition between reduction and hydrogen transfer is not easily compatible with independent mechanisms. For example, replacement of the α hydrogen by a methyl group as in α-phenylethylnitrile leads to an essentially statistical increase in reduction product. This is surprising since methyl substitution should stabilize the radical and destabilize the anion. Even more dramatically perhaps, replacement of a hydrogen by a phenyl group brings about an increase in reduced product by a factor of ~2.7 (statistically corrected) in spite of the large differences in the stability of any decyanated fragments. Also, reaction with isobutyronitrile leads to substantial quantities of dihydronaphthalene. Clearly the preference for hydrogen removal is dominant, and only when the nitrile is not enolizable is there complete or even predominant reduction. Finally, the effect of aromatic radical anion structure is supportive of the proposed scheme. The reaction of nitriles with sodium naphthalene bears only some similarity with the reaction of lithium anthracene and nitriles.[24] While hydrogen abstraction dominates for both reactions when there are α hydrogens, the reduction products differ considerably. For sodium naphthalene the exclusive electron transfer product is the reduced hydrocarbon, whereas for sodium anthracene, the alkylated product predominates. This difference is readily explained by the one-electron reduction with sodium anthracene leading to radical, and the proposed two-electron reduction with sodium naphthalene leading to anion.

In another context, considerable information can be extracted from the competition reaction with benzyl chloride and phenylacetonitrile for sodium naphthalene. One goal of this competition reaction was to compare the reduction reactivity of phenylacetonitrile with a documented electron transfer reaction. In this regard reduction of the nitrile is orders of magnitude slower than of the halide.

Several other competitive steps are revealing. Lee has found that addition of t-BuOH to benzyl chloride followed by reaction with sodium naphthalene leads to complete formation of toluene at the expense of bibenzyl.[16] Thus one can write the following steps and consider the relative rates.

$$Naph^-{\cdot} + PhCH_2Cl \rightarrow PhCH_2{\cdot} + Naph + Cl^- \quad (8)$$

$$Naph^-{\cdot} + PhCH_2{\cdot} \rightarrow PhCH_2^- + Naph \quad (9a)$$

$$PhCH_2^- + PhCH_2Cl \rightarrow PhCH_2CH_2Ph + Cl^- \quad (10)$$

$$PhCH_2^- + t\text{-BuOH} \rightarrow PhCH_3 + t\text{-BuO}^- \quad (14)$$

$$Naph^-{\cdot} + t\text{-BuOH} \rightarrow Naph\,H{\cdot} + t\text{-BuO}^- \quad (15)$$

To account for the effect of t-BuOH the rate of 14 must be greater than that of 10. Moreover to account for the products the rates of 8, 10, and 15 must be comparable.

The fact that phenylacetonitrile has no effect upon the production of bibenzyl when benzyl chloride reacts with sodium naphthalene adds additional steps that can be sequenced.

$$2Naph^-{\cdot} + PhCH_2CN \rightarrow Naph\,H^- + Ph\bar{C}HCN + Naph \quad (16)$$

$$2Naph^-{\cdot} + PhCH_2CN \rightarrow 2Naph + PhCH_2^- + CN^- \quad (17)$$

$$PhCH_2^- + PhCH_2CN \rightarrow PhCH_3 + Ph\bar{C}HCN \quad (18)$$

Interestingly, reaction 18 must be much slower than reaction 14 and slower than 11, 13, and 15 in spite of the similar pK_a

Table VII. Relative Rates Estimated from Competition Experiments

	Fastest					Slowest
Reaction no.[a]	9a >	14	> 8 ≃ 10 ≃ 15 >	16	>[b]	18 > 17
Log estimated rate constant	8[c]	5[d]	4–3[e]	2[f]		1[g]

[a] For reactions see text. [b] This order is based on some dihydronaphthalene formation in the competition experiment. [c] Estimated from data of Garst et al.; see reference. [d] Estimated by complete interruption of reaction 10 when *t*-BuOH is present. [e] Estimated from the rates of reaction of halides with sodium naphthalene (ref 1a,b) and the relative rates of reaction of sodium naphthalene with halide and *t*-BuOH (ref 16). [f] Estimated from known rate of reaction of chlorobenzene with sodium naphthalene and products from reaction of *p*-chlorophenylacetonitriles with sodium naphthalene. [g] From competition experiments in this work.

values of *t*-BuOH and $PhCH_2CN$. The effect could be kinetic. In this regard there is considerable analogy in the disparity between rates of protonation and equilibria which have been adequately accounted for by the principle of least motion.[25]

The remaining reactions may be sequenced to obtain the data shown in Table VII. These relative rates provide a potentially useful scale of reactivities. Of particular note in this table is the conclusion that the nucleophilic displacement reaction of benzyl anion with benzyl chloride competes with the electron transfer reaction of sodium naphthalene with benzyl chloride.

Summary and Conclusions

In reactions of sodium naphthalene with nitriles containing α hydrogens the predominant reaction is hydrogen transfer. Reduction and decyanation can be increased to a moderate degree by changes in solvent. This dampened ion-pairing effect upon competitive products differs from the effect observed in known independently competing paths.[26] The phenylacetonitrile radical anion, a likely common intermediate, can account for the several observations. Additionally from competition experiments a scale of relative reactivity has been constructed, covering some 8 power of 10 and including such diverse reactions as electron transfer, anion trapping, proton transfer, hydrogen atom transfer, cleavage, and nucleophilic displacement reactions.

Experimental Section

General. Reactants were commercial products often redistilled, and purity was checked via GLC analysis. Phenylacetonitrile-d_2 was prepared by three exchanges between the nitrile in CCl_4 and NaOD in D_2O (Stohler Isotope Chemicals), and was distilled from calcium hydride (Alfa Inorganics) prior to use. α,α-Dimethylphenylacetonitrile was prepared by successive alkylations of phenylacetonitrile in THF solution by the addition of butyllithium followed by methyl iodide, and was purified by GC trapping prior to use. Chromatoquality solvents were distilled from sodium benzophenone ketyl prior to use.

Gas chromatographic analyses were performed on a Hewlett-Packard Model 5750 chromatograph employing flame ionization detectors. Mass spectra were recorded on a AEI MS-902 high-resolution mass spectrometer, NMR spectra were recorded on a Varian Associates Model A-60A NMR spectrometer, and infrared spectra were recorded on a Beckman Model IR-10 spectrometer. Titrations were performed with a Fisher Model 36 Titrimeter.

Typical Procedures. Preparation and Standardization of Radical Anion. Solutions of sodium naphthalene (0.5 M) were prepared by stirring freshly cut sodium metal (4.8 g, 0.20 mol) with 16.0 g (0.13 mol) of naphthalene and 3.7 g (0.03 mol) of *tert*-butylbenzene internal standard in 250 mL of freshly distilled THF in a modified organometallic storage buret for 10 h under a dry nitrogen atmosphere. Aliquots (2 mL) of the sodium naphthalene solution were run from the buret into oven-dried, nitrogen-filled, septum-capped 4-dram vials and quenched with saturated aqueous ammonium chloride (1 mL) by syringe injection. Hexane (1 mL) was added by syringe and the organic phases analyzed by gas chromatography on a 4 ft, 10% Carbowax 20M column operating on a temperature program between 90 and 160 °C for *tert*-butylbenzene, dihydronaphthalene, and naphthalene. The completeness of radical anion formation and the mole ratio of radical anion to internal standard were then determined.

Reactions of Sodium Naphthalene. Direct addition reactions of sodium naphthalene with the various substrates examined were performed by introducing a 3-mL sample of the radical anion solution from the buret into an oven-dried, nitrogen-filled, septum-capped 5-dram vial fitted with a glass-coated magnetic stirring bar, allowing the solution to equilibrate for ~10 min in a bath at the appropriate temperature, and adding dropwise from a syringe with stirring a solution of the appropriate reactant (~3 mL) until the initially dark green sodium naphthalene solution decolorized (~3 min). Saturated aqueous ammonium chloride (1 mL) and hexane (1 mL) were added and the organic phase was analyzed by gas chromatography on a 4 ft, 10% Carbowax 20M column operating between 90 and 160 °C for low-boiling products and on a 4 ft, 10% silicon rubber SE-30 or UCW-98 column operating between 90 and 270 °C for any high-boiling products.

Inverse addition reactions were performed by syringing the nitrile solution (3 mL) into the vial and adding the radical anion solution dropwise with stirring until the theoretical amount had been added and the green color of the radical anion persisted for a few seconds. Saturated aqueous ammonium chloride (1 mL) and hexane (1 mL) were added and the organic phase was analyzed by gas chromatography.

Solutions of sodium naphthalene in solvent pairs were prepared by adding concentrated (0.75 M) THF or DME solutions (3 mL) of the radical anion to the reaction vials and diluting with an equal volume of the appropriate cosolvent. Aliquots (1 mL) were removed by hypodermic syringe and injected into septum-capped vials containing saturated aqueous ammonium chloride (1 mL) and hexane (1 mL), and the organic phases were analyzed by gas chromatography. Reactions with phenylacetonitrile in solvent pairs were accomplished by adding the nitrile solution in the same solvent pair (prepared in an analogous manner) dropwise from a syringe to the stirred radical anion solution.

Reactions of sodium naphthalene with phenylacetonitrile in the presence of added neutral naphthalene or added sodium tetraphenylboron were performed in a manner analogous to the reactions in solvent pairs, except that weighed quantities of the addenda were placed in the reaction vials prior to the addition of the radical anion solution.

Methyl Iodide Quench. To 5 mL of a 0.5 M THF solution of sodium naphthalene in a dry, nitrogen-filled, septum-capped 5-dram vial fitted with a glass-coated magnetic stirring bar was added 5 mL of a 0.5 M THF solution of phenylacetonitrile over a period of 5 min. The resulting solution was taken up in a dry 10-mL syringe and added dropwise to a solution of 9.1 g (0.06 mol) of methyl iodide in 50 mL of dry THF in a 100-mL, two-necked, round-bottomed flask fitted with a glass-coated magnetic stirring bar and septum stoppers. After quenching with saturated aqueous ammonium chloride, the reaction mixture was analyzed by gas chromatography. Regenerated nitrile was found to be composed of 78% α-methylphenylacetonitrile, 19% α,α-dimethylphenylacetonitrile, and 3% phenylacetonitrile. A control experiment indicated that no methylation occurred when phenylacetonitrile and methyl iodide were exposed to aqueous sodium hydroxide. Thus methylation of the reaction mixture must have occurred prior to the workup conditions.

Material balance and stoichiometry were determined for direct and inverse addition reactions between (0.5 M THF solutions of) sodium naphthalene and phenylacetonitrile, carried out and quenched in the usual manner, except that prior to reaction a second internal standard was added to the nitrile solution. The resulting organic solutions were analyzed by gas chromatography as were the initial nitrile solution and the organic solution resulting from water quenching of the radical anion solution. Multiple GLC traces were recorded and Xeroxed two to three times each, and the relevant peaks were cut out and weighed. Area ratios were then corrected to mole ratios by dividing by the appropriate molar response factors.

Titrations. A reaction between (3 mL each of 0.5 M THF solutions of) sodium naphthalene and phenylacetonitrile was performed in the usual manner, but was quenched by the addition of 1 mL of water. Hexane (1 mL) was added, and the aqueous and organic phases separated. The organic phase was extracted with two 1-mL portions of

Table VIII. Relative Intensities in the Mass Spectra of Isotopically Labeled Reaction Products

Substance	Rel intensity[c]				
$PhCD_2CN$[a]	117	118	119		
	11.04	35.90	96.77		
$PhCH_2CN$[b]	100.00	2.60	0.00		
Naphthalene		128	129		
		100.00	0.00		
Dihydro	130	131	132	133	134
	16.12	63.48	103.03	39.75	3.59
Toluene	92	93	94	95	
	0.18	0.16	32.66	97.53	

[a] Initial composition. [b] Nitrile recovered after reaction. [c] Corrected for ^{13}C and ^{15}N contributions. Calculated isotope effect of 1.6 ± 0.3; K_H/K_D = (yield dihydro H/toluene H)/(yield dihydro D/yield toluene D).

water, and the aqueous phases were combined, diluted to 40 mL with distilled and degassed water, and titrated with 0.10 M hydrochloric acid employing a Fisher Titrimeter to continuously monitor the pH of the solution. A titration curve was constructed and compared with standard titration curves obtained from known prepared mixtures of sodium cyanide and sodium hydroxide.

Isotopic Studies. A reaction between (0.5 M THF solutions of) sodium naphthalene and phenylacetonitrile-d_2 was performed and worked up in the usual manner. The organic products of the reaction were collected by preparative gas chromatography and analyzed by mass spectrometry at low ionizing voltages for isotopic composition. Relative intensities of the relevant molecular ion peaks (corrected for ^{13}C and ^{15}N contributions) are recorded in Table VIII from which the isotopic compositions in Table II were determined.

Competition Reaction with Phenylacetonitrile and Benzyl Chloride. To a solution of 7.1 g (0.06 mol) of phenylacetonitrile and 7.6 g (0.06 mol) of benzyl chloride in 50 mL of dry THF contained in a 100-mL round-bottomed flask fitted with a glass-coated magnetic stirring bar and a septum stopper was added 25 mL of a 0.5 M THF solution of sodium naphthalene (0.01 mol) over a period of 9 min. The reaction mixture was quenched with saturated aqueous ammonium chloride (3 mL), and the organic phase was analyzed by gas chromatography. The major reaction product was found to be bibenzyl with less than 10% of the theoretical amount of dihydronaphthalene being produced, indicating that in excess of 90% of the sodium naphthalene reacted with benzyl chloride.

NMR Exchange. In a dry, nitrogen-filled, septum-capped, 5-mL, pear-shaped flask fitted with a glass-coated magnetic stirring bar were placed 0.07 g (3.07 mmol) of sodium hydride, ca. 0.2 g (ca. 1.7 mmol) of phenylacetonitrile-d_2, and 1.0 g of THF-d_8. The mixture was allowed to stir for 4 h after which the supernatant liquid was transferred by cannula tubing with nitrogen pressure to a dry, nitrogen-filled NMR tube containing 0.10 g (0.81 mmol) of naphthalene and 0.15 g (1.15 mmol) of dihydronaphthalene. The NMR tube was evacuated at liquid nitrogen temperature and sealed. Spectra were obtained over a period of 4 h which were invariant with time and showed no loss of dihydronaphthalene protons or loss of phenylacetonitrile deuterons. After 4 h a precipitate accumulated in the NMR tube and spectra could no longer be taken. On aqueous workup, the reaction mixture was found to have produced significant quantities of the material identified as the nitrile dimer.

Nitrile Dimer Formation. To a dry, nitrogen-filled, septum-capped, 5-dram vial fitted with a glass-coated magnetic stirring bar were added 0.44 g (3.77 mmol) of phenylacetonitrile, 2 mL of THF, and 1.2 mL (1.8 mmol) of butyllithium in hexane (1.5 M). The resulting solution was stirred for 20 h and quenched with aqueous ammonium chloride. Benzene (1 mL) was added, and the organic phase was analyzed by gas chromatography. In addition to unreacted phenylacetonitrile, one major reaction product was observed. The aqueous and organic phases were separated, and the organic phase was dried over anhydrous magnesium sulfate. The dried organic phase was placed on a high vacuum line and benzene and unreacted phenylacetonitrile were removed at the pump leaving a dark red-brown oil. This material exhibited a molecular ion in the mass spectrometer at m/e 234 indicating a dimer of phenylacetonitrile. The NMR spectrum of this material consisted of a singlet at δ 3.82, 2 protons (benzylic protons), a broad singlet at δ 4.75, 2 protons (amine protons), and a resonance at δ 7.29, 10 protons (aromatic protons); the infrared spectrum (solution in CCl_4) exhibited major absorbances at 3500, 3400, 3360, 3240, 3220, 3075, 3040, 2960, and 2200 cm^{-1} indicating the presence of both amino and cyano functionalities. The infrared spectrum is in agreement with that reported[11] for β-amino-α,γ-diphenylcrotononitrile (KBr pellet), the known product of base-catalyzed dimerization of phenylacetonitrile, and the mass spectral and NMR data further confirm the assignment of this structure to the product of this reaction.

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Registry No.—Phenylacetonitrile-d_2, 935-66-0; sodium naphthalene, 3481-12-7; benzyl chloride, 100-44-7; β-amino-α,γ-diphenylcrotononitrile, 18029-64-6.

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