Å, $\beta = 90.99\ (3)°$, $Z = 4$, $d_c = 1.329\ g\cdot cm^{-3}$. Measurement: ω–2θ scan mode, $3° < \omega < 74°$; scan speed, $(\omega)0.03°\ s^{-1}$; scan width, $(\omega)(2.0 + 0.5 \tan \theta)°$; number of reflections measured, 4875.

Solution[20] and refinement[21] of the structure are based on 4153 reflections with $I > \sigma(I)$. Hydrogen atoms were found in difference Fourier syntheses. The number of parameters refined was 456: scale factor, extinction parameter, positional parameters of all atoms, and thermal parameters (isotropic for hydrogen atoms, anisotropic for others). The final R factor was 7.8%. The drawings have been made by ORTEP.[22]

Materials. **18C6·*t*-BuSC(NH_2)$_2$$ClO_4$ (1:1)** was prepared by extraction of an aqueous solution of *t*-BuSC(NH_2)$_2$Cl (4 mmol/mL) and $LiClO_4$ (1 mmol/mL) with a solution of 18C6 in chloroform. The compound was precipitated by addition of diethyl ether to the chloroform layer and recrystallized from ethanol/petroleum ether: mp 136–137 °C; 80-MHz ^1H NMR ($CDCl_3$) δ 8 (br s, 4 H, NH), 3.64 (s, 24 H, CH_2), 1.60 (s, 9 H, CH_3). Anal. Calcd for $C_{17}H_{37}ClN_2O_{10}S$ (M_r = 497.004): C, 41.08; H, 7.50; Cl, 7.13; N, 5.64; S, 6.45. Found: C, 41.15; H, 7.64; Cl, 7.00; N, 5.54; S, 6.36.

1,3X18C5·*t*-BuSC(NH_2)$_2$$ClO_4$ (1:1) was prepared by extraction of an aqueous solution of *t*-BuSC(NH_2)$_2$Cl (4 mmol/mL) and $LiClO_4$ (4 mmol/mL) with a solution of 1,3X18C5 (4 mmol/mL) in chloroform. The compound was precipitated by addition of diethyl ether to the chloroform layer and recrystallized from ethanol: mp 106–108 °C; 80-MHz ^1H NMR ($CDCl_3$) δ 8.04 (br s, 2 H, NH), 7.57 (s, 1 H, Ar H), 7.50 (br s, 2 H, NH_2), 7.23 (m, 3 H, Ar H), 4.56 (s, 4 H, Ar CH_2), 3.73 (s, 8 H, OCH_2), 3.65 (s, 8 H, OCH_2), 1.40 (s, 9 H, CH_3). Anal. Calcd for $C_{21}H_{37}ClN_2O_9S$ (M_r = 529.049): C, 47.68; H, 7.05; Cl, 6.70; N, 5.30; S, 6.06. Found: C, 47.51; H, 7.13; Cl, 6.60; N, 5.64; S, 5.96.

1,3X18C5·*t*-BuSC(NH_2)$_2$$PF_6$ (1:1) was prepared by extraction of an aqueous solution of *t*-BuSC(NH_2)$_2$Cl (4 mmol/mL) and $LiPF_6$ (4 mmol/mL) with a solution of 1,3X18C5 (4 mmol/mL) in chloroform. The compound was precipitated by addition of diethyl ether and was directly used: ^1H NMR ($CDCl_3$) δ 8.06 (br s, 2 H, NH), 7.57 (s, 1 H, Ar H), 7.26 (m, 5 H, Ar H′ and NH), 4.56 (s, 4 H, Ar CH_2), 3.76 (s, 8 H, OCH_2), 3.64 (s, 8 H, OCH_2), 1.38 (s, 9 H, CH_3). Elemental analyses were not performed because PF_6 salts are unstable.

Registry No. 18-C-6·*t*-BuSC(NH_2)$_2$$ClO_4$ (1:1), 98720-12-8; 1,3-X-18-C-5·*t*-BuSC(NH_2)$_2$$ClO_4$ (1:1), 98720-13-9; 1,3-X-18-C-5·*t*-BuSC(NH_2)$_2$$PF_6$ (1:1), 98720-15-1.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, bond distances, and bond angles (7 pages). Ordering information is given on any current masthead page.

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Substitution of Unactivated Aryl Halides by Thiolate Anions in Polyglymes

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Tetraglyme was found to be a suitable reaction medium to effect the substitution of hexa-, tetra-, tri-, di-, and monochlorobenzenes with sodium alkanethiolates. The substitution of hexa-, tetra-, and trichlorobenzenes by sodium benzenethiolate gave the corresponding (phenylthio)benzenes in tetraglyme, albeit in lower yield. The results of the substitution of chloro-, bromo-, and fluoro-substituted benzenes by an alkanethiolate suggest that an S_NAr mechanism is operative. The effectiveness of the polyglyme as a reaction medium was shown to decrease in the order tetraglyme > triglyme > diglyme > monoglyme.

Introduction

The substitution of aryl halides by thiolate anions continues to be an active area of interest from both a synthetic[1] and mechanistic[2] point of view, since the substitution products are the subject of considerable theoretical study.[3] In particular, hexasubstituted arylthiobenzenes have been shown to function as inclusion hosts,[4] e.g., the adduct of carbon tetrachloride with hexakis(phenylthio)benzene has a true clathrate structure.[5]

Tiecco and co-workers have advocated the use of hexamethylphosphoric triamide (HMPT) as the solvent of choice for the substitution of activated and unactivated aryl halides by thiolate anions.[6] Both *N*,*N*-dimethylacetamide (DMAC)[7] and *N*,*N*-dimethylformamide (DMF)[8] have been advanced as suitable replacements for the potentially carcinogenic HMPT. Quite recently, our laboratory reported the substitution of activated aryl halides by thiolate anions in triethyleneglycol dimethyl ether (triglyme)[9,10] including a single example of the substitution

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(8) Testaferri, L.; Tiecco, M.; Tingoli, M.; Chianelli, D.; Montanucci, M. *Synthesis* **1983**, 751.
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Table I. Reactions of Aryl Halides with Sodium Thiolates in Tetraglyme

entry	substrate	R in RSNa	molar equiv of RSNa	reaction temp, °C	reaction time, h	product	percent yield[a]
1	C_6Cl_6	phenyl	6.6	128	24	**1a**	23
2	C_6Cl_6	*n*-dodecyl	6.6	128	24	**1b**	95
3	C_6Cl_6	ethyl	7.0	143	24	**2**	25[b]
4	1,2,4,5-$C_6H_2Cl_4$	ethyl	4.4	145	20	**3a**	63
5	1,2,4,5-$Cl_6H_2Cl_4$	*n*-octyl	4.4	155	15	**3b**	87
6	1,2,4,5-$C_6H_2Cl_4$	*n*-dodecyl	4.4	162	22	**3c**	86
7	1,2,4,5-$C_6H_2Cl_4$	phenyl	4.4	157	18	**3d**	56
8	1,2,4-$C_6H_3Cl_3$	phenyl	3.3	140	22	**4a**	16[c]
9	1,2,4-$C_6H_3Cl_3$	*n*-dodecyl	3.6	135	22	**4b**	15
10	1,2,4-$C_6H_3Cl_3$	*n*-dodecyl	3.3	140	22	**4b**	25
11	1,2,4-$C_6H_3Cl_3$	*n*-dodecyl	4.3	150	19	**4b**	57
12	1,2,4-$C_6H_3Cl_3$	*n*-dodecyl	4.3	180	20	**4b**	96
13	1,2,4-$C_6H_3F_3$	*n*-dodecyl	4.3	150	19	**4b**	75
14	1,2,4-$C_6H_3Br_3$	*n*-dodecyl	4.3	150	20	**4b**	68
15	1,4-$C_6H_4Cl_2$	*n*-dodecyl	2.1	157	20	**5**	63
16	C_6H_5Cl	*n*-dodecyl	1.0	200	24	**6**	33

[a] Isolated yield (recrystallized). [b] Isolated by preparative HPLC. [c] Isolated by dry-column chromatography.

of an unactivated aryl halide by an alkanethiolate anion in tetraethyleneglycol dimethyl ether (tetraglyme),[10] albeit in low yield.

We report in this paper the results of an investigation on the reaction of unactivated aryl halides with thiolate anions in polyglyme solvents.

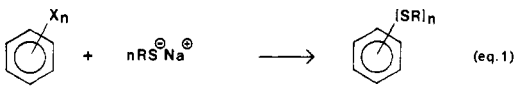
Results and Discussion

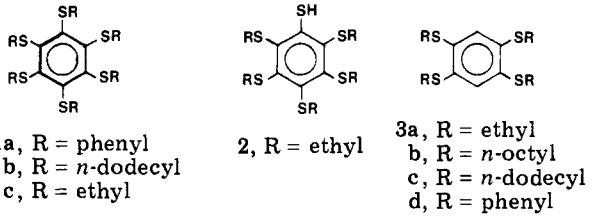
Substitution Reactions in Tetraglyme. The reaction of unactivated aryl halides with both sodium arene and alkanethiolates in tetraglyme (Scheme I; eq 1) was used to prepare a variety of aryl and alkylthiobenzenes (Table I). The reaction of hexachlorobenzene with 6.6 equiv of either sodium benzenethiolate or 1-dodecanethiolate in tetraglyme at 128 °C gave **1a** (23% recrystallized) and **1b** (95% recrystallized), respectively. From the reaction of 7 equiv of sodium ethanethiolate with hexachlorobenzene, however, the product of monodealkylation, **2**, rather than the expected **1c** was isolated by preparative HPLC.

The structure of **2** rests on the following observations. In the ^1H NMR spectrum of **2** an exchangeable singlet resonance was observed, which integrated to a single proton, assignable to the sulfhydryl proton. The ^1H NMR spectrum showed the presence of nonequivalent methyl and methylene group protons expected for structure **2**. The IR spectrum of **2** had a SH absorption at 2455 cm^{-1}. The MS displayed a molecular ion at m/z 410. The spectral and elemental analysis are fully in accord with structure **2**.

Previously, Tiecco *et al.* obtained **2** by the reaction of hexachlorobenzene with 12 equiv of sodium ethanethiolate in HMPT.[6c] Similar observations were reported by Peach and Rayner for the reaction of either hexachlorobenzene or hexafluorobenzene with sodium methanethiolate in HMPT with tetrahydrofuran as a cosolvent.[1e] The formation of **2** appears to be the result of a S_N2 nucleophilic dealkylation reaction by ethanethiolate anion. In agreement with the previous studies, this dealkylation reaction appears to be particularly favorable in the reaction of hexahalogenated benzenes with either methanethiolate or ethanethiolate anion. It has been suggested that S_N2 attack at the carbon atom adjacent to the sulfur of an alkylthio substituent competes with displacement of halogen in the case of sterically nondemanding alkanethiolate nucleophiles.[6c] Consistent with this interpretation, the reaction of the sterically large 1-dodecanethiolate anion with

Scheme I

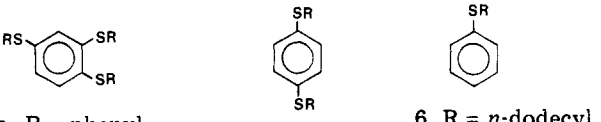




1a, R = phenyl
b, R = *n*-dodecyl
c, R = ethyl

2, R = ethyl

3a, R = ethyl
b, R = *n*-octyl
c, R = *n*-dodecyl
d, R = phenyl



4a, R = phenyl
b, R = *n*-dodecyl

5, R = *n*-dodecyl

6, R = *n*-dodecyl

hexachlorobenzene gave **1b** in high yield, although in this case the effect of a lower reaction temperature must be addressed (vide infra). The formation of **3a** from the reaction of 1,2,4,5-tetrachlorobenzene and sodium ethanethiolate at a slightly higher reaction temperature, however, strongly suggests that the explanation for the formation of **2** is primarily steric in nature. This would be the case, since steric hindrance to the displacement of halogen would be less in 1,2,4,5-tetrachlorobenzene than in hexachlorobenzene, thus minimizing competitive S_N2 attack on the ethylthio substituent by ethanethiolate anion. The formation of **3b,c** at significantly higher temperatures in high yield (entries 5 and 6) also supports the steric interpretation of these findings.

The alkylthiobenzenes **3a–c**, **4b**, **5**, and **6** were prepared similarly in generally high yield by the reaction of the corresponding halobenzene and alkanethiolate anion. The arylthiobenzenes **1a**, **3d**, and **4a** were obtained in lower yields which is presumably due to the reduced nucleophilicity of the resonance-stabilized benzenethiolate anion. The possibility of competing radical pathways due to single-electron transfer processes in the case of the benzenethiolate anion was not investigated.[11]

(10) Pastor, S. D.; Spivack, J. D.; Hughes, D. W. *Phosphorus Sulfur* **1984**, *21*, 39.

Table II. Effect of Polyglyme on Yield of (Alkylthio)benzene

entry	substrate	R in RSNa	molar equiv of RSNa	reaction temp, °C	reaction time, h	solvent	product	percent yield[a]
1	1,2,4-$C_6H_3Cl_3$	*n*-dodecyl	3.3	140	22	tetraglyme	**3c**	25
2	1,2,4-$C_6H_3Cl_3$	*n*-dodecyl	3.3	140	22	triglyme	**3c**	18
3	1,2,4-$C_6H_3Cl_3$	*n*-dodecyl	3.3	140	18	diglyme	*b*	
4	1,2,4-$C_6H_3Cl_3$	*n*-dodecyl	3.3	85 (reflux)	52	monoglyme	*c*	
5	1,2,4-$C_6H_6Cl_3$	*n*-dodecyl	4.3	150	19	tetraglyme	**3c**	57
6	1,2,4-$C_6H_3Cl_3$	*n*-dodecyl	4.3	150	20	triglyme	**3c**	27
7	C_6Cl_6	*n*-dodecyl	6.6	128	24	tetraglyme	**1b**	95
8	C_6Cl_6	*n*-dodecyl	6.6	128	24	triglyme	**1b**	77

[a] Isolated yields (recrystallized). [b] ^1H NMR and MS of the reaction product shows a mixture of mono- and disubstitution products. [c] ^1H NMR and MS of the reaction product shows a monosubstitution product and $C_6H_6Cl_3$.

The effect of the reaction temperature on the yield of **4b**, previously prepared in low yield using tetraglyme as the reaction medium,[10] was investigated. The yield of **4b**, prepared by the reaction of 1,2,4-trichlorobenzene and sodium 1-dodecanethiolate, increased dramatically from 15 to 96 percent with an increase of the reaction temperature from 135 °C to 180 °C (entries 9–12). In contrast, high yields of the *n*-dodecylthio-substituted benzenes **1b** and **3c** were obtained at significantly lower reaction temperatures. These observations are consistent with the previously reported activation of halogen displacement by thiolate anions of both chlorine and alkylthio substituents.[2a,6c]

The reaction of 1,2,4-trifluoro-, tribromo-, and trichloro-substituted benzenes with sodium 1-dodecanethiolate at 150 °C gave the expected product **4b** in 75, 68, and 57 percent yield, respectively (entries 11, 13, and 14). Since the substitution of aryl fluorides does not generally proceed by a $S_{RN}1$ mechanism due to the high energy of the C–F σ^* orbital, the substitution, at least in the case of 1,2,4-trifluorobenzene, proceeds by a S_NAr mechanism.[2,12] The higher yields of **4b** obtained from the fluoro- and bromo-substituted benzenes support the suggestion that a S_NAr mechanism is operative.

Variation of the Polyglyme. The ability of polyglyme solvents to solvate cations is known to depend upon the number of repeating glyme (ethyleneoxy) units.[13] Consistent with this increase in cation-solvating ability, the rate of the reaction of phenoxides with *n*-butyl chloride has been shown to markedly increase in the order monoglyme < tetraglyme < hexaglyme.[14]

The effect of varying the polyglyme upon the yield of the reaction of sodium 1-dodecanethiolate with both 1,2,4-trichlorobenzene and hexachlorobenzene was studied (Table II). Examination of entries 1, 2, 5, and 6 reveal a significant reduction in the yield of **3c** on changing from a tetraglyme to triglyme reaction medium. In the reaction of 1,2,4-trichlorobenzene with sodium 1-dodecanethiolate in diglyme, examination of the MS and ^1H NMR of the reaction product indicated products of mono- and disubstitution only, as evidenced by molecular ions at m/z 512 and m/z 346 in the mass spectrum. The ^1H NMR and MS of the reaction product obtained using monoglyme as the reaction medium showed evidence only for a monosubstitution product and unreacted starting materials.

A reasonable explanation for these observations is that tetraglyme can effectively solvate the sodium cation to generate a highly nucleophilic unsolvated thiolate anion, whereas the lower glymes exhibit reduced cation-solvating ability. This explanation is consistent with the previously determined cation-solvating ability of polyglymes.[13] Of course, the low boiling point of monoglyme limits the reaction temperature which should significantly reduce the rate of reaction, although increasing the duration of the reaction did not lead to a detectable di- or trisubstitution product.

A similar trend on the yield of **1b** was also observed in the reaction of hexachlorobenzene with 1-dodecanethiolate on changing from tetraglyme to triglyme solvent. The reduction of thiolate-anion nucleophilicity in triglyme was used effectively in a previous study from our laboratory to effect the substitution of halogenated phthalate esters without concurrent nucleophilic attack at the alkyl group of the ester functionality.

In summary, tetraglyme was found to be a suitable reaction medium to effect the substitution of a variety of unactivated aryl halides with both arene and alkanethiolate anions. These findings demonstrate that tetraglyme is a suitable alternative to HMPA, DMF, or DMAC.

Experimental Section

All melting points were determined in open capillary tubes with a Thomas-Hoover melting point apparatus and are uncorrected. ^1H NMR spectra were taken on a Varian Model CFT-20 or XL-200 spectrometer. All ^1H chemical shifts are reported relative to tetramethylsilane, where a positive sign is downfield from the standard. IR spectra (1% solution in dichloromethane; sodium chloride cells) were recorded on a Perkin-Elmer Model 1300 spectrometer. Mass spectra were obtained on a Finnegan Model 8200 mass spectrometer.

Preparative HPLC was carried out on a Waters Prep 500A HPLC. Whatman DCS-1F silica gel was used for dry-column chromatography. All solvents were dried prior to use. Reagents were purchased from Aldrich Chemical Company. Reactions were carried out in a flame-dried apparatus under a dry-nitrogen atmosphere. Elemental analyses were performed by Analytical Research Services, CIBA-GEIGY Corporation.

The preparation of **4b** is illustrative of the general method for the preparation of compounds **1–6**. The molar equivalents of thiol, reaction temperature, reaction duration, and yields of product are listed in Table I.

1,2,4-Tris(*n*-dodecylthio)benzene (4b). To a stirred suspension of 1.44 g (60 mmol) of sodium hydride in 50 mL of tetraglyme in a 1 L flask[15] was added dropwise a solution of 12.14 g (60 mmol) of 1-dodecanethiol in 150 mL of tetraglyme. After the addition was complete, the reaction mixture was stirred for 1 h at room temperature and then 2.54 g (14 mmol) of 1,2,4-trichlorobenzene was added. The reaction mixture was heated at 180 °C for 20 h. The cooled reaction mixture was partitioned between 1 L of dilute aqueous hydrochloric acid and 750 mL of diethyl ether. The organic phase was extracted twice with dilute sodium chloride solution.[16] The volatiles were removed in vacuo

(11) For a discussion of photostimulated $S_{RN}1$ reactions of aryl halides with thiolate anions see: Rossi, R. A.; Rossi, R. H. "Aromatic Substitution by the $S_{RN}1$ Mechanism" American Chemical Society: Washington, D.C., 1983; pp 218–224.

(12) Reference 11, pp 207–209.

(13) Chan, L. L.; Wong, K. H.; Smid, J. *J. Am. Chem. Soc.* **1970**, *92*, 1955.

(14) Ugelstad, J.; Berge, A.; Liston, H. *Acta Chem. Scand.* **1965**, *19*, 208.

(15) The large flask size was necessary due to frothing during the addition of the *n*-dodecanethiol.

and the residue was recrystallized from 2-propyl alcohol to give 9.09 g (96%) of a white solid: mp 58–59 °C (lit.[10] 57–59 °C). The spectral data was identical with that previously reported.[10]

Hexakis(phenylthio)benzene (1a). Light yellow solid; Purified by recrystallization from toluene; mp 183–184.5 °C (lit.[17] 182–185 °C) ^{1}H NMR ($CDCl_3$) (200 MHz) δ 7.00 (m, 12 H), 7.14 (m, 18 H). Anal. Calcd for $C_{42}H_{30}S_6$: C, 69.4; H, 4.2. Found: C, 69.3; H, 4.4.

Hexakis(*n*-dodecylthio)benzene (1b). White solid; Purified by recrystallization from a mixture of hexane and acetone; mp 39–41 °C; ^{1}H NMR ($CDCl_3$) (80 MHz) δ 0.96 (t, CH_3, 18 H), 1.27 (complex m, 120 H), 3.02 (t, SCH_2, 12 H). Anal. Calcd for $C_{78}H_{150}S_6$: C, 73.2; H, 11.8; S, 15.0. Found: C, 72.9; H, 11.8; S, 15.2.

Pentakis(ethylthio)benzenethiol (2). Colorless liquid; Purified by preparative HPLC (silica gel: heptane eluent); ^{1}H NMR ($CDCl_3$) (80 MHz) δ 1.15 (overlapping t, CH_3, 15 H), 2.96 (overlapping q, CH_2, 10 H), 6.77 (exchangeable s, SH, 1 H); IR ν 2455 cm^{-1} (SH); MS, *m/z* 410 ($M^{+\cdot}$). Anal. Calcd for $C_{16}H_{26}S_6$: C, 46.8; H, 6.4. Found: C, 47.0; H, 6.4.

1,2,4,5-Tetrakis(ethylthio)benzene (3a). White solid; Purified by recrystallization from 2-propyl alcohol; mp 65–67 °C (lit.[6c,10] 65–67 °C); ^{1}H NMR ($CDCl_3$) (80 MHz) δ 1.31 (t, CH_3, 12 H), 2.94 (q, CH_2, 8 H), 7.19 (s, ArH, 2 H).

1,2,4,5-Tetrakis(*n*-octylthio)benzene (3b). White solid; Purified by recrystallization from 2-propyl alcohol; mp 66–67 °C; ^{1}H NMR ($CDCl_3$) (200 MHz) δ 0.87 (t, CH_3, 12 H), 1.27–1.65 (complex m, 48 H), 2.89 (t, SCH_2, 8 H), 7.17 (s, ArH, 2 H). Anal. Calcd for $C_{42}H_{70}S_4$: C, 69.7; H, 10.8. Found: C, 69.9; H, 10.8.

1,2,4,5-Tetrakis(*n*-dodecylthio)benzene (3c). White solid; Purified by recrystallization from 2-propyl alcohol; mp 72–73.5 °C; ^{1}H NMR ($CDCl_3$) (200 MHz) δ 0.88 (t, CH_3, 12 H), 1.26–1.68 (complex m, 80 H), 2.90 (t, SCH_2, 8 H), 7.18 (s, ArH, 2 H). Anal. Calcd for $C_{54}H_{102}S_4$: C, 73.7; H, 11.7. Found: C, 73.7; H, 11.9.

1,2,4,5-Tetrakis(phenylthio)benzene (3d). White solid; Purified from a mixture of ethyl alcohol and toluene; mp 147–148.5 °C; ^{1}H NMR ($CDCl_3$) (80 MHz) δ 6.81 (s, 2 H), 7.19 (s, 20 H). Anal. Calcd for $C_{30}H_{22}S_4$: C, 70.6; H, 4.3. Found: C, 70.7; H, 4.7.

1,2,4-Tris(phenylthio)benzene (4a). Clear amber liquid; Purified by dry-column chromatography (silica gel; heptane eluent); ^{1}H NMR ($CDCl_3$) (200 MHz) δ 7.35 (dd, 1 H), 7.41 (dd, 1 H), 7.49 (dd, 1 H), 7.71 (complex m, 15 H). Anal. Calcd for $C_{24}H_{18}S_3$: C, 71.6; H, 4.5. Found: C, 71.2; H, 4.6.

1,4-Bis(*n*-dodecylthio)benzene (5). White solid; Purified by recrystallization from 2-propyl alcohol; mp 79–80 °C (lit.[18] 78–79.5 °C); ^{1}H NMR ($CDCl_3$) (200 MHz) δ 0.88 (t, CH_3, 6 H), 1.26–1.62 (complex m, 40 H), 2.90 (t, SCH_2, 4 H), 7.26 (s, ArH, 4 H). Anal. Calcd for $C_{30}H_{54}S_2$: C, 75.2; H, 11.4. Found: C, 74.8; H, 11.4.

(*n*-Dodecylthio)benzene (6). White solid; Purified by recrystallization from ethyl alcohol; mp 33–34 °C (lit.[17b,19] 33–34 °C); ^{1}H NMR ($CDCl_3$) (200 MHz) δ 0.89 (t, CH_3, 3 H), 1.07–1.63 (complex m, 20 H), 2.91 (t, SCH_2, 2 H), 6.99–7.59 (complex m, ArH, 5 H). Anal. Calcd for $C_{18}H_{30}S$: C, 77.6; H, 10.9. Found: C, 77.9; H, 10.5.

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(16) Since the product (in most cases) partially separated on standing, the organic phase was not dried.

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Reaction of Amines with Cyclopropylcarbinyl Halides: S_N2' or Solvolysis?[1a]

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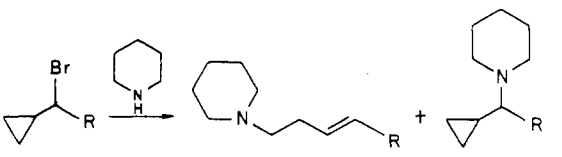
The cyclopropane ring can be opened by amines, under noncationic conditions, and without the requirement of electron-withdrawing groups on the ring. The pedant halide in cyclopropylcarbinyl halides, **1**, provides sufficient activation for the homoallylic ring opening to the corresponding alkenylamine. The substitution reaction of amines with a variety of increasingly sterically hindered halides follows second-order kinetics. This sharply contrasts with the S_N1-like behavior when the halides react with alkoxides in alcohol solvents. It appears that the reaction of **1** with amines proceeds via a homoallylic S_N2' pathway, analogous to Bordwell's description of the S_N2' reaction in allylic systems, rather than via a pathway involving solvent-separated ion pairs.

We have recently reported that cyclopropylcarbinyl halides, **1**, undergo facile substitution on reaction with piperidine to give mixtures of the homoallylic substitution product, **2**, and the direct substitution product, **3**, in good yield.[2] When the alkyl group on the bromine-bearing carbon provided sufficient steric hindrance, the major product of this reaction was **2**, which corresponds to the homoallylic analogue of the well-known S_N2' process observed with allylic halides.[3] Such a S_N2' process is unprecedented for the cyclopropylcarbinyl system. Indeed, only cyclopropane rings activated with two electron-with-



1 **2** **3**

a, R = Me; **b**, R = Et; **c**, R = *n*-Pr; **d**, R = *n*-Bu; **e**, R = *i*-Pr; **f**, R = *t*-Bu

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