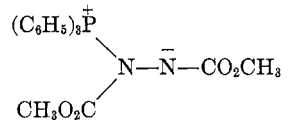
the esters rather than the azo linkage. Azobenzene was reported to be unreactive toward the phosphite esters. Triphenylphosphine reacted with diethyl azodicarboxylate in ether with Dry Ice cooling to give a red solid which formed a "sticky mass" at room temperature and was not characterized.[2]

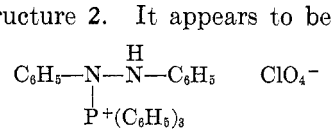
The adduct which formed between triphenylphosphine and dimethyl azodicarboxylate was produced in solution and found to undergo a variety of cycloaddition reactions with a number of reagents.[3] Apparently the adduct was not isolated. A quasi-1,3-dipole structure was suggested for the adduct as shown in **1**. The tri-



1

phenylphosphine–diethyl azodicarboxylate adduct was found to catalyze the reaction between the azo ester and several mercaptans to yield disulfides and diethyl hydrazodicarboxylate.[4] The phosphine was recovered unchanged. Formation of the phosphine–azo ester adduct was observed by the decrease in absorption of the azo group at 405 nm.

We have found that azobenzene reacts readily with triphenylphosphine at room temperature in aqueous ethanol or methanol containing perchloric acid to form a 1:1:1 adduct of the azo compound, phosphine, and perchloric acid. The reaction can be followed in dilute solution by observing the decrease in absorption of the azo group at 320 nm or the decrease in the polarographic reduction wave for the azo linkage, $E_{1/2} = -0.05$ V *vs.* sce, in perchloric acid solution. In higher concentrations the adduct precipitates in high yield (80–85%) after 5–10 min. The adduct is believed to have the following structure **2**. It appears to be stable, melts



2

to a red-brown liquid at 169–171°, and is very soluble in acetonitrile, dimethylformamide, and dimethyl sulfoxide and does not appear to dissolve in ethanol or water. The infrared spectrum of the compound has numerous peaks characteristic of the phenyl group and an absorption peak at 3200 cm^{-1} which is believed to be due to the N–H stretching mode. The nmr spectrum shows one signal with several peaks at δ 6.7–7.5, a second multipeak signal at δ 7.5–8.4, and a single peak at δ 9.4. These signals have relative areas, in the order given, of 10:14.6:1.3. The nmr spectrum is in agreement with the suggested structure. The uv spectrum has a maximum at 270 nm (ϵ 8000) and end absorption increasing from 240 nm.

The adduct was successfully titrated with KOH in acetonitrile, dimethylformamide, dimethyl sulfoxide, and pyridine. Glass and calomel electrodes were used and a reasonably large (250 mV) break in the potentiometric curve was found. The solutions turned yellow on reacting with base, presumably indicating the regeneration of azobenzene. The equivalent weight was found to be 530, as compared to the calculated value of 545. Other aromatic azo compounds, 4,4′-azodianiline and 4,4′-azodiphenetole, were found to react slowly with triphenylphosphine under the same conditions, but no products were isolated. No reaction was observed between azobenzene and tributylphosphine.

This reaction would appear to be similar to those involving the addition of tertiary phosphines to activated carbon–carbon double bonds.[5] Triphenylphosphine adds to the carbon–carbon double bond of benzalmalononitrile to form an adduct which then adds HCl to give a phosphonium chloride.[6]

(3) E. Brunn and R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **8**, 513 (1969).

(4) K. Kato and O. Mitsunobu, *J. Org. Chem.*, **35**, 4227 (1970).

Experimental Section

Materials.—Azobenzene and triphenylphosphine were Eastman Reagent chemicals. All other chemicals and solvents were the best available reagent grade materials.

Methods.—Infrared spectra were recorded with a Beckman IR-20 spectrophotometer. A Beckman DK-2A instrument was used to measure uv absorption. The nmr spectra were obtained with a Varian A-60A spectrometer.

Potentiometric titrations were done with a Corning Model 111 digital pH meter equipped with glass and calomel electrodes. A Hewlett–Packard Model 185 CHN analyzer was used for the C, H, and N analyses. The phosphorus analysis was by the Galbraith Laboratories, Knoxville, Tenn.

Preparation of the Adduct.—A solution of azobenzene (1.82 g, 10 mmol) and triphenylphosphine (2.62 g, 10 mmol) was prepared in 100 ml of 95% ethanol; 2 ml of 72% $HClO_4$ (23 mmol) was added to this solution. Precipitation of the adduct began within 5 min. The crystals were filtered after 1 hr and washed with ethanol. A yield of 4.63 g (85%) was obtained. The compound melts with decomposition to a red-brown liquid at 169–171°. The adduct was also prepared using aqueous methanol (10% H_2O) as solvent with about the same yield.

Anal. Calcd for $C_{30}H_{26}ClN_2O_4P$: C, 66.1; H, 4.82; N, 5.13; P, 5.69. Found: C, 65.8; H, 4.68; N, 5.28; P, 5.63.

Potentiometric Titrations.—Weighed amounts (0.05–0.2 mmol) of the adduct were titrated with standard solutions of KOH (0.02–0.04 *M*) in ethanol. Reaction was rapid and reasonably stable readings were obtained in dimethyl sulfoxide. The equivalent weight found was 530, compared with a calculated value of 545.

Registry No.—**2**, 32120-81-3; azobenzene, 103-33-3; triphenylphosphine, 603-35-0.

Acknowledgment.—The authors thank Dr. James E. Johnson of Texas Woman's University for recording the nmr spectra. The support of the Robert A. Welch Foundation of Houston, Texas, is gratefully acknowledged.

(5) S. Patai and Z. Rappoport in "The Chemistry of Alkenes," S. Patai, Ed., Interscience, New York, N. Y., 1964, pp 506–508.

(6) J. A. Ford, Jr., and C. V. Wilson, *J. Org. Chem.*, **26**, 1433 (1961).

A Novel Two-Step Synthesis of 10*H*-Benz[*b*]indeno[2,1-*d*]thiophene. Heterocyclopentadienes. III

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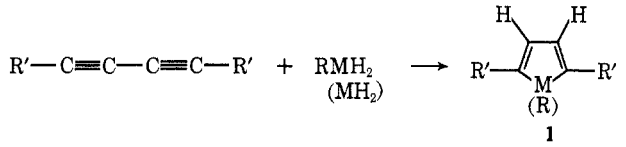
Received May 11, 1971

A particularly successful method for the synthesis of monoheterocyclopentadienes (**1**) is the addition of

(1) NASA Predoctoral Fellow, 1969–present.

RMH_2 (M = P,[2] As,[3] N[4]) and MH_2 (M = S,[5] Se,[6] Te[7]) to 1,3-diynes. An attractive extrapolation of this route to the synthesis of heterocycloheptatrienes would involve the addition of RMH_2 or MH_2 to 1,5-diyn-3-enes. We have investigated this route with H_2S and the readily available *o*-bis(phenylethynyl)benzene[8] (**2**) in hopes of preparing 2,4-diphenylbenzo[*b*]thiepin (**3**) in a convenient one-step synthesis. This reaction was originally planned as a model route for the unknown selenepin and tellurepin ring systems. However, when hydrogen sulfide was passed through a refluxing solution of **2** in aqueous acetone (135 ml of water and 15 ml of 1 *N* sodium hydroxide for 2.78 g of **2**) the sole isolable product was **2**. Likewise refluxing **2** in methanolic potassium sulfide afforded **2** as the only characterizable material. Further attempts to bring about the desired conversion of **2** → **3** by addition of hydrogen sulfide were not made.



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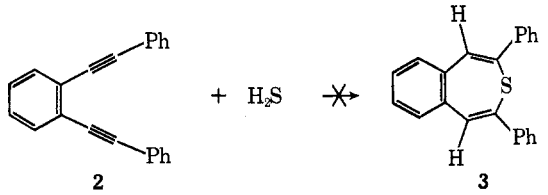
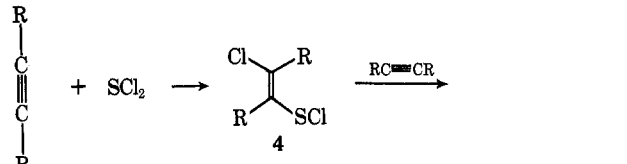


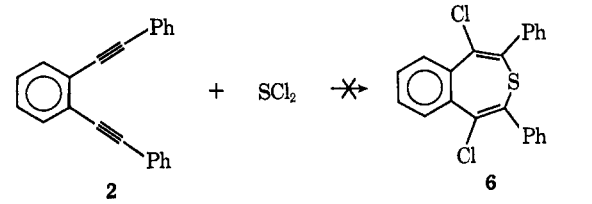
2 **3**

Another possible one-step route to a benzo[*d*]thiepin from **2** can be envisioned from the addition of sulfur dichloride. The addition of sulfur dichloride to acetylenes is known to proceed through an often isolable vinyl sulfenyl chloride (**4**)[9] which can add to another molecule of acetylene to afford a β,β'-dichlorodivinyl sulfide (**5**).[10] It has also been shown that SCl_2 will add to 1,3-diynes to yield 3,4-dichlorothiophenes.[11] It was therefore hoped that the conversion of **2** → **6** could be easily effected.

Since SCl_2 is an electrophilic reagent, whose reactions with acetylenes are thought to proceed through a thirene type intermediate which suffers nucleophilic attack by chloride anion,[9] one must consider the known behavior of **2** with electrophiles before predicting the course of this reaction. Whitlock[8] has reported that



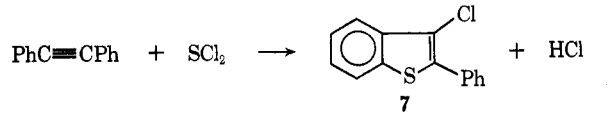
4 **5**



2 **6**

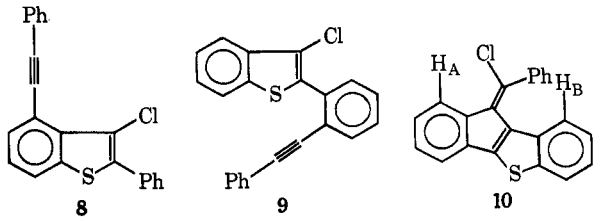
electrophilic attack on **2** results in formation of diphenylbenzofulvenes, or ring systems derived therefrom, without exception. This, of course, results from interaction of the triple bonds in the addition step. However, since it is questionable how much of the positive charge in the intermediate derived from SCl_2 addition to an acetylene resides on carbon, we could not confidently predict a similar course for SCl_2.

Several routes by which SCl_2 might react with **2** may be mechanistically envisioned and a choice between them is difficult. We therefore assumed that a mixture of products would likely result and hoped that **6** would represent a significant fraction of this mixture. Neither of these things turned out to be the case. Addition of SCl_2 to **2** provides a 90% yield of *one* product which analyzes for **6** less the elements of hydrogen chloride. The most striking feature of this orange, crystalline material is its nmr spectrum, which consists solely of two gross multiplets in the aromatic region (δ 8.5–8.3, 7.5–6.3; 12 H) and two peaks in the olefinic region (δ 5.6, 5.45; 1 H) which are actually multiplets upon high resolution. The loss of HCl is easily rationalized when one considers the known reaction of SCl_2 and diphenylacetylene to give 3-chloro-2-phenylbenzo[*b*]thiophene (**7**).[9]



7

Reasonable structures which can be drawn for the molecular formula, $C_{22}H_{13}SCl$, solely on mechanistic considerations are **8**, **9**, and **10**. However, examina-



8 **9** **10**

tion of models of these three molecules makes a choice of **10** very easy on the basis of the nmr spectrum. Regardless of the stereochemistry of the exocyclic chlorobenzylidene unit, either H_A or H_B is pushed into the

(2) E. A. Braye, IUPAC Symposium on Organo-Phosphorus Compounds, Heidelberg, 1964; G. Märkl and P. Potthast, *Angew. Chem.*, **79**, 58 (1967).

(3) G. Märkl and H. Hauptmann, *Tetrahedron Lett.*, 3257 (1968).

(4) J. Reisch and K. E. Schulte, *Angew. Chem.*, **73**, 241 (1961); K. E. Schulte, J. Reisch, and H. Walker, *Arch. Pharm. (Weinheim)*, **299**, 1 (1966).

(5) K. E. Schulte, J. Reisch, and L. Hörner, *Angew. Chem.*, **72**, 920 (1960); *Chem. Ber.*, **95**, 1943 (1962); K. E. Schulte, J. Reisch, W. Hermann, and G. Bohn, *Arch. Pharm., (Weinheim)*, **296**, 456 (1963); K. E. Schulte, J. Reisch, and W. Hermann, *Naturwissenshaften*, **50**, 332 (1963); K. E. Schulte and G. Bohn, *Arch. Pharm. (Weinheim)*, **297**, 179 (1964); K. E. Schulte, G. Rücker, and W. Meinders, *Tetrahedron Lett.*, 659 (1965).

(6) R. F. Curtis, S. N. Hasnain, and J. A. Taylor, *Chem. Commun.*, 365 (1968).

(7) W. Mack, *Angew. Chem., Int. Ed. Engl.*, **5**, 896 (1966).

(8) H. W. Whitlock, Jr., and P. E. Sandvick, *J. Amer. Chem. Soc.*, **88**, 4525 (1966).

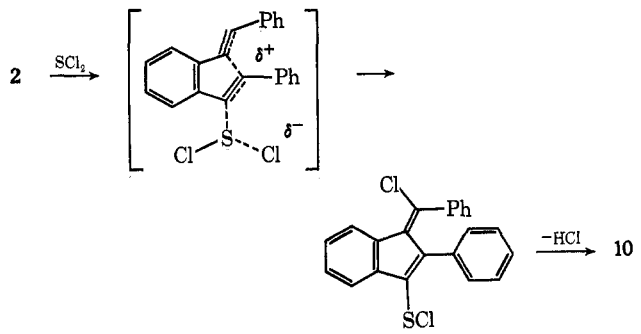
(9) T. J. Barton and R. G. Zika, *J. Org. Chem.*, **35**, 1729 (1970).

(10) L. Brandsma and J. F. Arens, *Recl. Trav. Chim. Pays-Bas*, **80**, 237 (1961).

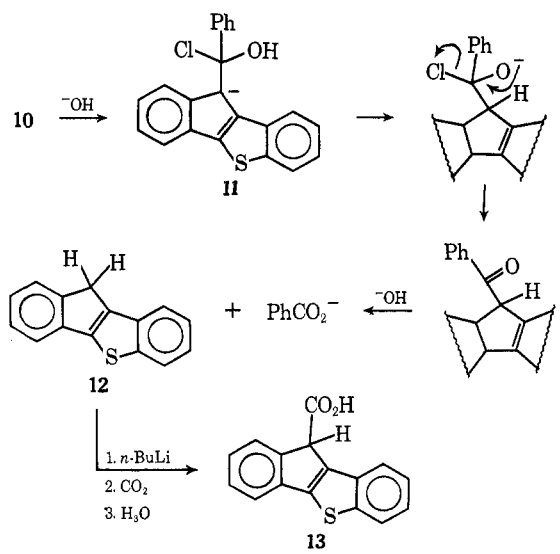
(11) K. E. Schulte, H. Walker, and L. Rolf, *Tetrahedron Lett.*, 4819 (1967). Reference 10 represents the first report of the addition of SCl_2 to an alkyne (divinyl sulfide preparations) while ref 11 reports the first additions of SCl_2 to 1,3-diynes (dichlorothiophene preparations). We were unaware of these two reports and thank Professor Schulte for informing us of his work.

shielding cone of the phenyl ring, thus explaining the prominent upfield shift of a single proton. Rotation of this phenyl ring is prevented by H_A or H_B.

A rational mechanism for the formation of **10** involves electrophilic attack of SCl_2 on one acetylenic linkage of **2** with concomitant involvement of the other triple bond as postulated by Whitlock[8] for the addition of bromine and hydrogen bromide. The intermediate sulfenyl chloride could then attack a phenyl ring to afford **10**.



As **10** represents to our knowledge the first example of the benz[*b*]indeno[2,1-*d*]thiophene ring system,[12] we were quite interested in converting it into the parent system. This was easily accomplished by treatment of **10** with potassium hydroxide in hot triethylene glycol. This procedure affords 10*H*-benz[*b*]indeno[2,1-*d*]thiophene (**12**) in *ca.* 50% yield. The conversion may be viewed as proceeding through initial attack by hydroxide ion on the exocyclic double bond so as to yield the indenyl anion (**11**) followed by several straightforward steps ending with a reverse condensation. The title compound (**12**) can be easily converted into the 10-acid (**13**) through treatment with *n*-butyllithium and then CO_2.



Final, conclusive proof of **12** was obtained by X-ray crystallography. The molecular structure of **12** is shown in Figure 1.

(12) See D. W. H. MacDowell and A. T. Jeffries, *J. Org. Chem.*, **35**, 871 (1970); D. W. H. MacDowell and T. B. Patrick, *ibid.*, **32**, 2441 (1967), for the synthesis and chemistry of indenothiophenes.

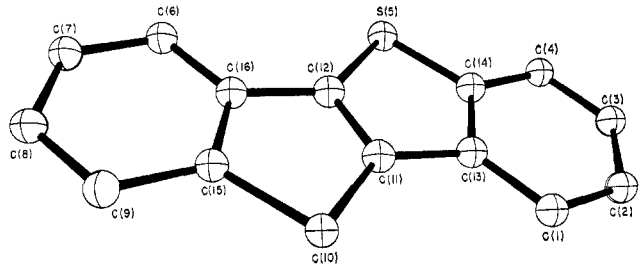


Figure 1.—The molecular structure of adduct **12**.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 21 spectrophotometer. Proton nmr spectra were determined on a Perkin-Elmer R-20-B instrument. Analyses were carried out by Ilse Beetz Mikroanalytisches Laboratorium, Kronach, West Germany.

Commercial sulfur dichloride (Matheson Coleman and Bell) was purified as in ref 9. *o*-Bis(phenylethynyl)benzene (**2**) was prepared by the method of Whitlock[13] and purified by chromatography on Woelm neutral alumina (hexane elution) followed by recrystallization from hexane [mp 49.1–50.5° (lit.[13] mp 49.5–51.5°)].

Addition of Sulfur Dichloride to *o*-Bis(phenylethynyl)benzene. 10-(Chlorobenzylidene)benz[*b*]indeno[2,1-*d*]thiophene (10).—Solutions of 1.19 g (4.27 mmol) of *o*-bis(phenylethynyl)benzene and 0.516 g (5.03 mmol) of freshly distilled sulfur dichloride each in 100 ml of dry methylene chloride were simultaneously added to 1.2 l. of stirred, refluxing methylene chloride. The addition was complete after 45 min and the resultant brilliant red solution was refluxed an additional 15 min. The solvent was removed *in vacuo* to leave a crude red solid. Recrystallization from methylene chloride–hexane afforded 1.323 g (90.3%, mp 169–171°) of orange, crystalline **10**: mp 175°; ir (KBr) 6.25, 6.95, 7.40, 8.15, 9.35, 9.75, 10.75, 11.05, 13.15, 13.35–13.55, 14.50 μ; nmr ($DCCl_3$) δ 8.5–8.3 and 7.5–6.3 (m, 12 H), 5.6 and 5.45 (m, 1 H); mass spectrum *m/e* 344 (100%, M^+), 346 (40.7%, $M + 2^+$).

Anal. Calcd for $C_{22}H_{13}SCl$: C, 76.62; H, 3.80; Cl, 10.28. Found: C, 76.58; H, 3.85; Cl, 10.31.

Oxidation of 10 with *m*-Chloroperbenzoic Acid. 10-(Chlorobenzylidene)benz[*b*]indenyl[2,1-*d*]thiophene 1,1-Dioxide.—To a solution of 0.501 g (1.46 mmol) of **10** in 30 ml of ice-bath cooled chloroform was added 0.453 g (2.63 mmol) of *m*-chloroperbenzoic acid in *ca.* 40 ml of chloroform. The reaction mixture was kept at ice-bath temperature for an additional 5 min and then allowed to stand at room temperature for 24 hr. After filtration the reaction solution was percolated through a 2.7 × 40 cm column of silica gel packed in hexane. The fraction eluted with hexane was stripped of solvent, dissolved in methylene chloride, washed with dilute potassium carbonate solution, dried over magnesium sulfate, and filtered, and the solvent was evaporated to a minimum volume. Addition of *n*-hexane and cooling afforded 0.302 g (55%) of the bright red crystalline sulfone of **10**: mp 210–211°; ir (KBr) 6.40, 6.95, 7.75, 8.70, 10.60 μ; nmr ($DCCl_3$) δ 8.6–8.4 and 7.8–6.8 (m, 12 H), 5.25 and 5.10 (m, 1 H); mass spectrum *m/e* 376 (100%, M^+), 378 (41.7%, $M + 2^+$).

Anal. Calcd for $C_{22}H_{13}O_2SCl$: C, 70.2; H, 3.48; O, 8.5; Cl, 9.42. Found: C, 69.82; H, 3.88; O, 8.58; Cl, 9.55.

10H-Benz[*b*]indeno[2,1-*d*]thiophene (12).—To a solution of 1.3 g of potassium hydroxide in 50 ml of triethylene glycol at *ca.* 150° was added 0.789 g (2.29 mmol) of **10**. The solution was heated intermittently with a Bunsen burner for *ca.* 5 min while stirring. After cooling, 100 ml of water was added and the solution was extracted with methylene chloride (two 100-ml portions). The organic layers were combined, washed with water, dried over magnesium sulfate, and filtered and the solvent was removed *in vacuo*. The residue was dissolved in a small amount of methylene chloride and percolated through a 6 × 6 cm column of silica gel packed with hexane. Concentration of the fraction eluted with hexane resulted in precipitation of 0.268

(13) H. W. Whitlock, Jr., P. E. Sandvick, L. E. Overman, and P. B. Reichardt, *J. Org. Chem.*, **34**, 879 (1969).

g (53%) of red **12**. Sublimation yielded a light yellow analytical sample: mp 201–202°; ir 6.25, 6.90, 8.0, 9.90, 10.10, 13.45, 13.75, 14.00 μ; nmr ($DCCl_3$) δ 7.9–7.2 (m, 8 H), 3.8 (s, 2 H); mass spectrum m/e 222 (100%, M^+), 224 (7.5%, $M + 2^+$).

Anal. Calcd for $C_{15}H_{10}S$: C, 81.04; H, 4.54; S, 14.42. Found: C, 81.00; H, 4.49; S, 14.33.

Benz[*b*]indeno[2,1-*d*]thiophene-10-carboxylic Acid (13).—To a stirred, ice-bath cooled solution of 0.073 g (0.33 mmol) of **11** in 75 ml of dry ether under argon was added 0.31 ml of a 1.6 *M* solution of *n*-butyllithium *via* syringe. Upon addition the solution turned from red-orange to green. After stirring for 10 min, 15 g of CO_2 was dispersed into the reaction mixture. The color immediately reverted to yellow. After evaporation of solvent, the residue was dissolved in methylene chloride and this solution was shaken with a small amount of 3 *N* hydrochloric acid. Extraction with aqueous sodium carbonate, acidification, extraction with methylene chloride, and recrystallization from methylene chloride–hexane afforded 0.042 g of white benz[*b*]indeno[2,1-*d*]thiophene-10-carboxylic acid (**13**): mp 217–219°; ir (KBr) 3.20–3.60 (br), 3.75 (sh), 5.95, 7.15, 7.85, 8.35, 10.75, 13.40 μ; nmr ($DCCl_3$) δ 7.20–8.0 (m, 8 H), 4.90 (s, 1 H), acid proton apparently too broad to observe; mass spectrum m/e 266 (M^+, 100%), 267 ($M + 1^+$ 17.9%), 268 ($M + 2^+$, 7.4%); high resolution mass spectrum 266.040656 (observed), 266.040147 (calculated), 0.000509 (Δ).

X-Ray Solution of Adduct 12.—The stout, circular crystals of **12** displayed $2/m$ Laue symmetry in oscillation and Weissenberg photographs. Systematic extinction on $h0l$ (for $l = 2m + 1$) and $0k0$ (for $k = 2m + 1$) uniquely require the common monoclinic space group $P2/c$ (C_{2h}^5). The cell constants are $a = 11.800$ (5), $b = 5.87$ (1), $c = 8.270$ (6) Å, and $\beta = 104.35$ (5)°. Measured and calculated densities require $Z = 2$ on one-half molecule per asymmetric unit. A molecular inversion center may be excluded by the elemental analysis and a disordered model was anticipated. Complete data in hkl and hkl octants with $\theta \leq 30°$ were collected on a fully automated Hilger–Watts four-circle diffractometer using Zr-filtered Mo Kα radiation (0.7107 Å). A total of 701 reflections were judged observed after background and Lp corrections. The molecular outline was found quite readily by standard heavy-atom techniques. Full structural details may be obtained from the author (J. C.). Figure 1 is a computer-generated drawing of one of the molecules in a disordered pair. The final R is 0.110 for the 701 observed reflections.

Registry No.—**10,** 32120-91-5; **10** (sulfone), 32120-92-6; **12,** 23421-93-4; **13,** 32120-93-7.

Acknowledgments.—The authors are grateful to the Petroleum Research Fund, administered by the American Chemical Society (PRF No. 1152-G1), the Public Health Service (Grant No. GM-6689-02, National Institutes of Health), and the Atomic Energy Commission for their generous and continuing support of this work.