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;

5, 372-64-5; 6, 1494-06-0; 7, 56717-64-7; 8, 14999-80-5; cyclohexane, 110-82-7; toluene, 108-88-3; ClC$_6$H$_{11}$-c, 542-18-7; CF$_3$SC$_6$H$_{11}$-c, 6476-52-4; ClCH$_2$C$_6$H$_5$, 100-44-7; n-C$_3$F$_7$SCH$_2$C$_6$H$_5$, 68409-04-1; CF$_3$SCH$_2$C$_6$H$_5$, 351-60-0; n-C$_3$F$_7$SC$_6$H$_{11}$-c, 68409-00-7; C$_6$F$_5$SCH$_2$C$_6$H$_5$, 33288-16-3; C$_6$F$_5$SH, 771-62-0; C$_6$F$_5$S$_2$C$_3$F$_7$-n, 75767-77-0.

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$_6$H$_5$S⁻, and I⁻ have been studied in dimethyl sulfoxide (Me$_2$SO) 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$_N$2) 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 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 C$_6$H$_5$S⁻. We have also examined briefly the reaction of **2b** with I⁻.

**1a**, X = S
b, X = O

2a, Y⁺ =

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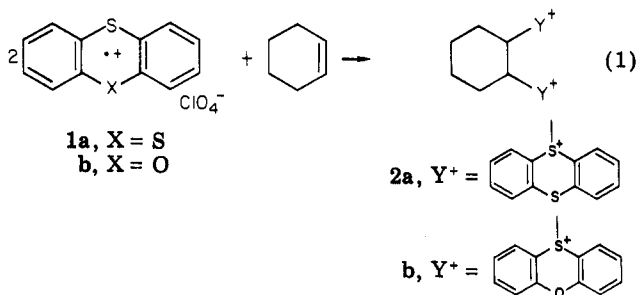
At first sight one might anticipate that the reaction of **2a** with nucleophiles would lead readily to other 1,2-disubstituted cyclohexanes (eq 2). This type of reaction was,
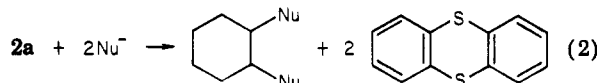

in fact, reported more recently by Chow and Iwai[4] between

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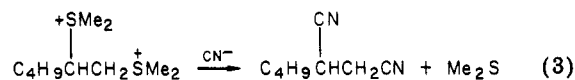
Results

Reaction of the Adduct 2a with Cyanide Ion. This reaction was successful only in dimethyl sulfoxide (Me$_2$SO). 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 Me$_2$SO after 6 h (eq 4) were thianthrene (**3**, 94%), 1-

cis-5   *trans*-5
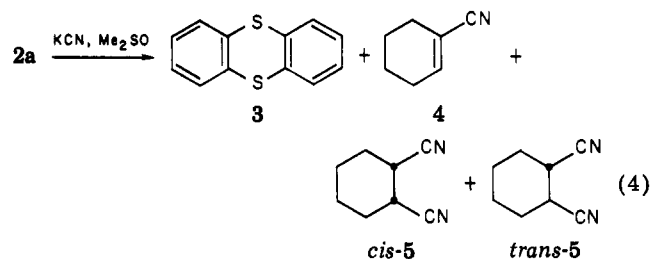
cyanocyclohexene (**4**, 72%), and the two isomers of 1,2-dicyanocyclohexane (**5**), in 19% (*cis*-5) and 8% (*trans*-5) yield. Insight into the course of the reaction was obtained by sampling the reaction mixture at timed intervals. The first products to be formed were **3** and **4**. In fact, within 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 1-cyanocyclohexene (**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/Chemical Society of Japan Meeting, Honolulu, HI, Apr 1979, No. ORGN 311, and personal communication from Professor Chow.

was demonstrated directly. Addition of HCN to 4 took place slowly in the reaction of 4 with potassium cyanide in Me₂SO at room temperature. Thus, after 3 h the composition of the products obtained from a suspension of potassium cyanide in a solution of 4 in Me₂SO was 84.7% of 4, 8.7% of cis-5, and 6.6% of trans-5. After 5 days, the composition was 7.1% of 4, 55.1% of cis-5, and 37.8% of trans-5. Here, too, the ratio of cis-5/trans-5 was in the range of 57/43 to 59/41 over the period of sampling.

Interconversion of cis- and trans-1,2-Dicyanocyclohexane (cis- and trans-5). Earlier workers found that these isomers were not interconvertible if boiled either in pyridine containing acetyl chloride for 6 h or in acetic anhydride containing acetyl chloride for 16 h.[5] We have found that interconversion does not occur during several hours if either isomer is stirred with potassium cyanide in Me₂SO at room temperature. But, if such a suspension is heated at 85 °C, interconversion occurs slowly and gives eventually a ratio of cis-5/trans-5 of 55/45 in the cooled solution. 1-Cyanocyclohexene was not detected in such interconversions by either TLC or GLC, the recovery of 5 being almost quantitative.

Reaction of trans-1,2-Dibromocyclohexane with Potassium Cyanide in Me₂SO. The preparation of 1,2-dicyanocyclohexane (5) is also possible by heating trans-1,2-dibromocyclohexane (6) with sodium cyanide in Me₂SO. This method was used by Applequist and Werner, who isolated cis-5 in 5.8% and trans-5 in 24.5% yield.[6] We have carried out the reaction of 6 with potassium cyanide in Me₂SO. No reaction occurs during 44 h at room temperature. After 16 h at 80 °C, 27% of cis-5 and 18.7% of trans-5 were isolated. The only other product identified was 2-cyanocyclohexanone (7) in about 1% yield. The greater yield of the cis isomer prompted us to examine the formation of the isomers by analytical GLC rather than by isolation. After 7.5 h of being heated at 90 °C with potassium cyanide in Me₂SO, the sample of 6 had disappeared. A substantial amount of 7 had been formed but was not assayed, while the yield of 5 was 35% with a cis/trans ratio of 54/46. After 22 h of heating, the yield was the same, and the ratio of isomers was 57/43.

Reaction of the Adduct 2a with Thiophenoxide Ion. Reaction of Me₂SO was complete in a short time, but no products of substitution were found. Instead, only thianthrene (94%) and cyclohexene (61%) were observed by TLC and GLC. The thiophenoxide ion was converted correspondingly into diphenyl disulfide (84%). Sodium thiophenoxide alone in Me₂SO was quite stable, so that the formation of diphenyl disulfide was related to reaction with 2a.

Reaction in dry ethanol, on the other hand, was very slow, so much so that even after 15 days 5% of the 2a remained unreacted and was recovered. The greater part of the 2a was converted into thianthrene and cyclohexene (respectively 94% and 59% of the 2a which reacted), while a small amount (2%) of 3-ethoxycyclohexene (8) was also obtained. Corresponding with the formation of thianthrene and cyclohexene was the formation of diphenyl disulfide (81%).

Reaction of the Adduct 2a with Iodide Ion. The only product of substitution obtained from reaction in Me₂SO was a trace of 1-iodocyclohexene (9) detected by TLC in the large amount of thianthrene (93%) which was isolated. The only other products which were found, corresponding with the cyclohexyl group of 2a, were cyclohexene (27%)

and, for the first time, 1,3-cyclohexadiene (22%). These two volatile products were identified and assayed by GLC with authentic samples.

Reaction of 2a with iodide ion in dry ethanol was, like that of thiophenoxide ion, very slow and incomplete. That is, after 5 days of contact, 15.3% of the 2a remained and was isolated not as 2a but as the diperiodide (10) corre-


10, Y⁺ =
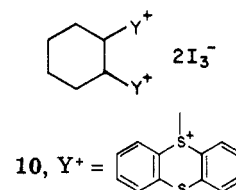
sponding with 2a. This salt 10 was identified by elemental analysis and by its conversion into 2a by reaction with silver perchlorate. The products of reaction (eq 5) of the

$$ \mathbf{2a} \xrightarrow[\text{EtOH}]{\text{I}^-} \quad + \quad + \quad + \quad (5) $$
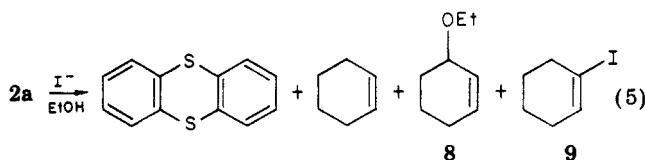
2a, in yields based on the 2a used, were thianthrene (90%), cyclohexene (24%), 1-iodocyclohexene (9, 11%), and 3-ethoxycyclohexene (8, 45%). The last three products were again identified and assayed by GLC using authentic compounds. The data account for 91% of the thianthrenyl and 83% of the cyclohexyl units of the 2a initially taken.

Reaction of the Adduct of 2b with Iodide Ion. This reaction was interrupted after a short time (30 min) and gave (eq 6) what we believe to be 5-(2-iodocyclohexyl)-

$$ \mathbf{2b} \xrightarrow[\text{EtOH}]{\text{I}^-} \quad \mathbf{11} \quad I_3^- \quad + \quad (6) $$
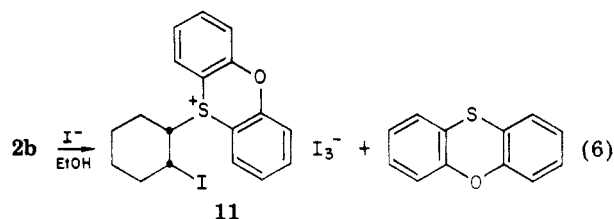
phenoxathiin periodide (11, 32%) and thianthrene (92%). In order for periodide ion to be formed, it is necessary that initially some of the 2b be reduced by iodide ion and that iodine be formed. This was indeed observed but not assayed. Compound 11 was identified by elemental analysis and its ¹H NMR and UV (I₃⁻) spectra.

Discussion

Products of Reactions. A complication that arises in discussing the products and their formation is that neither the configuration nor the conformation of the adducts 2a,b in solution are known. However, it is possible to deduce from the products formed that the configuration is very likely trans. A trans configuration for 2a would be expected also if the addition of the first thianthrene cation radical followed the same course as the addition of thiyl cations to alkenes,[7] and a bridged cation radical intermediate were formed. Consequently, also, the predominant conformation of 2a in solution may well be the axial–axial (aa) conformation, as in some other 1,2-disubstituted cyclohexanes containing polar substituents.[8]

(5) G. E. Ficken, H. France, and R. P. Linstead, *J. Chem. Soc.*, 3730 (1954).
(6) D. E. Applequist and N. D. Werner, *J. Org. Chem.*, 28, 48 (1963).

(7) (a) J. G. Tillet, *Chem. Rev.*, 76, 747, 769 (1976); (b) G. Capozzi, O. De Lucchi, V. Lucchini, and G. Modena, *Tetrahedron Lett.*, 2603 (1975).

Parker and co-workers[9] have shown that 1-substituted cyclohexenes are formed in reactions of bases with *cis*- but not *trans*-1,2-disubstituted cyclohexanes. For example, in reactions of ethoxide, acetate, and chloride ions with *cis*-2-bromocyclohexyl tosylate (12) in ethanol or acetone (eq 7), the two 1-substituted cyclohexenes 13 and 14 were

$$\text{(7)}$$
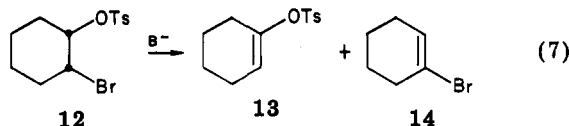
the major or only products. Further, reaction of *cis*-1,2-bis(tosyloxy)cyclohexane with chloride or acetate ion in acetone gave large amounts of 13.

The reaction of the adduct 2a with cyanide ion can then be understood if 2a has the trans configuration and undergoes successively S_N2 and E2 reactions to give 4 (eq 8,

$$\text{(8)}$$
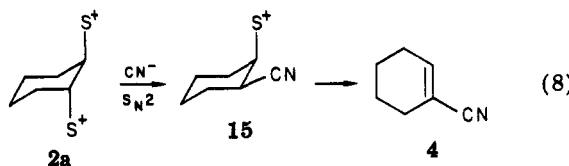
in which S^+ signifies a thianthrene unit). Although we have not isolated the intermediate 15 from reactions of 2a, an analogue (11, eq 6) was isolated as the periodide from the reaction of iodide ion with the adduct 2b in ethanol and is assumed to have, also, the cis configuration.

Further, the reactions of 2a with thiophenoxide ion can also be understood if 2a has the trans configuration. Parker[9] has found that reactions of *trans*-1,2-dibromocyclohexane (*trans*-6) with iodide and *p*-nitrothiophenoxide ion in acetone gave only cyclohexene. That is, only the E2Hal elimination was observed. In contrast, reaction of *cis*-1,2-dibromocyclohexane (*cis*-6) with *p*-nitrothiophenoxide ion gave greater than 95% of 1-bromocyclohexene. In our reaction of 2a with thiophenoxide ion in Me$_2$SO, 94% of the thianthrenyl units appeared as thianthrene, while the only other major product found was cyclohexene (61%). This reaction appears to follow the reductive elimination observed with *trans*-6[9] in compliance with which was our isolation of diphenyl disulfide in 84% yield. Reaction of 2a with thiophenoxide ion in ethanol gave the same results (94% of thianthrene and 59% of cyclohexene). The small amount (2%) of 3-ethoxycyclohexene (8) also obtained may have been formed by solvolysis of some 3-S$^+$-substituted cyclohexene, originating from an elimination (minor) reaction of 2a.

It is of interest that reaction of cyanide ion with *trans*-6 in acetone at 75 °C gave 78% of cyclohexene and 22% of 3-cyanocyclohexene (16).[9] Parker attributes this to a sequence of elimination and substitution reactions (eq 9).

$$\text{(9)}$$
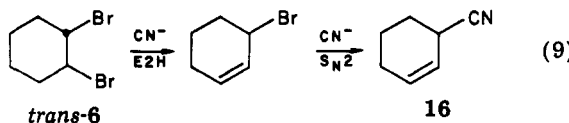
Why should the adduct 2a behave differently (eq 8) from *trans*-6? Our feeling is that this reflects the easy initial S_N2 displacement of S^+ as thianthrene, as compared with (the unobserved) S_N2 displacement of Br as bromide ion.

Scheme I
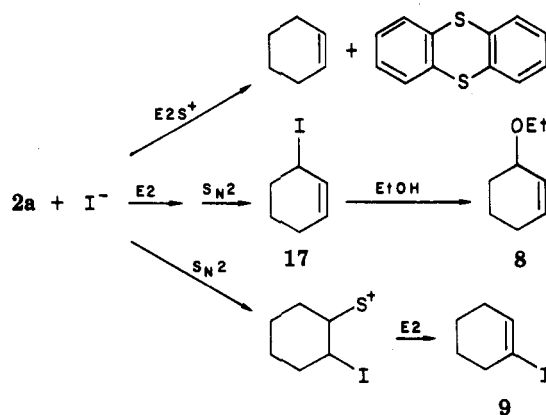
Reaction of 2a with cyanide ion proceeds easily, in fact, at room temperature, whereas no reaction occurred with *trans*-6 in the same solvent (Me$_2$SO) at room temperature within 44 h. Once displacement on 2a has occurred (forming 15) elimination follows to give 1-cyanocyclohexene, 4. Now, elimination from 15 (eq 8) appears not to give 1-S$^+$-substituted cyclohexene, in spite of the fact that the proton adjacent to the S$^+$ group is likely to be the more acidic.[10] Our conclusion about this is that, again, elimination to give 4 involves the departure of a much better leaving group (i.e., S$^+$ rather than CN).

Reactions of 2a with iodide ion leading to cyclohexene, 1-iodocyclohexene (9), and 3-ethoxycyclohexene (8) are also understandable (Scheme I). The 8 is believed to have been formed from 3-iodocyclohexene (17) which did not survive in the medium. We were unable to prepare pure 17 to check its solvolysis in ethanol, but we found that 3-bromocyclohexene was solvolyzed completely (to give 8) in ethanol under the conditions of reaction of 2a, and we assume, therefore, that the solvolysis of 17 is a reasonable expectation.

There are nuances in these reactions that go beyond complete explanation. Thus, in the reaction of 2a with iodide ion in Me$_2$SO some cyclohexadiene (22%) was formed. This is the only reaction in which we were able to find this product. Why it was not formed in detectable quantities in our other reactions with 2a remains unanswered. It is noteworthy that in reactions of *trans*-1,2-dibromocyclohexane with iodide, *p*-nitrothiophenoxide, cyanide, chloride, azide, and acetate ions, only the chloride and acetate ion reactions gave 1,3-cyclohexadiene (in 1% and 8% yields, respectively).[9]

We may ask: how do the reductive eliminations from the adduct 2a with iodide and thiophenoxide ion occur? Are they direct, bimolecular eliminations of the E2 type (designated E2S$^+$), or are they caused by electron transfer? Klein and Evans[11] have shown that cathodic reductive elimination of bromide from *trans*-1,2-dibromocyclohexane occurs more easily in fact in the axial–axial (aa) than the equatorial–equatorial (ee) conformation. This reduction must involve stepwise electron transfers. Similarly, reduction by thiophenoxide and iodide ion, particularly of 2a at room temperature, may involve stepwise electron transfer. The alternative, direct eliminative displacement, i.e., of leaving groups L by nucleophile Nu$^-$ (eq 10),[12] would

(8) F. R. Jensen and C. H. Bushweller, *Adv. Alicyclic Chem.*, **3**, 139 (1971).

(9) P. Beltrame, G. Biale, D. J. Lloyd, A. J. Parker, M. Ruane, and S. Winstein, *J. Am. Chem. Soc.*, **94**, 2240 (1972).

(10) See C. J. M. Stirling, *Acc. Chem. Res.*, **12**, 198 (1979). We base this statement on the analogy that a β-Me$_2$S$^+$ group is 2×10^3 times more effective than a β-CN group in activating alkene-forming eliminations.

(11) A. J. Klein and D. H. Evans, *J. Am. Chem. Soc.*, **101**, 757 (1979).

(12) As with amide ion and phenyldibromoalkanes: D. D. Davis and G. G. Ansari, *J. Org. Chem.*, **35**, 4285 (1970).

$$-\overset{|}{\underset{|}{C}}-\overset{\overset{L}{|}}{\underset{\overset{|}{L}}{C}}- \longrightarrow \text{NuL} + \text{L}^- + \overset{}{\underset{}{>}}C{=}C\overset{}{\underset{}{<}} \quad (10)$$

$$\text{Nu}^-$$
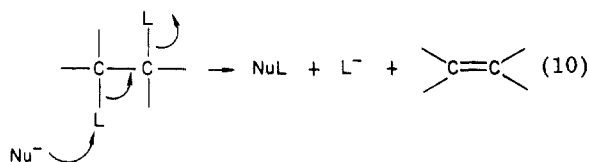
in our case lead to thianthrenium ions **18** and **19**, which

18, Nu = C$_6$H$_5$S
19, Nu = I
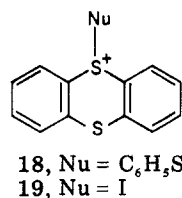
must again suffer S$_N$2 reaction with the nucleophile. The uncommon intermediate **18** particularly invites further interest in these reactions. The course of reductive elimination in adducts such as **2a,b** warrants further enquiry.

Formation of 1,2-Dicyanocyclohexane from 1,2-Dibromocyclohexane. We used the reaction of *trans*-1,2-dibromocyclohexane (*trans*-**6**) with cyanide ion as a way of preparing *cis*- and *trans*-1,2-dicyanocyclohexane (**5**).[6] This reaction, in Me$_2$SO at 85 °C, in giving the dicyanocyclohexanes, is quite different from Parker's reaction in acetone at 75 °C, although our yields of *cis*-**5** and *trans*-**5** are low, totaling from 35% to 46%. Parker[9] obtained mostly cyclohexene (78%) and some of **16** (22%). We did not look for cyclohexene; we obtained, but did not assay, 2-cyanocyclohexanone (**7**). The source of **7** is not known but may be the oxidative displacement of Br from 2-bromocyanocyclohexane (formed earlier) by Me$_2$SO.

Applequist and Werner[6] isolated *trans*-**5** in 24.5% and *cis*-**5** in 5.8% yields from reaction in Me$_2$SO. Our isolated yields were 27% *cis*-**5** and 18.7% *trans*-**5**. When the formation of *cis*- and *trans*-**5** was followed by GLC without isolation, the ratio of *cis*-**5**/*trans*-**5**, measured at room temperature, was 55/45. That is, in our experiments the cis isomer was formed in the greater amount. The same ratio of *cis*-**5**/*trans*-**5** was obtained from reaction of **2a** with cyanide ion, and, as discussed below, in reactions of **4** with cyanide ion and equilibrations of *cis*-**5** and *trans*-**5** with cyanide ion.

Reaction of 1-Cyanocyclohexene (4) with Cyanide Ion and Equilibration of *cis*- and *trans*-1,2-Dicyanocyclohexanes (*cis*- and *trans*-5). The reaction of **4** with cyanide ion in Me$_2$SO at room temperature, giving *cis*- and *trans*-**5**, represents a kinetically controlled reaction. Interconversion of *cis*- and *trans*-**5** was achieved only by heating with cyanide ion in Me$_2$SO at 85 °C and 95 °C. Both kinetic and equilibrium concentrations were about the same and were not very far from equal amounts. The data reflect, we feel, the small size of the cyano group and its small influence on the formation and relative stabilities of the isomers. The free-energy change $(-\Delta G°)$ in going from equatorial to axial CN in the cyclohexyl system is reported to be 0.15–0.25 kcal/mol.[8] It appears that this small difference is reflected also in the dicyanocyclohexanes, in which the balance between dipolar repulsions in the ee and ea forms and the eclipsing interactions in the aa conformation is slightly in favor of the ea form.

Effects of Solvent. Reactions of the adduct **2a** with the nucleophiles were faster in Me$_2$SO than in ethanol. Anions are not as well solvated in Me$_2$SO as in protic solvents, so that the anionic nucleophiles which were used have a comparatively greater reactivity in Me$_2$SO than in ethanol. The solvation of cations by Me$_2$SO, furthermore, makes the anionic nucleophiles even more reactive by

virtue of reducing ion pairing. Rates of S$_N$2 reactions are greatly enhanced, for example, in going from protic to dipolar aprotic solvents.[13] We can understand qualitatively, therefore, the differences observed in the reactions of **2a**, e.g., that 15% of **2a** survived reaction with iodide in ethanol after 5 days and was isolated as **10** and that 5% of **2a** remained from reaction with thiophenoxide ion in ethanol. In contrast, reactions with these nucleophiles in Me$_2$SO were comparatively fast and led to products of elimination.

Conclusions. The very large sulfonium groups in the adduct **2a** are easily displaced by nucleophiles, and the reactions fit into the patterns of reactions of 1,2-disubstituted cyclohexanes. Displacement, furthermore, is much easier than that of more common leaving groups, e.g., Br.

Experimental Section

Commercial thianthrene was found by TLC to contain a small amount of an impurity. This was removed by chromatography on silica gel, eluting with petroleum ether (bp 40–60 °C) and next crystallizing from ethanol; mp 159.5–160 °C. Cyclohexene (>99%, Phillips Petroleum Co.) was either distilled or passed through a column of silica gel (Davison Chemical Co., grade 950). Dimethyl sulfoxide (Me$_2$SO) was dried by distillation over calcium hydride and stored over molecular sieves (Linde, 4A) in a septum-capped bottle. Carbon tetrachloride was NMR grade from Norell Chemical Co. Absolute ethanol was distilled over magnesium turnings activated with iodine. Acetronitrile was Eastman Kodak's anhydrous grade (<0.05 % water) and was stored over molecular sieves in a septum-capped bottle. Reagent grade potassium cyanide and potassium iodide were each ground and kept in a dessicator over potassium hydroxide and phosphorus pentoxide. Sodium thiophenoxide was prepared from thiophenol and finely dispersed sodium. TLC plates were made from either alumina (E. Merck, neutral, Type E, GF 254) or silica gel (E. Merck, Type 60, GF 254). For preparative TLC, 20 g of alumina or silica gel was loaded onto 20 × 20 cm plates; for monitoring reactions, 5 g of alumina or silica gel on 5 × 20 cm plates was used.

Thianthrene cation radical perchlorate **1a** was made by the earlier method.[14,15] Iodometric assay gave 94% cation radical content.

Preparation of the Adduct 2a. A solution of 1.07 g (13.1 mmol) of cyclohexene in 15 mL of acetonitrile was added to a stirred suspension of 569 mg (1.69 mmol) of **1a** in 10 mL of acetonitrile. The color of **1a** disappeared after 15 min, but the mixture was stirred overnight. The pale yellow solution was then poured into 60 mL of dry ether to give a white precipitate. This was filtered, washed with ether, and dried under vacuum over potassium hydroxide and phosphorous pentoxide, giving 588 mg (0.825 mmol, 98%) of **2a**: mp 147–148 °C dec; ^{1}H NMR (liquid SO$_2$) δ 7.60–8.40 (m, 16 H, aromatic), 4.47 (br s, 2 H), 1.40–2.80 (br m, 8 H). Attempts to take the ^{1}H NMR spectrum in Me$_2$SO failed because the solution decomposed slowly on standing, giving the ^{1}H NMR spectrum of thianthrene and other unidentified peaks. Dilute (10^{-5} M) solutions in acetonitrile were also not stable and were not suitable for UV spectroscopy. The UV spectrum was obtainable with a 1.4 × 10^{-2} M solution and had the following [λ_{max} nm (e)]: 315 (br, 1 × 10^4), 254 (sh, 1.93 × 10^4), 237 (4.64 × 10^4), 233 (sh, 4.36 × 10^4).

Anal. Calcd for C$_{30}$H$_{26}$S$_4$Cl$_2$O$_8$: C, 50.5; H, 3.69; S, 18.0; Cl, 9.94. Found: C, 50.0; H, 3.59; S, 17.8; Cl, 10.2.

1-Cyanocyclohexene was made in 47% yield according to the method of Akhrem et al.[16] 3-Ethoxycyclohexene was made in 65% yield from reaction of 3-bromocyclohexene[17,18] with sodium ethoxide in dry ethanol according to the procedure used by

(13) A. J. Parker, *Adv. Org. Chem.*, **5**, 1–46 (1965).
(14) Y. Murata, and H. J. Shine, *J. Org. Chem.*, **34**, 3368 (1969).
(15) S. R. Mani and H. J. Shine, *J. Org. Chem.*, **40**, 2759 (1975).
(16) A. A. Akhrem, A. V. Kamernitskii, and N. S. Pavlova-Grinshina, *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)*, 984 (1962); *Chem. Abstr.*, **57**, 13635g (1962).
(17) M. C. Ford and W. A. Waters, *J. Chem. Soc.*, 2240 (1952).
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Berlande with 3-chlorocyclohexene.[19] 1-Ethoxycyclohexene was prepared by the method of Schmidt and Graffen[20] and was found by GLC to contain a very small amount of cyclohexanone diethyl acetal. The 1-ethoxycyclohexene was satisfactory, however, for use in characterizing by GLC the formation of 1-ethoxycyclohexene in reactions of **2a** with potassium iodide in ethanol.

Solvolyses of 3-Bromocyclohexene. These experiments were carried out to simulate the behavior of 3-iodocyclohexene which, itself, could not be made in satisfactory purity. A solution of 200 mg of 3-bromocyclohexene in 20 mL of ethanol was allowed to stand for 5 days at room temperature. GLC showed that the 3-bromocyclohexene had been converted into 3-ethoxycyclohexene. Very small unidentified peaks were also present in the chromatogram. The same result was obtained when a similar solution was stirred with solid potassium iodide for 5 days.

Preparation of cis- and trans-1,2-Dicyanocyclohexanes (5) from trans-1,2-Dibromocyclohexane (trans-6). Method A. The method of Applequist and Werner[6] was modified. To a suspension of 2.41 g (49.2 mmol) of dried, ground, sodium cyanide in 40 mL of Me$_2$SO was added dropwise over a period of 15 min 5 g (20.7 mmol) of *trans*-6. The mixture was stirred at room temperature for 45 min and then heated at 80 °C for 16 h. To the cooled brown mixture was added 200 mL of brine, and six extractions with methylene chloride (total 900 mL) followed. The dried methylene chloride solution was evaporated to give 13.4 g of a brown Me$_2$SO solution. This was taken up into ether, leaving behind a small amount of tarry material. The ether and Me$_2$SO were removed at low pressure, and the residue was distilled to give 1.35 g of a pale yellow oil which solidified in part in the condenser.

One gram of the product was chromatographed on alumina (Woelm neutral, activity III) with ether–petroleum ether, giving in succession 387 mg (18.7% yield) of *trans*-1,2-dicyanocyclohexane (mp 42–45.5 °C before crystallization), 560 mg (27.0% yield) of *cis*-1,2-dicyanocyclohexane as a sticky solid, and 16 mg of an oil which was shown by IR (C=O, C≡N), ^{1}H NMR, and mass spectrometry to be 2-cyanocyclohexanone, found *m/e* 123.06798, calcd *m/e* 123.06841.[21] Sublimation of the *trans*-5 gave a melting point of 45–46.5 °C (lit.[6] mp 47–48.5 °C). Crystallization of *cis*-5 from petroleum ether gave a melting point of 64–69.5 °C (lit.[6] mp 62–64 °C). Each of the products gave a single spot on TLC (alumina). Hydrolysis of the cis and trans products with 2 N nitric acid[6] gave the corresponding dicarboxylic acids.

Method B. To a suspension of 1.12 g (17.2 mmol) of potassium cyanide in 20 mL of Me$_2$SO was added 1.45 g (6.0 mmol) of *trans*-6. The mixture was stirred at room temperature for 44 h. TLC showed that no dicyanocyclohexane had been formed. The mixture was then heated at 90 °C. Samples (0.5 mL) were pipetted after 7.5 and 22 h and placed in 50 mL of water. The water solution was extracted twice with 50-mL portions of methylene chloride. To the methylene chloride solution, after it was dried over magnesium sulfate and filtered, was added 1 mL of 0.0498 M bibenzyl in methylene chloride to serve as an internal GLC standard. GLC (5% SE-30 on Chromosorb-W) showed the presence of small amounts of three unknown compounds and a substantial amount of 2-cyanocyclohexanone (retention time 1.55 min), but this was not assayed. Also present in both the 7.5- and 22-h samples were *cis*-5 and *trans*-5 in the ratios of 54/46 (7.5 h) and 57/43 (22 h). The total yields were 35% in each case. *trans*-5 and *trans*-6 had similar retention times under the column conditions used (1.85 and 1.90 min). However, TLC of the two samples showed that *trans*-6 was not present. The retention time for *cis*-5 was 3 min and for bibenzyl was 6.7 min.

Reaction of 2a with Cyanide Ion. Method A. Dry Me$_2$SO (10 mL) was added to a mixture of 1.02 g (1.43 mmol) of **2a** and 280 mg (4.31 mmol) of potassium cyanide at 10 °C. The mixture was then stirred for 3 h at room temperature, after which TLC on alumina showed that none of the adduct remained. The Me$_2$SO and volatile products were pumped off at 30–40 °C (<1 mmHg) after 6 h and trapped in liquid N$_2$. The solid residue was extracted

three times with 70 mL of methylene chloride, giving 619 mg of solids. Column chromatography on alumina (Woelm, neutral, activity III) with a petroleum ether–ether gradient gave 575 mg of thianthrene, 6.6 mg of *trans*-5, and 20.1 mg of *cis*-5.

The Me$_2$SO solution which had been pumped off was assayed by GLC (20% SE-30 on Chromosorb-P) and was found to contain 16 mg of *cis*-5, 9.4 mg of *trans*-5, 3 mg of thianthrene, and 111 mg of 1-cyanocyclohexene (4).

The summary is that the major products were thianthrene (94%), 1-cyanocyclohexene (72%), and *cis*- (19%) and *trans*-1,2-dicyanocyclohexane (8%).

Method B. The same starting procedure was used but with 1.07 g (1.5 mmol) of **2a**. After the mixture was stirred for 15 min at room temperature, all of the **2a** had dissolved, and some crystals of thianthrene (presumed) appeared. At intervals of 0.5, 1.0, 7.75, 24, and 48 h aliquots of 0.5 mL were drawn and placed in 50 mL of water. The aqueous solution was extracted with two 50-mL portions of methylene chloride which was washed with brine and dried over magnesium sulfate. Each methylene chloride solution was assayed by GLC. Aliquots taken at 0.5 and 1.0 h contained only 1-cyanocyclohexene (4). At 7.75, 24, and 48 h the compositions (in percent yield of 4, *cis*-5, and *trans*-5, respectively) were as follows: 7.75 h, 80, 7.6, and 5.7; 24 h, 55, 21.5, and 15.7; 48 h, 36.7, 33.6, 24.4. It can be seen that the cis/trans ratio was in each case about 57/43. The total yield of cyano products was 92–95% and shows the conversion of 4, the first product, into the *cis*- and *trans*-dicyanocyclohexanes.

Reaction of 1-Cyanocyclohexene (4) with Cyanide Ion. A solution of 150 mg (1.40 mmol) of 4 in 5 mL of Me$_2$SO was stirred with 180 mg (2.80 mmol) of potassium cyanide at room temperature. The mixture became dark brown after 1 h. Samples of 200 μL were removed after 1 and 2 h, placed on a small column of silica gel, and eluted with methylene chloride. Neither *cis*- nor *trans*-5 was detectable by GLC. Aliquots of 200 μL were removed at particular intervals thereafter, treated as before and analyzed by GLC, using 5% SE-30 on Chromosorb W. The results expressed as the percent composition of the sum of 4, *cis*-5 and *trans*-5 were as follows: 3.25 h, 84.7, 8.7, 6.6; 5.5 h, 76.2, 13.1, 10.6; 22 h, 44.3, 31.8, 23.9; 5 days, 7.1, 55.1, 37.8. The cis/trans ratio thus was in the range of 57/43 to 59/41.

Equilibration of cis- and trans-1,2-Dicyanocyclohexanes (5). Method A. A solution of 50 mg (0.373 mmol) of *cis*-5 in 1 mL of Me$_2$SO was stirred with 130 mg (2.0 mmol) of potassium cyanide at 95 °C. At particular time intervals a sample of the supernatant liquid was removed and placed in 50 mL of water, and the aqueous solution was extracted twice with 30 mL of methylene chloride. The cis/trans ratio of the dicyanocyclohexanes was measured by GLC and was 55/45 for 20, 44, 68, and 120 h. The same experiment was performed with *trans*-5 and gave at 21, 45, 73, and 118 h the ratio 55/45. In none of the samples was 4 detected.

Method B. Although the ratios of *cis*-/*trans*-dicyanocyclohexanes were measured in method A, the recovery of products was not monitored. Therefore, experiments were performed as follows.

A stirred suspension was made of 195 mg (3.0 mmol) of potassium cyanide in 10 mL of Me$_2$SO containing 134 mg (1.0 mmol) of *cis*-5. The experiment was designed for examining samples by TLC and quantitative GLC at timed intervals. After the reaction mixture was stirred for 3 h at room temperature, TLC showed only the presence of *cis*-5, and GLC sampling gave almost 100% recovery of this isomer. Thereafter, the reaction mixture was heated at 85 °C and was cooled briefly for sampling. The amounts of *cis*- and *trans*-5 in the samples totaled close to 100% recovery each time and were in ratios of 68/32 (18 h), 55/45 (42 h), and 54/46 (127 h).

The same experiment was performed with *trans*-5. Again, no conversion to *cis*-5 occurred during 3.5 h at room temperature. Conversion occurred at 85 °C and, with close to 100% recovery each time, had *cis*-5/*trans*-5 ratios of 45/55 (21 h), 52/48 (45 h), 53/47 (93 h).

In each experiment no other product, including 1-cyanocyclohexene, was detected by TLC or GLC.

Reaction of 2a with Sodium Thiophenoxide. Method A. In Me$_2$SO. A mixture of 930 mg (1.3 mmol) of **2a** and 412 mg (3.12 mmol) of sodium thiophenoxide was placed in a septum-

(19) M. A. Berlande, *Bull. Soc. Chim. Fr.*, **9**, 644 (1942).

(20) U. Schmidt and P. Graffen, *Justus Liebigs Ann. Chem.*, **656**, 97 (1962).

(21) We thank Dr. M. L. Gross and Dr. P. Lyon, Midwest Center for Mass Spectrometry, University of Nebraska at Lincoln, for this result.

capped flask under N_2, and 10 mL of Me_2SO, previously purged with N_2, was introduced by syringe. Monitoring the solution by TLC showed that none of the adduct remained after 1.5 h. The mixture was stirred, however, for 20 h. The Me_2SO was then pumped off at 45 °C at <1 mmHg and trapped in liquid N_2. Workup of the Me_2SO solution and the residue of preparative TLC (Merck alumina) and GLC (acid-washed Chromosorb W) gave 238 mg (84%, based on 2a) of diphenyl disulfide (identified by control TLC and melting point, 60.5–61.5 °C), 527 mg (94%) of thianthrene, and 65 mg (61%) of cyclohexene.

Method B. In Ethanol. Ten milliliters of anhydrous ethanol was purged with N_2, and to it were added, under N_2, 1.07 g (1.5 mmol) of 2a and 450 mg of sodium thiophenoxide. Disappearance of the 2a was found to be very slow by TLC monitoring, and 2a was present after 15 days when the stirring was stopped. Volatile materials were pumped off and trapped in liquid N_2.

The solid residue (1.27 g) was found to contain 66 mg of 2a, 244 mg (81%) of diphenyl disulfide, and 571 mg (94%) of thianthrene.

The ethanol solution of volatile materials was found by TLC to contain small amounts of diphenyl disulfide and thianthrene, but these were not assayed. The ethanol solution was found by GLC (20% SE-30 on acid-washed Chromosorb W) to contain 68 mg (0.829 mmol, 59%) of cyclohexene and 3.5 mg (0.0278 mmol, 2%) of 3-ethoxycyclohexene.

Reaction of 2a with Potassium Iodide. Method A. In Me_2SO. The 2a (1.07 g, 1.5 mmol) was added in the dark to a stirred suspension of 2 g of potassium iodide in 10 mL of Me_2SO. After 24 h the solvent and volatile products were pumped off and trapped in liquid N_2. The solid residue was washed with water to remove potassium iodide and dried in vacuo, giving 604 mg of solids. TLC showed this to be thianthrene (93% yield) containing a trace of 1-iodocyclohexene.[22] The distillate was assayed by GLC and contained 33 mg (27%) of cyclohexene and 26 mg (22%) of 1,3-cyclohexadiene.

Method B. In Ethanol. Twenty milliliters of ethanol was added to a mixture of 1.07 g (1.5 mmol) of 2a and 5 g of potassium iodide. The mixture was stirred for 5 days, after which the volatile materials were pumped off at 10 mmHg. Further pumping at 1 mmHg caused the trapping of brown crystals assumed to be iodine.

The brown solid remaining after removal of the volatiles was washed with water until the washings, initially brown, were colorless. The washings gave a positive starch–iodide test. The residue (816 mg), dried under vacuum, was washed with 900 mL of petroleum ether, leaving 302 mg of what was shown to be the diperiodide salt (10) of the original adduct (see later). The petroleum ether was evaporated to give 493 mg (2.28 mmol, 76%)

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(22) Prepared according to A. T. Bottini, F. P. Carson, R. Fitzgerald, and K. A. Frost, II, *Tetrahedron*, **28**, 4883 (1972).

of thianthrene.

The ethanolic solution of volatile products, pumped from the reaction mixture, was found by combinations of GLC and mass spectrometry[21] to contain cyclohexene, 1-iodocyclohexene, and 3-ethoxycyclohexene. 1-Ethoxycyclohexene was found, by GLC with the authentic compound, not to be present. The amounts of the volatile products were determined by GLC on 20% SE-30 on acid-washed Chromosorb W and the use of known solutions of the components in ethanol. The amount of iodine in the ethanolic solution was not assayed. The summation of yields was as follows: adduct diperiodide (10), 15.3%; cyclohexene, 20.3%; 3-ethoxycyclohexene, 38.6%; 1-iodocyclohexene, 9.4%; and thianthrene, 76.0%. These data account for 91% of the thianthrenyl units and 83% of the cyclohexyl units of the 2a used.

Identification of the Diperiodide 10. To a suspension of 65 mg (0.0495 mmol) of the diperiodide in ethanol was added 310 mg (1.5 mmol) of silver perchlorate in small portions. The mixture was stirred for 2 h, and 50 mL of water was added. The solids were filtered, washed with water, and dried, giving 82 mg of a mixture of silver iodide and 2a. The IR (Nujol) of this mixture was identical with that of 2a. Anal. Calcd for $C_{30}H_{28}S_4^{2+}$,$2I_3^-$·$2H_2O$ (mol wt 1312): C, 27.4; H, 2.29; S, 9.77; I, 58.1. Found: C, 27.0; H, 2.02; S, 10.1; I, 57.9.

Reaction of 2b with Potassium Iodide in Ethanol. Formation of 5-(2-Iodocyclohexyl)phenoxathiin Periodide (11). To a suspension of 383 mg (0.562 mmol) of 2b in 15 mL of ethanol was added an excess of solid potassium iodide. The mixture became dark yellow within 5 min. Water was added after 30 min to precipitate an oil which solidified to a brown solid. Filtration and drying gave 322 mg of product which was washed with petroleum ether until the washings, initially violet in color (iodine), were colorless, giving 145 mg of a brown solid (mp 115–116 °C dec) shown to be 11 (32% yield). Anal. Calcd for $C_{18}H_{18}SOI_4$·H_2O: C, 26.8; H, 2.50; S, 3.97; I, 62.8. Found: C, 27.3; H, 2.49; S, 3.74; I, 62.5.

The product had the following characteristics: λ_{max} (10^{-4} ϵ) (CH_3CN) 291 nm (5.07), 365 (2.08), characteristics of I_3^-; ^{1}H NMR [$(CD_3)_2S$=O] δ 8.3–7.0 (br m, 8 H, aromatic), 4.18 (br s, 1 H, assumed adjacent to S^+), 3.76 (br s, 1 H, assumed adjacent to I), 2.3–1.0 (br m, 8 H, cyclohexyl). A solution in Me_2SO gave a positive starch–iodide test.

The petroleum ether washings of the initial solid products were evaporated to give 177 mg (0.885 mmol) of phenoxathiin. This corresponds with 32% of 2b having given 11 and phenoxathiin and the remainder (68%) having undergone reductive elimination giving phenoxathiin (92%) and cyclohexene (unsought).