Reactions of the Radical Anions and Dianions of Aromatic Hydrocarbons

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Contents

I. Definitions and Scope of the Review

An aromatic radical anion may be defined simply as the specie which results from chemical, electrolytic, or photolytic reduction of an aromatic molecule.

$$\mathrm{Ar} + e^- \longrightarrow \mathrm{Ar}\cdot^- \qquad (1)$$

The dot appearing in $\mathrm{Ar}\cdot^-$ indicates that the new specie possesses an odd number of electrons, thus a radical nature; the minus sign indicates the presence of a negative charge characteristic of an anion. The added electron occupies the lowest unoccupied π orbital of the parent hydrocarbon. Reduction to the dianion produces a diamagnetic specie with a pair of electrons in the same molecular orbital.

$$\mathrm{Ar}\cdot^- + e^- \longrightarrow \mathrm{Ar}^{2-} \qquad (2)$$

All polynuclear, alternant aromatic hydrocarbons will accept two electrons under favorable conditions.

A variety of nomenclature is in use for these ions. The IUPAC nomenclature is illustrated by the official name of dihydronaphthylide for the naphthalene radical anion.[1] The dianion is dihydronaphthalendi-ide. Apparently only the British use these names. The designations more commonly encountered for the radical anion of naphthalene are the naphthalene radical anion, naphthalenide, naphthalide, or naphthalene. In this review the terms naphthalenide and naphthalene radical anion (the names of preponderant usage) shall be used, and other radical anions shall be named correspondingly. The dinegative specie shall be referred to as the dianion of the particular hydrocarbon.

Recently a number of reviews of the literature of anionic hydrocarbons have appeared.[2-12] However, the emphasis of these articles has been on physical properties; there has been no prior attempt to emphasize in a comprehensive way the synthetic applications.

This review covers the reactions of alkali metal radical anions and dianions of anthracene, biphenyl, naphthalene, perylene, phenanthrene, pyrene, and tetracene. Emphasis will be primarily focused on the chemistry of anthracene, biphenyl, and naphthalene *radical anions*, upon which most of the reports concentrate. Insofar as data permit, correlations will be made of the observed reaction trends with the nature of the aromatic compound. This review includes the literature through December 1972. The abbreviations used in this review are listed in Table I.

II. Physical Properties

There is much which needs to be considered to portray accurately the nature of radical anions and dianions, but emphasis here is placed on summarizing the physical characteristics most important in chemical reactions.

Radical anions and dianions are known to undergo two general types of reactions. The aromatic nucleus may serve simply as a "storehouse" for one or two electrons. In the presence of a receptor, C, an electron is transferred to C, which then may undergo a variety of product-forming transformations depending on its nature.

$$\begin{tikzcd}[column sep=small] \mathrm{Ar}\cdot^-\ (\mathrm{Ar}^{2-}) + \mathrm{C} \arrow[r] & \mathrm{C}\cdot^- \arrow[d] & + \mathrm{Ar}\ (\mathrm{Ar}\cdot^-) \qquad (3) \\ & \mathrm{D} & \end{tikzcd}$$

Radical anions and dianions are also powerful bases capable of abstracting a proton from weakly acidic substances.

$$\mathrm{Ar}\cdot^-\ (\mathrm{Ar}^{2-}) + \mathrm{HB} \longrightarrow \mathrm{B}^- + \mathrm{Ar{-}H}\cdot\ (\mathrm{Ar{-}H}^-) \qquad (4)$$

Of the two established functions of radical anions and dianions, electron transfer is by far the most common process. This occurs even in systems which are favorable to proton abstraction. As one might expect, the various radical anions and dianions undergo each of these two reactions with differing propensities. The reactivity of these ions depends in large part on the ease with which

TABLE I

Hydrocarbon	Abbreviation	Other	Abbreviation
Anthracene	A	Tetrahydrofuran	THF
Biphenyl	B	Dimethoxyethane	DME
Naphthalene	N	Hexamethylphosphoramide	HMPA
Perylene	Pe		
Phenanthrene	Pha	Dimethylformamide	DMF
Pyrene	Py		
Tetracene	Te	Solvent	SH

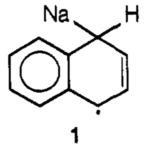
the negative ion is oxidized, which, in turn, is related to the electron affinity of the hydrocarbon.

A. Radical Anions

1. Historical Sketch

Formation of an aromatic radical anion was first recorded in 1867 when Berthelot described the appearance of a black addition product on fusing metallic potassium with naphthalene.[13] The first in-depth investigations were by Schlenk some years later.[14,15]

Early representation of the compounds formed from the addition of an alkali metal to aromatic hydrocarbons originated with Willstätter who visualized that the metal was bonded to the ring as shown for naphthalenide (**1**).[16]



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Use of this type of designation continued unquestioned until 1936 when it became evident the adduct was ionic rather than electrically neutral. Pertinent observations were that the adduct was formed in the more polar ether solvents such as dimethyl ether or tetrahydrofuran but not in diethyl ether or benzene,[17] and that solutions also conducted current.[18] Hückel and Bretschneider raised the first specific objection to Willstätter's formula, suggesting for the first time the idea that the adduct was formed *via* electron transfer.[19] Final verification of the radical anion nature of the adducts was made by Weissman and associates.[20,21]

2. Electron Affinity

The single characteristic most important in defining the reactivity of a radical anion is the ease with which the nucleus is reduced; one measure of this is given by the electron affinity in the gas phase. From Table II one may see that the difference in electron affinity between naphthalene and anthracene, two of the more commonly employed radical anions, is 0.40 eV with anthracene being the more easily reduced.

In solution the difference in electron affinity between any two compounds varies with the stabilization afforded by solvation. The degree of stabilization is not uniform and depends on the area of the radical anion; solvation is most important in those radical anions of rather small area but not as important in larger rings in which solvation becomes nearly constant.[6,22] Thus, in solution there is an increase in the difference between the electron affinities of small (*e.g.*, naphthalene) and large (*e.g.*, anthracene) molecules.

TABLE II. Electron Affinities[a]

Compound	Electron affinity, eV
Naphthalene	0.152 ± 0.016
Triphenylene	0.284 ± 0.020
Phenanthrene	0.308 ± 0.024
Chrysene	0.419 ± 0.036
Benzo[*e*]pyrene	0.486 ± 0.155
Picene	0.490 ± 0.110
Benzo[*c*]phenanthrene	0.542 ± 0.040
Anthracene	0.552 ± 0.061
Pyrene	0.579 ± 0.064
Dibenz[*a,h*]anthracene	0.676 ± 0.122
Dibenz[*a,j*]anthracene	0.686 ± 0.155
Benzo[*a*]anthracene	0.696 ± 0.045
Benzo[*a*]pyrene	0.829 ± 0.121
Azulene	0.587 ± 0.065

[a] W. E. Wentworth, E. Chen, and J. E. Lovelock, *J. Phys. Chem.*, **70**, 445 (1966); R. S. Becker and E. Chen, *J. Chem. Phys.*, **45**, 2403 (1966).

TABLE III. Potentiometric Titration with Biphenyl-Biphenylide

Aromatic hydrocarbon	Potential, V
Biphenyl	(0.0)
Naphthalene	0.043 ± 0.02
Triphenylene	0.132 ± 0.01
Phenanthrene	0.142 ± 0.01
Benzo[*c*]pyrene	0.484 ± 0.02
Pyrene	0.529 ± 0.01
Benzo[*e*]anthracene	0.590 ± 0.02
9,10-Dimethylanthracene	0.616 ± 0.01
Anthracene	0.642 ± 0.01
Benzo[*a*]pyrene	0.760 ± 0.02
Acenaphthylene	0.880 ± 0.03
Fluoranthrene	0.820 ± 0.02
Perylene	0.965 ± 0.01
Naphthacene	1.058 ± 0.02

3. Potentiometric and Polarographic Reduction

Another method of determining electron affinity was pioneered by Hoijtink and his associates.[23] Essentially the method involves potentiometric titration of aromatic compounds with a standard solution of biphenyl and biphenylide (biphenyl has a high reduction potential). One electrode was in the biphenyl-biphenylide solution, the other in the aromatic hydrocarbon to be reduced. The potential difference was measured as the biphenyl-biphenylide solution was added. Improvements in this technique were made by Slates and Szwarc;[24] their data are presented in Table III.

One further measure of the ease with which an aromatic nucleus will accept an electron is polarographic reduction. The $e_{1/2}$ values are frequently determined in a mixed aqueous solvent such as 75% aqueous dioxane. In a protic medium the radical anion, which is formed by rapid electron transfer, is protonated at a rate about 1000 times slower than electron transfer, so the polarographic value is a valid measure of the standard reduction potential. If the hydrocarbon accepts another electron the dianion is formed and a second wave is evident. The dianion is a much better base than the radical anion and is protonated at a rate comparable to its generation and therefore does not provide a standard value. For molecules accepting additional electrons (*e.g.*, crysene) the waves are often not clearly defined, and thus it is difficult to measure individual potentials.

Correlation of the half-wave potential and the energy of the lowest vacant molecular orbital as calculated by the simple Hükel method is fairly good. This is shown in Table IV[25,26] and Figure 1.

TABLE IV. Half-Wave Reduction Potential for Hydrocarbons and Energies of Lowest Vacant MO's[25,26]

No. in Fig 1	Hydrocarbon	$-m_{n+1}$[a]	$-e_{1/2}$ vs. sce[b]	$-e_{1/2}$[c]	$-e_{1/2}$[d,e]
1	Biphenyl	0.705	2.70		2.70
2	Naphthalene	0.618	2.50	2.60	2.63
3	Phenanthrene	0.605	2.46		
4	Pyrene	0.445	2.12	2.10	2.19 2.64
5	Anthracene	0.414	1.96	1.98	2.07 2.52
6	Perylene	0.347	1.67	1.43	1.73 2.21 2.70
7	Tetracene	0.295	1.58	1.58	

[a] $\alpha + m_{n+1}\beta$ is the energy of the lowest vacant orbital in units of standard β. [b] In 75% dioxane-water. [c] In 96% dioxane-water. [d] In acetonitrile. [e] T. A. Gough and M. E. Peover, "Polarography 1964," Proceedings of the Third International Congress, Southhampton, G. J. Hills, Ed., Vol. 2, Macmillan, New York, N. Y., p 1017. Reduction potentials determined by cyclic polarography in acetonitrile containing tetraethylammonium perchlorate and *vs.* sce. The second values refer to two-electron reduction.

It is seen from these results that some radical anions, such as biphenylide and naphthalenide, are almost as powerful reducing agents as the alkali metals themselves. Other radical anions (*e.g.*, anthracenide) possess appreciably less reducing strength. These potentials may be compared to those of other compounds listed in Table V. The potentials listed in this table will prove helpful in qualitatively interpreting a number of reactions. It is unfortunate that a comprehensive compilation of potentials is not available for solvent systems commonly used in radical anion reactions.

4. Structure and Solvation of Ion Pairs

The equilibrium constant for the reaction of an alkali metal with an aromatic hydrocarbon

$$M + Ar \rightleftharpoons Ar^{\cdot -}, M^{+} \tag{5}$$

depends upon the nature of the metal, the hydrocarbon, the solvent, and the temperature. These same factors also determine whether the cation–radical anion interaction will be as solvent-separated ("free") ions, solvent-separated (loose) ion pairs, contact (tight) ion pairs, or associated as larger aggregates.

Much of our understanding of the equilibria between alkali metals and aromatic hydrocarbons in ethereal solvents is attributable to Shatenshtein and associates.[27-29] The equilibrium constant for the electron-transfer reaction from alkali metal to aromatic hydrocarbon is often too large to permit quantitative studies. However, with naphthalene and particularly biphenyl the reduction potentials are sufficiently high that under proper conditions conversion to radical anions is only partial. Some of Shatenshtein's results are shown in Tables VI and VII. These tables show that steric factors in the coordinating solvent are more important than differences in basicity. The highest yield of radical anions is obtained for ethylene glycol ethers because of the ability of these solvents to form comparatively stable five-membered chelate rings. The influence of the identity of the metal on the equilibrium may be summarized by indicating that the highest equilibrium constant in a particular solvent is usually obtained for the smallest cation because of the higher heat of solvation ($Li^{+} > Na^{+} > K^{+} > Cs^{+}$).

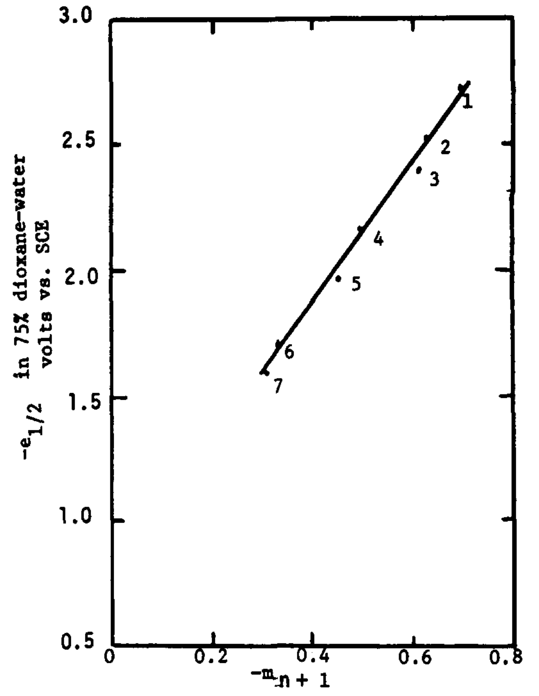


Figure 1. Half-wave potentials of aromatic molecules in 75% dioxane-water *vs.* energies of the lowest vacant orbitals.

As indicated previously, the type of ion pairing is dependent on the following factors: metal, hydrocarbon, temperature, and solvent. A number of techniques (epr, nmr, visible spectroscopy, and conductance measurements) all have proven valuable in determining the nature of the association between the cation and radical anion. For the most part, the conclusions drawn from one technique parallel those derived from others. For extensive discussions of the results of conductance and visible spectroscopy studies, the reader should consult especially ref 6. For thorough discussion of epr and nmr results, see ref 12, Chapters 5, 7, and 8. Only a very brief summarization of these discussions is given in this account.

The relationship between the identity of the alkali metal and the tendency to form *ion pairs* is highly dependent upon the solvent and anion. In situations where all the cations form contact ion pairs, lithium binds most strongly with the anions. But there are other cases, which are not uncommon, where Li^{+} compounds are solvent-separated ion pairs while their Na^{+}, K^{+}, or Cs^{+} counterparts form contact ion pairs.

Ion pairing is favored in the smaller hydrocarbons.[6] The charge is more concentrated, and therefore the interaction with the counterion becomes more important.[30] Hence there is a greater tendency for ion pairing in naphthalenide than there is for anthracenide or perylenide. This is demonstrated by Figure 2, which shows the dissociation constants of the sodium salts of naphthalene, biphenyl, anthracene, and perylene in THF over a range of temperature.

$$(Ar^{\cdot -},Na^{+})_{\text{ion pair}} \rightleftharpoons Ar^{\cdot -} + Na^{+} \quad K_D \tag{6}$$

The sodium salts of naphthalene, biphenyl, anthracene, and perylene have nearly identical dissociation constants at −70° in THF. As the temperature increases ion-pairing becomes more extensive; this reflects the observation that all of these dissociation processes are exothermic: sodium biphenylide (Table VIII) is more exothermic (7.3 kcal/mol at 20° in THF) than is sodium perylenide (2.2 kcal/mol). The smaller radical anions show greater attraction for the counterion than larger anions, so the sodium cation is more extensively solvated in the presence

TABLE V. Polarographic Reduction Values

Compound	$-e_{1/2}$	Solvent	Electrode	Ref
Styrene	2.35	0.175 *M* Bu_4NI 75% aq dioxane	Sce	*a*, p 648
Stilbene	2.26	0.175 *M* Bu_4NI 75% aq dioxane	Sce	*a*, p 648
Diphenylacetylene	2.20	0.175 *M* Bu_4NI 75% aq dioxane	Sce	*a*, p 648
Butadiene	2.59	Me_4NBr Dioxane	Sce	*b*, p 750
Acetaldehyde	1.87	Aq Me_4NOH	Sce	*a*, p 656
Propionaldehyde	1.92	Aq Me_4NOH	Sce	
n-Butyraldehyde	1.90	Aq Me_4NOH	Sce	
n-Valeraldehyde	1.91	Aq Me_4NOH	Sce	
Methyl ethyl ketone	2.25	Aq Me_4NI	Sce	*a*, p 661
Cyclohexanone	2.45	Et_4NI–75% aq dioxane	Sce	
Benzaldehyde	1.48	pH 11.3	Sce	*a*, p 679
p-Methoxybenzaldehyde	1.60	pH 11.98	Sce	
p-Chlorobenzaldehyde	1.18	Aq NH_4Cl	Nce	*a*, p 681
Cinnamaldehyde	0.78	Aq NH_4Cl	Nce	*a*, p 681
Benzophenone	1.42	pH 11.3		*a*, p 683
Bromobenzene	2.32	Et_4NBr 75% aq dioxane	Sce	*a*, p 648
Iodobenzene	1.62	Et_4NBr 75% aq dioxane	Sce	*a*, p 648
Benzyl chloride	1.94	Et_4NBr 75% aq dioxane	Sce	*a*, p 648
n-Butyl bromide	2.27	Et_4NBr 75% aq dioxane	Sce	*a*, p 648
n-Octyl bromide	2.38	Et_4NBr 75% aq dioxane	Sce	*a*, p 648
1,1-Dibromoethane	1.62	Et_4NBr 75% aq dioxane	Sce	*a*, p 648
1,2-Dibromoethane	1.52	Et_4NBr 75% aq dioxane	Sce	*a*, p 648
1,2-Dichloroethane	No wave	Et_4NBr 75% aq dioxane	Sce	*a*, p 648
Vinyl bromide	2.47	Et_4NBr 75% aq dioxane	Sce	*a*, p 648
Allyl chloride	1.91	Et_4NBr 75% aq dioxane	Sce	*a*, p 648
Methyl chloride	2.33	Me_4NBr in dioxane	Nce	*b*, p 747
Methylene chloride	2.33	Me_4NBr in dioxane	Nce	*b*, p 747
Chloroform	1.67	Me_4NBr in dioxane	Nce	*b*, p 747
Carbon tetrachloride	0.78	Me_4NBr in dioxane	Nce	*b*, p 747
Diphenyl disulfide	0.65	$(n\text{-}Bu)_4NOH$ in MeOH and i-PrOH	Sce	*c*, p 690
Diphenyl sulfone	2.04	Me_4NBr in aq EtOH	Sce	*c*, p 690
Diphenyl sulfoxide	2.07	Me_4NBr in aq EtOH	Sce	*c*, p 690
Fumaric acid diethyl ester	0.48	McIlvaine buffers in 4% EtOH	Sce	*c*, p 694
n-Hexyl hydroperoxide	0.12	LiCl in benzene–MeOH	Sce	*c*, p 695

[a] I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. II, 2nd ed, Interscience, New York, N. Y., 1952. [b] M. Brezina and P. Zuman, "Polarography in Medicine, Biochemistry, and Pharmacy," Interscience, New York, N. Y., 1958. [c] L. Meites, "Polarographic Techniques," 2nd ed, Interscience, New York, N. Y., 1965.

of the large perylenide anion and therefore dissociation is less exothermic.

The effect of solvent can be summarized as follows: free ions are preponderant only in highly polar solvents (HMPA), in DME loose ion pairs are most typical, and in solvents of low polarity and coordinating ability (THF, dioxane) contact ion pairs are most likely. It can be seen (Table VIII) that the dissociation constants of the sodium salts of radical anions are virtually independent of the anion if the pair is solvent-separated.[31] This is illustrated by data in DME and at low temperature in THF; the heat of dissociation of such pairs is low, *viz.*, between 0 and −2 kcal/mol. The entropy change, largely attributable to solvation of the free ions, is also largely independent of anion; free anions are not extensively solvated and little solvent reorganization is expected in the transition state.[31] THF does not coordinate well with the cation, so the degree of solvation is more dependent on the strength of the cation–anion attraction. When this attraction is weak, as with perylenide, cation solvation is sufficient for the formation of solvent-separated ion pairs. This is reflected in the small entropy change upon dissociation. On the other hand, when biphenylide is the anion, the attraction is more powerful and the cation is not extensively solvated; a contact ion pair is formed. Dissociation and solvation result in a large entropy change.

TABLE VI. Equilibrium Constant $K = [B\cdot^-,Na^+]/[B]$ for the Reaction Sodium + Biphenyl(sol) $\rightleftarrows$ $B\cdot^-,Na^+(sol)$[a,b]

T, °C	MME	1,2-DMPr	THF	MeTHF[c]	DEE	THP	1,3-DMPr
40	0.12	0.09	0.10				
30	0.28	0.20	0.20				
20	0.75	0.49	0.36	0.02	0.07		
10	2.55	1.40	0.66	0.036	0.11		
0	7.0	5.0	1.50	0.055	0.19	0.06	
−10			2.90	0.11	0.39	0.10	0.12
−20				0.20	1.25	0.17	0.34
−30				0.45	8.7	0.29	1.20
−40				1.18		0.48	

[a] MME = 1-methoxy-2-ethoxyethane; 1,2DMPr = 1,2-dimethoxypropane; THF = tetrahydrofuran; MeTHF = 2-methyltetrahydrofuran; DEE = 1,2-diethoxyethane; THP = tetrahydropyran; 1,3DMPr = 1,3-dimethoxypropane. [b] Data taken from A. I. Shatenshtein, E. S. Petrov, and M. I. Belousova, *Org. Reactiv. (USSR)*, **1**, 191 (1964). [c] Taken from ref 24.

TABLE VII. Effect of Solvent Structure on the Equilibria Na + Biphenyl $\rightleftarrows$ $Na^-,B\cdot^-$ and Na + Naphthalene $\rightleftarrows$ $Na^-,N\cdot^-$

Solvent[a]	$[Na^+,B\cdot^-]/[B]_0$	$[Na^+,N\cdot^-]/[N]_0$
CH_3OCH_3	0.02	0.2
$C_2H_5OC_2H_5$	0.01	0.02
$CH_3OC_2H_4OCH_3$	1.0	1.0
$CH_3OC_2H_4OC_2H_5$	0.6	1.0
$CH_3OC_2H_4OC_3H_7$	0.22	0.85
$C_4H_9OC_2H_4OC_4H_9$	0.1	0.2
$CH_3OCH_2OCH_3$	0	0
$CH_3O(CH_2)_2OCH_3$	1.0	1.0
$CH_3O(CH_2)_3OCH_3$	0.06	0.5
$CH_3O(CH_2)_4OCH_3$	0.03	0.2
$CH_3O(CH_2)_5OCH_3$	...	0.05

[a] Data taken from ref 28.

TABLE VIII. Dissociation Constants and Heats of Dissociation of Sodium Salts of Aromatic Radical Anions[6]

	$B\cdot^-$	$N\cdot^-$[a]	$A\cdot^-$[a]	$Pe\cdot^-$
	In DME			
10^6K_{diss} (25°)	4.6			6.0
10^6K_{diss} (−55°)	17.0			18.8
ΔH (20°), kcal/mol	−2.1			−2.5
ΔS (20°), eu	−31.5			−32.5
ΔH (−55°), kcal/mol	0.0			0.0
ΔS (−55°), eu	−22.0			−21.0
	In THF			
10^6K_{diss} (25°)	0.98	0.14	4.3	15.5
10^6K_{diss} (−55°)	24.5	13.1	28.7	28.5
ΔH (15°), kcal/mol	−7.3	−8.2	−6.1	−2.2
ΔS (15°), eu	−52	−58	−45	−29
ΔH (−65°), kcal/mol	−1.6	−1.8	0.0	0.0
ΔS (−65°), eu	−28	−30	−21	−21

[a] D. Nicholls, C. Sutphen, and M. Szwarc, *J. Phys. Chem.*, **72**, 1021 (1968).

An example of the relationship between solvent and temperature is illustrated by the observation that above −30°, $B\cdot^-,Na^+$ and $N\cdot^-,Na^+$ exist as contact ion pairs in DME;[32] at lower temperatures the loose pairs are detected. As previously stated, THF is less prone to form loose ion pairs than DME, but at −70° the process is sufficiently favorable that K_N = 4.5 for sodium naphthalenide.[32]

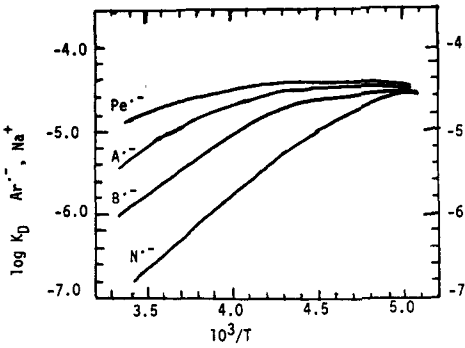


Figure 2. Dissociation constants, K_D, of ion pairs of sodium salts of aromatic radical anions at various temperature (range +25 down to −70°).

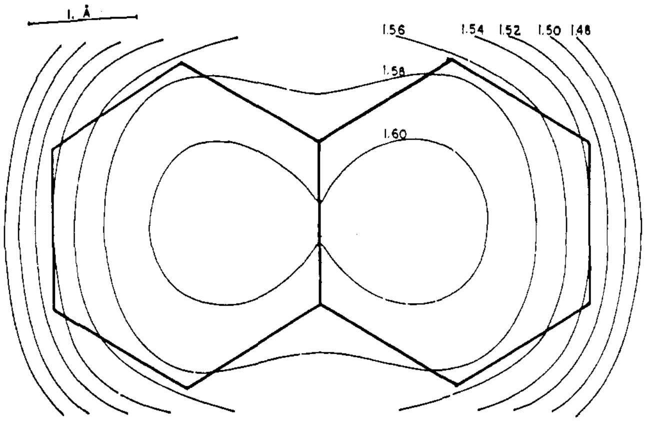


Figure 3. Electrostatic attraction between a positive point charge and naphthalenide where the positive charge is 3 Å above the nuclear plane. Energy in units of β.

$$(N\cdot^-,Na^+)_{tight} \rightleftarrows (N\cdot^-,Na^+)_{loose} \quad K_N \qquad (7)$$

The importance of solvation was further emphasized by the discovery that there is more than one form of a contact ion pair. Hirota found two forms of tight ion pairs for sodium naphthalenide and anthracenide, differing in the degree of solvation.[33]

Ion pairing is an important, though not well-defined, part of the reactions of radical anions. Later discussion will show that some reactions proceed more rapidly as free ions than as ion pairs, yet there are other examples in which the converse is true. Also, the course of reactions has been demonstrated to be dependent upon the state of aggregation. This is particularly the case in reactions forming dianions and in polymerization.

The position of the counterion in the ion pair has been calculated by Bolton.[34] For naphthalenide and anthracenide the sodium ion is positioned approximately 3 Å above the nuclear plane, depending on whether the ion pair is tight or loose. In naphthalenide the cation does not appear to be fixed over one ring but rather oscillates back and forth. In anthracenide the cation is largely confined to positions over the central ring. Figure 3 shows the distribution of calculated electrostatic attraction between naphthalenide and the sodium cation. Figures 4 and 5 also specify cation position by considering unpaired spin density. The electrostatic model shown in Figure 3 does not indicate the cation to be as much over the C_2–C_3 position as does the epr map. The electrostatic model does not appear to predict correctly the cation position because it does not consider the bonding between the radical anion molecular orbitals and the lithium p orbital.[35]

Additional types of interactions can be easily imagined. A sandwich interaction between a hydrocarbon and its

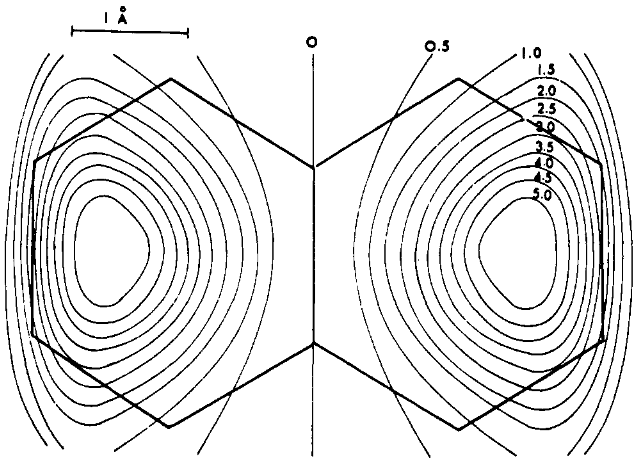


Figure 4. Calculated unpaired electron density on a sodium ion in an ion pair with naphthalenide. Sodium is 3 Å above the nuclear plane. Unpaired electron density is in units of 10^{-3}.

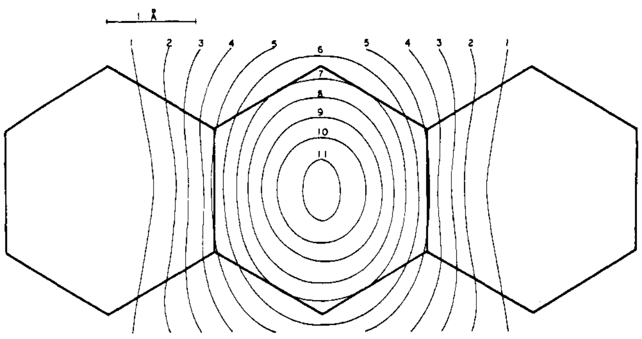


Figure 5. Calculated unpaired electron density on a sodium ion in an ion pair with anthracenide. Sodium is 3 Å above the nuclear plane.

radical anion is one of these. This has been observed between the (neutral) molecule and radical anion for both naphthalene[36] and anthracene.[37]

5. Visible Spectra

One of the techniques used in following the disappearance of the radical anion during the course of a reaction monitors light absorption. The wavelengths of the major absorptions observed in a variety of aromatic hydrocarbon radical anions are given in Table IX. These values, of course, may vary slightly depending on the conditions of the reaction.

TABLE IX. Visible Absorption Spectra (mμ) of Aromatic Hydrocarbon Radical Anions

Hydrocarbon anion	38	39	40	41
Biphenyl·$^-$	407	405	402	
	610	617		
	648	637		
Naphthalene·$^-$	368	366	366	369
	437	437	433	437
	466	465	463	
	775	735		735
Phenanthrene·$^-$	383	395	379	392
	421	415	415	417
	452	444	446	444
	665	654	637	649
Anthracene·$^-$	364[a]	369		
	400[a]	401	403	400
	510			513
	548	549	546	546
	595	599	595	595
	638		637	
	656	662	654	662
	693		694	
	725	714	725	719
Pyrene·$^-$	365	366	364	
	385	385	383	385
	450	455	450	455
	496	493	490	493
	742	719	735	730

[a] Parent molecules have absorptions in the same region.

B. Dianion Formation

Metal salts of the dianions can be prepared for all of the hydrocarbons which we have considered. Of the three most commonly employed hydrocarbons, anthracene, having the lowest reduction potentials, most easily forms the dianion. The lithium, sodium, potassium, and rubidium compounds have been prepared.[42] Biphenyl forms the dianion with lithium,[43] sodium,[44] and potassium.[45,46] The lithium salt is most stable, a consequence of its binding strength. The potassium salt decomposes in DME so that after 4 hr (apparently at room temperature) 90% of the initial concentration is destroyed.[45]

Formation of the dianion of naphthalene was first reported by Shatenshtein, *et al.*, Buschow and Hoijtink, and later by Smid.[47] Only the dilithium salt has been prepared in appreciable concentration.[48] Contacting potassium naphthalenide with metallic potassium in DME is reported to yield 1,4-dihydronaphthalene;[49] presumably naphthalenide is reduced by potassium to the dianion which is then protonated by DME. An explanation of why biphenyl forms the dianion with more alkali metals than naphthalene is not known, but this undoubtedly has its origin in the strength of the metal–dianion interaction. From X-ray studies on the crystalline complex, bis(tetramethylenediamine)lithium naphthalene dianion, it is known the dianion is situated between the cations with one cation positioned over one ring and the remaining cation positioned under the other ring.[35] The dianion is not planar with four atoms 0.15 Å off the mean plane of the group.[35]

A characteristic of the radical anions which must be evaluated when one is interpreting the results of a reaction is the tendency of many radical anions to disproportionate. Hence, a "radical anion" solution may contain dianion

$$2Ar^{\cdot -},M^+ \rightleftharpoons Ar^{2-},2M^+ + Ar \qquad (8)$$

which could account for a significant portion of the chemical activity. All of the hydrocarbons which are the subject of this review do form dianions under favorable conditions, so their presence in radical anion solutions and their effects upon ensuing reactions must be evaluated. Even in situations where the dianion is not formed in detectable concentrations, there may be present tiny quantities of the dianion in equilibrium with the radical anion. In principle, reactions of even these solutions may proceed, in part, through the dianion.

The most complete study of disproportionation is on tetraphenylethylene (T).[6] Studies on the disproportionation equilibria of alkali metal aromatic dianions such as dilithium, disodium, and dipotassium biphenyl and dilithium naphthalene have either not been performed or have received only cursory attention.

Szwarc and associates have recently elucidated the mechanism of electron transfer in the tetraphenylethylene disproportionation.[49a] Electron transfer occurs most rapidly from the free radical anion to the ion pair.

TABLE X. Calculated Spin Density Distribution in the Naphthalene Radical Anion by Various Authors and Methods[a]

Method position	Exptl values[66]	HMO[67]	McLachlan procedure[68]	SCF MO[69]	SCF MO with CI[69]	Open-shell SCF MO CI[70]	VB[71]	USCF MO[72]	Spin-extended SCF MO[73]	1/2 electron SCF MO[74]
1	0.185	0.181	0.222	0.191	0.243	0.223	0.196	0.262	0.252	0.185
2	0.069	0.069	0.047	0.059	0.036	0.047	0.066	0.026	0.027	0.065
9	0.000	0.000	−0.037	0.000	−0.056	−0.040	−0.024	−0.076	−0.059	0.000

[a] Considering the values arrived at in ref 66–74.

$$T^{\cdot -} + T^{\cdot -},Na^+ \rightleftharpoons T + T^{2-},Na^+ \quad (9)$$

The process indicated by eq 10 is slightly slower, and that by eq 11 is too slow to contribute significantly to the disproportionation process.

$$2T^{\cdot -},Na^+ \rightleftharpoons T + T^{2-},2Na^+ \quad (10)$$

$$2T^{\cdot -} \rightleftharpoons T^{2-} + T \quad (11)$$

Temperature is an important factor in the disproportionation equilibrium. DeBoer, using epr, found that lithium naphthalenide in 2-methyltetrahydrofuran existed as the radical anion at −120°. At higher temperatures the paramagnetism disappeared and the naphthalene dianion was formed.[6] The driving force for this endothermic process appears to be the increased binding of the cation in the dianion and the increased entropy due to less ion solvation. Ion pairing is "tighter" in dianions than in radical anions, and this is reflected by smaller dissociation constants.[6]

$$Ar^{2-},2M^+ \rightleftharpoons Ar^{2-},M^+ + M^+ \quad (12)$$

The solvent is also important in these equilibria. Solvents which form strong associations with the cations, such as DME or HMPA, favor formation of the free radical anions, which do not disproportionate.[50] The reduction potential of the free radical anion is higher than the ion pair. Less polar solvents such as dioxane do not bind strongly with the cation, so dianion formation is correspondingly more favorable.

C. Kinetics of Electron Transfer

Electron exchange between aromatic radical anions and their parent hydrocarbons is extremely rapid. Exchange rates[51-57] are determined from line-broadening in esr spectra and are found to be on the order of 10^8 M^{-1} sec^{-1}. This rate depends upon whether the cation–radical anion combination is "free" or an ion pair. Electron transfer in the exchange reaction between NaN and N was observed to be nearly two orders of magnitude slower for ion pairs than the free ions.[56] Electron transfer from the ion pair must also be accompanied by migration of the counterion; the net effect is that atom transfer occurs from ion pairs, and this is slower than simple transfer of an electron.[58]

It should be pointed out that the solvent separated (free) radical anion may not prove to be the most reactive specie in all electron transfer (or other) reactions. Some electron transfers proceed more rapidly through ion pairs. There are many examples in the inorganic literature where "bridging" groups are involved. It is likely that the first example from organic chemistry was noted by Garst and associates.[59] They observed that the air oxidation of the carbanion related to Koelsch's radical (2-phenylbis(biphenylene)allyl) proceeded more rapidly for ion pairs than the free anion. This result was interpreted as being consistent with a transition state in which the charge is more concentrated than in the reactant anion.

$$R:^- + O_2 \longrightarrow R\cdot + O_2^{\cdot -} \quad (13)$$

In this reaction the electron receptor is much smaller than in the exchange of an electron between naphthalene rings, so it would be anticipated that ion pairing would be more important in the transition state.

The factors involved in the rate of electron transfer from aromatic dianions are even less defined. From disproportionation studies of radical anions it is known that this must also be fast.[49]

There is also a fast rate of electron transfer from hydrocarbon radical anions to a variety of molecules bearing functional groups. The rates vary from 10^6 to 10^{10} M^{-1} sec^{-1}; this compares with the rate of proton transfer[60-64] which is about 10^4–10^6 M^{-1} sec^{-1}. The rate difference has a significant impact on the course of chemical reactions; there are a number of examples in which either proton abstraction or electron transfer is inherently possible on the basis of acidity and reduction potential. Because of the rate difference electron transfer from naphthalenide, for example, is significant even for some compounds having pK_a's as low as 20–23.

D. Spin and Charge Densities

Proton abstraction by the radical anion or dianion ultimately produces the dihydro derivative. Combination of either anion with other compounds forms derivatives in which the positions of attachment to the hydrocarbon correspond to those protonated, though for hydrocarbons forming more than one dihydro product the distribution may differ from that derived *via* protonation to reflect steric and electronic factors.

A precise determination of atomic charges (charge density) in the various hydrocarbon radical anions poses problems. No experimental method has been employed to determine this directly, though with significant improvements in resolving power X-ray photoelectron spectroscopy would appear to be of some help. It will be recalled that epr yields coupling constants which may be used to estimate spin density, but it must also be remembered that spin density is not the same as charge density. It turns out most often that the spin density is highest at the atom(s) having the greatest charge density, but this is not always the case.[65]

We shall first consider spin density. Spin density is calculated from the McConnell expression

$$a_H = Q\rho \quad (14)$$

where a_H is the coupling constant, ρ the spin density, and Q a constant. There is some uncertainty in this method because the value of Q may vary somewhat. The value 22.5 successfully describes the benzene ion, but greater values are necessary with larger hydrocarbons for there to be agreement with the total unpaired spin.

Numerous methods of calculating spin density distribution have been developed (Table X). For the most part there is only fair agreement with experimental results. In this report we shall consider mainly the experimentally determined coupling constants and the spin densities cal-

TABLE XI. Experimentally Derived Spin Densities

	ρ^{74}	a_H	Q	ρ^{75}	a_H	Q	ρ^{70}
Naphthalene							
1	0.185	4.95	31.2	0.158	4.90	27	0.223
2	0.069	1.87		0.060	1.83		0.047
Anthracene							
1	0.098	2.76	31.2	0.088	2.74	27	0.1068
2	0.044	1.53		0.049	1.57		0.0312
9	0.210	5.41		0.174	5.56		0.273
Phenanthrene							
1	0.132	3.71	31.2	0.119	3.60	27	0.128
2	0.003	0.43		0.014	−0.72		−0.024
3	0.105	2.88		0.093	2.88		0.099
4	0.001	0.63		0.020	0.32		0.037
9	0.158	4.43		0.142	4.32		0.223
Biphenyl							
2	0.080				2.75	27	0.100
3	0.013				−0.45		−0.011
4	0.160				5.50		0.170
Tetracene							
1	0.054	1.55	31.2	0.050			
2	0.032	1.15		0.037			
5	0.161	4.25		0.136			
Perylene							
1		3.53	31.2	0.114			
2		3.08		0.099			
3		0.46		0.015			
Pentacene							
1		0.88	31.2	0.028			
2		0.88		0.028			
5		3.01		0.097			
6		4.27		0.137			
Pyrene							
1					4.75	27	0.167
2					1.09		0.040
4					2.08		0.095

culated therefrom. Table XI lists the spin densities at the various positions in radical anions. From the examples in this table it is seen that the spin density in the radical anions is fairly localized. Thus, in naphthalenide the spin density at the α position is 2.7 times that in the β position.

Thus far we have considered the transfer of electron density from the metal to the aromatic nucleus to be complete. But this is not entirely true because under certain conditions the metal retains some of the unpaired spin density. This is detected as hyperfine coupling (epr or nmr) of the alkali metal and is often observed in the solution spectra of aromatic radical anions, especially in ethereal solvents. This phenomenon was first noted by Adam and Weissman when they found that each epr spectral component in the sodium ketyl of benzophenone was split into four as a result of coupling to ^{23}Na which has a nuclear spin of $3/2$; splitting by the metal indicated the presence of unpaired spin density.[58]

This spin coupling is always very small in the alkali metal aromatic radical anions, and there is considerable debate about its precise origin.[34,76-78] The important consideration for this discussion is that if splitting is detected this is taken to indicate the existence of ion pairing. The converse is not true.

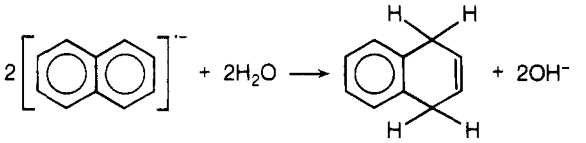
The largest metal hyperfine coupling ever reported is 36 G from potassium in isopropylamine at 135°, which corresponds to about 46% atomic character.[79] The metal hyperfine coupling constants for alkali metal aromatic radical anions are summarized by Symons,[65] and in no case is the coupling greater than 2.1 G, which means that the per cent atom character is less than 3.0%.

The lithium salts frequently give anomalous spectroscopic results when compared to the other alkali metal systems.[34] Recent evidence suggests formation of a three-center bond may be one factor.[35]

The solvent too may have an appreciable effect on the magnitude of the hyperfine splitting constants. In some cases the solvent has a large effect on the coupling constants, in other cases almost none. The effect of the solvent is not entirely predictable, though recently Tuttle has found a linear variation with the inverse cube of the dielectric constant for some solvents.[78] He therefore attributes the variations in hfs constants to changes in solvation of the cation in the ion pair.

More recently, nmr has proven to be a valuable adjunct to epr in the study of the nature of the radical anion-metal counterion interaction.[80-82] One of the more important observations is that the alkali metal coupling constants, measured either by nmr or epr, have been found to vary with temperature and that they may increase, decrease, or remain constant as the temperature is increased. No clear picture has emerged as to what causes these changes, although an increase in coupling constant has been generally assumed to indicate that the ions in an ion pair come closer together.

The determination of atomic charge (charge density) on the various carbons within radical anions is a factor of obvious importance in understanding the reactions in which addition, as in protonation, occurs to the aromatic nucleus.



(15)

As considered above, this may differ from the spin density. In lieu of a direct measurement of this quantity in radical anions, two methods are available which make it possible to calculate charge density with some reliability. Both of these use the Hückel description.

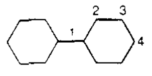
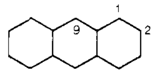
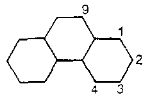
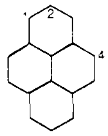
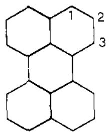
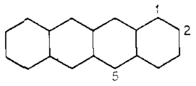
One method was developed some years ago by Hoijtink.[26,83] He assumed that the logarithm of the rate constant (using protonation as a model) is linearly proportional to the charge density at a particular atom, where the charge density is given by the square of the coefficient of the HMO for the first antibonding orbital. In protonation the position of highest electron density is considered to react first. The second protonation occurs with an ordinary carbanion, and again reaction is at the position of highest electron density. The charge density calculations are shown below for biphenyl, naphthalene, and anthracene. These calculations accurately predict the positions of protonation of naphthalenide to be 1,4, to mention just one example. Other calculations of electron density is shown in Figure 6 and Table XII. This method was successful in predicting the position of protonation, but was not satisfactory in explaining the relative rates among the different species.

A similar method of predicting the position of protonation was recently reported by Hayano and Fujihira.[84] In utilizing the Hückel method it likewise suffers from the shortcomings of this technique. Nonetheless, this method too predicts correctly the products of protonation, relying on calculation of changes in localization energies. The localization energy, L_r, is given by

$$L_r = M^- - M_r \qquad (16)$$

where the π energy of the radical anion is $(n + 1)\alpha + M^-\beta$, and that of the protonated radical is $(n - 1)\alpha +$

TABLE XII. Coefficients of the Energy of the Lowest Vacant MO, Charge Densities, and Localization Energies with Some Aromatic Hydrocarbons[25,84]

Molecule	$-m_{n+1}$	Position	c_r^2	L_{r-}
Benzene	1.000		0.167	1.536
Naphthalene	0.618	1	0.181	1.681
		2	0.069	1.862
Biphenyl	0.705	1	0.123	
 		2	0.090	1.695
		3	0.020	1.839
		4	0.158	1.742
Anthracene	0.414	1	0.096	1.84
 		2	0.047	1.99
		9	0.192	1.599
Phenanthrene	0.605	1	0.116	1.713
 		2	0.002	1.893
		3	0.099	1.849
		4	0.054	1.761
		9	0.172	1.694
Pyrene	0.445	1	0.136	1.745
 		2	0.000	2.10
		4	0.087	1.83
Perylene	0.347	1	0.083	
 		2	0.013	
		3	0.108	
Tetracene	0.295	1	0.056	
 		2	0.034	
		5	0.148	

$M_r\beta$, where r denotes the position of the carbon atom, and n, the number of π electrons of the parent molecule. It was assumed, and reasonably so, that protonation occurs at the position at which the change in localization energy is smallest. The predictions resulting from the application of this method are in agreement with those postulated originally by Hoijtink except for biphenyl (Table XII). The charge density in the biphenylide ion is greatest at position 4, but the localization energy change is lowest at position 2. The reduction products are reported to be 2,5-dihydrobiphenyl[85] or 1,4-dihydrobiphenyl.[86] This method is more successful in explaining relative rates, which would suggest that transition state energy differences parallel localization energy differences.

Nmr spectra of the sodium dianions of anthracene, tetracene, and perylene reveal information about electron densities.[87] The chemical shifts observed were quite large, and a calculation of charge density using the equation

$$\Delta\delta_r = Kq_r \tag{17}$$

where $\Delta\delta_r$ is the charge-induced chemical shift, K a constant, and q_r the excess charge, requires K values to range from 12 to 23 ppm per electron, or approximately twice the generally accepted value of 10 ppm per unit charge. Though an evaluation of charge densities is somewhat uncertain, a comparison with epr splittings in the radical anions indicates a qualitatively more uniform electron distribution in the dianions (Table XIII).

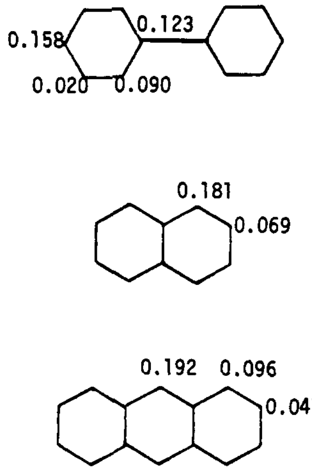


Figure 6. c_r^2 for the lowest vacant orbital of biphenyl, naphthalene, and anthracene.

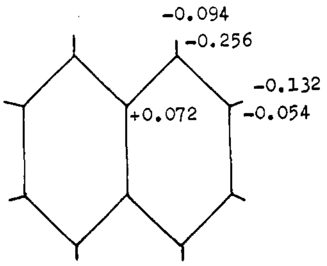


Figure 7. Charge distribution in the naphthalene dianion.

TABLE XIII. Comparison of Charge-Induced Chemical Shifts and Hyperfine Splittings in Aromatic Dianions and Radical Anions[79]

Compound	Position (r)	δ (dianion), ppm	$\Delta\delta_r$, ppm	a_H
Anthracene	1	3.36	4.61	2.74
	2	4.25	3.18	1.51
	9	1.89	6.56	5.34
Tetracene	1	4.46	3.54	1.54
	2	4.85	2.65	1.16
	9	3.00	5.63	4.23
Perylene	1	4.99	3.28	3.09
	2	5.93	1.52	0.46
	3	4.87	2.83	3.55

These authors did not make a similar study of the naphthalene dianion. A spectrum showing large chemical shifts for each proton would be expected on the basis of the calculated charge distribution in the dianion using the CNDO molecular orbital method.[35] However, this calculation does show that the carbon centers of high electron density in the dianion are the same as those in the radical anion and that there is actually greater charge concentration at the α carbon than in the radical anion (see Figure 7).

III. Chemical Properties

A. Basic Properties

1. Proton Abstraction

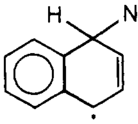
Adding an alkali metal to an alcoholic solution of an aromatic hydrocarbon causes reduction of the hydrocarbon.[88] Baeyer proposed that the metal reacted with the solvent to produce "nascent" hydrogen atoms which were very reactive and added to the organic compound before they coupled to form molecular hydrogen. This view was widely accepted until Willstätter suggested the reaction was initiated by the addition to metallic sodium to the double bond, followed by alcoholysis by the sol-

TABLE XIV. Metalations by Lithium Biphenylide in Tetrahydrofuran[91]

Hydrocarbon RH	Molar ratio, hydrocarbon: biphenyl	Time, hr	Temp, °C	Yield of RLi, %
Triphenylmethane[a]	1.0	9.0	30	92
	1.0	4.5	30	61
	1.0	3.5	66	98
	6.0	18.0	30	82
Diphenylmethane[b]	1.0	18.0	30	63
	1.0	3.5	66	43
	1.0	7.0	66	34
	6.0	27.0	30	52
Toluene[c]	1.0	18.0	30	~1

[a] $pK_a = 28-33$. [b] $pK_a = 33-35$. [c] $pK_a = 37$: H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, New York, N. Y., 1972, p 494.

vent. That is, the organometallic adduct (**2**) displayed basic properties.[16]



2

An early report which indicated the strength of these bases was made by Scott and associates, who determined that sodium naphthalenide abstracted a hydrogen from aniline, fluorene, and *tert*-butyl alcohol.[89] Later, Birch suggested that the reactive intermediate was formed by the transfer of one or two electrons to the aromatic nucleus, forming the radical anion or dianion, respectively.[90] These intermediates then reacted with proton donors. The presence of the radical anion in solution was later verified by Weissman and associates.[20,21]

From the limited data available concerning the basic properties of radical anions, it appears they are effective in abstracting a hydrogen from compounds having pK_a's $\leq$ 33. Certainly there should be some variation depending on the nature of the aromatic hydrocarbon, but this factor has not been quantitatively evaluated.

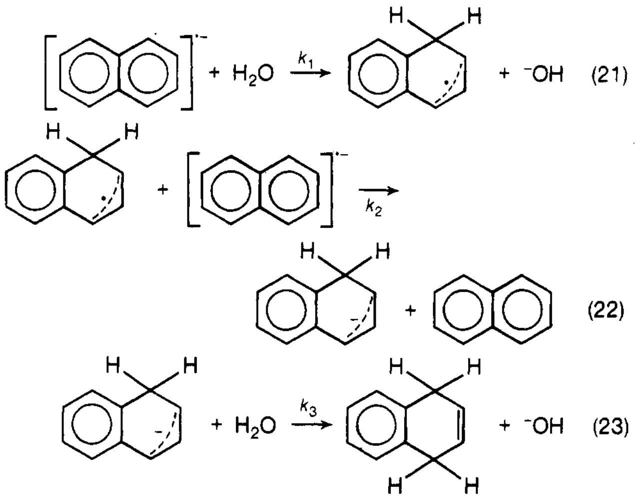
The examples investigated by Eisch and Kaska are instructive.[91] They found that sodium biphenylide is a sufficiently powerful base to remove almost quantitatively the acidic hydrogen from triphenylmethane, but that the reagent is quite ineffective when it comes to toluene. The degree to which proton abstraction occurred was determined indirectly by bubbling carbon dioxide into the solution of hydrocarbon and biphenylide, and the resulting acid derivative was isolated. (See Table XIV.)

The position of first protonation in the radical anion is at the carbon of greatest electron density (or which undergoes the least change in localization energy). A mechanism for this reaction was proposed by Weissman.[92]

$$Ar^{\cdot -} + BH \longrightarrow ArH^{\cdot} + B^- \qquad (18)$$

$$ArH^{\cdot} + Ar^{\cdot -} \longrightarrow ArH^- + Ar \qquad (19)$$

$$ArH^- + BH \longrightarrow ArH_2 + B^- \qquad (20)$$



This is detailed in eq 21-23 for the example of naphthalenide. The counterion is not included simply for clarity. The radical anion abstracts a proton in the first step, forming a hydronaphthyl radical (eq 21). This radical is rapidly reduced by naphthalenide to the anion (eq 22), which is protonated to form 1,4-dihydronaphthalene, the product of a kinetically controlled reaction. The slow step in the reaction is given by eq 21. Consistent with this is the rate expression

$$-d[N^{\cdot -}]/dt = 2k_1[N^{\cdot -}][H_2O] \qquad (24)$$

where k_1 at 20° in THF is $1.01 \times 10^4\ M^{-1}\ sec^{-1}$. The enthalpy and entropy of activation are $\Delta H^* = 10.0 \pm 1.9$ kcal/mol and $\Delta S^* = -6.3 \pm 2.5$ eu, respectively.[61] Electron transfer from the radical anion to the intermediate hydronaphthalene radical is very fast. Hoijtink has shown that the radical has a higher electron affinity than the parent molecule.[93] Completion of the reaction is brought about by protonation of the hydronaphthalene anion, which is a conjugated carbanion more basic than the radical anion. The mechanism of protonation of sodium anthracenide is directly analogous.[61a] Contrary to predictions based upon molecular orbital calculations, sodium anthracenide is appreciably less reactive than sodium naphthalenide. This is attributed to the state of ion pairing.

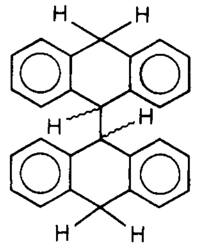
Protonation of sodium perylenide ($Pe^{\cdot -},Na^+$) in THF by a variety of alcohols is an instance in which a dianion is the specie protonated.[94] Quenching was second order in $Pe^{\cdot -},Na^+$ and inversely proportional to the concentration of added perylene (Pe). Despite its low concentration $Pe^{2-},2Na^+$ is protonated at a rate which exceeds by far that of the radical anion. Disproportionation of the radical anion is capable of maintaining a sufficient concentration of $Pe^{2-},2Na^+$ to account for the kinetics.

Other studies of protonation include reports by Hayano and Fujihira.[38,84] The radical anions of biphenyl, naphthalene, phenanthrene, anthracene, 1,2-benzanthracene, and pyrene were generated electrolytically in aqueous DMF solutions, and the rates of decomposition followed by measuring the decay in (visible) absorption spectra of the radical anions with time. For all of these radical anions the protonation reaction was first-order in radical anion concentration, consistent with the Paul, Lipkin, and Weissman mechanism. Umemoto's study confirms the observation that protonation of the anthracene radical anion occurs.[95] In a 1973 reference Szwarc[96] further verifies these results by determining that protonation is first order in DME with added methanol, ethanol, isopropyl alcohol, and water. Participation of the dianion is observed with *tert*-butyl alcohol (being the poorest solvating alcohol, it would favor ion pairing and dianion formation). Actually two types of dianion are observed: a "solvent-caged" complex ($A^{2-},2Na^+$; A) is present in higher concentration than the "diffused out-of-cage" complex ($A^{2-},2Na^+$).

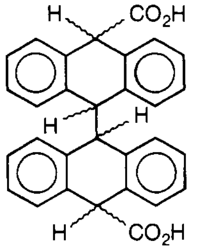
TABLE XV. Rate Constants and Derived Data for the Reaction of Sodium Naphthalenide and Water in Various Solvent Systems

System	Ion pair	$k^{20°}$ ($\times 10^{-4}$)	ΔE_a, kcal/mol	ΔH^*, kcal/mol	ΔS^*, eu
THF	Tight	1.06	10.6 ± 1.9	10.0 ± 1.9	−6.2 ± 2.5
DME	Loose	0.31	13.6 ± 3.4	13.0 ± 3.2	+13.2 ± 11
THF–tetraglyme	Glymated	0.0234	17.7 ± 5.0	17.3 ± 4.8	+22.5 ± 16.4
	(free)	0.0428			

Winkler and Winkler also report the photolytic hydrolysis of anthracenide to be consistent with the Weissman postulation.[97] Furthermore, at high concentrations of lithium anthracenide (2×10^{-2} *M* in diethyl ether) a solid was isolated which was identified as 9,9′,10,10′-tetrahydro-9,9′-bianthryl (**3**). This is very similar to the example

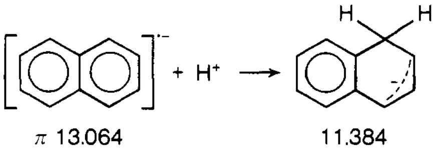


3



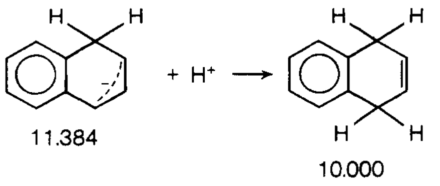
investigated by Schlenk and Bergmann who reported isolating the analogous dicarboxylic acid after treating anthracenide with CO_2.[15] Their assessment was challenged by Jeanes and Adams, who suggested the product actually isolated was fluorenecarboxylic acid.[98] There is no other reported example of a coupling product of this kind. If the specified product was actually formed, one would presume it to be the resultant of coupling of hydroanthracene radicals. This author is skeptical about the reported identity of the isolated compound on the basis of the analogous challenge by Jeanes and Adams and for reasons which are considered extensively in section III.B.4.

In a radical anion solution there may be as many as three bases functioning during the course of a protonation reaction: the radical anion, the dianion, and the hydroaromatic anion. The dianion is the strongest base; it appears that the naphthalene dianion is a stronger base than the benzyl carbanion.[35] The hydroaromatic anions of naphthalene[61] and anthracene[61a] are proven to be appreciably more basic than their corresponding radical anions. This increased basicity, *e.g.*, for the hydronaphthalene anion, is consistent with calculated MO energy changes.[61] For the radical anion the change in localization is 1.680 β (eq 25).[67] The change in the anion is 1.384 β (eq 26).



(25)

There is a greater loss in localization in the reaction of



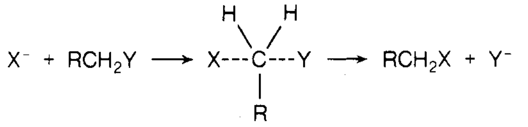
(26)

the radical anion. The difference of 0.296 β suggests the hydronaphthalene anion has a predicted reactivity of 10^3–10^4 that of the radical anion;[61] this value is consistent with experimental observations.

Streitwieser predicted that the transition state of protonation of radical anions involved only a perturbation of the original π-electron system, and that the transition state thus resembled starting material with little bond formation occurring.[99] For naphthalenide in aqueous THF solution the kinetic isotope effect was 1.37 ± 0.44, which is consistent with this interpretation.

The small isotope effect shown by the naphthalenide system is not shared by the perylene dianion. The isotope effect for the perylene dianion is about 10, indicating a substantial degree of O–H fission in the transition state.[94] The difference between these examples has not been explained.

Hayano and Fujihira studied the protonation of a variety of radical anions generated electrolytically in DMF containing small percentages of water.[84] Even at low concentration water was present in sufficient quantity to render the rate zero order in it. Adding more water had a striking rate-enhancing effect. This is opposite its effect upon typical substitution reactions, where the rate is much faster in dipolar aprotic solvents than in protic media.



$$X^- + RCH_2Y \longrightarrow X\text{---}\overset{H\ \ H}{\underset{R}{C}}\text{---}Y \longrightarrow RCH_2X + Y^- \qquad (27)$$

In the usual substitution reactions the negative charge of the anion (X^-) occupies a rather small volume and is highly stabilized by hydrogen-bonding solvents. In the transition state the charge is more diffused and solvation is not as powerful a stabilizing force. With dipolar aprotic solvents the anion is not as stabilized, so the free energy of activation is less than in protic media. The opposite trend shown in the radical anion reactions is likely due to greater charge localization in the transition state of the protonation reaction than in the ground state of the radical anion, where the charge is more diffused over the molecule. Greater localization of the charge during the transition state would be better stabilized by the more protic media.

The state of aggregation also has a direct influence on the rate of protonation. Bank and Bockrath[61] found that protonation of sodium naphthalenide occurs about 50 times faster for the tight ion pair than for free ions (Table XV). A similar trend was seen in the metalation of triphenylmethane[101] and phenylacetonitrile.[101a] Sodium naphthalenide effects both proton abstraction from and electron transfer to phenylacetonitrile. Electron transfer is a minor process in THF but major in THF–tetraglyme. Thus solvent systems which favor a loosening of ion pairs facilitate electron transfer. Results which may be in conflict with the above examples were reported by Solodovnikov.[102] He finds that the rate of deprotonation of diphenylmethane by various alkali metal salts of naphthalene and biphenyl is faster in DME than in THF. This, of

TABLE XVI. Base Condensation Reactions (I)

Acid	Base	Added reagent	Product	Yield, %	Ref
Phenylacetylene	NaN	CO_2	Phenylpropynoic acid	50	a
1-Hexyne	NaN	CO_2	2-Heptynoic acid	50	
Acetylene	NaN	Butanone	3-Methyl-1-pentyn-3-ol	80	
	NaN	Cyclohexanone	Ethynylcyclohexanol	90	
	NaN	CO_2	Propynoic acid	20	
	NaN	Ethanal	1-Butyn-3-ol	50	
	NaN	Propanal	1-Pentyn-3-ol	55	
Camphor	NaN	CO_2	Camphocarboxylic acid	70	
Phenylacetonitrile	NaN	CO_2	Cyanophenylacetic acid	40	
Diphenylmethane	NaN	CO_2	Diphenylacetic acid	70	
Fluorene	NaN	CO_2	Fluorene-9-carboxylic acid	72	
Diphenylmethane	NaPh	CO_2	Diphenylacetic acid	50	
	LiPh	CO_2	Diphenylacetic acid	50	
Acetylene	NaPh	2-Heptanone	3-Methyl-1-octyn-3-ol	90	
Propargyl alcohol	LiN	Mesityl oxide	4,6-Dimethyl-5-hepten-2-yne-1,4-diol	50	
	LiN	Cyclohexanone	1-(1′-Hydroxylcyclohexan-1′-yl)-1-propyn-3-ol	50	
	LiN	Citral	6,10-Dimethyl-5,9-undecadien-2-yne-1,4-diol	37	
	LiN	β-Ionone	1-(2′,6′,6′-Trimethyl-1′-cyclohexen-1′-yl)-3-methyl-1-hexen-4-yne-3,6-diol	50	
Propargyl alcohol	LiN	Methyl ethyl ketone	2,5-Dimethyl-3-heptyne-2,5-diol	80	b
		Pulegone		32	
3,7,11-Trimethyl-1-dodecen-3-ol	LiN	Methyl ethyl ketone	3,6,10,14-Tetramethyl-4-pentadecyne-3,6-diol	70	
Ethynyl-β-ionol	LiN	Methyl ethyl ketone	1-(2′,6′,6′-Trimethyl-1′-cyclohexen-1′-yl)-3,6-dimethyl-1-octen-4-yne-3,6-diol	55	
Acetone	LiN	Acetone	2,5-Dimethyl-3-hexyne-2,5-diol	20	
Cyclohexanone	LiN	Acetone	1-(1′-Hydroxyl-cyclohexan-1′-yl)-3-methyl-1-butyn-3-ol	50	
Cyclohexanone	LiN	Methyl ethyl ketone	1-(1′-Hydroxyl-cyclohexan-1′-yl)-3-methyl-1-pentyn-3-ol	52	
Acetophenone	LiN	Acetone	2-Phenyl-5-methyl-3-hexyne-2,5-diol	50	
Citral	LiN	Acetone	2,7,11-Trimethyl-6,10-dodecadien-3-yne-2,5-diol	39	
β-Ionone	LiN	Acetophenone	1-(2′,6′,6′-Trimethyl-1′-cyclohexen-1′-yl)-6-phenyl-1,6-dimethyl-1-hexen-4-yne-3,6-diol	30	
Acetylene	NaN	ϕ-Ionone	Ethynyl-ϕ-ionol	40	c
	NaN	Benzalacetone	1-Phenyl-1-penten-4-yn-3-ol	60	
	NaN	Acetophenone	3-Phenyl-1-butyn-3-ol	15	
	NaN	Carvone	Ethynylcarveol	40	
	NaN	Mesityl oxide	3,5-Dimethyl-4-hexen-1-yn-3-ol	35	
	NaN	Cinnamaldehyde	1-Phenyl-1-penten-4-yn-3-ol	15	
	NaN	Citral	5,9-Dimethyl-4,8-decadien-1-yn-3-ol	30	
Methylacetylene	NaN	β-Ionone	Propynyl-β-ionol	88	
	NaN	Carvone	Propynylcarveol	70	
	NaN	Benzalacetone	3-Methyl-1-phenyl-1-hexen-4-yn-3-ol	40	
	NaN	Pulegone	Propynylpulegol	30	
	NaN	Methyl ethyl ketone	4-Methyl-2-hexyn-4-ol	85	
Phenylacetylene	NaN	Cinnamaldehyde	1,5-Diphenyl-1-penten-4-yn-3-ol	20	
	NaN	Mesityl oxide	3,5-Dimethyl-1-phenyl-4-penten-1-yn-3-ol	40	
	NaN	Citral	2′-Phenylethynylgeraniol	50	
	NaN	Cyclohexanone	2′-Phenylethynylcyclohexanol	50	
	NaN	Methyl ethyl ketone	3-Methyl-1-phenyl-1-pentyn-3-ol	50	
2-Methyl-1-buten-3-yne	NaN	Methyl ethyl ketone	2,5-Dimethyl-1-hepten-3-yn-5-ol	15	c
3,7,11-Trimethyl-3-dodecen-1-yne	NaN	Mesityl oxide	2,4,7,11,15-Pentamethyl-2,7-hexadecadien-5-yn-4-ol	30	
	NaN	Crotonaldehyde	7,11,15-Trimethyl-2,7-hexadecadien-5-yn-4-ol	50	
	NaN	Methyl ethyl ketone	3,6,10,14-Tetramethyl-6-pentadecen-4-yn-3-ol	50	
Dibenzylamine	LiN	Hexyl bromide	Hexyldibenzylamine	90	d
	LiN	Ethyl bromide	Ethyldibenzylamine	50	
	LiN	Bromobenzene	Phenyldibenzylamine	70	
Aniline	LiN	Ethyl bromide	N-Ethylaniline	70	e
Cyclohexylamine	LiN	Butyl bromide	Butylcyclohexylamine	55	

TABLE XVI (Footnotes)

[a] H. Normant and B. Angelo, *Bull. Chem. Soc. Fr.*, 354 (1960). [b] S. Watanabe, K. Suga, and T. Suzuki, *Can. J. Chem.*, **47**, 2343 (1969). [c] K. Suga, S. Watanabe, and T. Suzuki, *ibid.*, **46**, 3041 (1968). [d] K. Suga, S. Watanabe, T. Pan, and T. Fujita, *Chem. Ind. (London)*, 78 (1969). [e] K. Suga, S. Watanabe, T. Pan, and T. Fujita, *Bull. Chem. Soc. Jap.*, **42**, 3606 (1969).

course, suggests that the "loose" ion pairs react more rapidly than "contact" pairs.

Considering only the reports comparing the reactivity of the free ions with ion pairs (loose and/or contact), it is possible to discern a reactivity pattern. Reactions in which the ion pair yields a kinetically faster rate than the free ions appear to have in common a transition state involving a fairly localized site. Electron transfer from the carbanion related to Koelsch's radical[59] to oxygen and proton abstraction appear to involve high charge concentration in the transition state. This charge would be stabilized by a close proximity of the cation. Electron transfer between two aromatic rings, which is faster for free ions,[56] would be anticipated to involve a transition state of low charge density and the cation would not be expected to effect much stabilization.

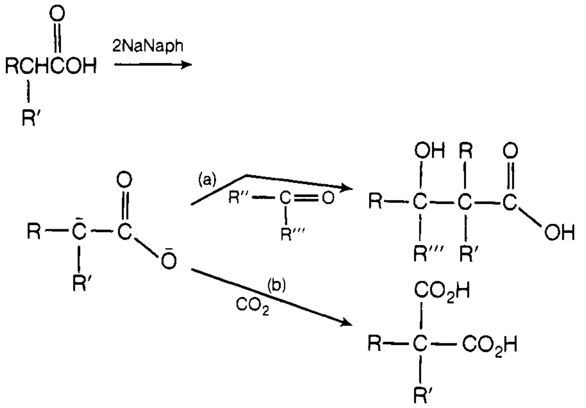
If we focus our attention on the overall change which has taken place in the aromatic nucleus as a result of protonation, we find the molecule is reduced. (On the basis of stoichiometry one-half of the radical anion concentration would form a dihydro product while the other half reverted to the aromatic compound.) The same transformation occurs in the Birch reduction, which differs from the previous examples in that an alkali metal is the electron source and the solvents of choice are liquid ammonia or a low molecular weight amine with an added proton source.[102a,103] In the Birch reduction the acidity of the protonating agent has a significant bearing on the overall yield of reduced aromatic product.[102] Use of acidic substances such as ammonium chloride or water in ammonia has a deleterious effect on the yield when the aromatic compound has a high reduction potential, whereas polynuclear aromatic compounds are reduced in high yield in the presence of the same substances. The difference in effectiveness is accounted for by the observation that ammonium chloride and water react rapidly with alkali metals dissolved in liquid ammonia; when the aromatic compound has a high reduction potential the metal reacts with the acid. With polynuclear compounds electron transfer is to the aromatic system in preference to the acid.

2. *Use in Condensation Reactions*

Alkali metal aromatic radical anions have synthetic advantages in some types of condensation reactions. One convenience is that stoichiometric amounts of base can be used because radical anions have a built-in indicator. The radical anions are highly colored, and since proton abstraction is very fast there is a rapid color change at equivalency. (Since the hydroaromatic anion is a stronger base than the radical anion, the disappearance of color also monitors the disappearance of this base.) Another advantage stems from the fact that radical anions are poor nucleophiles; thus combination with the reactants or products is not as likely as with other bases. The only major restriction is that they can be used only for those situations where electron transfer either does not occur, *i.e.*, the reduction potentials of the reactants and products are too high, or else that electron transfer is not detrimental to the desired reaction.

An early investigation by Scott and Walker inferred usefulness in base condensation reactions.[104] They treated acetonitrile with sodium naphthalenide and then added *n*-butyl bromide to form capronitrile, or with benzyl chloride to yield dibenzoacetonitrile. In more recent studies carbanion intermediates are generated from terminal alkynes, ketones, nitriles, or alkanes substituted with two or more phenyl groups. After generation of the carbanion, carbon dioxide or an aldehyde or ketone are typically added, forming a carboxylic acid in the first case and alcohols from the latter reagents. For some of the examples shown in Table XVI, the yield is fairly low, which may be caused by competing reactions such as electron transfer; this possibility has not been examined. See also Table XVII.

A similar reaction starts with carboxylic acids (eq 28 and 29). Path a is very similar to the Reformatsky method except that with the latter method esters are used. The advantage of using a radical anion is that hydrolysis of an ester is not necessary, a process which is often accompanied by decarboxylation and dehydration. It is also more generally favorable to the method of Hauser, which utilizes sodium amide.[105] Path b is a useful route to malonic acid derivatives.



(28)

(29)

B. Electron Transfer Reactions

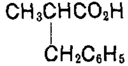
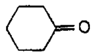
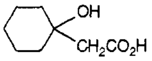
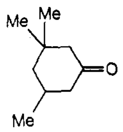
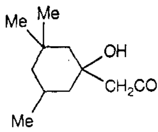
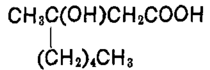
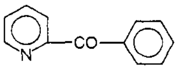
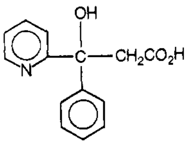
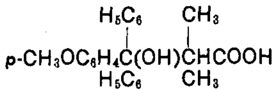
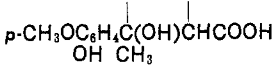
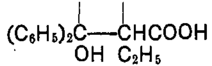
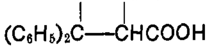
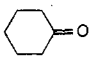
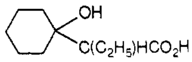
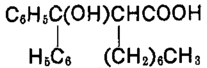
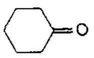
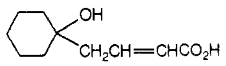
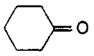
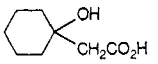
The more typical reaction of radical anions is not proton abstraction but electron transfer. This is true not only for naphthalenide, which is nearly as powerful a reducing agent as metallic sodium, but is also the usual mode of reaction for anthracenide, for example, which is a much weaker reducing agent. Radical anions react with a variety of compounds; the discussion which follows shall consider each type. Considerably less is known about the corresponding reactions of dianions, but this chemistry shall also be included.

1. *Alkanes*

Most alkanes are, of course, inert to radical anions. For a reaction to occur in the aliphatic portion of a hydrocarbon, there must be two or more aromatic substituents. Eisch and Szwarc have investigated examples, preceded by Ziegler's work of some years ago.[106-108] The reaction which these compounds undergo is cleavage.

The cleavage of 1,2-di(α-naphthyl)ethane (NN) with sodium biphenylide was found to proceed through the intermediacy of the dianion, generated by disproportionation of the NN radical anion (counterions are omitted for clarity);[108] eq 30–32.

TABLE XVII. Base Condensation Reactions (II)

Acid	Base	Added reagent	Product	Yield, %	Ref
CH_3CO_2H	NaN	CO_2	$HO_2CCH_2CO_2H$	5	*a*
$CH_3CH_2CO_2Na$	NaN	$C_6H_5CH_2Cl$	 $CH_3\underset{CH_2C_6H_5}{\underset{\vert}{C}}HCO_2H$	15	
$C_6H_5CH_2CO_2Na$	NaN	CO_2	$C_6H_5CH(CO_2H)_2$	55	
$(C_6H_5)_2CHCO_2H$	NaN	CO_2	$(C_6H_5)_2C(CO_2H)_2$	60	
CH_3COOH		$C_6H_5COC_6H_5$	$(C_6H_5)_2C(OH)CH_2COOH$	58	*b*
	NaN			38	
	NaN			57.5	
	NaN	$CH_3CO(CH_2)_4CH_3$	 $CH_3\underset{(CH_2)_4CH_3}{\underset{\vert}{C}}(OH)CH_2COOH$	37.3	
	NaN	$CH_3(CH_2)_6CHO$	$CH_3(CH_2)_6CHOHCH_2COOH$	80	
	NaN			62	
CH_3CH_2COOH	NaN	$p\text{-}CH_3OC_6H_4COC_6H_5$	 $p\text{-}CH_3OC_6H_4\overset{H_5C_6}{\overset{\vert}{C}}(OH)\overset{CH_3}{\overset{\vert}{C}}HCOOH$	38	
CH_3CH_2COONa	NaN	$p\text{-}CH_3OC_6H_4COC_6H_5$	 $p\text{-}CH_3OC_6H_4\overset{H_5C_6}{\overset{\vert}{C}}(OH)\overset{CH_3}{\overset{\vert}{C}}HCOOH$	44	
	NaN	$C_6H_5COC_6H_5$	 $(C_6H_5)_2\overset{OH}{\overset{\vert}{C}}—\overset{CH_3}{\overset{\vert}{C}}HCOOH$	60	
$CH_3CH_2CH_2COOH$	NaN	$C_6H_5COC_6H_5$	 $(C_6H_5)_2\overset{OH}{\overset{\vert}{C}}—\overset{C_2H_5}{\overset{\vert}{C}}HCOOH$	60	
	NaN			43	
$CH_3(CH_2)_6CH_2COOH$	NaN	$C_6H_5COC_6H_5$	 $C_6H_5\underset{H_5C_6}{\underset{\vert}{C}}(OH)\underset{(CH_2)_6CH_3}{\underset{\vert}{C}}HCOOH$	46.3	
$(CH_3)_2CHCOOH$	NaN	$C_6H_5COC_6H_5$	$(C_6H_5)_2C(OH)C(CH_3)_2COOH$	66.6	
$CH_3CH=CHCO_2H$	LiN			64	*c*
CH_3CO_2H	LiN			78	*d*

[a] H. Normant and B. Angelo, *Bull. Chem. Soc. Fr.*, 810 (1962). [b] B. Angelo, *ibid.*, 1848 (1970). [c] S. Watanabe, K. Suga, and K. Fujioshi, *Chem. Ind. (London)*, 80 (1972). [d] K. Suga, S. Watanabe, K. Fujiyoshi, and T. Nagase, *Nippon Kagaku Zasshi*, 92 (1971;) *Chem. Abstr.*, **76**, 58363f (1972).

TABLE XVIII. Alkane Cleavage Products

Compound	Organo-metallic	Major product	Other
1,1,1-Triphenylethane[a]	Li_2B	Triphenylacetic acid[b] (2%)	*c*
1,1,1,2-Tetraphenylethane[a]	Li_2B	Triphenylacetic acid[b] (93)	Phenylacetic acid
1,1,2,2-Tetraphenylethane[a]	Li_2B	Diphenylacetic acid[b] (83)	5,5-Diphenyl-1-pentanol
1,2-Di(α-naphthyl)ethane[d]	NaB	α-Methylnaphthalene	

[a] Reference 107. [b] Products isolated after CO_2 added. [c] A slow apparent gas evolution was observed. [d] Reference 108.

$$NN + B\cdot^- \longrightarrow NN\cdot^- + B \tag{30}$$

$$2NN\cdot^- \rightleftharpoons NN^{2-} + NN \tag{31}$$

$$NN^{2-} \longrightarrow 2N^- \tag{32}$$

This assessment was based on the stability of $NN\cdot^-$ in HMPA, a solvent known to preclude dianion formation by forming solvent separated ion pairs; these do not disproportionate. Also, the reaction obeys second-order kinetics with respect to $NN\cdot^-,M^+$, and the rate is inversely proportional to the concentration of nonreduced NN.

2. *Alkenes*

The most common reaction of alkenes is polymerization. (This will be treated in greater detail in section III.) Typically, active monomers contain an electron-withdrawing group, such as halogen, or an aromatic group. These reactions proceed almost exclusively by electron transfer.

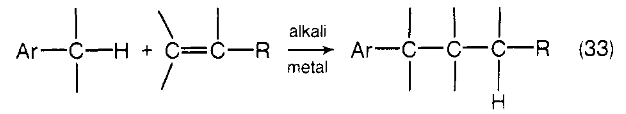
While polymerization is possible when the olefin is substituted with electron-donating groups, it is less likely and other reactions may occur. Isomerization of *cis*-2-butene to a mixture of 1- and *trans*-2-butenes occurs over a sodium film onto which an aromatic compound is sublimed.[109] The process appears to proceed through proton abstraction.

TABLE XIX. Side-Chain Ethylation of Alkylbenzenes by Sodium and Various Aromatic Hydrocarbons[112]

Electron acceptor	$-m_{n+1}$[a]	Relative conversion: Toluene	Ethylbenzene	Cumene
Biphenyl	0.705	1.0	1.0	1.8
Naphthalene	0.618	1.0	1.0	1.0
Phenanthrene	0.605	1.0	1.4	1.0
p-Terphenyl	0.593	1.0	1.5	1.0
Chrysene	0.520	3.4	3.1	4.0
Pyrene	0.445	9.7	5.1	8.0
Anthracene	0.414	6.9	3.5	4.0
Acenaphthylene	0.285	1.6	2.3	0.8

[a] Coefficient of lowest vacant orbital energy ($\epsilon = \alpha + m_{n+1}\beta$).

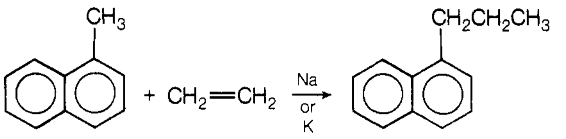
Olefins may be conveniently added to alkyl side chains of alkylbenzenes, naphthalenes, and pyridines with a metal catalyst. Equation 33 characterizes the general



$$\mathrm{Ar{-}\overset{|}{\underset{|}{C}}{-}H + \overset{\backslash}{C}{=}\overset{|}{C}{-}R \xrightarrow[\text{metal}]{\text{alkali}} Ar{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{H}{C}}{-}R} \quad (33)$$

reaction, the study of which is largely the result of work by Pines and associates.[110,111] As the length and branching of the alkylaromatic compound increases and as the steric hindrance of the olefin increases, the yields of aralkylation products decrease while dimerization and polymerization increase.

The intermediacy of a radical anion in this reaction is atypical, but when it is present the course of the reaction is altered significantly. An illustration of this is shown by the ethylation of 1-methylnaphthalene in the presence of catalytic amounts of metallic sodium or potassium.[111]



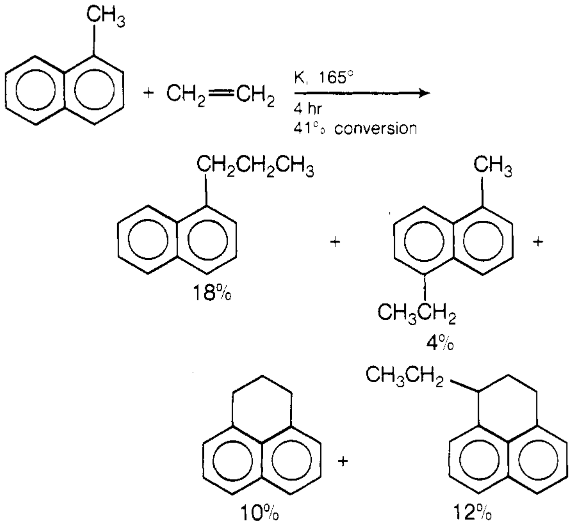
(34)

When sodium is used as catalyst, a promoter is required; typically this is o-chlorotoluene. In the absence of a stabilizing solvent like THF and at the high reaction temperatures (>100°), the naphthalene nucleus does not form its radical anion and the reaction proceeds *via* a carbanionic route.

$$\mathrm{ClC_6H_4CH_3 \xrightarrow{Na} C_6H_5CH_2Na \xrightarrow{C_{10}H_7CH_3} C_{10}H_7CH_2Na + C_6H_5CH_3} \quad (35)$$

$$\mathrm{C_{10}H_7CH_2Na \xrightarrow{CH_2{=}CH_2} C_{10}H_7CH_2CH_2CH_2Na \xrightarrow{C_{10}H_7CH_3} C_{10}H_7CH_2CH_2CH_3 + C_{10}H_7CH_2Na} \quad (36)$$

The differences are immediately apparent when potassium is used. No promoter is necessary and more than 15 products are formed, some of which are the result of nuclear alkylation (eq 37). Epr confirms the presence of the radical anion; this specie is thought to be an active base in methyl substitution reactions (eq 38). Pines has suggested a number of mechanistic possibilities which could account for the products of nuclear alkylation.[111] But existing experimental data are not really sufficient to permit a choice of these, or other, possibilities.



(37)

$$\mathrm{C_{10}H_7CH_3 \xrightarrow{K} C_{10}H_7CH_3{\cdot}^{-},K^{+} \xrightarrow{C_{10}H_7CH_3} [C_{10}H_8CH_3]{\cdot} + C_{10}H_7CH_2K} \quad (38)$$

Saegusa, *et al.*, have also studied side-chain ethylation to determine if the presence of a polynuclear aromatic compound might show a rate-enhancing effect.[112] The activity of each compound was indicated by the conversion of the alkylbenzene in an early reaction period. Chrysene, pyrene, and anthracene were the only aromatic compounds showing any rate-enhancing effect, and this is small (Table XIX and Figure 8). Catalyst activity was attributed to the formation of a "donor-acceptor" complex which aided in the abstraction of the benzylic hydrogen. No attempt was made to interpret why such a complex was formed by the three aforementioned compounds. One characteristic that these three compounds have in common is they readily form dianions. The dianions, if generated, would be expected to be more powerful bases than radical anions.

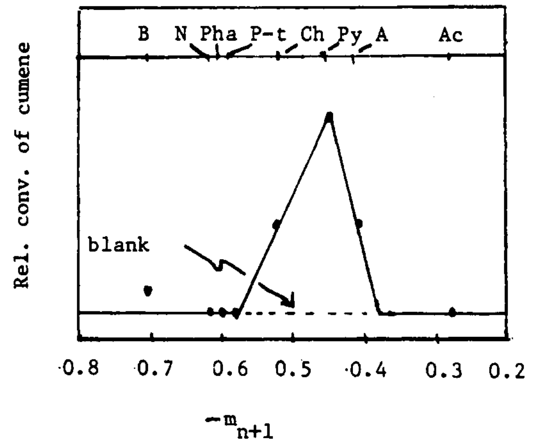
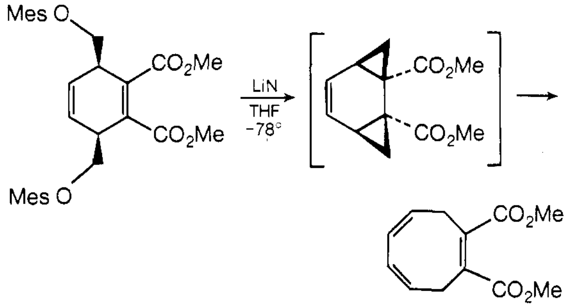


Figure 8. Relation of relative conversion rate of cumene *vs.* coefficient of lowest vacant MO energies in aromatic compound in the sodium catalyzed reaction of cumene with ethylene. Aromatic compound: *p*-terphenyl (P-t), chrysene (Ch), acenaphthalene (Ac).

It is reasonable to assume that electron transfer was involved in the novel ring expansion reported by Whitlock and Schatz (eq 39).[113] There was a 60% conversion to 1,4,6-cyclooctatriene-1,2-dicarboxylate (**4**).

3. Alkynes

Terminal alkynes lose a proton to radical anions. Diphenylacetylene, having no acidic hydrogens, accepts either one or two electrons from sodium biphenylide in THF to form the radical anion or dianion, respectively, eq 40.



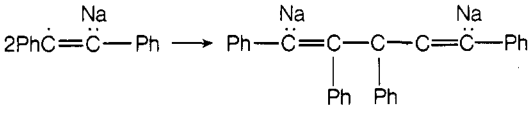
4

(39)

$$\mathrm{Ph{-}\overset{-}{\ddot{C}}{=}\dot{C}{-}Ph,\ Na^+ \overset{e,\ Na^-}{\rightleftharpoons} Ph{-}\overset{-}{\ddot{C}}{=}\overset{-}{\ddot{C}}{-}Ph,\ 2Na^+} \quad (40)$$

Originally it was reported that transfer of the second electron to the acetylene derivative was very slow,[114] but now it is known that this report was spurious and that electron transfer is rapid.[115,116] Equilibrium is rapidly established, but the concentration of the dianion is exceedingly low. In view of Szwarc's recent studies of the disproportionation of the tetraphenylethylene radical anion, the actual source of the electron for dianion formation is most likely free biphenylide or diphenylacetylene radical anion.[49]

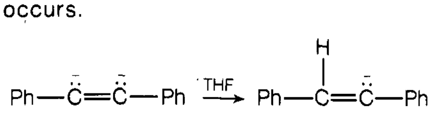
In THF solution the radical anion of diphenylacetylene slowly dimerizes to form the disodium salt of 1,2,3,4-tetraphenylbutadiene dianion.[115,116] Protonation of the dimeric dianion yields about 65% *cis,cis*-1,2,3,4-tetraphenylbutadiene and lesser amounts of other isomers. The extent of dimerization is temperature dependent; it is very limited at −80° but more extensive with increasing temperature. This is compatible with the coupling of ion pairs but not free ions.



$$\mathrm{2Ph\overset{Na}{\dot{C}}{=}\ddot{C}{-}Ph \longrightarrow Ph{-}\overset{Na}{\ddot{C}}{=}\underset{Ph}{C}{-}\underset{Ph}{C}{=}\overset{Na}{\ddot{C}}{-}Ph} \quad (41)$$

In hexamethylphosphoramide, diphenylacetylene accepts only one electron from sodium biphenylide and free ions are formed. The electron affinity of the free diphenylacetylene radical anion is rather low, and formation of the dianion becomes feasible only through association with its counterion. There is no detectable dimerization in HMPA.

The diphenylacetylene dianion is stable in THF below −78°, but at higher temperatures abstraction of a proton from THF occurs.



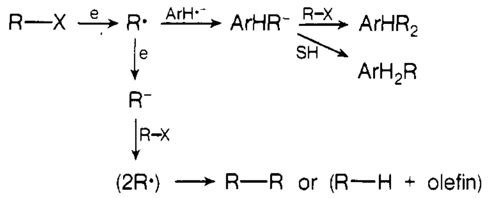
$$\mathrm{Ph{-}\overset{-}{\ddot{C}}{=}\overset{-}{\ddot{C}}{-}Ph \xrightarrow{THF} Ph{-}\overset{H}{C}{=}\overset{-}{\ddot{C}}{-}Ph} \quad (42)$$

The characteristics of methylphenylacetylene in the presence of biphenylide are similar to those of diphenylacetylene except that one additional reaction occurs.[117] The methyl hydrogens are sufficiently acidic that the dianion does effect proton abstraction.

$$\mathrm{Ph\overset{-}{\ddot{C}}{=}\overset{-}{\ddot{C}}CH_3 + PhC{\equiv}CCH_3 \longrightarrow Ph\overset{-}{\ddot{C}}{=}C{=}CH_2 + Ph\overset{-}{\ddot{C}}{=}CHCH_3} \quad (43)$$

4. Aliphatic and Aromatic Halides

SCHEME I

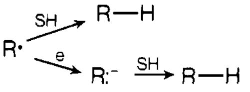


Alkyl halides react with radical anions to yield a variety of products. These products and the probable pathways to their formation are shown in Scheme I. Table XX lists the products with yields. Though there has been considerable research in this area, only the radical anions of naphthalene, biphenyl, and anthracene have received attention, and most data are from naphthalenide[118] reactions. There are no studies which examine the effects of changing radical anions. In the mechanism (*vide supra*) the individual steps seem reasonably certain except for formation of the "dimer," *i.e.*

$$\mathrm{R^- \xrightarrow{R\text{-}X} (2R\cdot) \longrightarrow R{-}R} \quad (44)$$

which is still subject to debate.

The first step is a fast electron transfer to the C-X bond; this is followed by rapid expulsion of halide ion. Only the rates of fluorides[119] have been measured, and these are found to have rate constants of about 5 × 10^4 M^{-1} sec^{-1}. Halogen expulsion is not only fast but also complete, as indicated by the use of sodium biphenylide for quantitative halogen analysis.[120] One product formed from the radical is an alkane. This is conceivably derived by either of two competing pathways.

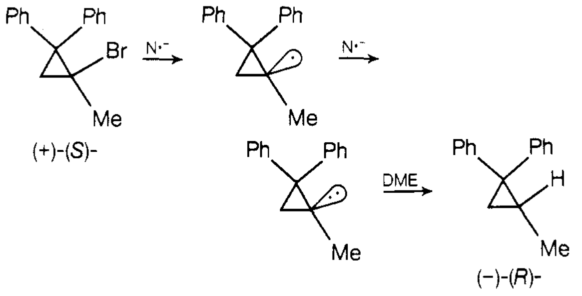


$$\mathrm{R\cdot \xrightarrow{SH} R{-}H} \quad (45)$$

$$\mathrm{R\cdot \xrightarrow{e} R{:}^- \xrightarrow{SH} R{-}H} \quad (46)$$

The carbanionic route predominates to the exclusion of the other. The carbanion may even be trapped by adding magnesium bromide which forms the Grignard reagent in good yield.[121]

The rate of electron transfer between naphthalenide and the alkyl radical is virtually diffusion controlled. This is substantiated nicely by the study of Jacobus and Pensak concerning the reduction of an optically active cyclopropyl bromide.[122] Treatment of optically pure (+)-(*S*)-1-bromo-1-methyl-2,2-diphenylcyclopropane with sodium naphthalenide in DME yields 29% optically pure (−)-(*R*)-1-methyl-2,2-diphenylcyclopropane (eq 47). Reduction of the optically active free radical must have a rate comparable to the inversion frequency of the cyclopropyl radical[123] (10^8–10^{10} sec^{-1}). In a similar reaction, Sargent and Browne were able to trap cis and trans isomers of vinyl radicals formed as intermediates in the reduction of *cis*- and *trans*-3-chloro-3-hexene with sodium naphthalenide.[124]



(47)

The intermediacy of an anion is further indicated by ^{19}F CIDNP. Reduction of *p*-fluorobenzyl halides (X = Cl,

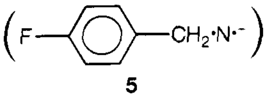


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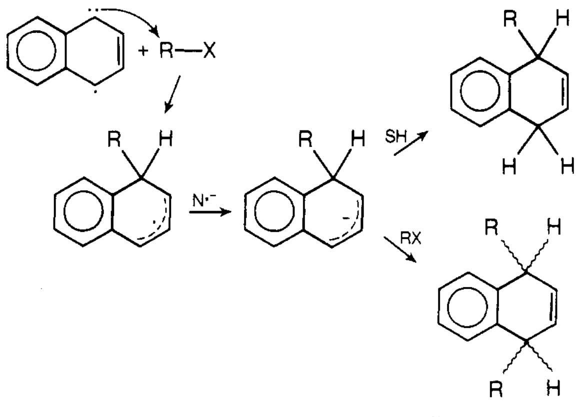
TABLE XX. Reactions of Alkyl Halides with Radical Anions

Alkyl halide (RX)	$Ar\cdot^-,M^+$	RH (%)	Olefin (%)	R–R (%)	Alkylate	Ref
5-Hexenyl chloride and bromide	$N\cdot^-,Na^+$	1-Hexene (40–70)	Not detectable 1,5-Hexadiene	(3–7)	Not analyzed	b
Cyclopentylmethyl chloride and bromide	$N\cdot^-,Na^+$					
n-Heptyl iodide	$N\cdot^-,Na^+$	Heptane (22)	1-Heptene (6)	Tetradecane (50)	Not analyzed	c
n-Pentyl iodide	$N\cdot^-,Na^+$	Pentane (17)	1-Pentene (4)	Decane (55)	Not analyzed	
n-Pentyl chloride		Pentane (44)	1-Pentene (4)		Not analyzed	
n-Pentyl bromide	$N\cdot^-,Na^+$	Pentane (29)		Decane (5)	Not analyzed	
Cholesteryl chloride	$B\cdot^-,Na^+$	5-Cholestene (58–84)				
β-Cyclocholestanyl chloride	$B\cdot^-,Na^+$	5-Cholestene (main)				d
5-Hexenyl iodide	$N\cdot^-,Na^+$	1-Hexene (41)		(7)[a]	(52)	e
5-Hexenyl bromide	$N\cdot^-,Na^+$	(47)		(5)	(48)	
5-Hexenyl chloride	$N\cdot^-,Na^+$	(55)		(0)	(45)	
5-Hexenyl fluoride	$N\cdot^-,Na^+$	(58)		(0)	(42)	
Neopentyl iodide	$N\cdot^-,Na^+$	Neopentane (17)		(72)	(11)	f
n-Pentyl iodide	$N\cdot^-,Na^+$	Pentane (16)	(3)	(46)	(35)	
sec-Pentyl iodide	$N\cdot^-,Na^+$	(17)	(4)	(22)	(48)	
tert-Pentyl iodide	$N\cdot^-,Na^+$	2-Methylbutane (22)	(8)	(3)	(61)	
1,4-Diiodobutane	$N\cdot^-,Na^+$		Ethylene (4)	Cyclobutane (51)	(44)	g
(+)-(*S*)-1-Bromo-1-methyl-2,2-diphenylcyclopropane	$N\cdot^-,Na^+$	(−)-(*R*)-1-Methyl-2,2-diphenylcyclopropane (29% optical purity)				h
cis-3-Chloro-3-hexene	$N\cdot^-,Na^+$	*trans*-3-Hexene				i
trans-3-Chloro-3-hexene	$N\cdot^-,Na^+$	*trans*-3-Hexene				
n-Hexyl chloride	$N\cdot^-,Na^+$	Hexane (30)		(3)		j
n-Hexyl bromide	$N\cdot^-,Na^+$	(37)		(5)		
n-Hexyl iodide	$N\cdot^-,Na^+$	(18)		(32)		
Variety	$N\cdot^-,M^+$ $B\cdot^-,M^+$ $A\cdot^-,M^+$					k
5-Hexenyl chloride	$N\cdot^-,Na^+$	1-Hexene (38–52) Methylcyclopentane (4–9)		(25)		l
5-Hexenyl bromide		1-Hexene (69) Methylcyclopentane (2)		(7)		
1,3- and 1,4-dichlorides	$N\cdot^-,Na^+$ $A\cdot^-,Na^+$ $Ar\cdot^-,Na^+$				Various alkylates	m
1,4-Dibromobutane	$N\cdot^-,Na^+$		Ethylene (22)	Cyclobutane (56)		n
1,4-Dichlorobutane	$N\cdot^-,Na^+$		(trace)	(59)		
1,5-Diiodopentane	$N\cdot^-,Na^+$	Pentane (trace)	1-Pentene (15)	Cyclopentane (42)		
1,5-Dibromopentane	$N\cdot^-,Na^+$	(1.6)	(2)	(53)		
1,5-Dichloropentane	$N\cdot^-,Na^+$	(1.8)	(trace)	(63)		

[a] Special reaction conditions were used to suppress dimer formation and multiple alkylation. [b] J. F. Garst, P. W. Ayers, and R. C. Lamb, *J. Amer. Chem. Soc.*, **88**, 4260 (1966). [c] G. D. Sargent, J. N. Cron, and S. Bank, *ibid.*, **88**, 5363 (1966). [d] S. J. Cristol and R. V. Barbour, *ibid.*, **88**, 4262 (1966). [e] J. F. Garst, J. T. Barbas, and E. Barton, II, *ibid.*, **90**, 7159 (1968). [f] G. D. Sargent and G. A. Lux, *ibid.*, **90**, 7160 (1968). [g] J. F. Garst and J. T. Barbas, *Tetrahedron Lett.*, 3125 (1969). [h] J. Jacobus and D. Pensak, *J. Chem. Soc. D*, 400 (1969). [i] G. D. Sargent and M. W. Browne, *J. Amer. Chem. Soc.*, **89**, 2788 (1967). [j] S. Bank and J. F. Bank, *Tetrahedron Lett.*, 4533 (1969). [k] N. D. Scott and J. F. Walker, U. S. Patent 2,150,039 (March 7, 1939); *Chem. Abstr.*, **33**, 4602^6 (1939). [l] J. F. Garst, *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, **13**, D65 (1968). [m] D. Lipkin, G. J. Davis, and R. W. Jordan, *ibid.*, **13**, D60 (1968). [n] J. F. Garst, *et al.*, *Accounts Chem. Res.*, **4**, 400 (1971).

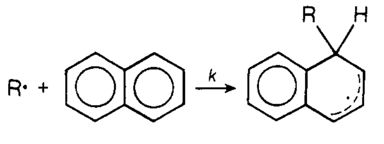
I) forms an intermediate which Rakshys interprets to be consistent with the collisional pair (**5**) of the *p*-fluorobenzyl radical and naphthalenide pair.[125]

Alkylation of the aromatic nucleus typically accounts for between 5 and 60% of the alkyl halide. A number of mechanisms could conceptually account for these derivatives. An SN2 displacement (eq 48) was postulated originally[126] but has since been ruled out for two principal reasons:[127-130] (1) the identity of the halogen has no effect on the amount of monoalkylation product; (2) the percentage of alkylate increases in going from primary to tertiary alkyl halides, exactly opposite of what would be expected on the basis of an SN2 reaction.



(48)

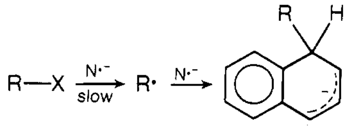
Another possible pathway involves direct attack of the alkyl radical on the aromatic nucleus, *i.e.*, on naphthalene itself (eq 49), but estimation of the rate constant, *k*,



(49)

from an analogous reaction reveals that it must be too small for this route to be significant.[131] Furthermore, variation of the amount of naphthalene in the reaction does not affect the product distribution.[130] (This is the mechanism, however, which at present has the greatest support in the silylation of naphthalene with silyl halides.)

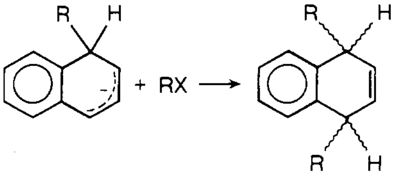
The first alkylation step is accounted for by eq 50. Coupling of the radical and the radical anion is consonant with the independence of the amount of monoalkylate with the identity of the halogen. It is also consistent with



(50)

kinetic observations; the rate is first order in both naphthalenide and alkyl halide.[10] Furthermore, as the reduction potential of the alkyl radical increases on going from primary to tertiary intermediates (meaning less reduction of R· → R:⁻), there is a corresponding increase in alkylate. Coupling with naphthalenide (and presumably other radical anions) must be virtually diffusion controlled for this reaction to compete effectively with reduction of the alkyl radical to anion.

The second alkylation is believed to be a simple SN2 displacement from the anion; this is represented by eq 51. Sargent and Lux determined that neopentyl and tertiary halides do not yield dialkylate, but instead give only monoalkylate; this behavior is consistent with what would be expected from a displacement reaction.[130] The percentage of cis and trans isomers has not been specified.



(51)

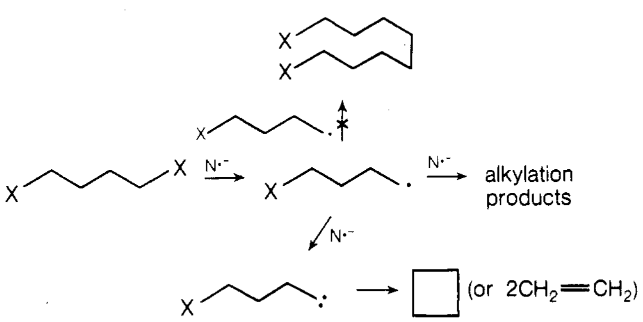
Reductive dimerization is the least understood of the various reactions of alkyl halides.

$$2R{-}X \xrightarrow{N^{\cdot -}} R{-}R + 2X^- \qquad (52)$$

"Dimer" formation is appreciable only with alkyl iodides; it is not uncommon for 50% of the alkyl iodide to be accounted for by this route. With bromides the yield is usually about 5%; for chlorides dimer formation is atypical and for fluorides this product apparently has not been observed. This trend was interpreted to imply a radical–radical coupling mechanism.[130,132] The high yields from iodides were viewed to be a consequence of the diminished reduction potentials of iodides compared to other alkyl halides which permitted such rapid production of free radicals that a sufficient radical concentration was achieved for appreciable coupling. A radical–radical coupling mechanism was further recommended by the observations that treatment of an equimolar mixture of *n*- and isopropyl iodides resulted in a statistical distribution of the possible dimers[132] and by the reaction of neopentyl iodide which forms a high yield of bineopentyl.[130]

Other investigations, however, suggest some other mechanism must be operative. The reaction of 1,4-diiodobutane forms no bimolecular reduction products, and, in fact, 99% of the starting material can be accounted for by the products cyclobutane, ethylene, and monalkylation derivatives.[128] The reaction is believed to take the course shown in Scheme II.[133] Thus the fate of the initially formed alkyl radicals is to be reduced by, or combine with, sodium naphthalenide. Coupling of two alkyl radicals does not occur.

SCHEME II



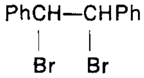
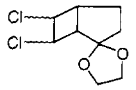
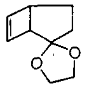
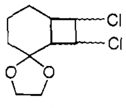
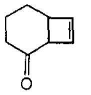
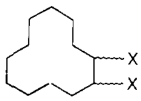
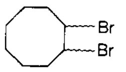
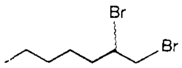
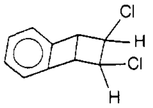
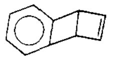
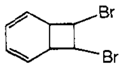
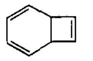
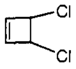
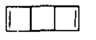
Thus there is something of a dilemma: there is evidence suggesting a radical pathway, and yet, according to other experimental data, it appears that it is not the radical which is the major pathway to bimolecular reduction product. A *modus vivendi* is possible when one considers the reactions of alkyllithium with alkyl halides. These reactions are known to have radical intermediates. Similar application of that mechanism to these reactions results in eq 53, in which radical pairs are generated in a

$$(R:^-,Li^+)_n + R'X \longrightarrow [R\cdot,R'\cdot,Li^+,X^-,(R:^-,Li^+)_{n-1}] \longrightarrow R{-}R' \qquad (53)$$

cage by electron donation from the alkyllithium. The radical pairs may then combine, disproportionate, or diffuse apart. The intermediate radicals have been trapped,[134] observed by esr,[135,136] inferred from chemically induced nuclear spin polarization,[137,138] and inferred from stereochemical experiments.[139]

The main thrust of research on alkyl halide reactions has used naphthalenide as the radical anion. Other radical anions, especially those which are less powerful reducing agents, should possibly lead to somewhat different product distributions. It would be reasonable to anticipate less unimolecular reduction product because the

TABLE XXI. Elimination of Vicinal Dihalides

Halide	MAr	Products	Yield, %	Ref
 $\underset{Br}{PhCH}-\underset{Br}{CHPh}$	NaN	*cis-* and *trans*-stilbene, α-bromostilbene, diphenylacetylene, bibenzyl		*a*
threo-2,3-Dibromo-3-methylpentane	NaN	*cis*-3-Methyl-2-pentene		*a*
erythro-2,3-Dibromo-3-methylpentane	NaN	*trans*-3-Methyl-2-pentene		*a*
	NaN		78	*b*
	NaN		68	*b*
 X = Cl, Br	NaN	Cyclododecene (*cis–trans*)	92 (X = Cl) >90 (X = Br)	*b*
	NaN	*cis*-Cyclooctene	>90	*b*
	NaN	1-Heptene	>90	*b*
1,3-Dichloropropane 1,4-Dichlorobutane 1,5-Dichloropentane	NaN	1,2-Dihydro fused rings 1,4-Dihydro bridged rings Alkylated aromatics		*c*
	Na_2Pha		88	*d*
		Naphthalene	12	
	Na_2Pha		95	*e*
	NaN (then MeOD)		4	*f*
cis		 syn and anti	20	
		cis- and *trans*-2-butenes	6	

[a] W. Adam and J. Arce, *J. Org. Chem.*, **37**, 507 (1972). [b] C. G. Scouten, F. E. Barton, Jr., J. R. Burgess, P. R. Story, and J. F. Garst, *Chem. Commun.*, 78 (1969). [c] D. Lipkin, J. G. Davis, and R. W. Jordan, *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, **13** (2), D40–D64 (1968). [d] R. N. McDonald and D. G. Frichey, *J. Amer. Chem. Soc.*, **90**, 5315 (1968). [e] E. Vogel, H. Kiefer, and W. R. Roth, *Angew. Chem., Int. Ed. Engl.*, 442 (1964). [f] J. S. McKennis, L. Brener, J. R. Schweiger, and R. Pettit, *Chem. Commun.*, 365 (1972).

radical anion would not as readily reduce the alkyl radical to anion. There is at least one sketchy report on reduction/alkylation which supports this possibility.[140] However, it is also entirely possible that little change in reduction/alkylation will be found as Bank has already observed.[61a]

In view of the facile reactions of alkyl halides, it is not surprising that vicinal dihalides react readily with sodium naphthalenide and the disodium salt of phenanthrene. The dihalide is converted to olefin by dehalogenation and this may occur by either cis or trans elimination. This technique has synthetic advantages compared to other vicinal dihalide eliminations,[141] namely high yields, convenience, and shorter reaction times.

Adam and Arce have found that upon treatment of *threo*- and *erythro*-2,3-dibromo-3-methylpentane with sodium naphthalenide dehalogenation occurs principally in a trans fashion.[142] Table XXII shows the threo isomer gives greater yields of the product derived *via* trans dehalogenation (Scheme III). This can be easily accounted for on the basis of lesser steric hindrance in the intermediates (**6b** and **7b**) derived from this isomer. The stereochemical integrity of the radical intermediates must be a

TABLE XXII. Stereochemical Course of the Reaction of *erythro*- and *threo*-2,3-Dibromo-3-methylpentane with Sodium Naphthalenide in DME

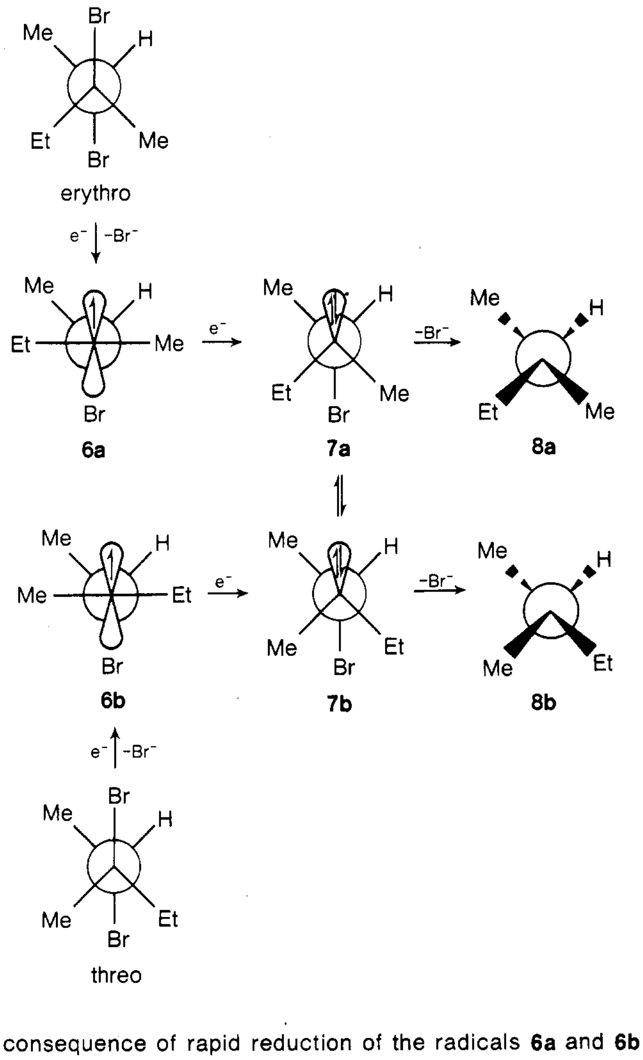
Reactant mixture, %		Product mixture, %		% trans elimination
Erythro	Threo	**8a**	**8b**	
12.2	87.8	15.6	84.3	92.2 ± 0.6
22.2	77.8	23.0	77.0	
78.6	21.4	61.9	38.1	75.6 ± 1.4
79.9	20.1	60.0	40.0	

TABLE XXIII. Percentages of Trans Product in 2-Butenes from Reactions of 2,3-Dihalobutanes with Sodium Naphthalenide in DME[a]

	2,3-Dichlorobutane				2,3-Dibromobutane			
	Excess $N\cdot^-$		Excess $C_4H_8Cl_2$		Excess $N\cdot^-$		Excess $C_4H_8Br_2$	
$N\cdot^-$, *M*	*meso*	*dl*	*meso*	*dl*	*meso*	*dl*	*meso*	*dl*
7.5×10^{-3}	78	*77*	76	*75*	73	*54*	66	39
6.8×10^{-2}	77	*76*	75	*76*	73	*67*	74	*53*
1.3×10^{-1}	77	*78*	76	*75*	79	*62*	76	48

[a] Italicized entries represent instances of dominant cis elimination. In experiments headed Excess $N\cdot^-$, alkyl halides were added to solutions containing a stoichiometric excess of sodium naphthalenide. In experiments headed Excess $C_4H_8X_2$, sodium naphthalenide was added to an excess of dihalide.

SCHEME III

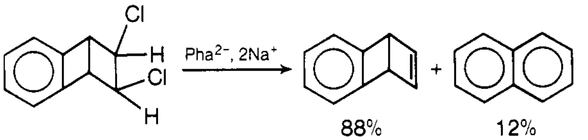


consequence of rapid reduction of the radicals **6a** and **6b** and of bridging by the neighboring bromine in the radicals to reduce the likelihood of bond rotation.[143]

Considering the results of Garst and associates,[144] a stereospecific reduction does not appear to be general. The dehalogenations of 2,3-dihalobutanes with sodium naphthalenide in DME show that either cis or trans elimination may predominate. See Table XXIII.

It is noted that 2,3-dichlorobutane dehalogenates with regioselectivity (same product mixture from *meso* and *dl* isomers) while there is a slight stereospecificity observed for the reactions of 2,3-dibromobutane (bromine being a better bridging atom than chlorine).

That pure cis dehalogenation occurs is seen in one of the reactions studied by McDonald and Frichey.[145] Treatment of **9** with disodium phenanthrene effects dechlorination.

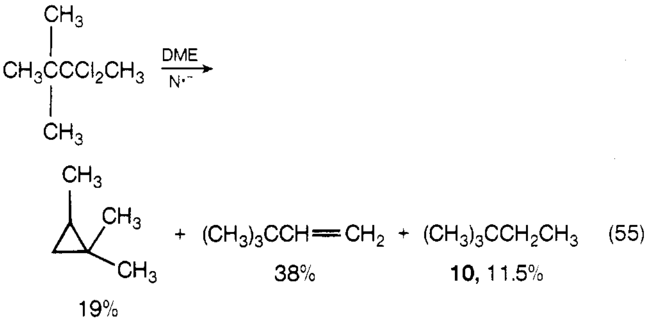


9 (54)

Considering again the results of Adam and Arce and those of Garst, *et al.*, it should be stated that while their observations differ it should not be concluded that there is necessarily a conflict between them (conformational factors are different in the two systems). But it does seem fair to say that dehalogenation, in general, is not highly stereospecific when both cis and trans dehalogenation mechanisms are possible.

Treatment of stilbene dibromides with sodium naphthalenide formed many products.[142] One of these was diphenylacetylene which likely has its origin as dehydrobromination. (It remains to be proven that E2 dehydrohalogenation is a possible reaction of these radical anions.)

Sargent[146] has reported the results of a *gem*-dichloride reaction and has found evidence for a carbene radical anion, hitherto an unreported intermediate. The overall equation is

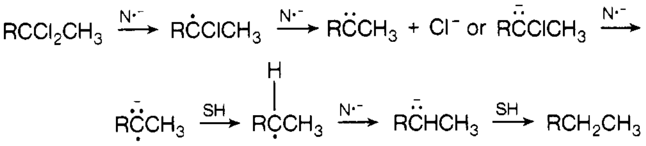


$$CH_3C(CH_3)_2CCl_2CH_3 \xrightarrow[N\cdot^-]{DME} \text{(cyclopropane, 19\%)} + (CH_3)_3CCH{=}CH_2 + (CH_3)_3CCH_2CH_3 \quad (55)$$

38% **10**, 11.5%

He suggests the cyclopropane derivate has a carbene or carbenoid origin, the alkene arising *via* "elimination and reduction reactions." The alkane **10** was proposed to be the product of a carbene radical anion intermediate (Scheme IV).

SCHEME IV



$$RCCl_2CH_3 \xrightarrow{N\cdot^-} R\dot{C}ClCH_3 \xrightarrow{N\cdot^-} R\ddot{C}CH_3 + Cl^- \text{ or } R\overset{-}{\ddot{C}}ClCH_3 \xrightarrow{N\cdot^-}$$

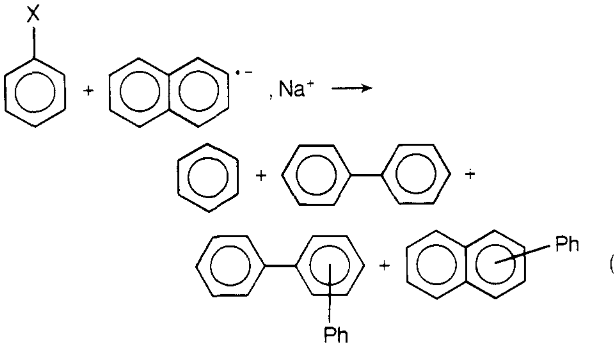
$$R\overset{-}{\underset{\cdot}{\ddot{C}}}CH_3 \xrightarrow{SH} R\overset{H}{\underset{\cdot}{C}}CH_3 \xrightarrow{N\cdot^-} R\overset{-}{\ddot{C}}HCH_3 \xrightarrow{SH} RCH_2CH_3$$

Reaction of aromatic halides with an electron source was apparently recorded first in 1862 when it was found these compounds form their corresponding hydrocarbons upon treatment with metallic sodium.[147] Another early study was that of White, who reduced chlorobenzene with sodium in liquid ammonia.[148] Benzene was the major product; the author presumed this product to be derived from attack of a phenyl radical on ammonia. Aniline, diphenylamine, and triphenylamine were also recovered. Apparently biphenyl was not formed.

Studies with radical anions as the electron source showed the reactions to be fast.[149] Product studies were completed recently by Cheng, Headley, and Halasa.[150] The overall reaction of various aromatic halides with sodium naphthalenide is summarized by eq 56 with yields given in Table XXIV.

TABLE XXIV. Relative Amounts of Identified Products from the Reaction of Sodium Naphthalene with Halobenzene before Hydrolysis

ArX	NaN/ ArX	Temp, °C	% benzene	% biphenyl	% o-terphenyl	% m-terphenyl	% p-terphenyl	% α-phenyl N	% β-phenyl N
Bromobenzene	1/1	−60	86.9	8.7	1.1	0.1	0.1	1.4	0.9
Bromobenzene	2/1	−60	86.5	6.4	0.7	0.2	0.2	0.8	1.0
Bromobenzene	1/1	27	89.7	6.3	0.5	0.3	0.3	0.9	0.7
Bromobenzene	2/1	27	85.0	7.3	1.4	0.4	0.5	1.6	0.7
Fluorobenzene	1/1	−60	72.2	16.9	2.6			1.7	2.0
Chlorobenzene	2/1	−60	82.4	8.6	1.7	0.3	0.2	2.4	1.5
Iodobenzene	1/1	27	84.8	9.8	0.6	0.3	0.3	1.1	0.2

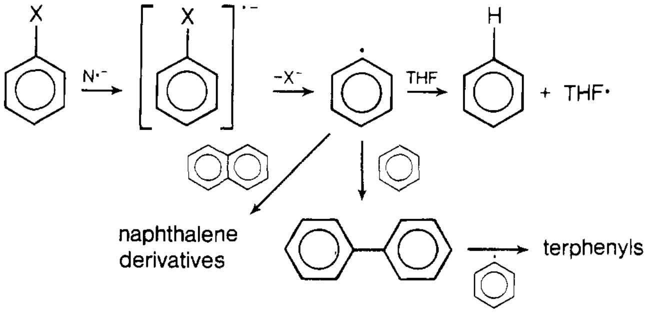


(56)

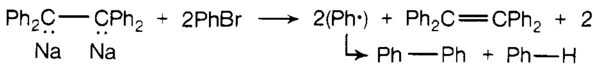
X = F, Cl, Br, I

From the yields it is evident that the product distribution, with the exception of the reaction of fluorobenzene, is independent of the halide. This suggests that the slow step in the reaction is not cleavage of the aryl-halogen bond. These results were interpreted by Cheng, *et al.*, to be accommodated by the mechanism in Scheme V. Cheng, *et al.*, found the following observations to be consistent with the proposed mechanism: (1) the product distribution is independent of the NaN/ArX ratio; (2) a small amount of THF dimer is seen by mass spectroscopy; (3) quenching the reaction with D_2O did not result in the formation of any deuterated benzene, providing evidence against the intermediacy of a phenyl anion.

SCHEME V



These results are compatible with those of Müller and Roscheisen,[151] who interpreted the reaction between disodium tetraphenylethylene and bromobenzene as being consistent with the scheme in eq 57. Müller and Roscheisen used CO_2 as a diagnostic for the presence of the phenyl anion. They isolated no benzoic acid and therefore concluded a radical mechanism was operative.



$$\underset{Na}{Ph_2\ddot{C}}-\underset{Na}{\ddot{C}Ph_2} + 2PhBr \longrightarrow 2(Ph\cdot) + Ph_2C{=}CPh_2 + 2NaBr \quad \llcorner\!\rightarrow Ph-Ph + Ph-H \qquad (57)$$

In a somewhat different environment there is direct evidence for the phenyl anion. After treating fluorobenzene with dilithium biphenyl, carbon dioxide was bubbled into the reaction mixture and benzoic acid was isolated.[107]

Studies more seriously questioning the validity of a radical pathway were published by Sargent.[152] His results are totally at odds with those of Cheng, *et al.* He cites the following observations.

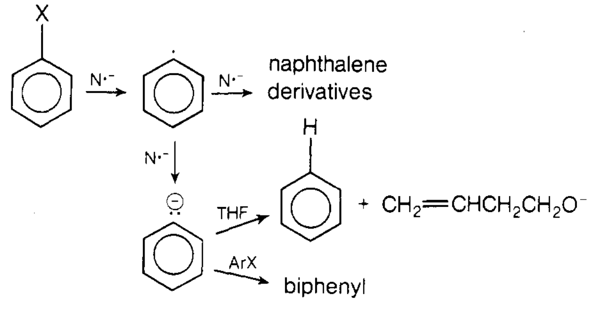
1. Garst has observed that abstraction of a hydrogen from THF by the 5-hexenyl radical does not compete with reduction of that radical to the corresponding anion.[127,153] Furthermore Sargent has determined that the sp^2-hybridized 3-hexen-3-yl radical is reduced to the anion more rapidly than it can extract a hydrogen from THF.[154] These results are in conflict with the proposed pathway to benzene (Scheme I).

2. It is difficult to account for the formation of biphenyl on the basis of the coupling of a phenyl radical with benzene. The benzene for this process can only come from a reaction of aryl halide with sodium naphthalenide, a reaction which concomitantly produces a molecule of naphthalene. Thus, the concentration of naphthalene must always be equal to or greater than that of benzene. Since the phenyl radical has greater affinity[155] for naphthalene than benzene by a factor of 24:1, more phenylnaphthalene than biphenyl would be anticipated by a radical mechanism. Increasing the concentration of benzene by performing the reaction in a solvent which was 40–60 vol % benzene-THF produced no significant difference in the yield of biphenyl.

3. Alkylation of naphthalene has clearly been demonstrated not to involve radical addition to naphthalene, but rather to be a consequence of alkyl radical-radical anion coupling. There are no *a priori* data which would suggest that phenyl radicals behave differently.

Sargent proposed a mechanism which is fully in agreement with the reactions of alkyl halides and sodium naphthalenide (Scheme VI).

SCHEME VI



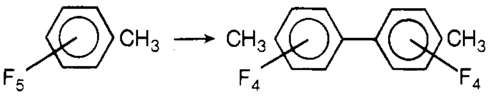
A comparison of the reactions of phenyllithium and sodium naphthalenide is of interest. Upon treatment with phenyllithium, fluorobenzene is converted to unstable *o*-fluorophenyllithium which decomposes to benzyne intermediates.[156] No evidence is seen in the results of Cheng, *et al.*, of similar behavior. Dilithium biphenyl does not preponderantly convert fluorobenzene to a benzyne intermediate either.[107] Electron transfer is the favored process for both the radical anion and dianion.

TABLE XXV. Yields for Reactions of Organic Halides and Trimethylsilyl Chloride with Sodium Naphthalenide[140]

Halide	Molar ratio Me_3SiCl/RX	Yield (%) of $RSiMe_3$
$PhCH_2Cl$	2	90
PhCl	2	60
PhBr	2	40[a]
$CH_2{=}CHCH_2Cl$	3	60
$CH_2{=}CHCH_2Br$	3	23[a]
$CH_3(CH_2)_4CH_2Cl$	2	20[b]
$CH_3CH{=}CHBr$	3	10

[a] The corresponding bromides give lower yields than the chlorides because of the competing reaction with the more reactive unreacted halide. [b] The other products are alkyldihydronaphthalenes and hexane arising from proton abstraction from solvent.

Pentafluorotoluene is reported to form a coupling product (**11**) upon treatment with potassium biphenylide or naphthalenide.[157]



(58)

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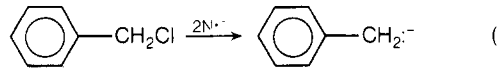
Very little work has been done to explore the possibilities which might arise out of selective electron transfer in an environment of two oxidizing agents. Bank and Bank have explored one such possibility.[158] The study in question concerned the reduction of benzyl chloride by sodium naphthalenide in the presence of trimethylsilyl chloride. Benzyl chloride alone with sodium naphthalene gives bibenzyl. In the absence of benzyl chloride, trimethylsilyl chloride forms disilylated dihydronaphthalenes[159] (see section II.B.5 for a discussion of the reactions of silyl halides), but when sodium naphthalenide is added to a solution of benzyl chloride and trimethylsilyl chloride in THF, a 90% yield of benzyltrimethylsilane is obtained.[158] The results are accounted for on the basis of reduction of benzyl chloride to the anion, which subsequently displaces chloride from the silyl chloride (present in 2:1 excess).



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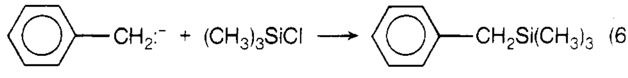


(60)

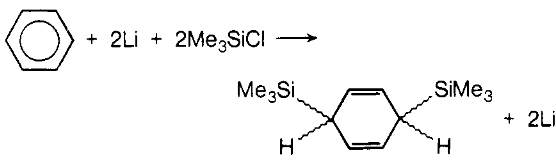
Other examples from the same study are listed in Table XXV.

Treatment of a 1:1 mixture of benzyl chloride and dimethylsilyl dichloride forms dibenzyldimethylsilane in 85% yield. Bank suggested phenyl-substituted silanes could not be prepared in good yield by this method because of "their tendency to form naphthalene derivatives." Also, phenyl-substituted silyl chlorides are prone to "reductive coupling" which forms 1,2-disilanes. This method was suitable, however, for the preparation of phenyl-substituted phosphanes. Benzyl chloride and diphenylchlorophosphine form benzyldiphenylphosphine in 85% yield.

5. Silyl Halides

While investigations abound for the reactions of alkyl halides, little is known about the reactions of silyl halides. The only detailed studies are of the compounds trimethylsilyl chloride and triphenylsilyl chloride. For these compounds the reactions are performed at quite different experimental conditions, the product distributions are certainly dissimilar, and the mechanisms proposed for silylation products are different.

Trimethylsilyl chloride adds to benzene in the presence of metallic lithium and forms, after 8 days, a 45% yield of 3,6-bis(trimethylsilyl)-1,4-cyclohexadiene and a 12% yield of the aromatized analog, 1,4-bis(trimethylsilyl)benzene.[160] The stereochemistry of the cyclohexadiene was not specified. It was also reported that toluene and anisole similarly gave high yields of 1,4-disilylation products (eq 62). The mechanism proposed for this reaction requires the intermediacy of a benzene radical anion (eq 63). This route is essentially the same as the original SN2 proposal for the reactions of alkyl halides.



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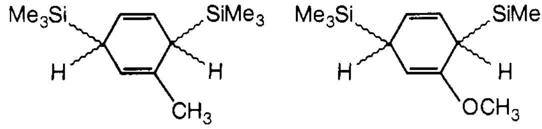

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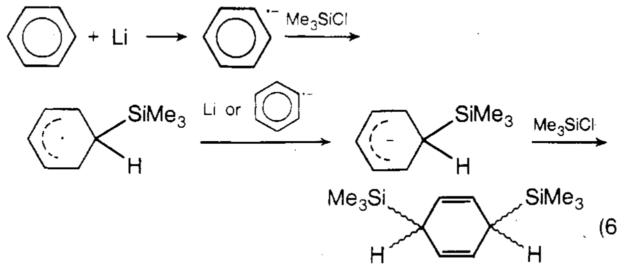
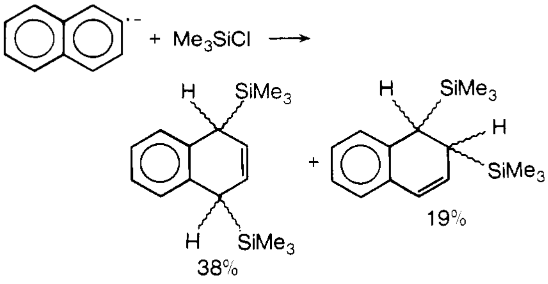


(63)

There are several troubling features concerning this mechanism. The investigators proffered no supportive evidence. There is no report of the fate of the balance of the silyl chloride; one might presume hexamethyldisilane to be a significant product. There was no epr signal of the benzene radical anion at experimental conditions, though this was seen at −80°. From the work of Pines in section II.B.2 one might also be a bit cautious about presuming a hydrocarbon radical anion in this reaction. It will be recalled that Pines found the ethylation of 1-methylnaphthalene with ethylene and sodium required a promoter because the naphthalene would not form a radical anion.

Displacement was also proposed to account for the reaction of sodium naphthalenide with trimethylsilyl chloride.[159]



(64)

Upon treatment with sodium naphthalenide, triphenylsilyl chloride forms hexaphenyldisilane as the major product (eq 65).[161] There is only a low percentage yield of the silylation product (Table XXVI), 1,4-bis(triphenylsilyl)-

TABLE XXVI. Reaction of Triphenylsilyl Chloride with Sodium Naphthalenide

Rxn no.[a]	$C_{10}H_8$-Na^+, mol	Ph_3SiX, mol	Additional reactants (mol)	Time, min	Ph_6Si_2, %	Ph_6Si_2O, %	Ph_3SiH, %	$Ph_3SiC_{10}H_7$, %	12, %
1	0.1	0.1, X = Cl		25	81.9	16.5			1.9
2	0.1	0.1, X = Cl		25	83	9.6			1.9
3	0.1	0.1, X = Cl		20	85.3	10.1			1.6
4	0.1	0.1, X = Cl	$C_{10}H_8$ (0.2)	45	74.0	10.1			4.4
5	0.1	0.1, X = Cl	$C_{10}H_8$ (0.5)	60	62.9	13.1	1.9		5.5
6	0.1	0.1, X = Cl	$C_{10}H_8$ (1.0)	75	61	11.6	1.5	1.3	9.0
7	0.1	0.1, X = F		120	77.6	7.9	1.7	0.9	4.4
8	0.1	0.1, X = F	$C_{10}H_8$ (0.5)	700	51.7	19.1	0.8	1.2	8.4
9	0.1 $C_{10}H_8$-Li^+	0.1, X = Cl		15	89.2				1.6

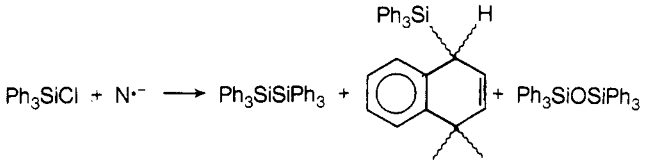
[a] In reactions 2 and 9, the solution of chlorotriphenylsilane was added to the radical anion. In all other cases the radical anion was added to the organosilyl halide. The time of addition is indicative of the relative rate.

TABLE XXVII. Reaction of Sodium Naphthalenide with Aromatic Carbonyl Compounds in THF

Compound	1,2-Diol (%)[a]	Alcohol (%)[a]
Benzaldehyde	1,2-Diphenyl-1,2-ethanediol (88)	Benzyl alcohol (7)
p-Tolualdehyde	1,2-Di(*p*-tolyl)-1,2-ethanediol (90)	*p*-Methylbenzyl alcohol (1)
p-Anisaldehyde	1,2-Di(*p*-methoxyphenyl)-1,2-ethanediol (90)	*p*-Methoxybenzyl alcohol (1)
p-Chlorobenzaldehyde[b]		
Cinnamaldehyde[b]		
Benzophenone	Tetraphenyl-1,2-ethanediol (7)	Benzhydrol (90)
p-Benzoquinone		Hydroquinone (92)

[a] Yields are based on carbonyl compound. [b] Polymeric product formed.

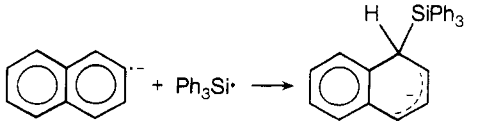
1,4-dihydronaphthalene (12). Attempts to eliminate the silyl ether were unsuccessful and this product was attributed to the oxide coating on the metallic sodium.



(65)

12

Fearon and Young concluded a SN2 mechanism similar to the one proposed for the reaction of trimethylsilyl chloride was not operative because of the dependency of **12** on the concentration of (neutral) naphthalene. Coupling of the triphenylsilyl radical and naphthalenide, the mechanism analogous to the one operative in alkylation, does not account for this reaction either.



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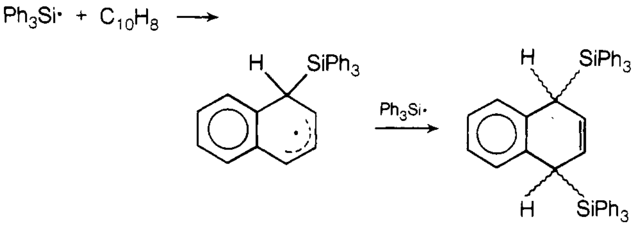
Inverse addition of chlorotriphenylsilane to naphthalenide does not change the amount of silylated naphthalene, and, unlike alkyl halides, the silylation yield is dependent on naphthalene; both observations militate against this path. Another possibility was discounted by the authors. Triphenylsilylithium is known to add to anthracene, and it was considered possible that the anion might add to naphthalene. However, experimental observations were not in accordance with this mechanism. The authors concluded that silylation must be a consequence of combination of the silyl radical with naphthalene.

SCHEME VII

$$Na^+C_{10}H_8^- + Ph_3SiX \longrightarrow Ph_3Si\cdot + C_{10}H_8 + Na^+X^-$$

$$2Ph_3Si\cdot \longrightarrow Ph_6Si_2$$



Thus, the results of the reactions of alkyl halides, trimethylsilyl chloride, and triphenylsilyl chloride are accounted by three distinct mechanisms. While such diversity is not impossible, one might reasonably hope for further verifications. An extremely sensitive mechanistic probe would be provided by the reactions of optically active silyl chlorides.

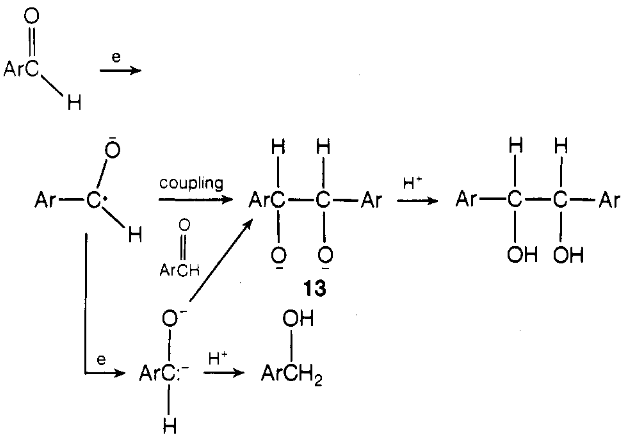
Other reports of the reaction of metal aromatic radical anions are limited. Brown reports the preparation of polydihydrosilylnaphthalenes.[162] 9,10-Dihydro-9-trimethylsilyl-10-triethylsilylanthracene is reported by Petrov.[163] Silylated products have also been cited from the reaction of dilithium naphthalene with dichlorodiphenylsilane.[164] This experiment apparently failed to produce any of the conceptually possible and interesting bridged 1,4-silanes, but resulted in disilylated dihydronaphthalenes.

Silyl radicals are likely intermediates during the reaction of triphenylsilyl bromide with ethylamine and lithium.[165]

6. *Aldehydes and Ketones*

Reactions of aromatic aldehydes and ketones with sodium naphthalenide lead to two products which in all likelihood reflect either a one- or a two-electron reduction.[166] Table XXIV shows that for benzaldehyde and related compounds the major product is diol. The two products likely arise *via* the Scheme VIII, which is consistent with electrolytic reduction. Alcohol could conceivably arise *via* disproportionation of the dianion **13**, but this is not probable in the view of the constancy of the yield with a variation in reaction time and method of quenching. It will be noted from Table XXVII that in those cases where only traces of alcohol are formed an electron-donating group

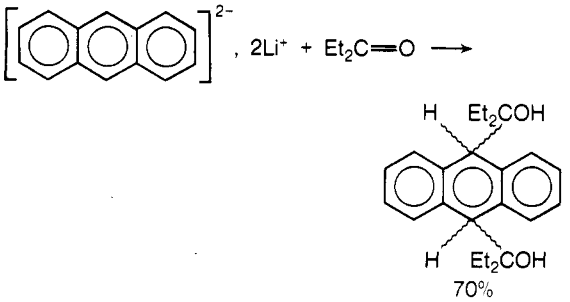
SCHEME VIII



is present para to the carbonyl function. This would, of course, raise the reduction potentials (Table V) and render two-electron reduction less likely. Benzophenone, having a low second reduction potential, is reduced almost entirely to alcohol. Reduction of a benzaldehyde containing an electron-withdrawing group, namely *p*-chlorobenzaldehyde, resulted only in polymer. Apparently the chlorine–aryl carbon was cleaved.

The reactions characteristic of aromatic aldehydes and ketones differ fundamentally from the reactions of their aliphatic analogs. Kaplan[167] reports that lithium biphenylide reacts with a variety of aldehydes and ketones to yield, among other products, derivatives resulting from addition to biphenyl. This author has investigated similar reactions with sodium naphthalenide and isolated products of 1- and 1,4-addition to naphthalene in low yield.[168]

One example of a dianion reaction is known. Dilithium anthracene reacts with 3-pentanone to form 9,10-bis-(pentan-3-ol)-9,10-dihydroanthracene in 70% yield.[169] No mechanism was proposed for this reaction.



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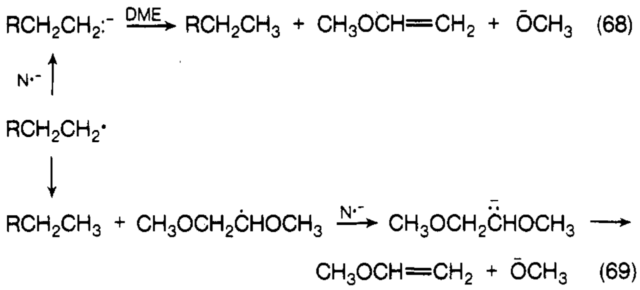
7. *Ether Cleavage*

Ethers are the solvents of choice in the preparation and reactions of alkali metal aromatic radical anions and dianions. As we have already seen, formation of these adducts is highly dependent on solvation, especially of the cation. But ethers themselves react with radical anions and dianions, albeit more slowly than other functional groups. The overall reaction of the ethers is cleavage, and this may occur by the aegis of electron transfer or proton abstraction.

The quenching of many of the intermediates considered earlier in this discussion was shown to occur by reaction between the intermediate and the solvent ether. One prominent example involved the quenching of intermediates derived from alkyl halides. In DME the possible routes are shown in eq 68 and 69.



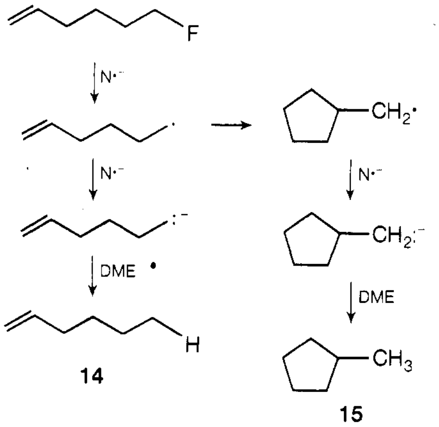
$$RCH_2CH_2:^- \xrightarrow{DME} RCH_2CH_3 + CH_3OCH{=}CH_2 + \bar{O}CH_3 \quad (68)$$

$$RCH_2CH_2\cdot \xrightarrow{N\cdot^-} RCH_2CH_2:^-$$

$$RCH_2CH_2\cdot \longrightarrow RCH_2CH_3 + CH_3OCH_2\dot{C}HOCH_3 \xrightarrow{N\cdot^-} CH_3OCH_2\ddot{\bar{C}}HOCH_3 \longrightarrow CH_3OCH{=}CH_2 + \bar{O}CH_3 \quad (69)$$

Studies on 5-hexenyl fluoride are helpful in choosing between (68) and (69). Garst found that the reduction of 5-hexenyl fluoride with sodium naphthalenide yielded 1-hexene (**14**) and methylcyclopentane (**15**); the reaction paths given in Scheme IX have been suggested.[170] With an excess of sodium naphthalenide the ratio 1-hexene: methylcyclopentane is as much as 40:1, it never falls below 2:1. Consequently, the reaction path *via* (69) is less likely than *via* (68) because it is known that cyclization of these radicals is much faster than hydrogen atom transfer.[153,171] Hence in this reaction the favored path involves proton abstraction.

SCHEME IX



In ethers having one or more components capable of undergoing reduction, the major cleavage mechanism appears to involve electron transfer. This conclusion is based entirely upon the products derived from the reactions found in extant reports because mechanistic studies have not been made.

Angelo[172] investigated the cleavage of several ethers (Table XXVIII). The most likely mechanistic possibility, using benzyl phenyl ether as a model, is analogous to the radical anion reactions elucidated by Kornblum, *et al.*[173] (Scheme X). Reduction of the ether would presumably form the radical anion in which the added electron is in the benzyl ring (**16**). Ejection of phenoxide would form the benzyl radical, which upon reduction and protonation is converted to toluene. Traces of bibenzyl might result from radical coupling, but this is not certain. The high

SCHEME X

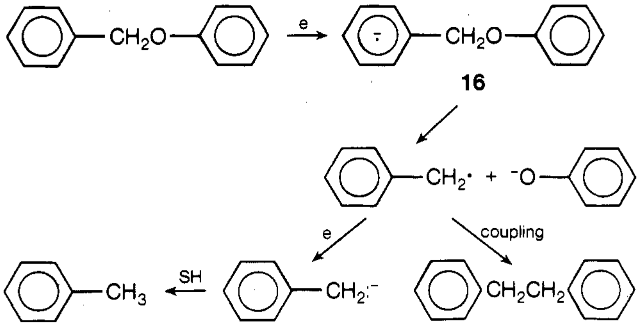


TABLE XXVIII. Cleavage of Ethers with Radical Anions

Ether	Reducing agent	Products	Yield, %
Allyl ethyl ether	Sodium naphthalenide	Biallyl	30
Biallyl ether	Sodium naphthalenide	Biallyl	50
		Allyl alcohol	30
n-Butyl benzyl ether	Sodium naphthalenide	Toluene	Traces
		Bibenzyl	Traces
Benzyl phenyl ether	Sodium naphthalenide	Toluene	30
		Phenol	44
Allyl phenyl ether	Sodium naphthalenide	Phenol	62
		Biallyl	40
Benzylhydryl methyl ether	Sodium naphthalenide	Diphenylacetic acid	50
Methyl triphenylmethyl ether	Sodium naphthalenide	Triphenylacetic acid	80
Dihydro-2,5-furan	Sodium naphthalenide	2-Buten-1-ol	45
	Lithium naphthalenide	Indefinite	
	Lithium biphenylide	Indefinite	

TABLE XXIX. Cleavage Reactions by the 2:1 Lithium-Biphenyl Adduct

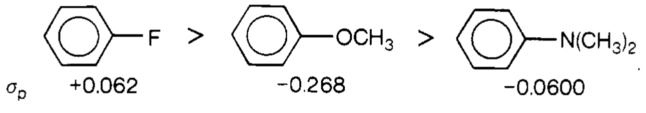
	Reaction conditions			Products[a] (%)	
Compound (mol)	Concn, M	Temp, °C	Reaction time, hr	Major	Other
Anisole (0.10)	0.57	66	2.0	Phenol (55)	*b*
	1.33	66	4.5	Phenol (80)	*b*
N,N-Dimethylaniline (0.10)	0.57	66	24	N-Methylaniline (2)	
Phenyl ether (0.10)	0.57	0	2.0	Phenol (96)	Benzoic acid
Triphenylamine (0.10)	0.57	66	10	Diphenylamine (58)	Aniline (1.6)
Dibenzothiophene (0.10)	0.30	0	2.0	3,4-Benzothiocoumarin (84)	
Carbazole (0.10)	0.57	66	20	Ammonia	
Tetrahydrofuran		66	8.0	*n*-Butyl alcohol	

[a] Products isolated after CO_2 added. [b] A slow, apparent gas evolution was observed.

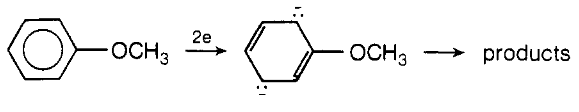
yields of dimer in many reactions raises considerable doubt about this. For example, biallyl ether forms 50% biallyl and 30% allyl alcohol. In view of the facile reduction of alkyl radicals by sodium naphthalenide, a 50% yield of dimer by radical coupling seems much too high. Perhaps dimer is actually the product of a displacement reaction between the allyl carbanion and the ether.

The reaction of benzyl phenyl ether presents the situation where the two aromatic rings have significantly different reduction potentials. The products of this reaction suggest that cleavage always occurs between the benzylic CH_2 and the oxygen, which would also be expected on the basis of the bond strengths of the aliphatic *vs.* aromatic carbon-to-oxygen bonds. Presumably somewhat different systems such as dibenzyl ethers or diphenyl ethers could be designed which would show cleavage at either or both ether links depending on substituent groups.

Eisch, using dilithium biphenyl, studied the cleavage of a variety of ethers, heterocyclics, and hydrocarbons.[107] The products of the various reactions are found in Table XXIX. The ease of cleavage of molecules of the type Ar–Z, where Z = F, OCH_3, or $N(CH_3)_2$, is consistent with the decrease in σ values of the substituents.[174] These



reactions are slow enough that kinetic studies are feasible and the results might best be accounted for by a new σ scale of radical anion values. These reactions were interpreted by Eisch to be the result of a two-electron transfer (shown in eq 70 for anisole). In view of more recent developments, a radical anion mechanism is more likely.



(70)

Electron transfer has also been proposed to account for the cleavage of β-trifluoroethyl ethers as a means of forming alcohols in high yield.[175]

$$ROCH_2CF_3 \xrightarrow{N\cdot^-} ROCH_2\dot{C}F_2 + F^- \xrightarrow{N\cdot^-} ROCH_2\underset{\overset{..}{-}}{C}F_2 \longrightarrow RO^- + CH_2{=\!=}CF_2 \quad (71)$$

There are inherent advantages in the use of alkali metal aromatic radical anions or dianions compared to the use of the metal in effecting ether cleavage. The homogeneous conditions permit the reactions to proceed faster and generally afford higher yields of the cleavage products. The rapidity of the reactions permits lower reaction temperatures. Use of a metal, especially lithium, usually requires an excess to be present, whereas ethers can be titrated with the highly colored radical anion solutions until the color persists, then quenched: this technique allows for the use of stoichiometric amounts of radical anion. Yet another advantage is that this method is successful for compounds which are inert to a metal.

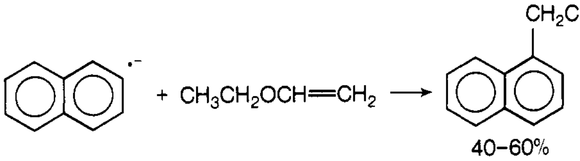
A variety of ether cleavage reactions have been performed with a metal in the absence of an electron carrier such as naphthalene or biphenyl. Mention is made of these reactions simply because mechanistically they ap-

TABLE XXX. Reaction of Sulfur Dioxide with Aromatic Radical Anions[179]

Aromatic	Red. pot., V	Electron affinity, Ev	% electron transfer	% addition
Naphthalene	2.48	−0.01	100	>1
Phenanthrene	2.44	+0.05	100	<1
Pyrene	2.11	+0.42	100	<1
Anthracene	1.96	+0.71	98	<1
Fluoranthene	1.77	+0.93	99	<1
Acenaphthylene	1.68	1.1	90	8

pear to be very similar to the reactions already considered. Some leading references are listed.[176]

In another type of reaction, Watanabe and associates report an alkylation reaction with ethyl vinyl ether.[177] No mechanism is specified.



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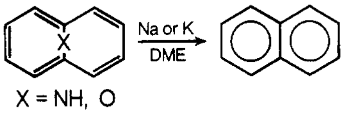
Reactions of the nonalternate hydrocarbons 1,6-imino- and 1,6-oxido[10]annulenes with sodium or potassium in DME are particularly interesting. Elimination of the heteroatom bridge occurs, leading to naphthalene (seen as naphthalenide). No mechanism is proposed for this reaction.[178]



(73)

8. *Sulfur Dioxide, Sulfonates, and Sulfonamides*

The reactions of alkali metal aromatic radical anions with compounds containing sulfur have been limited in scope to sulfur dioxide, sulfonates, and sulfonamides.

Sulfur dioxide combines with typical organometallic reagents such as Grignard reagents to form salts of sulfinic acids. The difference between the typical organometallic reagent and aromatic radical anions is again demonstrated by the observation that sodium naphthalenide undergoes almost exclusively electron transfer.[179] When electron transfer is favorable the aromatic radical anions are poor nucleophiles. The sulfur-containing products of this reaction are sodium thiosulfate (35%), sodium sulfite (35%), and sodium dithionite (30%) and are accounted for by Scheme XI. Dithionite (**17**) is formed by dimerization; this ion is unstable and is known to disproportionate.[180]

SCHEME XI

$$SO_2 \xrightarrow{e} SO_2^{\cdot-} \xrightarrow{\text{dimerize}} \underset{\mathbf{17}}{S_2O_4^{2-}} \xrightarrow{2e} S_2O_3^{2-} + SO_3^{2-}$$

Not unexpectedly, the extent of electron transfer depends upon the comparative electron affinities of the aromatic compound and sulfur dioxide. The electron affinity of SO_2 is 1.0 eV; Table XXX lists these for various aromatic compounds. A comparison of the values shows that only when the electron affinity of the aromatic compound nears that of SO_2, namely for acenaphthalene, any reaction other than electron transfer occurs.

The reaction of the dianion of anthracene (counterion = Na^+, presumably) with SO_2 is a bit puzzling.[179] Only electron transfer takes place. A comparison of the reduction potentials of anthracene shows they are comparable to those of tetraphenylethylene which combines with SO_2. Bank explains that the difference between these compounds is not a matter of charge densities at the reactive sites, because the calculated charge density at the 9 and 10 positions of anthracene is −0.386, whereas the charge density at the 1 and 2 positions of the tetraphenylethylene dianion is −0.312, or less than that of anthracene. The conditions of the reaction are not detailed but perhaps the explanation lies in the interaction of the counterions with the dianions.

N-Substituted aryl sulfonamides undergo facile cleavage with sodium naphthalenide to liberate amines.[181] The cleavage method may have some value in the preparation of pure secondary amines[182] and may conceivably have some applications in peptide synthesis. The overall equation is

$$ArSO_2NHR(Ar) \xrightarrow{N^{\cdot-}} ArSO_2^- + ArH + H_2NR(Ar) \qquad (74)$$

Like so many other reactions, only naphthalenide has been investigated. The results with 3–6 equiv of sodium naphthalenide at room temperature for 1 hr in DME are summarized in Table XXXI.

Several observations are noteworthy. Alkylmethanesulfonamides do not cleave at these experimental conditions. For example, even with 20 equiv of sodium naphthalenide, *N*-octylmethanesulfonamide shows <2% reaction and was recovered after quenching. This contrasts with the results of *N*-*p*-tolyl-*p*-toluenesulfonamide which forms cleavage products in 87% yield. Such disparity is attributable to the difference in reduction potentials; the dialkyl sulfonates do not as readily accept an electron as their aromatic counterparts. In a later paper it was determined that proton abstraction from *N*-octylmethanesulfonamide formed the anion, which, of course, is even less prone to reduction.[183] Treatment of *N*-*p*-tolyl-*p*-toluenesulfonamide with sodium naphthalenide, followed by quenching in air to prevent formation of dihydronaphthalene *via* hydrolysis, is reported to lead to 5 ± 2% dihydronaphthalenes. Thus, electron transfer is clearly the more favorable process even though the amide hydrogen is more acidic than in the N-alkyl analogs.

The reaction is amazingly selective. Conceivably the toluenesulfonamides of dipeptides could cleave at either the peptide or sulfonamide links. But cleavage is highly specific, occurring at the sulfonamide link to free the dipeptides in yields greater than 89% in every case. Aryl halogens do not remain intact, however; *N*-(*m*-chlorophenyl)-*p*-toluenesulfonamide is cleaved to form aniline.[181]

At room temperature 2–6 equiv of sodium naphthalenide is required for sulfonamide cleavage, but at −60 to −80° exactly 2 equiv is sufficient.[183] In fact, the endpoint can be titrated to the persistence of a faint green color. At −70° the only products are the sodium salt of the amine and the sodium arenesulfinate. At higher temperature the aromatic compound and a number of sulfur-containing salts are formed. Adding a large excess of sodium naphthalenide to *N*-ethyl-*N*-phenyl-*p*-toluenesulfonamide at 25° gave the products shown in Table XXXII. The products differ from those observed by Bank in his study of sulfur dioxide. No dithionite was detected and, unlike the SO_2 study, sulfide was one of the products. The products were consistent with the mechanism of eq 75–77 in which the differences with the SO_2 study are accounted for on the basis of the presence of a large excess of sodium naphthalenide in this reaction. High concentration of naphthalenide may permit reaction 76 to compete with 77. The sulfoxylate ion (**18**) is known to disproportionate rapidly to sulfide and sulfite.[184]

TABLE XXXI. Cleavage of Sulfonamides with Sodium Naphthalene[181]

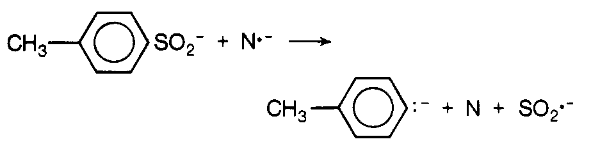
Sulfonamide	Yield of amine, %	Sulfonamide	Amine, %	Sulfonamide	Yield of amine, %
N-*p*-Tolylbenzene	99 (86)[a]	*N*-*p*-Tolyl-*p*-chlorobenzene	89	*N*-Octylmethane	<2
N-Methyl-*N*-phenylbenzene	100	*N*-Methyl-*N*-phenyl-*p*-chlorobenzene	67	*N*-*p*-Tolylmethane	9
N-Octylbenzene					
		N-*p*-Tolyl-*p*-bromobenzene	89	*N*-Methanesulfonylpiperidine	0
N-*p*-Tolyl-*p*-toluene	87 (93)	*N*-*p*-Tolyl-*p*-acetamidobenzene	80	*N*-Methyl-*N*-phenylmethane	92
Sodium salt	88				
N-*p*-Anisyl-*p*-toluene	98 (94)	*N*-*p*-Tolyl-*p*-methoxybenzene	95 (83)	*N*,*N*-Diphenylmethane	94
N-Phenyl-*p*-toluene	(97)				
N-Hexyl-*p*-toluene	(96)	*N*-Methyl-*N*-phenyl-*p*-methoxybenzene	92		
N-Octyl-*p*-toluene	98 (95)			*N*-*p*-Toluenesulfonylglycylglycine	87
N-(2-Heptyl)-*p*-toluene	(91)				
		N-*p*-Tolyl-β-naphthalene	89 (93)	*N*-*p*-Toluenesulfonyl-DL-alanyl-DL-leucine	95
N-(1-Phenylethyl)-*p*-toluene	(98)	*N*-Methyl-*N*-phenyl-β-naphthalene	91	*N*-*p*-Toluenesulfonyl-DL-leucyl-DL-alanine	93
N-(m-Chlorophenyl)-*p*-toluene	(94)	*N*-Octyl-α-toluene	84	*N*-*p*-Toluenesulfonyl-DL-alanyl-DL-valine	89
N-Methyl-*N*-phenyl-*p*-toluene	96 (68)	*N*-α-Toluenesulfonylpiperidine	62	*N*-*p*-Toluenesulfonyl-DL-alanyl-DL-phenylalanine	96
N-*p*-Toluenesulfonylpiperidine	82				

[a] Figures in parentheses refer to yields in THF.

TABLE XXXII. Products from the Cleavage of *N*-Ethyl-*N*-phenyl-*p*-toluenesulfonamide with Sodium Naphthalenide in DME at 25°[a]

Expt no.	Molar ratio of arenide to sulfonamide[b]	Toluene	Ethylaniline	Na_2S	Na_2SO_3	$Na_2S_2O_2$[c]
1	9	85	100	20	29	32
2	7	78	99	23	28	46

[a] Reaction time = 12 hr. [b] Yield based on sulfonamide. [c] Calculated on the basis of sulfur content. Reproduced by permission of the editors.


(75)

$$SO_2^{\cdot -} + N^{\cdot -} \longrightarrow \underset{\mathbf{18}}{SO_2^{2-}} + N \qquad (76)$$

$$2SO_2^{\cdot -} \longrightarrow S_2O_4^{2-} \qquad (77)$$

Absolute rate constants are difficult to obtain for sulfonamide cleavage because the reactions are so rapid. However, competition experiments have shown the rate to be given by[183]

$$d[\text{amine}]/dt = k[\text{sulfonamide}][\text{Ar}^{\cdot -}] \qquad (78)$$

Two mechanisms were considered to be consistent with experimental findings.

$$\text{Ar}^{\cdot -} + \text{sulfonamide} \xrightarrow{\text{slow}} \text{intermediate(s)} \xrightarrow[\text{fast}]{\text{Ar}^{\cdot -}} \text{products} \qquad (79)$$

$$\text{Ar}^{\cdot -} + \text{sulfonamide} \underset{}{\overset{\text{fast}}{\rightleftharpoons}} \text{Ar} + [\text{sulfonamide}]^{\cdot -} \xrightarrow{\text{slow}} \text{intermediate(s)} \xrightarrow[\text{fast}]{\text{Ar}^{\cdot -}} \text{products} \qquad (80)$$

To distinguish between these possibilities it was thought that the relative rates of cleavage of a pair of arenesulfonamides should be dependent on the electron source if the former mechanism applies, independent of the electron source if the latter mechanism applies. So the relative rates of cleavage of *N*-methyl-*N*-phenyl- and *N*,*N*-di-*n*-butyl-*p*-toluenesulfonamide were determined in the presence of four radical anions. The data in Table XXXIII show that the relative rate of cleavage is dependent on the source of electrons.

TABLE XXXIII. Relative Rates of Cleavage of *N*-Methyl-*N*-phenyl- (a) and *N*,*N*-Di-*n*-butyl-*p*-toluenesulfonamide (b) by Arene Anion Radicals in DME at 25°

k_a/k_b	Anion radical	$-\epsilon$ vs. sce[a]
1.31 ± 0.06	Sodium biphenylide	2.70
1.26 ± 0.06	Sodium naphthalenide	2.50
10 ± 2	Sodium pyrenide	2.11
36 ± 4	Sodium anthracenide	1.96

[a] Half-wave reduction potential of arene in 75% aqueous dioxane (from ref 25).

It was thus concluded the *modus operandi* was given by eq 79. However, the selection does not seem entirely justifiable on the basis of this experiment. For initial electron transfer to be the slow step is highly unusual, and the relative rate experiments can be interpreted in another way. The reduction potentials of the two amides would be expected to differ, with *N*-methyl-*N*-phenyl-*p*-toluenesulfonamide having the lower value. Biphenylide, by virtue of its intrinsic reducing power, would not be expected to be very selective in its reactions, and electron transfer to all amides would be essentially complete. The half-wave reduction potential of anthracene is closer to those of the amides, and thus electron transfer would be expected to be more selective. Formation of the radical anion of *N*-methyl-*N*-phenyl-*p*-toluenesulfonamide would be favored, so cleavage would occur preferentially in this compound.

Not surprisingly, the cleavage of toluenesulfonates also occurs readily, and alcohols are recovered in high yield (Table XXXIV). These reactions were performed at −80°

TABLE XXXIV. Cleavage of Toluenesulfonates with Sodium Naphthalenide

Toluenesulfonate	Sodium naphthalenide to toluenesulfonate, equiv	Yield of alcohol, %
Cyclohexyl	2–6	100
Cyclopentyl	6	98
cis-4-Cyclooctenyl	3	98
Menthyl	6	98
Phenyl	6	99
Stearyl	6	99
Neopentyl	5	85
2-Phenylethyl	6	99
2-(1-Naphthyl)ethyl	6	98
2-Octyl	6	99
exo-*cis*-Bicyclo[3.3.0]octan-2-yl	6	100
exo-Norbornyl	6	95
2,2-Dimethyldioxolane-4-methyl	6	98
Phenylcyclopentylcarbinyl	6	60

with 2–6 equiv of sodium naphthalenide.[185] Sodium phenanthrenide appears to work almost as well, whereas, sodium anthracenide reacts more slowly and gives lower yields.

As with sulfonamides, alkyl alkanesulfonates do not give good yields of cleavage alcohol. The sulfonates do react, however; for example, octadecylbutanesulfonate forms 44% octadecyl alcohol and 20% pentadecane, and about 30% is presumably converted to alkylated dihydronaphthalenes. The product distribution is sensitive to the concentration of sodium naphthalenide: as the naphthalenide increases there is formed an increasing percentage of alcohol. This result is consistent with the mechanism of eq 81–83,[186] with increasing naphthalenide favoring eq 83.

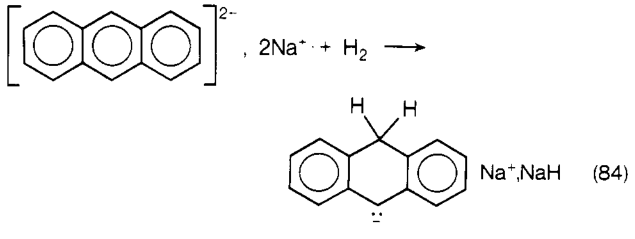
$$R'OSO_2R + N^{\cdot -} \rightleftharpoons R'OSO_2R^{\cdot -} + N \quad (81)$$

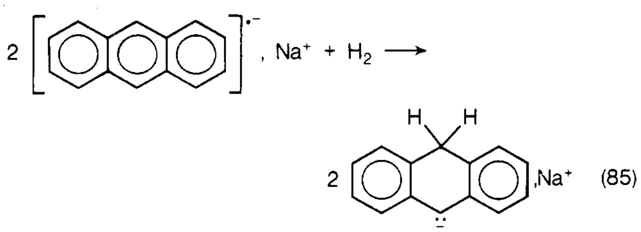
$$R'OSO_2R^{\cdot -} \longrightarrow R'^{\cdot} + RSO_3^- \quad (82)$$

$$R'OSO_2R^{\cdot -} + N^{\cdot -} \longrightarrow \longrightarrow R'O^- + RSO_2^- + N \quad (83)$$

9. *Hydrogen and Nitrogen*

The radical anion and dianion of anthracene react with molecular hydrogen to form adducts, but they do so by different routes. Heterolytic cleavage of hydrogen occurs in the presence of the dianion.[187] The radical anion causes both heterolytic and homolytic fission of hydrogen, the latter process being shown in eq 85. Whether these products are formed by direct combination or initial electron transfer has not been determined.


(84)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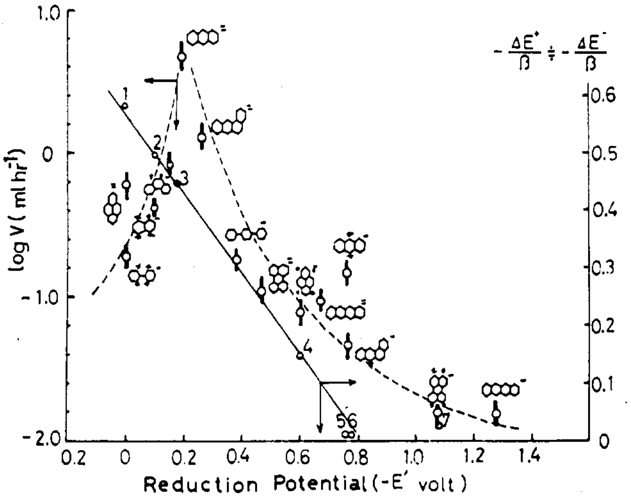
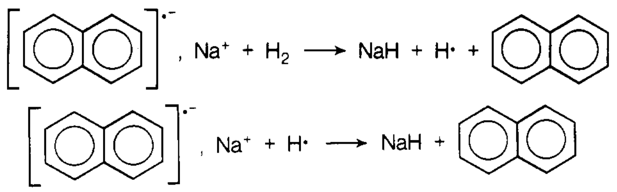


Figure 9. (– – –), the plot of the rate of hydrogen adsorption against the reduction potential for each anion radical and dianion; (——), the plot of the localization energy of each acceptor molecule against the reduction potential for its anion radical; (1) biphenyl, (2) naphthalene, (3) phenanthrene, (4) pyrene, (5) anthracene, (6) 1,2-benzoanthracene, (7) perylene. Reproduced by permission of the editors of the *Journal of the American Chemical Society.*

The 9-monohydroanthracene anion, under different conditions, does eliminate hydride.[188] Ejection of the hydride is a step in the hydrogenation of butadiene to 1- and 2-butenes with sodium anthracenide or the corresponding dianion.

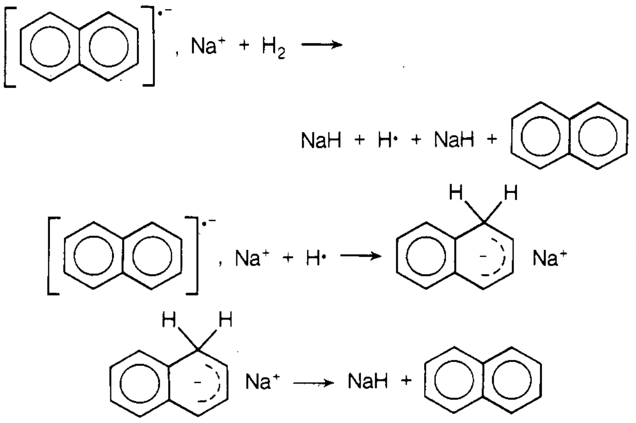
With naphthalenide an entirely different process predominates.[189] Naphthalenide donates an electron to hydrogen to effect its fission; this is shown in Scheme XII.

SCHEME XII



Naphthalenide also combines with atomic hydrogen (Scheme XIII). Experiments with deuterium indicate this route is minor.

SCHEME XIII



The rates of reaction have been measured for a number of radical anions and dianions.[190] These are shown in Figure 9. The rate of reaction seems to be a compromise

TABLE XXXV. Nitrogen Fixation in the Presence of Radical Anions

Transition metal complex	Metal radical anion	Pressure N_2	NH_3/mol of TM complex	Ref
Ti(O-isopropyl)$_4$	$N\cdot^-$ (generated electrolytically)			a
$FeCl_3$	Li_2N		0.82	b
$(C_5H_5)_2Ti$	NaN	1 atm	0.6	c
Ti(O-*n*-hexyl)$_2$	NaN	1 atm		
Ti(O-isopropyl)$_4$	NaN	1 atm	3.5	d
VCl_3	LiN	120	2.0	e
$CrCl_3$	LiN	120	1.2	
$TiCl_4$	LiN	120	1.3	
Cp_2TiCl_2	LiN			f

[a] E. E. van Tamelen and D. A. Seeley, *J. Amer. Chem. Soc.*, **91**, 5194 (1969). [b] L. G. Bell and H. H. Brintzinger, *ibid.*, **92**, 4464 (1970). [c] E. E. van Tamelen, R. B. Fechter, S. W. Schneller, G. Boche, R. H. Greeley, and B. Akermark, *ibid.*, **91**, 1551 (1969). [d] E. E. van Tamelen, G. Boche, and R. Greeley, *ibid.*, **90**, 1677 (1968). [e] G. Henrici-Olivé and S. Olivé, *Angew. Chem., Int. Ed. Engl.*, **6**, 873 (1967). [f] E. E. van Tamelen, D. Seeley, S. Schneller, H. Rudler, and W. Cretney, *J. Amer. Chem. Soc.*, **92**, 5251 (1970).

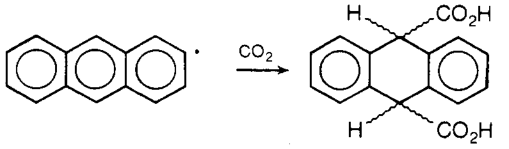
between the electron densities at particular carbons and the electron-donating ability.

Isolation of the first simple chemical complex of molecular nitrogen was reported in 1965 by Allen and Seroff.[191] The following year Vol'pin and Shur announced the chemical fixation of nitrogen.[192] Their technique involved treating $CrCl_3$, $MoCl_5$, WCl_6, $FeCl_3$, or $TiCl_4$ with ethylmagnesium bromide in ether solution under 150 atm of nitrogen. After quenching with acid they were able to recover an average of about 0.12 mol of ammonia/mol of transition metal.

Since this initial discovery, a number of refinements have been made. One of the most important of these has been the use of metal aromatic radical anions as the source of electrons. The advantages of radical anions compared to Grignard reagents include the following: (1) the electron transfer from a Grignard reagent is not as favorable as from a radical anion; (2) Grignard reagents are better bases and nucleophiles than are aromatic radical anions which means they undergo competitive reactions more readily. Some preparative results of the radical anion technique are summarized in Table XXXV.

10. Carbon Dioxide

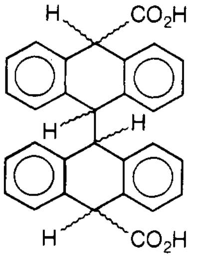
Carboxylation was one of the earliest reactions of radical anions investigated.[15,17,98,193,194] Much of the early work was done by Schlenk and Bergmann and Ziegler in the 1920's, and by Scott in the 1930's.[194] Anthracene, naphthalene, and phenanthrene radical anions have all been treated with carbon dioxide. The major products in these reactions are dicarboxylic acids. Anthracenide, for example, forms 9,10-dihydro-9,10-dicarboxyanthracene (eq 86).[15] It was also reported that 10,10′-dicarboxy-9,9′,10,10′-tetrahydro-9,9′-bianthryl (**19**) was formed.[97] This was discounted later by Adams.[98]



(86)

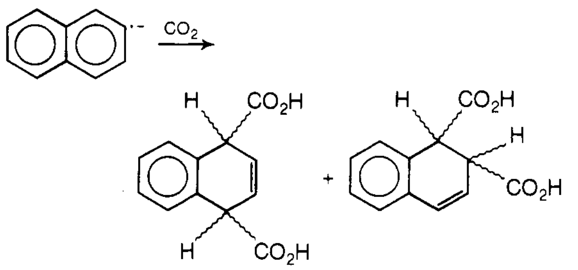
TABLE XXXVI. Yields of Dihydronaphthalene Dicarboxylic Acids Obtained by Carbonation of Preformed Sodium Naphthalenide[18]

Solvent	Carbonation temp, °C	1,4 acids	1,2 acids	Total acids
DME	29–36	7		51
Dimethyl ether	*Ca.* −30	25		74
Dimethyl ether	−68 to −73	44	32	94
DME	−60 to −70	44	30	83
DME	−76 to −82	51	29	84
DME	−60 to −70	28	63	91
	−65 to −70	28	64	92

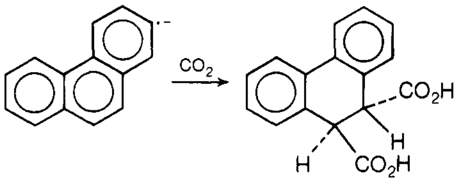


19

Naphthalenide[15,18,194] and phenanthrenide[98] also form dicarboxylic acids (eq 87 and 88). The mechanism of carboxylation is not established. Weissman proposed a nucleophilic path in 1956, but this route has not received experimental confirmation.[92] The lower yield in DME at higher temperature is likely attributable to decomposition of naphthalenide. Other differences between DME experiments probably are related to product isolation procedures.



(87)



(88)

Carbon monoxide is reported to react with the radical anions of naphthalene, anthracene, and biphenyl to form dihydroaromatic adducts.[195]

11. Aliphatic and Aromatic Esters

The only published study of the reaction of an ester with an alkali metal aromatic radical anion is by Machtinger, who reported a 60% yield of monolaurylnaphthalene obtained from reaction of sodium naphthalenide and ethyl laurate.[196]

Preliminary unpublished experimental results from our own laboratory suggest the alkylation product(s) to be a dihydronaphthalene derivative(s). Mono- and 1,2- and 1,4-dialkylated products are formed in varying amounts depending on the aliphatic ester. Reaction of ethyl benzoate with sodium naphthalenide results in conversion to benzoin and benzil, products originating *via* routes in which the naphthalenide functions as an electron donor.

TABLE XXXVII. Selected Polymer References

Authors	Reference	Date	Chem. Abstr.	Monomer	Metal aryl	Comment
A. Gourdenne, P. Sigwalt	Bull. Soc. Chim. Fr., 1967(10), 3678		68:13445c	Conjugated dienes, isoprene	NaN NaB	Block polymers
A. Gourdenne, P. Sigwalt	Bull. Soc. Chim. Fr., 1967(10), 3685		68:13446d	Butadiene, isoprene, ethylene sulfide	NaN, NaB	Block copolymers
H. Calvayrac, J. Gole	Bull. Soc. Chim. Fr., 1968(3), 1076		68:115299a	Vinyl chloride	LiN	
J. C. Favier, S. Boileau, P. Sigwalt	Eur. Polym. J., 1968, 4(1), 3		68:87616f	Propylene sulfide	NaN	
Y. Minoura, H. Hironaka, T. Kasabo, Y. Ueno	J. Polym. Sci., Part A-1, 1968, 6(10), 2773		68:78074w	Styrene, chlorinated ethylene	NaN	Copolymer
S. Okahe, K. Shiina, Y. Minouva	Kogyo Kagaku Zasshi, 1967, 70, 1247		68:13460d	*p*-Xylene dichloride	MAr	
T. Nakajima, Y. Nagai, H. Haung, Y. Kwon	Kogyo Kagaku Zasshi, 1968, 71(4), 568		69:59612d	Unsaturated aldehydes	NaN, KN	
I. V. Andreev, M. M. Koton, Yu. P. Germanchuk, L. Y. Madorskaya, E. I. Pokrovskii, A. I. Kol'tsov	Khim. Atsetilena, 1968, 386		70:115658h	Methacrolein	NaN	
A. F. Podol'skii, E. P. Skvortsevich, A. A. Korotkov	Vysokomol. Soedin., Ser. A, 1969, 11, 266		70:97250m	α-Methylstyrene	NaN	
B. J. Schmitt, G. V. Schulz	Makromol. Chem., 1969, 121, 184		70:78428k	Styrene	NaN	
Y. Tsunashima, K. Sakato, M. Fukatsu, M. Kurata	Bull. Inst. Chem. Res., 1968, 46, 37		70:12025v	α-Methylstyrene	NaN	
S. Numoto, Y. Yamashita	Kogyo Kagaku Zasshi, 1968, 71(12), 2067		70:47947z	Diphenylketene aldehydes	NaN	
M. Benes, J. Peska, O. Wichterle	J. Polym. Sci., Part C, 1967, (16), 555		70:20389g	Tetrolonitrile	LiN	
H. Naarmann, E. G. Kastning	Fr. 1,513,578, Badische Anilin	2/68	70:78964g	1,3-Dienes and isocyanates	NaN	Copolymer
Y. Iwakura, K. Uno, T. Takiguchi	J. Polym. Sci., Part A-1, 1968, 6(12), 3345		70:38316r	Polyketone	MAr	
K. Noro, H. Takida	Japan 68 18,149, Japan Syn. Chem.	8/68	70:38316r	Isobutyraldehyde	KN	
K. Noro, H. Takida	Japan 68 18,155	8/68	70:38317s	Aldehyde–isocyanate	MAr	
K. Ito, T. Sugie, Y. Yamashita	Makromol. Chem., 1969, 125, 291		71:50557y	Methyl methacrylate, benzyl methacrylate	NaN	Copolymer
K. S. Dennis	U. S. 3,458,491, Dow	7/69	71:71394h	α-Methylstyrene	NaA	
P. Rempp, H. Benoit, P. Weiss	Fr. 1,552,263, Centre Natl. Rech.	1/69	71:39754q	Styrene, methyl methacrylate, 2-vinylpyridine	NaN	
K. Hashimoto, H. Sumitomo	J. Polym. Sci., Part A-1, 1969, 7(6), 1549		71:71026q	β-Cyanopropionaldehyde	NaN	
L. N. Moskalenko, A. A. Arest-Yakubovich, S. S. Medvedev	Vysokomol. Soedin., Ser. B, 1969, 11(6), 395		71:82336s	Butadiene	MB	
L. N. Moskalenko, A. A. Arest-Yakubovich, S. S. Medvedev	Vysokomol. Soedin., Ser. B, 1969, 11, 395		71:82336s	Butadiene	MB	
H. Sato, T. Tsuruta	J. Macromol. Sci. Chem., 1970, 4(2), 295		72:55943b	α,β-Unsaturated aldimines	MAr	
K. Suga, S. Watanabe, T. Fujita, M. Kuniyoshi	Yukagaku, 1969, 18, 878		72:66508q	Styrene derivatives	LiN	
T. Goto, Y. Kishi, S. Yoshida	Japan 70 05,792, Electro. Chem. Ind.	2/70	72:133418a	Acetaldehyde	LiN	
	Bull. Chem. Soc. Jap., 1970, 43, 148		72:67321h	Butadiene, 1,1-diphenylethylene	MAr	Copolymer
J. E. Figueruelo	Makromol. Chem., 1970, 131, 63		72:79580g	Methyl methacrylate	MB	
J. C. Bevington, D. O. Harris, F. S. Rankin	Eur. Polym. J., 1970, 6(5), 725		73:25901g	Methyl and cyclohexyl methacrylates	NaN	
H. Takida	Japan 70 10,950, Japan Syn. Chem.	4/70	73:26066h	Aldehydes	LiN	
I. Mita, S. Yabe, I. Imai, H. Kambe	Makromol. Chem., 1970, 137, 133		73:88195h	Aldehydes	NaN	
P. Weiss, G. Hild, J. Herz, P. Rempp	Makromol. Chem., 1970, 135, 249		73:46169x	Styrene and divinylbenzene	NaN	Block copolymer
K. S. Dennis	U. S. 3,530,105, Dow	8/70	73:99386x	Styrene and derivatives	MAr	

TABLE XXXVII (Continued)

Authors	Reference	Date	Chem. Abstr.	Monomer	Metal aryl	Comment
M. Janic, J. Milan, J. Peska	Makromol. Chem., 1970, 138, 99		73:121004v	Phenylpropiolonitrile	NaN	
K. Suga, S. Watanabe, S. Tanaka	Japan 70 09,924, Mitsubishi	4/70	73:87400j	Isoprene	LiN	
A. A. Solov'yanov, K. S. Kazanskii	Vysokomol. Soedin., Ser. A, 1970, 12(9), 2114		73:13403p	Ethylene oxide	MN	
I. V. Kamenskii, V. V. Kulakov, N. M. Romanov	USSR 275,392	7/70	74:4180j	Furfurylidene ketone	NaN	
I. A. Livshits, Y. B. Podol'nyi	Vysokomol. Soedin., Ser. B, 1971, 13, 140		74:112502z	1,3-Butadiene, isoprene	NaN	
K. S. Dennis	U. S. 3,534,012	10/70	74:42847	Halogenated styrenes	NaN, NaB	
G. F. D'Alelio	U. S. 3,502,239	2/71	74:88371h	Styrene-2-butyn-1-yl methacrylate	NaN	
G. F. D'Alelio	U. S. 3,562,236, Geigy	2/71	74:88460m	Butyne methacrylates	NaN	
H. Yakida, T. Moriyama	Japan 71 02,264, Japan Syn. Chem.	1/71	74:2669j	Aldehydes	MAr	Graft polymers
P. Q. Tho	J. Polym. Sci., Part B, 1970, 723		74:23186g	Isoprene	LiN NaN	
R. L. Williams, D. H. Richards, D. A. Salter	Brit. 1,211,193, Natl. Res. Dev. Corp.	11/70	74:13572r	α-Methylstyrene	NaN	
H. Takida	Japan 70 31,468, Japan Syn. Chem.	10/70	74:13614f	Acetaldehyde	LiN	
I. A. Livshits, Yu. B. Podol'nyi	Vysokomol. Soedin., Ser. A, 1970, 12(12), 2655		74:42730w	Conjugated dienes	NaN, NaB	
T. Warakai	Ger. Offen. 1,950,312	1/71	74:63886s	Propene ethers	K Py K B	
I. A. Livshits, Yu. B. Podol'nyi	Vysokomol. Soedin., Ser. A, 1970, 12, 2655		74:42730w	Butadiene	NaN NaB	
A. I. Soshko			74:112565x	Tetrafluoroethylene	LiN	
T. Warakai, H. Kawaguchi, T. Saegusa	Ger. Offen. 1,950,312	1/71	74:63886s	Propylene, ethylene	NaPy KB	
M. Amagasa, T. Goto, K. Maramori, T. Saito	Kobunshi Kagahu, 1971, 28, 60		75:22056y	Isoprene	LiAr	
Japan Oil Co., Ltd.	Brit. 1,248,549	10/71	75:151342n	Propene, ethene	KB	
V. N. Zgonnih, L. A. Shibaev, N. I. Nikolaev	Kinet, Mech. Polyreactions, Int. Symp. Macromol. Chem. Prepr., 1969, 4, 319		75:64363b	Ethylene oxide, styrene	NaB	
V. V. Kulahov, I. V. Kamenshii, I. G. Maslekha	Tr. Mosk. Khim-Teknol. Inst., 1970, 187–9		75:77374f	Monofurfurylideneacetone	MAr	
M. Amagasa, T. Goto, K. Muramori, T. Saito	Kobunshi Kagaku, 1971, 28, 60–9		75:22056y	Isoprene	MAr	
T. Cheng, A. F. Halasa	Fr. 2,066,564, Firestone	9/71	76:142116k	Butadiene	NaN	
S. Horiie, S. Kurematsu, S. Asai	Ger. Offen. 2,120,232, Electro Chem.	12/71	76:114502q	Styrene, butadiene	LiB	
C. P. Pinzaai, J. Brossas, F. Clouet, D. Reyx	C. R. Acad. Sci., Ser. C, 1972, 274(5), 502		76:142032e	Isoprene, butadiene	LiN	
Y. Avny, G. Marom, A. Zilkha	Eur. Polym. J., 1971, 7(8), 1037		76:34623q	Vinylnaphthalene, styrene	MAr	

This pattern is consistent with that observed with aliphatic and aromatic aldehydes and ketones.

12. *Miscellaneous Reactions*

One of the problems encountered in synthesis with hydrocarbon radical anions is that separation of the hydrocarbon (*e.g.*, naphthalene) from the products is often difficult. Bank[197] has found that α-dimethylaminonaphthalene reacts similarly to sodium naphthalenide and is easily recoverable by extraction. Use of this reagent in future research appears highly attractive.

Sodium biphenylide transfers an electron to triphenylborazine.[198]

$$(C_6H_5)_3B_3N_3H_3 + B\cdot^- \longrightarrow (C_6H_5)_3B_3N_3H_3\cdot^- + B \quad (89)$$

This behavior is consistent with the reactions of borazine in metal–ammonia[199] and one electron polarographic reduction.[200] When the resulting solution is treated with methyl iodide, sodium iodide precipitates.[198] Apparently the borazine radical anion serves as the electron donor and the borazine is not methylated in the process. Quite a different reaction occurs with tetramethylborazine: treatment with sodium biphenylide results in proton abstraction.

$$(CH_3)_4B_3N_3H_2 + B\cdot^- \longrightarrow (CH_3)_4B_3N_3\bar{H} + BH\cdot \quad (90)$$

Adding methyl iodide to this solution causes methylation of the borazine.

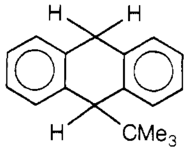
$$(CH_3)_4B_3N_3{}^-H + CH_3I \rightleftharpoons (CH_3)_4B_3N_3(CH_3)H + I^- \quad (91)$$

Compton and Lagowski[198] also investigated the reactions of $Mn(CO)_5Br$, $(C_6H_5)_3SnCl$, and $(C_6H_5)_2PCl$ with biphenylide, determining that the reactions had the stoichiometry given in eq 92.

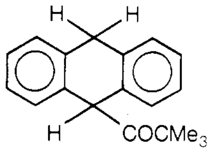
$$2B^{\cdot -} + 2MX \longrightarrow 2B + MM + 2X^- \qquad (92)$$

$$MX = Mn(CO)_5Br,\ (C_6N_5)_3SnCl,\ (C_6H_5)_2PCl$$

Lithium anthracenide[201] is reported to react with trimethylacetonitrile to yield, after hydrolysis, **20** and **21**.



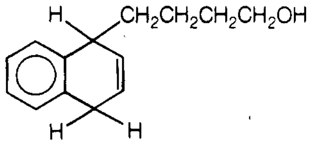
20, 22%



21, 43%

The minor product suggests the intermediacy of the nitrile radical anion, which appears to have expelled CN^- to leave a tertiary butyl radical; the radical then combines with anthracenide. The major product could arise either by nucleophilic attack by anthracenide on the neutral nitrile or by coupling of the nitrile radical anion with anthracenide or anthracene.

Photolyzing lithium naphthalenide in THF brings about ring opening of THF and combination with the naphthalene nucleus.[202] Similar products are derived from anthracenide, phenanthrenide, and pyrenide. Cleavage of an iron complex is reported by Nesmeyanov and Vol'kenau.[203] Sodium naphthalenide is the electron source.

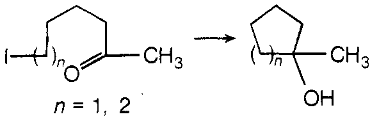


22

$$2[C_6H_6FeC_5H_5]BF_4 + 2[C_{10}H_8]^{\cdot -},Na^+ \xrightarrow{THF} (C_5H_5)_2Fe + 2C_6H_6 + [Fe] + 2NaBF_4 + 2C_{10}H_8 \qquad (93)$$

Group VIb metal carbonyls are conveniently prepared with the aid of sodium naphthalenide. Chromium hexacarbonyl was prepared by treating $CrCl_3$ with sodium naphthalenide under a pressure of 3500 psi of CO.[204] In similar reactions, $W(CO)_6$ and $Mo(CO)_6$ were prepared from WCl_6 and $MoCl_5$. The advantages of this method are (1) the reducing agent can be handled in solution and pumped into the metal-salt CO solution and (2) the reagent can be mixed at room temperature without excessive reduction of the metal salt to free metal.

Nickel tetraphenylporphine is reduced to $NiTTP^{2-}$ by lithium naphthalenide. $NiTTP^{2-}$ is an effective reagent for the cyclization shown in eq 94.[205]



(94)

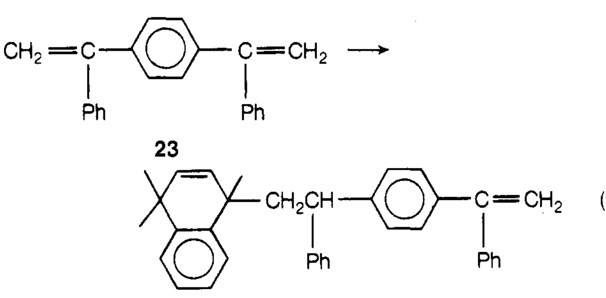
Cobalt(II) chloride was reduced to metal with sodium naphthalenide.[206]

Reductive coupling occurs in the reaction of an aromatic nitro compound with sodium naphthalenide. Nitrobenzene forms azobenzene and/or azoxybenzene, depending on the ratio of sodium naphthalenide employed in the reaction. The C–N bond is not cleaved.[207]

IV. Polymerization

Under many polymerization conditions the polymer chains are terminated spontaneously, but Szwarc has pioneered a use for alkali metal aromatic radical anions in which this is not true. *Via* techniques developed principally by him, "living polymers" are formed. That is, polymerization proceeds to the point where an equilibrium is established between the polymer and its monomer and this solution is stable. Adding monomer at a later time results in additional polymerization. This method is particularly suited to formation of block polymers. Some selected works of Szwarc are listed in ref 208.

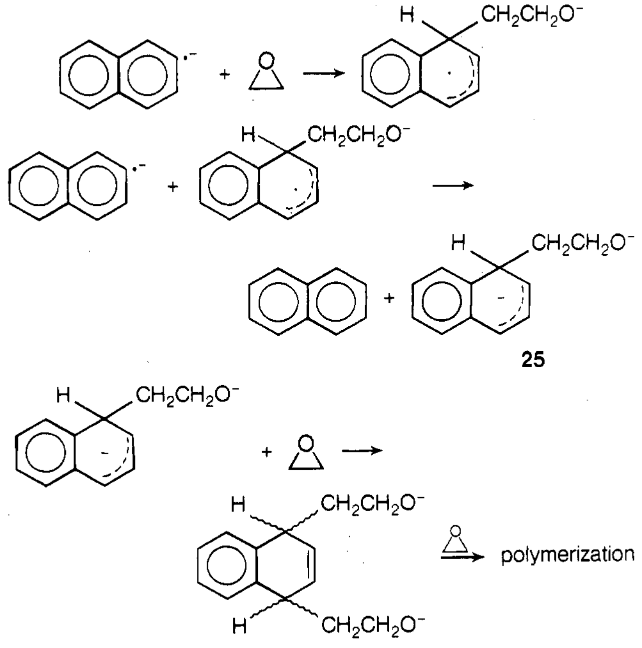
What is to be examined briefly in this section is the role of the radical anion in effecting dimerization and polymerization. The function of the radical anion in the reactions of hydrocarbon monomers, *e.g.*, styrene and/or butadiene, essentially is restricted to electron transfer to the monomer, which then grows through combination with other monomer units. For the initiator to become incorporated in the polymer is definitely the exception, though it is not entirely without precedent. Hoecker and Lattermann have recently investigated the oligomerization of *p*-di(1-phenylvinyl)benzene (**23**) with alkali metals and sodium naphthalenide.[209] Sodium naphthalenide gave all oligomers through the decamer and also a compound which they believed to be **24**. Nonolefinic monomers are more likely to incorporate the initiator. Ethylene oxide, for example, reacts with sodium naphthalenide;[210] Scheme XIV was proposed. Consistent with this description are the observations that naphthalene is present in the polymer, a



(95)

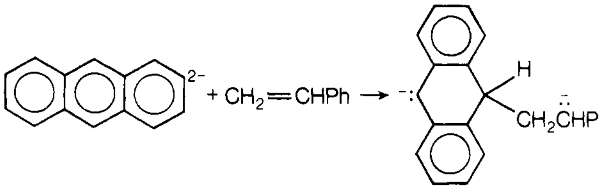
24

SCHEME XIV



transient red color is attributed to **25**, and only one-half of the added sodium naphthalenide was converted to naphthalene. A similar mechanism was proposed for the reaction of cyclic siloxanes.[211] Formaldehyde is reported to form a polymer with sodium naphthalenide; the product contains a naphthalene moiety.[212]

In a situation where coupling of a hydrocarbon moiety with a monomer conceptually could occur *via* either the radical anion or dianion, coupling has been shown to involve the dianion. The dianion of anthracene, for example, combines directly with vinyl monomers[213] and does



(96)

not take place through the sequence of two steps.

$$\text{anthracene}^{2-} + \text{styrene} \rightleftharpoons \text{anthracene}^{\cdot-} + \text{styrene}^{\cdot-} \quad (97)$$

$$\text{anthracene}^{2-} + \text{styrene} \rightleftharpoons {}^{-}\text{anthracene-styrene}^{-} \quad (98)$$

Table XXXVII gives selected polymerization references listed in *Chemical Abstracts* from 1968 through 1972. The table is not meant to be exhaustive but to illustrate the varied applications of radical anions.

V. Conclusion

The synthetic reactions of radical anions are many and varied. Most of these reactions utilize naphthalenide, and it would be of interest to extend the range. Perhaps it would then be possible to interpret differences in reaction behavior on the basis of electron affinity, charge or spin density, and/or ion pairing. Other roles besides electron transfer and proton abstraction are conceivable though unproven for radical anions and dianions. A nucleophilic function seems to be one of the most likely.

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