The recrystallized product weighed 1.1 g., m.p. 179–180°. Infrared absorption bands noted were 3.01 $\mu[\nu(NH_2)]$ and 3.1 $\mu[\nu(CH)]$.

Anal. Calcd. for $C_5H_7N_3S$: C, 42.53; H, 5.00; S, 22.71. Found: C, 42.35; H, 5.08; S, 22.53.

2-Cyano-3-dimethylaminothiocrotonamide.—2-Cyano-3-methoxythiocrotonamide (0.75 g.) was suspended in a mixture of benzene and ethyl ether. Anhydrous dimethylamine was bubbled into the suspension until most of the solid had dissolved. This solution was filtered and evaporated to dryness. The residue was then recrystallized from methanol. Analytical data indicated that this material was not pure.

This material was then recrystallized from methanol and found to melt at 152–154° (softened at 150°). The infrared spectrum was in agreement with the structure given.

Anal. Calcd. for $C_7H_{11}N_3S$: C, 49.68; H, 6.55; N, 24.82. Found: C, 49.63; H, 6.24; N, 24.57.

2-Cyano-3-phenylthioacrylamide.—2-Cyanothioacetamide (1.0 g., 0.01 mole) was mixed with 1.06 g. (0.01 mole) of benzaldehyde in 10 ml. of ethyl alcohol containing 2 drops of piperidine. The mixture was stirred, and the reaction was noted to be slightly exothermic. The reaction mixture was then placed on the steam bath for 5 min. and then set aside overnight. The solvent had evaporated by the next morning. The sticky residue was washed with hexane then with ethyl ether and dried, m.p. 140–190°. This crude product was recrystallized from ethyl alcohol and water to obtain a yellow solid, m.p. 149–150°. The infrared spectrum was in agreement with the proposed structure.

Anal. Calcd. for $C_{10}H_8N_2S$: C, 63.80; H, 4.28; N, 14.89. Found: C, 63.22; H, 4.33; N, 14.41.

2-Cyano-3-(2-thienyl)thioacrylamide.—(2-Thienylmethylene)malononitrile (5.0 g., 0.03 mole) was dissolved in benzene and 3 drops of triethylamine was added. Hydrogen sulfide was bubbled into the mixture until most of the solvent was evaporated. The resulting solid was treated with Darco G-60 and recrystallized from benzene to obtain a yellow solid, m.p. 169–171°. The molecular weight, determined by boiling point elevation in benzene, was 229. The theoretical molecular weight was 193.19. The infrared spectrum was in agreement with the proposed structure.

Anal. Calcd. for $C_8H_6N_2S_2$: C, 49.46; H, 3.11; N, 14.42; S, 33.00. Found: C, 49.54; H, 3.38; N, 14.34; S, 32.29.

2-Cyano-3-(2-furyl)thioacrylamide.—(2-Furylmethylene)-malononitrile (7.20 g., 0.05 mole, m.p. 72.5–73°) was dissolved in 50 ml. of dry benzene and 3 drops of triethylamine was added to the mixture. The mixture was stirred with a magnetic stirrer, and hydrogen sulfide was bubbled into this solution until most of the benzene was evaporated. The resulting solid was filtered, treated with Darco G-60, and recrystallized from benzene. The product (6.3 g.) melted at 155–156°.

Anal. Calcd. for $C_8H_6N_2OS$: C, 53.94; H, 3.39; N, 15.72; S, 17.99. Found: C, 54.07; H, 3.39; N, 15.70; S, 17.76.

Acknowledgment.—The author is indebted to Dr. H. W. Coover and Dr. N. H. Shearer for helpful discussions and suggestions throughout this study. Thanks are also due Mr. M. V. Otis for infrared analyses, Dr. V. W. Goodlett for NMR studies, Mr. C. L. Harrison for gas chromatographic analyses, and Mr. J. S. Lewis for mass spectrometric analyses.

Organic Sulfur Compounds. VII. Some Addition and Co-oxidation Reactions of Thiols with 2,5-Dimethyl-2,4-hexadiene

ALEXIS A. OSWALD,[1a] B. E. HUDSON, JR.,[1b] GEORGE RODGERS,[2] AND FERNAND NOEL[3]

Esso Research and Engineering Company, Linden, New Jersey

Received January 12, 1962

Aromatic and aliphatic thiols were added to 2,5-dimethyl-2,4-hexadiene by a radical mechanism to yield the 1,2-monoadducts in better than 80% yield. On low temperature co-oxidation of aromatic thiols and 2,5-dimethyl-2,4-hexadiene by molecular oxygen, crystalline 2,5-dimethyl-5-arylmercapto-3-hexen-2-yl hydroperoxides were obtained according to a 1,4-radical mechanism. In the addition reaction, the hydrogen of the mercaptan is abstracted predominantly at the more reactive, secondary carbon of the allylic radical intermediate. In the co-oxidation reaction, most of the product is derived from the tertiary resonance form which contributes more than the secondary to the structure of the allylic radical intermediate. Co-oxidation reactions, important in the chemistry of fuel instability, also occur in severely cracked naphtha of high diene content with added aromatic thiols.

A previous paper of this series reported that an aromatic thiol (4-chlorobenzenethiol) can be selectively added to the more reactive double bond of some unconjugated diolefins (dicyclopentadienes, Aldrin).[4a] The same thiol and diolefins could also be co-oxidized by oxygen in hydrocarbon solutions. Again only the more reactive double bond was affected and unsaturated hydroperoxides containing sulfur were formed. These unsaturated hydroperoxides rearranged to substituted 2-hydroxyethyl sulfoxides, as did the hydroperoxide derived from monoölefin–thiol co-oxidation[4a,5] according to the following reaction equation:

$$\mathrm{RSH} + \mathrm{CR_2'{=}CR_2''} + \mathrm{O_2} \longrightarrow \mathrm{R{-}S{-}CR_2'{-}CR_2''{-}O_2H} \longrightarrow \mathrm{R{-}SO{-}CR_2'{-}CR_2''{-}OH}$$

---

[1] Esso Research and Engineering Co., (a) Central Basic Research Laboratory, P.O. Box 45, Linden, New Jersey; (b) Analytical Research Division, P.O. Box 121, Linden, New Jersey.

[2] Present address: 56 Sigwin Circle, Wallingford, Connecticut.

[3] Imperial Oil Ltd., Research Department, P.O. Box 3022, Sarnia, Ontario, Canada.

[4] A. A. Oswald and F. Noel, (a) *J. Org. Chem.*, **26**, 3948 (1961); (b) *Chem. Eng. Data*, **6**, 294 (1961).

[5] A. A. Oswald, *J. Org. Chem.*, **24**, 443 (1959); **26**, 842 (1961).

This type of reaction may be important in the instability of hydrocarbon fuels containing thiols and reactive monoölefins.[4b]

It was of interest from the viewpoint of gum formation in cracked gasolines to determine whether similar reactions of conjugated diolefins and mercaptans may occur. Conjugated diolefins are common components in steam cracked naphtha.[6] Early studies summarized by Ellis[7] and Gruse[8] concluded that they cause rapid gum formation in gasolines because they are peroxidized and polymerized readily. Gum residues from autoxidized cracked gasolines also contain relatively high percentages (about 0.5–3%) of sulfur.[9] Work on the oxidation of pure conjugated diolefins and cracked gasolines[10,11] indicated that thiols may be important in color and haze formation of fuels containing conjugated diolefins. This initiated a study of addition and co-oxidation reactions of thiols and conjugated diolefins in our laboratories.

Addition of a thiol to a conjugated diolefin was first reported by Posner in 1905.[12] The uncatalyzed addition of benzenethiol to 1-phenyl-1,4-butadiene gave liquid 1-phenyl-4-phenylmercapto-2-butene which, after oxidation was isolated as the corresponding crystalline sulfone:

$$C_6H_5SH + C_6H_5{-}CH{=}CH{-}CH{=}CH_2 \longrightarrow$$

$$C_6H_5{-}CH_2{-}CH{=}CH{-}CH_2{-}S{-}C_6H_5 \xrightarrow{KMnO_4} C_6H_5{-}CH{-}CH{=}CH{-}CH_2{-}SO_2{-}C_6H_5$$

More recently, other workers[13–16] also reported 1,4-addition of thiols to conjugated dienes.

Autoxidation reactions of conjugated diolefins usually give polyperoxides by 1,2- or 1,4-mechanism.[17–23] No cooxidation reactions of conjugated diolefins with thiols have been reported to our knowledge.

In the first part of our studies reported here, 2,5-dimethyl-2,4-hexadiene (1,1,4,4-tetramethyl-1,3-butadiene) was chosen as a conjugated diolefin because it is symmetrical in structure, highly reactive, fairly stable, and readily available.

Addition.—A few addition reactions to 2,5-dimethyl-2,4-hexadiene were reported in the literature. However, none of them was definitely of free radical type. Low temperature addition of bromine yielded a mixture of the 1,2- and the 1,4-dibromide[24] while hydrogen chloride addition occurred exclusively in a 1,4-manner.[25] Addition of ethyl diazoacetate with a 1,2-mechanism resulted in the formation of *d,l-cis* and *d,l-trans*-2,2-dimethyl-3-isobutenylcyclopropane - 1 - carboxylic acid ethyl ester.[26,27]

No addition reaction of thiols to 2,5-dimethyl-2,4-hexadiene has been reported in the literature. As expected, we have found that one mole of an aromatic thiol readily added to 2,5-dimethyl-2,4-hexadiene when their equimolar mixture was heated by a water bath. The reaction could be catalyzed by ultraviolet light and peroxides (Table I). Less reactive aliphatic thiols could also be added under the influence of ultraviolet light.

TABLE I

CATALYSIS OF THIOL ADDITION TO 2,5-DIMETHYL-2,4-HEXADIENE[a]

	Thiol reacted, %[b]		
Catalyst	Benzene-	4-Toluene-	4-Butylbenzene-
None	14	19	30
t-Butyl hydroperoxide[c]	30.5	69.5	75
Ultraviolet light[d]	92	100	100

[a] *n*-Heptane solutions containing 2,5-dimethyl-2,4-hexadiene and one of the three thiols, both in 0.3 mole/l. concentration, were stored for three hours at room temperature. [b] The residual mercaptan contents were determined by potentiometric titration with silver nitrate. [c] 0.1 mole/l. [d] 5-cm. distance.

The products were isolated by distillation as high boiling, almost colorless liquids. Their elemental analyses (Table II) indicated the addition of one mole of thiol per one mole of dimethylhexadiene. NMR spectra (Table III) showed that the adducts are predominantly 5-substituted mercapto-2,5-dimethyl-2-hexenes formed by 1,2-addition:

$$RSH + C(CH_3)_2{=}CH{-}CH{=}C(CH_3)_2 \longrightarrow$$

$$RS{-}C(CH_3)_2{-}CH_2{-}CH{=}C(CH_3)_2$$

I

(and *trans*-$RS{-}C(CH_3)_2{-}CH{=}CH{-}CH(CH_3)_2$)

II

The difference between the NMR spectrum of the 1,2-adduct (I) and the 1,4-adduct (II) is illustrated by the 2-naphthalenethiol adducts (R = 2-naph-

---

(6) S. F. Birch and W. D. Scott, *Ind. Eng. Chem.*, **24**, 49 (1932).

(7) C. Ellis, "The Chemistry of Petroleum Derivatives," Vol. I, The Chemical Catalogue Co., Inc., New York, N. Y., 1934, pp. 893–903.

(8) W. A. Gruse, "Science of Petroleum," Vol. II, Oxford University Press, New York, N. Y., 1938, p. 1016.

(9) C. G. Dyer, C. D. Lowry, Jr., J. C. Morrell, and G. Egloff, *Ind. Eng. Chem.*, **26**, 885 (1934).

(10) J. C. Morrell, W. L. Benedict, and G. Egloff, *ibid.*, **28**, 449 (1939).

(11) G. Egloff, J. C. Morrell, W. L. Benedict, and C. Wirth, III, *ibid.*, **27**, 323 (1935).

(12) T. Posner, *Ber.*, **38**, 646 (1905).

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

(14) C. S. Marvel and H. N. Cripps, *J. Polymer Sci.*, **8**, 313 (1952).

(15) J. A. Reeder, Ph.D. thesis, University of Colorado, 1958.

(16) S. J. Cristol and K. L. Nagpal, *J. Org. Chem.*, **26**, 365 (1961).

(17) R. Criegee, "Preparative Methoden der Organischen Chemie," Vol. 8, Houben-Weyl, ed., Thieme Verlag, Stuttgart, Germany, 1952, p. 14.

(18) K. Bodendorf, *Arch. Pharm.* **271**, 1 (1933).

(19) (a) W. Kern, H. Jokusch, and A. Wolfram, *Makromol. Chem.*, **3**, 223 (1949); (b) W. Kern and J. Stallmann, *ibid.*, **7**, 199 (1951); (c) W. Kern, A. Heinz, and J. Stallmann, *ibid.*, **16**, 21 (1955); (d) W. Kern and A. R. Heinz, *ibid.*, **16**, 81 (1955).

(20) F. K. Kawahara, *J. Am. Chem. Soc.*, **79**, 1447 (1957).

(21) C. T. Handy and H. S. Rothrock, *ibid.*, **80**, 5306 (1958).

(22) H. Hock and F. Depke, *Ber.*, **84**, 349 (1951).

(23) R. Jacquemain, *Compt. rend.*, **215**, 200 (1942).

(24) C. Prevost, *ibid.*, **184**, 1460 (1927).

(25) A. L. Henne, H. Chanan, and A. Turk, *J. Am. Chem. Soc.*, **63**, 3474 (1941).

(26) H. Staudinger, O. Muntwyler, L. Ruzicka, and S. Seibt, *Helv. Chim. Acta*, **7**, 390 (1924).

(27) T. G. M. Campbell and S. H. Harper, *J. Chem. Soc.*, 28 (1945).

TABLE II

ADDUCTS OF THIOLS AND 2,5-DIMETHYL-2,4-HEXADIENE AND DERIVATIVES

$R—SO_x—C(CH_3)_2—CH_2—CH{=}C(CH_3)_2$ and $R—S—C(CH_3)_2—CH{=}CH—CH(CH_3)_2$

1,2-Adduct, Main Product (0 = nil) 1,4-Adduct, By-product

R	X	Formula	Yield,[a] %	Conversion,[b] %	1,4-Adduct by-product determined by, % G.C.	n.m.r.	B..p[c] (m.p.), °C./mm.	n^{20}_D	Calcd. C	H	S	Found C	H	S
Phenyl	0	$C_{14}H_{20}S$	96	91[d]	25	23	91–93/1	1.5354	76.30	9.15	14.55	76.11	8.96	14.58
4-Tolyl	0	$C_{15}H_{22}S$	94	93[d]	15	17	92–94/1	1.5415	76.86	9.46	13.68	76.75	9.27	13.81
4-*t*-Butylphenyl	0	$C_{18}H_{28}S$	96	88[d]	16	14	109–111/1	1.5295	79.94	9.39	10.67	79.50	9.52	11.02
	2	$C_{18}H_{28}O_2S$	79	. . .	0	0	(88–89)	. . .	70.09	9.15	10.39	69.98	9.41	10.27
2-Naphthyl	0	$C_{18}H_{22}S$	93	85[d]	. .	8	125–127/1	. . .	79.94	8.20	11.86	79.84	8.25	12.11
			74[f]	. . .	0	0	(39–41)	. . .				79.78	8.18	12.09
	2	$C_{18}H_{22}O_2S$	67	. . .	0	0	(91–92.5)	. . .	71.84	7.33	10.60	71.66	7.31	. . .
Methyl	0	$C_{19}H_{18}S$	78	32[e]	28	23	85–86/22	1.4788	68.29	11.46	20.25	68.16	11.29	20.12
Ethyl	0	$C_{20}H_{20}S$	81	23[e]	35	29	95–97/22	1.4771	69.70	11.69	18.61	69.87	11.75	18.39

[a] On the basis of the thiol converted. [b] On the basis of the decrease of the thiol content of the reaction mixture. [c] Uncorrected. [d] After three hours at 95°. [e] After 12 hours ultraviolet irradiation. [f] By recrystallization of the mixture of isomers from ethanol.

TABLE III

PARAMETERS OF NMR SPECTRA OF THIOL–2,5-DIMETHYL-2,4-HEXADIENE ADDUCTS

1,2-Adduct 1,4-Adduct Dimethylhexadiene adduct of	Type of addition	R—S— R—S—	—C(CH₃)₂—	—C(CH₃)₂—	—CH₂—	—CH=CH—	—CH=	—C(CH₃)₂—	—C(CH₃)₂	H
		Chemical shifts of structural units downfield from tetramethylsilane internal reference: p.p.m. s singlet; d doublet; t triplet; q quartet; m multiplet: p.p.m.								
Benzenethiol	1,2	m (7–7.5)	s 1.18		d 2.18[a]		t 5.30[a]		s 1.50,[c] s 1.68[c]	m[d]
	1,4	m (7–7.5)		s 1.29		m[b]		d 0.85[a]		m[d]
4-Toluenethiol	1,2	q 7.10,[e,f] s 2.18[g]	s 1.15		d 2.14[a]		t 5.30[a]		s 1.52,[c] s 1.68[c]	
	1,4	q 7.10,[e,f] s 2.18[g]		s 1.28		m[h]		d 0.86[a]		m[d]
4-Butylbenzenethiol	1,2	q 7.25,[e,i] s 1.23[j]	s 1.17		d 2.18[a]		t 5.30[a]		s 1.53,[c] s 1.68[c]	
	1,4	q 7.25,[e,i] s 1.23[j]		s 1.30		m[h]		d 0.86[a]		m[d]
	1,2[l]	q 7.63,[c,k] s 1.32[j]	s 1.16		d 2.30[a]		t 4.98[a]		s 1.57,[c] s 1.68[c]	
2-Naphthalenethiol	1,2	m (7.4–8.1)	s 1.19		d 2.16[a]		t 5.28[a]		s 1.54,[c] s 1.72[c]	
	1,4	m (7.4–8.1)		s 1.32		m[h]		d 0.86[a]		m[d]
Methanethiol	1,2	s 1.80	s 1.18		d 2.22[a]		t 5.20[a,m]		s 1.58,[c] s 1.70[c,m]	
	1,4	s 1.80		s 1.27		s 5.25		d 0.98[a]		m[d]
Ethanethiol	1,2	t 1.15,[a] q 2.43[a]	s 1.20		d 2.17[a]		t 5.20[a,m]		s 1.58,[c] s 1.70[c,m]	
	1,4	t 1.15,[a] q 2.43[a]		s 1.28		s 5.30		d 0.97[a]		m[d]

[a] $J = 7$ c.p.s. [b] Unsymmetrical six-line pattern representing the AB portion of an ABX type spin system. $\delta_{AB} = 0.55$ p.p.m., $J_{AB} = 16$ c.p.s., $J_{AX} = 2$ c.p.s., $J_{BX} = 6$ c.p.s. [c] The two separate methyl peaks represent position *cis* and *trans* to the vinyl proton. [d] This proton is theoretically split into a 28-component multiplet which could not be recognized in the spectrum. [e] AB type quartet. [f] $\delta = 0.4$ p.p.m., $J = 8$ c.p.s. [g] Due to the protons of the 4-methyl group on the benzene ring. [h] The multiplet peaks of the two *trans* vinyl protons overlap with the triplet of the single vinyl proton of the 1,2 adduct and therefore parameters could not be determined with certainty. [i] $\delta = 0.22$ p.p.m., $J = 8$ c.p.s. [j] Due to the protons of the 4-*t*-butyl groups on the benzene ring. [k] $\delta = 0.27$ p.p.m., $J = 8$ c.p.s. [l] The corresponding sulfone prepared by the oxidation of the adduct. [m] Remote splitting occurs between the vinyl proton and the protons of the *trans*-methyl groups. $J_r = 1.7$ c.p.s.

TABLE IV

INFRARED ABSORPTION PEAKS OF THIOL–2,5-DIMETHYL-2,4-HEXADIENE ADDUCTS

$R—SO_X—C(CH_3)_2—CH_2—CH{=}C(CH_3)_2$ AND $R—S—C(CH_3)_2—CH{=}CH—CH(CH_3)_2$

Absorption Peaks (Microns; vs Very

R	(Reference Compound)	X	Olefinic			
			$—CH{=}C(CH_3)_2$	General	*trans*-Disubstituted (and unassigned)	
(2,5-Dimethyl-2,4-hexadiene[a])			11.9vs	5.9m,6.1w,6.2m	10.15	
	(Benzenethiol[a])					6.3vs
Phenyl		0[a]	11.8m	6.0m	10.2i,10.3m	6.3m
	(4-Toluenethiol[b])	0[a]	11.8m	6.0m	10.2i,10.3m	6.1w,6.25w
4-Tolyl						6.1w,6.3m
	(4-Butylbenzenethiol[a])					6.25w
4-Butyl		0[a]	11.8i,12.05vs	6.0m	10.2i,10.3m	6.3m
4-Butyl		2[b]	11.8s	6.0vw	10.3m	6.3m
	(2-Naphthalenethiol[b])	0[b]	11.75s	6.0w	10.4m	6.2m,6.3m
2-Naphthyl					10.2w 10.4m	6.3m
2-Naphthyl		2[d]	11.7m,11.8s	6.0w	10.4m	6.3m
Methyl		0[a]	11.8m	6.0w,6.1vw	10.1m,10.3s	
	(Ethanethiol[a])					
Ethyl		0[a]	11.7m,11.8m	6.0m,6.1vw	10.2i,10.3s	

[a] Without solvent. [b] Melted on sodium chloride plate. [c] Sulfone absorption. [d] In chloroform solution.

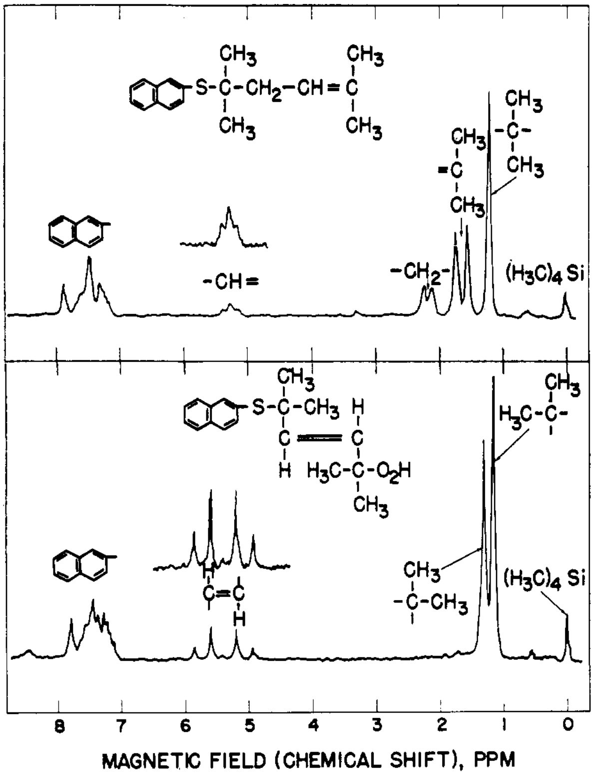


Fig. 1.—Proton nuclear magnetic resonance spectra of addition and co-oxidation products of 2-naphthalenethiol and 2,5-dimethyl-2,4-hexadiene.

thyl) as examples (Fig. 1). The spectrum of the 1,2-adduct (I) shows a characteristic doublet at 2.16 p.p.m. downfield from the tetramethylsilane internal reference. This doublet represents the methylene protons, which are absent in the 1,4-adduct. The two structures are also readily distinguished on the basis of the relative chemical shifts and splittings of their methyl group absorption. The geminal methyls on the carbon atom adjacent to sulfur produce singlet peaks of six-proton intensity in both cases, but with a greater downfield shift for the 1,4- (II) than for the 1,2-adduct (I). The methyl groups on the unsaturated carbon in structure I produce separate singlet peaks as a result of their *cis* and *trans* locations with respect to the single vinyl proton. The corresponding methyl groups of structure II are geometrically identical. Their protons, spin coupled to a single methine proton, exhibit doublets with less downfield shift than the olefinic methyl peaks of structure I.

The vinyl proton resonance pattern of the pure 1,2-adduct shows a characteristic triplet at 5.28 p.p.m. as a result of spin splitting by the adjacent methylene group. The vinyl patterns in the spectra of product mixtures of aromatic thioldimethylhexadiene additions are frequently indistinct.

However, the isomer mixture of benzenethiol–dimethylhexadiene addition clearly showed both the triplet of the vinyl proton of the 1,2-adduct and a six-line pattern of the *trans*-vinyl protons of the 1,4-adduct. The latter represent the AB portion of an ABX type spin system[28] in which the *trans*-vinyl protons (AB) are coupled to the methine proton. This six line pattern collapsed to an apparent singlet in the 1,4-adduct components of the aliphatic thiol–dimethylhexadiene addition products.

On the basis of the relative strength of the characteristic methyl peaks of the NMR spectra, the amount of 1,2- and 1,4-adducts in mixtures can be determined. The 1,2- and 1,4-adducts could be

---

(28) 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, p. 138.

TABLE IV (*Continued*)

Strong, m Medium, w Weak, i Inflection

Aromatic			Other characteristic peaks above 7.5 μ		
			7.6vw,8.0vw,8.6s	9.5s	12.3m
	13.6vs	14.4vs,14.6vs	7.7w,8.5w	8.9s,9.15s,9.35m	9.75vs
12.6vs	12.9s,13.3vs	14.2vs,14.4vs	7.7m,8.0m,8.4m	8.9vs,9.1vs,9.2s	9.8s
11m,12.5vs			7.65m,8.3w	8.9s,9.1s,9.6s	9.8m
12.3vs,12.6s	12.9m	14m	7.7w,8.0s,8.3m	9.8vs, 9.1s,9.2s	9.8s
12.2vs	13.5m	13.9m	7.9s,8.3m	8.9vs	9.9vs
1.6vs	12.9m,13.4w	13.6m	7.8m,8.0s,8.4m	8.9s,9.0vs,9.1s	9.9s
12.5m	12.9w,13.1m	14.7s	7.7s[c],7.8vs[c],8.3m,8.6vs[c]	8.8vs[c],8.9s,9.0vs,9.3vs	9.9m
10.6m,11.7s,12.3vs	13.4vs		7.9w,8.4w	8.8s,9.2s	
11.5vs,12.1vs	13.45vs		7.7m,7.9m,8m,8.4m	8.9vs,9.3w	9.8w,11s
			7.7vs,[c]7.9m,8.1m,8.4m	8.7vs,[c]9.0vs,9.4vs	9.9m
			7.7w,7.9m,8.3m	8.8vs,9.0s,9.4w	
			7.9vs	9.15m	
			7.8vs,8.0s,8.4m	8.9vs,8.9vs,9.1s,9.5m	

also separated by gas-liquid phase chromatography using a silicone rubber column.[29] The 1,2-adducts have longer retention times. The relative amounts of the two isomers correspond rather well to the values predicted by NMR. Simple distillation does not result in a good separation although the 1,2-addition products boil at somewhat lower temperatures.

Studies of the infrared spectra of thiol–dimethylhexadiene adducts confirmed that the addition occurred mainly by a 1,2-mechanism. A characteristic spectrum of a thiol–dimethylhexadiene addition product is shown in Fig. 2. This spectrum and the infrared spectra of other similar adducts all showed absorptions at about 11.8, 6.0, and 10.3 μ (Table IV) which could be assigned to olefins.

Characteristic out of plane —CH= deformations of trisubstituted ethylenes have been reported to have a wave length range of 11.9–12.5 μ.[30] All the thiol adducts had a definite absorption at a slightly lower wave length, namely at 11.7–12.0 μ. This indicates that the reaction products contain some 1,2-adduct. The presence of absorption due to the C=C stretching vibration at about 6 μ, which is characteristic of a trisubstituted ethylene[31] supports this indication.

It is known that *trans*-disubstituted olefins have out of plane —CH= deformation vibrations between 10.1–10.4 μ[32] The observed absorption of the thiol–olefin adducts could be attributed to the *trans*-vinyl hydrogens resulting from *trans*-1,4-addition. The relative intensities of absorption at 10.3 μ are qualitatively proportional to the amount of the 1,4-*trans*-addition product. It is noted, however, that 2,5-dimethyl-2,4-hexadiene itself and its 1,2-thiol addition products all absorb at 10.3 μ.

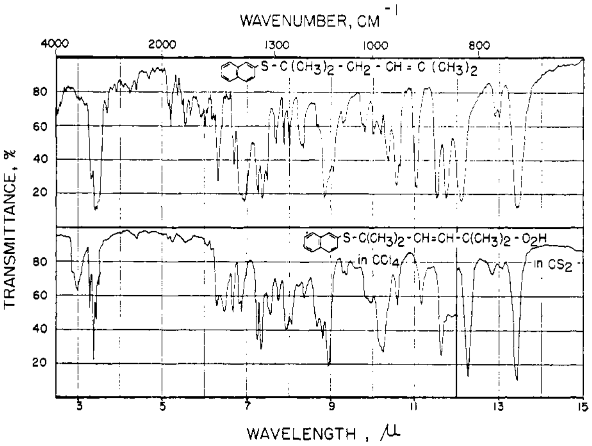


Fig. 2.—Infrared absorption spectra of the addition and co-oxidation product of 2-naphthalene thiol and 2,5-dimethyl-2,4-hexadiene.

It is known that *cis*-disubstituted olefins show absorption between 13.75 and 14.8 μ.[32] The spectra of our thiol–dimethylhexadiene adducts, however, did not show any absorption in that range, except those which were also present in the parent (aromatic) thiols.

To confirm further the 5-substituted mercapto-2,5-dimethyl-2-hexene structure of the products of addition with a 1,2-mechanism, equimolar adducts of 4-*t*-butylbenzenethiol and 2-naphthalenethiol were oxidized by peracetic acid to the corresponding crystalline sulfones:

---

[29] Silicone gum rubber column with Chromosorb P (F & M Model 500).

[30] H. L. McMurry and V. Thornton, *Anal. Chem.*, **24**, 318 (1952).

[31] N. Sheppard and G. B. M. Sutherland, *J. Chem. Soc.*, 1540 (1947).

[32] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," J. Wiley and Sons, Inc., New York, N. Y., 1959, pp. 45–49.

$$R{-}S{-}C(CH_3)_2{-}CH_2{-}CH{=}C(CH_3)_2 \xrightarrow[(AcOH)]{2H_2O_2} R{-}SO_2{-}C(CH_3)_2{-}CH_2{-}CH{=}C(CH_3)_2$$

$$R = \text{4-tolyl, 4-}t\text{-butylphenyl}$$

NMR spectrum of the sulfone from the oxidation of 4-butylbenzenethiol-2,5-dimethyl-2,4-hexadiene adduct showed again the characteristic triplet for the single vinyl proton at 4.98 p.p.m. and the doublet for the methylene protons at 2.30 p.p.m. (Table III). The infrared absorption spectra of these sulfones (Table IV) showed again the peaks at 11.8 and 6.0 μ which can be attributed to the trisubstituted ethylenic structure of the 1,2-adducts. Characteristic sulfone absorption bands,[33] not present before oxidation, appeared at about 7.7 and 8.7 μ.

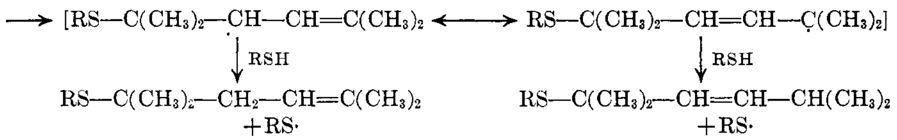
It is known since the work of Burkhardt,[34] Kharasch, Read, and Mayo[35] in the thirties that mercaptans add to olefins by the following chain mechanism:

$$(RSH \longrightarrow)\ RS\cdot + CH_2{=}CR_2' \longrightarrow RS{-}CH_2{-}CR_2'\cdot$$

$$RS{-}CH_2{-}CR'_2\cdot + RSH \longrightarrow RS{-}CH_2{-}CHR_2' + RS\cdot$$

The first step of a similar mechanism in the case of dimethylhexadiene, is apparently the addition of the thiol radical to the second carbon to form an allylic radical. The 1,2- and 1,4-addition product can be derived from the latter as shown in the following equation:

$$(RSH \longrightarrow)\ RS\cdot + C(CH_3)_2{=}CH{-}CH{=}C(CH_3)_2 \longrightarrow$$

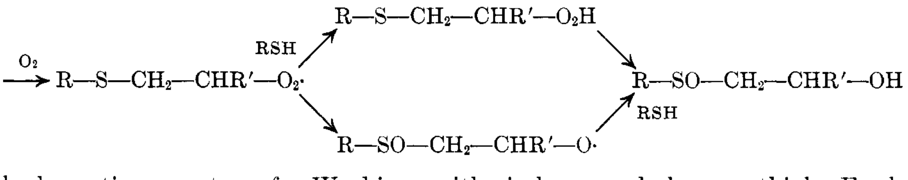


Our work indicates that most of the addition products are derived from the allylic radical at the secondary carbon atom. This reflects the higher hydrogen abstraction rate of the thiol by the allylic radical at the more reactive secondary carbon than at the less reactive tertiary carbon. Since the hydrogen abstraction from the thiol has a significant activation energy, the reaction proceeds at a faster rate at the secondary carbon.

Co-oxidation.—2,5-Dimethyl-2,4-hexadiene is readily oxidized by molecular oxygen at room temperature to yield a solid polyperoxide of unknown structure.[36] Thiols alone are oxidized only at a very slow rate by molecular oxygen at ambient temperatures.

It was first reported by Kharasch and co-workers[37] that hydrocarbon solutions containing both a reactive olefin (styrene) and a mercaptan are readily co-oxidized by molecular oxygen at room temperature. In the case of styrene, Kharasch obtained substituted 2-hydroxyethyl phenyl sulfoxides by the reaction and proposed the following mechanism:

$$(RSH \longrightarrow)\ RS\cdot + CH_2{=}CHR' \longrightarrow R{-}S{-}CH_2{-}CHR'\cdot \longrightarrow$$



Working with indene and benzenethiol, Ford, Pitkethly, and Young have shown the formation of the hydroperoxide intermediate.[38] A number of such intermediates have been isolated at about 0° by Oswald and co-workers.[4,5]

The co-oxidation of 2,5-dimethyl-2,4-hexadiene with thiols was carried out by molecular oxygen in dilute hydrocarbon solutions in a manner previously used.[4,5] On oxygenation of aliphatic hydrocarbon solutions containing equimolar amounts of an aromatic thiol and 2,5-dimethyl-2,4-hexadiene, about 0.3 mole/l. each, well defined hydroperoxides were formed. When the oxygenation of such solutions was carried out with ice cooling between 0–10°, practically all of the aromatic thiol was co-oxidized within three hours and most of the hydroperoxides precipitated in crystalline form. They could be isolated in good yields by filtration of the cold solutions and could be recrystallized from aliphatic solvents.

Elemental composition of these hydroperoxides (Table V) indicated that one mole of aromatic thiol was co-oxidized with one mole of dimethylhexadiene by one mole of oxygen. Peroxide determination indicated the presence of one hydroperoxy group per molecule.

NMR spectra of all the hydroperoxides (Table VI) show two very strong singlet peaks originating from the protons of the two pairs of geminal methyl groups. A characteristic spectrum is shown in Fig. 2. The downfield peak is at about the same posi-

---

[33] K. C. Schrieber, *Anal. Chem.*, **21**, 1168 (1949).

[34] G. N. Burkhardt, *Trans. Faraday Soc.*, **30**, 18 (1934).

[35] M. S. Kharasch, A. T. Read, and F. R. Mayo, *Chem. Ind.* (London), 752 (1938).

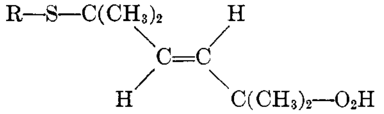
[36] S. H. Harper, H. W. B. Reed, and R. A. Thompson, *J. Sci. Food Agr.*, **2**, 94 (1951).

[37] M. S. Kharasch, W. Nudenberg, and G. H. Mantell, *J. Org. Chem.*, **16**, 524 (1951).

[38] J. F. Ford, R. C. Pitkethly, and V. O. Young, *Tetrahedron*, **4**, 325 (1958).

TABLE V

HYDROPEROXIDES OF AROMATIC THIOL–2,5-DIMETHYL-2,4-HEXADIENE CO-OXIDATION



R	Formula	Yield, %	M.p.,[a] °C.	Calculated C	Calculated H	Calculated S	Found C	Found H	Found S	Hydroperoxide,[b] %
Phenyl	$C_{14}H_{20}O_2S$	77	38.5–40	66.63	7.99	12.70	66.94	8.19	12.71	105
4-Tolyl	$C_{15}H_{22}O_2S$	83	40–41.5	67.67	8.32	12.04	67.59	8.47	12.27	99
4-*t*-Butylphenyl	$C_{18}H_{28}O_2S$	76	64–66	70.09	9.15	10.39	69.86	8.99	10.61	104
4-Chlorophenyl	$C_{14}H_{19}O_2S$	67	44–45	58.62	6.68	11.18	59.17	7.06	10.98	103
2-Naphthyl	$C_{18}H_{22}O_2S$	75	58.5–59.5	71.48	7.33	10.61	71.55	7.38	10.95	103

[a] Uncorrected. [b] Per cent hydroperoxide content of the calculated value.

TABLE VI

PARAMETERS OF NMR SPECTRA OF THIOL–2,5-DIMETHYL-2,4-HEXADIENE CO-OXIDATION PRODUCTS

Chemical shifts: downfield from tetramethylsilane internal reference: p.p.m.
s singlet, q AB quartet, m multiplet

R	RS—	$—C(CH_3)_2—$	—CH=CH[b]—	$—C(CH_3)_2—$	$—O_2H$[c]
Phenyl	m 71.5[a]	s 1.30	q 5.35	s 1.18	...
4-Tolyl	m 7.42[d], s 2.28[e]	s 1.30	q 5.34	s 1.19	...
4-Butylphenyl	s 7.29, s 1.29[f]	s 1.31	q 5.43	s 1.22	...
4-Chlorophenyl	q 7.33[g]	s 1.30	q 5.40	s 1.22	...
2-Naphthyl	m 7.0–8.1[h]	s 1.34	q 5.45	s 1.16	...

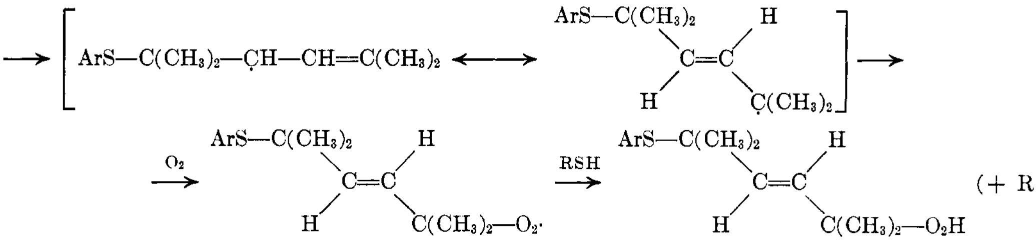
[a] Unresolved. [b] δ_{AB} = 0.55–0.60 p.p.m. J_{AB} = 16 c.p.s. [c] Proton of hydroperoxide group could not be observed in spectrum. [d] Five component. [e] Due to protons of 4-methyl group on benzene ring. [f] Due to protons of 4-*t*-butyl group on benzene ring. [g] δ_{AB} = 0.25 p.p.m., J_{AB} = 9 c.p.s. [h] Partially resolved.

tion (Table VI) as the peak of the methyl groups on the carbon α to the sulfur in the 1,4-adduct (Table III). As expected, the upfield peak is at a lower field than the peak of the terminal methyls in the 1,4-adduct. A very characteristic AB quartet is observed in the vinyl region of the spectrum:[39] The magnitude of the coupling constant (15–16 c.p.s.) of the vinyl protons is characteristic of *trans*-internal olefins. However, the difference in chemical shift for the two vinyl protons (0.6 p.p.m.) is greater than the difference in position of the two pairs of geminal methyl peaks (0.09 to 0.18 p.p.m.). The signal of the proton of the hydroperoxy group could not be observed; it may have been obscured by multiple resonances of the aromatic protons.

Infrared absorption spectra of the low temperature co-oxidation products (Table VII) confirm the presence of a hydroxyl (hydroperoxy) group (absorption at 3, 7.6, 8, 8.9, and 9.8 μ).[40] Strong absorption at 10.3 μ may be characteristic of a *trans* CHR=CHR′ structure[32] although 2,5-dimethyl-2,4-hexadiene also absorbs in this region.

On the basis of elemental, group, NMR and infrared absorption spectral analyses, it is proposed that the 2,5-dimethyl-2,4-hexadiene thiol co-oxidation products are *trans*-2,5-dimethyl-3-hexen-2-yl hydroperoxides. The radical addition of thiols to 2,5-dimethyl-2,4-hexadiene and earlier studies on the co-oxidation of olefins and thiols[5] suggest the following reaction mechanism for their formation:

$$(ArSH \longrightarrow)\ ArS\cdot + C(CH_3)_2{=}CH{-}CH{=}C(CH_3)_2 \longrightarrow$$



The hydroperoxide was apparently derived by combination of the allylic radical intermediate with molecular oxygen at the tertiary carbon atom. Such a radical combination reaction between an allylic radical and an oxygen diradical would not be expected to have a significant activation energy. This could account for the preferential combination with oxygen at the tertiary carbon since the tertiary resonance form makes a greater contribution than the secondary to the structure of the allylic radical intermediate.

On standing at room temperature, these hydroperoxides decomposed and yielded the corresponding diaryl disulfides and unidentified peroxides

$$2ArS{-}C(CH_3)_2{-}CH{=}CH{-}C(CH_3)_2{-}O_2H \longrightarrow (ArS{-})_2 + \text{Peroxide}$$

---

[39] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance Spectra," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp. 122, 238.

[40] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," J. Wiley and Sons, Inc., New York, N. Y., 1959, p. 95.

TABLE VII

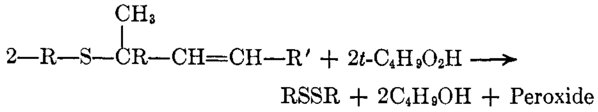
INFRARED ABSORPTION SPECTRA OF THIOL-2,5-DIMETHYL-2,4-HEXADIENE CO-OXIDATION PRODUCTS

$R—S—C(CH_3)_2—CH=CH—C(CH_3)_2—O_2H$

R	Absorption peaks[a] (μ; vs, very strong, m, medium, w, weak)							
	Hydroxyl	Olefinic		Aromatic		Other characteristic peaks above 7.5 μ		
		General	*trans*-Disubstituted (and unassigned)					
Phenyl	3.0m	6.05w	10.25s	6.3m	11.9w,13.3vs,14.4vs	7.6m,7.9m,*8.0s*,8.1s	8.7s,8.8s,*8.95vs*,9.2m,9.4w	*9.75s*,10m
4-Tolyl	3.0m	6.05w	10.25s	6.3m	12.3vs	7.6m,7.8m,*8.0s*,8.1s	8.5m,8.7s,8.8s,*8.95vs*,9.15m,9.6w	*9.8s*,10m
4-Butylphenyl	3.0m	6.05w	10.25s	6.3m	12.05vs	7.6m,7.8m,*7.95s*,8.1m	8.7s,8.8s,*9vs*,9.3m,9.6m	*9.85s*
4-Chlorophenyl	3.0m	6.05w	10.25s	6.3m	11.8w,12.2vs,12.8m,13.4s	7.55m,7.7m,*7.95s*,8.05m	8.7s,8.8s,*8.9vs*,9.1vs	*9.8vs*
2-Naphthyl	3.0m	6.05w	10.25s	6.3m	11.2m,11.7vs,12.3vs,13.45vs	7.6m,7.8m,*8.0s*,8.1s	8.4w,8.7s,8.8s,*8.95vs*,9.4w	*9.9m*

[a] Absorption peaks below 11 μ were obtained using chloroform solutions, at higher wave lengths carbon disulfide solutions were used.

The formation of the disulfides also supports the proposed structure of the hydroperoxides since according to Barnard[41] 1-methyl-alk-2-enyl sulfides react with *t*-butyl hydroperoxide in an analogous manner to yield the corresponding disulfides:



$$2—R—S—\overset{CH_3}{\overset{|}{C}}R—CH=CH—R' + 2t\text{-}C_4H_9O_2H \longrightarrow RSSR + 2C_4H_9OH + \text{Peroxide}$$

It is also known that unsaturated sulfides autoxidize readily.[42,43] Therefore, it is suggested that intermediates similar to the 5-arylmercapto-2,5-dimethyl-2-hex-3-enyl hydroperoxides may be formed in such autoxidations.

Co-oxidation of Conjugated Diolefins and Thiols in Petroleum Products.—Since the co-oxidation of aromatic mercaptans and conjugated diolefins proceeds quickly, it was thought that such relations might be used for the removal of either type of the co-oxidation components from petroleum fractions, which are known to cause oxidation instability. It is known that severely thermally cracked naphtha contains a high concentration of diolefins but very little, if any, aromatic mercaptans. Therefore, the addition of aromatic mercaptans is necessary for successful co-oxidation.

When 100 ml. of a severely cracked naphtha containing 0.1 mole/liter of 2-naphthalenethiol was aerated for four hours, a rapid co-oxidation took place and 24 g. of a mixture of peroxides containing a high percentage of sulfur separated (Table VIII, Fig. 3). Concurrently, the diene number of the naphtha phase decreased from 14 to 1.6 and on subsequent distillation, it yielded a water-white, stable product. A control experiment without added 2-naphthalenethiol yielded an unstable product of a diene number of 13.

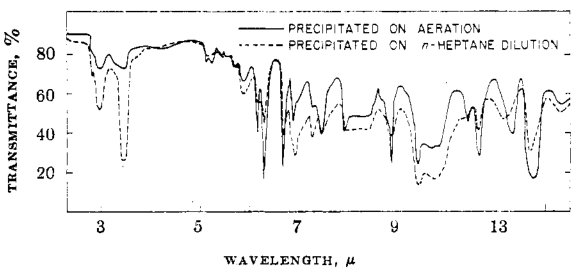


Fig. 3.—Infrared spectra of co-oxidation products from steam-cracked naphtha.

Experimental

Materials and Methods.—The reactants used were purified by recrystallization or distillation before using. The solvents were all C.P. reagents. Some characteristics of the severely cracked naphtha used in some experiments are shown in Table VIII.

All oxygenations and aerations were carried out by bub-

---

(41) D. Barnard, *J. Chem. Soc.*, 489 (1956).

(42) L. Bateman and J. C. Cunneen, *ibid.*, 1596 (1955).

(43) L. Bateman and F. W. Shipley, *ibid.*, 1996 (1955).

TABLE VIII

REMOVAL OF DIOLEFINS BY CO-OXIDATION

	Steam-cracked naphtha		
	Air oxidized[a]	Co-oxidized[a]	Co-oxidized[b]
Added 2-naphthalenethiol, mole/l.	Nil	1	1
Period of aeration, hr.	4	4	6
Peroxide separated, g./100 ml.	Nil	20[c]	24[d]
Diene numbers:			
original (before aeration)	14	14	34
final (after redistillation)	13	1.6	11[e]
Reduction of diene number, %	7	88.5	67.6

[a] Boiling range 43–217°. [b] Boiling range 135–221°. [c] On cooling to −73°. [d] On dilution with *n*-heptane. [e] Without redistillation.

bling oxygen or air at a rate of 0.3 l./min., through a sintered glass bubbler with 7.5-cm.^{2} sintered area, into the reaction mixture which was in a measuring cylinder with a height diameter ratio of 6 to 1.

The peroxide analyses were done according to the method of Wagner and co-workers.[44] Hydroperoxide contents were determined on the basis of the amount of 2-naphthalenethiol oxidized in the presence of an alkylamine catalyst.[45] The mercaptan concentrations of the reaction mixtures were determined by potentiometric titration with silver nitrate. Diene number determinations were carried out according to an ASTM method.[46]

The NMR spectra were recorded with a Varian Model A-60 proton resonance spectrometer. Carbon tetrachloride was used as a solvent for the solid compounds examined. The infrared spectra were obtained using a Baird recording spectrophotometer, Model B. Liquid-gas chromatography was carried out on an F & M Model 500 linear programmed temperature gas chromatograph, using the 2-ft. Chromosorb P–silicone gum rubber column.

Addition of Aromatic Thiols to 2,5-Dimethyl-2,4-hexadiene.—A mixture of 0.1 mole of an aromatic thiol and 11 g. (0.1 mole) of 2,5-dimethyl-2,4-hexadiene were heated in a 50-ml. round-bottom flask equipped with a water-cooled condenser for 3 hr. on a water bath. The top of the condenser was closed airtight to avoid extensive air oxidation. By the end of the 3 hr. a mercaptan number determination[39] showed that most of the thiol had reacted. The reaction mixture was taken up in 50 ml. of benzene and washed with 50 ml. of 4% aqueous sodium hydroxide solution to remove the rest of the thiol. The benzene phase was then fractionally distilled. The isomeric mixtures of the addition products were collected at 1 mm. pressure as colorless liquid condensates.

5-β-Naphthylmercapto-2,5-dimethyl-2-hexene crystallized out of the isomeric mixture on standing. It was recrystallized from ethanol to yield a colorless, crystalline solid of m.p. 39–41°.

Some physical and analytical data of the aromatic thiol-dimethylhexadiene adducts are shown in Tables II–IV.

Addition of Aliphatic Thiols to 2,5-Dimethyl-2,4-hexadiene.—A mixture of 0.16 mole of an aliphatic thiol (methane- and ethanethiol) and 16.7 g. (0.15 mole) of 2,5-dimethyl-2,4-hexadiene was irradiated in a 50-ml. Vycor (98% silica) round-bottom flask equipped with a chilled water-cooled, closed condenser by a 100 w. ultraviolet light (high pressure Hanovia utility lamp) from 5-cm. distance for 24 hr. By the end of that period about one third of the original thiol had reacted with the diene. The addition products were isolated as colorless liquids by distillation at 22 mm. pressure. Some physical and analytical data of the methane- and ethanethiol adducts are shown in Tables II–IV.

5-(4-*t*-Butylphenylsulfonyl)-2,5-dimethyl-2-hexene.—In 5 ml. of glacial acetic acid, 6.9 g. (0.025 mole) of a mixture of the two isomeric addition products (85% 1,2-adduct, 15% 1,4-adduct) of the reaction of 4-*t*-butylbenzenethiol and 2,5-dimethyl-2,4-hexadiene were dissolved. To the solution, 2 g. (0.055 mole) of 90% hydrogen peroxide was then added. The temperature of the reaction mixture was slowly raised to 70° and kept there for 0.5 hr. to complete the oxidation. When raising the temperature exothermicity was observed at about 35° and 70°; the temperature was kept under control by water cooling until the exothermic reaction subsided. After the 0.5 hr. heating, the reaction mixture was allowed to cool, mixed with 5 ml. of ethanol, and left to stand on a watchglass. Crude 5-(4-*t*-butylphenylsulfonyl)-2,5-dimethyl-2-hexene oxidation product (5 g.) crystallized on standing. On recrystallization from 90% ethanol, 4 g. (60%) of the colorless pure sulfone, m.p. 88–89°, was obtained.

5-β-Naphthylsulfonyl-2,5-dimethyl-2-hexene.—A mixture (7 g., 0.025 mole) of isomeric 2-naphthalenethiol-2,5-dimethyl-2,4-hexadiene adducts (90% 1,2-adduct, 10% 1,4-adduct) was oxidized to the corresponding sulfones by a 10% excess of aqueous 90% hydrogen peroxide in glacial acetic acid in a manner described above to yield 5.1 g. (75%) of colorless, crystalline 5-β-naphthylsulfonyl-2,5-dimethyl-2-hexene, m.p. 91–92.5°.

Co-oxidation of Aromatic Thiols with 2,5-Dimethyl-2,4-hexadiene.—Oxygen (air) was introduced into a stirred *n*-heptane solution, containing 5.5 g. (0.05 mole) of 2,5-dimethyl-2,4-hexadiene and 0.05 mole of an aromatic thiol, with ice water-cooling between 0–10°. The introduction of oxygen was continued until the thiol content of the solution had decreased to less than 5% of the original. This took between 2 and 3 hr. By that time most of the hydroperoxide product of the reaction usually crystallized on the walls of the reaction vessel. If crystallization did not occur, it was initiated by scratching and cooling a sample of the mixture in a solid carbon dioxide–acetone bath. After the crystallization had started at room temperature, the solution was slowly cooled to −20° to obtain a better yield of the crystals. The crystalline product was then isolated by filtration of the cold solution with suction, subsequently washing with cold *n*-pentane and drying at 1 mm. for 1 hr. at room temperature. Some physical properties, analytical data and the yields of the 2,5-dimethyl-5-arylmercapto-3-hexen-2-yl hydroperoxides obtained are shown in Tables V–VII.

Decomposition of 5-(2-Naphthylmercapto)-2,5-dimethyl-3-hexene-2-yl Hydroperoxide.—A solution of 2.1 g. (0.007 mole) of the hydroperoxide (IV) in a mixture of 30 ml. of *n*-heptane and 10 ml. of benzene was left to stand in a tightly stoppered flask at room temperature for 5 days. By the end of this period, the solution was yellow and contained a voluminous platelike crystalline precipitate. These crystals were removed by filtration, recrystallized from a toluene–*n*-heptane mixture to yield 0.6 g. of bis-2-naphthyl disulfide which was identified by the comparison of its infrared spectrum with that of an authentic sample and by mixed melting point. On concentrating the filtrate, 0.2 g. more of the disulfide was isolated to yield a total of 0.8 g. (0.0025 mole) of disulfide.

The liquid residue was dried in a vacuum desiccator to yield 0.75 g. of a yellow oil with a peroxide equivalent of 534.

Other 5-arylmercapto-2,5-dimethyl-3-hexene-2-yl hydroperoxides also decomposed in a similar manner on standing.

Change of the infrared spectrum of the hydroperoxide with time was studied in carbon tetrachloride. The inten-

---

[44] C. D. Wagner, R. H. Smith, and E. D. Peters, *Anal. Chem.*, **19**, 976 (1947).

[45] A. A. Ostwald, F. Noel, and A. J. Stephenson, *J. Org. Chem.*, **26**, 3969 (1961).

[46] 1958 Book of ASTM Standards, American Society for Testing Materials, Philadelphia, Pennsylvania, D-555-58, Part 8, p. 271.

sity of the bands at 3, 7.6, 8.0, 8.9, 11.9 μ which may be associated with the vibration of the hydroperoxy group were decreased. The band at 9.8 μ shifted to 9.9 μ indicating decomposition of the hydroperoxide to a peroxide.

Removal of Dienes from Severely Cracked Naphtha by Co-oxidation with 2-Naphthalenethiol.—a. 2-Naphthalenethiol (16 g., 0.1 mole) was dissolved in 100 ml. (82 g.) of severely cracked naphtha of diene number 34. Air was introduced into the solution at room temperature for 3 hr. Then the solution was cooled to 0° and the air introduction was continued for another 3 hr. At the end of this period, the clear orange-colored reaction mixture was placed in a cold box at −15°. At this temperature, an almost colorless solid precipitated. It was filtered off by suction and washed with cold *n*-heptane. In this manner, 0.4 g. of substance having peroxide equivalent 242 was obtained. When the filtrate (65.3 g.) was diluted with an equal volume of *n*-heptane, 24 g. of orange-colored co-oxidation product separated as a bottom phase at room temperature. The latter product had a peroxide equivalent of 393. The diene number of the severely cracked naphtha decreased to one third of the original as a result of the treatment.

The solid peroxidic product showed the following composition on analysis: C, 72.72; H, 5.05; S, 7.2; 0 (by difference), 15.03. The liquid peroxide isolated had a sulfur content of 8.35%. The infrared spectrum of both is shown in Fig. 3.

b. In 100 ml. of severely cracked naphtha of diene number 14, 16 g. (0.1 mole) of 2-naphthalenethiol was dissolved while air was introduced into the mixture. Then the solution was cooled by ice water to about 0°, while the introduction of air was continued. At 0°, however, some of the naphthalenethiol precipitated. Therefore the mixture was allowed to come to room temperature. During the second cooling period, no precipitation was observed. This showed the progress of the reaction. After a total of 4 hr. of air introduction, the solution was kept overnight at −29°, when 4.4 g. of light yellow liquid separated. On further cooling to −73°, 16 g. more substance crystallized, which turned to a yellow liquid at room temperature. These liquids gave a positive qualitative peroxide test.

The naphtha filtrate after this treatment was distilled at 10 mm. on a steam bath to yield 80 ml. of a colorless distillate with a diene number of 1.6. This distillate remained colorless for 5 days when left standing in an open Erlenmeyer flask at 43°. The distillation residue deposited 2.4 g. of crystals which had a peroxide equivalent of 1692.

Air Oxidation of Severely Cracked Naphtha.—A 100-ml. sample of the severely cracked naphtha used in experiment b was air oxidized in the same manner as in (b), but at 0° without the addition of naphthalenethiol. After 8 hr. of air introduction, the naphtha was distilled at 10 mm. (maximum bath temperature 100°). The distillate obtained (89 ml.) contained more low boiling constituents than the corresponding distillate of experiment b above, but was colored (Rob. 18.5) and had a diene number of 13.

Acknowledgment.—The authors wish to thank T. Vicai and T. G. Jermansen for technical help, P. B. Gerhardt for the elemental, and J. A. Hinlicky for the infrared analyses.

Sulfobenzoic Acid Esters. III. The Correct Structures of the Aryl Esters

BERNARD LOEV AND MINERVA KORMENDY

Research and Development Division, Smith Kline and French Laboratories, Philadelphia 1, Pennsylvania

Received January 5, 1962

The structures of the compounds previously assumed to be phenyl 2-sulfamylbenzoate and its isomer, phenyl 2-sulfobenzamide, have both been shown to be incorrect; the various reactions involving these compounds have been elucidated.

Previous papers in this series[1] described the synthesis of aliphatic esters of 2-sulfamylbenzoic acid for evaluation as potential anticonvulsant agents. As part of this study the corresponding aryl esters were also desired.

The preparation of such a compound (*4*) and its isomer (*8*) (Fig. 1) was reported by Remsen[2,3] more than 60 years ago. We have discovered, in repeating Remsen's work, that certain of the structures which he assigned to his products are incorrect.

The reactions carried out by Remsen and the structures which he assigned to his products are shown in Fig. 1.

According to Remsen,[2] the diacid chloride of *o*-sulfobenzoic acid on heating with phenol gave an oil (*1*) which on stirring with ammonium hydroxide gave a mixture of the diphenyl ester (*3*) and another substance (*4*), m.p. 130°, whose analysis agreed with the structure he assigned to it (Fig. 1). Subsequently,[3] the half ester (*2*) was isolated from

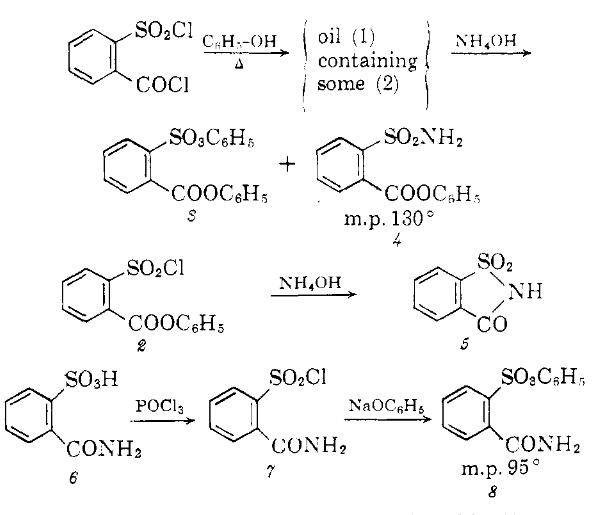


Fig. 1.—Reactions showing structures assigned by Remsen.

---

[1] B. Loev and Minerva Kormendy, Part I, *J. Org. Chem.*, **27**, 1703 (1962); Part II, *ibid.*, **27**, 2177 (1962).

[2] I. Remsen and S. R. McKee, *Am. Chem. J.*, **18**, 794 (1896).

[3] I. Remsen and R. E. Humphreys, *ibid.*, **30**, 292 (1903).