famyl-*N*-methylacetamide by reaction with potassium cyanate.[4b,28]

4-Methyl-1,2,4,2H-thiadiazine-3,5(4H,6H)-dione-1,1-dioxide by thermal decomposition of the pyridinium salt. Approximately 0.5 g. of the pyridinium salt obtained by the cyclization procedure described previously,[4b] was heated in a sublimation block at 120–125° and 0.2 mm. After several minutes the salt decomposed without charring, releasing a gas. At the end of the decomposition the fused mass solidified and sublimed, leaving no residue. The white sublimate, m.p. 124–134° dec. was sublimed again, yielding analytically pure product, m.p. 130–131.5° dec., which was identical to material obtained in low yield by treatment of a methanolic solution of the pyridinium salt with a cation exchange resin. (In aqueous solution complete hydrolysis of the pyridinium salt to *N*-methylsulfamylacetamide took place during treatment by the ion exchange resin.)

6,6-Dimethyl-1,2,4,2H-thiadiazine-3,5-(4H)-dione-1,1-dioxide. Compound VIb (0.09 g.) was dissolved in 0.2*N* sodium hydroxide solution and allowed to stand for 45 min. The alkaline solution was passed down a column of Dowex-50-X4 resin and the strongly acidic eluant was evaporated under a current of air. The crude material (0.08 g.) melted at 157–165° dec. and showed strong bands at 1695, 3240, 3350, and 3470 cm.$^{-1}$ A weak band at 1740 cm.$^{-1}$ showed the presence of thiadiazine. The ultraviolet spectrum of the crude material in 0.1*N* sodium hydroxide contained a peak at 241 mμ. Vacuum sublimation (120–138° at 0.35 mm.) gave three fractions. The first melted at 152–153° and showed greatly increased absorption at 1740 cm.$^{-1}$ By titration it was shown to contain 28% of Id. The second fraction melted at 153–154° and contained 50% Id. The third fraction melted at 188–190° dec. and showed no peak at 1740 cm.$^{-1}$ Absorption at 1680, 3340, and 3440 cm.$^{-1}$ had increased greatly. This fraction contained no strongly acidic material and its basic solution showed no maximum in the ultraviolet. This fraction apparently consisted of a mixture of the hydrolysis products, Vb and VIb.

pK_a' Measurements. The apparent pK_a values of the sulfonamides and sulfonylureas were determined at 25° by titration, with the aid of a Model G Beckman *p*H meter equipped with calomel and glass electrodes and standardized before use with standard buffer at *p*H 7.00. Two-milliliter aliquots of aqueous stock solutions (ca. $1.6 \times 10^{-2}M$) of the compounds were titrated with 0.1020*N* sodium hydroxide solution. The *p*Ka′ was calculated from the *p*H at approximately 20%, 40%, and 60% neutralization by means of the Henderson equation.[29] The *p*Ka values of the more acidic thiadiazines (Ia–d) were calculated from the *p*H values of solutions of known concentration (about 0.01*M*). The values reported for the thiadiazines and their precursors are the means of at least two determinations. The average deviation $\leqq$ 0.06 *p*K unit, with the exception of Id, for which the a.d. $\sim \pm 0.5$.

For the spectrophotometric determination of pK_a' of Ia and for determination of all other ultraviolet spectra, the following buffers were used: *p*H 1, 0.1*N* hydrochloric acid–potassium chloride; *p*H 5, 0.14*N* acetate; *pH* 8–10, 0.05*M* borate; *p*H 10–11.75 *ca.* 0.05*M* glycine (and sodium hydroxide).

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(28) This synthesis, together with the preparation of both isomeric amide ureides of sulfoacetic acid,[4b] establishes clearly that potassium cyanate attacks the sulfonamide group rather than the carboxamide group under these conditions.

(29) S. Glasstone, *The Electrochemistry of Solutions*, Methuen and Co., Ltd., London, 1930, p. 207.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MICHIGAN STATE UNIVERSITY]

The Preparation and Desulfurization of Some Unsymmetrically Substituted Thiiranes

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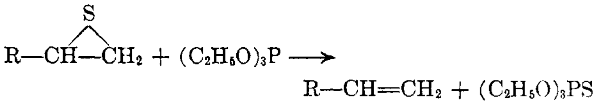
Received July 15, 1960

A number of unsymmetrically substituted thiiranes, 2-alkoxymethylthiiranes, 2-thioalkylmethylthiiranes, and 2-diethylaminoethylthiirane, have been prepared. The reaction of triethyl phosphite with the 2-alkoxymethylthiiranes as well as with several known thiiranes has been investigated and found to result, in all cases, in the desulfurization of the thiirane with the formation of triethyl thionophosphate and an olefinic compound corresponding to the thiirane. Desulfurization of the 2-alkoxymethylthiiranes was also noted in their reactions with phenyllithium, butyllithium and with methyl iodide, yielding again an olefinic compound corresponding to the thiirane.

Recently[2] it was reported, from these laboratories, that heating an equimolar mixture of triethyl phosphite and a thiirane at its reflux temperature, for a short period, results in the formation of triethyl thionophosphate with the simultaneous conversion of the thiirane to its corresponding unsaturated compound.



$$\mathrm{R{-}\overset{S}{CH{-}CH_2} + (C_2H_5O)_3P \longrightarrow R{-}CH{=}CH_2 + (C_2H_5O)_3PS}$$

$R = CH_3, ClCH_2, CH_3OCH_2$

Davis,[3] at the same time, described the formation of cyclohexene and triethyl thionophosphate from the reaction of 2,3-tetramethylenethiirane and triethyl phosphite in ether.

This paper reports on further investigations of this desulfurization reaction with the thiiranes,

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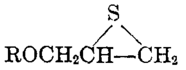
(1) Abstracted in part from the doctoral thesis of R. L. Jacobs.

(2) R. D. Schuetz and R. L. Jacobs, *J. Org. Chem.*, **23**, 1799 (1958).

(3) R. E. Davis, *J. Org. Chem.*, **23**, 1767 (1958).

TABLE I

2-ALKOXYMETHYLTHIIRANES



$ROCH_2\overset{S}{CH—CH_2}$

R	Formula	B.P.	Mm.	n_D^{25}	Yield, %	Carbon, %		Hydrogen, %		Sulfur, %	
						Calcd.	Found	Calcd.	Found	Calcd.	Found
CH_3	C_4H_8OS	60–61	16–17	1.4791	$92.5^{a,d}$; $85.5^{b,d}$	46.15	46.30	7.69	7.94	30.77	30.56
C_2H_5	$C_5H_{10}OS$	50	11	1.4725	90^a; 83^b	50.84	51.05	8.47	8.76	27.12	27.32
n-C_3H_7	$C_6H_{12}OS$	63	11	1.4691	59^a; 90^b	54.54	54.21	9.09	9.01	24.24	23.95
i-C_3H_7	$C_6H_{12}OS$	54	11	1.4651	38^a; 81^b	54.54	54.49	9.09	8.96	24.24	24.07
n-C_4H_9	$C_7H_{14}OS$	80	11	1.4679	40^a; 90^b	56.70	56.90	9.46	9.56	21.70	21.90
C_6H_5	$C_9H_{10}OS$	106	1	1.5735	61^a; 0^c	65.11	65.16	6.07	6.26	19.31	19.33

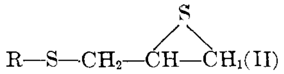
[a] Potassium thiocyanate procedure. [b] Thiourea and acid procedure. [c] Thiouronium salt formed but it failed to hydrolyze. [d] Average yield for two preparations.

2-phenylthiirane, 2,2-diethoxymethylthiirane, and a series of 2-alkoxymethylthiiranes; R = $C_2H_5OCH_2$, $n = C_3H_7OCH_2$, i-$C_3H_7OCH_2$, n-$C_4H_9CH_2$, $C_6H_5OCH_2$. In addition, two other desulfurization reactions of these thiiranes are described as well as the synthesis of the 2-alkoxymethylthiiranes.

Convenient laboratory methods for the synthesis of thiiranes[4] involve the transformation of an epoxide into its corresponding thiirane, by reaction with aqueous alkali thiocyanates or thiourea.

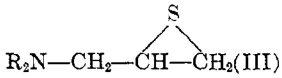
Advantage was taken of these procedures for the synthesis of the 2-alkoxymethylthiiranes, described here for the first time. The 1-alkoxy-2-hydroxy-3-chloropropanes, $ROCH_2CHOHCH_2Cl$(I), were obtained, in excellent yields, by the acid catalyzed interaction of a four molar excess of the alcohol to epichlorohydrin. Glycidyl ethers were isolated in high yields, by the dehydrohalogenation of the 1-alkoxy-2-hydroxy-3-chloropropanes(I) with finely powdered sodium hydroxide, at 0°, in anhydrous ether. The interaction of the glycidyl ethers with either aqueous potassium thiocyanate, or thiourea,[5] at room temperature gave the desired thiiranes. In general, the thiocyanate procedure gave higher yields of the 2-methoxymethyl- and 2-ethoxymethylthiirane whereas the thiourea procedure gave better results with the other members of the series. The physical properties, yields, and analysis of the 2-alkoxymethylthiiranes are summarized in Table I. These thiiranes are stable for long periods of time, at room temperature. Within the series, the 2-alkoxymethylthiiranes were more stable than 2-phenoxymethylthiirane.

Attempts were made to extend the general types of reactions, described, to the preparation of 2-thioalkylmethylthiiranes



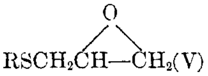
$R—S—CH_2—\overset{S}{CH—CH_2}(II)$

and 2-dialkylaminomethylthiiranes



$R_2N—CH_2—\overset{S}{CH—CH_2}(III)$

The 1-thioalkyl-2-hydroxy-3-chloropropanes, $RSCH_2$-$CHOHCH_2Cl$(IV) obtained readily from the acid catalyzed reaction of mercaptans with epichlorohydrin gave good yields, on basic dehydrohalogenation, of the glycidyl thioethers,



$RSCH_2\overset{O}{CH—CH_2}(V)$

The latter thioethers (V) were also readily obtained from the interaction of sodium mercaptans and epichlorohydrins. However, while the 2-thioalkylmethyl thiiranes (II) were obtained, by reactions of the glycidyl thioethers (V) with either potassium thiocyanate or thiourea, they were quite unstable, rapidly polymerizing on attempted purification by vacuum distillation, and could not be isolated as chemically pure compounds.

Only a single member of the 2-dialkylaminomethylthiiranes(III), (R = C_2H_5) was prepared. It was obtained by the interaction of diethylamine with epichlorohydrin to yield 3-diethylamino-1,2-epoxypropane

$(C_2H_5)_2NCH_2\overset{O}{CH—CH_2}$

and reaction of the latter with potassium thiocyanate. While the aminothiirane(III) was isolated as the monomer (60%), it polymerized in a few days in dark storage at room temperature.

As only the 2-alkoxymethylthiiranes were reasonably stable, they were used in the studies of the reactions of the thiiranes with nucleophilic reagents.

In a previous paper[2] the desulfurization of 2-methyl-, 2-chloromethyl-, and 2-methoxymethylthiiranes with the nucleophilic reagent triethyl phosphite was described with a few comments on the mechanism of this desulfurization reaction. The results obtained by the interaction of this

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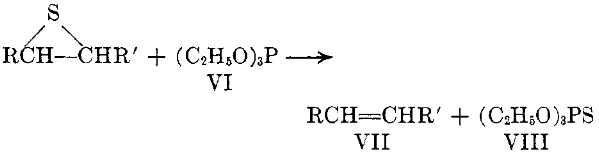
[4] A. Schonberg, Houben-Weyl, *Methoden der Organischen Chemie, Vol. IX*, Verlag, Stuttgart, 1955, pp. 148–169.

[5] F. G. Bordwell and H. M. Andersen, *J. Am. Chem. Soc.*, 75, 4959 (1953).

reagent and several additional thiiranes are summarized in Table II. The lowest yields of the unsaturated products were obtained in these desulfurization reactions when the thiirane contained a phenyl or phenoxy group. This decrease in yield parallels the lower stability of the 2-phenylthiirane and 2-phenoxymethylthiirane as compared with 2-alkyl- or 2-alkoxymethylthiiranes.

TABLE II

Desulfurization of Thiiranes by Triethyl Phosphite[v]



Thiirane	Yields %, VII	Product[t] VIII
Thiirane[m]	91[a]	94
Methylthiirane[n]	97[b]	99
2,3-Tetramethylenethiirane[o]	88[c]	91
Phenylthiirane[p]	57[d]	60
2-Chloromethylthiirane[r]	95[c]	100
2-Methoxymethylthiirane[s]	94[f]	96
2-Ethoxymethylthiirane	96[g]	98
2-*n*-Propoxymethylthiirane	93[h]	97
2-Isopropoxymethylthiirane	91[i]	95
2-*n*-Butoxymethylthiirane	97[j]	100
2-Phenoxymethylthiirane[u]	73[k]	77
2,2-Diethoxymethylthiirane[q]	87[l]	93

Identified by the physical properties of the dibromide of VIII. [a] I. Heilbron, *Dictionary of Organic Compounds*, Vol. **II,** Oxford University Press, New York, 1953, p. 502. [b] M. S. Kharasch, J. C. McNab, and M. C. McNab, *J. Am. Chem. Soc.*, **57,** 2463 (1935). Identified by the physical properties of VIII. [c] B. A. Karanokii and N. F. Glushnev, *J. Gen. Chem., U.S.S.R.*, **8,** (1938). [d] I. Heilbron, *Dictionary of Organic Compounds*, Vol. **IV,** Oxford University Press, New York, 1953, p. 379. [e] C. A. Vernon, *J. Chem. Soc.*, 4462 (1952). [f] S. C. Irvine, J. A. MacDonald, and C. W. Sautar, *J. Chem. Soc.*, **107,** 337 (1915). [g] S. W. Bruhl, *Ann*, **200,** 178 (1880); M. T. Rogers and M. B. Panish, *J. Am. Chem. Soc.*, **77,** 4230 (1955). [h] D. N. Kursanov and D. M. Shemyakina, *Doklady Akad. Nauk. U.S.S.R.*, **62,** 341 (1948). [i] I. Heilbron, *Dictionary of Organic Compounds*, Vol. **III,** Oxford University Press, New York, 1953, p. 108. [j] E. A. Tully, A. S. Hunter, and E. Zanovsky, *J. Am. Chem. Soc.*, **73,** 3528 (1951). [k] D. S. Tarbell, *Org. Reactions*, Vol. **II,** 26, 1944. D. I. Weisblatt, B. J. Magerlein, D. R. Meyers, A. R. Hanz, E. I. Fairburn, and S. T. Rolfsum, *J. Am. Chem. Soc.*, **75,** 5893 (1953). Thiiranes obtained by methods described in the literature. [m] G. I. Branz, *J. Gen. Chem., U.S.S.R.*, **21,** 757 (1951). [n] F. G. Bordwell and H. M. Andersen, *J. Am. Chem. Soc.*, **75,** 4959 (1953). [o] E. E. VanTamlen, *Org. Synthesis*, **32,** 39 (1952). [p] C. O. Guss and D. L. Chamberlain, Jr., *J. Am. Chem. Soc.*, **74,** 1342 (1952). [q] J. B. Wright, *J. Am. Chem. Soc.*, **79,** 1691 (1957). Desulfurization of thiiranes with XIII previously reported. [n,r,s] R. D. Schuetz and R. L. Jacobs, *J. Org. Chem.*, **23,** 1799 (1958). [o] R. E. Davis, *J. Org. Chem.*, **23,** 1767 (1958). [t] Product IX identified by its physical properties. C. Walling and R. Rabinowitz, *J. Am. Chem. Soc.*, **79,** 5326 (1957). [u] Polymeric sulfide also formed. [v] Molar ratio of thiiranes to VI was 1:1 in all cases and the reaction conditions were distillation of the reactants at atmospheric pressure, with the exception of 2-phenoxymethylthiirane where the distillation was done at 20 mm.

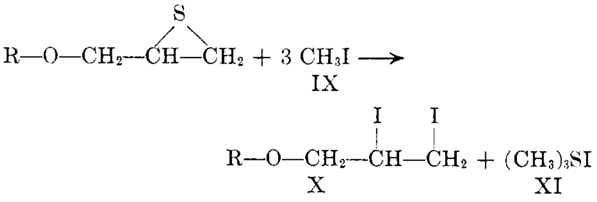
As reported previously[2] the failure of epoxides to undergo deoxygenation when treated with triethyl phosphite under the same conditions as the thiiranes undergo desulfurization was further substantiated by the observation that epichlorohydrin, methyl glycidyl ether, and *n*-butyl glycidyl ether were recovered quantitatively on distillation from an equal molar quantity of triethyl phosphite.

In the present investigation, a study was made of the reaction of methyl iodide with the 2-alkoxymethylthiiranes. In general, a ten-fold excess of methyl iodide was employed and the reactants were set aside, at room temperature, for periods varying from one to two weeks. In every instance, trimethylsulfonium iodide was the only product obtained. All efforts to isolate the 1-alkoxy-2,3-diiodopropanes, a presumed intermediate,[6] in this reaction were without success. Little or no polymer formation was detected and the yields of trimethylsulfonium iodide were in the range of 65–70%. When an excess of methyl iodide was not employed, the average yields of the trimethylsulfonium iodide decreased to 17–23%, (Table III). These results are in agreement with previous investigators.[6–8]

The desulfurization of 2-alkoxymethylthiiranes with organolithium compounds was investigated.

TABLE III

Yields of Trimethylsulfonium Iodide from the Reaction of 2-Alkoxymethylthiiranes with Methyl Iodide



Reaction	R	Mole Ratio IX[a]/Thiirane[b]	Reaction Time Weeks	Yield, % XI
1	CH_3	3.5	2	23
2	CH_3	30.0	2	71
3	CH_3	30.0	1	57
4	C_2H^5	3.0	2	18
5	C_2H^5	3.5	1	22
6	C_2H^5	30.0	2	72
7	C_2H^5	30.0	1	56
8	*n*-C_3H_7	3.5	1	22
9	*n*-C_3H_7	30.0	2	66
10	*i*-C_3H_7	3.5	1	20
11	*i*-C_3H_7	30.0	2	67
12	n-C_4H_9	3.5	2	18
13	n-C_4H_9	30.0	2	65

[a] Moles of IX = 1.50 or 0.175. [b] Moles of thiiranes = 0.05.

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(6) C. G. J. Culvenor, W. Davies, and N. S. Heath, *J. Chem. Soc.*, 282 (1949).

(7) M. Delepine and P. Jafferex, *Compt. rend.*, **172,** 158 (1921).

(8) M. Delepine and S. Eschenbrenner, *Bull. Soc. Chim. France*, **33,** 703 (1923).

(9) F. G. Bordwell, H. M. Anderson, and B. M. Pitt *J. Am. Chem. Soc.*, **76,** 1082 (1954).

(10) A. Schönberg, *Ann.*, **454,** 37 (1927).

It was observed that both phenyllithium and butyllithium caused a sulfur elimination reaction to occur, giving rise to alkyl allyl ethers and lithium mercaptides. The yields of the allyl ethers varied from 45 to 75% and those of the mercaptanes from 70–85 %. These results are in agreement with Bordwell[9] and others.[10]

EXPERIMENTAL

Materials. Epichlorohydrin, phenol, alcohols, and mercaptans were obtained from commercial sources and were used as received. Triethyl phosphite was obtained from the Virginia-Carolina Chemical Corporation and purified prior to use by distillation from metallic sodium. Methyl iodide was obtained from Eastman Organic Chemicals and redistilled just prior to use.

1-Alkoxy-2-hydroxy-3-chloropropanes. The halohydrins were prepared by the interaction of an alcohol with epichlorohydrin, under acid-catalyzed conditions, employing modifications of the method of Flores-Gallardo and Pollard.[11] In general, 15 to 20% higher yields were obtained by employing longer reaction periods, lower reaction temperatures and a higher mole ratio of alcohol to epichlorohydrin.

1,2-Epoxy-3-alkoxypropanes. The methyl, ethyl, *n*-propyl, isopropyl, and *n*-butyl glycidyl ethers were prepared by the dehydrohalogenation of the corresponding 1-alkoxy-2-hydroxy-3-chloropropanes with sodium hydroxide, using the procedure of Flores-Gallardo and Pollard,[11] except that longer reaction periods were employed, resulting in a 10 to 15% increase in yields.

1,2-Epoxy-3-phenoxypropane. This epoxy aryl ether was synthesized, in a 56% yield, according to the method of VanZyl and his collaborators.[12]

2-Alkoxymethylthiiranes. A series of 2-alkoxymethyl thiiranes were prepared, for the first time, and their properties are summarized in Table I. The methods of their preparation are similar, and the experimental procedures for obtaining 2-methoxymethylthiirane are given as representative of these syntheses.

Method A. To a vigorously stirred solution, held at 20–30°, and containing 97 g. (1.0 mole) of potassium thiocyanate dissolved in 100 ml. of water, was added dropwise 88 g. (1.0 mole) of 1,2-epoxy-3-methoxypropane, during 1.75 hr. The turbid reaction solution was stirred for 2 hr. following the addition of the epoxide and set aside overnight. The water layer was separated, set aside, and the organic layer was treated with a second aqueous solution of potassium thiocyanate (50.0 g. of salt in 100 ml. of water) as described, for an additional 5 hr. The aqueous layer was separated, combined with the first aqueous phase and these were extracted with three 25-ml. portions of ether. The ether extracts and organic phase were combined, dried over anhydrous calcium chloride and the ether was removed. The crude product was vacuum distilled (1 × 40 cm. Fenske-type column packed with 3/16″ glass helices). The 2-methoxymethylthiirane boiled at 60.5–61° (16 mm.), n_D^{25} 1.4791. Yields from three preparations averaged 92% based on the 1,2-epoxy-3-methoxypropane.

Method B. A 1-l. three-necked flask was charged with 76 g. (1.0 mole) of thiourea and 30 ml. of a sulfuric acid solution (1.0 eq. of acid in 350 ml. of water). The vigorously stirred reaction mixture was cooled to 5–10° and held in this temperature range while 88 g. (1.0 mole) of 1,2-epoxy-3-methoxypropane was added dropwise during 2 hr. After the epoxide had been added the reaction mixture was stirred for 0.25 hr., warmed to room temperature and hydrolyzed with 106 g. (1.0 mole) of sodium carbonate dissolved in 450 ml. of water. The aqueous phase was separated and extracted with two 25-ml. portions of ether. After being set aside for several hours, additional oily material had separated from the aqueous phase and the ether extraction was repeated. The ether extracts were combined with the organic layer, dried over anhydrous sodium sulfate, and the ether was removed. The residue was vacuum distilled (1 × 40 cm. column packed with 3/16″ glass helices). An 87% yield of 2-methoxymethyl thiirane, distilling at 60° (16 mm.), n_D^{25} 1.4791, was obtained. A second preparation of this thiirane gave similar results.

1-Thioethyl-3-chloropropanol-2. This compound was prepared in a 66.3% yield, essentially as described by Todsen, Pollard, and Rietz.[13]

1-n-Thioalky-2,3-epoxypropanes. A modification of the procedure of Nenitzescu and Scarlatescu[14] was used to obtain these materials. The *n*-thiopropyl and thioethyl-2,3-epoxypropanes were obtained in increased yields of 10–15% by using lower reaction temperatures and longer reaction periods.

1,2-Epoxy-3-diethylaminopropane. This epoxy amine was prepared, in a 67.0% yield, using procedures described in the literature.[15]

2-Diethylaminomethylthiirane. A 500-ml. three necked flask was charged with 42 g. (0.55 mole) of thiourea and 140 ml. of methanol. The stirred solution of thiourea and alcohol was cooled to 0–5°, and 65 g. (0.50 mole) of 1,2-epoxy-3-3-diethylaminopropane was added dropwise during 1.5 hr. The reaction mixture was stirred, at 5°, for an additional 0.5 hr., warmed to room temperature, and poured into 300 ml. of water. The crude product was extracted with four 50-ml. portions of chloroform; these were combined, dried over anhydrous sodium sulfate, and the chloroform was removed. The liquid residue was vacuum distilled. (1 × 30 cm. column packed with 3/16″ glass helices). The pure product, obtained in a 60% yield, distilled at 75° (11 mm.), n_D^{25} 1.4832.

Anal. Calcd. for $C_7H_{15}NS$: C, 57.93; H, 10.34; N, 10.00; S, 22.07. Found: C, 57.14; H, 10.45; N, 9.89; S, 21.96.

Reaction of 2-alkoxymethyl- and alkylthiiranes with triethyl phosphite. The experimental procedure employed was essentially that described previously,[2] and involved the distillation of an equimolar mixture of triethyl phosphite and the alkoxymethyl- or alkylthiirane. The results are summarized in Table II. The unsaturated products, resulting from these desulfurization reactions, were in all cases known compounds which were identified by their physical properties. In two cases of low boiling olefinic products they were converted to their dibromide derivative and identified as such.

Reaction of 2-alkoxymethylthiiranes with methyl iodide. The best results were obtained using the following experimental procedures. In a 300-ml. one-necked flask, equipped with a reflux condenser and calcium chloride drying tube, were placed 0.05 mole of the 2-alkoxymethyl thiirane and 1.5 moles of freshly distilled methyl iodide. The reaction mixture was set aside, with occasional stirring, for 2 weeks, filtered, and the recovered solid was washed several times with acetone. After recrystallization from absolute ethanol, the trimethylsulfonium iodide melted at 215° (lit.[6] m.p. 215°). Isolation of the 1,2-diiodo-3-alkoxypropane, presumably the other product of this reaction, was unsuccessful. In each case, after removal of the excess methyl iodide, vacuum distillation of the residual liquid resulted in its rapid and extensive decomposition. Variations in the yields of the trimethylsulfonium iodide isolated due to changes, in the mole ratio of methyl iodide to alkoxymethylthiirane,

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(11) H. Flores-Gallardo and C. B. Pollard, *J. Org. Chem.*, **12,** 831 (1947).

(12) G. VanZyl, G. D. Ziuden, J. F. Zack, Jr., and P. B. Kromann, *J. Am. Chem. Soc.*, **75,** 5002 (1953).

(13) T. K. Todsen, C. B. Pollard, and E. G. Rietz, *J. Am. Chem. Soc.*, **72,** 4000 (1950).

(14) C. D. Nenitzescu and N. Scarlatescu, *Ber.*, **68,** 587 (1935).

(15) H. Gilman and L. Fullhart, *J. Am. Chem. Soc.*, **71,** 1478 (1949).

interacting, their time of interaction, and structural alterations in the thiirane, are summarized in Table III.

Reaction of 2-alkoxymethylthiiranes with organolithium compounds. The experimental procedures employed in these reactions were modified from those described by Bordwell, Anderson, and Pitt.[9] The reaction of 2-butoxymethylthiirane with butyllithium is given as representative of these reactions. To an ether solution of butyllithium, prepared by the method of Gilman *et al.*[16] from 60.0 g. (0.44 mole) of *n*-butyl bromide and 8.6 g. (1.23 g-atom) of lithium, was added, during 0.75 hr., to 26.28 g. (0.18 mole) of 2-butoxymethyl thiirane dissolved in 30 ml. of anhydrous ether. Following the addition of the thiirane the reaction mixture was stirred for 3.0 hr., set aside overnight and then it was poured into an equal volume of ice water. The ether layer was separated, washed twice with 50-ml. portions of 2*N* sodium hydroxide solution and the washings were combined with the aqueous phase. The ether phase was washed, till neutral, with small portions of water, dried over Drierite and the ether was removed *in vacuo*. The residual liquid was fractionated (1 × 30 cm. Fenske-type column packed with 3/16″ glass helices). Butyl allyl ether was obtained in a 77% yield, b.p. 114–116° (741 mm.), n_D^{20} 1.4053 (lit.[17] b.p. 117.8–118° (763 mm.), n_D^{20} 1.4057).

The aqueous phase was acidified with concentrated hydrochloric acid to precipitate 1-butanethiol as an oil, which was separated. The aqueous phase was extracted with three 25-ml. portions of pentane. The oil and pentane extracts were combined and dried over Drierite. Distillation of the residual oil, after removal of the pentane, through an 18″-Vigreux column afforded an 81% yield of 1-butanethiol, boiling at 94–96° (747 mm). The mercaptan was characterized as *n*-butyl-2,4-dinitrophenyl sulfide, m.p. 66–67.5° (lit.,[9] b.p. 95–97° (760 mm.), m.p. of 2,4-dinitro derivative 66–68°).

The reaction of 23.76 g. (0.18 mole) of 2-isopropoxymethylthiirane with butyllithium (0.44 mole), gave a 58% yield of isopropyl allyl ether, b.p. 80–82° (741 mm), (lit.,[18] 82–83° (731 mm.). The 1-butanethiol, was obtained in a 74% yield. A 67% yield of *n*-propyl allyl ether, b.p. 90–91° (743 mm.), n_D^{20} 1.3917, and a 78% yield of 1-butanethiol were obtained from the reaction of 23.76 g. (0.18 mole) of 2-propoxymethyl thiirane with *n*-butyllithium (0.44 mole), (lit.,[19] values for *n*-propyl allyl ether, b.p. 90–92° (760 mm.), n_D^{20} 1.3919).

The reaction of 21.24 g. (0.18 mole) of 2-ethoxymethylthiirane with butyllithium (0.44 mole) afforded ethyl allyl ether, b.p. 66–67° (747 mm.), n_D^{25} 1.3892, in a 47% yield (lit. b.p. 66–67° (743 mm.),[20] n_D^{25} 1.3892[21]). The 1-butanethiol was obtained in an 84% yield.

A 70% yield of 1-butanethiol resulted from the reaction of 20.8 g. (0.20 mole) of 2-methoxymethyl thiirane with an ether solution of butyllithium (0.44 mole). Because of the low boiling point of the methyl allyl ether, only a small quantity of this ether was isolated, b.p. 42° (746.5 mm.), n_D^{20} 1.3786 (lit.,[22] b.p. 42.5–43° (757 mm.), n_D^{20} 1.3778–1.3803). The reaction of 2-alkoxymethylthiiranes with phenyllithium was carried out using the experimental procedures described above for the reaction of butyllithium with 2-butoxymethylthiirane, except that 40.0 g. (0.25 mole) of bromobenzene and 3.5 g. (0.50 g-atom) of lithium were used to prepare the phenyllithium.[9]

The reaction of 26.28 g. (0.18 mole) of 2-butoxymethylthiirane with phenyllithium (0.25 mole) gave a 74% yield of butyl allyl ether,[17] b.p. 114–116° (741 mm.), n_D^{20} 1.4054. The other product of this reaction, thiophenol, was obtained in an 83% yield, b.p. 70–73° (33 mm.), and was characterized as its 2,4-dinitrophenyl phenyl sulfide, m.p. 119–121° (lit.,[9] m.p. 119–121°).

The reaction of 23.76 g. (0.18 mole) 2-propoxymethylthiirane with phenyllithium (0.25 mole) in ether solution, resulted in a 53% yield of isopropyl allyl ether and a 71% yield of thiophenol. The isopropyl allyl ether distilled at 82–84° (741 mm.).[18]

The reaction of 23.76 g. (0.18 mole) 2-propoxymethylthiirane with phenyllithium (0.25 mole) gave a 70% yield of *n*-propyl allyl ether, b.p. 89–91° (737 mm.), n_D^{20} 1.3920[20] and an 86% yield of thiophenol. The interaction of 21.24 g. (0.18 mole) 2-ethoxymethylthiirane with phenyllithium (0.25 mole) produced ethyl allyl ether, b.p. 66–67° (745.3 mm.)[20,21] in 42% yield, and thiophenol in an 81% yield.

The reaction of 20.8 g. (0.20 mole) of 2-methoxymethylthiirane with an ether solution of phenyllithium (0.25 mole) gave a 74% yield of thiophenol. Because of the high volatility of methyl allyl ether,[22] it was not actually isolated.

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