

Organic Sulfur Compounds. XII. Factors Determining a 1,2- vs. 1,4-Mechanism of Radical Reactions of Conjugated Diolefins. Co-oxidation with Thiols by Oxygen

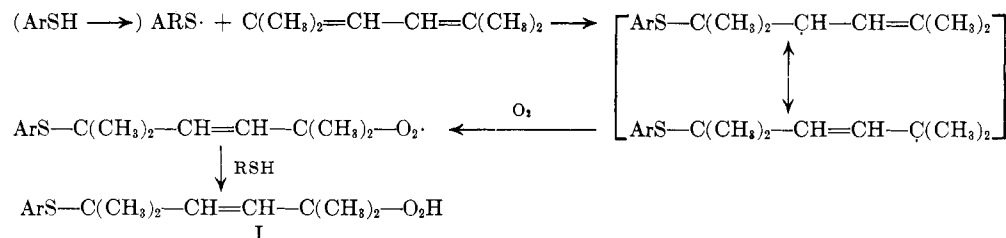
ALEXIS A. OSWALD,¹ KARL GRIESBAUM,¹ AND B. E. HUDSON, JR.¹

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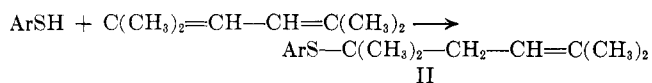
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Co-oxidation of thiols and conjugated diolefins by molecular oxygen *via* a chain mechanism has been studied to find possible correlations between the diene structure and the course (1,2- or 1,4-mechanism) of the reaction. 1,3-Butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, and simple aromatic and aliphatic thiols were used as reactants. The first propagation step in each case is the addition of a mercapto radical to one end of the conjugated system to form an allylic radical intermediate. In the second propagation step, this radical, we have found, then combines with oxygen at the more highly substituted allylic carbon atom to form a peroxy radical. The last propagation step is the abstraction of a hydrogen from the thiol by the peroxy radical to form an allylic hydroperoxide. In the presence of an alkylamine catalyst the latter is reduced *in situ* by an excess of the thiol to the more stable alcohol. The combination of an allylic radical with oxygen at the more highly substituted allylic carbon atom in the co-oxidation reaction is in contrast with the hydrogen abstraction from a thiol. In the latter case, the same allylic radical reacts at the less highly substituted allylic carbon atom in the addition reaction of thiols to conjugated dienes. This indicates that the 1,2- vs. 1,4-mechanism of radical reactions of conjugated diolefins is determined mainly by the activation energy of the reaction of the allylic radical intermediates. In combination reactions, which have negligible activation energies, reaction occurs with a minimum reorganization of the structure of the allylic radical. In abstraction reactions, which have significant activation energies, reaction occurs with reorganization of the allylic radical structure in the transition state to form the thermodynamically more stable product.

A previous paper of this series² reported that 2,5-dimethyl-2,4-hexadiene, a conjugated diolefin, is readily co-oxidized with aromatic thiols by molecular oxygen at 0° to yield crystalline 5-arylmercapto-2,5-dimethyl-3-hexen-2-yl hydroperoxides (I) by a radical type "1,4-mechanism."

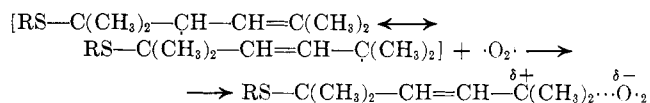


However, the same thiols and diolefin yielded, in the absence of oxygen, mainly the 1,2-adducts (II).



A systematic study was initiated in this laboratory to ascertain what factors determine whether diolefins react by a 1,2- or 1,4-mechanism. In the first phase of this study, the radical addition of thiols to various conjugated diolefins was examined.³ It was proposed that as a consequence of the significant activation energy,⁴ the hydrogen abstraction from the thiol occurs at the less highly substituted of the two reaction centers of the intermediate allylic radical. However, in radical combination reactions with oxygen, which have no significant activation energy,⁵⁻⁷ the reaction was thought to occur at the more substituted (or more stable) carbon

atom of the intermediate allylic radical. In the case of alkyl substitution, this alkylated allylic carbon atom is also the more electron-rich one. Therefore, the attack of the oxygen diradical to form a sort of an ion pair in the transition state is more likely to occur at that carbon.



Consequently, it was expected that co-oxidation reactions of thiols and conjugated diolefins would take a course opposite to that of addition reactions.

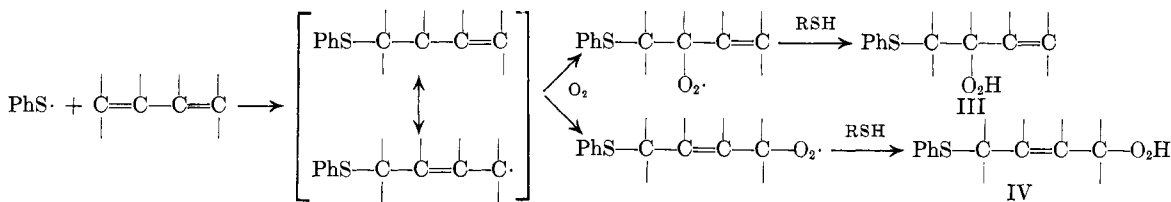
This paper describes the results of such thiol-diolefin co-oxidation studies using simple aromatic and aliphatic thiols in reactions with 2,3-dimethyl-1,3-butadiene, isoprene, and 1,3-butadiene. These reactions were carried out in the liquid phase at room temperature with or without solvents. Pure molecular oxygen at atmospheric pressure was used as the oxidant.

Elemental analysis (Tables I and IV), nuclear magnetic resonance (Tables II and V), and infrared absorption spectroscopy (Table III) were used to establish the structures of the hydroperoxide co-oxidation products and the corresponding alcohol reduction products.

Results

Exploratory experiments were carried out in *n*-heptane containing benzenethiol and a diolefin, each in 0.3 mole/l. concentration, to see whether the thiol-diene co-oxidation reaction could be generalized. Furthermore, an investigation of the products was planned

- (1) Esso Research Center, P. O. Box 45, Linden, N. J.
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to determine whether the reaction occurred by a 1,2- and/or 1,4-mechanism (see above).

Oxygen was bubbled into the stirred co-oxidation mixture, while the temperature was kept below 5° by ice-water cooling. The reaction occurred readily without external initiation under these conditions. Within a few hours, a heavy, colorless oil separated. This oil

had 50–90% of the hydroperoxide content expected for III or IV.

N.m.r. spectra showed that the products of benzenethiol co-oxidation with 2,3-dimethyl-1,3-butadiene, isoprene, and 1,3-butadiene had structures of type III as indicated by the signals of the terminal vinyl protons. Infrared absorption peaks, characteristic of terminal vinylic unsaturation, supported the n.m.r. evidence. This suggested that 1,3-butadienes with internal (2,3-) substitution are co-oxidized with thiols by a 1,2-mechanism. This is in contrast to the 1,4-co-oxidation of a terminally (1,4-) substituted butadiene, namely 2,5-dimethyl-2,4-hexadiene (1,1,4,4-tetramethyl-1,3-butadiene).

However, the liquid hydroperoxides derived from the internally substituted diolefins could not be obtained in a pure state in contrast to the crystalline hydroperoxides from 2,5-dimethyl-2,4-hexadiene which were reported earlier.² These oils were unstable at room temperature. Infrared spectra indicated the formation of carbonyl groups. Attempts at purification were unsuccessful. Consequently, we decided to convert these hydroperoxides into the corresponding alcohols by reduction through hydroperoxide-amine complex intermediates.^{8,9} Such a reduction is illustrated by the following equations.

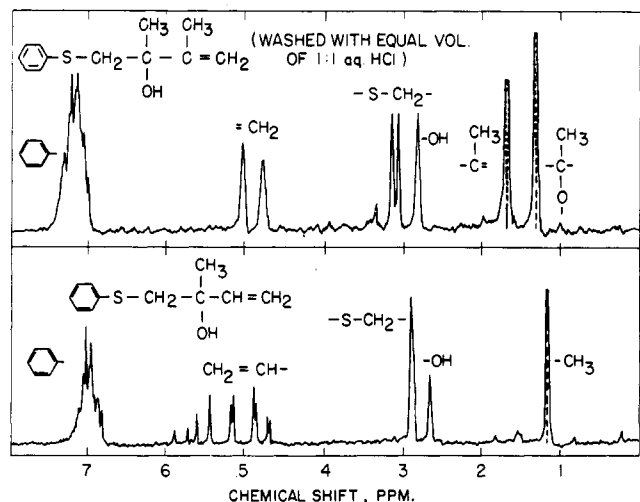


Fig. 1.—Proton n.m.r. spectra of alcohols of co-oxidation of benzenethiol with 2,3-dimethyl-1,3-butadiene and isoprene.

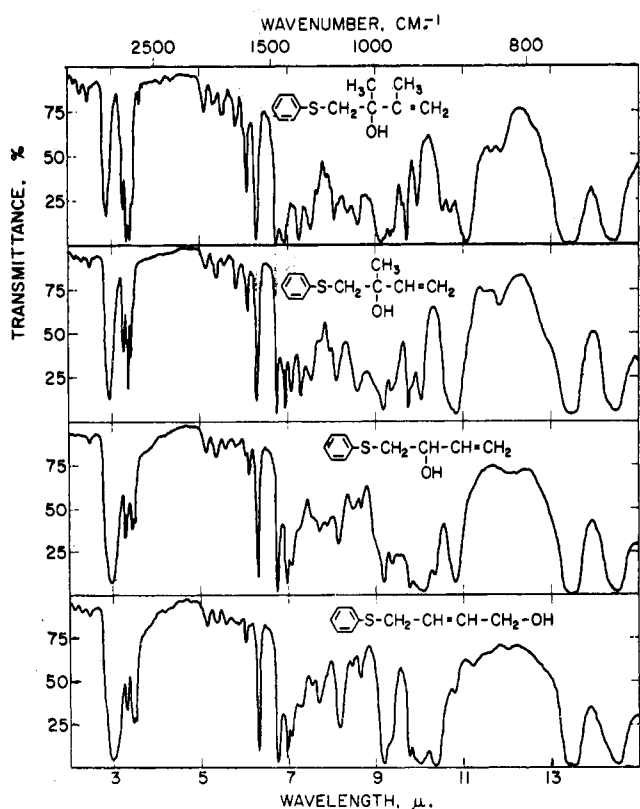
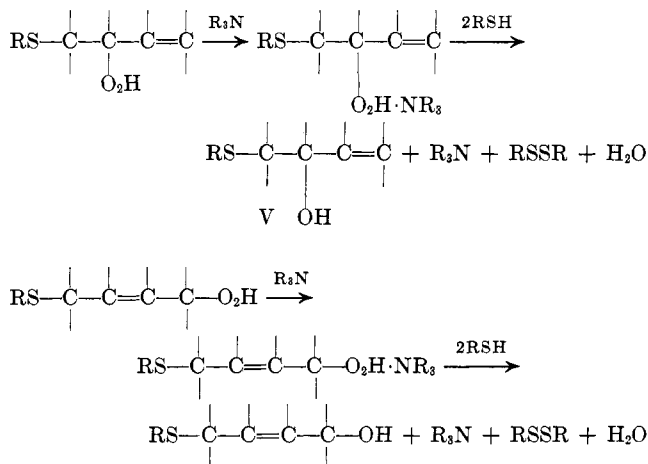


Fig. 2.—Infrared spectra of alcohols of benzenethiol-diene co-oxidation.

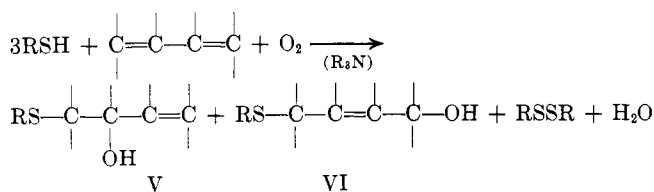


A reduction procedure for the hydroperoxides from thiol-2,5-dimethyl-2,4-hexadiene co-oxidation was reported in the previous paper of this series.¹⁰ Alkylamines could be used as catalysts for such reductions of hydroperoxides by thiols. When solutions containing a thiol and a conjugated diolefin were oxygenated in the presence of an aliphatic amine, co-oxidation and reduction of the hydroperoxides by the unchanged thiol to the corresponding alcohols (V, VI) occurred simultaneously.

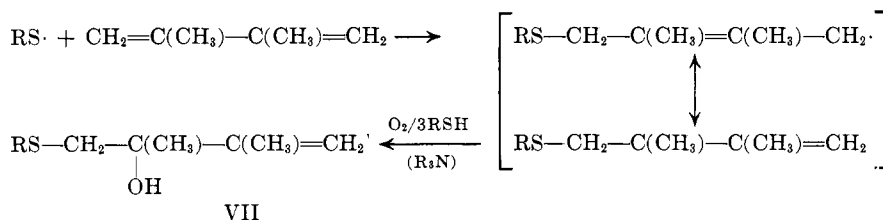
(8) A. A. Oswald, F. Noel, and A. J. Stephenson, *J. Org. Chem.*, **26**, 3969 (1961).

(9) A. A. Oswald, F. Noel, and G. Fisk, *ibid.*, **26**, 3974 (1961).

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2,3-Dimethyl-1,3-butadiene.—The one-pot co-oxidation and reduction reaction of thiols and 2,3-dimethyl-1,3-butadiene took the following course. Capillary g.c. analysis of the distilled products (Table I) showed that in each case one of the two possible isomeric alcohols predominated.



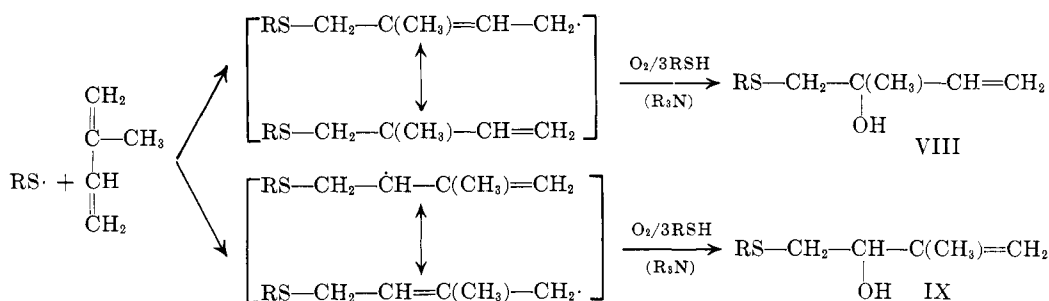
N.m.r. spectra (Table II and Fig. 1) showed that the products were 4-substituted mercapto-2,3-dimethyl-2-buten-3-ols (VII). The two vinyl protons of such alcohols produced separate singlet peaks because of their *cis* and *trans* locations with respect to substantially dissimilar substituents. The proton appearing at higher field showed some remote coupling¹¹ and, there-

up at about 8.7 μ .¹⁴ The higher wave length observed is probably due to the presence of α,β -unsaturation.¹⁵

From this it is apparent that the combination of the intermediate allylic radical occurred at the tertiary allylic carbon atom. A similar observation was made earlier for 2,5-dimethyl-2,4-hexadiene. However, while the tertiary carbons of the latter are at the two ends of the basic butadiene skeleton, 2,3-dimethyl-1,3-butadiene has its "inner" carbon atom substituted. This means that the co-oxidation reactions may take a 1,4- or 1,2-course depending on the structure of the conjugated diolefin.

Isoprene.—The co-oxidation of isoprene is a some-

what similar problem to that of 2,3-dimethyl-1,3-butadiene since both compounds can be regarded as internally substituted butadienes. However, the unsymmetrical structure of isoprene can give rise to the formation of additional isomeric products; attack of the thiyl radical at carbon 1 *vs.* carbon 4 leads to different products.



fore, is located *trans* to the methyl group. The protons of the two methyl groups show up as two separate singlets, the signal at lower field originating from the methyl attached to the unsaturated carbon atom. The methylene group which is not spin coupled to other protons exhibits an AB-type quartet as is frequently the case for Q-CH₂-C(XYZ) structures with free rotation of the-CH₂-bonds.¹²

The infrared spectra (Table III and Fig. 2) of the products also support the assumed structure VII. A very strong band at 11.1 μ and its overtone at 5.6 μ can be assigned to the out-of-plane deformation vibrations of the terminal vinyl hydrogens.¹³ A rather sharp peak at 2.95 μ and the appearance of a very strong band at 9.1 μ indicate that these compounds had a tertiary hydroxyl group. The strong band at 9.1 μ may be due to the CO stretching and OH deformation vibrations. The latter vibrations of tertiary alcohols usually show

The alcoholic products obtained from co-oxidations using various thiols were isolated by distillation *in vacuo*. Their examination by g.c. showed that in each case only one major product was present. The product of benzenethiol-isoprene co-oxidation could be isolated in a pure state. Distillates of aliphatic thiol-isoprene co-oxidation showed the presence of minor impurities.

N.m.r. spectra (Table II and Fig. 1) showed that the products were 4-substituted mercapto-3-methyl-2-buten-3-ols (VIII). The vinyl protons showed the characteristic multiplet pattern of an ABM spin system.¹⁶ Although the methylene group is attached to an asymmetric center, as was the case for co-oxidation products of 2,3-dimethyl-1,3-butadiene, it exhibits a singlet rather than an AB-type quartet. Evidently, either the conditions of unequal population of rotameric states and/or the conditions of unequal chemical shift for the geminal protons in the rotameric states is not met, or accidental averaging to $\delta = 0$ has occurred.

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(14) H. H. Zeiss and M. Tsutsui, *J. Am. Chem. Soc.*, **75**, 897 (1953).

(15) A. V. Stuart and G. B. B. M. Sutherland, *J. Chem. Phys.*, **24**, 559 (1956).

(16) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp. 241-245.

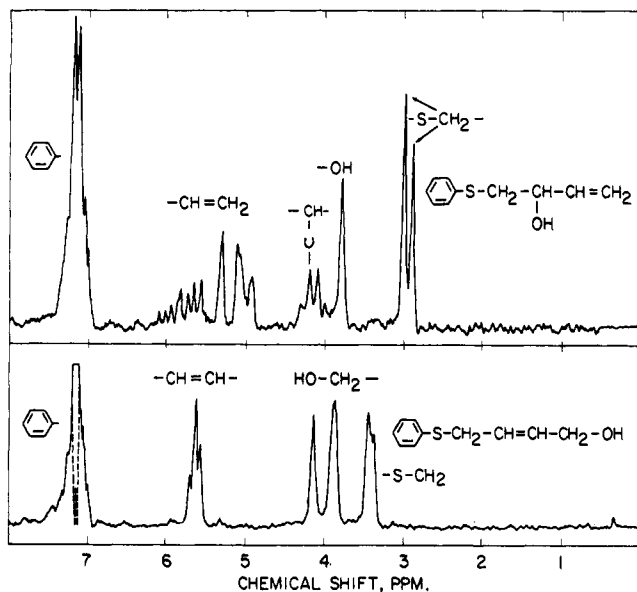
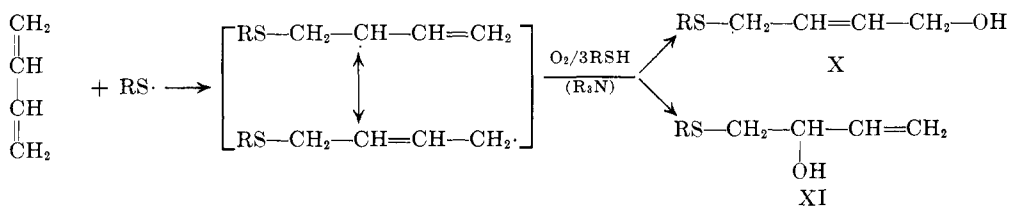


Fig. 3.—Proton n.m.r. spectra of alcohols of co-oxidation of benzenethiol with 1,3-butadiene.

Infrared spectra of the products (Table III and Fig. 2) also supported structure VIII. Strong absorption peaks at about 10.1 and 10.8 μ , with an overtone at about 5.4 μ , are clear indications of the presence of $-\text{CH}=\text{CH}_2$ groups.^{13b} The sharp peaks at 2.95 μ were assigned to the OH stretching vibrations of the tertiary hydroxyl group.^{13c} The presence of absorption at about 5.8 μ is probably due to the CO stretching vibrations of carbonyl compounds.^{13b} These impurities, which could be formed by decomposition of the hydroperoxides and oxidation of the alcohols, also were indicated by g.c.

1,3-Butadiene—On co-oxidation of thiols and butadiene in the presence of *t*-butylamine both alcohols (X and XI) were formed in major amounts by reduction of the hydroperoxides *in situ*. The boiling points of the primary 1,4-alcohols (X) were considerably higher than those of the corresponding secondary 1,2-isomers (XI) probably because of stronger hydrogen bonding of the former.^{13c} The isomeric products could be isolated by distillation *in vacuo* (Table IV).



N.m.r. spectra of the isomeric alcohols clearly showed the two types of structures (Table V and Fig. 3). The 1,2-alcohols all showed the characteristic multiplet pattern of an ABM spin system due to the $-\text{CH}=\text{CH}_2$ group.¹⁶

The vinyl protons of the 1,4-alcohol gave a narrow multiplet as did the two pairs of methylene groups in this isomer.

Infrared absorption spectra of the isomeric alcohols (Table III and Fig. 2) also showed characteristic differences. The 1,2-alcohols showed strong peaks at 10.1 and 10.8 μ , with an overtone at 5.4 μ which is

characteristic of the $-\text{CH}=\text{CH}_2$ group.^{13b} The 1,4-alcohols showed a stronger absorption peak at 10.3 μ than the 1,2-alcohols. This is probably due to the out of plane $-\text{CH}=\text{CH}_2$ deformation of the *trans*-1,4-alcohol.^{13d} It is assumed that most of the 1,4-co-oxidation products have *trans* structures. It is recalled that 1,4-addition of thiols to 1,3-butadiene also gives mostly *trans* products.^{3,17,18}

In view of the isolation of both 1,2- and 1,4-products it is apparent that in the co-oxidation of butadiene, the intermediate allylic radical apparently combined with oxygen at both the secondary and primary allylic carbon atoms. The difference in reactivity between these carbon atoms is expected to be less than that between the tertiary and primary carbon atoms of allylic radicals derived from 2,3-dimethyl-1,3-butadiene and isoprene. Nevertheless, the corresponding thiol-butadiene addition reactions take place in quite a selective manner to yield the 1,4-products.³ To explain this difference it is suggested that besides the activation energy of the reactions of intermediate allylic radicals, steric factors also influence the course of these reactions. These steric effects tend to increase the relative amount of 1,4-products of butadiene.

Discussion

The course of co-oxidation reactions of thiols and conjugated diolefins by molecular oxygen is evidently affected by the stability and structure of the intermediate allylic radical formed on thiol radical addition to the diene. In the first reversible propagation step, thiol radicals add selectively to the first carbon atom of unsymmetrically substituted butadienes so as to yield the more stable intermediate allylic radical. The latter then irreversibly combines with the oxygen diradical preferentially at the more highly substituted allylic carbon atom. The peroxy radical formed then abstracts hydrogen from the thiol to yield an olefinic hydroperoxide in the third propagation step.

Combination of the intermediate allylic radical with the more electrophilic oxygen at the more highly substituted position is favored by the higher electron density although it is sterically less favorable. It should be recalled that hydrogen abstraction from thiols by the

same allylic radical occurs preferentially at the less highly substituted C-4. We propose that this change of the reacting allylic position can be best explained by Hammond's correlation between the rates and free energies of chemical reactions.¹⁹ In contrast to the hydrogen abstraction reaction, the combination of an allylic radical with oxygen has no significant activation energy. Consequently, in the co-oxidation reaction, the transition state has a character resembling that of

(17) J. Longfield, R. Jones, and C. Sivertz, *Can. J. Res.*, **28B**, 373 (1950).

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TABLE I
SUBSTITUTED 4-MERCAPTO-1-BUTEN-3-OLS OF CO-OXIDATION OF THIOLS WITH 2,3-DIMETHYL-1,3-BUTADIENE AND ISOPRENE
 $R-S-CH_2-C(CH_3)=C(X)-CH_2-OH$

Diene	Co-oxidation product of Thiol	X	Adduct formula	Yield, ^a %	Conversion, ^b %	Product ^c purity	B.p., ^d °C. (1 mm.)	n _D ²⁰	Elemental analyses, %					
									Calcd.			Found		
									C	H	S	C	H	S
2,3-Dimethyl-1,3-butadiene	Methane	CH ₃	C ₇ H ₁₄ OS	27	45	87	43-45	57.49	9.64	21.93	57.43	9.60	22.05
	Ethane	CH ₃	C ₈ H ₁₆ OS	31	40	88	63-65	1.4908	59.95	10.06	20.01	59.82	9.92	19.90
	Benzene	CH ₃	C ₁₂ H ₁₆ OS	81	76	96	101-102	1.5602	69.21	7.74	15.37	69.42	7.60	15.45
Isoprene	4-Chlorobenzene	CH ₃	C ₁₂ H ₁₅ OS	71	100	97	109-110	1.5804	59.37	6.22	13.21	59.53	6.37	13.05
	Methane	H	C ₆ H ₁₂ OS	25	95	95	41-43	1.5016	54.51	9.14	24.25	54.23	9.07	24.13
	Ethane	H	C ₇ H ₁₄ OS	34	85	89	57-59	1.4928	57.49	9.64	21.93	57.18	9.52	22.05
	Benzene	H	C ₁₁ H ₁₄ OS	73	99	98	90-92	1.5720	67.99	7.26	16.50	67.78	7.15	16.73

^a Based on conversion. ^b On oxygenation of an *n*-heptane solution containing 0.9 mole/l. of thiol, 0.3 mole/l. of diene and 0.03 mole of *t*-butylamine. ^c As determined using a capillary g.c. unit. ^d Uncorrected.

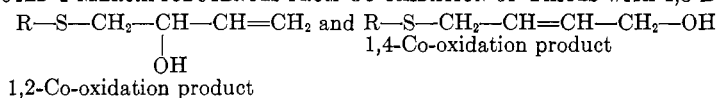
TABLE II
PROTON NUCLEAR MAGNETIC RESONANCE SPECTRA OF PRODUCTS OF THIOL CO-OXIDATION WITH 2,3-DIMETHYL-1,3-BUTADIENE AND ISOPRENE

Diene	Starting compounds	Thiol	X	RS-	Chemical shifts of structural units, p.p.m., downfield from tetramethylsilane internal reference				
					s, singlet, t, triplet, q, quadruplet, m, multiplet	-CH ₂ -	-C(OH)-	-C(X)-	
2,3-Dimethyl-1,3-butadiene	Methanethiol	CH ₃	CH ₃	s 2.08	q 2.62 ^{a,b}	s 3.18	s 1.31	s 1.75	s 5.06, s 4.79 ^c
	Ethanethiol	CH ₃	CH ₃	t 1.18, ^d q 2.50 ^d	q 2.68 ^{a,e}	s 3.15	s 1.28	s 1.73	s 5.05, s 4.80 ^c
	Benzenethiol	CH ₃	CH ₃	m 6.8-7.4	q 3.12 ^{a,f}	s 3.50	s 1.32	s 1.72	s 4.95, s 4.75 ^c
Isoprene	4-Chlorobenzenethiol	CH ₃	CH ₃	s 7.0	q 3.10 ^{a,g}	s 3.20	s 1.30	s 1.68	s 5.0, s 4.60 ^c
	Methanethiol	H	H	2.11	s 2.65	s 3.42	s 1.30	m 4.8-5.5 ^h	m 5.7-6.3 ⁱ
	Ethanethiol	H	H	t 1.20, ^d q 2.55 ^d	s 2.68	s 3.30	s 1.28	m 4.8-5.5 ^h	m 5.7-6.3 ⁱ
	Benzenethiol	H	H	m 6.8-7.4	s 3.05	s 2.60	s 1.30	m 4.6-5.3 ^h	m 5.4-5.8 ⁱ

^a AB type, *J* = 12.5 c.p.s. ^b δ_{AB} = 0.25 p.p.m. ^c This hydrogen is probably *trans* to the methyl group; the remote coupling constant is 2 c.p.s. ^d *J* = 7 c.p.s. ^e δ_{AB} = 0.27 p.p.m. ^f δ_{AB} = 0.25 p.p.m. ^g δ_{AB} = 0.13 p.p.m. ^h Four peaks, M portion of an ABM spin system, *J* = 10 c.p.s. and 17 c.p.s. ⁱ AB portion of an ABM spin system, *J*_{AB} = 2 c.p.s.

TABLE III
 INFRARED ABSORPTION SPECTRA OF ALCOHOLS OF THIOL-DIENE CO-OXIDATION

Compounds			Characteristic absorption peaks, μ :				
Co-oxidation product of		Isomer type	OH and =C-H stretching region		Over tone	C=C stretching region	
Diene	Thiol					Olefinic	Aromatic
2,3-Dimethyl-1,3-butadiene	Benzenethiol	1,2	2.9 s, 3.25 s			6.1 m	6.3 s, 6.7 vs
	4-Chlorobenzenethiol	1,2	2.9 s, 3.25 m			5.85 ms, 1 s	6.35 s, 6.75 vs
	Methanethiol	1,2	2.9 s, 3.2 m		5.5 vw	5.95 s, 6.1 s	
	Ethanethiol	1,2	2.9 s, 3.25 m		5.5 vw	5.9 m, 6.1 s	
Isoprene	Benzenethiol	1,2	2.9 s, 3.25 m			6.1 w	6.3 s, 6.7 vs
	Methanethiol	1,2	2.9 s, 3.25 m		5.4 vw	5.8 s, 6.1 m	
	Ethanethiol	1,2	2.9 s, 3.2 m		5.4 vw	5.8 w, 6.1 m	
1,3-Butadiene	Benzenethiol	1,2	2.95 s, 3.25 s			6.1 w	6.3 s, 6.75 vs
		1,4	3.0 s, 3.3 s			6.05 w	6.3 s, 6.75 vs
	4-Toluenethiol	1,2	2.95 vs, 3.25 s			6.1 m	6.2 m, 6.3 w, 6.7 vs
		1,4	3.0 vs, 3.3 s			6.1 w	6.2 s, 6.3 m, 6.7 vs
	Methanethiol	1,2	2.9 vs, 3.3 s		5.4 vw	5.9 vw, 6.1 m	
		1,4	3.0 vs, 3.35 i			6.1 m	
	Ethanethiol	1,2	3.0 vs, 3.2 s			5.8 m, 6.1 m	
	1,4	3.0 vs, 3.3 i			5.9 w, 6.0 m		

 TABLE IV
 SUBSTITUTED 4-MERCAPTOBUTENOLS FROM CO-OXIDATION OF THIOLS WITH 1,3-BUTADIENE


Co-oxidation product			Yield, %	Conversion, % in 24 hr.	Ultra-violet irradiation	Product purity, %	B.p., °C. (mm.)		Elemental analyses, %						
Starting	Formula	Type					°C. (mm.)	n_D^{20}	Calcd.			Found			
Methane	$\text{C}_8\text{H}_{10}\text{OS}$	1,2	51	42	95	Yes	91	35-36 (1)	1.5025	50.81	8.52	27.13	50.96	8.37	27.02
		1,4	49				95	60-62 (1)	1.5213				50.91	8.46	26.90
Ethane	$\text{C}_8\text{H}_{12}\text{OS}$	1,2	52	46	90	Yes	92	37-39 (1)	1.4959	54.50	9.15	24.25	54.36	9.19	24.03
		1,4	48				97	64-66 (1)	1.5124				54.70	9.40	24.09
Benzene	$\text{C}_{10}\text{H}_{12}\text{OS}$	1,2	73	83	90	No	99	107-108	1.5921	66.63	6.70	17.79	66.61	6.89	17.81
		1,4	27				97	125-127	1.6005				66.55	6.61	17.93
4-Toluene	$\text{C}_{11}\text{H}_{14}\text{OS}$	1,2	75	85	100	No	96	108-110	1.5829	68.00	7.26	16.51	67.92	7.23	16.64
		1,4	25				97	127-130	1.6036				67.86	7.17	16.45

^a Based on conversion. ^b On oxygenation of a *n*-heptane solution containing 0.9 mole/l. of thiol, 0.3 mole/l. of diene, and 0.03 mole/l. of *t*-butylamine. ^c As determined using a capillary g.c. unit. ^d Uncorrected.

the intermediate allylic radical and the product is derived with a minimum reorganization as the antipodal structure which more closely resembles the structure of the allylic radical.

Experimental

Materials and Methods.—The 1,3-butadiene used was a C.P. chemical of 99% minimum grade. 2,3-Dimethyl-1,3-butadiene from Houdry Corporation and isoprene from Eastman were redistilled before use. The thiols and the *t*-butylamine were C.P. chemicals. The oxygen used was of a 99.6% purity.

The oxygenations and analyses were carried out using methods described in the previous paper of this series.¹⁰

Co-oxidation of 2,3-Dimethyl-1,3-butadiene, Isoprene, and 1,3-Butadiene with Benzenethiol.—A solution of 0.1 mole of the diene

in about 330 ml. of *n*-heptane was cooled by a salt-ice bath and purged with oxygen. To the solution 11.0 g. (0.1 mole) of benzenethiol was added dropwise in an hour. Oxygenation of the solution with stirring was continued for about 5 hr. at or below 5°. By that time more than 80% of thiol was oxidized and a heavy, viscous phase was formed. This lower phase was purged for an hour with nitrogen at 0°, and then analyzed. The sulfur and hydroperoxide values were 80-95% of the theoretical for the corresponding phenylmercaptobutenyl hydroperoxides. N.m.r. and infrared spectra of these hydroperoxides showed the presence of terminal vinyl groups.

Co-oxidation of Aromatic Thiols and Conjugated Dienes in the Presence of *t*-Butylamine.—To an oxygenated and stirred solution of 0.11 mole of the diene and 0.7 g. (0.01 mole) of *t*-butylamine in 330 ml. of *n*-heptane, 0.3 mole of an aromatic thiol was added in the course of 3 hr. Oxygenation of the reaction mixture was continued for about a day to complete the reaction. The

TABLE III (Continued)

Fingerprint region (C—O stretching and —OH deformation included)		Characteristic absorption peaks, μ : vs, very strong, s, strong, m, medium, w, weak, i, inflection		=C—H deformation region	
		Olefinic		Aromatic and others	
8.0 s, 8.4 s, 8.6 s, 9.1 vs, 9.2 s, 9.7 s		10.0 s, 10.5 s, 10.7 s, 11.0 vs		11.8 w	13.4 vs, 14.5 vs
7.75 m, 8.1 s, 8.4 s, 8.6 s, 9.1 vs, 9.4 s, 9.65 s		9.9 vs, 10.5 s, 10.7 s, 11.1 vs		12.2 vs, 12.5 vs, 13.4 s	
8.0 s, 8.3 s, 8.6 s, 9.1 vs, 9.4 s, 9.65 s		10.0 s, 10.7 s, 11.1 vs		12.0 w, 13.0 m, 15.1 m	
7.9 s, 8.1 s, 8.4 s, 8.6 s, 9.2 vs, 9.4 s, 9.7 s		10.0 m, 10.6 s, 10.7 s, 11.1 vs		11.8 m, 12.6 m, 12.8 m	
8.1 s, 8.6 s, 9.1 s, 9.4 s, 9.7		10.0 s	10.8 vs	11.8 w	13.4 vs, 14.5 vs, 15.0 m
8.1 s, 8.6 s, 9.1 s, 9.4 s, 9.8 s		10.0 s	10.8 vs	11.9 m	12.6 m, 12.9 m, 14.6 s, 15.0 s
8.1 s, 8.6 s, 9.1 s, 9.4 s, 9.8 s		10.0 s	10.8 vs	11.8 w,	13.1 s, 14.5 s, 15.0 s
7.7 m, 8.15 s, 8.65 m, 9.2 vs, 9.4 s, 9.75 vs		10.0 vs, 10.3 s	10.8 vs		13.4 vs, 14.5 vs, 15.0 i
7.7 m, 8.15 s, 8.65 m, 9.2 vs, 9.4, 9.75 vs		10.0 vs, 10.3 vs			13.4 vs, 14.5 vs
7.9 s, 8.2 s, 8.5 s, 8.9 s, 9.1 vs, 9.6 s, 9.8 vs		10.0 vs, 10.3 s	10.8 vs		12.5 vs, 13.2 s
7.7 s, 8.2 s, 8.5 s, 8.9 s, 9.1 vs, 9.6 s, 9.8 vs		10.0 vs, 10.3 vs			12.5 vs, 14.2 s
7.9 s, 8.1 s, 8.5 m, 9.0 s, 9.5 s, 9.8 s		10.1 vs, 10.4 s	10.8 vs	12.2 w	13.0 m, 14.1 m
8.2 s, 8.6 w, 9.2 s, 9.4 m		10.0 s, 10.4 vs			
7.9 s, 8.1 s, 8.4 s, 9.0 vs, 9.5 s		10.1 vs	10.8 vs	12.1 m, 12.8 s	14.3 s
7.9 s, 8.2 s, 9.2 s, 9.4 s		10.0 vs, 10.4 vs		11.3 m, 12.8 m, 13.3 s, 14.1 s	

TABLE V

PROTON NUCLEAR MAGNETIC RESONANCE SPECTRA OF 4-MERCAPTOBUTENOLS FROM THIOL-BUTADIENE CO-OXIDATION

Structural fragments of co-oxidation products	Starting thiol	Product type	Chemical shifts of structural units, p.p.m., downfield from tetramethylsilane as internal reference:													
			RS—	RS	—CH ₂ —	—CH ₂ —	—CH—	—CH=CH—	(—OH)	—CH ₂ —	—CH=	—OH	=CH ₂			
Methanethiol	1,2	s	2.10		d 2.55 ^a		q 4.16 ^b		s 3.75		m 5.60-5.62 ^c		m 4.9-5.5 ^d			
	1,4			s 1.98		m 3.08 ^e		m 5.63 ^e		m 4.05 ^e		s 4.30				
Ethanethiol	1,2	t	1.19 ^f	q	2.51 ^f	d	2.56 ^a	q	4.18 ^b	s	4.25	m	5.6-6.2 ^c	m	4.9-5.5 ^d	
	1,4			t	1.20, ^f 2.43 ^f		m	3.10 ^e		m	5.63 ^e		m	4.04 ^e	s	4.30
Benzenethiol	1,2		7.0-7.4			d	2.95 ^a	q	4.16 ^b	s	3.48	m	5.6-6.2 ^c		m	4.9-5.5
	1,4			m	7.0-7.4		m	3.40 ^e		m	5.63 ^e		m	3.88 ^e	s	4.19
4-Toluenethiol	1,2	m	6.8-7.2 ^g	s	2.25 ^h	d	2.90 ^a	q	4.08 ^b	s	3.40	m	5.6-6.2 ^c		m	4.9-5.5 ^d
	1,4			m	6.8-7.2 ^g	s	2.25 ^h	m	3.40 ^e		m	5.60 ^e		m	3.90 ^e	s

^a $J = 6$ c.p.s. ^b Split by CH₂ and —CH=; the apparent coupling constant is 6-7 c.p.s. ^c Eight peaks; M portion of ABMX spin system, $J = 17.5, 10$ and 5.5 c.p.s. ^d AB portion of ABMX spin system. ^e Width of peak at half-height is approximately 10 c.p.s. ^f $J = 7$ c.p.s. ^g Due to aromatic protons of 4-tolyl group. ^h Due to methyl protons of 4-tolyl group.

mixture was then cooled in a Dry Ice-isopropyl alcohol mixture and the precipitated disulfide was filtered off by suction. After the removal of the solvent, the raw alcoholic product was purified by fractional distillation at a pressure of about 1 mm.

Methanol can also be used in these reactions and the concentration of the total reactants can be increased. Methanol is a poor solvent for the aromatic disulfide by-products of the reactions. The complete removal of these disulfides by filtration of the cold reaction mixtures results in obtaining purer alcohols during the subsequent distillations. The reaction can also be carried out in the absence of any solvent. This, however, results in the formation of some thiol-diene adducts as products of competing side reactions.

The disulfide-free allyl alcohol products are colorless liquids. They are thermally stable at room temperature, but on prolonged exposure to air, they become slightly yellow.

Co-oxidation of Aliphatic Thiols and Conjugated Dienes in the Presence of *t*-Butylamine.—These co-oxidation reactions were

carried out in a manner described for similar reactions of aromatic thiols. The hydroperoxide intermediates and the alcohol products of the reaction with aliphatic thiols are, however, less soluble in heptane than the corresponding derivatives of aromatic thiols. Cleaner products and better yields were obtained by working in *n*-heptane-benzene solvent mixtures, methanol, or in the absence of any solvent. However, even in this case, a large proportion of the total raw product (about 40%) remains as distillation residue.

The products of these aliphatic thiol-diene co-oxidations are colorless liquids with characteristically unpleasant odors. The 1,2-isomeric alcohols are very unstable. On standing in the presence of air they turn first yellow then brown with the formation of oxidation products containing carbonyl groups.

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