For **2f**, 0.1 M acetone-d_6 solution and 1,1,2,2-tetrachloroethane as an internal standard were used.

Acknowledgment. We gratefully acknowledge support by the Ministry of Education, Science, and Culture (Grant-in-Aid No. 505026).

Registry No. 1a, 121-46-0; **1b**, 947-57-9; **1c**, 15872-28-3; **1d**, 826-62-0; **1e**, 79632-14-7; **1f**, 78941-78-3; **1g**, 79632-15-8; **1h**, 79632-16-9; **1i**, 79632-17-0; **1j**, 79632-18-1; **1k**, 79632-19-2; **2a**, 278-06-8; **2b**, 714-53-4; **2f**, 78941-77-2; **2g**, 79632-20-5; **2h**, 79632-21-6; **2i**, 79632-22-7; **2j**, 79632-23-8; **2k**, 79632-24-9; **3**, 25753-80-4; **4**, 14751-81-6; **5**, 79647-68-0; **6**, 25753-77-9; $(Ph_3P)_3CuBPh_4$, 34013-06-4; $[Ph_3PCuCl]_4$, 25895-58-3; CuOTf, 25535-55-1; $Rh_2(CO)_4Cl_2$, 14523-22-9; CuCl, 7758-89-6; aniline, 62-53-3; 1-naphthylamine, 134-32-7; *p*-anisidine, 104-94-9.

Photostimulated Reactions of Alkanethiolate Ions with Haloarenes. Electron Transfer vs. Fragmentation of the Radical Anion Intermediate[1]

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The photostimulated reactions of RS^- ions (R = methyl, *n*-butyl, *tert*-butyl, and benzyl) with haloarenes in liquid ammonia were studied. Two main products were formed: alkyl aryl sulfide and arenethiolate ions. The formation of these compounds is explained by the $S_{RN}1$ mechanism of aromatic nucleophilic substitution. The radical anion intermediate formed in the coupling of an aryl radical with an alkanethiolate ion undergoes two competing reactions: transfer of the odd electron to the substrate leading to the substitution product or bond fragmentation leading to arenethiolate ion and an alkyl radical. It is concluded that the ratio of these products depends mainly on changes in the rate of fragmentation and not on changes in the electron-transfer reaction.

The photostimulated reaction of iodobenzene (**1**) with benzenethiolate ion (**2**) in liquid ammonia has been shown to give diphenyl sulfide (**3**) in nearly quantitative yield by $S_{RN}1$ mechanism of aromatic nucleophilic substitution (eq 1).[2] The photostimulated reaction of **1** with ethanethiolate

$$\underset{\mathbf{1}}{\mathrm{PhI}} + \underset{\mathbf{2}}{\mathrm{PhS^-}} \xrightarrow{h\nu} \underset{\mathbf{3}}{\mathrm{PhSPh}} + \mathrm{I^-} \qquad (1)$$

ion (**4**) is much slower, releasing only 60% of the theoretical amount of iodide ion after 90 min of irradiation. When this reaction is carried out for 200 min and then quenched with benzyl chloride, the products are phenyl ethyl sulfide (**8**, 30%), phenyl benzyl sulfide (**10**, 44%), and diphenyl sulfide (**3**, 3%). These results were interpreted by the $S_{RN}1$ mechanism shown in Scheme I.[3-5]

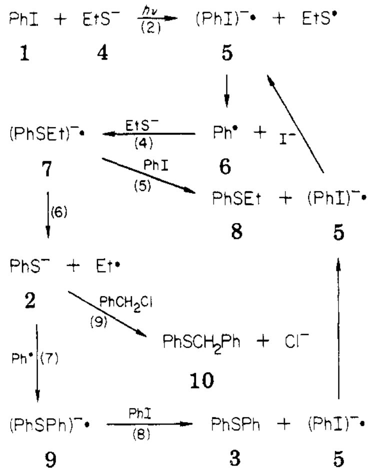
The principal course of the chain reaction is by eq 5 (in Scheme I). The formation of ethyl radical in eq 6 is a chain-terminating step, which depresses the overall reaction. The reaction of **2** to give **3** via eq 7 and 8 is minor, but the presence of **2** is shown by trapping with benzyl chloride to give **10** (eq 9).

The photostimulated reaction of the sodium salts of *n*-butanethiolate and 2-hydroxyethanethiolate ions with 1-chloro- or 1-bromonaphthalene in liquid ammonia has been shown to give naphthalene and the alkyl naphthyl sulfides in good yields without any product derived from fragmentation of the radical anion intermediate formed in the sense of eq 6.[6]

$$C_{10}H_7X + RS^- \xrightarrow{h\nu} C_{10}H_7SR + X^-$$
$$X = Cl, Br;\ R = n\text{-Bu},\ OHCH_2CH_2$$

In the electrochemically induced $S_{RN}1$ reaction of 4-bromobenzophenone with PhS^-, CH_3S^-, or t-BuS^- ions in $(Me)_2SO$ or acetonitrile, the only products reported were benzophenone and the 4-benzoylphenyl sulfides resulting from substitution; no products resulting from bond fragmentation were obtained.[7]

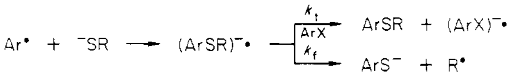
Scheme I



The contrasting behavior of iodobenzene compared with 1-halonaphthalenes and 4-bromobenzophenone in the reaction with RS^- ions prompted us to investigate the reactions of several aryl halides with alkanethiolate ions to determine the factors that affect the balance between the electron-transfer reaction (eq 10) and bond fragmentation (eq 11) of the aryl alkyl sulfide radical ion intermediates.

Results

Equations 4–6 in Scheme I can be generalized as shown in eq 10 and 11, where k_t and k_f are rate constants for the



(10)

(11)

electron transfer and the bond fragmentation reactions,

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[1] Research supported in part by the Consejo Nacional de Investigaciones Científicas y Técnicas and the Subsecretaría de Ciencia y Tecnología, Argentina.

(2) Bunnett, J. F.; Creary, X. *J. Org. Chem.* **1974**, *39*, 3173.

(3) Bunnett, J. F.; Creary, X. *J. Org. Chem.* **1975**, *40*, 3740.

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

(5) Bunnett, J. F. *Acc. Chem. Res.* **1978**, *11*, 413.

(6) Rossi, R. A.; de Rossi, R. H.; López, A. F. *J. Am. Chem. Soc.* **1976**, *98*, 1252.

(7) Pinson, J.; Saveant, J. M. *J. Am. Chem. Soc.* **1978**, *100*, 1506.

respectively. The competition between these two reactions is affected by the nature of both the aryl and alkyl groups in the radical anion intermediate.

Iodobenzene (1) gave only the substitution product with PhS^- ion as the nucleophile[2] ($k_t \gg k_f$). In the reaction of 1 with methyl, ethyl, *n*-butyl, or *tert*-butyl sulfide ions, almost equal amounts of substitution and fragmentation products were found ($k_t \approx k_f$), while with the benzenethiolate ion, only the fragmentation product was formed, and hence $k_t \ll k_f$ (eq 12).

$$Ph\cdot + RS^- \xrightarrow{h\nu} PhSR + PhS^- \qquad (12)$$

R	rel yield, % PhSR	rel yield, % PhS^-	tot yield, %
Ph	100	0	94
Me, Et, *n*-Bu, *t*-Bu	50	50	30-70
$PhCH_2$	0	100	4

The differences in total yields in eq 12 reflect the fact that PhSR is formed by an electron-transfer chain reaction (eq 10), whereas PhS^- is formed by a chain-terminating fragmentation reaction (eq 11).

Differences in product composition are also observed when the aryl group is changed while the alkyl group is kept the same. With n-BuS^- ion, iodobenzene gave equal amounts of both kinds of reaction products ($k_t \approx k_f$), while the proportion of electron transfer product increased with 2-chloropyridine and even more with 1-chloronaphthalene ($k_t > k_f$; eq 13).

$$Ar\cdot + n\text{-}BuS^- \xrightarrow{h\nu} n\text{-}BuSAr + ArS^- \qquad (13)$$

Ar	rel yield, % *n*-BuSAr	rel yield, % ArS^-	tot yield, %
phenyl	50	50	30
2-pyridyl	84	16	86-100
1-naphthyl	100	0	81

More dramatic changes were found in reactions of various aryl radicals with $PhCH_2S^-$ ion (eq 14).

$$Ar\cdot + PhCH_2S^- \xrightarrow{h\nu} ArSCH_2Ph + ArS^- \qquad (14)$$

Ar	rel yield, % $ArSCH_2PH$	rel yield, % ArS^-	tot yield, %
phenyl	0	100	4
9-phenanthryl	12	88	5-12
1-naphthyl	15	85	17-24
2-pyridyl	21	79	39
2-quinolyl	100	0	69

Both eq 13 and 14 confirm the trend of decreasing total yield as the proportion of bond fragmentation increases.

The photostimulated reaction of 1-iodonaphthalene with $PhCH_2S^-$ ion gave, in addition of the substitution and fragmentation products, 15–20% of dibenzyl sulfide (11). The formation of 11 might be ascribed to reaction of benzyl radical formed in the fragmentation of the radical anion intermediate (eq 15) with $PhCH_2S^-$ ion (eq 16). However,

$$(C_{10}H_7SCH_2Ph)^{-}\cdot \rightarrow C_{10}H_7S^- + PhCH_2\cdot \qquad (15)$$

$$PhCH_2\cdot + PhCH_2S^- \rightarrow (PhCH_2SCH_2Ph)^{-}\cdot \qquad (16)$$

$$(PhCH_2SCH_2Ph)^{-}\cdot + C_{10}H_7I \rightarrow \underset{11}{PhCH_2SCH_2Ph} + (C_{10}H_7I)^{-}\cdot \qquad (17)$$

this seems unlikely because the resulting radical anion should be able to sustain the chain reaction (eq 17), whereas the overall reaction yield was considerably lower than with other thiolate ions.

Moreover, Bunnett and Gloor have found that the benzyl radical does not react with cyanomethyl anion in liquid ammonia.[8] In the reaction of phenyl radical with cyanomethyl anion, the radical anion intermediate fragments into cyanide ion and benzyl radical, which dimerizes to 1,2-diphenylethane. However, in the reaction of 1-iodonaphthalene and 1-bromonaphthalene with $PhCH_2S^-$ ion, no 1,2-diphenylethane could be detected.

A more likely source of dibenzyl sulfide is the reaction of benzyl radical with the radical 12 formed in the initiation step.

$$C_{10}H_7I + PhCH_2S^- \xrightarrow{h\nu} (C_{10}H_7I)^{-}\cdot + \underset{12}{PhCH_2S\cdot}$$

$$\underset{12}{PhCH_2S\cdot} + PhCH_2\cdot \rightarrow \underset{11}{PhCH_2SCH_2Ph}$$

The observed formation of about equal amounts of naphthalenethiolate ion and dibenzyl sulfide supports this mechanism.

Photostimulation of $PhCH_2S^-$ ion and 4-chlorobenzophenone produced no reaction, possibly because of addition of the nucleophile to the carbonyl group, as has been suggested in the reaction of phenylselenide ion with this ketone.[9] *p*-Iodonitrobenzene reacted with $PhCH_2S^-$ ion, both with irradiation and in the dark, to liberate a high yield of iodide ion and to give a complex mixture of products. It is probable that other mechanisms compete with the $S_{RN}1$ reaction in this case, as was found with acetone enolate ion,[10] and this reaction was not investigated further.

Discussion

The radical anion formed as an intermediate in these reactions can undergo two competing reactions: transfer of the odd electron to the substrate or bond fragmentation. It is unlikely that the differences in the proportions of both reaction products among the different pairs of aryl halide–alkanethiolate ion combinations can be attributed to changes in electron-transfer rates. For instance, in eq 18

$$\underset{13}{(PhSR)^{-}\cdot} + PhI \xrightarrow{k_t} PhSR + (PhI)^{-}\cdot \qquad (18)$$

the half-wave reduction potential of the parent of the radical anion 13 is −2.549 V when R = phenyl,[11] and the reduction potential of iodobenzene is −1.21 V.[12a] Thus, the electron-transfer reaction is thermodynamically favored by more than 1 V,[12b] and the rate of eq 18 should be diffusion controlled;[13] the only reaction observed is electron transfer.[2] However, when R = benzyl, the reduction potential of the parent molecule is −2.569 V,[11] and electron transfer to iodobenzene should also be diffusion controlled,[13] whereas *only* bond fragmentation occurs. When R = methyl ($E_{1/2}$ = −2.751 V),[11] ethyl ($E_{1/2}$ = −2.734 V),[11] or *tert*-butyl ($E_{1/2}$ = −2.638 V),[11] about equal proportions of electron-transfer and bond-fragmentation products are formed.

In all these reactions, while the rate of electron transfer should be about the same and be diffusion controlled,[13]

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[8] Bunnett, J. F.; Gloor, B. F. *J. Org. Chem.* **1973**, *38*, 4156.

[9] Pierini, A. B.; Rossi, R. A. *J. Org. Chem.* **1979**, *44*, 4667.

[10] Bunnett, J. F.; Sundberg, J. E. *Chem. Pharm. Bull.* **1975**, *23*, 2620.

[11] The reduction potential is in DMF vs. Ag/AgCl with 0.15 Mm n-Bu_4NI as the supporting electrolyte: Gerdill, R. *J. Chem. Soc. B* **1966**, 1071.

[12] (a) The reduction potential is in DMF vs. Ag/AgBr with 0.02 M Et_4NBr as the supporting electrolyte: Sease, J. W.; Bunton, F. G.; Nickol, S. L. *J. Am. Chem. Soc.* **1968**, *90*, 2595. (b) Although care must be taken when comparing electrochemical data from different sources, the magnitude of the differences in the data presented here is significantly larger than the uncertainly expected in them.

[13] Dorfman, L. M. *Acc. Chem. Res.* **1970**, *3*, 224.

Table I. Photostimulated Reaction of Haloaromatic Compounds with Thiolate Ions in Liquid Ammonia

ArX[a]	$-E_{1/2}$ (ArH)[b]	RS⁻	$h\nu$, min	$D_{\mathrm{PhS\text{-}R}}$[c]	% yield ArSR	% yield ArS⁻
PhI[d]	>3.0	PhS⁻	70	76	94	0
PhI	>3.0	MeS⁻	180	65	12	19
PhI[e]	>3.0	EtS⁻	200	62	30	44
PhI	>3.0	*n*-BuS⁻	180	60	14	16
PhI	>3.0	*t*-BuS⁻	180	59	36	33
PhI	>3.0	$\mathrm{PhCH_2S^-}$	180	51	0	4
2-ClPyr[f]	2.7	*n*-BuS⁻	180	60	72-85	14-15
2-ClPyr	2.7	$\mathrm{PhCH_2S^-}$	180	51	8	31
2-ClPyr[g]	2.7	$\mathrm{PhCH_2S^-}$	180	51	11	23
1-INaph[d]	2.5	PhS⁻	75	76	85	0
1-ClNaph[h]	2.5	*n*-BuS⁻	170	60	81	0
1-INaph[h]	2.5	$\mathrm{HOCH_2CH_2S^-}$	150		74	0
1-INaph	2.5	*t*-BuS⁻	180	59	88	0
1-BrNaph[f]	2.5	$\mathrm{PhCH_2S^-}$	180	51	2-4	15-20
9-BrPhen[f]	2.4	$\mathrm{PhCH_2S^-}$	180	51	0-2	5-10
2-ClQ	2.1	$\mathrm{PhCH_2S^-}$	90	51	69	0
2-ClQ	2.1	$\mathrm{PhCH_2S^-}$	90[i]	51	0	0

[a] Pyr = pyridine, Naph = naphthalene, Phen = phenanthrene, and Q = quinoline. [b] Reduction potential of the parent aromatic compound (DMF vs. SCE). [c] Reference 17. [d] Reference 2. [e] Reference 3. [f] Average of two or more runs. [g] Tenfold excess of the substrate. [h] Reference 6. [i] Dark reaction.

the products obtained are quite different. We conclude that the differences depend on the different bond-fragmentation rates of the radical anion **13** and not on differences in electron-transfer rates to the substrate.

It has been suggested that at the beginning of the three-electron coupling of an aryl radical with a nucleophile, the bond being formed involves a doubly occupied σ molecular orbital (MO) and a singly occupied σ* MO. As the reactants approach each other, the energy of the σ MO decreases while the energy of the σ* MO increases; if there is no antibonding MO (σ* or π*) of lower energy, the odd electron will not be transferred. However, if there is another antibonding MO with lower energy than the incipient σ* MO of the bond being formed, there should be a point in the reaction coordinate where both antibonding MO's have equal energies, and, by intersystem crossing, the odd electron can be transferred to the second antibonding MO.[14]

Our results on the competition between electron-transfer and bond-fragmentation rates in the reaction of aryl radicals with alkanethiolate ions can be explained along the same lines.

Consider the reaction with $\mathrm{PhCH_2S^-}$ ion. When a phenyl radical couples with it, the lowest antibonding MO of the system should be that of the σ* MO of the S–CH₂Ph bond. Thus, when the phenyl radical approachs the nucleophile, σ and σ* MO's are built in the coupling process. As they approach each other, the gap between the MO's increases, there should be a point where the energy of the σ* MO of the Ph–S bond equals that of the σ* MO of the S–$\mathrm{CH_2Ph}$ bond, and fragmentation of the radical anion occurs (eq 19).

$$\mathrm{Ph}\cdot + {}^-\mathrm{SCH_2Ph} \rightarrow \underset{\sigma^*\ \text{radical anion}}{\mathrm{Ph}\overset{\cdot -}{\cdots}\mathrm{SCH_2Ph}} \rightarrow \underset{\sigma^*\ \text{radical anion}}{\mathrm{PhS}\overset{\cdot -}{\cdots}\mathrm{CH_2Ph}} \rightarrow \mathrm{PhS^-} + \cdot\mathrm{CH_2Ph} \tag{19}$$

Despite the fact that the electron-transfer reaction to iodobenzene should be diffusion controlled, it cannot compete with the bond-fragmentation rate.

Consider the coupling of the same nucleophile with the 2-quinolyl radical. Now the lowest energy antibonding MO corresponds to the π* MO of the quinolyl moiety. Thus, when it couples with the nucleophile, the odd electron of the incipient σ* MO of the quinolyl–S bond is transferred to the π* MO of the quinolyl moiety and stays there. Because the difference in energy between the π* and σ* MO's is large enough, intramolecular electron transfer to the σ* MO to produce bond fragmentation does not compete with intermolecular electron transfer to the substrate.

$$\mathrm{C_9H_6N}\cdot + {}^-\mathrm{SCH_2Ph} \rightarrow \underset{\sigma^*\ \text{radical anion}}{\mathrm{C_9H_6N}\overset{\cdot -}{\cdots}\mathrm{SCH_2Ph}} \rightarrow \underset{\pi^*\ \text{radical anion}}{(\mathrm{C_9H_6N})^{-}\cdot\mathrm{SCH_2Ph}}$$

$$(\mathrm{C_9H_6N})^{-}\cdot\mathrm{SCH_2Ph} + \mathrm{C_9H_6NCl} \rightarrow \mathrm{C_9H_6NSCH_2Ph} + (\mathrm{C_9H_6NCl})^{-}\cdot$$

In the coupling of the $\mathrm{PhCH_2S^-}$ ion with 2-pyridyl, 1-naphthyl, or 9-phenanthryl radicals, the differences in energy of the π* and σ* MO's are not as high as those with the 2-quinolyl radical, and both processes compete.

The electrochemical reduction of *p*-nitrophenyl diphenylmethyl sulfide in DMF leads to bond fragmentation according to eq 20 and 21, with an activation energy of 21

$$p\text{-}\mathrm{O_2NC_6H_4SCHPh_2} + e^- \rightarrow \underset{\mathbf{14},\ \pi^*\ \text{radical anion}}{(p\text{-}\mathrm{O_2NC_6H_4})^{-}\cdot\mathrm{SCHPh_2}} \tag{20}$$

$$(p\text{-}\mathrm{O_2NC_6H_4})^{-}\cdot\mathrm{SCHPh_2} \rightarrow p\text{-}\mathrm{O_2NC_6H_4S^-} + \cdot\mathrm{CHPh_2} \tag{21}$$

kcal/mol. Since ESR studies indicate that in the radical anion **14** the odd electron is located in the π* MO, the high activation energy probably reflects the unfavorable tendency from transfer of the odd electron from the π* MO of the *p*-nitrophenyl moiety to the σ* MO of the C–S bond.[15]

The half-wave reduction potential of arenes is a measure of the π* MO energy,[16] and as the $E_{1/2}$ of benzene has the highest negative value of the series, only bond fragmentation is observed. With pyridine, naphthalene, and phenanthrene, with $E_{1/2}$ values between −2.7 and −2.4 V (Table I), both processes are observed. The lowest π* MO corresponds to quinoline (−2.1 V), which is in agreement

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(14) Rossi, R. A., in press.

(15) Farnia, G.; Severin, M. G.; Capobianco, G.; Vianello, E. *J. Chem. Soc., Perkin Trans. 2* **1978**, 1.

(16) Streitwieser, A. "Molecular Orbital Theory for Organic Chemistry"; Wiley: New York, 1961.

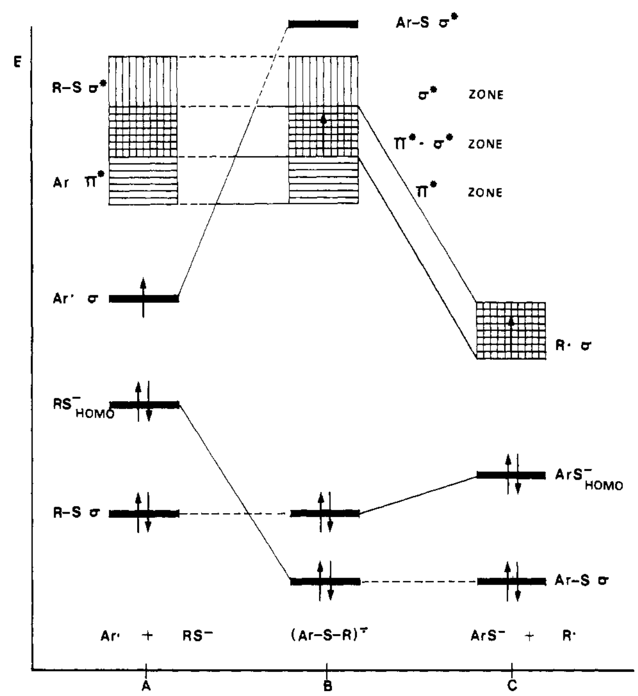

Figure 1. Schematic representation of the MO's involved when an aryl radical couples with an alkanethiolate ion to form a radical anion that fragments.

with the results obtained. The reaction with *n*-butanethiolate ion (eq 13) can be explained along the same lines: phenyl radical gave about equal proportions of both reactions, pyridyl radical more electron transfer than bond fragmentation and naphthyl radical only electron transfer.

From the results in Table I it can be seen that the competition between electron transfer and bond fragmentation depends not only on the π^* MO of the aryl moiety but also on the nature of the R group (eq 12), which determines the strength of the S–R bond, which is also related to the σ^* MO energy. Thus, if R = phenyl ($D_{\mathrm{PhS-Ph}}$ = 76 kcal/mol[17]), only electron transfer is observed; if R = Me, Et, *n*-Bu, or *t*-Bu ($D_{\mathrm{PhS-R}}$ = 59–65 kcal/mol; see Table I), both reactions are observed; if R = CH_2Ph ($D_{\mathrm{PhS-CH_2Ph}}$ = 51 kcal/mol[17]), only bond fragmentation is observed.

The nitrogen hyperfine splittings in the radical anions of *p*-(alkylthio)nitrobenzenes, which are certainly π^* radical anions, are decreased because of electron transfer between the π^* MO of the *p*-nitrophenyl moiety containing the unpaired electron and the σ^* MO of the S–R bond; the electron transfer increases with the bulkiness of the alkyl substituent.[18] This interpretation is supported by INDO calculations.[19]

Figure 1 is a schematic representation of the coupling of an aryl radical with an alkanethiolate ion, the bond fragmentation of the radical anion intermediate which leads to arenethiolate ion and alkyl radical, and the MO's involved in this transition.[14]

In Figure 1, A is the initial state of the system when no interaction exists between the reactants and represents the MO's involved in the highest perturbation of the coupling process (the singly occupied molecular orbital, SOMO, of the σ aryl radical and the highest occupied molecular orbital, HOMO, of the nucleophile),[20] the σ–σ^* MO's of the S–R bond and the π^* MO of the aryl moiety.

Differences in the values of the SOMO's of the aryl radicals[21] and in the HOMO's of the nucleophiles[22] are not expected, while there are differences in the values of the π^* MO's of the aryl moieties (for instance between benzene and quinoline systems) and the σ^* MO's.

As the reactants approach each other, σ and σ^* MO's are built. In B of Figure 1 the radical anion intermediate is formed, and in the antibonding zone we can distinguish σ^*, π^*, and a σ^*–π^* zones.

In the σ^* zone, the σ^* MO energy is higher than the π^* MO energy (π^* zone); thus the odd electron never reaches that zone, the radical anion intermediate is of π^* nature, and only electron transfer is observed. In the σ^*–π^* zone, the odd electron can be in any of these orbitals, resulting in variable amounts of fragmentation competing with the electron-transfer reaction. The relative rates of these two reactions depend on the differences in the σ^* and π^* MO energies.

C of Figure 1 is the final state of the system when the fragmentation process has concluded, being the SOMO of the alkyl radical with an energy that depends on the nature of R and the HOMO of the arenethiolate ion, both MO's being of lower energy than the SOMO and HOMO of the starting reactants.

It is concluded that when an aryl radical couples with an alkanethiolate ion, electron transfer will be observed as the only reaction when the substitution product has an antibonding π^* MO of low energy and the σ^* MO of the S–R bond has high energy (high bond dissociation energy). On the other hand, bond dissociation will be the only reaction when the lowest lying antibonding MO is the σ^* MO of the S–R bond. When the σ^* and π^* MO's are of comparable energies, both processes compete.

Experimental Section

General Methods. NMR spectra were recorded on a Varian T-60 nuclear magnetic resonance spectrometer, and all spectra are reported in parts per million relative to Me_4Si (δ) with CCl_4 as the solvent. Mass spectral measurements were obtained with a Hitachi Perkin-Elmer Model RMU-6 E mass spectrometer, and the GC/MS data were obtained in a Varian MAT CH 7A or a Finnigan Model 4000 mass spectrometer. Gas chromatographic analyses were performed on a Varian Aerograph Series 2400 with a flame-ionization detector and a column packed with 4% silicon rubber SE-30 on Chromosorb G, (80–100 mesh, 1.5 m × 3 mm) or 1.5% OV-101 on Chromosorb P (1.5 m × 3 mm). Irradiation was conducted in a reactor equipped with two 250-W UV lamps emitting maximally at 350 nm (Philips, Model HPT, water refrigerated).

Materials. Reagents were all commercially available materials unless otherwise noted and were purified by standard procedures. Liquid ammonia was dried over sodium and distilled under nitrogen into the reaction flask. Sodium was cut into small pieces and washed free of oil with dried diethyl ether immediately before addition to the reaction flask. RS^- ions (R = *n*-butyl, *tert*-butyl, and benzyl) were prepared by the acid–base reaction of the thiols[23] and sodium *tert*-butoxide prepared in situ[24] in liquid ammonia. Methanethiolate ion was prepared by the reaction of benzyl methyl sulfide and Na metal in liquid ammonia.

Photostimulated Reaction with Alkanethiolate Ions. The photostimulated reaction of $PhCH_2S^-$ ion with 2-chloroquinoline

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[17] Estimated values from: Benson, S. W. *Chem. Rev.* **1978**, *78*, 23.

[18] Alberti, A.; Martelli, G.; Pedulli, G. F. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1252.

[19] Alberti, A.; Guerra, M.; Bernardi, F.; Mangini, A.; Pedulli, G. F. *J. Am. Chem. Soc.* **1979**, *101*, 4627.

[20] Rossi, R. A.; de Rossi, R. H.; Lôpez, A. F. *J. Org. Chem.* **1976**, *41*, 3367.

[21] Kasai, P. H.; Clark, P. A.; Whipple, E. B. *J. Am. Chem. Soc.* **1970**, *92*, 2640.

[22] The differences in pK_a of arenethiols are only on the order of 1–2 p*K* units (March, J. "Advanced Organic Chemistry", 2nd ed.; McGraw-Hill: New York, 1977; p 228) or 1–2 kcal/mol at −33 °C.

[23] Vogel, A. I. "A Text Book of Practical Organic Chemistry", 3rd ed.; Longmans: London, 1959; p 497.

[24] Rossi, R. A.; de Rossi, R. H. *J. Org. Chem.* **1974**, *39*, 855.

is representative. Into a three-necked 500-mL, round-bottomed flask, equipped with a cold-finger condenser charged with solid CO_2 and ethanol, a nitrogen inlet, and a magnetic stirrer, was condensed ~250 mL of ammonia. To the ammonia was added *t*-BuOH (9.74 mmol) and Na metal (9.74 mol) to form sodium *tert*-butoxide and then $PhCH_2SH$ (9.74 mmol). To this solution was added 2-chloroquinoline (4.86 mmol), and the solution was irradiated for 90 min. The reaction was quenched by adding MeI (9.7 mmol), and the ammonia was allowed to evaporate. Water (100 mL) was added to the residue, and the mixture was extracted three times with 50 mL of diethyl ether. The ether extracts were dried and distilled. The residue was column-chromatographied on silica gel and eluted with petroleum ether. 2-Quinolyl benzyl sulfide was obtained as a white solid and was recrystallized from petroleum ether: mp 39–41 °C (lit.[25] mp 44–45 °C); hydrochloride, mp 183–186 °C (lit.[25] mp 187–190 °C); NMR δ 4.48 (s, 2 H), 6.6–6.8 (m, 11 H); mass spectrum, *m/e* (relative intensity) 251 (100), 218 (75), 160 (12), 129 (50), 116 (12), 91 (75).

The photostimulated reaction with methanethiolate ion was quenched with benzyl chloride and quantified by GC (1-chloronaphthalene as internal standard). The photostimulated reaction of 2-chloropyridine with *n*-butanethiolate ion was quenched with benzyl chloride, and the products were column chromatographed on silica gel and eluted with petroleum ether. *n*-Butyl 2-pyridyl sulfide [NMR δ 0.5–1.8 (m, 7 H), 2.8–3.3 (m, 2 H), 6.5–8.4 (m, 4 H)] and 2-pyridyl benzyl sulfide [NMR δ 3.46 (s, 2 H), 6.6–7.3 (m, 9 H)] were isolated.

The photostimulated reaction of t-BuS$^-$ ion with iodobenzene was quenched with benzyl chloride, and the products were quantified by GC, with 1-chloronaphthalene as internal standard, and compared with authentic samples. The photostimulated reaction of 1-iodonaphthalene and t-BuS$^-$ ion gave only the substitution product, *tert*-butyl 1-naphthyl sulfide, which was isolated by column chromatography (silica gel, eluted with petroleum ether) as a white solid and recrystallized from petroleum ether: mp 55–56 °C; NMR δ 1.26 (s, 9 H), 7.2–8.7 (m, 7 H); mass spectrum, *m/e* (relative intensity) 216 (65), 161 (36), 160 (100), 128 (24), 115 (100).

The photostimulated reaction of iodobenzene and $PhCH_2S^-$ ion was quenched with MeI, and by GC (internal standard 1-methylnaphthalene) there was obtained only methyl phenyl sulfide (4% yield). The photostimulated reaction of 2-chloropyridine with the same nucleophile was quenched with MeI. The products were column chromatographed (silica gel, eluted with petroleum ether) and gave 2-pyridyl benzyl sulfide and 2-pyridyl methyl sulfide: NMR δ 2.53 (s, 3 H), 6.6–8.4 (m, 4 H). The photostimulated reaction with 1-bromonaphthalene (quenched with MeI) was analyzed by GC/MS: 1-naphthyl benzyl sulfide, *m/e* (relative intensity) 250 (8), 115 (16), 91 (100), 65 (15); 1-naphthyl methyl sulfide, *m/e* (relative intensity) 174 (82), 159 (50), 115 (100); dibenzyl sulfide, *m/e* (relative intensity) 214 (79), 91 (100), 65 (24). The dark reaction of $PhCH_2S^-$ ion with 2-chloroquinoline was quenched with MeI and analyzed by GC with 2-methylnaphthalene as an internal standard. The photostimulated reaction with 9-bromophenanthrene was analyzed by GC.

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Registry No. PhI, 591-50-4; 2-ClPyr, 109-09-1; 1-INaph, 90-14-2; 1-ClNaph, 90-13-1; 1-BrNaph, 90-11-9; 9-BrPhen, 573-17-1; 2-ClQ, 612-62-4; PhS$^-$, 13133-62-5; MeS$^-$, 17302-63-5; EtS$^-$, 20733-13-5; n-BuS$^-$, 20733-16-8; t-BuS$^-$, 20733-19-1; $PhCH_2S^-$, 1492-49-5; $HOCH_2CH_2S^-$, 57966-62-8; phenyl radical, 2396-01-2; 2-pyridyl radical, 15905-71-2; 1-naphthyl radical, 2510-51-2; 9-phenanthryl radical, 20199-82-0; 2-quinolyl radical, 54978-39-1.

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Alkylation of Allylic Derivatives. 3. The Regiochemistry of Alkylation of the Isomeric *trans*-α,γ-Methylphenylallyl Acetates with Lithium Dialkylcuprates

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Alkylation of the isomeric *trans*-α,γ-methylphenylallyl acetates (**1-OAc** and **2-OAc**) with lithium dimethylcuprate or di-*n*-butylcuprate is regioselective but not regiospecific. Both isomers give essentially the same product mixture which contains 95% of the trans conjugated alkylation product (**3**). The starting acetates do not rearrange under the conditions for these reactions. These results show that the isomeric acetate give the same product-forming intermediate(s). Presumably the key intermediate that is common to the two isomers is a π-allyl copper(III) complex (**7**).

We have extended our studies[1] of the regio- and stereochemistry of alkylation of allylic derivatives with organocopper reagents to the *trans*-α,γ-methylphenylallyl system. This paper reports an investigation of the regiochemistry of alkylation of the isomeric acetates (**1-OAc** and **2-OAc**) with lithium dimethylcuprate and di-*n*-butylcuprate. Possible alkylation products include two conjugated isomers, (*E*)- and (*Z*)-3-alkyl-1-phenyl-1-butene (**3** and **4**) and two unconjugated isomers, (*E*)- and (*Z*)-1-alkyl-1-phenyl-2-butene (**5** and **6**).

Product distributions for alkylation of the acetates in ether at 0 °C are presented in Table I. These compositions were determined by capillary GC and in all cases base line resolution of all components was observed. The yields included in the table are GC yields obtained with (*E*)-1-phenyl-1-pentene as an internal standard for the **3a**–**5a** mixtures and 1-phenyloctane for the **3b**-**5b** mixture. Mixtures were isolated in yields of 64–68%. Normally only **3**, **4**, and **5** were detected in product mixtures and unidentified contaminants, if any, were present in only trace amounts. (*Z*)-1-Alkyl-1-phenyl-2-butene (**6**) was not de-

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[1] Previous paper in this series is Goering, H. L.; Kantner, S. S. *J. Org. Chem.* **1981**, *46*, 2144.