Methyl *m*-(2-Phenoxyethoxy)-benzoate (XXIII).—Seventy grams (0.461 mole) of methyl *m*-hydroxybenzoate, 100 g. (0.498 mole) of β-phenoxyethyl bromide, 80 g. of potassium carbonate and 350 cc. of dioxane were mixed in a 1-l. three-necked flask and refluxed with stirring for 35.5 hours. An additional 5 g. of β-phenoxyethyl bromide was added after 13 hours of refluxing had elapsed. The solution was chilled and poured slowly and with stirring into 1200 cc. of cold water. The product precipitated as a yellow oil which solidified upon being chilled overnight. The solution was filtered, and the product, with the exception of a small amount which was reserved for purification and analysis, was saponified directly to (XXIV) using an alcohol-aqueous sodium hydroxide mixture. The product (XXIII), after several recrystallizations from absolute methyl alcohol, melted at 69.5–70.5°.

Anal. Calcd. for $C_{16}H_{16}O_4$: C, 70.58; H, 5.92. Found: C, 70.53; H, 6.07.

S-Benzylpseudothiuronium Salts of Polyalkoxybenzoic Acids (Table II).—The polyalkoxybenzoic acids were characterized by the formation of the solid S-benzylpseudothiuronium salts. One gram of S-benzylpseudothiuronium chloride was dissolved in 20 cc. of warm absolute alcohol. An equivalent quantity of the organic acid was dissolved in 50 cc. of warm absolute alcohol, and the alcoholic solution was carefully neutralized with either 0.5% aqueous sodium hydroxide or 0.5% alcoholic sodium hydroxide until just pink to phenolphthalein. In a few cases a small amount of water was added to the boiling alcoholic solution in order to keep the sodium salt in solution. The alcoholic solution of S-benzylpseudothiuronium chloride was then added to the alcoholic sodium salt solution of the acid slowly and with shaking. The solution was chilled and the precipitate was filtered and recrystallized. In a number of cases it was necessary to evaporate the solution either to one-third of its original volume or to dryness in a hood in order to obtain the desired derivative.

Acknowledgment.—One of us (M.B.W.) wishes to express his appreciation to Dr. Robert L. McKee for his helpful suggestions in the preparation of this paper.

CHAPEL HILL, N. C. RECEIVED OCTOBER 29, 1951

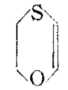
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

Heterocyclic Vinyl Ethers. I. *p*-Oxathiene[1]

BY WILLIAM E. PARHAM, IRVING GORDON AND JEROME D. SWALEN

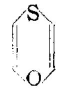
The synthesis of *p*-oxathiene was achieved by the acid-catalyzed dealkoxylation of 2-methyoxy-*p*-oxathiane. Experimental conditions for the dealkoxylation reaction were established by a preliminary study with a series of 2-tetrahydropyranyl ethers using various acidic catalysts. The mode of addition of unsymmetrical reagents to *p*-oxathiene furnishes direct chemical evidence to indicate that oxygen releases electrons more readily in the direction of its covalent bonds than does sulfur. Other properties of *p*-oxathiene are described.

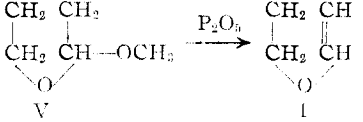
The heterocyclic vinyl ethers I–IV represent an interesting class of compounds in that a knowledge of their properties might furnish valuable information regarding the relative electronic effects of oxygen and sulfur. This paper is concerned with the synthesis and properties of the first member of this series, *p*-oxathiene (I), prepared in 76% yield by slow distillation of 2-methoxy-1,4-oxathiane (V) from a small quantity of phosphorus pentoxide. The acetal V was prepared in 72% yield from monothioglycol and dimethyl chloroacetal by a procedure previously described.[2] Previous attempts to dealkoxylate acetals by this procedure have either resulted in failure, or low yields of products.[3] The choice of catalyst and reaction conditions for the dealkoxylation of V was established by a preliminary study with a series of 2-tetrahydropyranyl ethers (VI) using $ZnCl_2$, P_2O_5, *p*-CH_3–$C_6H_4SO_3H$ and AlCl as catalyst. These experiments are described in the Experimental section of this report. The best results were realized by employing phosphorus pentoxide as a catalyst with acetals whose boiling point was 200° or higher.

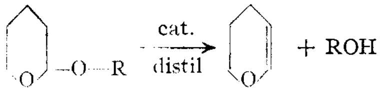

I


II

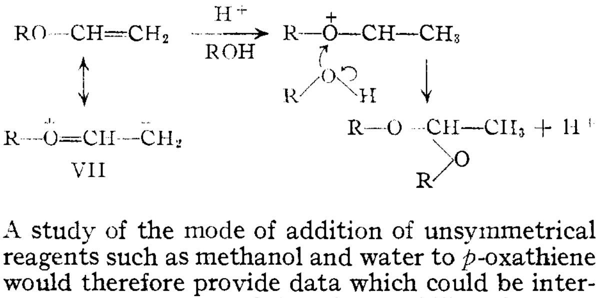

III


IV


V I


VI
R = C_1–C_5

Acid-catalyzed additions to vinyl ethers takes place[4] essentially as shown in the equations



A study of the mode of addition of unsymmetrical reagents such as methanol and water to *p*-oxathiene would therefore provide data which could be interpreted as a measure of the relative ability of oxygen and sulfur to release electrons in the direction of their covalent bonds (structures Ia and Ib).

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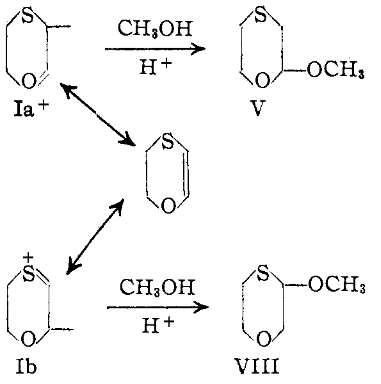
[1] Part of this work was supported by aid received from the research funds of the Graduate School of the University of Minnesota.

[2] W. E. Parham, THIS JOURNAL, **69**, 2449 (1947).

[3] D. B. Killian, G. F. Hennion and J. A. Nieuwland, *ibid.*, **57**, 544 (1935); L. Claisen, *Ber.*, **31**, 1019 (1898).

[4] *Cf.* Hoaglin and Hirsch, THIS JOURNAL, **71**, 3468 (1949), for the mechanism of the acid-catalyzed addition of acetals to vinyl ethers. The β-carbon atom in VII is analogous to the ortho and para positions in anisole.



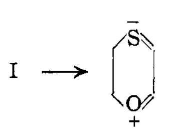
When *p*-oxathiene reacted with cold methanol containing a catalytic quantity of dry hydrogen chloride, the acetal, obtained in 87% yield, was shown to be V by the identity of its boiling point, refractive index and infrared absorption spectrum with those of an authentic sample prepared by the cyclization of 2-(β-hydroxyethylthio)-dimethyl acetal.[2]

Additional evidence regarding the mode of addition to *p*-oxathiene was obtained by a study of the nature of the product obtained upon hydrolysis. The hydrolysis was effected in aqueous ethanol containing hydrochloric acid, and the resulting aldehyde was isolated as a 2,4-dinitrophenylhydrazone. The product, easily purified by recrystallization

$$\text{I} \xrightarrow[\text{RNHNH}_2]{\text{H}_2\text{O, H}^+} \begin{array}{c} \text{HOCH}_2\text{CH}_2\text{S—CH}_2\text{CH=N—NH—R} \\ \text{IX} \\ \text{HS—CH}_2\text{—CH}_3\text{—O—CH}_2\text{—CH=N—NHR.} \\ \text{X} \end{array}$$

from aqueous ethanol, was β-hydroxyethylthioacetaldehyde 2,4-dinitrophenylhydrazone (IX). There was no evidence that the product contained any of the isomeric hydrazone (X) which would have resulted from Ib. These results indicate that oxygen releases electrons more readily in the direction of its covalent bonds than does sulfur—a conclusion arrived at independently by Baddeley[5] by an interpretation of other reactions of sulfur and oxygen compounds which were reported in the literature. These results lend indirect support to the conclusions of Schomaker and Pauling[6] who, on the basis of measurements of dipole moment, proposed that an expansion of the valence shell of sulfur in thiophene occurs. If it is accepted that resonance structures involving a positively charged oxygen atom contribute more to the activated state than structures involving a positively charged sulfur atom, then it can be concluded that resonance of a different type must exist in thiophene to account for the increased resonance energy of thiophene relative to furan. Such an explanation is consistent with the observed sensitivity of furan relative to thiophene to electrophilic reagents.

The ultraviolet spectra of *p*-oxathiene, dihydropyran and dihydrothiopyran were determined. The spectra of dihydropyran and dihydrothiopyran show no absorption maxima above[7] 227 mμ (the limit of our instrument in these determinations), whereas that of *p*-oxathiene shows a distinct maximum at 229 mμ (ϵ = 3820). Assuming a relationship to exist between a bathochromic effect and the contribution of excited resonance forms to the main hybrid form,[8] additional resonance such as that shown in formula XI is indicated for *p*-oxathiene. Resonance of this type may be sufficient to effect considerable stability in molecules such as III and IV and this possibility is under investigation.



XI

Samples of *p*-oxathiene slowly polymerize; the product is colorless and melts over a wide range (200–220°). When I was kept free of all traces of acids or peroxides, it was apparently quite stable; however, addition of boron trifluoride caused immediate polymerization. Attempts to convert *p*-oxathiene to a sulfone were not successful.

Action of 2,4-dinitrobenzenesulfenyl chloride in glacial acetic acid upon *p*-oxathiene resulted in an excellent yield of a crystalline derivative (m.p. 148–149°) which had the composition calculated for 2-acetoxy-3-(2,4-dinitrobenzenesulfenyl)-*p*-oxathiane.

Experimental

2-Alkoxytetrahydropyran (VI).—The acetals in which the R group is methyl, ethyl, *n*-propyl and *n*-butyl have been previously reported.[9] The properties and yields of new acetals are as follows:

2-*n*-Hexoxytetrahydropyran: b.p. 119° (20 mm.), n^{20}_D 1.4401, yield 55%. *Anal.* Calcd. for $C_{11}H_{22}O_2$: C, 70.91; H, 11.91. Found: C, 71.12; H, 12.21.

2-*n*-Octoxytetrahydropyran: b.p. 146° (20 mm.), n^{20}_D 1.4426, yield 73%. *Anal.* Calcd. for $C_{13}H_{26}O_2$: C, 72.83; H, 12.23. Found: C, 72.36; H, 12.23.

2-*n*-Decoxytetrahydropyran: b.p. 175° (20 mm.), n^{20}_D 1.4452, yield 52%. *Anal.* Calcd. for $C_{15}H_{30}O_2$: C, 74.35; H, 12.48. Found: C, 74.14; H, 12.66.

Cleavage of VI to Dihydropyran.—Approximately 0.1 g. of catalyst was added to 20 g. of the acetal and the mixture was distilled slowly at atmospheric pressure, through a 12-inch column packed with glass helices. The cleavage of each acetal was first studied qualitatively by measuring the amount of material distilling below 100°. This fraction contained all of the dihydropyran (b.p. 86°) and, when R was larger than butyl, practically no alcohol. With the lower molecular weight acetals (R = $C_1 - C_3$) little cleavage was observed. The following catalysts were found to be effective: phosphorus pentoxide > *p*-toluenesulfonic acid > zinc chloride.

TABLE I

		Dihydropyran		Alcohol[a]	
VI, R	Catalyst	Yield, %	Boiling range, °C.	Yield, %	Boiling range, °C.
n-C_4H_9–	P_2O_5	42[b]	82–85	33	110–115
n-C_6H_{13}–	P_2O_5	68	80–86	61	150–155
n-C_8H_{17}–	P_2O_5	75	82–85	58	185–190
n-C_4H_9–	TSA	57	80–87	52	110–116
n-C_8H_{17}–	TSA	54	80–87	52	183–187
n-$C_{10}H_{21}$–	TSA	53	80–85	58	100–235

[a] The alcohols were characterized by formation of their phenylurethan derivatives. [b] Considerable unchanged acetal was recovered.

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(5) G. Baddeley, *J. Chem. Soc.*, 663 (1950).

(6) V. Schomaker and L. Pauling, THIS JOURNAL, **61**, 1769 (1939).

(7) One point at 226 mμ indicates that dihydrothiopyran may have a maximum at 227 mμ (ϵ 1927).

(8) K. Bowden, E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 948 (1946).

(9) G. F. Woods and D. N. Kramer, THIS JOURNAL, **69**, 2246 (1947).

The results of a more quantitative study using phosphorus pentoxide and *p*-toluenesulfonic acid as catalysts are summarized in Table I.

2-Methoxy-*p*-oxathiane (V) was prepared by a modification of the procedure previously described.[2] Dimethyl-(2-hydroxyethylthio)-acetal (prepared from 7.5 moles of monothioglycol) was not distilled but treated directly with 105 ml. of methanolic hydrogen chloride. The acidified reaction product was protected from moisture and allowed to stand overnight. The product was then neutralized with anhydrous potassium carbonate. There was obtained 734 g. (72.3%) of V; b.p. 57° (5 mm.) or 85° (20 mm.), $n^{23}\text{D}$ 1.4911.

Anal. Calcd. for $C_5H_{10}O_2S$: C, 44.75; H, 7.51. Found: C, 44.85; H, 7.48.

***p*-Oxathiene** (I).—In a distilling flask fitted with a 5-inch column packed with glass helices was placed 102 g. (0.76 mole) of 2-methoxy-*p*-oxathiane and one gram of P_2O_5. The mixture was heated slowly to 160° and held at this temperature as long as methanol distilled (about five hours). The residue was then distilled at reduced pressure to give 58.6 g. (76%) of *p*-oxathiene, b.p. 54° (20 mm.), $n^{20.7}\text{D}$ 1.5357, and 18.6 g. of unchanged starting material, b.p. 81° (20 mm.).

Anal. Calcd. for C_4H_6OS: C, 47.03; H, 5.92. Found: C, 47.18; H, 6.25.

Reaction of *p*-Oxathiene with Methanol.—A solution of 16.05 g. of *p*-oxathiene in 25 ml. of anhydrous methanol was cooled to 0° and 3 drops of 7 *N* methanolic hydrogen chloride was added. The mixture was allowed to warm to room temperature, and was maintained at this temperature for 20 hours. During this time the reaction mixture was protected from all sources of moisture. The mixture was then heated at the reflux temperature for five minutes, cooled and made alkaline with methanolic sodium methoxide. Distillation of the product gave 18.33 g. (87%) of product boiling at 85° (20 mm.), $n^{23}\text{D}$ 1.4915–1.4910.

This product had an infrared absorption spectrum identical to that shown for V; furthermore, it was easily converted[1] to 2-hydroxyethylthioacetaldehyde 2,4-dinitrophenylhydrazone (m.p. and mixed m.p. with that obtained from V[1] was 74–75°).

The Hydrolysis of *p*-Oxathiene.—A solution containing 0.80 g. (0.0097 mole) of 2,4-dinitrophenylhydrazine, 4 ml. of concd. sulfuric acid, 6 ml. of water and 20 ml. of ethanol was added to a solution containing 1.0 g. (0.0097 mole) of *p*-oxathiene in 41 ml. of ethanol. The resulting solution was allowed to stand for 24 hours, 7 ml. of water was added and the resulting solution was allowed to stand at 0° for 70 hours. The crude hydrazone was filtered, washed with water and allowed to dry (wt. 0.96 g., m.p. 65–71°). An additional 0.19 g. (m.p. 67–71°) was obtained from the filtrate by the addition of 25 ml. of water. The hydrazone was purified by several recrystallizations from ethanol–water, m.p. 74–75°.

An identical experiment using 0.0097 mole of V gave 1.29 g. of crude hydrazone (m.p. 65–71°). The pure hydrazone (m.p. 74–75°) obtained from V did not depress the melting point of the hydrazone obtained from I.

The reaction of I with hydrogen peroxide was carried out in the usual manner using acetone as the solvent. When the reaction mixture was added to ice, no precipitate was formed. The resulting mixture was extracted with methylene chloride, and a small quantity of white solid was obtained from the organic layer. The solid was purified by sublimation (m.p. 91°); however, it did not have the composition calculated for the sulfone or sulfoxide of I. The structure of this product is undetermined.

Anal. Found: C, 48.48; H, 8.21.

The Reaction of I with 2,4-Dinitrobenzenesulfenyl Chloride.—A solution of 1.4 g. (0.006 mole) of the sulfenyl chloride and 1.44 g. (0.014 mole) of I in 30 ml. of glacial acetic acid, was heated for 20 minutes on a steam-bath. The reaction mixture was cooled, poured upon 100 g. of ice and the yellow precipitate was collected. The precipitate turned to a gum which gave orange needles (m.p. 144–148°, 75% yield) from 95% ethanol. The product melted at 148–149° after recrystallization from 95% ethanol.

Anal. Calcd. for $C_{12}H_{12}O_7N_2S_2$: C, 40.00; H, 3.36. Found: C, 40.20; H, 2.91.

MINNEAPOLIS 14, MINN. RECEIVED OCTOBER 19, 1951

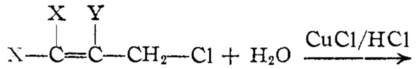
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

Allylic Chlorides. XVI. Copper(I) Chloride Catalyzed Acid Hydrolysis of the 1,3-Dichloropropenes Containing Cl^{36} [1]

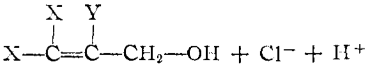
BY LEWIS F. HATCH, LEON O. MORGAN AND VIRGIL L. TWEEDIE[2]

Both *cis*- and *trans*-1,3-dichloropropene containing radioactive chlorine have been prepared and shown to be labeled exclusively in the allylic position. The rate of copper(I) chloride catalyzed acid hydrolysis has been determined with each isomer at 40° and also with the *cis* isomer at 60°. Complete hydrolysis of either isomer gave chloride ion in solution corresponding to 100% removal of one chlorine atom from the 1,3-dichloropropene molecule. From the *trans* isomer approximately 10% of the vinylic chlorine was removed during the reaction; from the *cis* isomer 17% of the vinylic chlorine appeared as chloride ion in solution. A rapid exchange reaction occurred between the labeled allylic chlorine atom and the inactive chloride ion of the hydrolytic medium. It was shown that the vinylic chlorine of the dichloride became partially labeled during the hydrolysis reaction. A reaction mechanism is presented.

In studies concerning the relative reactivities and geometrical configuration of certain allylic chlorides the copper(I) chloride acid hydrolysis has been a useful and interesting reaction.[3] With monochloro compounds unambiguous results were obtained in following the extent of hydrolysis by titration of the chloride ion produced in solution during the course of the reaction.



$$X-\overset{X}{C}=\overset{Y}{C}-CH_2-Cl + H_2O \xrightarrow{CuCl/HCl}$$



$$X-\overset{X}{C}=\overset{Y}{C}-CH_2-OH + Cl^- + H^+$$

However, when the allylic compounds under study contained both allylic and vinylic chlorine atoms (X or Y was chlorine), there arose a question as to the source of chloride ion being titrated.[4] In the present investigation this difficulty has been resolved for the copper(I) chloride acid hydrolysis of the 1,3-dichloropropenes through the use of radioactive chlorine to label the allylic position.

Both *cis*- and *trans*-1,3-dichloropropene containing Cl^{36} in the allylic position ($CHCl{=}CH{-}CH_2Cl^{36}$) were prepared by treatment of the corresponding 3-chloro-2-propen-1-ols with radioactive

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[1] Presented in part at the 118th Meeting of the American Chemical Society, Chicago, Ill., September, 1950.

[2] Research Corporation Fellow 1949–1950.

[3] L. F. Hatch, A. N. Brown and H. P. Bailey, THIS JOURNAL, **72**, 3198 (1950).

[4] L. F. Hatch and S. G. Ballin, *ibid.*, **71**, 1041 (1949).