Free-Radical Reactions of Fluoroalkanesulfenvl Halides. 4.¹ Reactions of Perfluoroalkane- and Pentafluorobenzenesulfenyl Chlorides with Hydrocarbons in the Presence of Fluorinated Disulfides

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Free-radical reactions of perfluoroalkanesulfenyl chlorides and pentafluorobenzenesulfenyl chloride with cyclohexane and toluene were carried out in the presence of bis(perfluoroalkyl) disulfides and bis(pentafluorophenyl) disulfide to assess the competition between the disulfide and the sulfenyl chloride for reaction with hydrocarbon radicals. With added bis(perfluoroalkyl) disulfides, radical attack occurs only on the sulfenyl chloride, but with added bis(pentafluorophenyl) disulfide, attack occurs on both sulfenyl chloride and disulfide.

In recent years, free-radical chain reactions of highly halogenated alkane- and benzenesulfenvl chlorides with hydrocarbons have been reported.^{1,3-8} Depending upon the structure of the sulfenyl chloride and the hydrocarbon, these reactions yield as major products up to three of the following four types of organic compounds: thiols, disulfides, sulfides, and chlorocarbons (eq 1). Steric effects

$$RSCI + R'H \xrightarrow{n\nu} RSH + RSSR + RSR' + R'CI + HCI$$
(1)

have been proposed as the chief factors determining the product mix in many of these reactions.^{1,3}

It is generally agreed that steps a through e of Scheme I account for the formation of thiol, disulfide, and chlorohydrocarbon in these reactions.^{3,4,6,7} Step f, the attack of the hydrocarbon radical on the sulfur atom of the sulfenyl chloride, has been suggested as the step producing sulfide in the reactions of CF₃SCl and C₆Cl₅SCl.^{3,4} Step g, the attack of the radical on disulfide, has also been considered as an alternative to step f for producing sulfide in the reactions of C_6F_5SCl and C_6Cl_5SCl , and evidence suggests that some sulfide is produced via step g in the C_6F_5SCl -cyclohexane reaction.^{7,8} Step g seems especially attractive in those cases where disulfide is a major product in view of the well-known reactions of free radicals with hydrocarbon disulfides.⁹ This paper presents results of a study of several perfluoroalkanesulfenyl chloride- and pentafluorobenzenesulfenyl chloride-hydrocarbon freeradical reactions carried out with added bis(perfluoroalkyl) or bis(pentafluorophenyl) disulfide to assess the competition between the sulfenyl chloride and the added disulfide for reaction with hydrocarbon radicals.

Results and Discussion

Photoinitiated reactions of sulfenyl chlorides 1-3 with

$$\begin{array}{ccc} \mathrm{CF_3SCl} & n\mathrm{-}\mathrm{C_3F_7SCl} & \mathrm{C_6F_5SCl} \\ 1 & 2 & 3 \end{array}$$

excess cyclohexane or toluene in the presence of an ap-

- (5) H. Kloosterziel, Recl. Trav. Chim. Pays-Bas, 80, 1234 (1961).
 (6) H. Kloosterziel, Recl. Trav. Chim. Pays-Bas, 82, 497, 508 (1963).
- (7) D. D. Tanner, N. Wada, and B. G. Brownlee, Can. J. Chem., 51,

Scheme I

$$RSCI \xrightarrow{h\nu} RS \cdot + CI \cdot$$
 (a)

CI+ R'H ----- R'+ HCI (b)

RS+ R'H ----- RSH + R'+ (c)

RSCI + RSH ------ RSSR + HCI (d)

+ R'CI + RS-(e) (f)

proximately equimolar quantity of a disulfide, usually derived from one of the other two sulfenyl chlorides, were examined. The results are tabulated in Table I and discussed below.

Previously, it has been reported that free-radical reactions of $CF_3SCl(1)$ and $n-C_3F_7SCl(2)$ with cyclohexane are chain reactions which yield a perfluoroalkyl cyclohexyl sulfide, a bis(perfluoroalkyl) disulfide, and chlorocyclohexane, the relative proportions depending upon the sulfenyl chloride (eq 2).^{1,3}

$$R_{\dagger}SCI + \bigwedge \stackrel{h_{\bullet}}{\longrightarrow} R_{\dagger}S \bigwedge + R_{\dagger}SSR_{\dagger} + CI \bigwedge + HCI (2)$$

In the current study, it has been found that when an approximately equimolar mixture of $CF_3SCl(1)$ and (n- C_3F_7 ₂ S_2 (4) is irradiated in a large excess of cyclohexane, the same products in essentially the same yields as seen in the reaction without the added disulfide were obtained. No product arising from attack by a hydrocarbon radical on the added disulfide was detected. Since it has been shown previously that the CF_3SCl -cyclohexane reaction is a long chain reaction which can be initiated either photochemically or by means of an azo initiator^{3a} and since in the current study comparable yields of the same products were obtained under comparable conditions both in the presence and absence of added disulfide, it is obvious that the reaction in the presence of the added disulfide is also a chain reaction.

Similar results were obtained when the reaction of n- C_3F_7SCl (2) with cyclohexane was carried out in the presence of $(CF_3)_2S_2$ (5): i.e., the same products in approximately the yields were obtained as with no added disulfide, and no product deriving from the added disulfide was seen. Further, in a reaction of $n-C_3F_7SCl$ (2) with cyclohexane in the presence of added disulfide related to 2, i.e., $(n-C_3F_7)_2S_2$ (4), the yield of the sulfide product, i.e., heptafluoro-n-propyl cyclohexyl sulfide, relative to the yield of chlorocyclohexane, did not increase when com-

⁽¹⁾ Paper 3: J. F. Harris, Jr., J. Org. Chem., 44, 563 (1979).

⁽²⁾ Contribution no. 2602.

^{(3) (}a) J. F. Harris, Jr., J. Org. Chem., 31, 931 (1966); (b) U.S. Patent

⁽⁸⁾ J. F. Harris, Jr., J. Org. Chem., 43, 1319 (1978).
(9) R. M. Kellogg, "Thiyl Radicals", in "Methods in Free-Radical Chemistry", Vol. 2, E. S. Huyser, Ed., Marcel Dekker, New York, 1969, pp 11-14.

pared with a reaction with no added disulfide. An increase would have been expected if cyclohexyl radical attack on the disulfide 4 were occurring. From this group of experiments, it is concluded that cyclohexyl radical attack on bis(perfluoroalkyl) disulfides does not compete successfully with attack on the perfluoroalkanesulfenyl chlorides 1 and 2.

Analogous results were obtained in reactions of toluene with CF₃SCl (1) and n-C₃F₇SCl (2) with added (n-C₃F₇)₂S₂ (4) and (CF₃)₂S₂ (5), respectively.

However, when the added disulfide is bis(pentafluorophenyl) disulfide (6), products derived from this disulfide were obtained in addition to the products normally expected from the reaction of the sulfenyl chloride and the hydrocarbon alone. For example, in the reaction of CF₃SCl (1) with cyclohexane in the presence of 1 equiv of the disulfide 6, cyclohexyl pentafluorophenyl sulfide (7) and trifluoromethyl pentafluorophenyl disulfide (8) were among the major products. The two cyclohexyl sulfides were produced in comparable amounts (eq 3).

$$CF_{3}SCI + \bigcirc + (C_{6}F_{5})_{2}S_{2} \xrightarrow{h_{*}} CF_{3}S \bigcirc + 6$$

$$1 \qquad 6$$

$$(CF_{3})_{2}S_{2} + CI \bigcirc + CF_{3}SSC_{6}F_{5} + C_{6}F_{5}S \bigcirc + 8$$

$$7$$

$$HCI (3)$$

Analogous results were obtained in the reactions of $CF_3SCl(1)$ with toluene and $n-C_3F_7SCl(2)$ with cyclohexane and toluene, all in the presence of the disulfide 6. In the $CF_3SCl(1)-(C_6F_5)_2S_2$ (6)-cyclohexane reaction,

the cyclohexyl sulfide 7 is presumably formed via attack by the cyclohexyl radical on 6 (eq 4). Subsequent reac-

$$\begin{array}{c} & & & \\ &$$

tions of the pentafluorophenylthiyl radical thus formed can account for the presence of trifluoromethyl pentafluorophenyl disulfide (8) (eq 5 and 6). Alternatively, the

$$C_6F_5S' + \bigcirc - C_6F_5SH + \bigcirc (5)$$

$$C_6F_5SH + CF_3SCl \rightarrow CF_3SSC_6F_5 + HCl \qquad (6)$$

sulfide 7 could be produced by cyclohexyl radical attack upon the disulfide 8, which in turn could be formed by the attack of the (trifluoromethyl)thiyl radical upon the disulfide 6 (eq 7 and 8).¹⁰

$$CF_{3}S \cdot + (C_{6}F_{5})_{2}S_{2} \rightarrow CF_{3}SSC_{6}F_{5} + C_{6}F_{5}S \cdot$$
(7)

$$\bigcirc + CF_3SSC_6F_5 \longrightarrow \bigcirc SC_6F_5 + CF_3S \cdot (8)$$

Presumably the pathway represented by eq 4–6 is preferred since in the reaction of CF_3SCl (1) with cyclohexane in the presence of 1 equiv of the unsymmetrical disulfide 8, the yield of the cyclohexyl sulfide 7 is much less than that in the corresponding reaction containing disulfide 6. It thus appears that attack by the cyclohexyl radical on the unsymmetrical disulfide 8 does not compete very well with attack upon CF₃SCl (1)—in contrast to the competition between attack on 6 and 1. In the analogous reaction of CF₃SCl (1) with toluene in the presence of the unsymmetrical disulfide 8, only a trace of benzyl pentafluorophenyl sulfide was detected, indicating that benzyl radical attack upon 1 occurs almost to the exclusion of attack on 8.

Not unexpectedly, reactions of pentafluorobenzenesulfenyl chloride (3) with cyclohexane and toluene in the presence of $(n-C_3F_7)_2S_2$ (4) or $(CF_3)_2S_2$ (5) yielded no cyclohexyl or benzyl perfluoroalkyl sulfides. The products were those expected from the reactions of the sulfenyl chloride (3) with the hydrocarbon alone.¹¹

In summary, these results show the following in hydrocarbon solution at ambient temperatures.

(1) Bis(perfluoroalkyl) disulfides do not compete successfully with perfluoroalkanesulfenyl chlorides 1 and 2 or pentafluorobenzenesulfenyl chloride (3) in reactions with cyclohexyl or benzyl radicals.

(2) Bis(pentafluorophenyl) disulfide does compete successfully with perfluoroalkanesulfenyl chlorides 1 and 2 for reaction with these same radicals, and reactions with both substrates occur on a comparable scale.

(3) The ability of $CF_3S_2C_6F_5$ to compete with sulfenyl chlorides 1 and 2 for these radicals is intermediate, i.e., less than that of $(C_6F_5)_2S_2$ (6), but greater than that of $(CF_3)_2S_2$ (5).

With respect to the mechanism of free-radical reactions of fluorinated sulfenyl chlorides with hydrocarbons (Scheme I), these studies suggest that in reactions of perfluoroalkanesulfenyl chlorides, sulfide production must occur overwhelmingly via attack by hydrocarbon radicals on the sulfur of the sulfenyl chloride rather than by attack on disulfide that may have been produced in the reaction, i.e., via step f rather than step g of Scheme I. However, when the sulfenyl chloride is an aromatic one, then some sulfide production occurs via attack upon the aromatic disulfide that is made during the reaction.

Experimental Section

I. Irradiation Experiments. All of these experiments were carried out in essentially the same manner and are illustrated by two detailed examples given below. The reaction mixtures were analyzed by gas chromatography and the principal products were identified by comparison of retention times with those of materials of known structure.¹² Although the gas chromatography analyses were qualitative, each experiment with an added disulfide was compared with an experiment without the added disulfide done either immediately before or immediately after in the same equipment. All of the experiments without added disulfides have been analyzed quantitatively and reported in previous publications.^{1,3a,8} In all cases in which the added disulfide was a bis-(perfluoroalkyl) disulfide, the GC analyses showed that the yields of the products were essentially the same as those in the experiments with no added disulfide. The results of the experiments are tabulated in Table I.

a. Reaction of Trifluoromethanesulfenyl Chloride and Bis(heptafluoro-n-propyl) Disulfide with Cyclohexane. A mixture of 1.626 g (0.0119 mol) of trifluoromethanesulfenyl chloride (1), 3.40 g (0.00845 mol) of bis(heptafluoro-n-propyl) disulfide (4), and 10 mL of cyclohexane contained in a quartz tube

⁽¹⁰⁾ The formation of unsymmetrical disulfides by thiyl radical displacement upon disulfides is well-known: K. U. Ingold and B. P. Roberts, "Free Radical Substitution Reactions", John Wiley and Sons, Inc., New York, 1971, pp 209-217.

⁽¹¹⁾ In the reaction of $C_8F_5SCl(3)$, $(CF_3)_2S_2(5)$, and cyclohexane, a very small yield of $CF_3S_2C_6F_5(8)$ was detected, presumably arising by a displacement reaction of the pentafluorophenylthiyl radical on the disulfide 5^{10}_{10}

⁽¹²⁾ All of the sulfide products have been reported previously.^{1,3,8} In some cases, the identities of compounds corresponding to the GC peaks were confirmed by mass spectroscopy.

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chloride	amount, g (mol)	disulfide	(mol)	(mL)	time, min	sulfenyl chloride	added disulfide
CF ₃ SCl	1.626 (0.0119)	$(n \cdot C_3 F_7)_2 S_2$	3.40 (0.00845)	cyclohexane (10)	12	$\frac{CF_3SC_6H_{11}-c,^a}{ClC_6H_{11}-c,}$ $(CF_3)_2S_2$	none
CF₃SCl	1.626 (0.0119)	$(n-C_3F_7)_2S_2$	4.79 (0.0120)	toluene (30)	17	$CF_3SCH_2C_6H_5, a,b$ $CICH_2C_6H_5, (CF_3), S,$	none
CF ₃ SCl	1.626 (0.0119)	$(C_6F_5)_2S_2$	4.74 (0.0119)	cyclohexane (30)	39	$CF_3SC_4H_{11}^{-1}-c, b$ $ClC_4H_{11}^{-1}-c,$ $(CF_3)_2S,$	$\begin{array}{c} C_6F_5SC_6H_{11}\text{-}c,\\ C_6F_5S_2CF_3 \end{array}$
CF_3SCl	1.951 (0.0143)	$(C_6F_5)_2S_2$	4.74 (0.0119)	toluene (25)	20	$C\dot{F}_{3}SC\dot{H}_{2}\dot{C}_{6}H_{5}^{,b,c}$ (CF ₄) ₂ S,	$C_{6}F_{5}SCH_{2}C_{6}H_{5},$ $C_{4}F_{5}S_{3}CF_{3}$
CF ₃ SCl	1.626 (0.0119)	C ₆ F ₅ S ₂ CF ₃	3.57 (0.0119)	cyclohexane (30)	4	CF ₃ SC ₆ H ₁₁ -c, ClC ₆ H ₁₁ -c, (CF ₃) ₂ S,	C ₆ F ₅ SC ₆ H ₁₁ -c (low yield)
CF,SCl	1.626 (0.0119)	$C_6F_5S_2CF_3$	3.57 (0.0119)	toluene (30)	7	$CF_3SCH_2C_6H_5,$ (CF_1),S,	$C_6F_5SCH_2C_6H_5$ (trace)
n-C ₃ F ₇ SCl	1.50 (0.00634)	$(CF_3)_2S_2$	2.34 (0.0116)	cyclohexane (20)	6	$n \cdot C_{3}F_{7}SC_{6}H_{11} \cdot c, a$ $ClC_{6}H_{11} \cdot c, (n - C_{3}F_{7})_{2}S_{2}$	none
n-C ₃ F ₇ SCl	1.50 (0.00634)	(CF ₃) ₂ S ₂	2.34 (0.0116)	toluene (20)	9	$n \cdot C_3 F_7 SCH_2 C_6 H_5, ^a$ CICH ₂ C ₆ H ₅ , (n- C ₃ F ₇) ₂ S ₂	none
$n-C_3F_7SCl$	1.00 (0.00423)	$(n-C_3F_7)_2S_2$	1.70 (0.00423)	cyclohexane (20)	18.5	$n-C_{3}F_{7}SC_{6}H_{11}-c,^{a}$ CIC ₆ H, 1-c	none
$n-C_3F_7SCl$	1.00 (0.00423)	$(C_6F_5)_2S_2$	1.68 (0.00422)	cyclohexane (20)	17	$n - C_{3}F_{7}SC_{6}H_{11} - c, b$ $ClC_{6}H_{11} - c, (n - C_{3}F_{7})_{2}S_{2}$	$C_{6}F_{5}SC_{6}H_{11}-c, C_{6}F_{5}S_{2}C_{3}F_{7}-n$
$n-C_3F_7SCl$	1.00 (0.00423)	$(C_6F_5)_2S_2$	1.68 (0.00422)	toluene (20)	33	$\begin{array}{c} n\text{-}C_{3}F_{7}SCH_{2}C_{6}H_{5}, \\ ClCH_{2}C_{6}H_{5}, (n-2)G_{3}F_{7})_{2}S_{2} \end{array}$	$C_{6}F_{5}SCH_{2}C_{6}H_{5}$ $C_{6}F_{5}S_{2}C_{3}F_{7}-n$
C ₆ F ₅ SCl	2.00 (0.00853)	$(\mathbf{CF}_3)_2\mathbf{S}_2$	4.14 (0.0205)	cyclohexane (25)	22	$C_{s}F_{5}SC_{s}H_{11}-c, a, b$ $CIC_{s}H_{11}-c, (C_{5}F_{5})_{2}S_{2}$	$C_6F_5S_2CF_3$ (very little)
C ₆ F ₅ SCl	2.00 (0.00853)	(CF ₃) ₂ S ₂	3.60 (0.0178)	toluene (20)	10	$C_6F_5SCH_2C_6H_5$, a,b ClCH ₂ C ₆ H ₅ (trace)	none
C ₆ F ₅ SCl	1.00 (0.00426)	$(n-\mathbf{C}_3\mathbf{F}_7)_2\mathbf{S}_2$	1.71 (0.00425)	cyclohexane (20)	21	$C_{6}F_{5}SC_{6}H_{11}-c,^{a}$ ClC_{6}H_{11}-c, (C_{6}F_{6})_{3}S_{3}	none
C ₆ F ₅ SCl	2.92 (0.0124)	$(n-C_3F_7)_2S_2$	5.00 (0.0124)	toluene (30)	12	$\begin{array}{c} C_{6}F_{5}SCH_{2}\hat{C}_{6}H_{5},^{a,b}\\ ClCH_{2}C_{6}H_{5}\\ (trace), (C_{6}F_{5})_{2}\\ S_{2} \ (trace) \end{array}$	none

^a The yields of these products, as determined by GC, are essentially the same as those in an analogous experiment with no added disulfide. ^b The product peaks were examined by GC/MS and their identities confirmed: Du Pont Model 21-490 spectrometer interfaced to a Varian Model 1440 gas chromatograph and a VG 2040 data system. ^c No α-chlorotoluene was detected. Under the GC conditions used, its retention time was very close to that of another product.

 $(9 \times 1.5 \text{ in.})$ fitted with an acetone-dry ice condenser and a magnetic stirrer was irradiated under nitrogen with a sunlamp positioned several inches from the tube until no further color change was evident and the evolution of HCl had ceased (12 min). The reaction mixture was analyzed by gas chromatography (6 ft 20% SE-30 on 60-80-mesh WAWDMCS, 80 °C) and shown to contain chlorocyclohexane, trifluoromethyl cyclohexyl sulfide and bis(trifluoromethyl) disulfide as well as bis(heptafluoro-n-propyl) disulfide.

For comparison, a mixture of 1.626 g (0.0119 mol) of trifluoromethanesulfenyl chloride (1) and 10 mL of cyclohexane was irradiated in the same equipment under the same conditions until the characteristic yellow color of the sulfenyl chloride was gone (7 min). A gas chromatogram showed the presence of the same products as those in the experiment with added bis(heptafluoro-n-propyl) disulfide, and by comparing the sizes of the peaks, it was evident that the yields of these products are essentially the same in the two experiments.¹³

b. Reaction of Heptafluoro-1-propanesulfenyl Chloride and Bis(trifluoromethyl) Disulfide with Toluene. A mixture of 1.50 g (0.006 34 mol) of heptafluoro-1-propanesulfenyl chloride (2), 2.34 g (0.0116 mol) of bis(trifluoromethyl) disulfide, and 20 mL of reagent-grade toluene was irradiated as described above until the mixture was essentially colorless (9 min). In the same apparatus under the same conditions, a mixture of 1.00 g of the sulfenyl chloride 2 and 15 mL of toluene was irradiated until essentially colorless (8 min). Gas chromatographic analysis showed that the yields of α -chlorotoluene, heptafluoro-*n*-propyl benzyl sulfide, and bis(heptafluoro-n-propyl) disulfide were essentially the same in the two reactions. A quantitative analysis of the reaction mixture from an experiment without the added disulfide has been reported previously.14

II. Preparation of Trifluoromethyl Pentafluorophenyl Disulfide (8).¹⁵ In a 150-mL vessel equipped with a magnetic stirrer, a dry ice condenser capped with a nitrogen bubbler, and a gas-inlet tube was placed a solution of 5.00 g of pentafluorobenzenethiol in 25 mL of toluene. The condenser was filled with dry ice and 2.7 mL (at -76 °C) of liquid CF₃SCl was vapor transferred into the vessel via the gas-inlet tube. Heat was evolved and the yellow color disappeared quickly. GC showed one major

⁽¹³⁾ In a previous study, it was reported that the yields of chlorocyclohexane, trifluoromethyl cyclohexyl sulfide, and bis(trifluoromethyl) disulfide obtained in a UV-initiated CF₃SCI-cyclohexane reaction done under comparable conditions were 28%, 45% and 25%, respectively.^{3a}

⁽¹⁴⁾ Yields were as follows: α-chlorotoluene, 34%; heptafluoro-n-propyl benzyl sulfide, 54%; bis(heptafluoro-n-propyl) disulfide, 46%.¹
(15) M. E. Peach, Can. J. Chem., 45, 429 (1967).

product. Distillation of the reaction mixture through a small Vigreux still gave 5.32 g of trifluoromethyl pentafluorophenyl disulfide (8), distilling at 72-73 °C (20 mm).

Registry No. 1, 421-17-0; 2, 662-42-0; 3, 27918-31-6; 4, 356-07-0;

Ion Radicals. 46. Reactions of the Adducts of Thianthrene and Phenoxathiin Cation Radicals and Cyclohexene with Nucleophiles^{1,2}

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Thianthrene cation radical perchlorate 1a reacts with cyclohexene to give an adduct [2a, 1,2-bis(5-thianthreniumyl)cyclohexane diperchlorate]. Reactions of 2a with CN^- , $C_gH_sS^-$, and I⁻ have been studied in dimethyl sulfoxide (Me₂SO) and ethanol at room temperature. Reaction of the analogous adduct of cyclohexene and phenoxathiin cation radical perchlorate 2b with I⁻ in ethanol was also studied. The reactions indicate that the adducts have the trans-1,2 structure and undergo facile substitution (S_N2) and subsequent elimination (E2) reactions at room temperature.

Recently, the addition of the thianthrene and phenoxathiin cation radicals to alkenes and alkynes was reported.³ The products of addition to alkenes were the then unknown alkane 1,2-disulfonium ions, which were isolated as their perchlorates. The chemistry of these ions is, for the most part, unknown. They contain very large sulfonium groups which would appear to be ideally suited leaving groups in reactions with nucleophiles. Therefore, we have investigated the reactions of the adduct 2a obtained from thianthrene cation radical perchlorate 1a and cyclohexene (eq 1) with the representative, strong nucleophiles CN⁻, I⁻, and C₆H₅S⁻. We have also examined briefly the reaction of 2b with I⁻.



At first sight one might anticipate that the reaction of **2a** with nucleophiles would lead readily to other 1,2-disubstituted cyclohexanes (eq 2). This type of reaction was,

$$2a + 2Nu^{-} \rightarrow \bigvee_{Nu}^{Nu} + 2 \bigvee_{S}^{S} (2)$$

in fact, reported more recently by Chow and Iwai⁴ between

cyanide ion and the adduct of the dimethylsulfonium cation radical with 1-hexene. A quantitative yield of 1,2dicyanohexane was obtained (eq 3). Our experience with 2a, however, has been quite different.

+SMe₂ CN

$$\downarrow$$
 \downarrow CN
C4H9CHCH₂SMe₂ $\xrightarrow{CN^{-}}$ C4H9CHCH₂CN + Me₂S (3)

Results

Reaction of the Adduct 2a with Cyanide Ion. This reaction was successful only in dimethyl sulfoxide (Me₂SO). Many attempts in acetonitrile led only to an almost quantitative yield of thianthrene, that is, as if electron transfer had occurred. The isolated products of reaction in Me₂SO after 6 h (eq 4) were thianthrene (3, 94%), 1-



cyanocyclohexene (4, 72%), and the two isomers of 1,2dicyanocyclohexane (5), in 19% (cis-5) and 8% (trans-5) yield. Insight into the course of the reaction was obtained by sampling the reaction mixture at timed intervals. The first products to be formed were 3 and 4. In fact, within 15 min of starting the reaction, 2a, initially in suspension, had dissolved completely, and crystals of 3 began to appear. Samples taken at 0.5 and 1 h showed the presence of 4 but not of 5. With progressing time, quantitative GLC showed that the amount of 4 decreased while the amounts of cis- and trans-5 increased. At the end of sampling (48 h) the yields were as follows: 4, 36.7%, cis-5, 33.6%; and trans-5, 24.4%. During the period of sampling (7.5-48 h) the ratio of cis-5/trans-5 was always 57/43.

The formation of 1,2-dicyanocyclohexane (5) from 1cyanocyclohexene (4), as indicated by the results with 2a,

⁽¹⁾ Part 45: H. J. Shine, A. G. Padilla, and S.-M. Wu, J. Org. Chem., 44, 4069 (1979).

⁽²⁾ Supported by the National Science Foundation, Grant No. CHE 78-00813.

⁽³⁾ H. J. Shine, B. K. Bandlish, S. R. Mani, and A. G. Padilla, J. Org. Chem., 44, 915 (1979).
(4) Y. L. Chow and K. Iwai, Abstracts, American Chemical Society/

⁽⁴⁾ Y. L. Chow and K. Iwai, Abstracts, American Chemical Society/ Chemical Society of Japan Meeting, Honolulu, HI, Apr 1979, No. ORGN 311, and personal communication from Professor Chow.