reflux for 2 hr. It was then cooled, poured onto 1000 g. of ice, and extracted three times with a total of 200 ml. of pentane. The pentane solution was washed with water and dried over magnesium sulfate. The pentane was removed by distillation through a 30-cm. column packed with glass helices and the residue was analyzed by gas–liquid chromatography using a silicone oil on Chromosorb-P column. The retention time of the main peak (small solvent peaks were present also) was identical with that of an authentic norbornane sample. The infrared spectrum of a collected sample of the main peak was identical with the spectrum of norbornane.

Treatment of Compound I with Silver Nitrate.—A solution of compound XVI in saturated ethanolic silver nitrate was sealed in a test tube and heated at 100° for 30 hr. A shiny film formed on the walls of the tube dissolved completely on addition of 1:1 nitric acid and no nitric acid-insoluble material was formed in the reaction.

Acknowledgment.—The authors wish to thank the National Science Foundation for support of this research.

Reactions of Enol Ethers with Carbenes. III.[1] Vinyl Sulfides and Δ^3-Dihydrothiapyran[2]

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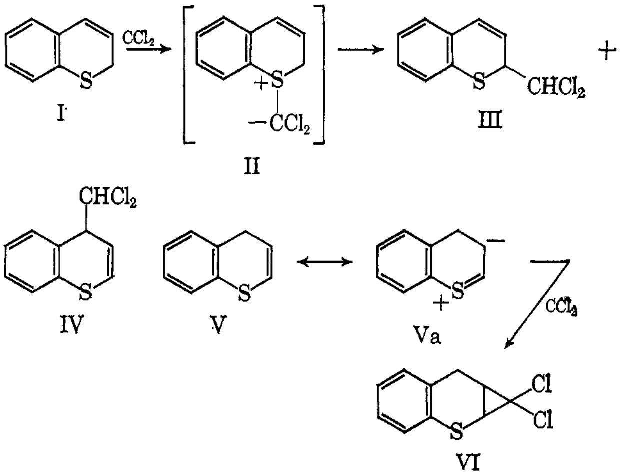
Received December 16, 1963

The reactions of cyclic and noncyclic vinyl sulfides with ethyl trichloroacetate and sodium methoxide lead to the formation of cyclopropanes in high yields (60–77%). The reaction of cyclic allyl sulfides with these reagents leads to the formation of unsaturated insertion products.

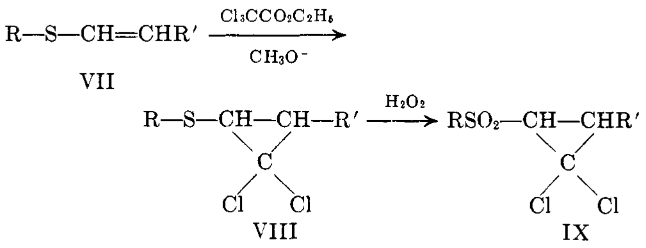
In a previous study[5] we observed that the reaction of 2H-1-benzothiapyran (I) with dichlorocarbene[6] produced the insertion products III and IV, while reaction of the isomeric 4H-1-benzothiapyran (V), under identical conditions, produced only the cyclopropane VI.



The remarkable difference in behavior of these two isomeric olefins was attributed to the difference in nucleophilic character of the two double bonds (*i.e.*, V ↔ Va) relative to sulfur, and it was suggested that the reaction with I may involve the "ylid" intermediate II. Evidence was cited to indicate the carbanion derived directly from I or V was not an intermediate in either reaction.

In order to learn more about the generality and mechanism of these interesting transformations, an investigation of the reaction of saturated sulfides, and the reaction of α,β-, β,γ-, and γ,δ-unsaturated sulfides, with dichlorocarbene precursors was undertaken. This paper describes our preliminary findings with vinyl sulfides and the isomeric Δ^2- and Δ^3-dihydrothiapyrans.

The reactions of the α,β-unsaturated sulfides VIIa–d (1 mole) with ethyl trichloroacetate (1.1–1.6 moles) and sodium methoxide (1.3–2.0 moles) was carried out in olefin-free petroleum ether (b.p. 30–60°) using conditions previously described for other olefins.[6] In each case high yields of the corresponding cyclopropanes VIII (60–77%) were obtained.[7] The dichlorocyclopropanes were characterized by their composition and spectra (infrared, ultraviolet, and n.m.r., see Experimental), and by conversion to the corresponding sulfones IX. The olefins VIIb–d were mixtures of *cis* and *trans* isomers, prepared by isomerization[8] of the corresponding allyl sulfides; the corresponding cyclopropanes VIIIb–d were, as expected, mixtures of *cis* and *trans* isomers (by n.m.r. and v.p.c.).



$$\underset{\text{VII}}{R{-}S{-}CH{=}CHR'} \xrightarrow[CH_3O^-]{Cl_3CCO_2C_2H_5} \underset{\text{VIII}}{R{-}S{-}\underset{CCl_2}{CH{-}CH}{-}R'} \xrightarrow{H_2O_2} \underset{\text{IX}}{RSO_2{-}\underset{CCl_2}{CH{-}CHR'}}$$

VIIa, R = C_6H_5; R′ = H
b, R = C_6H_5; R′ = CH_3, *cis–trans*
c, R = n-C_4H_9; R′ = CH_3, *cis–trans*
d, R = t-C_4H_9; R′ = CH_3, *cis–trans*

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[1] For the proceeding article in this series, see W. E. Parham and M. O. Bhasvar, *J. Org. Chem.*, **29**, 1575 (1964).

[2] Supported in part by a grant (No. GP 159) from the National Science Foundation.

[3] In part from the Master's Thesis of L. Christensen, University of Minnesota, 1962.

[4] In part from the dissertation of S. H. Groen, University of Groningen, The Netherlands. O.E.C.D. Postgraduate Travel Grant awarded by Netherlands Organization for the Advancement of Pure Research (Z.W.O.).

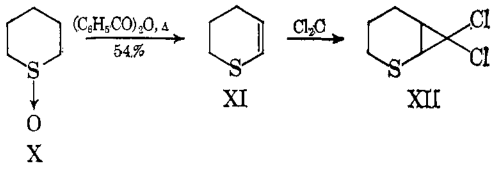
[5] W. E. Parham and R. Koncos, *J. Am. Chem. Soc.*, **83**, 4034 (1961).

[6] The reaction was carried out with ethyl trichloroacetate and sodium methoxide and is assumed to involve formation of trichloromethyl anion, dichlorocarbene, and methyl ethyl carbonate. *Cf.* W. E. Parham and E. Schweizer, *J. Org. Chem.*, **24**, 1733 (1959).

[7] Subsequent to the completion of our work E. P. Prilezhaeva, N. P. Petukhova, and M. F. Shostakovskii [*Dokl. Akad. Nauk SSSR*, **144**, 1059 (1962); *Chem. Abstr.*, **57**, 13,632 (1962)] described the preparation of the 1,1-dichlorocyclopropanes from ethyl vinyl sulfide and phenyl vinyl sulfide in 40 and 25.9% yield, respectively, by reaction with chloroform and potassium t-butylate. These authors also describe the sulfoxide and sulfone derivatives of the cyclopropyl adducts.

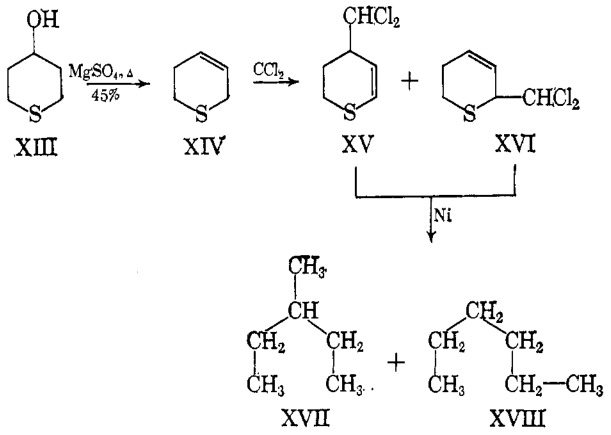
[8] D. S. Tarbell and M. A. McCall, *J. Am. Chem. Soc.*, **74**, 48 (1952).

A study of the reactions of the isomeric olefins Δ^2-dihydrothiapyran (XI) and Δ^3-dihydrothiapyran (XIV) with dichlorocarbene was of particular interest in view of the structural relationship of these olefins with the benzthiapyrans I and V. Δ^2-Dihydrothiapyran (XI) had previously been prepared by reaction of hydrogen sulfide with dihydropyran over activated alumina at 425°.[9] In our hands this procedure gave a product in variable yields and of questionable purity. A product of higher purity and stability was prepared from tetrahydrothiapyran 1-oxide (X) as shown in the accompanying equation. The usual procedure of using



acetic anhydride in the Pummerer reaction[1,10] gave unsatisfactory results since the product was contaminated with acetic anhydride and acetic acid, and was more difficult to purify; use of benzoic anhydride proved to be preferable for preparation of this olefin. The olefin reacted readily with ethyl trichloroacetate and sodium methoxide to give the expected 7,7-dichloro-2-thia[4.1.0]heptane (XII) in 70% yield. There was no evidence for the formation of unsaturated insertion products.

Δ^3-Dihydrothiapyran (XIV) was prepared from tetrahydrothiapyran-4-ol (XIII), and the infrared, ultraviolet, and nuclear magnetic resonance spectra



of this product were all consistent with the assigned structure. Reaction of the olefin XIV with ethyl trichloroacetate and sodium methoxide gave an unstable oil which showed considerable unsaturation. A distilled sample of the product had composition in close agreement with that calculated for the insertion products XV and/or XVI, and spectral data (see Experimental) suggested that the product was a mixture of XV and XVI. While their instability precluded separation of XV and XVI, further evidence relative to the composition of the mixture was obtained by desulfurization with Raney nickel. The reaction was effected in alcohol solvent, and the volatile hydrocarbons were analyzed by vapor phase chromatography. 3-Methylpentane and n-hexane were found in approximately equal amounts, data consistent for the presence of both XV and XVI. A third component (one-fourth the intensity of n-hexane) was also present. The latter material was not identified; however, it was shown not to be 2-methylpentane.

It can be concluded, therefore, that the reaction of ethyl trichloroacetate and sodium methoxide with α,β-unsaturated sulfides leads generally to the corresponding 1,1-dichlorocyclopropanes, while reactions involving cyclic β,γ-unsaturated sulfides leads to insertion products.

Experimental

Vinyl Sulfides (VIIa–d).—Phenyl vinyl sulfide (VIIa, b.p. 84–86° at 12 mm., n^{20}D 1.5882, 74% yield; lit.[11] 83.7%, b.p. 94–97° at 25 mm.) was prepared as previously described[11] from β-chloroethyl phenyl sulfide; $\lambda_{\max}^{95\%\ \mathrm{alc}}$ 247 mμ (ϵ 8020), 264 mμ (ϵ 7740). *cis,trans*-**Phenyl propenyl sulfide** (VIIb, b.p. 48–51° at 0.5 mm., n^{20}D 1.5870, 79% yield; lit.[8] b.p. 61–69° at 1.3 mm., n^{20}D 1.5860, 95%) was prepared as previously described[8]; $\lambda_{\max}^{95\%\ \mathrm{alc}}$ 248 mμ (ϵ 10,180), 264.5 mμ (ϵ 10,800). *cis,trans-n*-**Butyl propenyl sulfide** (VIIc, 72% yield, b.p. 78.5–79.5° at 26 mm., n^{25}D 1.4742) was prepared by a procedure similar to that described[12] for the preparation of *t*-butyl propenyl sulfide. The vinyl sulfide VIIc showed $\lambda_{\max}^{95\%\ \mathrm{alc}}$ 225 mμ (ϵ 6340), 244 mμ (shoulder) (ϵ 3480); ν^{neat} C═C (1610 cm.$^{-1}$), *trans* CH═CH- (940 cm.$^{-1}$); n.m.r. spectrum[13] (20% in CCl_4): —CH═ (multiplet between 279–338 c.p.s., weight 2.0), S–CH_2 (multiplet, 133–154 c.p.s., weight 1.9), ═C—CH_3 and —CH_2— (complex 68–103 c.p.s., weight 6.9), CH_3—CH_2— (multiplet, 45–85 c.p.s., weight 3.1).

Anal. Calcd. for $C_7H_{14}S$: C, 64.54; H, 10.83. Found: C, 64.30; H, 10.95.

cis- **and** *trans-t*-**butyl propenyl sulfide** (VIId, 23% yield, n^{27}D 1.4647, b.p. 140–142°; lit.[12] 66% yield, b.p. 139.1–140.8, n^{20}D 1.4700) was prepared as previously described[12] and showed $\lambda_{\max}^{95\%\ \mathrm{alc}}$ 249 mμ (ϵ 3260), 226 mμ (ϵ 3390); ν^{neat} C═C (1610 cm.$^{-1}$), *trans* —CH═CH— (940 cm.$^{-1}$); n.m.r. spectrum[13] (20% in CCl_4): —CH═ (multiplet, 299–347 c.p.s., weight 2.0), *cis* and *trans* —CH_3 (multiplet, 85–96 c.p.s., weight 3.1), *cis* and *trans* $(CH_3)_3C$— (two nearly superimposed singlets, 66 and 68 c.p.s., weight ~9).

1,1-Dichlorocyclopropanes VIIIa–d. 1,1-Dichloro-2-phenylmercaptocyclopropane (VIIIa).—A 500-ml. flask was equipped with a nitrogen-inlet tube and a condenser equipped with a calcium chloride tube. Dry methanol (150 ml.) was added to the flask and sodium (6.5 g., 0.28 g.-atom) was added in small pieces. Nitrogen gas was admitted to the flask during the entire course of the reaction. When the sodium had dissolved, the excess methanol was removed from the stirred solution, and the residual solid was heated at 100° (12 mm.) for 30 min. Dry thiophene-free benzene (100 ml.) was added to the solid, and most of the benzene was evaporated. Olefin-free petroleum ether (200 ml., b.p. 30–60°) and phenyl vinyl sulfide (Ia, 29.5 g., 0.217 mole) were added; the resulting mixture was cooled in an ice bath and ethyl trichloroacetate (46.0 g., 0.240 mole) was added dropwise over a 30-min. period. The mixture was stirred under a nitrogen atmosphere for 6 hr. at ice-bath temperature, and then was allowed to warm to room temperature overnight. Water (80 ml.) was added to the reaction mixture, the organic layer was separated, and the aqueous phase was extracted with petroleum ether (50 ml., b.p. 30–60°). The combined organic extracts were dried ($MgSO_4$) and concentrated in a rotatory evaporator. Distillation of the residue through a 3-in. Vigreux column gave (a) recovered Ia, 3.0 g., and (b) the cyclopropane VIIIa, 29.0 g. (61% yield, b.p. 95–99° at 1 mm., n^{20}D 1.5905).

A sample of VIIIa was redistilled (b.p. 86–87° at 0.4 mm., n^{20}D 1.5915, m.p. 24–24.5°) for analysis; $\lambda_{\max}^{95\%\ \mathrm{alc}}$ 240 mμ (ϵ 7640),

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[9] (a) R. F. Naylor, *J. Chem. Soc.*, 2749 (1949); (b) Yu K. Yur'ev, T. B Dubrovina, and E. P. Tregribov, *J. Gen. Chem. USSR* (Engl. Trans.), **16,** 843 (1946); *Chem. Abstr.*, **41,** 1654 (1947).

[10] W. E. Parham and M. D. Bhavsar, *J. Org. Chem.*, **28,** 2686 (1963).

[11] F. Montanari, *Boll. sci. fac. chim. ind. Bologna*, **14,** 55 (1956); *Chem. Abstr.*, **51,** 5723 (1957).

[12] D. S. Tarbell and W. E. Lovett, *J. Am. Chem. Soc.*, **78,** 2259 (1956).

[13] The n.m.r. spectra were determined on a Varian V 4302 at 56.44 Mc. (reference, tetramethylsilane). Weights are estimates obtained by using a planimeter.

250 mμ (ϵ 7300); n.m.r. spectrum[14] (pure liquid): aromatic H (multiplet, 419–445 c.p.s., weight 5), —S—CH (quartet, 157, 164, 167, and 174 c.p.s., weight 1.0), (*cis*)H—C—H(*trans*) [(part of an ABX system in which second-order effects are apparent in intensities), H (*cis*) (quartet, 94, 101, 104, and 111 c.p.s., weight 1), H (*trans*) (triplet, 68, 76, and 83 c.p.s., weight 1), J (*gem*) = J (*trans*) = 7.3 c.p.s., J (*cis*) = 10.1 c.p.s.].[15]

Anal. Calcd. for $C_9H_8Cl_2S$: C, 49.33; H, 3.68; Cl, 32.36; S, 14.63. Found: C, 49.21; H, 3.71; Cl, 32.26; S, 14.75.

cis- **and** *trans-***1,1-Dichloro-2-phenylmercapto-3-methylcyclopropane (VIIIb)**.—The reaction was carried out as described for VIIIa using sodium (3.0 g., 0.13 g.-atom), phenyl propenyl sulfide (13.0 g., 0.087 mole), ethyl trichloroacetate (23.0 g., 0.120 mole), and olefin-free petroleum ether (100 ml., b.p. 30–60°). The yield of VIIIb (b.p. 95–105° at 0.6 mm., n^{20}_{D} 1.5844) was 15.5 g. (77%). The sample was redistilled for analysis; b.p. 90–91.5° (0.3 mm.); n^{20}_{D} 1.5852 (12.0 g., 59% yield); $\lambda_{\max}^{95\%\text{ alc}}$ 240 mμ (ϵ 8030), 251 mμ (ϵ 8270); n.m.r. spectrum[14] (pure liquid) of *cis-* and *trans-*VIIIb: aromatic H (multiplet, 417–440 c.p.s., weight 5), —S—CH (doublet, 173 and 163 c.p.s., J (*cis*) = 10 c.p.s., and doublet, 135 and 142 c.p.s., J (*trans*) = 7.0 c.p.s., combined weight 1), C*H*CH$_3$ (multiplet, 77–127 c.p.s., weight 1), CHC*H*$_3$ [doublets (?), 63, 65, 69, 71 c.p.s., weight 2.8]; v.p.c. of *cis–trans-*VIIIb: one peak with shoulder (8.9% Reoplex on Chromosorb 60–80 M at 200°).

Anal. Calcd. for $C_{10}H_{10}Cl_2S$: C, 51.51; H, 4.32; Cl, 30.42; S, 13.75. Found: C, 51.45; H, 4.40; Cl, 30.10; S, 13.75.

1,1-Dichloro-2-*n*-butylmercapto-3-methylcyclopropane (VIIIc).—The procedure was essentially that described for VIIIa except commercial sodium methoxide was employed. From *n*-butyl propenyl sulfide (10.0 g., 0.077 mole), ethyl trichloroacetate (19.1 g., 0.100 mole), sodium methoxide (7.0 g., 0.13 mole, weighed in a drybox), and petroleum ether (100 ml.) there was obtained 9.8 g. (60% yield) of VIIIc (b.p. 74–76° at 1.6 mm., n^{25}_{D} 1.4967); $\lambda_{\text{sh}}^{95\%\text{ alc}}$ 226 mμ (ϵ 260). The n.m.r. spectrum[13] of *cis-* and *trans-*VIIIc (20% in CCl_4) showed no absorption above 162 c.p.s. (no unsaturation).

Anal. Calcd. for $C_8H_{14}Cl_2S$: C, 45.07; H, 6.62. Found: C, 44.79; H, 6.67.

1,1-Dichloro-2-*t*-butylmercapto-3-methylcyclopropane (VIIId).—The reaction of *t*-butyl propenyl sulfide (6.0 g., 0.046 mole), ethyl trichloroacetate (14.0 g., 0.073 mole); commercial sodium methoxide (5.0 g., 0.093 mole) and petroleum ether (50 ml.) was carried out as described for VIIIc, and gave 6.5 g. (66% yield) of VIIId (b.p. 62–67° at 1.5 mm., n^{26}_{D} 1.4943). A sample was redistilled (b.p. 56–57° at 1.0 mm., n^{26}_{D} 1.4935) for analysis; $\lambda_{\text{sh}}^{95\%\text{ alc}}$ 225 mμ (ϵ 440); n.m.r. spectrum[13] (20% in CCl_4) showed no peaks above 152 c.p.s. (no unsaturation).

Anal. Calcd. for $C_8H_{14}Cl_2S$: C, 45.07; H, 6.62. Found: C, 44.87; H, 6.40.

Preparation of the Sulfones IXa–d. 1,1-Dichloro-2-phenylsulfonylcyclopropane (IXa).—A stirred mixture of sulfide VIIIa (3.0 g., 0.014 mole), acetic acid (20 ml.), and hydrogen peroxide (6 ml., 30%) was heated at 100° for 3 hr. The mixture was cooled and water (100 ml.) was added. The solid obtained (3.3 g., 94% yield) melted at 87–88° when crystallized from water–ethanol.

Anal. Calcd. for $C_9H_8Cl_2O_2S$: C, 43.04; H, 3.21. Found: C, 43.04; H, 3.29.

cis- **and** *trans-***1,1-Dichloro-2-phenylsulfonyl-3-methylcyclopropane (IXb)**.—The procedure used for oxidation of VIIIb was essentially that described for IXa. The oil obtained subsequent to addition of water was extracted with ether and the ether extract was washed with saturated sodium carbonate and finally with water. The oily mixture of *cis-* and *trans-*IXa (3.2 g., 92% yield) obtained from the dried ether was crystallized by cooling (−70°) a solution prepared by dissolving the mixture in ethanol (two parts)–petroleum ether (one part). The mixture melted at 67–77°.

Anal. Calcd. for $C_{10}H_{10}Cl_2O_2S$: C, 45.29; H, 3.80. Found: C, 45.10; H, 4.01.

cis- **and** *trans-***1,1-Dichloro-2-*n*-butylsulfonyl-3-methylcyclopropane (IXc)**.—*cis,trans*-Sulfone IXc was obtained from VIIIc as an oil (2.4 g., 83% yield). The infrared spectrum of the crude product was essentially identical with that of a sample obtained by redistillation (1.4 g., 46% yield, n^{26}_{D} 1.4930, b.p. 81–82.5° at 0.05 mm.).

Anal. Calcd. for $C_8H_{14}Cl_2O_2S$: C, 39.19; H, 5.75. Found: C, 39.04; H, 5.76.

cis- **and** *trans-***1,1-Dichloro-2-*t*-butylsulfonyl-3-methylcyclopropane (IXd)**.—The product was obtained as a solid, 94% yield, m.p. 106–112° (from ethanol).

Anal. Calcd. for $C_8H_{14}Cl_2O_2S$: C, 39.19; H, 5.75. Found: C, 39.29; H, 5.82.

The sample used for analysis (m.p. 106–112°) was recrystallized three times from ethanol; the melting point was raised to 134–137°.

Anal. Found: C, 39.19; H, 5.72.

Δ^2-Dihydrothiapyran (XI).—A mixture of tetrahydrothiapyran 1-oxide (52.7 g., 0.45 mole), prepared in 92% yield by oxidation of tetrahydrothiapyran with 30% hydrogen peroxide in absence of solvent,[16] and benzoic anhydride (117 g., 0.52 mole) in dry benzene (75 ml.) was heated at the reflux temperature for 14 hr. The benzene was removed by distillation at atmospheric pressure using an oil-bath temperature of 100–110°. When all of the benzene had been removed, the pressure was reduced, and the product XI was distilled rapidly at 66–69° (55–60 mm.). The product was redistilled through a small spiral wire column to give pure Δ^2-dihydrothiapyran (24.5 g., 54% yield, b.p. 66° at 57 mm., n^{25}_{D} 1.5363; lit.[9b] b.p. 143.6–144.2°, n^{20}_{D} 1.5328); $\lambda_{\max}^{95\%\text{ alc}}$ 229 mμ (ϵ 5420), 249 mμ (ϵ 2810); ν^{neat} C=C (1604 cm.$^{-1}$).

Anal. Calcd. for C_5H_8S: C, 59.95; H, 8.05. Found: 59.93; H, 8.35.

Tetrahydrothiapyran-4-one.—Several procedures and combinations of procedures previously described[17] were employed; however, yields were inconsistent and varied from 0–39%. Methyl thiodipropionate[18] (103 g., 0.50 mole) was added dropwise over a period of 1 hr. to a cold (0–5°) stirred (magnetic) suspension of fresh commercial sodium methoxide (60 g., 1.11 mole, weighed in a drybox) in dry ether (400 ml.). The mixture was kept cold for 6–8 hr. and then allowed to stir at room temperature for 20–22 hr. Sulfuric acid (15%, 1 l.) was then added, the ether was distilled, and the resulting mixture was heated with stirring at the reflux temperature for 12 hr. The mixture was cooled and extracted with three 300-ml. portions of ether. The ether was washed free of acid with strong aqueous bicarbonate, and the ether extract was dried ($MgSO_4$) and concentrated. The yellow oil crystallized when cooled and was recrystallized from ether–petroleum ether (b.p. 30–60°) to give the ketone as a white solid (23 g., 39%, m.p. 62–65°, lit.[17b] m.p. 64–66°).

Tetrahydrothiapyran-4-ol (XIII).—Tetrahydrothiapyran-4-one (24.0 g., 0.21 mole) was reduced with sodium borohydride (4.0 g., 0.11 mole) in 95% ethanol (100 ml.). The hydride was added at room temperature over a 2-hr. period, and the resulting mixture was heated at reflux for 4 hr. The cooled mixture was neutralized (litmus) with dilute hydrochloric acid, and the resulting mixture was dried (K_2CO_3) and distilled. Tetrahydrothiapyran-4-ol (XIII, 18 g., 73% yield, b.p. 72° at 1 mm.; lit.[19] b.p. 84–85° at 1.8 mm., m.p. 49°) was obtained as a liquid which solidified in the receiver.

Δ^3-Dihydrothiapyran (XIV).—Crushed tetrahydrothiapyran-4-ol (10.0 g., 0.085 mole) and anhydrous magnesium sulfate (100 g., 0.84 mole) were heated in a nitrogen atmosphere at 200° for 4 hr. in a flask equipped with a condenser. The olefin, containing some water, was distilled from the magnesium sulfate. The olefin from three runs was dissolved in ether, dried with magnesium sulfate, and distilled. Δ^3-Dihydrothiapyran (11.5 g., 45% yield) was obtained as a clear liquid (b.p. 75° at 58 mm., $n^{24.5}_{D}$ 1.5305; lit.[9a] b.p. 35–36° at 12 mm., n^{20}_{D} 1.5328); $\lambda^{95\%\text{ alc}}$ no absorption above 220 mμ; ν^{neat} C=C (1652 cm.$^{-1}$).

Anal. Calcd. for C_5H_8S: C, 59.95; H, 8.05. Found: C, 59.92; H, 8.16.

7,7-Dichloro-2-thiabicyclo[4.1.0]heptane (XII).—The reaction of Δ^2-dihydrothiapyran (XI, 12.86 g., 0.13 mole), ethyl trichloroacetate (47.69 g., 0.25 mole), and commercial sodium methoxide (14.0 g., 0.26 mole) in olefin-free petroleum ether was carried out as described for the other vinyl sulfides. 7,7-Dichloro-2-thia-

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[14] Taken on a Varian A60 at 60 Mc. (reference, tetramethylsilane). Weights were obtained by use of an integrator.

[15] Compare T. D. Graham and M. T. Rogers, *J. Am. Chem. Soc.*, **84**, 2249 (1962).

[16] D. S. Tarbell and C. Weaver, *ibid.*, **63**, 2939 (1941).

[17] (a) C. Barkenbus, V. C. Midkiff, and R. M. Newman, *J. Org. Chem.*, **16**, 232 (1951); (b) C. M. Bennett and L. V. D. Scorah, *J. Chem. Soc.*, 199 (1927).

[18] L. L. Gershbein and C. D. Hurd, *J. Am. Chem. Soc.*, **69**, 241 (1947).

[19] M. Protiva and E. Adlerova, *Chimia* (Aarau), **12**, 145 (1958).

bicyclo[4.1.0]heptane (XII, 16.35 g., 70% yield, b.p. 71° at 0.75 mm., n^{25}_D 1.5604) was distilled through a spiral-wire column.

The infrared and n.m.r. spectrum of XII were consistent with the assigned structure and showed absence of any unsaturation (no insertion detected).

Anal. Calcd. for $C_6H_8Cl_2S$: C, 39.36; H, 4.40. Found: C, 39.53; H, 4.76.

Reaction of Δ^3-Dihydrothiapyran (XIV) with Dichlorocarbene.—The reaction of XIV (6.64 g., 0.066 mole) with ethyl trichloroacetate (25.24 g., 0.13 mole) and commercial sodium methoxide (7.5 g., 0.14 mole) was carried out by a procedure identical with that employed with XI. The product was distilled rapidly (b.p. 65–110° at 0.25 mm., 4.3 g., 35% calcd. as XV or XVI) without use of a fractionating column. The black tarry residue was not further processed. The distillate was fractionated through a spiral-wire column to give (a) 1.0 g., b.p. 52–64° (0.4 mm.), n^{25}_D 1.5717, yellow oil which rapidly turned brown; (b) 1.87 g., clear, b.p. 64–68° (0.4 mm.), n^{25}_D 1.5700; and (c) 1.28 g., mostly hold up in column, n^{25}_D 1.5899. The infrared spectra of all of these fractions showed the presence of considerable unsaturation in the 1608–1680-cm.$^{-1}$ region.

Fraction b showed $\lambda_{\max}^{95\%\ \text{alc}}$ 233 mμ (ϵ 4970), 248 mμ (ϵ 4330); ν^{neat} C=C (1608 s and 1665 w cm.$^{-1}$); n.m.r. spectrum[13]: strong broad absorption in the region τ 3.6–4.6 (317–362 c.p.s.), consistent with the unsaturated insertion products XV and XVI.

Anal. Calcd. for $C_6H_8Cl_2S$: C, 39.36; H, 4.40. Found: C, 39.62; H, 4.37.

Desulfurization Reactions. A. XV and XVI.—The mixture of XV and XVI (1.4 g., fraction b, above) in 75% ethanol–water (100 ml.) and Raney nickel (about 6 g.)[5] was heated at the reflux temperature for 1.5 hr. Water (25 ml.) was added, and the resulting mixture was distilled. The distillate was diluted with water and then was extracted with ether (5 ml.).

Vapor phase chromatography of the ether extract using a diisodecyl phthalate column (set at 55°, carrier gas helium, flow 15 p.s.i.) showed the presence of three components in addition to solvents. Two of the compounds were identified as n-hexane and 3-methylpentane (approximately equal amounts). The other product (approximately 0.25 peak intensity of n-hexane) was not identified; however, it was shown not to be 2-methylpentane.

B. XII.—Reaction of XII (1.7 g.) with Raney nickel ($\sim$6.0 g.) was carried out as described in A, above. Analysis of the ether solution by v.p.c. (same conditions as above) showed n-hexane and 2-methylpentane to be present in the approximate ratio, 3:1.

Reaction of Enol Ethers with Carbenes. IV.[1] Allyl Sulfides and Saturated Sulfides[2]

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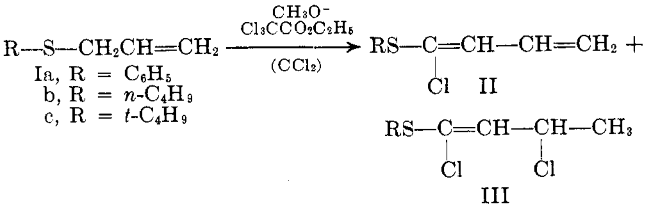
Received December 16, 1964

The reaction of ethyl trichloroacetate and sodium methoxide with noncyclic allyl sulfides leads to the formation of 1-chloro 1-substituted mercaptobutadienes in high yields, together with some olefins derived by addition of hydrogen chloride to the butadienes. The course of these reactions is discussed, and additional data concerning reaction of saturated sulfides with ethyl trichloroacetate and sodium methoxide is presented. It is shown that saturated sulfides inhibit the formation of dichlorocyclopropyl adducts from olefins such as cyclohexene. Evidence is also presented for a minor chlorination process in reactions involving ethyl trichloroacetate and sodium methoxide.

In previous reports we have described evidence which shows that dichlorocarbene, generated from ethyl trichloroacetate and sodium methoxide,[4] reacts with vinyl sulfides to give cyclopropanes,[1] and with cyclic allyl sulfides[1,5] to give insertion products. This paper describes reactions of open-chain allyl sulfides with dichlorocarbene precursors, and presents preliminary data concerning reactions of dichlorocarbene with saturated sulfides.

The reaction of the allyl sulfides (I, 1 mole) with ethyl trichloroacetate (1–1.5 moles) and sodium methoxide (1–2 moles) were carried out at ice-bath temperature, and the reaction mixtures were allowed to warm to room temperature overnight. The allyl sulfides studied were allyl phenyl sulfide (Ia), allyl n-butyl sulfide (Ib), and allyl t-butyl sulfide (Ic); evidence will be presented showing that the principal reaction in each case is properly summarized by the equation I → II + III.



A. Reaction of Allyl Phenyl Sulfide.—The reaction of allyl phenyl sulfide (Ia) with ethyl trichloroacetate and sodium methoxide afforded as a principal product a liquid A (IIa) in 46–60% yield with the empirical formula $C_{10}H_9ClS$. Vapor phase chromatography of this product on Reoplex and on Carbowax columns showed only one peak.

The infrared spectrum of the product showed no alkyl hydrogen, but did show olefinic absorption at 1610, 900–910, 980, and 1835 cm.$^{-1}$ characteristic of the —CH=CH$_2$ grouping. The ultraviolet spectrum of IIa (95% alcohol) showed $\lambda_{\max}$ 244 mμ (ϵ 16,370), (shoulder), 274 mμ (ϵ 8680); the n.m.r. spectrum[6] (neat) was complex but showed =CH$_2$ (complex 282–312 c.p.s., weight 2.0), —CH= (complex 363–405 c.p.s., weight 1.9), and aromatic H (complex 408–430 c.p.s., weight 5.4).

The product gave a colorless polymeric sulfone when treated with hydrogen peroxide in acetone, or with 1 equiv. of perbenzoic acid in benzene or chloroform; however, a solid derivative (m.p. 143–144°, >40%

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(1) For the preceeding article in this series, see W. E. Parham, L. Christensen, S. H. Groen, and R. M. Dodson, *J. Org. Chem.*, **29**, 2211 (1964).

(2) Supported in part by a grant (no. GP-159) from the National Science Foundation, and by a grant from the U. S. Army Research Office (Durham), Contract No. DA-ORD-31-124-61-GB.

(3) From the dissertation of S. H. Groen, the University of Groningen, The Netherlands. O.E.C.D. Postgraduate Travel Grant awarded by the Netherlands Organization for the Advancement of Pure Research (Z.W.O.).

(4) W. E. Parham and E. E. Schweizer, *J. Org. Chem.*, **24**, 1733 (1959).

(5) W. E. Parham and R. Koncos, *J. Am. Chem. Soc.*, **83**, 4034 (1961).

(6) The n.m.r. spectra were taken on Varian A60 at 60 Mc. (reference tetramethylsilane). Weights were obtained by integration.