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THE ROLE OF MERCAPTANS IN POLYMERIZATION OF DIENES AND THE COPOLYMERIZATION OF STYRENE AND DIENES[1]

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Received July 12, 1955

Mercaptans are commonly used in the preparation of synthetic polymers because they are supposed to serve a dual purpose. In the low temperature (5° and below) and high temperature (50°) copolymerizations of butadiene and styrene, these mercaptans are usually assumed to function as follows. First, in the presence of an oxidant, mercaptans give rise to free RS• radicals which initiate polymerization. Second, they serve as "modifiers" because of their ability to react with the long chain free radicals (eq. 1).

1. $$R(M)_n\bullet + RSH \rightarrow R(M)_nH + RS\bullet$$

This "modification" is important, from a practical standpoint, because of the physical properties essential for a useful polymer.

In the present paper, data are presented which suggest that mercaptans act as "modifiers" by two entirely different mechanisms at 50° and at 5° (or below), respectively.

Reaction of mercaptans with styrene and with butadiene. In order to fully understand the mechanism whereby mercaptans may function as "initiators" and "modifiers" of the copolymerization of styrene and butadiene, it is necessary to consider the reaction of these latter substances with equimolar portions of mercaptans in the presence of small amounts of an oxidant (1*d*). The products formed when styrene or butadiene reacts with a mercaptan depend upon the mercaptan, the temperature and the amount of oxidant (equations 2 to 7) used.

2. $$RSH + Ox \rightarrow RS\bullet + HOx$$

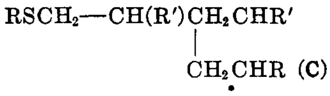
3. $$RS\bullet + CH_2{=}CHR' \rightarrow RSCH_2{-}\underset{\bullet}{C}HR'$$

4. $$RSCH_2{-}\underset{\bullet}{C}HR' + RSH \rightarrow RSCH_2{-}CH_2R'\ (A) + RS\bullet$$

5. $$RSCH_2{-}\underset{\bullet}{C}HR' + CH_2{=}CHR' \rightarrow RSCH_2{-}CH(R')CH_2{-}\underset{\bullet}{C}HR'$$

6. $$RSCH_2{-}CH(R')CH_2{-}\underset{\bullet}{C}HR' + RSH \rightarrow RSCH_2{-}CH(R')CH_2{-}CH_2R'\ (B) + RS\bullet$$

7. $$RSCH_2{-}CH(R')CH_2{-}\underset{\bullet}{C}HR' + CH_2{=}CHR' \rightarrow$$



$$RSCH_2{-}CH(R')CH_2CHR'\ (\text{branch: } CH_2\underset{\bullet}{C}HR)\ (C)$$

8. $$C + RSH \rightarrow CH + RS\bullet$$

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[1] The work discussed herein was performed as a part of the research project sponsored by the Federal Facilities Corporation, Office of Synthetic Rubber, in connection with the Government Synthetic Rubber Program.

The schemes indicated in equations 2 to 8 adequately represent the reaction of equimolar quantities of styrene with *n*-propyl or with *n*-lauryl mercaptan in the presence of a trace of an oxidant at 30–50°. Compounds corresponding to structures **A** and **B** have been isolated and identified (1*b*). Note that, with styrene, even in the presence of an equimolar quantity of the mercaptan, a considerable quantity of **B** is produced, along with small amounts of a material formed as indicated in equations 7 and 8. When small amounts of the mercaptan are used, the products of types **B** and **C** (and higher adducts formed from **C** in the manner indicated in equation 7) are formed at the expense of **A**. In other words, the reaction is one involving addition-polymerization of styrene. Similar results have been obtained with butadiene (1*b*).

Furthermore, since mercaptans which are readily oxidized (thioglycolic acid, thiophenol) react with styrene or butadiene to give high yields of the 1:1 adduct (**A**, eq. 4) in homogeneous solution (1*a*), and little (if any) of the adducts of the type **B** and [CH] (eq. 8), these mercaptans, when used in a polymerization recipe, should "inhibit" polymerization. Such indeed is the case when these mercaptans are substituted for lauryl mercaptan or long chain tertiary mercaptans.[2]

The elucidation of the mechanism of addition of mercaptans to olefins (1*a*), and the determination of the factors influencing this simple reaction have proved helpful in understanding (a) the mechanism of the mercaptan-initiated and "modified" copolymerization of styrene and butadiene in emulsion at 50°; (b) the inhibitory effect of oxygen (1*c*); and (c) the photochemical initiation of the emulsion copolymerization of styrene and butadiene by disulfides at 50°, but not at a lower temperature (2).

Reaction of mercaptans with styrene and with butadiene at low temperatures in the presence of an oxidant. There is no *a priori* reason why mercaptans in conjunction with appropriate oxidants should not be satisfactory initiators, promotors and/or modifiers in low temperature emulsion polymerizations. However, attempts to initiate polymerization at a reasonable rate at 5° with mercaptans and oxidants have (in our hands) been unsuccessful or at best unsatisfactory. Thus, lauryl mercaptan, although rapidly oxidized by potassium ferricyanide at 5°, does not initiate the copolymerization of styrene and butadiene at that temperature (15 hours), in the presence of 5% of an emulsifier. Even with the easily oxidized thiol, anisyl mercaptan, there is only 10–15% conversion in 15 hours.

Furthermore, it can be shown that although, in emulsion, mercaptans add to styrene at an appreciable rate at 30° in the presence of a small amount of an oxidant (Table I), little or no chain-addition takes place at 5°. Rather disulfide is

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[2] The relative ease of oxidation of a series of mercaptans was determined by dissolving equivalent amounts of the mercaptans in acetic acid and then adding equivalent quantities of ferric chloride dissolved in acetic acid. The rate of oxidation was measured by adding *o*-phenanthroline to the reaction mixture and noting, from the color change, the rate at which the ferrous *o*-phenanthroline complex was formed. The following order of decreasing rate of oxidation was observed:

thiophenol > thioglycolic acid ≫ propyl, lauryl ≫ *tert*-butyl,
3-B mercaptan (a commercial sample of a *tert*-mercaptan).

TABLE I

ADDITION OF LAURYL MERCAPTAN TO STYRENE IN THE PRESENCE OF $K_2S_2O_8$ (3 HOURS) AT 30° (IN EMULSION)

Conditions	Per cent Reaction in Vacuum
Control ($K_2S_2O_8$, none)	0
0.2 equivalent—% $K_2S_2O_8$	51
2.0 equivalent—% $K_2S_2O_8$	47

formed at this temperature in an amount corresponding roughly to the amount of oxidant used (1*b*). The formation of disulfide and the non-formation of adducts may be due to: (a) the very slow rate at which free mercaptyl radicals add to the olefin in question at 5° (or below), or (b) the inability of the radical $R'\underset{\bullet}{C}HCH_2SR$ to abstract a hydrogen atom from the mercaptan. This latter possibility would imply that mercaptans should not act as "modifiers" in the copolymerization of monomers at low temperature, if the reaction is initiated by free $RO\cdot$ radicals which add rapidly to the monomers (desirably R should be a tertiary radical, and the hydroperoxide should be little soluble in water). Yet, tertiary mercaptans, which are insoluble in water, act as "modifiers" in the low temperature emulsion copolymerization of styrene and butadiene. An obvious implication to be drawn from these data is that although mercaptans act as "modifiers" at 30–50° in accordance with the mechanism indicated in equation 1, they must, at low temperatures (5° or below), act as "modifiers" by some other mechanism.

Reaction of butadiene with a mercaptan and tert-butyl hydroperoxide and ferrous salts in the presence of water and an anti-freeze at −10°. The experiments described in this section were designed with the object of ascertaining the mechanism of the "modifying" action of mercaptans in low temperature polymerizations or copolymerizations.

It has been established (3) that, when a mixture of butadiene, *tert*-butyl hydroperoxide and water (containing an anti-freeze, and maintained at about −10°) is treated with a water solution of a ferrous salt, a reaction takes place which may be formulated as follows:

9. $$(CH_3)_3COOH + Fe^{++} \rightarrow (CH_3)_3CO\cdot + Fe^{++}OH$$

10. $$(CH_3)_3CO\cdot + C_4H_6 \rightarrow (CH_3)_3COC_4H_6\cdot \ (\mathbf{E})$$

11. $$2\mathbf{E} \rightarrow (CH_3)_3COC_4H_6C_4H_6OC(CH_3)_3 \ (\mathbf{F})$$

Reactions 9 and 10 show how the "low temperature" polymerization is initiated; equation 11 shows one type of termination of polymerization. If it is assumed that the free radical **E** is about the same reactivity (4) as the growing free radicals, $(CH_3)_3CO(C_4H_6)_n\cdot$, then valid conclusions regarding the probable mechanism of "modification" (and/or reactions) of the growing free radical $RO(M)_n\cdot$ may be drawn from the behavior of the free radical **E**. The reactions of the free radical **E**, generated as here described, was studied in the presence of (a) thiophenol, (b) *n*-propyl mercaptan, and (c) *tert*-butyl mercaptan.

Reaction of butadiene, thiophenol, and tert-butyl hydroperoxide in the presence of ferrous salts. To a well stirred mixture of butadiene (1.9 moles), water (150 ml. containing 75 g. of urea, to serve as an anti-freeze), *tert*-butyl hydroperoxide (0.358 mole), and thiophenol (0.358 mole) (externally cooled to −10°) a water solution of ferrous ammonium sulfate (0.0716 mole; 20 mole-% on the basis of the hydroperoxide) was added over a two-hour period. The following products, in the amounts stated, were isolated from the reaction mixture.

(**H**) $(CH_3)_3COC_4H_6SC_6H_5$ (76% on the basis of the C_6H_5SH)

(**K**) $C_6H_5SC_4H_6SC_6H_5$ (6% on the basis of the C_6H_5SH)

(L) $(CH_3)CO(C_4H_6)_2OC(CH_3)_3$ (*ca.* 5% on the basis of the $(CH_3)_3COOH$)

(M) $CH_3CH{=}CHCH_2SC_6H_5$ (less than 10% on the basis of C_6H_5SH)

When propyl mercaptan or *tert*-butyl mercaptan was used instead of thiophenol, larger amounts of ferrous salt were needed (40 and 60% on the basis of the hydroperoxide, respectively). The products formed are indicated below.

n-Propyl Mercaptan	*tert*-Butyl Mercaptan
(**N**) $CH_3CH_2CH_2SC_4H_7$ (*ca.* 4%)	(**R**) $(CH_3)_3COC_4H_6SC(CH_3)_3$ (9%)
(**O**) $(CH_3)_3COC_4H_6SC_3H_7$-(*n*) (*ca.* 63%)	(**S**) $(CH_3)_3CO(C_4H_6)_2OC(CH_3)_3$ (25%)
(**P**) *n*-$C_3H_7SC_4H_6SC_3H_7$-(*n*) (*ca.* 5–10%)	
(**Q**) $(CH_3)_3CO(C_4H_6)_2OC(CH_3)_3$ (less than 5%)	

The yields of all products, except **Q** and **S** were calculated on the basis of the mercaptan used. Products **Q** and **S** were calculated on the basis of the amount of hydroperoxide used in the reaction.

A reasonable explanation of the data here recorded is presented by the following reaction scheme.

I. $(CH_3)_3COOH + Fe^{++} \rightarrow (CH_3)_3CO\cdot + Fe^{+++} + OH^-(Fe^{++}OH)$

II. $(CH_3)_3CO\cdot + CH_2{=}CHCH{=}CH_2 \rightarrow (CH_3)_3COC_4H_6\cdot$

IIIa. $Fe^{+++} + RSH \rightarrow Fe^{++} + RS\cdot + H^+$

IIIb. $(CH_3)_3CO\cdot + RSH \rightarrow RS\cdot + (CH_3)_3COH$ or $(CH_3)_2CO + CH_4$

IV. $RS\cdot + (CH_3)_3COC_4H_6\cdot \rightarrow (CH_3)_3COC_4H_6SR$

V. $RS\cdot + CH_2{=}CHCH{=}CH_2 \rightarrow RSC_4H_6\cdot$

VI. $RS\cdot + RSC_4H_6\cdot \rightarrow RSC_4H_6SR$

VII. $RSC_4H_6\cdot + RSH \rightarrow RS(C_4H_6)H + RS\cdot$

VIII. $2\ (CH_3)_3COC_4H_6\cdot \xrightarrow{\text{Dimerization}} (CH_3)_3CO(C_4H_6)_2OC(CH_3)_3$

The differences in the yields, and the ferrous salt requirements, of the mercaptans here cited are readily understood if the differences in the ease of oxidation of the mercaptans are taken into account. Thus, the readily oxidized mercaptan (thiophenol) reacts fast according to scheme IIIa leading to a rapid regeneration of the ferrous salt (the ferrous salt requirement is therefore small), and since II and IIIa are fast, a large yield of compound IV is obtained. With *n*-propyl mercaptan, which is not as readily oxidized by ferric ion, larger amounts of ferrous salts are needed, and still larger amounts of ferrous salts are needed in the case of the tertiary mercaptans. The ratio of the products formed is therefore essentially the one expected from the ease oxidation of the mercaptans, and the differences in the amounts of ferrous salts used.

Other important aspects of the schemes I to VIII deserve some comment: (a) note that the alkoxy radicals generated as in equation I preferentially add to butadiene (II) instead of abstracting a hydrogen atom from the mercaptan. This behavior accounts for the high yields of products in which alkoxy radicals have been incorporated into butadiene. The findings also suggest that free *tert*-alkoxy radicals add faster to butadiene than do free mercaptyl radicals. (b) The free radical [$(CH_3)_3COC_4H_6\cdot$] does not abstract a hydrogen atom even from such a ready hydrogen donor as thiophenol. (c) The free mercaptyl radicals must be generated by the oxidation of the mercaptan by the ferric salt. (d) Although free mercaptyl radicals add at low temperatures to butadiene, the rate of addition is very slow; the major reaction is "coupling" with the free $(CH_3)_3COC_4H_6\cdot$ radical. (e) We are still uncertain whether reaction VII takes place at the low temperature here used, or at the higher temperature (20–30°) employed in working up the reaction mixture. (f) The extent of reaction VIII depends on the amount of iron used. The larger the amount of iron used, the more of this material is formed. (g) There is a remarkable difference in the nature of the products obtained at 30–50° and at −10°. At the higher temperatures (30−50°) high yields of adducts of the type indicated in equations 4, 6 and 8 are obtained, whereas at lower temperatures the major reaction is the "dimerization" of the free radicals of the type $(CH_3)_3CO(C_4H_6)_n\cdot$ with the mercaptyl radicals (see eq. IV).

The most significant aspect of the data here recorded is that with all the mercaptans here studied (particularly with thiophenol which so readily donates a hydrogen atom) no products of the type $(CH_3)_3CO(C_4H_6)_n\cdot H$ (where $n = 1$ or some larger number) were found, in spite of a careful search. If the observations here recorded are applicable to polymerizations carried out at low temperatures, they would preclude the current hypothesis that the low temperature "modification" by mercaptans takes place in a manner similar to "modification" 50° (see equation 1). Although it is difficult to assess the importance of other methods of radical destruction (disproportionation, etc.), it would nevertheless appear that "coupling" of like (or unlike) free radicals plays a major role in the "modification" of polymerization at low temperatures.[3]

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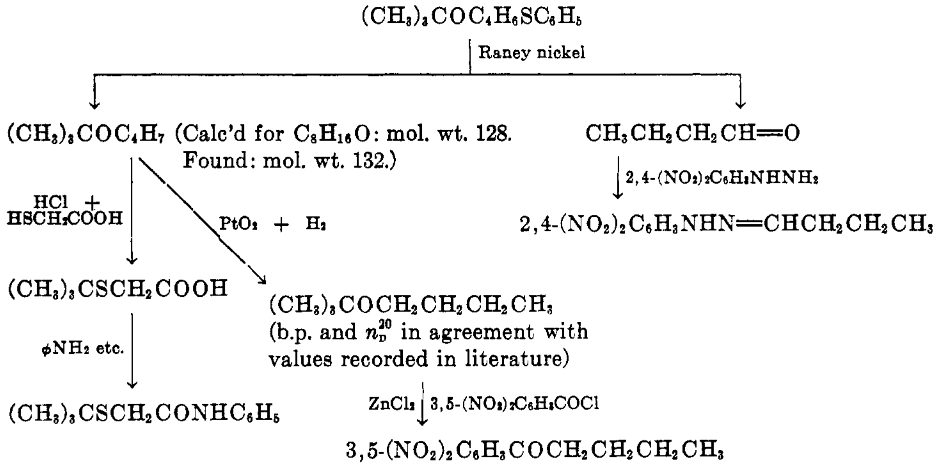
[3] Note that Brown and Winkler [*Can. J. Chem.*, **31,** 13 (1953)] in a kinetic study of redox polymerization claim "that two types of non-mercaptan termination have been found to occur to appreciable extents; mutual termination of free radicals and a termination process involving the emulsifier" (Dresinate 731). However, the data here recorded indicates that the free radical $RO(M)_n\cdot$ is so weak that under no circumstances could it abstract a hydrogen atom from the soap. Hence some other substance (or substances) must account for the "termination" assumed by Brown and Winkler.

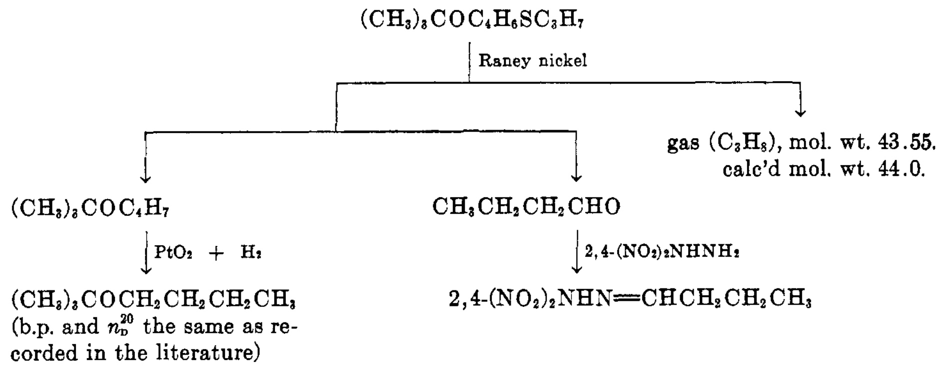
Proof of structure of compounds H to Q. The experimental part of the paper should be consulted for details. In general, the structures were established by desulfurization with Raney nickel and identification of resulting products. The procedures used in the proof of structure of the major reaction products **H** and **O** are indicated below.

Proof of Structure of Compound **H** [$(CH_3)_3COC_4H_6SC_6H_5$]



Similarly, the proof of structure of compound **O** [$(CH_3)_3COC_4H_6SCH_2CH_2CH_3$] was established by the series of reactions indicated below.

Proof of Structure of Compound **O** [$(CH_3)_3COC_4H_6SC_3H_7$]



EXPERIMENTAL

General procedure. The reactions were carried out in a one-litre three-necked flask equipped with a Tru-Bore stirrer, Dry-Ice condenser and a pressure-compensating dropping-funnel. The air in the apparatus was displaced by nitrogen gas. The contents of the flask were cooled, by immersing the flask in a large Dewar, to −10°.

An aqueous solution (20% solution) of ferrous ammonium sulfate hexahydrate was added dropwise to a vigorously stirred mixture of redistilled water (150 ml.), urea (75 g. as anti-freeze), butadiene (100 g.; 1.9 moles), *tert*-butyl hydroperoxide (18–36 g.; 0.2–0.4 mole),

TABLE II

REACTIONS OF MERCAPTANS, *tert*-BUTYL HYDROPEROXIDE AND BUTADIENE IN THE PRESENCE OF FERROUS AMMONIUM SULFATE AT −10°

Exp	Mercaptan	Moles RSH	Moles *t*-BuOOH	Moles Butadiene	Moles of Ferrous Ammonium Sulfate (%)	Products moles—(%)				
						RSC_4H_6O-*t*-Bu	RSC_4H_6SR	RSC_4H_7	[*t*-$BuOC_4H_6]_2$	RSH recovered, %
1	Thiophenol	0.358	0.358	3.5	20	76	6	10	5	0
2	Thiophenol	.136	.136	1.9	24	64	17	10	5	0
3	Thiophenol	.136	.136	1.9	100	—	36	—		0
4	n-Propylmercaptan	.5	.5	1.9	42	63	*ca* 10	*ca* 5	*ca* 5	5
5	*tert*-Butylmercaptan	.2	.2	1.9	60	9	—	—	25	72

and mercaptan (0.2–0.4 mole). It took two hours for the addition of the iron salt. The amount of ferrous ammonium sulfate solution used depended on the mercaptan used (see Table II). After all the ferrous solution was added the reaction mixture was stirred for an additional period of time at −10°. With thiophenol the additional time of stirring was one-half to one hour, while with the more difficultly oxidized mercaptans stirring was continued for two hours in the case of propyl mercaptan and six hours (or longer) in the case of *tert*-butyl mercaptan. The cooling bath then was removed and the excess butadiene was allowed to evaporate. The reaction mixture then was extracted with petroleum ether, the extract was washed with water and was dried over sodium sulfate, and the petroleum ether was removed by distillation at reduced pressure.[4] The oils remaining after removing the petroleum ether were separated by distillation at reduced pressure and the various fractions identified (see below). A summary of the experimental conditions and the nature and amount of the products formed is indicated in Table II.

Reaction of thiophenol with tert-butyl hydroperoxide in the presence of butadiene and ferrous ammonium sulfate (100 mole-%) (Exp. 3). After removal of the ligroin (see general procedure), some colorless crystals deposited from the residual oil. The whole was cooled in an ice-bath and the crystals (Compound **K**) (3.1 g., m.p. 72–79°) were collected on a filter. The filtrate (27.7 g.) was distilled at reduced pressure, and the following fractions were collected: (*1*) 59–83°/0.01 mm., 4.6 g., n_D^{20} 1.4977; (*2*) 84–93°/0.02 mm., 9.6 g., n_D^{20} 1.5054; (*3*) 94–106°/0.05 mm., 7.4 g., n_D^{20} 1.5492; (*4*) 106°/0.05 mm., 0.6 g., n_D^{20} 1.5788; Residue, 3.6 g. (crystallized on cooling). The residue, after washing with petroleum ether, was shown to be identical with Compound **K**. The two batches of crystals (**K**) (6.7 g. in total, 36% calculated as 1,4-bisthiophenoxy-2-butene) were therefore combined. The crystals, after two recrystallizations from ethanol, melted at 79–80°, and showed no depression when mixed with an authentic sample of 1,4-bisthiophenoxy-2-butene (see below for preparation of authentic sample). Since Fractions *1* and *2* were collected over such a large temperature range, they were carefully redistilled. Fraction *1* when distilled gave the following fractions: (*a*) 44–47°/0.005 mm., 1.2 g., n_D^{20} 1.5068, molecular weight 183; (*b*) 48–50°/0.005 mm., 0.7 g., n_D^{20} 1.5039; (*c*) 51–54°/0.01 mm., 0.9 g., n_D^{20} 1.4963; (*d*) 55–60°/0.01 mm., 0.7 g., n_D^{20} 1.47880; (*e*) Residue, 1.2 g. The analyses for carbon and hydrogen of these fractions were: (*a*) C, 73.38; H, 9.66. (*b*) C, 73.17; H, 9.50. (*c*) C, 73.27; H, 9.86. (*d*) C, 74.18; H, 10.58. It was surmized from these data that these fractions were mixtures of phenyl butenyl thioether (Compound **M**), $C_{10}H_{12}S$, b.p. 52–53°/0.1 mm., n_D^{20} 1.5688; Mol. wt. calc'd 164. *Anal.* Calc'd C, 73.17, H, 7.32, and the

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[4] With *tert*-butyl mercaptan and propyl mercaptan, an aliquot of the petroleum ether extract was titrated with silver nitrate for unused mercaptan before removing the petroleum ether.

bis-*tert*-butoxyoctadienes (Compound L), $C_{16}H_{30}O_2$, b.p. 55–70°/0.05 mm., n_D^{20} 1.4432–1.4485; Mol. wt. calc'd 254, C, 75.60, H, 11.83. Fraction *d* appears richer in Compound L content than the earlier fractions.

Fraction *2* was added to residue *1d* above and distilled. The following fractions were collected: (*2a*) 41–63°/0.01 mm., 0.6 g., n_D^{20} 1.4884; (*2b*) 64–67°/0.02 mm., 1.6 g., n_D^{20} 1.4793, mol. wt. 202; (*2c*) 75–77°/0.02 mm., 2.7 g., n_D^{20} 1.4855, mol. wt. 232; (*2d*) 78–81°/0.02 mm., 3.1 g., n_D^{20} 1.5095; (*2e*) residue, 1.2 g. Analyses for carbon and hydrogen on these fractions were: (*2a*) C, 73.63; H, 7.95. (*2b*) 73.85; H, 10.35. (*2c*) C, 73.06; H, 10.21. (*2d*) C, 72.34; H, 9.54. Fractions *2a*, *b*, *c*, were likewise surmized to be mixtures of phenyl butenyl thioether (Compound M) and the bis-*tert*-butoxyoctadienes (Compound L) (richer in octadiene than Fraction *1*). That Fractions *1* and *2* contained the constituents indicated was shown by treatment with Raney nickel in ethanol. Under these conditions the thioether was desulfurized and butene gas was isolated and identified by molecular weight (57, calc'd 54). Compound L was then separated by distillation and identified by molecular weight, boiling point, and refractive index.

Fraction *3*, from its refractive index, and boiling point was assumed to be mostly the thiophenoxy-*tert*-butoxybutene, $\phi\text{-}SC_4H_6OC(CH_3)_3$ (Compound H) (b.p. 81–83°/0.02 mm., n_D^{20} 1.5340–1.541) contaminated with some of the 1,4-bis-thiophenoxy-2-butene (Compound **K**). Fraction *4* was not investigated. Fraction *2d*, from its boiling point, analysis, and refractive index, was assumed to be a mixture of Compounds **H** and **L**. Fraction *2e* was not investigated. No attempt was made to separate the various fractions obtained in this experiment into their individual components since it was found that the reaction products formed, when smaller amounts of ferrous salts (*ca.* 20 mole-%) were used, could be more readily separated into analytically homogenous fractions. The formation of appreciably large amounts of Compounds **K** and **L** when large amounts of iron are used is perhaps not surprising in view of the large concentration of mercaptyl and *tert*-butoxy radicals generated under these conditions.

Reaction of thiophenol with tert-butylhydroperoxide in the presence of butadiene and ferrous ammonium sulfate (24 mole-%) (Exp. 2). In Table II are listed the amounts of reactants used. The *tert*-butyl hydroperoxide (56% titre) was used without purification. After removal of the petroleum ether (see general procedure), there remained a nearly colorless oil (29.3 g.). The oil was distilled at reduced pressure and the fractions collected: (*1*) 61–69°/0.005–0.01 mm., 4.0 g., mol. wt. 185; (*2*) 83–88°/0.005–0.1 mm., 12.3 g., mol. wt. 235; (*3*) 105–114°/0.05 mm., 9.1 g., mol. wt. 228; (*4*) residue (crystallized on cooling) (3.3 g.) melted at 78–80°; this product was somewhat impure Compound **K** (17% yield on basis of thiophenol used). The residue was crystallized from absolute ethanol to give shiny white plates (m.p. 80–81°). This material was shown to be pure 1,4-bis-thiophenoxy-2-butene (Compound **K**) (see below).

Anal. Calc'd for $C_{16}H_{16}S_2$: C, 70.57; H, 5.92; Mol. wt. 272.
Found: C, 69.93; H, 5.77; Mol. wt. 267.

The identity of the crystals, m.p. 80–81°, was confirmed by the melting point (80–81°) on admixture with an authentic sample of 1,4-bis-thiophenoxy-2-butene. The authentic bis-thiophenoxy-2-butene was prepared from the sodium salt of thiophenol (2.65 g., 0.02 mole, made from sodium ethoxide in ethanol and thiophenol) and *trans*-1,4-dibromo-2-butene (2.14 g., 0.01 mole) in absolute ethanol. An exothermic reaction ensued on mixing the reagents and sodium bromide separated. After warming for 15 minutes (steam-bath) the reaction mixture was poured into water and extracted with ether. The ether solution was washed with water and dried. After removal of the ether, a white crystalline residue remained which was crystallized from absolute ethanol to give 1.7 g. of pure (m.p. 80–81°) 1,4-bis-thiophenoxy-2-butene (Compound **K**).

Anal. Calc'd for $C_{16}H_{16}S_2$: C, 70.57; H, 5.92.
Found: C, 70.59; H, 6.22.

It was surmized from the boiling point and molecular weight of Fraction *1* that this fraction was a mixture of Compound **M** (phenyl butenyl thioether) and Compound **L** (bis-

tert-butoxyoctadiene). Fractions *2* and *3* appeared to be (at least from molecular weight) largely Compound **H** (*tert*-butoxythiophenoxy-butenes). In order to establish the homogeneity of these fractions, they were distilled. Fractions *1* and *2* were combined and carefully distilled and the following fractions collected: (*2a*) 67–72°/0.007 mm., 2.1 g., n_D^{20} 1.5278; (*2b*) 72–74°/0.007 mm., 3.1 g., n_D^{20} 1.5198; (*2c*) 75–80°/0.02 mm., 4.3 g., n_D^{20} 1.5225; (*2d*) 81–83°/0.02 mm.; 5.1 g., n_D^{20} 1.5339. The carbon and hydrogen analyses of these fractions were: (*2a*) C, 72.50; H, 8.83. (*2b*) C, 71.81; H, 9.05. (*2c*) C, 71.89; H, 9.15. (*2d*) C, 71.07; H, 8.69. Fraction *2a* was shown to contain Compound **M**, phenyl butenyl thioether (calc'd for $C_{10}H_{12}S$, C, 73.17; H, 7.32; n_D^{20} 1.5688) contaminated with Compound **L** (bis-*tert*-butoxyoctadienes) by desulfurization with Raney nickel (method described in later section). Fractions *2b* and *2c* were substantially Compound **H** (*tert*-butoxythiophenoxybutenes) contaminated with small amounts of Compound **L** (bis-*tert*-butoxyoctadienes) (note analyses and refractive indices). Fraction *2d* was shown to be Compound **H** (*tert*-butoxythiophenoxybutene, mostly 1-*tert*-butoxy-4-thiophenoxy-2-butene containing some 4-*tert*-butoxy-3-thiophenoxy-1-butene) by desulfurization with Raney nickel (see later experiments), and the analyses for carbon and hydrogen.

Anal. Calc'd for $(CH_3)_3COC_4H_6SC_6H_5$ ($C_{14}H_{20}SO$): C, 71.15; H, 8.53.
Found: C, 71.07; H, 8.69.

Fraction *3*, although its molecular weight 228 corresponds well to that calculated for Compound **H**, *tert*-butoxythiophenoxybutenes ($C_{14}H_{20}SO$, mol. wt. calc'd 236), it boiled higher (presumably due to entrainment by Fraction *4*) than expected for this compound (see Fraction *2d*). Accordingly, Fraction *3* was redistilled and the major portion (8.0 g.) now boiled at 81–84°/0.01–0.02 mm., n_D^{20} 1.5340. This fraction was assumed to be pure Compound **H** (*tert*-butoxythiophenoxybutenes). The small residue (*ca.* 1 g.) from this distillation was not investigated. In this experiment the yield of Compound **H** was 64%.

Reaction of thiophenol with tert-butyl hydroperoxide in the presence of butadiene and ferrous ammonium sulfate (20 mole-%) (Exp. 1). In Table II is listed the amount of each reagent used for this experiment. The aqueous phase consisted of a solution of 150 g. of urea in 300 ml. of redistilled water rather than the amounts indicated in the general procedure. The ferrous ammonium sulfate (20 mole-%) was added dropwise over a period of 20 minutes as a solution [28.0 g. $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in 113 ml. of solution]. The reaction mixture then was worked up as indicated in the general procedure. After removal of most of the petroleum ether by distillation at atmospheric pressure, the last traces were removed at water pump pressure. There was no indication of low-boiling materials, such as the ether $(CH_3)_3COC_4H_7$. A nearly colorless oil (84.5 g.) remained after complete removal of the petroleum ether. The oil was distilled and the following fractions were collected: (*1*) 64–74°/0.02 mm., 7.6 g.; (*2*) 87–93°/0.02 mm., 31.0 g.; (*3*) 93–94°/0.03 mm., 22.8 g.; (*4*) 95–110°/0.03 mm., 13.8 g.; (*5*) residue (crystallized on cooling), 3.0 g.

Fraction *5*, the residue, after recrystallization from ethanol, deposited shiny white crystals (Compound **K**) which melted at 80–81°. This material did not depress the melting point of an authentic sample of 1,4-bis-thiophenoxy-2-butene (m.p. 80–81°), prepared from *trans*-1,4-dibromo-2-butene and sodium thiophenoxide. The yield of crude dithioether, Compound **K**, based on the thiophenol used, was 6%.

Fractions *1* and *2* were combined and redistilled: (*2a*) 56–64°/0.03 mm., 3.5 g., n_D^{20} 1.5198, mol. wt. 182; (*2b*) 65–77°/0.03 mm., 4.9 g., n_D^{20} 1.5276, mol. wt. 188; (*2c*) 78–81°/0.03 mm., 9.0 g., n_D^{20} 1.5188, mol. wt. 214; (*2d*) 82–83°/0.04 mm., 6.5 g., n_D^{20} 1.5227, mol. wt. 227; (*2e*) residue, 14.9 g.

Fraction *2e* was added to fraction *3* above and the whole was distilled: (*3a*) 88–89°/0.05 mm., 9.5 g., n_D^{20} 1.5309, mol. wt. 230; (*3b*) 90–92°/0.05 mm., 5.3 g., n_D^{20} 1.5344, mol. wt. 228; (*3c*) 93–95°/0.05 mm., 17.0 g., n_D^{20} 1.5374, mol. wt. 228; (*3d*) 96°/0.04 mm., 3.9 g., n_D^{20} 1.5399, mol. wt. 228; (*3e*) residue, 1.9 g.

The residue, *3e*, was combined with Fraction *4* (above) and the whole was distilled: (*4a*) 84–88°/0.02 mm., 1.3 g., n_D^{20} 1.5396, mol. wt. 228; (*4b*) 89–90°/0.02 mm., 11.3 g., n_D^{20} 1.5410, mol. wt. 227; (*4c*) 90°/0.02 mm., 0.4 g., n_D^{20} 1.5433, mol. wt. 229; (*4d*) the residue (2.7 g.) was discarded.

Identification of fractions. Fractions *2a* and *2b* correspond in boiling point, refractive index, and molecular weight to the fraction in experiment #2 (in which 24 mole-% of iron was used) (Fraction *2a*) which was shown to be a mixture of Compound **M** (phenyl-butenylthioether), and Compound **L** (bis-*tert*-butoxyoctadienes). Furthermore, when these fractions were combined and treated with Raney nickel, butene was evolved (identified by mol. wt.) and bis-*tert*-butoxyoctadienes (19%) were isolated (identified by b.p. and refractive index). Fractions *2c, 2d, 3a, 3b, 3c, 3d, 4a, 4b,* and *4c* have molecular weights, boiling points, and refractive indices corresponding essentially to those observed for Compound **H** (*tert*-butoxythiophenoxybutenes) (mol. wt. calc'd 236) which was isolated and characterized by analysis in experiment #2; although these fractions were not analyzed for carbon and hydrogen their constitution was established by using Raney nickel desulfurizations. Although the earlier fractions appear (from Raney nickel desulfurization) to contain small amounts of Compound **L** (bis-*tert*-butoxyoctadienes) these fractions and the later ones were substantially mixtures of the *tert*-butoxythiophenoxy-butenes, $(CH_3)_3COC_4H_6SC_6H_5$ (Compound L).

Raney nickel desulfurizations. The desulfurization experiments described below are representative of the treatment to which all the fractions were subjected.

To Fraction *2c*, b.p. 78–81°/0.03 mm., 8.1 g., was added eight teaspoonfuls of freshly prepared Raney nickel (5) and 15 ml. of redistilled water. An exothermic reaction ensued immediately. After the initial vigorous reaction subsided, the reaction mixture was refluxed for 3½ hours on a steam-bath. The reaction mixture then was steam-distilled and the oil layer (1.8 g.) in the steam-distillate was separated and dried over calcium chloride. The aqueous layer of the steam-distillate was extracted with ether, and the ether extract was washed with saturated sodium chloride, and finally dried over calcium chloride. The ether was removed from the dried ether extract by careful fractional distillation, and there remained, after removing the ether, a higher-boiling residue (1.6 g.). The residue from the ether extract was combined with the oil which had separated from the steam-distillate. The whole was distilled and the following fractions were collected: (*1*) 63–78°/atm. pressure, 0.6 g., n_D^{20} 1.3891; (*2*) 78–119°/atm. pressure, 0.6 g., n_D^{20} 1.3888; (*3*) 120–122°/atm. pressure, 0.7 g., n_D^{20} 1.3990; (*4*) 62–64°/0.01 mm., 0.2 g., n_D^{20} 1.4334; (*5*) 64–65°/0.01 mm., 0.5 g., n_D^{20} 1.4308. Fractions *1* and *2* were largely ethanol (introduced with the Raney nickel). Fraction *3*, 0.5199 g., which was assumed to be *tert*-butyl butenyl ether $[(CH_3)_3COC_4H_7]$ was hydrogenated in 5 ml. of ethanol in the presence of platinum oxide (0.0120 g.). Only 6.05 ml. (corrected) of hydrogen was absorbed, while 91.7 ml. should have been absorbed by *tert*-butyl butenyl ether. Apparently, almost complete hydrogenation of Fraction *3* occurred during the desulfurization treatment with Raney nickel. The completely hydrogenated Fraction *3* was recovered from the hydrogenation reaction by diluting with water (40 ml.), extracting with petroleum ether, washing the petroleum ether extract with water, drying the petroleum solution, and finally removing the petroleum ether by distillation. The residue, distilled at atmospheric pressure from an Emich microfractioning tube, boiled at 115–117° (uncorr.), n_D^{20} 1.3946. Norris and Rigby (6) report the following physical constants for *tert*-butyl n-butyl ether: b.p. 124° (corr.), n_D^{25} 1.3928. The distillate (0.2 g.) was heated with zinc chloride (0.15 g.) and 3,5-dinitrobenzoyl chloride (0.2 g.) at 110° for one hour, according to the procedure of Underwood (7). Upon working up this mixture, a material (0.33 g.) which melted at 61–65° was obtained. After two crystallizations of this substance from carbon tetrachloride-petroleum ether, the material (40 mg.) melted at 66–67°. This material did not depress the melting point of an authentic sample of the 3,5-dinitrobenzoate of *n*-butanol (m.p. 66–67°). These results establish the presence of the *n*-butoxy moiety in the original compound. The *tert*-butoxy moiety was shown to be present by treatment of another portion of the distillate with thioglycolic acid in the presence of hydrochloric acid (see below for method) and conversion of the S-*tert*-butylthioglycolic acid thus formed to the anilide (m.p. 79°). The melting point was not depressed when mixed with authentic anilide of S-*tert*-butylthioglycolic acid.

Fractions *4* and *5*, i.e. b.p. 62–64°/0.01 mm. and b.p. 64–65°/0.01 mm., were free of sulfur. Hydrogenation of these fractions indicated only a trace of unsaturation. These fractions were surmized to be the hydrogenated bis-*tert*-butoxyoctadienes (hydrogenated during the Raney nickel treatment). The physical constants of these fractions correspond to constants previously reported, *i.e.* b.p. 65°/0.1 mm., n_D^{20} 1.4301 (3).

Desulfurization of fractions 2d and 3b. Fraction *2d*, b.p. 82–83°/0.04 mm., n_D^{20} 1.5227, 5.6 g. and fraction *3b*, b.p. 90–92°/0.05 mm., n_D^{20} 1.5344, 4.4 g. were combined (10 g. in all) and treated with ten teaspoonfuls of Raney nickel and 35 ml. of redistilled water. The whole was heated on a steam-bath for six hours and then was steam-distilled. The steam-distillate was extracted with petroleum ether, the petroleum ether extract washed with water, dried, and the petroleum ether removed by distillation. A residue, 6.7 g., remained which gave the following fractions on distillation: (*1*) 76–80°/atm. pressure, 0.79 g.; (*2*) 81–105°/atm. pressure, 1.44 g., n_D^{20} 1.4039; (*3*) 120–124°, 1.7 g., n_D^{20} 1.4063; (*4*) 61–62°/0.01 mm., n_D^{20} 1.4368, 0.3 g. Fraction *3*, after hydrogenation, was treated with zinc chloride and 3,5-dinitrobenzoyl chloride, as described in the previous example, to give the 3,5-dinitrobenzoate of *n*-butanol, m.p. 66–67°. Fraction *4*, which contained no sulfur, was assumed from its boiling point and refractive index, to be partially hydrogenated bis-*tert*-butoxyoctadienes, small amounts of which were suspected to be present in Fraction *2d*. Fractions *1* and *2* were not investigated.

Desulfurization of fraction 3a. To Fraction *3a*, b.p. 88–89°/0.05 mm., n_D^{20} 1.5309, 7.31 g., was added five teaspoonfuls of freshly prepared Raney nickel and ten ml. of redistilled water and the whole was heated on a steam-bath for four hours. After the reaction mixture had cooled, it was extracted with petroleum ether, and the petroleum ether extract was washed with water, dried over calcium chloride, and finally the petroleum ether was removed by distillation. The residue, when distilled, gave the following fractions: (*1*) 54–102°, 0.5 g., n_D^{20} 1.4238; (*2*) 103–121°, 0.9 g., n_D^{20} 1.4289; (*3*) 121–122°, 1.2 g., n_D^{20} 1.4071; (*4*) 122°, 0.2 g., n_D^{20} 1.4068; (*5*) residue, 1.5 g., n_D^{20} 1.5267, contained sulfur by sodium fusion test and a *tert*-butoxy group by the Denige reagent test. Fraction *5* was thus probably unreacted starting material. It was not further investigated. All the fractions contained carbonylic material in small amounts as indicated by treatment with 2,4-dinitrophenyl hydrazine reagent. The dinitrophenyl hydrazone was shown by melting in admixture with an authentic sample to be the hydrazone of butyraldehyde (m.p. 124–125°). The formation of butyraldehyde during the desulfurization reaction will be discussed in a later section.

A portion of Fraction *3* (b.p. 121–122° g.) was treated with 5 ml. of 20% hydrochloric acid and the mixture was warmed at 60° for two hours under an efficient reflux condenser. The reaction mixture then was distilled and two fractions were collected: (*a*) 66–83°, gave a positive test for chlorine (copper wire test) and a positive test for the *tert*-butoxy group; (*b*) 85–100°, gave the same tests as fraction *a*. Fraction *a* was distilled giving as the main fraction a material which boiled at 47–55° (0.5 g.) which was assumed to be crude *tert*-butyl chloride and was accordingly treated with freshly distilled thioglycolic acid (1.5 g., b.p. 110–113°/20 mm.) and 30 ml. of 2 *N* hydrochloric acid. The whole was heated on a steam-bath for 17 hours, worked up as usual (3), and finally was distilled at 65–69°/0.005 mm. (0.65 g.). A neutral equivalent on this fraction indicated some contamination, probably with dithioglycolide. This was removed by shaking the samples with cold alkali, ether, and finally acidification and extraction with ether. After drying and removal of the ether, there was obtained 0.3 g. of product, neut. equiv. 147, calculated for S-*tert*-butyl thioglycolic acid, $C_6H_{12}SO_2$, neut. equiv. 148. The sodium salt obtained from the neutral equivalent determination was heated with aniline (1.0 g.) and conc'd hydrochloric acid (0.3 ml.) at 150–160° for one hour. The anilide thus formed was worked up in the usual manner (3) to give a solid m.p. 77–79° (0.1 g.) which after crystallization from ligroin melted at 79°. The melting point was not depressed by admixture with authentic sample of the anilide of S-*tert*-butyl thioglycolic acid (m.p. 80–81°). Fraction *3* was therefore considered to be *tert*-butyl butenyl ether.

Desulfurization of Fraction 3c. To Fraction *3c* (b.p. 93–95°/0.05 mm., n_D^{20} 1.5374, 10.4 g.) was added freshly prepared Raney nickel (five teaspoonfuls) and absolute ethanol (2 ml.). The reaction mixture was refluxed on a steam-bath for five hours and then was steam-distilled. The steam-distillate was extracted with petroleum ether, and the petroleum ether extract was washed several times with water, dried over calcium chloride, and finally the petroleum ether was removed by careful distillation. The residue (4.0 g.) upon distillation gave the following fractions: (*1*) 79–98°, 0.4 g., n_{D}^{20} 1.4382; (*2*) 101–114°, 0.6 g., n_{D}^{20} 1.4359; (*3*) 115–121°, 0.8 g., n_{D}^{20} 1.4098; (*4*) 121–122°, 1.7 g., n_{D}^{20} 1.4004. Each of these fractions gave a positive qualitative test for carbonylic compound when treated with 2,4-dinitrophenylhydrazine reagent. In order to identify the carbonyllic contaminant, a portion (0.1 g.) of fraction *4* was treated with 2,4-dinitrophenylhydrazine reagent. A solid separated which melted at 105–111°. After several crystallizations from ethanol the hydrazone melted at 119–120°. When mixed with a known sample of the 2,4-dinitrophenylhydrazone of butyraldehyde (m.p. 120–121°) the mixture melted at 119–120°. The formation of aldehydes during reductive treatment of allylic ethers appears quite common. It has been observed in this laboratory that hydrogenation of *tert*-butyl allyl ether with Adams catalyst and hydrogen in ethanol gave propionaldehyde (35%). Also, treatment of diallyl ether with Raney nickel in ethanol gave propionaldehyde. The formation of butyraldehyde during the desulfurization reaction is therefore indicative of the presence of the group $-CH_2-CH=CH-CH_2OR$ in the compound(s) making up fraction *3c*. The cryoscopic molecular weight (in benzene) for fraction *4* was 132, calc'd for *tert*-butyl butenyl ether, $C_8H_{16}O$, 128. The hydrogenation equivalent on Fraction *4* was 145, calc'd for $C_8H_{16}O$, 128. The high hydrogenation equivalent may be due to partial hydrogenation of Fraction *4* during the desulfurization.

Another portion of Fraction *4* when treated with thioglycolic acid and 2 *M* hydrochloric acid (as described in the previous section) gave the S-*tert*-butyl thioglycolic acid anilide derivative of correct melting point and mixture melting point.

Desulfurization of Fraction 4b. Fraction *4b*, b.p. 89–90°/0.02 mm., n_{D}^{20} 1.5410 (9.1 g.) was treated with Raney nickel (eight teaspoonfuls) and 15 ml. of water and the whole was refluxed for four hours. The reaction mixture was steam-distilled and the steam-distillate was extracted with petroleum ether, the extract dried, and the petroleum ether removed by distillation. The residue (a few drops) when treated with 2,4-dinitrophenylhydrazine deposited yellow crystals which melted at 105–107°. After three recrystallizations from ethanol the material melted at 119–120°, and no depression was noted by admixture with an authentic sample of the 2,4-dinitrophenylhydrazone of butyraldehyde.

The reaction of n-propylmercaptan, tert-butyl hydroperoxide, and butadiene in the presence of ferrous ammonium sulfate (Exp. 4). The procedure used for carrying out the reaction was the same as that described in the general procedure. The amounts of reagents used are shown in Table II. The *n*-propyl mercaptan was distilled prior to use (b.p. 67–68°). The *tert*-butyl hydroperoxide used was of high titer (98–99%). The aqueous solution of ferrous ammonium sulfate was added dropwise (82.1 g. of the salt in 245 ml. of redistilled water) over a period of about three hours. The petroleum ether extract was tested for unused mercaptan and hydroperoxide. The hydroperoxide test was negative. Titration of an aliquot of the petroleum ether extract (using excess silver nitrate and back titrating with potassium thiocyanate) indicated that the petroleum ether contained 1.7 g. (4.5%) of unused *n*-propyl mercaptan. After removal of the bulk of the petroleum ether by distillation at atmospheric pressure and the last traces at water pump pressure at 55°, there remained a nearly colorless oil (79.4 g.). The oil was distilled (rapidly) at reduced pressure and the following fractions were collected: (*1*) 53–67°/0.008–0.5 mm., 8.65 g.; (*2*) 68–74°/0.01–0.5 mm., 14.6 g.; (*3*) 74–57°/0.5–0.02 mm., 39.5 g.; (*4*) 57°/0.02 mm., 5.2 g.; (*5*) 63–81°/0.02 mm., 8.4 g., n_{D}^{20} 1.4831, mol. wt. 224; (*6*) residue, 1.0 g.; (*7*) low boilers (caught in Dry Ice trap), 2.01 g., n_{D}^{20} 1.4625. Since the pressure did not remain constant during part of the distillation fractions *1*, *2*, *3*, and *4* (total 67.9 g.) were combined and redistilled through a small Fenske column (16 in. long). The fractions collected were: (*R1*) 36–38°/0.1 mm., 1.3 g., n_{D}^{20} 1.4578, mol. wt. 197; (*R2*) 42–46°/0.12 mm., 0.8 g., n_{D}^{20} 1.538, mol. wt. 200; (*R3*) 41–44°/0.1 mm., 9.9 g., n_{D}^{20} 1.4609, mol. wt. 199; (*R4*) 45–47°/0.12 mm., 2.3 g., n_{D}^{20} 1.4570, mol. wt. 217; (*R5*) 45–48°/0.05 mm., 4.3 g., n_{D}^{20} 1.4599, mol. wt. 208; (*R6*) 45–48°/0.03 mm., 4.8 g., n_{D}^{20} 1.4703, mol. wt. 201; (*R7*) 51°/0.05 mm., 0.1 g.; (*R8*) 54–55°/0.07 mm., 10.7 g., n_{D}^{20} 1.4694, mol. wt. 201; (*R9*) 47–48°/0.05 mm., 10.7 g.,

n_D^{20} 1.4719, mol. wt. 199; (*R10*) 54–55°/0.07 mm., 7.1 g., n_D^{20} 1.4720, mol. wt. 199; (*R11*) Residue, 9.3 g., n_D^{20} 1.4792; (*R12*) low boilers (caught in Dry Ice trap) 2.9 g., n_D^{20} 1.4681.

Fraction *R11* (the residue) was distilled from a flask fitted with a take-off head for cutting fractions (but with no column): (*R11a*) 68°/0.04 mm., 2.9 g., n_D^{20} 1.4782, mol. wt. 213; (*R11b*) 68–69°/0.05 mm., 1.2 g., n_D^{20} 1.4790, mol. wt. 205; (*R11c*) 70–73°/0.06 mm., 2.0 g., n_D^{20} 1.4816, mol. wt. 202; (*R11d*) 81°/0.11 mm., 0.70 g., n_D^{20} 1.4863, mol. wt. 216; (*R11e*) residue, 1.1 g., n_D^{20} 1.4917.

The two low-boiling fractions caught in the Dry-Ice traps, i.e. fraction *7* and fraction *R12*, were combined and distilled at 20 mm. The major fraction distilled from 68–72°/20 mm. n_D^{20} 1.4602. This distillate was assumed to be largely *n*-propyl butenyl thioether (n-$C_3H_7SC_4H_7$) contaminated with *tert*-butoxy-*n*-thiopropoxy-butenes. An authentic sample of $CH_3CH_2CH_2SC_4H_7$, prepared from butadiene and *n*-propyl mercaptan, boiled at 67–74°/19 mm. (n_D^{20} 1.4751–1.4773).

Fraction *5* (b.p. 63–81°/0.02 mm., n_D^{20} 1.4831) was surmized from its boiling point, refractive index, and molecular weight to be a mixture of the di-thioether, n-$C_3H_7SC_4H_6SC_3H_7$-n, and the bis-*tert*-butoxyoctadienes (*tert*-$BuOC_4H_6C_4H_6O$-*tert*-Bu). Bis-1,4-*n*-thiopropoxy-2-butene (n-$C_3H_7SCH_2CH{=}CHCH_2SC_3H_7$-$n$), prepared from the sodium salt of *n*-propyl mercaptan and 1,4-dibromo-2-butene had the following properties: b.p. 70–71°/0.04 mm., n_D^{20} 1.5138, mol. wt. found 202, calc'd for $C_{10}H_{20}S_2$, 204. That fraction *5* was actually made up of the mixture assumed above was shown by desulfurization experiments. To Fraction *5* (7.8 g.) was added Raney nickel (four teaspoonfuls) in 20 ml. of ethanol and 10 ml. of distilled water. The whole was heated on a steam-bath for four hours and the gas (1200 ml., corrected) (presumably a mixture of propene and butene) evolved was collected over saturated sodium chloride. The reaction mixture was steam-distilled, the steam-distillate was extracted with petroleum ether. The petroleum ether extract was washed with water, and then dried over calcium chloride. After removal of the petroleum ether by distillation, there remained a residue (2.0 g.). The residue did not distill at atmospheric pressure. At water pump pressure (19 mm.) there was collected in a Dry Ice trap 0.3 g. of material (n_D^{20} 1.4062). In order to distill the bulk of the residue it was necessary to reduce the pressure to 0.01 mm. At that pressure the following fractions were collected: (*1*) 61–63°/0.01 mm., 0.5 g., n_D^{20} 1.4360; (*2*) 64–73°/0.01 mm., 0.7 g., n_D^{20} 1.4376. Neither of these fractions contained sulfur; from the boiling point, refractive index, and absence of sulfur it was assumed that these fractions were bis-*tert*-butoxyoctadienes. The 0.3 g. of material (n_D^{20} 1.4062) caught in the Dry-Ice trap may have been *tert*-butyl butenyl ether. The isolation, after desulfurization, of bis-*tert*-butoxyoctadienes, and the evolution of gas but isolation of essentially no *tert*-butyl butenyl ether indicate the original fraction was made up of bis-thiopropoxy-butene and bis-*tert*-butoxyoctadienes.

Fractions *R1* to *R10* inclusive had molecular weights (cryoscopic in benzene, see above for values) corresponding to those calculated for the *tert*-butoxy-*n*-thiopropoxybutenes (*cis* and *trans* 1,4- and 1-*tert*-butoxy-2-thiopropoxy-1-butene), $(CH_3)_3COC_4H_6SC_3H_7$ (mol. wt. calc'd for $C_{11}H_{22}OS$, 202). Representative fractions were desulfurized with Raney nickel in order to establish their identity.

Desulfurization of Fraction R3. To fraction *R3* (b.p. 41–44°/0.1 mm., n_D^{20} 1.4609, 8.84 g.), contained in a flask provided with a nitrogen inlet tube, was added Raney nickel (five teaspoonfuls), ethanol (10 ml.), and redistilled water (10 ml.). The whole was refluxed for four hours and the gas (1000 ml., corrected) evolved during the reaction was collected over saturated sodium chloride solution. After the heating period the apparatus was flushed with nitrogen gas and the displaced gas was collected in the same vessel as the gas evolved during the reaction. The gas, after removal of the nitrogen, had a molecular weight of 43 (calculated for propane, C_3H_8, 44).

The reaction mixture from the desulfurization was steam-distilled, the steam-distillate was extracted with petroleum ether, and the petroleum ether extract was washed with water and dried over calcium chloride. The petroleum ether was removed by distillation leaving a residual oil which was distilled and the following fractions were collected: (*1*) 119–125°, n_D^{20} 1.4034, 0.2 g.; (*2*) 127–133°, n_D^{20} 1.4095, 0.9 g.; (*3*) 135–137°, n_D^{20} 1.4127, 1.6 g.; (*4*) residue, n_D^{20} 1.4459, 2.1 g. Fraction *4*, the residue, gave a positive test for sulfur (sodium fusion). That it was undesulfurized starting material was shown by distillation of this material (b.p. 45–47°/0.02 mm., n_D^{20} 1.4542). Fractions *1*, *2*, and *3* were shown to contain *tert*-butyl butenyl ether by the methods described in the section on the thiophenol adducts. The higher boiling point of Fractions *2* and *3* here recorded for *tert*-butyl butenyl ether is undoubtedly due to "entrainment" by the high-boiling residue of the undesulfurized material.

Desulfurization of Fraction R8. To fraction *R8* (b.p. 54–55°/0.07 mm., n_D^{20} 1.4694, 10.3 g.) was added Raney nickel (4½ teaspoonfuls) and absolute ethanol (10 ml.). Provision was made to collect evolved gases. The reaction mixture was refluxed on a steam-bath for four hours during which time gas (1300 ml., corrected) was evolved. The gas had a molecular weight of 43.6; calc'd for C_3H_8, 44. After the heating period the reaction mixture was steam-distilled, and the steam-distillate was extracted with petroleum ether. The petroleum ether extract was worked up in the usual fashion and finally the petroleum ether was removed by careful distillation at atmospheric pressure. The residue upon distillation gave the following fractions: (*1*) 92–117°, 0.3 g., n_D^{20} 1.3971; (*2*) 117–121°, 0.1 g., n_D^{20} 1.4050; (*3*) 122–124°, 1.5 g., n_D^{20} 1.4059; (*4*) 125–127°, 2.6 g., n_D^{20} 1.4077; (*5*) residue, 0.8 g., n_D^{20} 1.4366. Fractions *1*, *3*, and *4*, when treated with 2,4-dinitrophenyl hydrazine reagent, deposited small amounts of 2,4-dinitrophenyl hydrazone of butyraldehyde (m.p. 120° after several recrystallizations from ethanol). These fractions were assumed to be *tert*-butyl butenyl ether (b.p. 125–127°, n_D^{20} 1.4077). Upon hydrogenation of these fractions (1.4452 g.) in the presence of platinum oxide (0.0615 g.) and absolute ethanol (10 ml.) 123.7 ml. of hydrogen gas (corrected for catalyst and STP) was absorbed (hydrogenation equivalent 262; calculated for *tert*-butyl butenyl ether, $C_8H_{16}O$, 128). The high observed hydrogenation equivalent indicates some hydrogenation had occurred during the desulfurization reaction. The hydrogenated product was recovered (after removal of the catalyst) by pouring the reaction mixture into water. The whole then was extracted with petroleum ether (b.p. 35°), and the petroleum ether extract washed with water. The petroleum ether solution then was dried over calcium chloride, and the petroleum ether was removed by distillation. The residue then was distilled and the major fraction (1.2 g.) was collected at 119–122°, n_D^{20} 1.3956. *tert*-Butyl *n*-butyl ether (see earlier section) boils at 123° (n_D^{25} 1.3928, n_D^{20} 1.3952).

Fractions *R11a*, *R11b*, *R11c*, *R11d* were not investigated. From the boiling points, refractive indices and molecular weights of these fractions it was assumed that they were mixtures of $C_3H_7SC_4H_6SC_3H_7$ and bis-*tert*-butoxyoctadienes (see Fraction *5*, of original distillation above).

The reaction of tert-butyl mercaptan with tert-butyl hydroperoxide in the presence of butadiene and ferrous ammonium sulfate (*Exp. 5*). In contrast to the results of the experiments with thiophenol and *n*-propyl mercaptan, the major product formed, when *tert*-butyl mercaptan was used, was bis-*tert*-butoxyoctadiene ("dimer"), rather than the *tert*-butoxythioalkoxybutenes. The extremely slow rate of oxidation of *tert*-butyl mercaptan by ferric ion to produce mercaptyl radicals and to regenerate ferrous ion is responsible for the observed results (*i.e.* low mercaptan consumption, low conversion to products when small amounts (<60%) of ferrous ammonium sulfate were used).

The amounts of reagents used are shown in Table II. The ferrous ammonium sulfate (60 mole-%) was added over a period of 16 hours and the reaction mixture was worked up in the manner indicated in the general procedure. The petroleum ether distillate was shown by titration with silver nitrate to contain 0.144 mole (72%) *tert*-butyl mercaptan (unused). The residue remaining after removal of the last traces of petroleum ether at 10 mm. pressure and 90° weighed 12.5 g. The residue was distilled and the following fractions were collected: (*1*) 43–58°/0.02 mm., 0.5 g., n_D^{20} 1.4408; (*2*) 59–62°/0.02 mm., 2.0 g., n_D^{20} 1.4438; (*3*) 63°/0.02 mm., 4.2 g., n_D^{20} 1.4482; (*4*) 78–82°/0.02 mm., 2.7 g., n_D^{20} 1.4534; (*5*) residue, 2.1 g.

Fractions *1* and *2* were combined and redistilled to give the following fractions: (*2a*) 49–52°/0.01 mm., 1.1 g., mol. wt. 215.7, n_D^{20} 1.4460; (*2b*) 55.5–56°/0.015 mm., 0.5 g., n_D^{20} 1.4457; (*2c*) 59–61°/0.015 mm., 0.3 g., n_D^{20} 1.4472.

Fractions *3* and *4* were combined and redistilled: (*4a*) 61–63°/0.003 mm., 1.5 g., n_D^{20} 1.4478, mol. wt. 238.4; (*4b*) 63°/0.01 mm., 2.9 g., n_D^{20} 1.4494, mol. wt. 240.6; (*4c*) 66.5–68°/0.01 mm., 1.6 g., n_D^{20} 1.4523, mol. wt. 243.0; (*4d*) 68°/0.01 mm., 0.2 g., n_D^{20} 1.4528; (*4e*) residue, 0.3 g.

Fraction *5*, the residue, 2.1 g., was distilled from a molecular still (10^{-5} mm.) at 45° to give a distillate, mol. wt. 249.8.

Fraction *2a*, b.p. 48–52°/0.01 mm., n_D^{20} 1.4460, mol. wt. 215.7 was surmized to be *tert*-butoxy-*tert*-thiobutoxy butene, $(CH_3)_3COC_4H_6SC(CH_3)_3$, $C_{12}H_{24}SO$, mol. wt. calc'd 216. It was, therefore, desulfurized with Raney nickel in the usual fashion. During the treatment with Raney nickel 1000 ml. of gas (mol. wt. 55) was evolved. The gas, since it was not absorbed by sulfuric acid containing nickel sulfate and silver sulfate, was a saturated hydrocarbon, presumably isobutane, calc'd for C_4H_{10}, mol. wt. 58. In view of the small amount of sample desulfurized no attempt was made to isolate products other than the gas.

Fraction *4a*, b.p. 61–63°/0.003 mm., was treated with Raney nickel in the usual fashion. A small amount of gas was evolved (mol. wt. 54.2, contained no unsaturation) and, after working up the reaction mixture, there was obtained a residue corresponding to 75% of the weight of the starting product. The residue, bis-*tert*-butoxyoctadiene (partially hydrogenated), was distilled at 65–75°/0.05 mm., n_D^{20} 1.4278.

Fractions *4b* and *4c* were combined and treated with Raney nickel. From the reaction with Raney nickel was recovered essentially the same weight of product as charged. This was partially hydrogenated bis-*tert*-butoxyoctadiene and it was distilled as follows: 63–70°/0.01 mm., n_D^{20} 1.4279.

Fraction *5*, from its molecular weight and boiling point, was assumed to be bis-*tert*-butoxyoctadienes.

SUMMARY

1. The reactions of mercaptans with styrene and with butadiene in the presence of an oxidant at 5° (and below) and at 30° have been investigated.

2. It has been established that the following principal types of compounds are formed when a ferrous salt is added to a mixture of butadiene, *tert*-butyl hydroperoxide, and a mercaptan, maintained at −10°: (*a*) $(CH_3)_3COC_4H_6SR$; (*b*) RSC_4H_6SR; (*c*) $(CH_3)_3CO(C_4H_6)_2OC(CH_3)_3$.

3. It is suggested that "modification" by mercaptans at 50° takes place in the following manner: $R(M)_n\cdot + RSH \rightarrow R(M)_nH + \cdot SR$, whereas, at −10° "modification" takes place by "dimerization", $R(M)_n\cdot + \cdot SR \rightarrow R(M)_nSR$.

4. Synthetic routes for the preparation of a number of new compounds are described.

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