Anal. Calcd. for $C_{26}H_{26}N_2O_2$ (398.49): C, 78.36; H, 6.57. Found: C, 78.41; H, 6.50.

Oxime of III. Ten milliliters of 95% alcohol containing 0.246 g. of III, 0.167 g. of hydroxylamine hydrochloride, and 0.5 ml. of pyridine were heated to boiling. The solution was cooled, and the solid which separated was purified from 95% alcohol (m.p. 148–149°).

Anal. Calcd. for $C_{20}H_{21}O_3$ (323.38): C, 74.27; H, 6.55; N, 4.33. Found: C, 74.29; H, 6.40; N, 4.37.

Hydrolysis of III. (*dl-3,4-Diphenyladipic acid*). One gram of III in 10 ml. of 5% sodium hydroxide–ethanol solution was warmed on a steam bath for 1 hr. The solution was allowed to cool and was acidified with hydrochloric acid. Water was added to precipitate the product. The product was purified from 95% alcohol and water (m.p. 186°). A mixed melting point of this compound with known sample prepared by the procedures of Badger[10] showed no depression. Neut. equiv. Calcd. for $C_{18}H_{18}O_4$ (298.32): 149.16. Found: 150.7.

dl-3,4-Diphenylcyclopentanone (II). Five grams of III in 25 ml. of 20% hydrobromic acid and 20 ml. of 95% alcohol was refluxed for 1 hr. The hard lumpy substance was washed with water and purified from 95% alcohol, followed by recrystallization from ether. The colorless sawtooth-like crystals melted at 177°.

Anal. Calcd. for $C_{17}H_{16}O$ (236.30): C, 86.40; H, 6.80. Found: C, 86.69; H, 6.97.

Oxime of dl-3,4-diphenylcyclopentanone. One gram of II, 2 ml. of pyridine, 0.3 g. of hydroxylamine hydrochloride, and 20 ml. of 95% alcohol was refluxed for 2 hr. The solution was concentrated and the product purified from 95% alcohol (m.p. 117–118°).

Anal. Calcd. for $C_{17}H_{17}NO$ (251.32): C, 81.24; H, 6.81. Found: C, 81.38; H, 6.91.

Acknowledgments. The authors are greatly indebted to Dr. R. H. Eastman for his interest in this work and very helpful discussions. We also wish to thank Miss Brigitte Bach for the infrared and ultraviolet spectral measurements.

STANFORD, CALIF.

[CONTRIBUTION FROM THE DIAMOND ALKALI COMPANY RESEARCH DEPARTMENT]

Chlorinated Derivatives of Butadiene Sulfone and Diels-Alder Reactions of 3,4-Dichlorothiophene 1,1-Dioxide

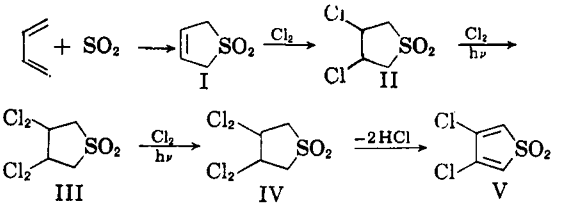
HENRY BLUESTONE, RUSSELL BIMBER, REYNOLD BERKEY, AND ZOLTAN MANDEL[1]

Received May 3, 1960

Chlorination of butadiene sulfone (I) has produced *cis*- and *trans*-3,4-dichlorotetrahydrothiophene 1,1-dioxide (*cis*-II and *trans*-II), 3,3,4-trichlorotetrahydrothiophene 1,1-dioxide (III), and 3,3,4,4-tetrachlorotetrahydrothiophene 1,1-dioxide (IV). Treating *cis*-II and *trans*-II with an equivalent of alkaline material yielded 3-chloro-2,3-dihydrothiophene 1,1-dioxide (VI); alkaline treatment of IV yielded 3,4-dichlorothiophene 1,1-dioxide (V) and 3,3,4-trichloro-2,3-dihydrothiophene 1,1-dioxide (VII). Diels-Alder reactions of 3,4-dichlorothiophene 1,1-dioxide (V) with butadiene, isoprene, and cyclopentadiene each produced two types of products wherein the diene-dienophile relationships were interchanged. Reactions of V with benzoquinone, bicycloheptadiene, two *N*-substituted maleimides, and with itself are also reported.

The investigation of the chemistry and biological activity of chlorinated derivatives of butadiene sulfone was undertaken because of the expected reactivity of such compounds with various substrates. This report concerns the intermediates involved in the preparation of 3,4-dichlorothiophene 1,1-dioxide (V) and Diels-Alder reactions of V. Reports on the biological activity of some of these materials[2,3] have been or will be published elsewhere.

The synthetic route to V is straightforward and is represented by the following series of reactions:



The chlorination of 2,5-dihydrothiophene 1,1-dioxide (I) under a variety of conditions[4-7] produced 3,4-dichlorotetrahydrothiophene 1,1-dioxide (II) as the main product.

Chlorination of I produced a mixture of the *cis* and *trans* isomers of II. Prochazka and Horak[7] reported a 75% yield of *trans*-II *via* chlorination in aqueous hydrochloric acid, but isolation of *cis*-II has not been reported. We have found chlorination conditions which favor formation of each isomer and have isolated both pure isomers. The *cis* isomer was the major product when the chlorination of I was conducted in an essentially nonpolar environment, whereas the *trans* isomer predominated when the chlorination was carried out under polar conditions. Thus, chlorinating a solution or suspension of I in anhydrous carbon tetrachloride using only gaseous chlorine produced the

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[1] Present address: Experimental Station, E. I. du Pont de Nemours & Co., Wilmington, Del.

[2] P. H. Schuldt and H. Bluestone, *Contrib. Boyce Thompson Inst.*, 19, 63 (1958).

[3] P. H. Schuldt, unpublished paper, Gordon Research Conferences, 1959.

[4] E. de Roy Van Zuydewijn, *Rec. trav. chim.*, 57, 443 (1938).

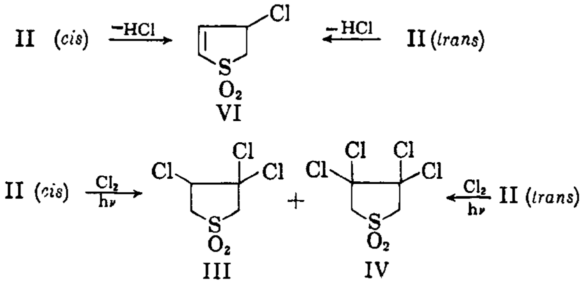
[5] T. E. Jordan and F. Kipnis, *J. Am. Chem. Soc.*, 71, 1875 (1949).

[6] F. H. Firsching and I. Rosen, *J. Org. Chem.*, 23, 502 (1958).

[7] M. Prochazka and V. Horak, *Chem. listy*, 52, 1768 (1958).

cis isomer in about 65% yield; chlorinating I under similar conditions but with the addition of a small quantity of ferric chloride, aluminum chloride, antimony chloride, or iodine, produced the *trans* isomer in about 80% yield. The predominant isomer was separated from the crude chlorination product by fractional crystallization from water or methanol. The two isomers had almost identical melting points (*cis*: 129.5–130.5°; *trans*: 129.5–130°) but the melting point of their mixture was depressed about 20°, and they differed in crystalline form.

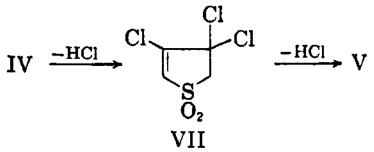
Proof that the two substances were indeed *cis-trans* isomers was established by the fact that (1) monodehydrochlorination of either isomer produced the identical 3-chloro-2,3-dihydrothiophene 1,1-dioxide (VI), and (2) photochlorination of either isomer produced the identical trichloro (III) and tetrachloro (IV) derivatives, in good yield.



The assignment of *cis* and *trans* configurations to the separate isomers was based on measurements of their relative dipole moments in dioxane solution. The isomer with the smaller dipole moment was designated *trans* and this was in agreement with the tentative geometric assignment based on mode of preparation; that is, the isomer which predominated when the addition chlorination of I was carried out in the presence of metal chlorides and would accordingly be expected to result from *trans* addition, was found to have the smaller dipole moment. The two pure isomers were also found to have a marked difference in thermal stability. Thus the *cis* isomer, on heating at 220 ± 10° for six hours, decomposed with loss of one equivalent of acidic vapor, whereas the *trans* isomer was stable under the same conditions.

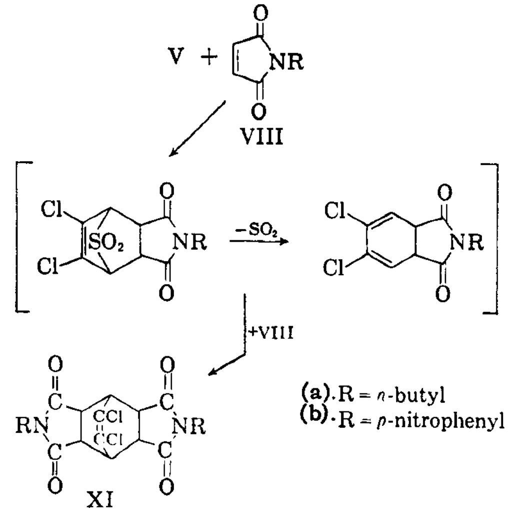
An infrared spectrophotometric method was developed for determining the compositions of mixtures containing *cis*-II, *trans*-II, and VI, based on their absorption maxima at 8.25 μ, 8.33 μ, 13.03 μ, respectively.[8]

The substitutive chlorination of II is in apparent contradiction to the report of Jordan and Kipnis,[5] but their report did not include free radical catalysis. We have found that II in the presence of benzoyl peroxide or ultraviolet light was chlorinated to either III or IV, depending on chlorination time. IV distilled without decomposition at 222° and 100 mm. pressure. The dehydrochlorination of IV with base produced either 3,3,4-trichloro-2,3-dihydrothiophene 1,1-dioxide (VII) or 3,4-dichlorothiophene 1,1-dioxide (V).



VII

Thiophene 1,1-dioxides such as V are of particular interest in Diels-Alder reactions. They exemplify a unique system wherein a heterocyclic conjugated diene has properties of a reactive diene as well as of a reactive dienophile.[9-14] Reactions of these compounds as the diene component in Diels-Alder reactions are generally accompanied by loss of the sulfonyl bridge from the 1:1 adduct, generating a new conjugated diene system, whereupon reaction with a second mole of dienophile frequently occurs.[9-11,14] We have isolated such 2:1 products (IX) in good yields from reactions of V with *N*-substituted maleimides (VIII). Maleic anhydride appeared to react similarly.



(a). R = *n*-butyl
(b). R = *p*-nitrophenyl

When benzoquinone was chosen as the dienophile the product was not a 2:1 adduct but instead 6,7-dichloronaphthoquinone (XI) was obtained. The course of this reaction is believed to be

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(8) I. E. Smiley and J. J. Mannion, unpublished results; *cis*- and *trans*-II were measured in acetonitrile and VI in nitromethane.

(9) W. J. Bailey and E. W. Cummins, *J. Am. Chem. Soc.*, **76**, 1932–1942 (1954).

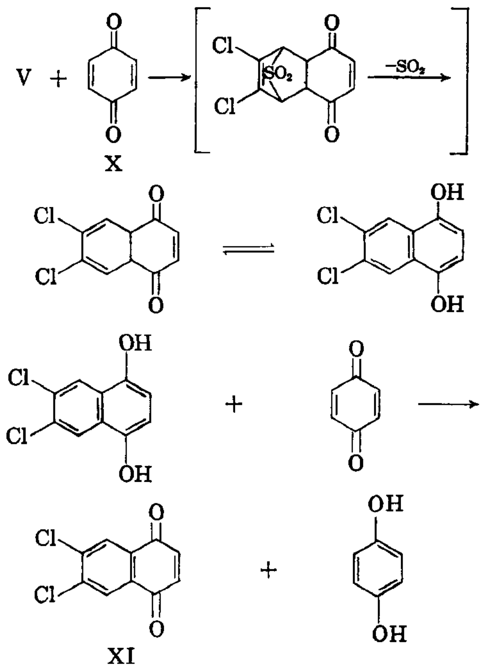
(10) J. L. Melles, *Rec. trav. chim.*, **71**, 869 (1952); *Chem. Abstr.*, **47**, 7485f.

(11) H. J. Backer and J. L. Melles, *Koninkl. Ned. Akad. Wetenschap. Proc.*, **54B**, 340 (1951) (in English); *Chem. Abstr.*, **47**, 6932b.

(12) W. Davies and Q. N. Porter, *J. Chem. Soc.*, 459 (1957).

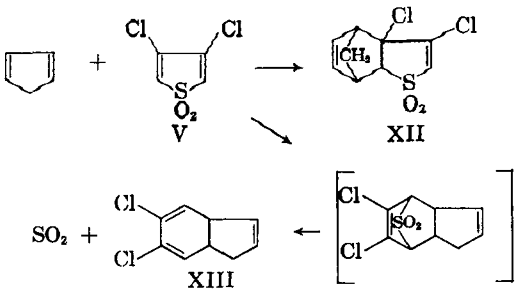
(13) W. Davies, F. C. James, S. Middleton, and Q. N. Porter, *J. Chem. Soc.*, 1565 (1955).

(14) J. M. Whelan, Jr., *Dissertation Abstr.*, **20**, 1180 (1959).



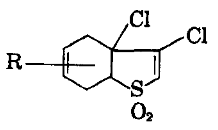
This is analogous to reactions of cyclopentadienones with quinones.[15] In the workup of this reaction quinhydrone was also isolated. When the reaction was repeated, hydrogen peroxide was used to convert the quinhydrone to benzoquinone, which was more readily separated from the product, XI.

When reactions of V with conjugated diene hydrocarbons were carried out we were interested to learn which of the two conjugated reactants would participate as the diene and which as the dienophile. Since it was reasonable to expect the elimination of the sulfonyl bridge as sulfur dioxide from those 1:1 adducts where V had functioned as the diene, the presence of sulfur in the product would indicate that V had reacted as the dienophile. Using the reaction of V with cyclopentadiene as an example, two types of 1:1 adducts (exclusive of *exo-endo* isomerism) might result:

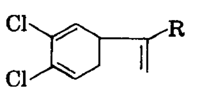


Thus XII would result if V behaved as the dienophile whereas XIII would be expected if cyclopentadiene functioned as the dienophile. Actually, both XII and XIII were produced, with XII predominating.

Butadiene and isoprene produced similar pairs of products XIV and XV.

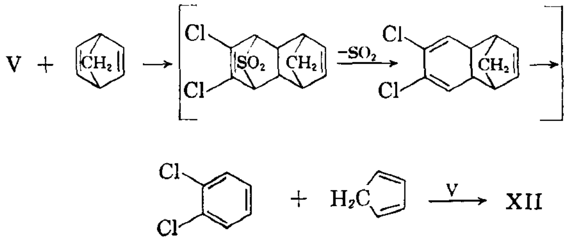


XIVa. R = H
b. R = CH_3

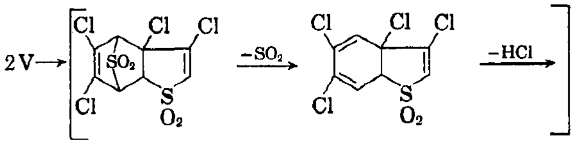


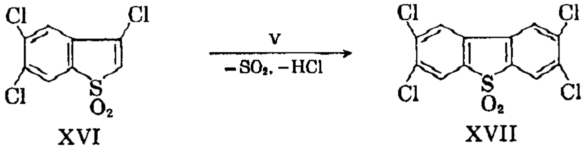
XVa. R = H
b. R = CH_3

The reaction of V with bicyclo[2.2.1]hepta-2,5-diene produced an unexpected result in that the only solid product isolated was XII. However, when *o*-dichlorobenzene was identified as a reaction product, it became apparent that the course of the reaction must have been as follows:



It having been established that 3,4-dichlorothiophene 1,1-dioxide, V, behaved both as a diene and as a dienophile in reactions with other conjugated dienes at low to moderate temperatures, its thermal polymerization was attempted in inert solvents. In one attempt, V in refluxing xylene was rapidly converted to a mixture of products from which XVI, XVII, and a third product, melting at 231.5–232°, were isolated. XVII was also prepared separately by refluxing a trichlorobenzene solution of V and XVI.





Based on the elemental analysis and molecular weight determination, the product melting at 231.5–232° had a molecular formula of $C_8H_4Cl_4S_2O_4$, corresponding to a dimer of V. The infrared absorption spectra of this material contained an absorption maxima at 3.26 μ which was attributed to an ethylenic H atom. Two pairs of isomeric structures were considered for this dimer: XVIII-a and XVIII-b, the *endo* and *exo* pair of Diels-Alder adducts; and XIX-a and XIX-b, obtainable by a 1,2 to 1,2 or a 1,2 to 2,1-adduction.

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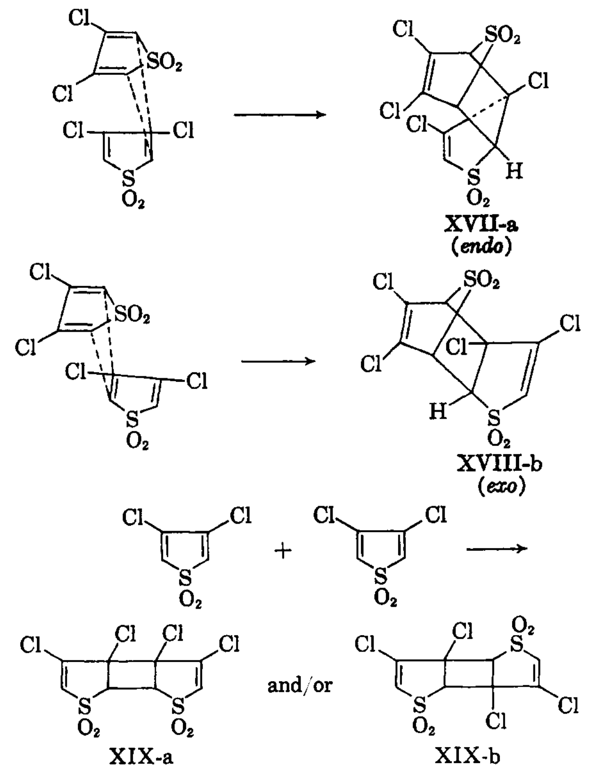
[15] W. Dilthey and F. Quint, *J. prakt. Chem.*, [2] 128, 139 (1930).



XVII-a (*endo*)

XVIII-b (*exo*)

XIX-a

XIX-b

Although sulfonyl bridged cyclohexane rings[16] and carbonyl bridged cyclohexene rings[17] have been previously reported, there appears to be no prior mention of the existence of a stable compound containing a sulfonyl bridged cyclohexene ring. Accordingly, structures XVIII appeared unlikely.

The chemical literature shows that the *endo* isomer is by far the more common product of Diels-Alder reactions under mild conditions.[18] Therefore we believe the production of XVI proceeds via the *endo* adduct XVIII-a, which loses sulfur dioxide and hydrogen chloride to produce XVI.

Structures XVIII and XIX were expected to be distinguishable *via* NMR measurements since XIX contains only two types of C—H bonds whereas XVIII has three. The NMR spectrum of the dimer of V was obtained and found to contain peaks corresponding to two different C—H bond types. In addition, crystals of the dimer were found to exhibit zero piezoelectricity by Dr. Leroy Alexander of the Mellon Institute and it was concluded that the structure was completely centrosymmetric. We therefore believe the dimer of V has the structure represented by XIX-b, wherein the two sulfonyl rings are fused *trans* to the cyclobutane ring.

EXPERIMENTAL[19]

cis-3,4-Dichlorotetrahydrothiophene 1,1-dioxide (*cis*-II). A suspension of 118 g. (1.0 mole) of I in 500 ml. of carbon tetrachloride was stirred while 90 g. (1.27 moles) of chlorine was bubbled in over a 2-hr. period. The mixture was cooled to keep it below 35°. The solid product was filtered and air dried, leaving 173 g. of II. An additional 15 g. (total 99%) of II was obtained from the filtrate. Infrared spectrophotometric analysis showed this II to be about 65% *cis*-II and 30% *trans*-II. Four recrystallizations from mixtures of methanol and water produced a first crop of 23.7 g. (12.5%) of needle-shaped crystals of pure *cis*-II, m.p. 129.5–130.5°.

Anal. Calcd. for $C_4H_6Cl_2O_2S$: C, 25.4; H, 3.2; Cl, 37.5; S, 16.9. Found: C, 25.2; H, 3.2; Cl, 37.9; S, 16.9.

trans-3,4-Dichlorotetrahydrothiophene 1,1-dioxide (*trans*-II). A suspension of 118 g. (1.0 mole) of I and 5.9 g. of anhydrous ferric chloride in 410 ml. of carbon tetrachloride was stirred and heated at reflux temperature while 95 g. (1.34 moles) of chlorine was added during a 2-hr. period. The mixture was cooled to room temperature, filtered, and the filtrate evaporated to dryness. The 200 g. of brown solid obtained was stirred briefly in 200 ml. of boiling water, then cooled to 10° and filtered. Infrared analysis of the 172 g. of dried crude product showed it to be about 83% *trans*-II. Two recrystallizations from 2500 ml. portions of water gave 85 g. (45%) of tetragonal plates of pure *trans*-II, m.p. 129.5–130.0°.

Anal. Calcd. for $C_4H_6Cl_2O_2S$: C, 25.4; H, 3.2; S, 16.9. Found: C, 25.2; H, 3.2; S, 16.9.

3,3,4-Trichlorotetrahydrothiophene 1,1-dioxide (III). A 400-g. sample (2.12 moles) of mixed *cis* and *trans* isomers of II was dissolved in 3 l. of carbon tetrachloride at reflux temperature. This was illuminated by a 100-watt Hanovia No. 8A1 ultraviolet lamp in a quartz immersion well while 325 g. (4.6 moles) of chlorine was passed into the mixture; this required 4.5 hr. Air was blown through the hot product suspension to remove hydrogen chloride and excess chlorine. Cooling in ice-water, filtering, and washing with cold carbon tetrachloride, left 350.2 g. of crude product. This produced 343 g. (72.5%) of III, m.p. 102–104°, when recrystallized from carbon tetrachloride. Several additional recrystallizations from methanol produced pure III, m.p. 110–111°.

Anal. Calcd. for $C_4H_5Cl_3O_2S$: C, 21.5; H, 2.3; Cl, 47.6. Found: C, 21.7; H, 2.2; Cl, 47.2.

III was also prepared by chlorinating the separate *cis* and *trans* isomers of II in acetic acid solution containing benzoyl peroxide.

3,3,4,4-Tetrachlorotetrahydrothiophene 1,1-dioxide (IV). A refluxing solution of 400 g. (2.12 moles) of II in 3000 ml. of carbon tetrachloride was exposed to ultraviolet radiation from a Hanovia No. 8A1 lamp in a quartz immersion well for 11 hr. while 1500 g. (21.2 moles) of chlorine was passed into the solution. Cooling and filtering gave a first crop of 390 g. (71%) of crude IV, m.p. 174–177°. Recrystallizing this from methanol produced pure IV, m.p. 178.5–179.5°.

Anal. Calcd. for $C_4H_4Cl_4O_2S$: C, 18.6; H, 1.6; Cl, 55.0. Found: C, 18.7; H, 1.7; Cl, 55.7.

3,4-Dichlorothiophene 1,1-dioxide (V). A solution of 50 g. (0.194 mole) of IV in 500 ml. of methanol was stirred while 30 ml. (0.45 mole) of 29% ammonia water was added portionwise. The solution was stirred 0.5 hr. longer and then 280 ml. of cold water and 120 g. of ice were added. Stirring was continued until the ice had just melted and then the product was filtered. The dried V was in the form of pale orange, needle-shaped crystals weighing 29.6 g. (82%), m.p. 112–113°. One recrystallization of this colored product from methanol, with a Nuchar treatment, produced colorless crystals of pure V, m.p. 112–113°.

Anal. Calcd. for $C_4H_2Cl_2O_2S$: C, 26.0; H, 1.1; Cl, 38.3. Found: C, 26.0; H, 1.5; Cl, 38.0.

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(16) S. F. Birch, R. A. Dean, and N. J. Hunter, *J. Org. Chem.*, 23, 1026 (1958).

(17) C. F. H. Allen and J. Van Allen, *J. Am. Chem. Soc.*, 64, 1260 (1942).

(18) R. B. Woodward and T. J. Katz, *Tetrahedron*, 5, 70 (1958).

(19) All melting points are uncorrected.

3-Chloro-2,3-dihydrothiophene 1,1-dioxide (VI). A solution of 1 g. (0.005 mole) of *cis*-II and 2 g. (0.025 mole) of pyridine in 5 ml. of chloroform was refluxed for 2 hr. The cooled solution was shaken with 10 ml. of aqueous 10% hydrochloric acid and the layers were separated. The chloroform layer, combined with three 10-ml. chloroform extracts of the aqueous layer, was dried over anhydrous potassium carbonate, filtered, and the chloroform was allowed to evaporate. Adding 25 ml. of ether to the brown oily residue precipitated a trace of brown powder; this was removed by filtration, leaving a colorless soluton. Adding 25 ml. of hexane and evaporating almost to dryness produced 0.50 g. (62%) of crystals of VI, m.p. 82 to 84°.

Anal. Calcd. for $C_4H_5ClO_2S$: C, 31.5; H, 3.3; Cl, 23.2. Found: C, 31.5; H, 3.3; Cl, 24.2.

3,3,4-Trichloro-2,3-dihydrothiophene 1,1-dioxide (VII). Pyridine (46 g., 0.58 mole) was added in one portion to a refluxing solution of 100 g. (0.388 mole) of IV in 500 ml. of methanol and refluxing was continued 10 min. Pouring this hot solution into 3000 ml. of cold water caused a solid to precipitate; this was reprecipitated from methanol by adding water. The precipitate was recrystallized from 250 ml. of benzene and then from 200 ml. of 1:1 benzene:cyclohexane, giving a first crop of 40.8 g. (43%) colorless crystalline VII, m.p. 108.5–109.5°.

Anal. Calcd. for $C_4H_3Cl_3O_2S$: C, 21.7; H, 1.4; Cl, 48.0. Found: C, 21.8; H, 1.4; Cl, 48.2.

N,N'-Dibutyl 5,6-dichlorobicyclo[2.2.2]-oct-5-ene-2,3,7,8-tetracarboxylic diimide (IXa). A solution of 9.3 g. (0.05 mole) of V in 200 ml. of xylene was added to 15 g. (0.98 mole) of *N*-butylmaleimide at room temperature. The solution was heated at reflux for 2.5 hr. and then left at room temperature overnight. The flaky solid which had separated was filtered and the mother liquor was concentrated, giving a total of 18.2 g. (87%) of crude product, m.p. 250–252°. This was recrystallized once from 700 ml. of xylene (Nuchar treatment) and then twice from 1400-ml. portions of methanol, producing a first crop of 11.8 g. (56.5%) of tetragonal plates of IXa, m.p. 257.5 to 258.5°.

Anal. Calcd. for $C_{20}H_{24}Cl_2N_2O_4$: Cl, 16.5; N, 6.5; S, absent. Found: Cl, 16.4; N, 6.4; S, absent.

N,N'-Bis(p-nitrophenyl)-5,6-dichlorobicyclo[2.2.2]-oct-5-ene-2,3,7,8-tetracarboxylic diimide (IXb). A solution of 18.5 g. (0.1 mole) of V and 43.6 g. (0.2 mole) of *N*-(*p*-nitrophenyl)maleimide in 1100 ml. of benzene was stirred at reflux overnight. An additional 9.3 g. (0.05 mole) of 3,4-dichlorothiophene 1,1-dioxide was then added and the mixture was stirred 4.5 hr. longer. The hot mixture was filtered, removing 49 g. of purple powder. Soluble impurities were extracted from this powder with chloroform in a Soxhlet apparatus, leaving 45.2 g. (81%) of light purple IXb, which blackened above 420°, but did not melt below 500°. Part of this recrystallized twice from dimethylformamide, giving colorless crystals of IXb, which blackened above 440° but did not melt below 500°.

Anal. Calcd. for $C_{24}H_{14}Cl_2N_4O_8$: C, 51.8; H, 2.5; Cl, 12.7; S, absent. Found: C, 52.0; H, 2.7; Cl, 12.7; S, absent.

6,7-Dichloro-1,4-naphthoquinone (XI).[20] A solution of 37 g. (0.20 mole) of V and 108 g. (1.0 mole) of benzoquinone in 250 ml. of benzene was heated at 65–70° for 88 hr. The benzene was removed under reduced pressure and the solid residue was slurried in 500 ml. of cold methanol and filtered, leaving 86.8 g. of solid. The solid was resuspended in methanol and 30% hydrogen peroxide was added to oxidize the hydroquinone present and thereby prevent separation of quinhydrone. Cooling and filtering produced 55.6 g. of solid, m.p. 148–164°. Two recrystallizations from ethanol, with a decolorizing carbon treatment, yielded 43.6 g. (96% based on V) of XI, m.p. 182–184°. Orange and reddish brown impurities were removed on a column of 60–200 mesh desiccant grade silica gel (Davison Chemical Co.) by eluting the product with benzene. The 27.1 g. (60%) of pure canary yellow platelets of XI melted at 185.0–186.5°. An additional recrystallization from benzene raised the m.p. to 186–187°.

Anal. Calcd. for $C_{10}H_4Cl_2O_2$: C, 52.9; H, 1.8; Cl, 31.2. Found: C, 52.7; H, 1.9; Cl, 31.4.

3,3a-Dichloro-3a,4,7,7a-tetrahydro-4,7-methanothianaphthene 1,1-dioxide (XII) and *5,6-dichloro-3a,7a-dihydroindene* (XIII). A solution of 185 g. (1 mole) of V in 850 ml. of acetone was stirred below 5° while 101.8 g. (1.5 moles) of freshly prepared monomeric cyclopentadiene was added over a period of 25 min. The reaction was strongly exothermic. The acetone was allowed to evaporate. Filtering the partly crystalline residue and triturating the solid with methanol left 153.7 g. (61%) of purplish crystals of crude XII, m.p. 148–151°. One recrystallization from methanol, including a Nuchar treatment, produced colorless XII, m.p. 150.5–151.5°.

Anal. Calcd. for $C_9H_8Cl_2O_2S$: C, 43.0; H, 3.2; Cl, 28.2. Found: C, 43.0; H, 3.2; Cl, 28.2.

The mother liquors from the crude XII were concentrated by removing the methanol under reduced pressure, leaving 73.3 g. of brown liquid. Distilling this produced 30.4 g. (16%) of colorless liquid XIII, b.p. 74–77° at 0.7 mm. The XIII had a refractive index (n_D^{27}) of 1.5600 and a density (d_4^{27}) of 1.273.

Anal. Calcd. for $C_9H_8Cl_2$: C, 57.8; H, 4.3; S, absent. Found: C, 57.8; H, 4.0; S, absent.

Reaction of bicycloheptadiene with V. A solution of 7.4 g. (0.04 mole) of V and 4.05 g. (0.044 mole) of redistilled bicyclo[2.2.1]hepta-2,5-diene in 50 ml. of chloroform was heated at reflux for 18 hr. while the system was swept with dry nitrogen. The exit gases were passed through an ammoniacal-pyridine solution of cuprous chloride in water. Since no precipitate formed in the cuprous chloride solution, no acetylene had formed. The cooled reaction mixture, which smelled like *o*-dichlorobenzene and contained a little solid, was triturated with portions of cold heptane and filtered. The resulting 3.4 g. of solid was extracted with boiling benzene, leaving a trace of insoluble material. Evaporating the benzene and washing the solid with heptane left 2.8 g. (28%) of crude XII, m.p. 144–149°. When mixed with pure XII, m.p. 150.5–151.5°, this product melted at 147–150°. Most of the heptane was distilled from the wash solution. The infrared spectrum and a vapor chromatogram of the residue confirmed the presence of *o*-dichlorobenzene.

3,3a-Dichloro-3a,4,7,7a-tetrahydrothianaphthene 1,1-dioxide (XIVa) and *2,3-dichloro-5-vinyl-1,3-cyclohexadiene* (XVa). A solution of 46.3 g. (0.25 mole) of V in 500 ml. of methanol was stirred and heated at 50 to 60° for 5 hr. while 68 g. (1.26 moles) of butadiene was bubbled into the solution. The methanol was then distilled under reduced pressure. The residual liquid crystallized when 100 ml. of petroleum ether (b.p. 35–60°) was added, giving 21.2 g. (35.5%) of crude XIVa, m.p. 68–80°. This produced a first crop of 12 g. (20%) of pure XIVa, m.p. 90–91°, when recrystallized from methanol.

Anal. Calcd. for $C_8H_8Cl_2O_2S$: C, 40.2; H, 3.4; Cl, 29.6. Found: C, 40.1; H, 3.4; Cl, 30.3.

The mother liquor from the crude XIVa was distilled twice. The 10.2 g. of colorless product, b.p. 72–76° at 4.2 mm., had a refractive index (n_D^{25}) of 1.5315 and a density (d_4^{25}) of 1.195. Analysis showed this to be XVa; the yield was 23%.

Anal. Calcd. for $C_8H_8Cl_2$: C, 54.9; H, 4.6; S, absent. Found: C, 54.0; H, 4.2; S, absent.

The infrared spectrum of the product had an absorption peak at 3.24 μ which was attributed to a terminal methylene group and it did not contain any absorption peaks which might indicate the presence of an aromatic ring.

3,3a-Dichloro-3a,4,7,7a-tetrahydro-5(and/or 6)-methylthianaphthene 1,1-dioxide (XIVb) and *2,3-dichloro-5-isopropenyl-*

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[20] The infrared spectrum of our product was consistent with the structure XI, although K. Babu Rao and N. V. Subba Rao, *J. Sci. Ind. Research (India)*, 17B, 225 (1958), report a m.p. of 199° for 6,7-dichloro-1,4-naphthoquinone.

1,3-cyclohexadiene (XVb). A solution of 111 g. (0.6 mole) of V in 1360 ml. of methanol was stirred at 45–55° while 68 g. (1.0 mole) of isoprene was added. The solution was stirred at 50° for 1 hr., then a second mole of isoprene was added and stirring was continued 3 hr. longer at 50°. The solution was left overnight at room temperature and then distilled. About 47 g. of crude liquid distilled from 70° at 1.5 mm. to 90° at 0.8 mm. This was redistilled, yielding 26 g. (23%) pale yellow liquid XVb, b.p. 84–85° at 3.5 mm., having a refractive index (n_D^{27}) of 1.5302 and a density (d_4^{27}) of 1.164.

Anal. Calcd. for $C_9H_{10}Cl_2$: C, 57.2; H, 5.3; S, absent. Found: C, 57.5; H, 5.3; S, absent.

Further distillation of the reaction mixture produced an additional 48.2 g. of distillate before slow decomposition of the residual tar ended the distillation. Redistilling this produced 29.5 g. (19%) of pale yellow liquid XIVb, b.p. 133–136° at 0.6 mm., having a refractive index (n_4^{25}) of 1.5550 and a density (d_4^{25}) of 1.4215.

Anal. Calcd. for $C_9H_{10}Cl_2O_2S$: C, 42.8; H, 3.98; S, present. Found: C, 43.2; H, 3.87; S, present.

3,5,6-Trichlorothianaphthene 1,1-dioxide (XVI), *2,3,7,8-tetrachlorodibenzothiophene 5,5-dioxide* (XVII), and *3,3a,6,6a-tetrachloro-3a,3b,6a,6b-tetrahydrocyclobuta[1,2-b,3,4-b′]dithiophene 1,1,4,4-tetroxide* (XIXb). A solution of 25.8 g. (0.1 mole) of IV in 150 ml. of xylene was stirred and cooled for 2 hr. to keep it below 30° while about 7 g. (0.4 mole; 100% excess) of anhydrous ammonia was bubbled through the solution to convert IV to V. The resulting suspension was heated at reflux temperature, with continued stirring, for 1 hr. The ammonium chloride was filtered from the hot solution and rinsed with hot benzene. The crude ammonium chloride was found to contain a small amount of water-insoluble solid; this was recrystallized from chloroform, producing colorless needle-shaped crystals of XVII, m.p. 380°.

Anal. Calcd. for $C_{12}H_4Cl_4O_2S$: Cl, 40.0; S, 9.1. Found: Cl, 39.7; S, 9.1.

Chilling the xylene filtrate overnight at −20° caused 2.3 g. (12%) of XIXb, m.p. 227–231°, to crystallize. One recrystallization from methanol, with a Nuchar treatment, afforded pure XIXb, m.p. 231.5–232°.

Anal. Calcd. for $C_8H_4Cl_4S_2$: C, 26.0; H, 1.1; Cl, 38.3; mol. wt., 370. Found: C, 26.1; H, 1.4; Cl, 38.2; mol. wt. (*via* Rast method in camphor), 236 and 414.

Evaporating the filtrate produced 6.6 g. (49%) of crystalline XVI, m.p. 167–171°, after recrystallization from isopropanol. Two recrystallizations from methanol, with decolorizing carbon treatments, produced pure XVI, m.p. 170–171°.

Anal. Calcd. for $C_8H_3Cl_3O_2S$: C, 35.7; H, 1.1; Cl, 39.5. Found: C, 35.7; H, 1.5; Cl, 39.4.

Improved preparation of 2,3,7,8-tetrachlorobenzothiophene 5,5-dioxide (XVII). A solution of 22.6 g. (0.084 mole) of XVI in 400 ml. of 1,2,4-trichlorobenzene was stirred and heated at 200–215° for 2 hr. while a solution of 32.2 g. (0.174 mole) of V in 240 ml. of chloroform was added dropwise. Chloroform was allowed to distill during the addition. The resulting solution was refluxed for an hour, then the solvent was distilled under reduced pressure until a solid began to form; about 150 ml. of material remained. Triturating this residue with 150 ml. of petroleum ether (b.p. 35–60°) and filtering produced 15.6 g. of brown solid. An additional 4 g. of similar appearing solid was obtained from the filtrate. This 19.6 g. of crude solid was recrystallized twice from benzene and then twice from chloroform, yielding a first crop of 9.4 g. (23%) of fine colorless needle-shaped crystals of XVII, m.p. 380–381°.

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PAINESVILLE, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MAINE]

The Anhydrous Chlorination of Some Mercapto Acids and Analogous Disulfides[1,2,3]

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o-Thiolbenzoic acid, *m,m′*-dithiodibenzoic acid, 3-thiolpropanoic acid, and 4,4′-dithiodibutanoic acid react with anhydrous chlorine to form chlorosulfinylacyl chlorides of the type ClS(O)—R—COCl by a process which is believed to involve the intramolecular solvolysis of an intermediate organosulfur trichloride.

Investigations carried out in this laboratory have shown that certain bivalent sulfur compounds can be converted by the action of anhydrous chlorine at low temperatures to the corresponding alkylsulfur trichlorides.[5] The latter compounds upon controlled solvolysis with water, alcohols, or carboxylic acids yield sulfinyl chlorides.[6] In view of these reactions, it appeared possible that compounds containing both sulfhydryl (or disulfido) and carboxyl groups within their molecular structures might form sulfur trichlorides which would undergo intramolecular solvolysis to form com-

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