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Halogen Interchange during Complex Formation between *N*-Halosuccinimides and Quaternary Ammonium Halides

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N-Halosuccinimides and quaternary ammonium halides form both 1:1 and 2:1 complexes. Where two different halogen atoms are involved, the complex, in every case studied, has the more electronegative halogen atom associated with the quaternary ammonium ion and the less electronegative halogen atom bonded to the imide nitrogen. Where necessary a halogen interchange reaction occurs to satisfy this requirement. A mechanism for this halogen interchange reaction is proposed.

Introduction

N-Bromosuccinimide, SBr, forms stable, crystalline complexes with quaternary ammonium imides, e.g., tetrabutylammonium succinimide, Bu_4NS, tetrabutylammonium phthalimide, and tetrabutylammonium maleimide,[1] and the complex with Bu_4NS was shown to be an intermediate in the electron-transfer-mediated reduction of SBr by the succinimide anion, S^-.[2] The initial electron-transfer step between SBr and S^- forms a cage radical anion/radical pair. Nitrogen–bromine bond cleavage within the cage produces a pair of succinimidyl radicals, $S\cdot$, which react with disproportionation to yield succinimide, SH, and maleimide. The latter then undergoes predominant radical polymerization to give polymaleimide.[3]

Complexes between SBr and quaternary ammonium halides, R_4NX, were briefly studied by Braude and Waight[4] and had SBr to R_4NX ratios of 2:1. We have found that SBr–R_4NBr complexes play an important catalytic role in the oxidation of ferrocene to ferrocinium ion by SBr[5] and therefore decided to study these species in more detail. We find that SBr forms both 1:1 and 2:1 complexes with R_4NBr. The 1:1 SBr–Bu_4NBr complex decomposes via an X-philic mechanism[6] to form SH, polymaleimide, and tetrabutylammonium tribromide. The tribromide, thus formed, is the reagent responsible for the facile bromination of olefins by SBr in combination with bromide ion.[7]

During complex formation between *N*-chlorosuccinimide, SCl, and tetraethylammonium bromide a facile halogen interchange takes place, and the product is the same 2:1 complex obtained starting with SBr and tetraethylammonium chloride. It has the structure, 2SBr–Et_4NCl.[8] We now report that these halogen interchange reactions occur frequently where different halogens are involved in the starting *N*-halosuccinimide, SX, and the starting R_4NX, that they occur in the formation of both 1:1 and 2:1 complexes, that they follow a discernible, predictable pattern, and that they occur by a reaction mechanism involving X-philic attack of X^- on the halogen atom of S–X.

Results

The reaction of SCl with Et_4NBr results in a 2:1 complex having the empirical formula $C_{16}H_{28}Br_2ClN_3O_4$.[8] Two structures, 2SBr–Et_4Cl and SBr–SCl–Et_4NBr, are consistent with this empirical formula. The same product is obtained from the reaction of SBr with Et_4NCl. Treatment of the complex with cold water dissolves the quaternary ammonium halide portion of the complex and leaves only SBr. In addition, evidence from cyclic voltammetry indicates that SBr but no SCl is present in this complex. The complex, thus, combines two SBr and one Et_4NCl, and halogen interchange has occurred only in the reaction of SCl and Et_4NBr.[8]

The foregoing results are indicated by the first two entries in Table I. The subsequent eight entries summarize four sets of paired experiments in which the same 1:1 complex was obtained from two different pairs of reagents and in which the reaction of one of the reaction pairs must necessarily involve a halogen interchange reaction. Since a 1:1 complex was obtained in all eight of the reactions involved, determination of the empirical formulas provided no clue as to which pair of reagents entailed a halogen interchange.

One source of evidence for the structures indicated in column 4 of Table I was provided by the reaction of the complexes with silver nitrate in acetonitrile. The *N*-haloamides are inert to this reagent, but the quaternary ammonium halide moiety of the complex reacts almost quantitatively to precipitate the appropriate silver halide. Thus the complex prepared from SBr and Et_4NI (entry 4 in Table I) gives silver bromide in 99.8% yield, and the atomic ratio of I/Br in this precipitate was 0.002, as determined by the electron microprobe. We conclude that a halogen interchange was involved in this reaction and that the complex is SI–Et_4NBr. Similarly, the complex prepared from SBr and Bu_4NI (entry 5 in Table I) gave a 99% yield of silver bromide which shows a I/Br atomic ratio of 0.005. In this example, too, a halogen interchange has occurred, and the structure of the complex is SI–Bu_4NBr. All of the complexes indicated in Table I were subjected to this diagnostic reaction, and in every case the silver halide obtained was consistent with the product

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Table I. Complexes of *N*-Halosuccinimides, SX, and Quaternary Ammonium Halides, R_4NX

								anal.							
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entry	SX	R_4NX	product	ratio SX:R_4NX	mp, °C	yield, %	solvents for crystallizatn	C	H	N	OE[a]	C	H	N	OE[a]
1	SBr	Et_4NCl	$2SBr{\cdot}Et_4NCl$	2:1	140–143 dec	86	CH_3CN–CH_3OH–ether	36.83	5.41	8.06		36.83	5.52	8.03	
2	SCl	Et_4NBr	$2SBr{\cdot}Et_4NCl$	2:1	139–141 dec	95	$CHCl_3$–CH_3OH–ether	36.83	5.41	8.06	261	36.88	5.44	8.01	267
3	SI	Et_4NBr	$SI{\cdot}Et_4NBr$	1:1	127–128 dec	93	$CHCl_3$–ether	33.12	5.56	6.44	435	33.24	5.57	6.19	434
4	SBr	Et_4NI	$SI{\cdot}Et_4NBr$	1:1	127–128 dec	88	$CHCl_3$–CH_3OH–ether	33.12	5.56	6.44	435	32.93	5.63	6.26	436
5	SBr	Bu_4NI	$SI{\cdot}Bu_4NBr$	1:1	100–102 dec	93	acetone–ether	43.88	7.37	5.12	547	43.96	7.23	5.06	550
6	SI	Bu_4NBr	$SI{\cdot}Bu_4NBr$	1:1	102–104 dec	92	acetone–ether	43.88	7.37	5.12	547	44.31	7.51	4.99	563
7	SBr	$C_6H_5CH_2NEt_3Cl$	$SBr{\cdot}C_6H_5CH_2NEt_3Cl$	1:1	115–117	86	CH_3CN–ether	50.32	6.46	6.90	406	50.15	6.06	6.72	408
8	SCl	$C_6H_5CH_2NEt_3Br$	$SBr{\cdot}C_6H_5CH_2NEt_3Cl$	1:1	115–118	93	CH_3CN–ether	50.32	6.46	6.90		50.55	6.62	6.92	
9	SI	$C_6H_5CH_2NEt_3Cl$	$SI{\cdot}C_6H_5CH_2NEt_3Cl$	1:1	103–105	86	CH_3CN–ether	45.10	5.79	6.19		45.23	5.97	6.04	
10	SCl	$C_6H_5CH_2NEt_3I$	$SI{\cdot}C_6H_5CH_2NEt_3Cl$	1:1	103–105	93	CH_3CN–ether	45.10	5.79	6.19		45.06	5.88	6.35	
11	SBr and SI	Et_4NBr	$SBr{\cdot}SI{\cdot}Et_4NBr$	1:1:1	115–118	66	$CHCl_3$								
12	SBr	Et_4NI	$SBr{\cdot}SI{\cdot}Et_4NBr$	1:1:1	114–116	75	$CHCl_3$	31.34	4.60	6.85	307	31.32	4.55	6.76	306
13	SI	Et_4NBr	$2SI{\cdot}Et_4NBr$	2:1	138–141 dec	91	$CHCl_3$–CH_3CN–ether	29.11	4.28	6.37	330	29.44	4.26	6.23	334

[a] The designation "OE", the oxidation equivalent, refers to the values obtained by iodometric titration of the SBr or SI moieties of the complexes. For a 1:1 complex the value is equivalent to the molecular weight; for a 2:1 complex the value is equal to half the molecular weight.

Table II. Electron Bonding Energies (eV)[a] for Different Atoms in S•••X Complexes with Halide Ion and Some Reference Compounds

compd	N	O	Cl	Br	I
Et_4NCl	401.8		196.7		
Bu_4NBr	401.8			180.8	
Et_4NI	401.8				617.5
SCl	400.3	532.2	201.5		
SBr	400.4	532.1		184.6	
TMSBr[b]	400.3	531.9		184.5	
SI	399.9	531.6			620.9
$Bu_4NBr_3^-$	401.6			182.1[c]	
SBr, Et_4NBr	401.6 399.4	531.2		183.7 181.0	
SBr, Et_4NBr[d]	401.6[e]	531.5		183.3 181.2	
SBr, Bu_4NBr	402.0 399.8	531.5		183.4 180.8	
SBr, Et_4NCl	400.9 399.6	531.2	197.0	183.7	
SBr, Et_4NCl (exch)[f]	401.1 400.0	531.3	196.8	184.0	
SBr, $PhCH_2NEt_3Cl$	401.2 399.8	531.3	197.3	183.7	
SBr, $PhCH_2NEt_3Cl$ (exch)[f]	401.7 399.9	531.6	197.3	183.7	
SI, Et_4NBr	401.3 398.6	530.9		180.4	620.0
SI, Et_4Br (exch)[f]	401.3[e]	531.1		181.1	620.0
SI, Bu_4NBr	401.8 399.9	531.6		181.0	620.8
SI, Bu_4NBr (exch)[f]	401.5[e]	531.3		181.2	620.0
SI, $PhCH_2NEt_3Cl$	401.7 399.7	531.4	197.8		621.1
SI, $PhCH_2NEt_3Cl$ (exch)[f]	401.6 399.3	531.4	197.8		620.6
SBr, SI, Et_4NBr	401.4 400.0	531.3		183.6 181.7	620.4
SBr, SI, Et_4NBr (exch)[f]	401.0[e]	531.2		183.2 181.2	620.0

[a] The bonding energy of C $1s_{1/2}$ was fixed at 285.2 eV according to standard for CH_2 carbon. [b] TMSBr = tetramethyl-*N*-bromosuccinimide. [c] Broad peak. [d] Recrystallized from acetonitrile. [e] Unresolved peak. [f] Prepared via halogen exchange.

structures indicated in column 3 of the table.

In addition to the foregoing there is the supporting evidence obtained from melting point determinations and infrared spectra. In every case where the same complex is obtained from two different pairs of starting reagents, the products have the same melting points and identical infrared spectra. Thus the two preparations of the SI–benzyltriethylammonium chloride complex (entries 9 and 10 in Table I), whether from SI and benzyltriethylammonium chloride, which involves no halogen interchange or from SCl and benzyltriethylammonium iodide, which does require a halogen interchange, show identical melting points and superimposable infrared spectra.

In order to demonstrate unambiguously that halogen exchange has taken place in the mode described above, X-ray photoelectron spectroscopy (ESCA for electron spectroscopy for chemical analysis) was used for measuring the electron bonding energies for some of the elements of these complexes and a few reference compounds. The kinetic energy of the emitted electrons from the 1s (C, O, and N), $2p_{3/2}$ (Cl), $3p_{3/2}$ (Br), and $3d_{5/2}$ (I) levels was recorded, and the electron bonding energy calculated from these data. The calibration of the energy scale was based on C 1s (285.2 eV) according to the standard for methylene carbons.

The results are presented in Table II. One can first note the respectable change in electron bonding energy in going from X^- to SX, 4.8 eV for Cl, 3.8 for Br, and 3.4 for I, showing the influence of the appreciable difference in

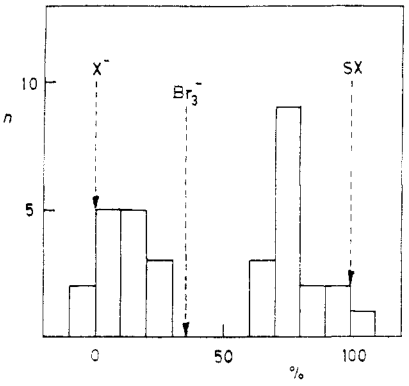

Figure 1. Histogram showing the distribution of halogen electron bonding energies of the complexes of Table II. To be comparable, the energies have been normalized with respect to the difference between those of SX and the corresponding X^- (4.8 eV for Cl, 3.8 eV for Br, and 3.4 eV for I) and expressed in percent of the difference.

Table III. ^{13}C NMR Data for SX and Their Halide Complexes in CD_3CN

compd	^{13}C shift/ppm CH$_2$	^{13}C shift/ppm CO
SCl	28.2	172.9
SCl, Et_4NCl	28.2	173.0
SBr	29.0	175.1
SBr, Bu_4NBr	29.3	177.7
SBr, Et_4NCl	29.2	177.7
SBr, Et_4NCl (exch)	29.2	177.2
SBr, Bu_4NCl (exch)	29.3	177.9
SI	29.6	179.8
SI, Et_4NI[a]	30.4	*b*
SI, Et_4NBr	30.3	183.4
SI, Et_4NBr (exch)	30.3	183.4
SI, $PhCH_2NEt_3Cl$	30.2	183.5
SI, $PhCH_2NEt_3Cl$ (exch)	30.2	183.4

[a] Iodine precipitated copiously. [b] Too low concentration to be detectable.

charge on the halogen in these situations. In the complexes, the difference in electron bonding energy between the two types of halogen is smaller, indicating that some redistribution of charge between the halogen occurs in the complexes. This effect is best shown in a histogram where electron bonding energies for each halogen have been normalized with respect to the interval in electron bonding energy between X^- and SX (see above) and are expressed in percent (Figure 1).

Five pairs of heterohalogen 1:1 complexes are listed in Table II, and within each pair both complexes are identical according to their ESCA spectra. In none of the cases is there any indication of the presence of the opposite halogen types in the exchanged complexes, as shown by the example of Figure 2.

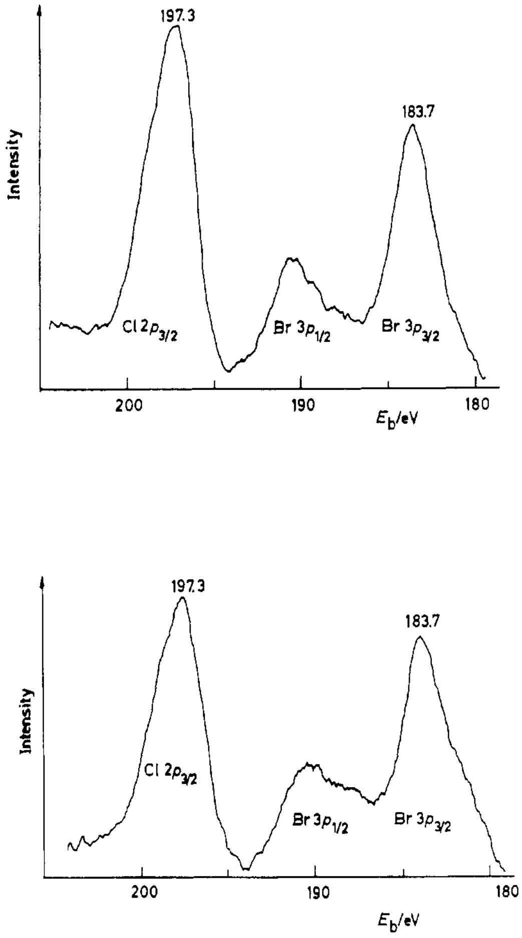

Figure 2. ESCA spectra for the halogen atoms of SBr, $PhCH_2NEt_3Cl$ complexes. The lower spectrum was obtained for a complex prepared by halogen exchange.

Additional evidence was obtained from ^{13}C NMR spectra of SX, X^- complexes in CD_3CN solution (Table III). In the SBr, Br^- complex the ^{13}C NMR shift of the CO carbon moves 2.6 ppm toward lower field upon complexation, and similar shifts are seen in all the heterohalogen complexes with one expected exception, SCl, Cl^-. It has not been possible to isolate this complex in the solid state in spite of many attempts, and in view of the insignificant ^{13}C NMR shift upon complexation it may well be that such a complex does not exist or at least is only a minor component of the equilibrium. The SI, I^- complex is not obtainable in the solid state either due to extensive further reaction to give iodine; a ^{13}C CH_2 signal 0.8 ppm downfield with respect to that of SI is one indication that the complex might be present in solution in very low concentration.

When a solution of SCl in CD_3CN was mixed with one equivalent of Bu_4NBr in CD_3CN, halogen exchange took place at such a rate that it was essentially over by the time the first ^{13}C NMR spectrum could be taken (ca. 5 min). With only half an equivalent of the bromide, the same result was obtained and signals of both the complex and remaining SCl were seen in the NMR spectrum. Thus the halogen exchange process is a fast one, requiring other kinetic techniques for measuring its rate constant.

The last three entries in Table I warrant some additional discussion. The complex prepared from SBr and Et_4NI was first reported by Braude and Waight.[4] It melted at 115–116 °C, analyzed correctly for $C_{16}H_{28}Br_2IN_3O_4$, and was assigned the structure, $2SBr-Et_4NI$. We repeated this preparation and duplicated these results (entry 12 in Table I). However, when this complex in acetonitrile was treated with silver nitrate the product was silver bromide rather than the silver iodide that would be expected from the assigned structure. This suggests that a halogen interchange reaction may have been involved in the reaction. The analytical results and the resultant empirical formula clearly indicate that the complex contains two bromine atoms and one iodine atom. The only structure that is consistent with all of these observations is a 1:1:1 complex made up one SBr, one SI, and one Et_4NBr. This has been confirmed by preparation of the complex from equivalent quantities of SBr, SI, and Et_4NBr and by the ESCA results in Table II (the last two entries). In the paired set of reactions, SBr with Et_4NI and SI with Et_4NBr (entries 12 and 13 in Table I) the reaction of SI with Et_4NBr results in a 2:1 complex, which also gives silver bromide with silver nitrate, but involves no halogen interchange. This complex is 2SI–$\mathrm{Et_4NBr}$ and melts at 138–141 °C dec.

Discussion

The halogen interchange reactions follow a readily identifiable pattern. Using Pauling's electronegativity values (3.0 for Cl, 2.8 for Br, and 2.5 for I),[9] it becomes possible to predict both the occurrence of a halogen interchange and its direction. The changes are always such as to combine the most electronegative halogen atom with the quaternary ammonium ion and attach the less electronegative halogen atom to the imide nitrogen of the complex. Thus, starting with SCl and $\mathrm{R_4NBr}$ the 1:1 complex formed will be SBr–$\mathrm{R_4NCl}$ and a halogen interchange accompanies the reaction. Starting with SBr and $\mathrm{R_4NCl}$ the same complex will be obtained and halogen interchange does not occur. With SI and $\mathrm{R_4NBr}$ as the starting reagents the 1:1 complex formed will be SI–$\mathrm{R_4NBr}$ and no halogen interchange is involved. The same complex can be prepared from SBr and $\mathrm{R_4NI}$, but with this pair of reagents a halogen interchange occurs. All of the complex forming reactions in both Tables I and II, both those that involve halogen interchanges and those that do not, can be successfully rationalized by these simple considerations.

An alternate way of expressing the foregoing is to suggest that the stable complex that results is in every case the product that would result from reaction of a quaternary ammonium succinimide, $\mathrm{R_4NS}$, with an interhalogen compound, BrCl, IBr, or ICl. We have noted that the ^{13}C NMR studies indicate that the halogen interchange reactions occur very rapidly, in less than 5 min, and at a rate too rapid to be followed by NMR. We would also note that when, for example, $\mathrm{Et_4NI}$ and SBr are added to a mixture of chloroform and methanol the dark brown color of iodine monobromide is immediately generated and quickly fades to a light orange as solution is completed. Addition of ether precipitates the SI–$\mathrm{Et_4NBr}$ complex.

The foregoing observations are consistent with an X-philic reaction mechanism[6] for effecting the halogen interchange. We would formulate the reaction as shown in (1), where X is one halogen and Y is another. For the case

$$[\mathrm{SX, Y^-}] \rightleftharpoons [\mathrm{>N^{\delta-}\cdots X^{\delta+}\cdots Y^{\delta-}}]^{\ddagger} \rightleftharpoons \mathrm{S^-} + \mathrm{XY} \rightleftharpoons [\mathrm{SY, X^-}] \tag{1}$$

where Y is the more electronegative halogen, the complex formed would be SX–$\mathrm{R_4NY}$. Where X is the more electronegative halogen, the complex formed would be SY–$\mathrm{R_4NX}$.

The system of equilibria shown in (1) is such that one side is always strongly favored. The favored side, as has been noted, is that in which the more electronegative halogen atom will end up associated with the quaternary ammonium ion. Support for this one-sided position of the equilibria is provided by the reaction with silver nitrate in acetonitrile, in which the silver halide precipitated is from the halogen associated with the quaternary ammonium ion. In every case the silver halide precipitated is actually the more soluble rather than the less soluble of the two silver halide possibilities.[10] This must be a resultant of the equilibria being very strongly to one side.

Support for the above hypothesis is provided by the result obtained by reacting tetrabutylammonium succinimide with iodine monobromide. The product, obtained in 88.5% yield, was the SI–$\mathrm{Bu_4NBr}$ complex and had an infrared spectrum that was indistinguishable from the spectrum given by either the product obtained from SI and $\mathrm{Bu_4NBr}$ or the complex formed from SBr and $\mathrm{Bu_4NI}$ (see entries 6 and 5 in Table I).

Experimental Section

Preparations of SX–$\mathrm{R_4NX}$ complexes have been described.[4,5,7] Only a few representative preparations need be included herein.

Preparation of the SI–$\mathrm{Bu_4NBr}$ Complex from SBr and $\mathrm{Bu_4NI}$. SBr (3.56 g, 0.02 mol) and $\mathrm{Bu_4NI}$ (7.38 g, 0.02 mol) were dissolved in a mixture of ether (100 mL) and acetone (100 mL). The addition of more ether (400 mL) precipitated crystals. The mixture was cooled in the freezer, and more ether (100 mL) was added. The yield was 10.16 g (93%); mp 100–102 °C dec. The same procedure applied to SI and $\mathrm{Bu_4NBr}$ as the starting materials gave the SI–$\mathrm{Bu_4NBr}$ complex in 92% yield; mp 102–104 °C dec.

Preparation of the SI–$\mathrm{Bu_4NBr}$ Complex from $\mathrm{Bu_4NS}$ and IBr. A solution of $\mathrm{Bu_4NS}$ in acetonitrile (25.0 mL of a 0.942 M solution, 0.0235 mol) in a 125-mL Erlenmeyer flask was cooled in an ice bath. IBr (4.88 g, 0.0237 mol) in dry acetonitrile (5 mL) was added portionwise. During the early stages of addition the IBr was immediately decolorized. In the latter stages the orange color persisted. Ether (10 mL) and acetonitrile (1 mL) were used to wash all of the IBr into the reaction flask. The reaction mixture was filtered by gravity into a 500-mL Erlenmeyer flask. Ether (150 mL) was added portionwise. This resulted in turbidity and precipitation of some oily product. The mixture was cooled in the freezer, and a seed of the SI–$\mathrm{Bu_4NBr}$ complex was added. This resulted in crystallization of the product; yield 11.41 g (88.5%). The infrared spectrum of this product was identical with that of the product obtained from SI and $\mathrm{Bu_4NBr}$ above, and a mixed melting point of the two products showed no depression.

Reaction with Silver Nitrate. The SI–$\mathrm{Bu_4NBr}$ complex, prepared as above (2.74 g, 0.005 mol) was dissolved in acetonitrile (50 mL). The solution was stirred magnetically, and a solution of silver nitrate (0.85 g, 0.005 mol) in acetonitrile (15 mL) was added. The yellow precipitate was filtered with suction by using a sintered glass funnel. The precipitate was washed several times with acetonitrile, then with distilled water, and finally with acetone. It was then oven dried at 125 °C for 1.5 h. The yield of silver bromide was 0.864 g (92%). The atomic ratio of I/Br, determined on the precipitate with the electron microprobe, was 0.015 ± 0.007.

Preparation of the 1:1:1 SI–SBr–$\mathrm{Et_4NBr}$ Complex. A mixture of SI (2.25 g, 0.01 mol), SBr (1.78 g, 0.01 mol), and $\mathrm{Et_4NBr}$ (2.10 g, 0.01 mol) was dissolved in chloroform (200 mL). The solution was filtered and refrigerated. On scratching the product precipitated: yield 4.13 g (66%); mp 115–118 °C.

This product was also prepared from SBr and $\mathrm{Et_4NI}$ as described by Braude and Waight[4] in 75% yield; mp 114–116 °C.

Instrumental Analyses. The ESCA spectra were recorded by an AEI-100 spectrometer with AlK (1486.6-eV) X-ray radiation. The pressure of the sample compartment was 10^{-6}–10^{-7} torr. The samples were spread thinly on a Pt foil and were cooled to −60 °C to minimize decomposition. ^{13}C NMR spectra were recorded on a Varian XL-300 instrument.

The atomic ratios of the halogens present in the silver halides were determined by electron microprobe analysis using an ARL SEMQ. A small amount of collodion was mixed with the specimens and served as an adhesive; disks of fused KCl, KBr, and KI were used as standards.

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Registry No. SBr, 128-08-5; SCl, 128-09-6; SI, 516-12-1; $\mathrm{Et_4NCl}$, 56-34-8; $\mathrm{Et_4NBr}$, 71-91-0; $\mathrm{Et_4NI}$, 68-05-3; $\mathrm{Bu_4NI}$, 311-28-4; $\mathrm{Bu_4NBr}$, 1643-19-2; $\mathrm{C_6H_5CH_2NEt_3Cl}$, 56-37-1; $\mathrm{C_6H_5CH_2NEt_3Br}$, 5197-95-5; $\mathrm{C_6H_5CH_2NEt_3I}$, 5400-94-2; 2SBr·$\mathrm{Et_4NCl}$, 104549-34-0; SI·$\mathrm{Et_4NBr}$, 104549-35-1; SI·$\mathrm{Bu_4NBr}$, 104549-36-2; SBr·$\mathrm{C_6H_5CH_2NEt_3Cl}$, 104549-37-3; SI·$\mathrm{C_6H_5CH_2NEt_3Cl}$, 104549-38-4; SBr·SI·$\mathrm{Et_4NBr}$, 104549-39-5; 2SI·$\mathrm{Et_4NBr}$, 104549-40-8; $\mathrm{Bu_4NBr_3^-}$, 38932-80-8; $\mathrm{Bu_4NS}$, 74830-30-1; IBr, 7789-33-5.

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