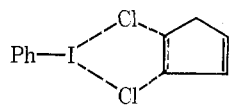
The steric requirements of the large anion (Ph–I–Cl$^-$) can also be used to explain the fact that Cristol et al.[11] obtained trans addition of chlorine in the reaction of acenaphthylene with iodobenzene dichloride. Tanner and Gidley[2] concluded that this reaction must be going by a radical mechanism since ionic addition of molecular chlorine to acenaphthylene gave only cis addition. However, the large anion from iodobenzene would probably prefer to add trans while the small chloride ion could add cis.

The increase in trans 1,4 addition and the decrease in cis 1,2 addition in the reaction between **1** and antimony pentachloride has also been rationalized on the basis of a large anion ($SbCl_4^-$ or $SbCl_6^-$) in the ion pair.[5]

The small amount of cis 1,2 addition (**1a, 2a**) which does occur in the reaction of **1** and **2** with iodobenzene dichloride is probably not the result of a concerted, molecular process (**5**, shown with diene **1**) since cis 1,2-dichloride formation with this chlorinating agent in the case of other olefins has been interpreted in other ways,[2] or simply has not been observed.[11,12] The cis 1,4-dichlorides (**1c** and **2c**) can not be formed by a concerted cis 1,4 addition since this suprafacial addition would be forbidden with iodobenzene dichloride as has been explained with antimony pentachloride.[13]



5

Experimental Section

Materials. Both iodobenzene dichloride[14] and trichloramine[15] were prepared as described in *Organic Syntheses*. Antimony pentachloride was obtained from Alfa Products.

Reaction Conditions. Reactions were carried out under nitrogen (unless oxygen was required as an inhibitor) and at the following temperatures: trichloramine and antimony pentachloride, −10 °C; and iodobenzene dichloride, room temperature. The dienes were dissolved in the appropriate amount of solvent to give a mole fraction of 0.02. The chlorinating agents were added to a stirred solution of the dienes in such amounts to consume 10 and 20% of the diene in dilute and neat solutions, respectively. The method of addition of the chlorinating agent depended on the reaction conditions: with dilute solutions, antimony pentachloride and iodobenzene dichloride were added as ca. 5% solution in the appropriate solvent; and in neat reactions, antimony pentachloride was added neat, and iodobenzene dichloride as a solid. Under all conditions trichloramine was added as a solution (0.6–0.7 M) in the appropriate solvent. The approximate volumes of dilute reaction mixtures are (ml): CH_2Cl_2, 22; CCl_4, 32; and C_5H_{12}, 38.

Identification and Analysis of Products. The cyclopentadiene dichlorides have already been reported,[3] and the procedures for establishing the structures of the cyclohexadiene dichlorides are described elsewhere.[4] The dichlorides from both dienes were analyzed by VPC under the following conditions: (cyclopentadiene), 7 ft × 0.125 in. column (SS) at 62 °C packed with β,β-oxydipropionitrile (2.5%) on 80–100 mesh Chromosorb W (AWDMCS) with retention times (min) of 4.4, 7.4, 20.6, and 22.6 for **1b, 1d, 1c,** and **1a,** respectively; and (cyclohexadiene),[16] 6 ft × 0.125 in. column (SS) at 57 °C packed with SE-30 (2.5%) on 80–100 mesh Chromosorb W (AWDMCS) with retention times (min) of 5.8, 7.2, 7.9, and 9.2 for **2b, 2d, 2c,** and **2a,** respectively. The stability of the dichlorides under these reaction and analysis conditions have been discussed elsewhere.[3–5]

Acknowledgment. Support for this work was provided by the Research Corporation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Atlantic Richfield Foundation.

Registry No.—**1a,** 51502-28-4; **1b,** 31572-43-7; **1c,** 31572-45-9; **1d,** 31572-44-8; **2a,** 53921-00-9; **2b,** 53920-98-2; **2c,** 54112-34-4; **2d,** 53920-99-3; cyclopentadiene, 542-92-7; 1,3-cyclohexadiene, 592-57-4; iodobenzene dichloride, 932-72-9; trichloroamine, 10025-85-1.

References and Notes

(1) K. W. Field and P. Kovacic, *J. Org. Chem.*, **36,** 3566 (1971).
(2) D. D. Tanner and G. C. Gidley, *J. Org. Chem.*, **33,** 38 (1968).
(3) V. L. Heasley, G. E. Heasley, P. D. Davis, D. M. Ingle, and K. D. Rold, *J. Org. Chem.*, **39,** 736 (1974).
(4) G. E. Heasley, V. L. Heasley, D. Strickland, G. McClung, D. M. Ingle, P. D. Davis, T. S. Ungermann, K. D. Rold, and D. Hayse, *J. Org. Chem.*, in press.
(5) The mechanisms of the reactions of antimony pentachloride with olefins and dienes (including cyclopentadiene) is discussed in the following article: V. L. Heasley, G. E. Heasley, K. D. Rold, D. Titterington, C. Leach, D. McKee, and B. Gipe, unpublished work. A study on the reaction of butadiene with antimony pentachloride has recently been reported.[13]
(6) Molecular oxygen also had no effect on the product ratios. Field and Kovacic (ref 1) observed that solvents had no effect on the meso/*dl* ratio in the reaction between *cis*-2-butene and trichloramine, and that inhibitors did not affect the reactions with cyclohexene.
(7) We observed in a separate study that radical addition of methyl hypochlorite to isoprene resulted primarily in 1,4 addition (CH_3OC–C–C=C–C–Cl) although the main contributor to the intermediate resonance system must be the tertiary radical (CH_3OC–C–C–C=C). Apparently steric preference is involved in the attack of the radical on methyl hypochlorite.
(8) Although this chlorination was done under radical conditions, we feel that the addition may be occurring primarily by an ionic mechanism since the product ratios are so similar to the ionic reactions. Under the conditions of entry 4 cyclohexane was chlorinated to give chlorocyclohexane confirming a radical component to the reaction, but it may be a minor one. At least there is no major change in product composition in going from radical to ionic conditions as was observed by Poutsma in the chlorination of butadiene [M. L. Poutsma, *J. Org. Chem.*, **31,** 4167 (1966)].
(9) Tanner and Gidley[2] found that in their reactions with iodobenzene dichloride *sym*-tri-*tert*-butylphenol was ineffective as a radical inhibitor. In our case 2,6-dimethyl-4-*tert*-butylphenol was much more effective at retarding rate and altering product composition than oxygen. However, the concentration of the phenol that we used was approximately 300 times greater than was used by Tanner and Gidley.
(10) Our evidence for the ionic addition of the chlorines from iodobenzene dichlorides to **1** and **2** under the conditions described in entries 5, 6, and 7 is as follows. (a) There is a significant change in product ratios between ionic conditions (entries 5, 6, and 7) and radical conditions (8 and 9) with an increase in trans 1,2 addition (**1b** and **2b**) under radical conditions which correlates with the radical addition of trichloramine. (b) The inhibitor, 2,6-dimethyl-4-*tert*-butylphenol, greatly retarded the rate of reaction of iodobenzene dichloride. Under radical conditions the reaction is complete in a few minutes whereas with the inhibitor a couple of days is required for complete reaction. (c) In a separate study butadiene reacted with iodobenzene dichloride in the presence of the inhibitor to give the ratio of dichlorides expected from ionic addition, and in the absence of the inhibitor (and in the presence of N_2 and ultraviolet illumination) the ratio of dichlorides indicated radical addition. [For a discussion of the ratio of dihalides expected from ionic and radical additions to butadiene see the studies on the chlorination[6] and bromination [V. L. Heasley and S. K. Taylor, *J. Org. Chem.*, **34,** 2779 (1969)] of this diene.] Further evidence confirming the ionic addition of iodobenzene dichloride in the presence of the inhibitor came from a comparison of the rates of addition to butadiene and cyclopentadiene (**1**). The latter was found to be immensely faster; this appears reasonable on the basis of the relative stabilities of the allylic cation (chloronium ion) intermediates.
(11) S. J. Cristol, F. R. Stermitz, and P. S. Ramsey, *J. Am. Chem. Soc.*, **78,** 4939 (1956).
(12) J. G. Traynham and D. B. Stone, Jr., *J. Org. Chem.*, **35,** 2025 (1970).
(13) R. P. Vignes and J. Hamer, *J. Org. Chem.*, **39,** 849 (1974).
(14) H. J. Lucas and E. R. Kennedy, "Organic Syntheses", Collect. Vol. III, Wiley, New York, N.Y., 1955, p 482.
(15) P. Kovacic and S. S. Chudhary, "Organic Syntheses", Collect. Vol. V, Wiley, New York, N.Y., 1973, p 35.
(16) During the course of the present study it was determined that dichlorides **2a–d** could be separated under simpler conditions (a shorter column) than was reported in an earlier study.[4]

A Convenient Synthesis of 2,3,12,13-Tetrathia[4.4]metacyclophanes and 2,3,12,13-Tetrathia[4.4]paracyclophanes

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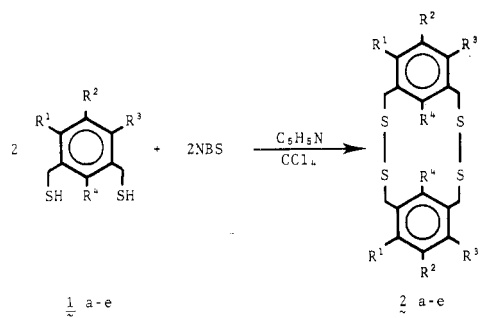
The potential of tetrathia[4.4]cyclophanes as useful synthetic precursors of bridged aromatic ring systems has been

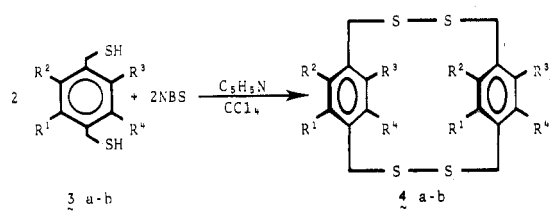
Table I. Preparation of 2 and 4 by Oxidation of 1 and 3 with NBS–Pyridine in CCl_4

Compd	Reaction time, h (temp, °C)	Mp, °C (recrystn solvent)	Yield,[a] %	Molecular formula[b]	Method of isolation[c]
2a	10 (40)	170–171[d] (ethanol)	56		A
2b	12 (50)	209–210 (hexane)	60	$C_{18}H_{20}S_4$	A
2c	15 (40)	252–254 (acetone)	72	$C_{20}H_{24}S_4$	A
2d	18 (76)	283–285 (benzene)	62	$C_{22}H_{28}S_4$	A
2e	16 (25)	265–267 dec (benzene)	22	$C_{22}H_{28}S_4$	B
4a	20 (25)	250–252 dec (benzene)	8	$C_{16}H_{16}S_4$	B
4b	18 (76)	286–288 (CCl_4)	15	$C_{24}H_{32}S_4$	B

[a] Yields are for isolated and purified products. [b] Confirmed by mass spectral data, and satisfactory analytical values (±0.3% for C, H, and S) were reported for all new compounds listed in the table. [c] A, by direct crystallization; B, by chromatography over silica gel using benzene–petroleum ether (bp 50–75 °C) (1:4 or 1:5) followed by recrystallization from the solvent specified. [d] Lit.[1] mp 171.5–172.5 °C.

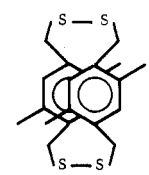
realized by the conversion of 2,3,12,13-tetrathia[4.4]metacyclophane (**2a**) and its 10,20-dimethyl derivative (**2**, $R^1 = R^2 = R^3 = H$; $R^4 = CH_3$) into the corresponding 2,11-dithia[3.3]metacyclophanes[1] which were the key intermediates for a series of interesting hydrocarbons including 15,16-dihydropyrenes.[2] In principle, this type of medium-size cyclic bisdisulfide can be prepared directly by oxidative coupling of appropriate *m*- and *p*-xylylene dimercaptans, but a general procedure is lacking in the literature. We report here a convenient method which not only provides reasonably good yields of symmetrical tetrathia[4.4]metacyclophanes **2**, thus complementing the two-step synthesis reported by Boekelheide and Mondt,[1] but also permits the preparation of 2,3,12,13-tetra[4.4]paracyclophanes (**4**) for the first time.



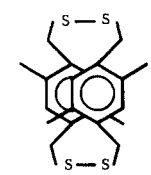


The procedure involves treatment of xylylene dimercaptans **1** or **3** with the appropriate molar quantity of *N*-bromosuccinimide (NBS) in carbon tetrachloride containing slight excess of pyridine. Isolation of products is effected by direct crystallization or column chromatography.

Seven successful cyclizations (Table I) were observed from nine xylylene dimercaptans examined in the present investigation. The lower yields for the formation of tetrathia[4.4]paracyclophanes **4** are readily accountable by their increased ring size. The only instance where the desired cyclization failed was with 4,6-bis(mercaptomethyl)isodurene (**1**, $R^1 = R^2 = R^3 = R^4 = CH_3$), which gave only polymeric products. In addition, 2,5-bis(mercaptomethyl)-*p*-xylene (**3**, $R^1 = R^3 = H$; $R^2 = R^4 = CH_3$) gave a coupling product with mp 249–251 °C and parent mass peak at *m/e* 392 whose structure can either be the syn (**5a**) or anti (**5b**) isomer. Inspection of molecular models reveals that these two isomers are not interconvertible by ring flipping. Unfortunately, its NMR spectrum ($CDCl_3$), which displayed singlets at δ 2.34 (3 H), 3.64 (2 H), and 6.82 (1 H), cannot distinguish between these two possibilities.



5 a



5 b

The facile oxidative coupling observed with NBS is remarkable since our earlier attempts to prepare **2** and **4** by employing other oxidants such as hydrogen peroxide, iodine, ferric chloride, and atmospheric oxygen under various conditions failed in almost all cases. Either polymerization occurred in such serious extents that product isolation was precluded or starting materials were recovered unchanged. The only exception was **1c**, which was cyclized into **2c** in 80% yield by air oxidation in ethanol containing excess sodium ethoxide.

Experimental Section[3]

Preparation of Dimercaptans 1 and 3. Compounds **1c–e** and **3b** were prepared by standard procedure[4] from the corresponding xylylene dichlorides which were in turn obtained by bischloromethylation of appropriately substituted methylbenzenes.[5] Compounds **1a, b** and **3a** were prepared similarly from the corresponding dibromides. All dimercaptans exhibited NMR spectra consistent with the assigned structures.

General Procedure for the Preparation of [4.4]cyclophanes 2 and 4. An equal molar mixture of **1** or **3** and NBS in a large volume of dry carbon tetrachloride (distilled over P_2O_5) containing a slight excess of pyridine was stirred at the temperature and for the durations specified in Table I. Removal of succinimide and pyridine hydrobromide from the reaction mixture was effected by extraction or washing with water. Product isolation from the residue was carried out by crystallization or column chromatography. Representative preparations are illustrated below.

6,7,8,16,17,18-Hexamethyl-2,3,12,13-tetrathia[4.4]metacyclophane (2d). To a solution of **1d** (1.70 g, 8 mmol) in 350 ml of dry carbon tetrachloride containing pyridine (2.0 g, excess) was added NBS (1.41 g, 8 mmol) in one portion and the mixture was stirred under reflux for 18 h. The reaction mixture was filtered hot and the cooled filtrate was extracted with water and dried over anhydrous $MgSO_4$. Removal of solvent in vacuo gave a fluffy white solid which was recrystallized from benzene to afford 1.05 g (62%) of pure **2d** as white, fluffy needles: mp 283–285 °C; NMR (CS_2) δ 6.45 (s, 1 H), 3.70 (s, 4 H), 2.21 (s, partially overlapped, ca. 6 H), and 2.11 (s, partially overlapped, ca. 3 H); mass spectrum (70 eV) *m/e* 420 (M^+).

2,3,12,13-Tetrathia[4.4]paracyclophane (4a). To a solution of **3a** (1.70 g, 10 mmol) in 400 ml of dry carbon tetrachloride containing pyridine (2.2 g, excess) was added NBS (1.78 g, 10 mmol) in

one portion, and the mixture was stirred at room temperature for 20 h during which period a white solid gradually formed. The resulting mixture was carefully evaporated to dryness under reduced pressure and the residue was successively washed with water and methanol followed by repeated extraction with warm chloroform. The dried (anhydrous $MgSO_4$) chloroform solution was concentrated to ca. 10 ml and poured into a column of silica gel. The fractions eluted by benzene–petroleum ether (bp 50–75 °C) (1:4) on evaporation left a white solid which was recrystallized from benzene to give 130 mg (8%) of pure **4a**: mp 250–252 °C dec; NMR ($CDCl_3$) δ 6.84 (s, 1 H), 3.62 (s, 1 H); mass spectrum (70 eV) *m/e* 336 (M^+).

Acknowledgment. We are grateful to Mr. K. W. Ho for providing mass spectral data.

Registry No.—**1a**, 41563-69-3; **1b**, 42082-63-3; **1c**, 58074-29-6; **1d**, 58074-30-9; **1e**, 10074-13-2; **2a**, 27929-85-7; **2b**, 58074-31-0; **2c**, 58074-32-1; **2d**, 58074-33-2; **2e**, 58074-34-3; **3a**, 105-09-9; **3b**, 10519-84-3; **4a**, 58074-35-4; **4b**, 58074-36-5; NBS, 128-08-5.

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(3) All melting points were determined on a Koefler hot stage and are uncorrected. Nuclear magnetic resonance spectra were taken on a JEOL 60HL spectrometer using tetramethylsilane as internal standard. Mass spectral data were obtained on a Varian M66 instrument. Elemental analyses were performed by Australian Microanalytical Service, Melbourne.
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Protic Acid Catalyzed Thiono–Thiolo Rearrangements of Phosphorus Esters

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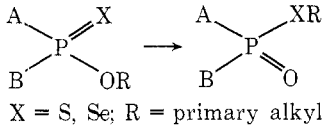
The thiono–thiolo rearrangement of organophosphorus thionoesters (eq 1) is known to be effected thermally as well as by alkyl halides, Lewis acids,[1] and electron impact.[2]

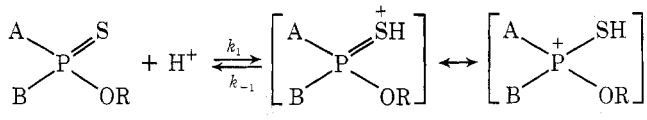


(1)

X = S, Se; R = primary alkyl

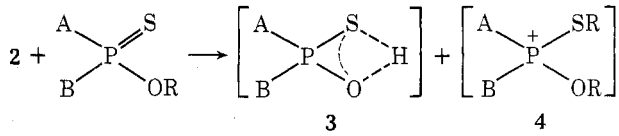
We have found that protic acids can also cause this type of rearrangement with the rate of reaction depending on the nature of the A, B, and R substituents and also on the strength of the acid used. The rearrangement can be monitored by means of either ^{31}P NMR[3] or by ^1H NMR.[4] The main limitation of our new procedure for thiono–thiolo rearrangements lies in its inapplicability to compounds with P–N bonds; such bonds are labile in acidic conditions.[5] Those esters when R is secondary or tertiary alkyl are also unsuitable reactants. The described method of rearrangement of phosphorothionates into isomeric phosphorothiolates under the influence of protic acids possesses one main advantage; it gives very clean and easily isolable products. Simple removal of trifluoroacetic acid by distillation and neutralization of the 1:1 complex[6] (>P=O·····$HOCOCF_3$) allows isolation of pure phosphorothiolate. For example, dissolving trimethyl phosphorothionate and trifluoro- or trichloroacetic acid (1:10 mol/mol) results in rearrangement to *O,O,S*-trimethyl phosphorothiolate. The half-life times $t_{1/2}$, measured at 55 °C, were 5.95 and 82.9 h, respectively. It has been also found that $t_{1/2}$ of conversion at 55 °C of trimethyl phosphorothionate, *O,O*-dimethyl phenylphosphonothionate, and *O*-methyl diphenylphosphonothionate diluted in trifluoroacetic acid (1:10 mol/mol) were respectively 0.46, 1.2, and 3.91 h.

Our preliminary observations allow us to draw some conclusions about the mechanism of the rearrangement. Intermolecular character has been demonstrated in the following experiment. The mixture of trimethyl and triethyl phosphorothionate (1:1) in trifluoroacetic acid solution gave the following products: $(MeO)_2P(O)SMe$, $(EtO)_2P(O)SEt$, $(MeO)_2P(O)SEt$, and $(EtO)_2P(O)SMe$. The last two compounds clearly indicate an intermolecular type of process. In addition $(EtO)_2P(O)SEt$ and $(MeO)_2P(O)SMe$, when stored in CF_3COOH solution under the same conditions, did not lead to detectable amounts of $(MeO)_2P(O)SEt$ or $(EtO)_2P(O)SMe$. It seems reasonable that the protonation of thiophosphoryl sulfur takes place in the first step of the reaction. The absorption band for the thiophosphoryl group, $\nu_{P=S}$ 635 cm^{-1} in $Ph_2P(S)OMe$ measured in CCl_4 solution (10%) shifts to 628 cm^{-1} when an equimolar amount of CF_3COOH is added, while the $\nu_{P=O}$ 1030 cm^{-1} of the bridging oxygen remains unchanged. Consequently, the formation of a quasi-phosphonium cation has to be considered:



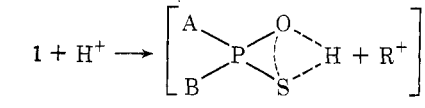
1 2

Equilibrium between **1** and **2** depends on the pK_a of the acid and the nature of the substituents A, B, and R. Quasi-phosphonium cation **2** possesses strong alkylating properties[7] and a "soft" base in the reaction medium would be immediately alkylated. The sulfur atom of the thiophosphoryl group can be considered as a "soft" base, which, in the presence of **2** would be alkylated immediately with formation of another ion **4** and free acid **3**.



3 4

Cationic species **4** would also possess alkylating properties[7] and could alkylate another molecule of thionoester **1** or the free thio acid **3**, with liberation of rearranged thioloester–trifluoroacetic acid complex. The formation of 1:1 complexes of phosphoryl compounds with protic acids is known.[6] It has to be emphasized that in several experiments the presence of dialkyl hydrogen phosphorothioate **3** has not been detected. Also methyl trifluoroacetate is not formed in the reactions investigated. *O-n*-Propyl diphenylphosphinothionate rearranges in CF_3COOH solution to *S-n*-propyl derivative. No traces of *S*-isopropyl ester were found among the reaction products. Thus, carbocation R^+ is then presumably not responsible for the S-alkylation process.



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