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THE STEREOCHEMISTRY OF THE REACTION OF TETRACHLOROETHYLENE WITH *p*-TOLUENE-THIOLATE REAGENT[1]

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Abstract—Sodium *p*-toluenethiolate reacts with tetrachloroethylene (I) in refluxing ethanol to give *trans*-1,2-bis(*p*-tolylthio)-1,2-dichloroethylene (V). The structure is assigned on the basis of crystallographic and supporting data.

ALTHOUGH the stereospecific reaction of thiolate with tetrachloroethylene[3] has been known for some time, there has been almost no work published concerning the geometry of the product. Baganz and Kruger[4] reported the preparation of 1,2-bis-(ethylthio)-1,2-dichloroethylene, but did not mention the problem of geometrical isomerism, (even though they did draw a *cis* structure for the reaction product). Based on the fact that additive halogenations have frequently been reported to give predominantly the *trans* isomer,[5] a *cis* configuration was assumed[6] for the 1,2-bis-(*p*-tolylthio)-1,2-dichloroethylene (V), m.p. 101–101·5°, derived from tetrachloroethylene, because a stereoisomeric material VIII, m.p. 82–83°, was produced by chlorination of 1,2-bis(*p*-tolylthio)ethyne (VII). However, further investigation[7] showed that the dipole moment of the higher melting isomer (V) is smaller than the dipole moment of the lower melting isomer (VIII) and revealed the need to review and, perhaps, to reverse the configurations which were originally assumed.

Data are now available which require that the higher melting isomer (V), derived from tetrachloroethylene (I), be assigned the *trans* configuration and the lower melting isomer (VIII), derived from 1,2-bis(*p*-tolylthio)ethyne (VII), be assigned the *cis* configuration.

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[1] This investigation was supported by Public Health Service Research Grant No. CA-04536-06 from the National Cancer Institute, by the U.S. Army Research Office-Durham, and National Science Foundation Grant No. GB02905. For preceding paper see J. Flynn, Jr., V. V. Badiger and W. E. Truce, *J. Org. Chem.* **28**, 2298 (1963).

[2] Taken from Mr. F. M. Perry's Ph.D. thesis.

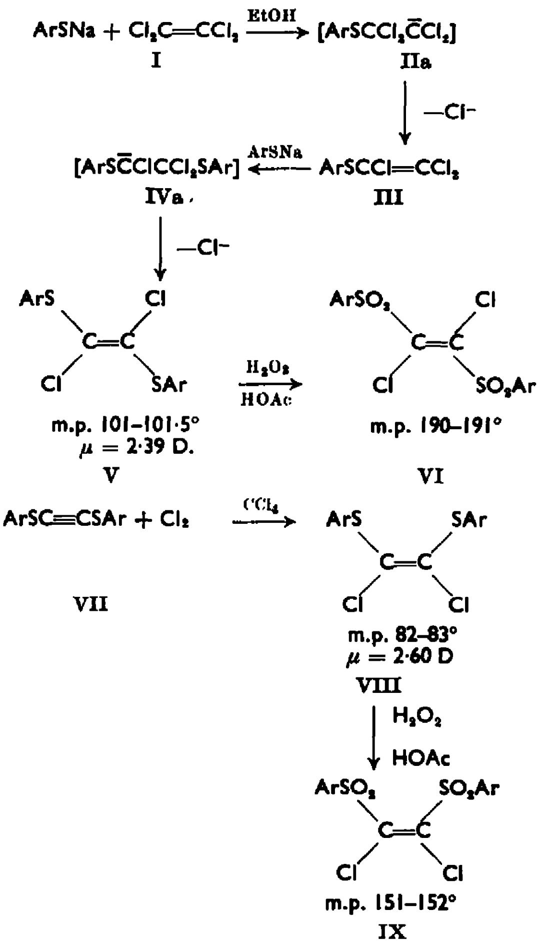
[3] N. W. Cusa and H. McCombie, *J. Chem. Soc.* 767 (1937).

[4] H. Baganz and K. E. Kruger, *Chem. Ber.* **91**, 809 (1958).

[5] E. Bergmann, *J. Chem. Soc.* 402 (1936); A. T. Morse and L. Leitch, *Canad. J. Chem.* **33**, 6 (1955); A. Leitch, *Ibid.* **31**, 385 (1953); G. F. Hennion and C. E. Welsh, *J. Amer. Chem. Soc.* **62**, 1367 (1940); G. F. Hennion and G. M. Wolf, *Ibid.* **62**, 1368 (1940); H. Sinn, *Angew. Chem.* **69**, 754 (1957); R. A. Raphael, *Acetylenic Compounds in Organic Synthesis* p. 35. Butterworths, London (1955).

[6] W. E. Truce and R. Kassinger, *J. Amer. Chem. Soc.* **80**, 6450 (1958).

[7] W. E. Truce and B. Groten, *J. Org. Chem.* **27**, 128 (1962).



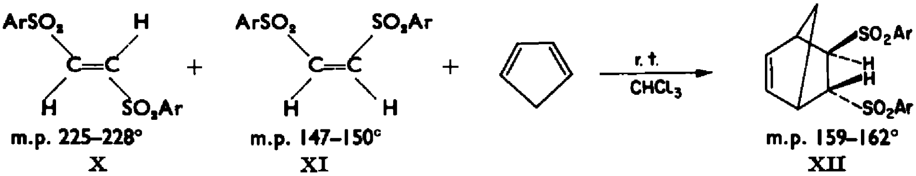
where Ar = $p\text{-}CH_3C_6H_4$

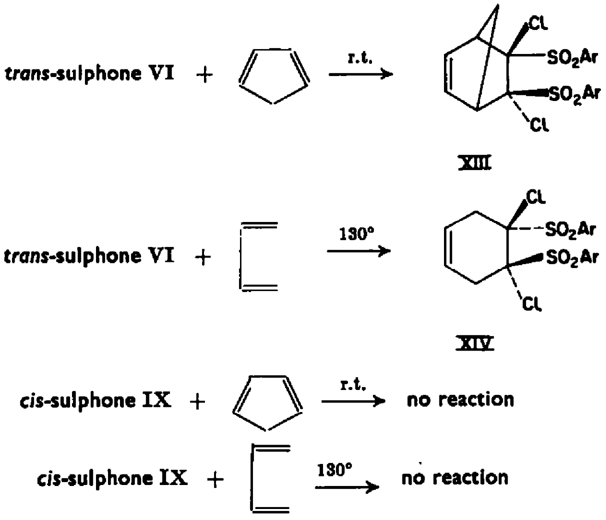
Crystals of the *trans*-sulphide (V), m.p. 101–101·5°, and *cis*-sulphide (VIII), m.p. 82–83°, of mol. wt. 341·32 were photographed on a Buerger Precession camera. Their space groups were determined as $P2_1/a$ for the higher melting isomer, and as either P1 or $P\bar{1}$ for the lower melting isomer. Unit cell dimensions and density measurements showed that there were two molecules per unit cell in each case. Since the space group $P2_1/a$ has four asymmetric units related by centres of symmetry, the higher melting isomer must possess a *trans* configuration. By elimination the lower melting isomer must have the *cis*-configuration. Its molecular symmetry must be m or 2. Since the two-fold configuration is likely to have less energy, the two enantiomorphs are possibly related by a centre of symmetry in $P\bar{1}$.

The above crystallographic data are consistent with the dipole moments which have been observed for V and VIII. The *cis*-sulphide (VIII, μ = 2·60 D.) would be expected to have the higher dipole moment, in spite of the complications presumably caused by the non-linearity of the carbon-sulphur-carbon bond angle.[7] This expectation is further supported by the fact that the dipole moment of the *trans*-sulphide (V, μ = 2·39 D.) is the same (within experimental error of ±0·03 D.) as the dipole moments of *trans*-1,2-bis(*p*-tolylthio)-ethylene, $\mu = 2{\cdot}37$ D., and 1,2-bis(*p*-tolylthio)-ethyne, $\mu = 2{\cdot}39$ D.

This assignment is also in line with a correlation between m.p. and configuration.[8] In eight out of nine cases for which data are available, the *trans*-1,2-bis(arylthio)-ethylene was higher melting than the *cis*-1,2-bis(arylthio)ethylene.[9] Also, in eleven out of twelve cases for which data are available, the *trans*-1,2-bis[alkyl(or aryl) sulphonyl]ethylene was higher melting than the *cis*-1,2-bis[alkyl(or aryl) sulphonyl]-ethylene.[10] With the 1,2-bis(*p*-tolylthio)-1,2-dichloroethylenes, the *trans*-sulphide (V) and the *trans*-sulphone (VI) are higher melting than the *cis*-sulphide (VIII) and the *cis*-sulphone (IX) respectively.

As suggested by data in the literature[11] and verified by a competitive reaction of *trans*-1,2-bis(*p*-tolylsulphonyl)ethylene (X) and *cis*-1,2-bis(*p*-tolysulphonyl)ethylene (XI) with cyclopentadiene, the *trans*-sulphone (X) reacts faster with cyclopentadiene than does the *cis*-sulphone (XI). The relative Diels-Alder reactivity of the *cis*-sulphone (IX) and *trans*-sulphone (VI) agrees with the above data as indicated by the fact that *trans*-sulphone(VI) forms Diels-Alder adducts with cyclopentadiene and 1,3-butadiene, whereas the *cis*-sulphone (IX) does not react with either diene under the same conditions.





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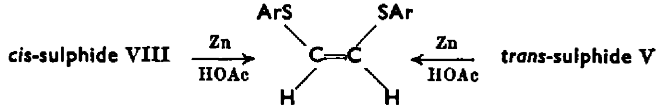
[8] L. Crombie, *Quart. Revs.* **6**, 101 (1952).

[9] F. Montanari, *Gazz. Chim. Ital.* **86**, 420 (1956).

[10] W. E. Parham, R. F. Motten and G. L. O. Mayo, *J. Amer. Chem. Soc.* **81**, 3386 (1959); M. F. Shostakovskii, E. N. Prilezhaeva, L. V. Tsymbal and L. G. Stolyarova, *Zh. Obshch Khim.* **30**, 3143 (1960); F. Montanari, *Gazz. Chim. Ital.* **86**, 428 (1956); F. Montanari, *Ibid.* **86**, 420 (1956).

[11] H. R. Snyder and D. P. Hallada, *J. Amer. Chem. Soc.* **74**, 5595 (1952); W. E. Truce and R. J. McManimie, *Ibid.* **75**, 1672 (1953).

It should be noted that both *cis*-sulphide (VIII) and *trans*-sulphide (V) were reduced by zinc in acetic acid in very poor yield to *cis*-1,2-bis(*p*-tolylthio)ethylene.



In order to study the extent of the stereoselectivity of the reaction of thiolate with tetrachloroethylene, the sodium n-propanethiolate–tetrachloroethylene system was adopted because the resulting compounds are liquids and could be analysed by vapour phase chromatography (vpc). Analysis of the mixture from the sodium n-propanethiolate–tetrachloroethylene reaction showed that the product consisted of n-propylthiotrichloroethylene (XV; 11%) and 1,2-bis(n-propylthio)-1,2-dichloroethylene (XVI; 89%), which was 94% the *trans*-sulphide (the major component was assumed to have a *trans* configuration by analogy with the sodium *p*-toluenethiolate–tetrachloroethylene system). The reaction mixture from the chlorination of 1,2-bis(n-propylthio)ethyne (XVII) contained 1,2-bis(n-propylthio)-1,2-dichloroethylene (XVI) which consisted of 45% *trans*-sulphide and 55% *cis*-sulphide. An analytically pure sample of 1,2-bis(n-propylthio)-1,2-dichloroethylene (94% *trans*) after irradiation with UV light was found to contain less *trans*-isomer (83%) and more *cis*-isomer (17%).

$$\begin{array}{lcc} \mathrm{PrSNa + Cl_2C{=}CCl_2 \rightarrow} & \mathrm{PrSCCl{=}CCl_2} & \mathrm{+\ PrSCCl{=}CClSPr} \\ & 11\% & 89\%\ (94\%\ \textit{trans},\ 6\%\ \textit{cis}) \\ & \mathrm{XV} & \mathrm{XVI} \end{array}$$

For the nucleophilic replacements by thiolates on tetrachloroethylene, a mechanism[12] involving carbanion intermediates was originally proposed.[6]

Initial addition of thiolate to form carbanion IIa followed by loss of chloride ion gives the intermediate, *p*-tolylthiotrichloroethylene (III) which has been isolated. Repetition of the process on III with formation of intermediate carbanion (IVa) results in *trans*-sulphide (V). The formation of an unstable intermediate analogous

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[12] There are at least two other possible mechanisms which can be envisaged and which cannot be entirely ruled out. One mechanism is a charge-transfer process involving charge-transfer complexes, such as $[\mathrm{ArS{\cdot}(Cl_2C \doteq CCl_2)^-}]$ and $[\mathrm{ArS{\cdot}(Cl_2C \doteq CClSAr)^-}]$. Colour formation is often observed in organic charge-transfer processes (R. Foster, *Photoelectric Spectrometry Group Bulletin* No. **15**, 413 (1963); E. M. Kosower and P. E. Klinedinst, Jr., *J. Amer. Chem. Soc.* **78**, 3493 (1956)); however, no colour formation was observed in the thiolate-tetrachloroethylene reaction. A second mechanism is a nucleophilic attack on chlorine with the formation of dichloroacetylene and *p*-toluenesulphenyl chloride which subsequently react to form III. Repetition of this process on III would give *p*-tolylthiochloroacetylene and *p*-toluenesulphenyl chloride which then react to form *trans*-sulphide (V). The addition of arylsulphenyl chloride to acetylene and chloroacetylene is known to proceed in a *trans* fashion (F. Montanari, *Gazz. Chim. Ital.* **86**, 406 (1956); G. Leandri, G. Modena and F. Montanari, *Boll. sci. fac. Chim. Ind. Bologna* **12**, 170 (1954); F. Montanari, *Ricerca Sci.* **25**, 3107 (1955); F. Montanari and A. Negrini, *Gazz. Chim. Ital.* **87**, 1061 (1957); W. E. Truce and R. Kassinger, *J. Amer. Chem. Soc.* **80**, 1916 (1958)) which, in this case, would produce *cis*-sulphide (VIII) rather than the observed *trans*-sulphide (V). *cis*-Sulphide (VIII) was not isomerized by treatment with sodium *p*-toluenethiolate in refluxing ethanol. However, the possibility remains that arylsulphenyl chloride could behave anomalously with arylthiochloroacetylenes.

to anions IIa and IVa (drawn in the Newman notation[13] in Fig. 1) having sp^3-hybridization was previously suggested by a number of workers.[14] Loss of chloride ion from carbanion IVa must occur in a stereospecific manner to give the *trans*-sulphide (V). This may be accounted for by assuming that the unstable carbanion (IVa) which is in equilibrium with such other conformations as IVb and IVc, will react by the path most energetically favourable. This path is *via* a transition state resembling IVc because a transition state resembling IVb would require more energy to eclipse the rather bulky groups attached to sulphur.

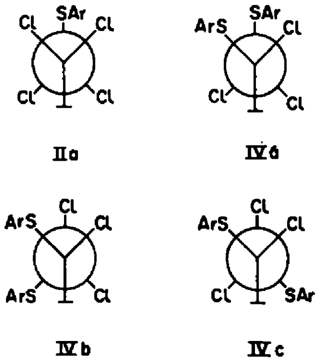

FIG. 1.

EXPERIMENTAL

All m.ps were taken in capillary tubes and are uncorrected. IR spectra were obtained in $CHCl_3$ solution or as nujol mulls with an Infracord spectrophotometer. Elemental analyses and mol. wt. determinations by a Mechrolab vapour phases osmometer (Model 301A) were performed by Dr. C. S. Yeh and assistants, Lafayette, Indiana.

trans-1,2-*Bis*(p-*tolylthio*)-1,2-*dichloroethylene* (V). This sulphide, m.p. 101–101·5°, was prepared[6] by reaction of sodium *p*-toluenethiolate with tetrachloroethylene (I) in refluxing EtOH.

trans-1,2-*Bis*(p-*tolylsulphonyl*)-1,2-*dichloroethylene* (VI). This sulphone, m.p. 188–189°, was prepared[6] by oxidation of V with H_2O_2 in acetic acid.

cis-1,2-*Bis*(p-*tolylthio*)-1,2-*dichloroethylene* (VIII). This sulphide, m.p. 82–83°, was prepared[6] by chlorine addition to 1,2-bis(*p*-tolylthio)ethyne (VII).

cis-1,2-*Bis*(p-*tolylsulphonyl*)-1,2-*dichloroethylene* (IX). A mixture of 1 g (0·00293 m) VIII, 25 ml glacial acetic acid and 7 ml 30% H_2O_2 at 0° was allowed to come to room temp and then heated on a steam bath for 3 hr. The reaction mixture was poured into 50 g ice water and the white solid which formed collected by filtration. Recrystallization from EtOH gave 0·92 g IX, m.p. 146–147°, in 77% yield. Further recrystallization from ether gave IX, m.p. 151–152°. (Found: C, 47·52; H, 3·50; Cl, 17·60; S, 15·75 $C_{16}H_{14}Cl_2O_4S_2$ requires: C, 47·41; H, 3·48; Cl, 17·50; S, 15·82%.) The IR spectrum of IX is identical with that of VI except that it shows an absorption band at 10·4 μ which is not present in the IR spectrum of VI. Also it is to be noted that the IR spectra of V and VIII are identical.

X-ray crystallography data. Crystals of *trans*-sulphide V, m.p. 99–101°, were grown from 2-propanol. They were colourless prisms with well developed {1, 0, 0} and {0, 0, 1} faces. Photographs of the (h, 0, l), (h, 1, l) and (0, k, l) reflections from a crystal of dimensions 0·07 × 0·2 × 0·07 cm

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[13] M. S. Newman, *J. Chem. Ed.* 37, 344 (1955).

[14] V. Gold, *J. Chem. Soc.* 1430 (1951); J. F. Bunnett and D. E. Zahler, *Chem. Revs.* 49, 273 (1951); D. E. Jones, O. R. Morris, C. A. Vernon and R. F. M. White, *J. Chem. Soc.* 2349 (1960); J. Hine, *Physical Organic Chemistry* p. 233. McGraw-Hill, New York (1962). However, this explanation would not be altered if carbanions adjacent to divalent sulphur were planar.

showed the symmetry to be monoclinic. The only systematic absences were for the (h, 0, l) reflections when h was odd and (0, k, 0) when k was odd. Therefore the space group was $P2_1/a$. The cell dimensions were a = 18·29 Å, b = 5·97 Å, c = 7·66 Å, β-105° 45′. Assumption of two molecules per unit cell gave a calculated density of 1·40 g/cm^3 in agreement with the measured density of 1·4 ± 0·1 g/cm^3. Since the cell contains four asymmetric units, the molecule must possess a centre of symmetry, and can only have the *trans* configuration.

Crystals of *cis*-sulphide VIII, m.p. 82–83°, were grown from diethyl ether and were opaque, yellowish prisms with well developed {0, 0, 1} and {1, 0, 0} faces. Photographs of the (h, 0, l) and (0, k, l) reflections, as well as cone axis photographs down the a and b axes, were taken. The triclinic crystals had dimensions 0·05 × 0·18 × 0·13 cm, with cell parameters a = 10·05 Å, b = 9·24 Å, c = 9·32 Å, α = 107° 24′, β = 96° 18′, γ = 98° 30′. Assumption of two molecules per unit cell gave a calculated density of 1·41 g/cm^3 in agreement with the measured density 1·4 ± 0·1 g/cm^3. Since the cell contained two molecules the space group was $P1$ or $P\bar{1}$.

Reduction of cis-*1,2-bis(*p*-tolylthio)-1,2-dichloroethylene* (VIII). A mixture of 1·5 g *cis*-sulphide VIII, 5 g Zn dust and 50 ml glacial acetic acid was refluxed for 4 hr and filtered while hot. The hot filtrate was poured into water and the water solution extracted with CH_2Cl_2. After washing with water the CH_2Cl_2-extract was dried (Na_2SO_4) and evaporated to dryness. The residue was dissolved in CH_2Cl_2 and purified by chromatography on an alumina column eluting with 1 l. hexane and with 400 ml CH_2Cl_2. A solid, m.p. 78–83° after recrystallization from 2-propanol, failed to give a $AgNO_3$ test for Cl-ion when fused with Na, was collected from the CH_2Cl_2-eluent. This material, obtained in 10% yield, was identified as *cis*-1,2-bis(*p*-tolylthio)ethylene on the basis of its IR spectrum which was superimposable with the spectrum of an authentic sample of *cis*-1,2-bis(*p*-tolylthio)ethylene, lit.[15] m.p. 92°.

Diels–Alder reaction between trans-*sulphone* (VI) *and cyclopentadiene.* To a solution of 2 g (0·0049 m) *trans*-sulphone (VI) dissolved in 40 ml benzene at room temp was added 13 ml freshly distilled cyclopentadiene. After 2·5 hr a white solid precipitated. The solid, collected by filtration, afforded an 87% yield of the adduct XIII, m.p. 252–254° with dec. (Found: C, 53·66; H, 4·36; Cl, 14·91; S, 13·40 $C_{21}H_{20}Cl_2O_4S_2$ requires: C, 53·50; H, 4·25; Cl, 15·07; S, 13·59%.)

Diels–Alder reaction between cis-*sulphone* (IX) *and cyclopentadiene.* To a solution of 0·6 g (0·0015 m) *cis*-sulphone (IX) dissolved in 12 ml benzene at room temp was added 6 ml freshly distilled cyclopentadiene. After standing 18 hr the benzene solution was evaporated to dryness and the residue m.p. 132–150° identified as IX by its IR spectrum.

Diels–Alder reaction between trans-*sulphone* (VI) *and* 1,3-*butadiene.* Two sealed Carius tubes, each containing 6 g (0·0148 m) *trans*-sulphone (VI), 12·4 g (0·23 m) 1,3-butadiene, 0·1 g hydroquinone and 40 to 50 ml toluene, were heated to 130° for 24 hr. The sealed Carius tubes were opened and the combined reaction mixture evaporated to dryness. The residue was boiled with 600 ml EtOH and filtered while hot. Unreacted *trans*-sulphone (VI, 54%) was recovered from the hot EtOH extract and identified by its IR spectrum. The hot EtOH insoluble residue was recrystallized from toluene to give XIV, m.p. 218–219°, in 33% yield. (Found: C, 52·74; 52·78; H, 4·66, 4·66; Cl, 15·72, 15·64; S, 13·99, 13·82; mol. wt., 469, 456 $C_{20}H_{20}Cl_2O_4S_2$ requires: C, 52·29; H, 4·36; Cl, 15·43; S, 13·94%; mol. wt. 459.)

Diels–Alder reaction between cis-*sulphone* (IX) *and* 1,3-*butadiene.* A sealed Carius tube, containing 1·3 g (0·0032 m) *cis*-sulphone (IX), 15 ml (0·172 m) 1,3-butadiene, 0·05 g hydroquinone and 40 ml toluene was heated to 130° for 24 hr. The reaction mixture was evaporated to dryness and the residue after recrystallization from absolute EtOH gave *cis*-sulphone (IX), m.p. 147–150°, in 69% recovery as identified by IR spectrum. The remaining unreacted *cis*-sulphone (IX, 31%) was recovered by evaporation of the mother liquor and identified by IR spectrum.

Diels–Alder competition experiment. To a solution of 1 g (0·00295 m) *trans*-sulphone (X)[11] and 1 g (0·00295 m) *cis*-sulphone (XI)[11] in 200 ml $CHCl_3$ at 28° was added 0·25 ml (0·201 g, 0·0030 m) freshly distilled cyclopentadiene and the solution stirred for 1 hr. The reaction mixture was evaporated under red. press. at 40°. The residue after chromatography on an alumina column afforded the *trans*-adduct (XII), m.p. 159–160° (lit.[11] m.p. 162–163°), in 59% yield (no *cis*-adduct was isolated).

1,2-*Bis(*p*-tolylsulphonyl)benzene.* A solution of 3 g (0·00654 m) 4,5-bis(*p*-tolylsulphonyl)-4,5-dichlorocyclohexene and 1·3 g (0·0196 m) 85% KOH dissolved in 50 ml EtOH was refluxed for 2 hr

[15] W. E. Truce, M. M. Boudakian, R. F. Heine and R. J. McManimie, *J. Amer. Chem. Soc.* **78**, 2743 (1956).

and evaporated to dryness. The residue was extracted with CH_2Cl_2 and the yellow solution treated with charcoal. The white solid, remaining after evaporation of the CH_2Cl_2, was recrystallized from 95% EtOH and afforded 1 g 1,2-bis(*p*-tolylsulphonyl)benzene, m.p. 162–164°, as indicated by its elemental analysis, mol. wt, IR spectrum and NMR spectrum. (Found: C, 62·05; H, 4·78; S, 16·77; mol. wt., 400 $C_{20}H_{18}O_4S_2$ requires: C, 62·18; H, 4·66; S, 16·58%, mol. wt., 386.)

Thiolate treatment of cis-*sulphide* (VIII). To a solution of 1 g (0·00293 m) *cis*-sulphide (VIII) in 25 ml abs. EtOH was added a sodium *p*-toluenethiolate solution, prepared by dissolving 0·04 g (0·0029 g atom) Na and 0·11 g (0·001 m) *p*-toluenethiol in abs. EtOH. The resulting mixture was refluxed under N_2 atm. for 12 hr followed by evaporation of the solvent. The residue was dissolved in ether and the ether solution was washed with KOH aq. Recrystallization of the ether residue afforded unreacted VIII, m.p. 82–83°, in 70% yield.

trans-1,2-*Bis*(*n-propylthio*)-1,2-*dichloroethylene*. A solution of 16·5 g (0·10 m) tetrachloroethylene in EtOH was added dropwise to a sodium n-propanethiolate solution prepared by dissolving 5·6 g (0·20 g atom) Na and 15·2 g (0·20 m) n-propylmercaptan in 200 ml abs. EtOH. After refluxing under a N_2 atm. for 19 hr, the reaction mixture was filtered while hot (affording a 92% yield of salt). The filtrate was evaporated to dryness, dissolved in CH_2Cl_2, washed with water, dried ($MgSO_4$) and evaporated under red. press. to yield *trans*-1,2-bis(n-propylthio)-1,2-dichloroethylene in 64% yield.

Vpc analysis of the product on a Silicone SE-30 column at 200° showed the presence of XV and XVI in the relative amounts of 11% and 89%, respectively. Vpc analysis of the product on a phenyldiethanolamine succinate column at 190° showed the presence of *trans*- and *cis*-1,2-bis(n-propylthio)-1,2-dichloroethylene in the relative amounts of 94% and 6%, respectively. Compound XV, b.p. 35–36°/0·3 mm, n_D^{29} 1·5310, and XVI, b.p. 90–92°/0·4 mm, n_D^{29} 1·5542, could be separated easily by vacuum distillation. Analytical samples of XV and XVI were obtained by preparative vapour phase chromatography. (Found: C, 29·38; H, 3·70; Cl, 52·20; S, 15·45; mol. wt., 221 $C_5H_7Cl_3S$ requires: C, 29·27; H, 3·42; Cl, 51·95; S, 15·61%; mol. wt., 205·5.) (Found: C, 39·50; H, 5·68; Cl, 29·20; S, 26·00; mol. wt., 242 $C_8H_{14}Cl_2S_2$ requires: C, 39·18; H, 5·71; Cl, 28·98; S, 26·12%; mol. wt., 245.)

cis-1,2-*Bis*(*n-propylthio*)*ethylene*. A solution of 42 g (0·25 m) *cis*-1,2-dichloroethylene in EtOH was added dropwise over a 3 min period to a solution of sodium n-propanethiolate, prepared by dissolving 13 g (0·566 g atom) Na and 38 g (0·5 m) n-propylmercaptan in 600 ml abs. EtOH. After refluxing for 24 hr the reaction mixture was diluted with 2 l. water and extracted 3 times with 300 ml CH_2Cl_2. The CH_2Cl_2 extract was washed with water, dried ($MgSO_4$) and evaporated under red. press. Distillation of the residue afforded *cis*-1,2-bis(n-propylthio)ethylene, b.p. 138–140°/20 mm, n_D^{27}1·5316 (lit.[16] b.p. 141°/18 mm), in 65% yield. (Found: C, 54·79, H, 9·37; S, 36·00; mol. wt., 182 Calc. for $C_8H_{16}S_2$: C, 54·55; H, 9·08; S, 36·35%; mol. wt., 176.)

Bis(*n-propylthio*)*ethyne*. To a solution of 28 g (0·159 m) *cis*-1,2-bis(n-propylthio)ethylene in 100 ml CCl_4, cooled in an ice bath, was added dropwise over a 30 min period a solution of 25·5 g (0·16 m) Br_2 dissolved in 50 ml CCl_4. After the addition of the Br_2 was complete, a solution of 31·6 g (0·48 m) 85% KOH aq was added and the mixture refluxed for 3 hr. After filtration the reaction mixture was diluted with 3 l. water and extracted twice with 300 ml CH_2Cl_2. The organic extracts were washed with water, dried ($MgSO_4$) and evaporated under red. press. Distillation of the residue gave bis(n-propylthio)ethyne, b.p. 134–142°/20 mm, n_D^{27} 1·5145, in 55% yield. Vpc analysis showed the presence of a substantial amount of unreacted *cis*-1,2-bis(n-propylthio)ethylene.

Chlorination of bis(*n-propylthio*)*ethyne*. A solution of 6·0 g (0·084 m) Cl_2 in 40 ml cold CCl_4 was added dropwise over a 30 min period to a cold solution of 14 g (0·081 m) bis(n-propylthio)ethyne, b.p. 138–1420/20 mm, in CCl_4. The reaction mixture was stirred for 1 hr at 0° and evaporated under red. press. Vpc analysis of the residue on a phenyldiethanolamine succinate column at 190° showed the presence of *trans*- and *cis*-1,2-bis(n-propylthio)-1,2-dichloroethylene in relative amounts of 45% and 55%, respectively.

Isomerization of sulphide XVI. Forty microliters of 1,2-bis(n-propylthio)-1,2-dichloroethylene (94% *trans*, 6% *cis*) was irradiated with UV light from a 500 watt Hg-arc lamp for 20 hr. Vpc analysis after irradiation showed the presence of only 1,2-bis(n-propylthio)-1,2-dichloroethylene (83% *trans*, 17% *cis*).

[16] Pittsburgh Coke and Chemical Co., British patent 819,069 (1959); [*Chem. Abstr.* **54**, P9193d (1959)].