Anal. Calcd. for $C_{48}H_{56}N_6O_{12}S_2$: C, 59.24; H, 5.80; N, 8.64; S, 6.59. Found: C, 59.38; H, 5.76; N, 8.53; S, 6.71.

S-Trityl-L-cysteinylglycine *p*-Nitrophenyl Ester Hydrochloride (XXI).—To the suspension of 0.78 g. (0.001 mole) of XIII in 5 ml. of acetone was added 0.4 ml. of 5 *N* HCl. The mixture was shaken for 30 minutes, and the resulting clear solution was evaporated to dryness. Upon adding ether, 0.52 g. (90%) of XXI was obtained as a microcrystalline not hygroscopic powder; it was dissolved in ethyl acetate and precipitated again with ether; $[\alpha]^{27}D$ +39.6° (*c* 3, ethanol).

Anal. Calcd. for $C_{30}H_{28}N_3O_5SCl$: N, 7.27; S, 5.55; Cl, 6.13. Found: N, 7.35; S, 5.65; Cl, 5.97.

L-Cystinyldiglycine (XXII).—The solution of 0.688 g. (0.002 mole) of XIVb and 0.4 g. of phenol in 3 ml. of trifluoroacetic acid was refluxed for 20 minutes and then it was concentrated to dryness *in vacuo*.[54] The L-cysteinylglycine thus formed was oxidized by aeration to XXII. For the isolation of the dipeptide the general procedure described by Weygand and Steglich[26] was followed. The yield was 0.25 g. (70%), $[\alpha]^{25}D$ −67° (*c* 1, water), reported[55] $[\alpha]^{27}D$ −67.5° (*c* 1, water).

N-Trifluoroacetyl-L-valyl-S-diphenylmethyl-L-cysteinylglycine Ethyl Ester (XXIII).—Compound XV (2 g., 0.005 mole) was deformylated in the same manner as the corresponding trityl derivative XI. The amorphous S-diphenylmethyl-L-cysteinylglycine ethyl ester hydrochloride (1.6 g., 0.004 mole) thus obtained was dissolved in chloroform and to this solution were added successively 0.56 ml. of triethylamine, 0.89 g. (0.0042 mole) of N-trifluoroacetyl-L-valine[33] and 0.88 g. of dicyclohexylcarbodiimide. After standing for 24 hours at room temperature the mixture was worked up as usual (compare above). The crude product XXIII thus obtained was repeatedly recrystallized from ethanol to constant m.p. 175° and $[\alpha]^{27}D$ −23.3° (*c* 3, dimethylformamide); the yield of pure[56] XXIII was 0.58 g. (23%).

Anal. Calcd. for $C_{27}H_{32}N_3O_5SF_3$: N, 7.40; S, 5.65. Found: N, 7.40; S, 5.28.

N-Trifluoroacetyl-L-valyl-L-cysteinylglycine Ethyl Ester (XXIV).—The solution of 1.7 g. (0.003 mole) of XXIII and 0.6 g. of phenol in 4.5 ml. of trifluoroacetic acid was refluxed for 30 minutes and then evaporated to dryness *in vacuo*. Upon dissolving the residue in 8 ml. of acetic acid[54] and adding 16 ml. of water, crystalline XXIV separated; it was collected, dried and washed with ether. The yield was 0.84 g. (70%), m.p. 193–195° and 194–196° after recrystallization from ethanol; $[\alpha]^{27}D$ −18° (*c* 3, dimethylformamide).

Anal. Calcd. for $C_{14}H_{22}N_3O_5SF_3$: N, 10.47; S, 7.99. Found: N, 10.33; S, 8.08.

N,N'-Bistrifluoroacetyl-L-valyl-L-cystinyldiglycine Diethyl Ester (XXV).—The solution of 0.4 g. (0.001 mole) of XXIV in 80% acetic acid was titrated with 0.1 *N* iodine; the theoretical amount of iodine solution was consumed and the cystine peptide XXV separated out; the yield was 95%, m.p. 238–239°, $[\alpha]^{27}D$ −92° (*c* 3, dimethylformamide), after recrystallization from ethanol.

Anal. Calcd. for $C_{28}H_{42}N_6O_{10}S_2F_6$: N, 10.49; S, 8.01. Found: N, 10.71; S, 8.14.

(54) Iodine titration of an aliquot revealed a 97% formation of sulfhydryl derivative.

(55) H. S. Loring and V. du Vigneaud, *J. Biol. Chem.*, 111, 385 (1935).

(56) Whether peptide XXIII consisted of D- or L-valine was not determined. The low yield of pure product may result from racemization during coupling.

[CONTRIBUTION FROM THE CENTRAL BASIC RESEARCH LABORATORY OF THE ESSO RESEARCH AND ENGINEERING CO., LINDEN, N. J.]

Organic Sulfur Compounds. VIII. Addition of Thiols to Conjugated Diolefins

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Radical addition of simple aliphatic and aromatic thiols and of thiolacetic acid to 1,3-butadiene, 2,3-dimethyl-1,3-butadiene, isoprene and chloroprene yields predominantly the 1,4-*trans*-monoadducts.

In the case of unsymmetrically substituted butadienes (isoprene, chloroprene and piperylene), the addition of aromatic thiyl radicals is highly selective to the first carbon atom. Aliphatic thiyl radicals are less selective; their addition to carbon four leads to significant amounts of the "reverse adducts" as by-products. The adducts are derived from the intermediate allylic radical through subsequent hydrogen abstraction from the thiol by the more reactive primary carbon atom.

Thiols add to piperylene to yield both 1,2- and 1,4-adducts. This is expected since both reactive carbons of the intermediate allylic radical are of the secondary type.

Addition of ionic and free radical reagents to conjugated dienes usually gives rise to both normal 1,2-addition and 1,4-conjugate addition. Kharasch and co-workers reported about a quarter of a century ago [3,4] that in the presence of peroxides the addition of hydrogen bromide and hydrogen chloride to butadiene resulted predominantly in 1,4-adducts while in the absence of peroxides mainly the 1,2-adducts were formed. Carbon tetrachloride and butadiene also formed a 1,4-addition product under free radical conditions, along with larger amounts of telomeric products.[5]

The first addition of a thiol to a conjugated diolefin was reported by Posner[6] in 1905. On treating benzenethiol with 1-phenyl-1,3-butadiene, he obtained an unidentified liquid adduct. On oxidation with potassium permanganate, this yielded a crystalline sulfone corresponding to the 1,4-adduct in an unreported yield.

$$C_6H_5SH + CH_2{=}CHCH{=}CHC_6H_5 \longrightarrow C_6H_5SCH_2CH{=}CHCH_2C_6H_5 \xrightarrow{KMnO_4} C_6H_5SO_2CH_2CH{=}CHCH_2C_6H_5$$

In 1949, Behringer described the addition of thiolacetic acid to 2,3-dimethyl-1,3-butadiene.[7] He did not determine, however, whether the 1,2- or 1,4-adduct was formed. In the last twelve years, free radical addition of thiols to butadiene,[8,9] 3-methylenecyclohexene and 1,2-dimethylenecyclo-

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(3) M. S. Kharasch, E. T. Margolis and F. R. Mayo, *J. Org Chem.*, **1**, 393 (1936).

(4) M. S. Kharasch, J. Kritchevsky and F. R. Mayo, *ibid.*, **2**, 489 (1937).

(5) W. R. Peterson, U. S. Patent 2,401,099 (1946).

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

(7) H. Behringer, *ibid.*, **82**, 219 (1949).

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

(9) J. A. Reeder, Ph.D. Thesis, University of Colorado, 1958.

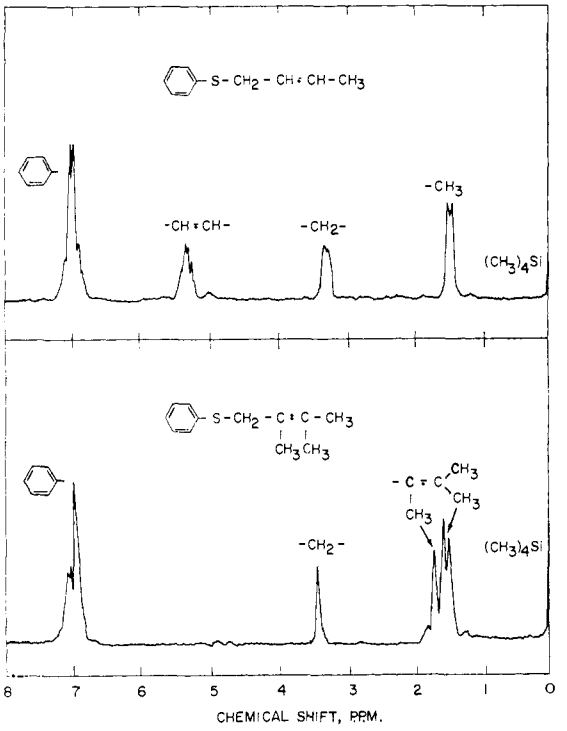


Fig. 1.—Nuclear magnetic resonance spectra of thiol-butadiene adducts.

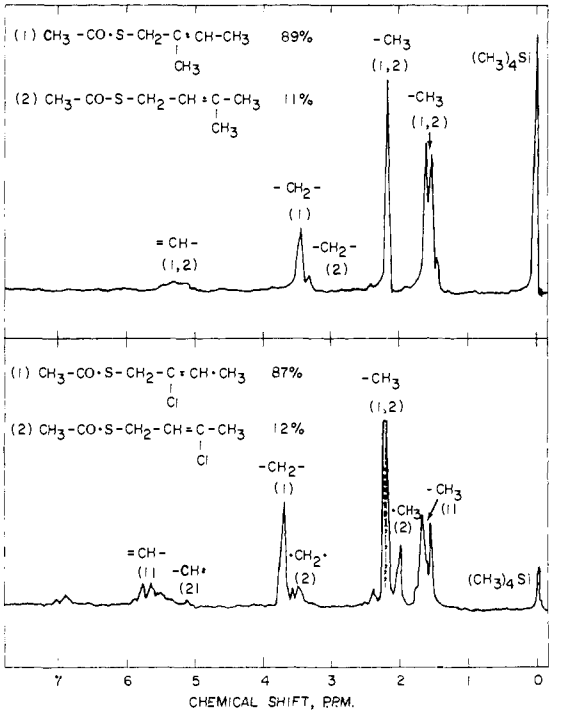


Fig. 2.—Nuclear magnetic resonance spectra of thiol-isoprene and thiol-chloroprene adducts.

hexane[10] has been described. These latter reactions yielded almost entirely the 1,4-adducts.

It was reported in the previous paper of this series[11] that the free radical addition of thiols to

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

(11) A. A. Oswald, B. E. Hudson, Jr., G. Rodgers and F. Noel, *ibid.*, **27**, 2439 (1962).

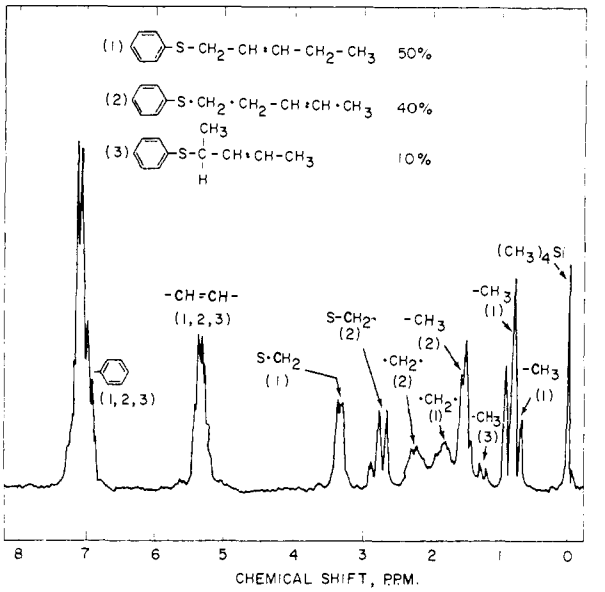


Fig. 3.—Nuclear magnetic resonance spectra of benzenethiol–piperylene adducts.

2,5-dimethyl-2,4-hexadiene yielded predominantly the 1,2-adducts. The structure of the diolefin apparently affected the ratio of the 1,2- and 1,4-adducts formed on thiol addition.

It was proposed in this Laboratory that most of the thiol–diene adduct is derived from the intermediate allylic radical at the less highly substituted (primary or secondary) allylic carbon atom. For example, in the case of 1,3-butadiene and 2,5-dimethyl-2,4-hexadiene the main addition products are formed by the propagation mechanisms

$$CH_2{=}CHCH{=}CH_2 \xrightarrow{RS\cdot} \left[RSCH_2\dot{C}HCH{=}CH_2 \leftrightarrow RSCH_2CH{=}\dot{C}HCH_2\right] \xrightarrow{RSH} RSCH_2CH{=}CHCH_3$$

$$C(CH_3)_2{=}CHCH{=}C(CH_3)_2 \xrightarrow{RS\cdot} \left[RSC(CH_3)_2\dot{C}HCH{=}C(CH_3)_2 \leftrightarrow RSC(CH_3)_2CH{=}\dot{C}HC(CH_3)_2\right] \xrightarrow{RSH} RSC(CH_3)_2CH_2CH{=}C(CH_3)_2$$

To gain further evidence regarding this hypothesis, the addition of simple aliphatic and aromatic thiols and thiolacetic acid to 1,3-butadiene, 2,3-dimethyl-1,3-butadiene, isoprene (2-methyl-1,3-butadiene), chloroprene (2-chloro-1,3-butadiene) and piperylene (1,3-pentadiene) were studied. The thiol-butadiene reaction product was re-examined using n.m.r. technique. No addition reaction of thiols to the other dienes had yet been studied to our knowledge.

Results

It was found that the addition of an aromatic thiol, benzenethiol, to the above dienes is complete in a few days, when an equimolar mixture of the

reactants is allowed to stand at room temperature in the absence of any catalyst. When the reaction mixture was heated on a water-bath or irradiated with ultraviolet light, the reaction was substantially complete in a few hours. As expected, thiolacetic acid was found to be somewhat less reactive. Aliphatic thiols, methanethiol and ethanethiol, react extremely slowly with these dienes at room temperature in the absence of a catalyst. In the presence of ultraviolet light, however, the reaction is completed in a few days.

The resulting adducts are colorless, mobile liquids. They can be purified by distillation *in vacuo*. But ordinary fractionation does not result in a complete separation of the 1,2- and 1,4-adduct isomers. However, these isomers can be conveniently separated for quantitative analytical determination by gas chromatography on a Carbowax 20 M (polyethylene glycol of 20,000 average molecular weight) column.

The isomeric adduct mixtures were analyzed without separation. Elemental analysis of these mixtures and some of their physical properties are reported in Table I.

The nuclear magnetic resonance and infrared spectra of the isomeric adduct mixtures are shown in Tables II, III, IV and V. The n.m.r. spectra of representative benzenethiol-diolefin adducts are shown in Figs. 1, 2 and 3. The n.m.r. spectra usually indicated the structure of the adduct isomers in an unequivocal manner and were also used for semi-quantitative determination of the isomer distribution.

Butadiene.—The addition of 1-butanethiol and 4-toluenethiol to 1,3-butadiene was reported to yield *trans*-1,4-addition products.[8,9] Our experiments using methane-, ethane-, benzene-thiol and thiolacetic acid also yielded the 1,4-adduct of butadiene in greater than 95% yield.

$$RSH + CH_2{=}CHCH{=}CH_2 \longrightarrow RSCH_2CH{=}CHCH_3$$

The disubstituted ethylene structure of the adducts is clearly indicated by their n.m.r. spectra (Table II, Fig. 1). They all show the two vinyl protons as a partially resolved multiplet of the MN portion of a A_2MNX_3 spin system.[12] The two methylene protons on the carbon α-(alpha)- to the sulfur show a doublet split as expected by the vinyl proton on the adjacent carbon. Methyl protons of the 2-buten-1-yl groups can also be clearly recognized as a doublet at about 1.6 p.p.m. downfield from the tetramethylsilane internal reference.

The infrared spectra of the thiol–butadiene addition products are also characteristic of 1,4-adducts. They show a very strong absorption at 10.4 μ Table V. This is assigned to the out of plane —CH= deformation vibrations of *trans*-disubstituted ethylenes.[13] None of the starting materials absorb in this region. Even though absorption occurs between 12.5 and 14 μ, none of these bands can be definitely assigned as a *cis*-band, since little is known about the effect of α-alkylmercapto substitution on the wave lengths of out-of-plane —CH= deformation vibrations of *cis*-disubstituted olefins.[13]

Gas chromatographic analyses of the products of each reaction show a single major peak which accounts for more than 95% of the total. Consequently, it is assumed that the 1,4-addition of thiols to butadiene yielded essentially the *trans*-butene derivatives.

Bands of much smaller intensity and inflections at about 10.85 μ may be due to the deformation vibrations of vinylic hydrogens in small amounts of 1,2-adduct.[13] The presence of small amounts of minor products is also indicated by vapor phase chromatography.

Dimethylbutadiene.—Gas chromatography (Table I) of our thiol– and thiolacetic acid–dimethylbutadiene adducts showed that the main component of the addition products was formed in more than 95% yield. This was shown by n.m.r. (Table II and Fig. 1) to be the 1,4-adduct, formed by the reaction sequence

$$RS\cdot + CH_2{=}C(CH_3{+})C(CH_3){=}CH_2 \longrightarrow \left[RSCH_2C(CH_3){=}CH_2 \leftrightarrow RSCH_2C(CH_3){=}C(CH_3)CH_2\cdot \right] \xrightarrow{RSH} RSCH_2C(CH_3){=}C(CH_3)CH_3.$$

No vinylic protons resulting from 1,2-addition could be observed in the spectra. The virtual absence of 1,2-addition is also indicated by the singlet methylene signal. The protons of the three methyl groups of the aromatic thiol adducts show three separate unsplit peaks. This is attributable to long range shielding and deshielding by the magnetically anisotropic aromatic rings. In the n.m.r. spectra of aliphatic thiol adducts, the corresponding three methyl groups give one signal of triple intensity.

Infrared spectra of the adducts are also in accord with 1,4-addition. Bands of varying but in all cases low intensity between 11.0 and 11.25 μ may indicate the presence of very small amounts of 1,2-addition products.[13]

Isoprene.—Gas chromatography (Table I) of thiol–isoprene adducts showed two main components, n.m.r. analyses (Table III and Fig. 2) indicated that the larger component (60–96% depending on thiol) was the 1,4-adduct. The formation of this product could be rationalized by the reaction mechanism

$$RS\cdot + CH_2{=}C(CH_3)CH{=}CH_2 \longrightarrow \left[RSCH_2C(CH_3)CH{=}CH_2 \leftrightarrow RSCH_2C(CH_3){=}CHCH_2\cdot \right] \xrightarrow{RSH} RSCH_2C(CH_3){=}CHCH_3.$$

The smaller component was the "reverse" 4,1-adduct

$$RS\cdot + CH_2{=}CHC(CH_3){=}CH_2 \longrightarrow \left[RSCH_2.CHC(CH_3){=}CH_2 \leftrightarrow RSCH_2CH{=}C(CH_3)CH_2\cdot \right] \xrightarrow{RSH} RSCH_2CH{=}C(CH_3)CH_3.$$

(12) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., N. Y., 1959, p. 242.

(13) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," J. Wiley and Sons, Inc., New York, N. Y., 1959, pp. 45–49.

TABLE I

SOME PHYSICAL AND ANALYTICAL DATA OF THIOL–DIENE ADDUCTS

Adduct of: Diene	Thiol	Adduct formula	Conversion[a]: %	After days	At temp., °C.	Ultraviolet	Yield,[b] %	Adduct isomers by G.C., %: 1,2	1,4	4,1	B.p., °C. mm.	$n^{25}D$	Elemental analyses, % Calculated: C	H	S	Found: C	H	S
Butadiene	Methanethiol	$C_5H_{10}S$	...	...	...	....	95	3[c]	96	...	67–68 /100	1.4790	58.77	9.86	31.37	58.85	9.83	31.12
	Ethanethiol	$C_6H_{12}S$	...	...	...	...	96	4[c]	90	...	64–65 /40	1.4755	62.01	10.40	27.59	61.97	10.58	27.67
	Benzenethiol	$C_{10}H_{12}S$	100	5	Ambient	No	98	1[c]	99	...	128–129/28	1.5706	73.12	7.36	19.52	72.84	7.49	18.99
	Thiolacetic acid	$C_6H_{10}OS$	77	1	Ambient	Yes	91	2[c]	98	...	25–26 /5	1.4890	55.35	7.74	24.63	55.15	7.72	24.52
2,3-Dimethyl-butadiene	Methanethiol	$C_7H_{14}S$	50	1	Ambient	Yes	97	2.5[c]	97	...	55–56 /20	1.4919	64.55	10.83	24.62	64.46	10.83	24.79
	Ethanethiol	$C_8H_{16}S$	35	1	Ambient	Yes	98	3[c]	96	...	112–115/80	1.4874	66.60	11.17	22.23	66.82	11.12	22.30
	Benzenethiol	$C_{12}H_{16}S$	100	1/4	95	No	99	1[c]	98	...	82–84 /2	1.5637	74.95	8.38	16.67	75.23	8.60	16.40
	Naphthalenethiol	$C_{16}H_{18}S$	100	1/4	95	No	97	...	99	...	162–164/3	1.6328	79.29	7.48	13.23	79.33	7.31	13.49
	Thiolacetic acid	$C_8H_{14}OS$	84	1/4	95	No	94	1[c]	99	...	45–46 /1	1.4986	60.72	8.91	20.27	60.71	8.95	20.10
Isoprene	Methanethiol	$C_6H_{12}S$	...	...	...	...	80	...	76	22[d]	146–148	1.4826	62.04	10.41	27.55	62.18	10.39	27.67
	Ethanethiol	$C_7H_{14}S$	58	4	Ambient	Yes	88	...	75	25[d]	58–60 /20	1.4805	64.55	10.83	24.62	65.17	11.27	25.42
	Benzenethiol	$C_{11}H_{14}S$	100	1/8	Ambient	Yes	96	...	97.5	2.5[d]	60–62 /1	1.5654	74.11	7.91	17.98	73.99	7.08	17.76
	Thiolacetic acid	$C_7H_{12}OS$	76	1/8	Ambient	Yes	89	...	89	10[d]	30–31 /1	1.4933	58.31	8.39	22.20	58.12	8.10	21.92
Chloroprene	Methanethiol	C_5H_9ClS	...	...	...	...	77	...	75	25[d]	69–71 /20	1.5088	43.95	6.63	23.47	43.81	6.72	23.59
	Ethanethiol	$C_6H_{11}ClS$	60	1	Ambient	Yes	75	...	72	28[d]	87–89 /20	1.5023	47.83	7.35	21.28	47.69	7.31	21.35
	Benzenethiol	$C_{10}H_{11}ClS$	88	1/8	Ambient	Yes	90	...	95	5[d]	73–74 /1	1.5800	60.45	5.57	16.13	60.52	5.75	15.92
	Thiolacetic acid	C_6H_9ClOS	75	1/8	Ambient	Yes	67	...	86	13	50–51 /2	1.5122	43.77	5.50	19.48	43.80	5.40	15.65
Piperylene	Methanethiol	$C_6H_{12}S$	...	...	...	...	81	31[f]	49	20[e]	64–68 /42	1.4745	62.04	10.41	27.55	61.95	10.51	27.70
	Ethanethiol	$C_7H_{14}S$	95	15	Ambient	Yes	75	34[f]	52	16[e]	54–59 /14	1.4723	64.55	10.83	24.62	64.80	11.11	24.62
	Benzenethiol	$C_{11}H_{14}S$	100	1/8	Ambient	Yes	95	46[f]	47	7[e]	87–93 /1	1.5589	74.11	7.91	17.98	73.98	7.73	17.89
	Thiolacetic acid	$C_7H_{12}OS$	90	7	Ambient	Yes	80	...	...	...	44–46 /1	1.4840	58.31	8.39	22.20	58.38	8.49	22.62

[a] On the basis of the decrease of the mercaptan content of the reaction mixtures. [b] On the basis of the converted reagents. [c] The 1,2-adduct has a shorter retention time than the 1,4. [d] The 1,4-adduct has a longer retention time than the 4,1. [e] The 4,1-adduct has the shortest retention time. [f] The 1,2-adduct has the longest retention time.

TABLE II

PARAMETERS OF NUCLEAR MAGNETIC RESONANCE SPECTRA OF THIOL–DIENE ADDUCTS

Adduct of: Diene	Thiol	In General Formula: R	X	Chem. shifts of structural units downfield from tetramethylsilane intern. ref., p.p.m. (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet): RS—	—CH_2—	—CX=	=CX—	—CH_3
1,3-Butadiene	Methanethiol	CH_3	H	s1.92	d2.95[a]	m5.44[b]	m5.44[b]	d1.70[a]
	Ethanethiol	C_2H_5	H	t1.18,[c] q2.38[c]	d2.98[a]	m5.43[b]	m5.43[b]	d1.68[a]
	Benzenethiol	C_6H_5	H	s7.2	m3.40	m5.45[b]	m5.45[b]	d1.52[a]
	Thiolacetic acid	CH_3CO	H	s2.19	d3.38[a]	m5.42[b]	m5.42[b]	d1.58[a]
2,3-Dimethyl-1,3-butadiene	Methanethiol	CH_2	CH_3	s1.88	s3.05	s1.68	s1.68	s1.68
	Ethanethiol	C_2H_5	CH_3	t1.19,[c] q2.36[c]	s3.13	s1.70	s1.70	s1.70
	Benzenethiol	C_6H_5	CH_3	m7.12	s3.42	s1.72	s1.56	s1.47
	2-Naphthalenethiol	$C_{10}H_7$	CH_3	m7.1–7.6	s3.48	s1.67	s1.49	s1.42
	Thiolacetic acid	CH_3CO	CH_3	s2.18	s3.51	s1.60	s1.60	s1.60

[a] Coupling constant $J = 5$ c.p.s. [b] Partially resolved MN portion of A_2MNX_3 spin system. [c] $J = 7$ c.p.s.

TABLE III

PARAMETERS OF NUCLEAR MAGNETIC RESONANCE SPECTRA OF THIOL–ISOPRENE AND THIOL–CHLOROPRENE ADDUCTS

Starting compounds: Diene	Thiol	1,4-Adduct / 4,1-Adduct: Adduct type	X	RS—	RS—	—CH_2—	—CH_2—	—CX—	—CH=	=CH—	—CX—	—CH_3	—CH_3
				Chem. shifts of structural units, p.p.m. downfield from tetramethylsilane intern. ref. s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet									
Isoprene	Methanethiol	1, 4		s1.87		s3.00		s1.68		q5.28[a]		d1.62	
		4, 1	CH_3		s1.96		d3.08[a]		t[b]		s1.75		s1.68
	Ethanethiol	1, 4		q2.28,[a] t1.17[a]		s2.97		s1.63		q5.20[a]		d1.58[a]	
		4, 1	CH_3		q2.28,[a] t1.17[a]		d3.03[a]		t5.12[a]		s1.68		s1.53
	Benzenethiol	1, 4		m7.10		s3.38		s1.65		q5.22		d1.42	
		4, 1	CH_3		m7.10		d3.40[a]		t[b]		s1.74		s1.55
	Thiolacetic acid	1, 4		s2.20		s3.50		s1.64		q5.38		d1.52	
		4, 1	CH_3		s2.20		d3.40		t5.10[a]		s1.64		s1.57
Chloroprene	Methanethiol	1, 4		s2.20		s3.30		...		q5.68[a]		d1.76[a]	
		4, 1	Cl		s2.06		d3.23		t[b]		...		s2.15
	Ethanethiol	1, 4		q2.48,[a] t1.22[a]		s3.35		...		q5.80[a]		d1.76[a]	
		4, 1	Cl		q2.48,[a] t1.22[a]		d3.28		t[b]		...		s2.13
	Benzenethiol	1, 4		m7.15		s3.58		...		q5.43[a]		d1.54[a]	
		4, 1	Cl		m7.15		d[b]		t[b]		...		s1.87
	Thiolacetic acid	1, 4		s2.25		s3.69		...		q5.75[a]		d1.68[a]	
		4, 1	Cl		s2.25		d3.52[a]		t5.50		...		s2.06

[a] J = c.p.s. [b] Indistinct peaks due to low concentration of components.

TABLE IV

PARAMETERS OF NUCLEAR MAGNETIC RESONANCE SPECTRA OF THIOL–PIPERYLENE ADDUCTS

Piperylene adduct of	Type of addition: 1,2-Adduct / 1,4-Adduct / 4,1-Adduct	RS—	RS—	RS—	—CH_2—	—CH—	—CH_2—	—CH=CH— (—CH_3)	—CH=CH—	—CH_2—	—CH=CH	—CH_3	—CH_3	—CH_3
		Chem. shifts of structural units, p.p.m. downfield from tetramethylsilane intern. ref. s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet												
Methanethiol	1, 2	s2.00			t2.32		...[d]		*m5.35*			d1.60[a]		
	1, 4		s1.96			d3.00[a]		*m5.35*		...[d]			t0.98[c]	
	4, 1			s1.93		...[b]		d1.28[c]			*m5.35*			d1.67[a]
Ethanethiol	1, 2	q2.35,[c] t1.15[c]			...[d]		...[d]		*m5.33*			d1.58[a]		
	1, 4		q2.35,[c] t1.15[c]			d2.96[a]		*m5.33*		...[d]			t0.96[c]	
	4, 1			q2.35,[c] t1.15[c]		...[d]		d1.25[c]			*m5.33*			d1.62[a]
Benzenethiol	1, 2	m7.08			t2.77[c]		m2.22		*m5.22*			d1.58[a]		
	1, 4		m7.08			d3.36[a]		*m5.22*		m1.75			t0.84[c]	
	4, 1			m7.08		...[b]		d1.30[c]			*m5.22*			d1.49[a]
Thiolacetic acid	1, 2	s2.24			t2.88[c]		...[d]		*m5.45*			d1.60[a]		
	1, 4		s2.28			d3.45[a]		*m5.45*		...[d]			t0.95[c]	
	4, 1			s2.28		m4.03		d1.37[c]			*m5.45*			d1.65[a]

[a] J = 5 c.p.s. [b] Indistinct due to low concn. of component. [c] J = 7 c.p.s. [d] These peaks of the component cannot be recognized because of the complexity of the spectrum.

TABLE V

INFRARED ABSORPTION PEAKS OF THIOL-DIENE ADDUCTS

Adduct of: Diene	Thiol	General olefinic (and CO)	Absorp.					
1,3-Butadiene	.....	6.25s	6.7m,	7.2s,	7.3s,	7.8m		
	Methanethiol	6.05m, 6.15w		7.6m,		8.2s	8.5m,	9.2w
	Ethanethiol	6.05m, 6.15w		7.7m,	7.9s,	8.2s	8.5w	9.2w
	Benzenethiol	6.05m, 6.15w	6.5,[a]	7.7m,	7.9w,	8.2s	8.5w 8.7w,	9.2s
	Thiolacetic acid	(5.95vs)		7.65w		8.15m	8.9vs,	9.1vs
2,3-Dimethyl-1,3-butadiene	.....	6.22s	6.9s,	7.3s		8.45m		
	Methanethiol	6.0w, 6.1vs		7.6w,	7.85w,	8.1s	8.35m, 8.6m,	9.0s
	Ethanethiol	6.1m, 6.2i			8.0s,	8.2s	8.5s, 8.7s,	9.1s
	Benzenethiol	6.05m, 6.15w	6.3s,[a]	7.7m,	7.9w,	8.2s	8.4s, 8.65s,	9.2s
	2-Naphthalenethiol	6.05m, 6.15w	6.2s,[a]	6.3vs[a]	7.9m,	8.2s	8.4s, 8.65s,	8.85s
	Thiolacetic acid	(5.95vs)			7.85vs,	8.15w	8.4w, 8.8vs,	9.05vs
Isoprene	.....	6.25vs	6.8m,	6.9s,	7.05m,	7.3m		
	Methanethiol	6.05m, 6.1i			8.1m,	8.3m		9.2w
	Ethanethiol	6.05m, 6.1vw		7.9s,	8.15s,	8.3m		9.2w
	Benzenethiol	6.0m, 6.1vw	6.3s,[a]	7.7w,	8.1m,	8.3s	8.45w, 8.65w,	9.2s
	Thiolacetic acid	(5.95vs)			8.1m,	8.3w	8.8vs,	9.05vs
Chloroprene	.....	6.15s, 6.2s, 6.3s				8.2s		
	Methanethiol	6.05s, 6.15vw		7.65s,		8.15s	8.4m, 8.9s,	9.15m
	Ethanethiol	6.05s, 6.15vw		7.65s,	7.9s,	8.1s	8.4m, 8.9m,	9.15m
	Benzenethiol	6.0s, 6.1w	6.3s,[a]	7.7s		8.1s	8.5m, 8.95s,	9.2s
	Thiolacetic acid	(5.95)		7.7s		8.15m	8.4w, 8.9vs,	9.1vs
Piperylene	.....	6.05m, 6.2m	6.9s,	7.1m,	7.3m,	7.7m	8.4m	
	Methanethiol	6.05w, 6.15i		7.6w,	7.95s,	8.2m	8.3m	9.1s
	Ethanethiol	5.9m, 6.1w		7.75i,	7.9vs,	8.2s	8.3m, 8.7w,	9.1m
	Benzenethiol	6.0w, 6.1i	6.3[a]	7.7m,	7.9m,	8.2s	8.45w, 8.65w,	9.2s
	Thiolacetic acid	(5.95vs)		7.6vw	7.8vw,	8.2w	8.3vw,	8.9vs

[a] Absorption of the aromatic ring. [b] Absorption of the 2-substituted naphthyl ring system. [c] Absorption of *trans*-di-

Methylene protons of the 1,4-adduct are represented by an unsplit peak. One methyl group signal appears as a singlet while the other is split into a doublet by the single vinyl proton. The methylene protons of the 4,1-adduct, on the other hand, are split into a doublet by the vinyl proton, while the methyl groups are unsplit but show up at different positions as a result of their *cis* and *trans* locations with respect to the single vinyl proton. No terminal vinyl unsaturation corresponding to a 1,2- or 4,3-adduct could be observed in the n.m.r. spectra. On the basis of the relative strength of these characteristic n.m.r. signals, the amount of 1,4- and 4,1-adducts in mixtures was estimated and assignments of gas chromatography peaks were made. The ratio of 1,4- to 4,1-adducts formed on the addition of aliphatic thiols and thiolacetic acid to isoprene is below 3 while the same ratio is above 10 in the case of the adducts of benzenethiol and isoprene.

The infrared spectra of each of the thiol–isoprene addition products exhibit bands of medium intensity in the region between 11.9 and 12.3 μ which can be assigned to the —CH= deformation vibrations of the trisubstituted ethylene[14] resulting from 1,4- and 4,1- addition. The absence of bands of significant intensity around 11.0 μ, on the other hand, indicates that no significant amount of 1,2-adduct was formed in these reactions.[13]

Addition of thiyl radicals, leading to the "straight" 1,4-adduct, is expected to occur preferentially since this results in a more stable allylic radical than addition at carbon four. The formation of a greater proportion of a 1,4-adduct on addition of an aromatic thiol can be attributed to the enhanced stability of thiyl radicals derived from aromatic thiols. Consequently, benzenethiyl radical adds with an increased selectivity to carbon one to form the more stabilized allylic radical.

Chloroprene.—Gas chromatography (Table I) of the thiol–chloroprene adducts like those of isoprene showed a large (72–95% area) and a smaller peak which were shown by n.m.r. (Table III and Fig. 2) to be 1,4- and 4,1-structures, respectively: $RSCH_2CCl{=}CHCH_3$ and $RSCH_2CH{=}CClCH_3$. The singlet methylene and doublet methyl signals of the chlorobutenyl moiety in the 1,4-adducts could be distinguished easily from the doublet methylene and singlet methyl signals of the 1,4-adducts. The virtual absence of 1,2- or 4,3-addition of thiols to chloroprene is indicated by the absence of signals of terminal vinylic protons.

The infrared spectra of the thiol–chloroprene adducts also indicate that the addition took place to the end carbon atoms of chloroprene. Each of the addition products shows the —CH= deformation vibration between 12.25 and 12.4 μ of a trisubstituted ethylene.[14] No evidence for the presence of any significant amounts of 1,2-adduct can be obtained in the infrared spectra around 11 μ.

The 1,4- and 4,1-adducts of thiol–chloroprene reactions were apparently formed by mechanisms analogous to those shown for thiol–isoprene systems. The 1,4- to 4,1-adduct isomer ratios of chloroprene adducts were generally lower than those of the corresponding isoprene adducts. However, benzenethiol again gave mainly (90%) the 1,4-adduct. This indicates that the main factor determining whether the thiyl radical adds to carbon one or four of the diolefin is, in both cases, the stability of the intermediate allylic radical.[15] The unfavorable polar effect of the electronegative chlorine atom[16] is apparently negligible.

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

(15) C. Walling and W. Helmreich, *J. Am. Chem. Soc.*, **81**, 1137 (1959).

(16) C. Walling, D. Seymour and K. B. Wolfstirn, *ibid.*, **70**, 2559 (1948).

TABLE V (*continued*)

tion peaks, μ (vs, very strong; m, medium; w, weak; i, inflection

Other characteristic peaks above 7.5 μ, plus aromatic and *trans*-disubstituted-olefinic peaks

	9.75i,	9.85vs	10.05i,	11.05vs,			12.7m,	13.1w	13.8m,	14.9s	
9.4m,		9.65w	*10.4vs*,[c]	10.9s,	11.8wv						
9.4m,	9.55m,	9.65m	*10.4vs*,[c]	10.9s,	11.6vw		12.8m,	13.2w	13.35m,	14.3m	
9.4s		9.75s	*10.4vs*,[c]	10.85s,	11.6vw,	12.0vw	12.9w		*13.5vs*,[d]	*14.5vs*[d]	
	9.4m		*10.4vs*,[c]				12.8w			14.4m	
			10.05m,	11.05vs							
		9.9w	10.25m,	10.45m,	11.15m,	11.8vw		13.5m	14.1m,	14.55m,	15.0m
	9.55m		10.4s,	10.8i,	11.2m,	11.8m	12.8m,	13.4m	13.9s,	15.3m	
9.4s,	9.8s,	10.0w	10.4w,	11.0i	11.2s,	11.7m			*13.5vs*,[d]	*14.5vs*[d]	
9.35s,		9.85s	10.45m,	*10.65vs*,[b]	11.25s,	*11.8vs*[b]	*12.35vs*,[b]	13.15m	*13.45vs*,[b]	*14.15*m[b]	
		9.9m	10.5s,	11.0w						13.95m	
9.3m			10.0s,		11.2vs						
		9.75m	10.3m,	10.45m,	11.6m,	11.85m	12.1m,	12.8m	13.65m,	14.7s	
	9.5w,	9.85m	10.35m		11.25w,	11.9m	12.15m,	12.8m	13.35m,	14.1s	
9.35m,	9.75vs,	10.0i	10.4w	11.0i,	11.2m,		12.1m,	12.8m	*13.5vs*,[d]	*14.5vs*[d]	
	9.8m		10.5vs,		11.35w,	11.9m	12.8m,	13.1vw		14.3s	
	9.8m		10.3s,	10.9s,	11.4vs						
	9.65 vw,	10.1vs	10.4s,	10.65vs		11.75m	12.3s,	13.13m	13.5s,	14.45s	
9.5m,	9.6w		10.3s,	10.55vs	11.4m		12.3s,	13.3m	13.75s,	14.45m	
9.35s,	9.75s,	10.0w	10.55vs		11.3m,	12.1i	12.3s,	*13.4vs*[d]	*14.5vs*,[d]	15.05s	
		10.0m	10.5vs	11.5w,				13.35m	13.85s,	15.05s	
	9.45m,	9.95vs	10.55s	11.1vs			12.25m,	12.9m	13.25w,	13.8w	
		9.8vs	*10.4vs*,[c]	11.0w,	11.3w,	11.6w	12.4s,	13.3vw	13.8w,	14.8m	
9.3m,	9.5s,	9.9s	*10.4vs*,[c]	10.95m,	11.3w,	11.6w	12.75m,	13.15m	13.35m,	14.5m	
9.35s,	9.75s,	10.0m	*10.4vs*,[c]	11.0m,	11.2m,	11.5w	12.3w		*13.5vs*,[d]	*14.5vs*[d]	
	9.8s		*10.45vs*,[c]		11.3w,	11.6vw	12.3vw,	13.3w		14.6m	

substituted olefin. [d] Absorption of the monosubstituted benzene ring.

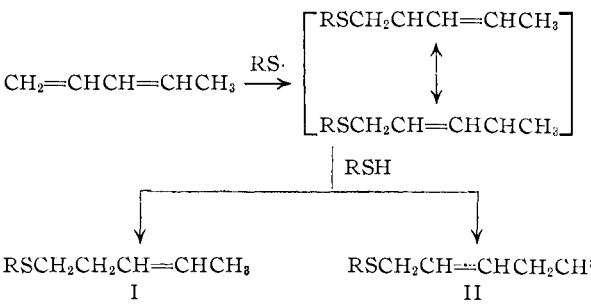
Piperylene.—As a starting material for the thiol additions, a 2:7 commercial mixture of *cis*- and *trans*-piperylene was used. The different structural isomers were separated by gas chromatography. Structural assignments of the g.c. peaks were made on the basis of the n.m.r. spectra of the adduct mixtures.

N. m. r. (Table IV and Fig. 3) indicated that the two major components of the product mixtures were the 1,2- and the 1,4-adduct (I and II). The 1,2-isomer could be recognized easily from the doublet signal of the single methyl group of the pentenyl moiety. The other major component, the 1,4-adduct, as expected had a doublet methylene signal, split by the adjacent vinyl proton, and a methyl triplet split by the adjacent methylene protons. The 4,1-adduct (III), a minor component, had two methyl group doublets split by single protons on the neighboring saturated and unsaturated carbon, respectively. No significant amount of 4,3-adduct was formed since signals of terminal vinylic protons were absent *from* the infrared and n.m.r. spectra of the products.

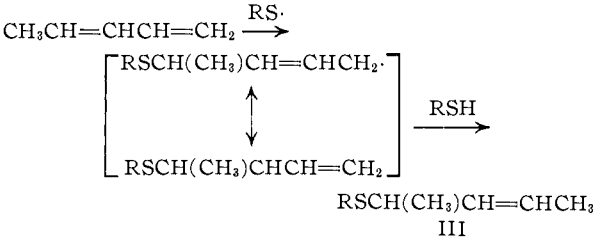
The amount of the 4,1-adduct formed was somewhat dependent on the thiols used in the addition reaction. Benzenethiol which gives a stable radical again gave much less of the reverse 4,1-adduct than the other thiols. Other differences in isomer composition were also observed. A more detailed study of the stereochemistry of radical addition to dienes using pure *cis*- and pure *trans*-piperylene is in progress and will be reported in a subsequent paper.

Infrared spectra of the thiol–piperylene adducts again show a very strong band at 10.4 μ which is usually characteristic of *trans*-disubstituted olefins. The presence of a definite *cis*-band could not be established. This indicates the presence of large amounts of *trans* isomer in at least one of the isomeric adducts.

The formation of the 1,2- and 1,4-adducts as major products in similar quantities can be explained by the preferential attack of a thiyl radical at the first carbon atom of piperylene to yield the more stable allylic radical intermediate, having both of its reactive positions at a secondary carbon



The side reaction, the addition of the thiyl radical to carbon four, results in a 4,1-adduct by subsequent hydrogen abstraction at the primary carbon



Discussion

The course of radical additions of thiols to conjugated diolefins probably is affected by the stability of the thiyl radical derived from the thiol and of the allylic radical formed on radical addition to the diene. Thiyl radicals of increasing stability add with increasing selectivity to the first carbon

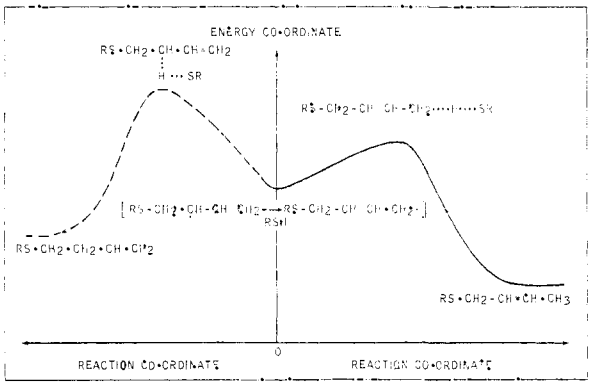


Fig. 4.—Energy relationships in hydrogen abstraction from thiol by allylic radical.

atom of unsymmetrically substituted butadienes so as to yield the more stable intermediate allylic radical. The latter then abstracts a hydrogen from the thiol, in a step of significant activation energy,[17] predominantly at the less highly substituted of the two allylic positions. This means that the transition state of this reaction has a lower energy than that of a similar reaction at the more highly substituted position. It is known that reaction at the less highly substituted position of the allylic radical yields the thermodynamically more stable product and is sterically favored. In the case of thiol–butadiene additions, these energy relationships are qualitatively pictured in Fig. 4.

It is believed that our observations may be explained by Hammond's correlation between the rates and free energies of chemical reactions.[18] The abstraction of hydrogen from a thiol by an allylic radical should be a reaction of significant activation energy. Therefore, the stability of the final product should make an important contribution to that of the transition state. Indeed, the thermodynamically more stable olefinic product is formed in such reactions; *i.e.*, the allylic radical is considerably reorganized in the transition state and the product is derived from its less contributing resonance form.

This hypothesis is further supported by the data of the previous paper of this series.[11] Addition of thiols to 2,5-dimethyl-2,4-hexadiene yielded mainly the 1,2-adducts, which are derived from hydrogen abstraction by the intermediate allylic radical at the less substituted carbon. On the other hand, on co-oxidation of thiols with the same diolefin the 1,4-products were obtained. The co-oxidation of diolefins yields different products since it involves the combination of the intermediate allylic radical with oxygen, a step of insignificant activation energy. Further results in this respect will be discussed in detail in the next paper of this series.

(17) C. Walling, "Free Radicals in Solution," J. Wiley & Sons, Inc., New York, N. Y., 1957, p. 314.

(18) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

Experimental

Materials.—The butadiene used was a C.P. chemical of 99%+ minimum grade. 2,3-Dimethyl-1,3-butadiene of Houdry Corporation, isoprene of Eastman Kodak Co. and chloroprene of du Pont de Nemours and Co. were redistilled before use. The piperylene used was a purified Enjay product containing 70% *trans*-piperylene, 20% *cis*-piperylene and 10% cyclopentene.

Methods of Analyses.—The n.m.r. spectra were recorded with a Varian model A-60 proton resonance spectrometer. 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 10 ft. Carbowax 20 M (20% polyethylene glycol of 20,000 average molecular weight) column.

Addition of Thiols to Dienes.—A mixture of 0.25 mole of a thiol and 0.25 mole of a diene was placed into a 100-ml. Vycor (98% silica) flask equipped with a magnetic stirrer and a condenser. In the case of reaction mixtures containing methanethiol and/or butadiene, a solid carbon dioxide–isopropyl alcohol cooled condenser was used. In the other cases the reaction flasks were equipped with chilled water–cooled condensers. All the condensers were closed at the end. The reaction flasks were irradiated by a 100 w. ultraviolet light (high pressure Hanovia utility lamp) from 5-cm. distance.

After an arbitrary length of time, the reaction was discontinued and the extent of the reaction was determined on the basis of the decrease of mercaptan content. The reaction mixture was then worked up. The unreacted aromatic mercaptans were removed by washing with 4% aqueous sodium hydroxide solution. The aliphatic mercaptans and dienes were distilled off at atmospheric pressure from a water-bath. The adducts were fractionated at reduced pressure (100–1 mm.). They were obtained as colorless, mobile liquids. The aliphatic thiol– and thiol-acetic acid–diene adducts had characteristic odors. The aromatic thiol–diene adducts were almost odorless. No attempt was made to separate the different isomers by super fractionation. The amount of the main isomers was determined by gas–liquid phase chromatography. Boiling ranges, refractive indices of the isomeric adduct mixtures and their elemental analyses are shown in Table I. Their n.m.r. spectra are shown in Tables II, III and IV and Figs. 1, 2 and 3. Infrared spectral data are given in Table IV.

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