tive to structure **1** and explain the product distribution found. The result is the same whether the transition state resembles the intermediates **1** and **2** or the close approach of the ion pair to the anhydride. The energy difference between the common ground state and transition state **1** is smaller and therefore the rate is greater.

The extension of this interpretation to the additions of thiols and alcohols to isocyanates[3c] is obvious and may prove helpful.

Experimental

Materials.—Untreated analytical reagent grade xylene (boiling range 137–140°) obtained from Mallinckrodt was used as the reaction solvent. Because of the high dilution of reactants it was felt that traces of water might affect the rate of reaction. Freshly distilled sodium-treated solvent was used for a kinetic run to test the influence of water. The results were no different from those observed with untreated xylene. The commercially available thiols used were distilled prior to use and made up as 2% stock solutions. The uncorrected boiling points are: 1-butanethiol, 96–97°; 2-methyl-2-propanethiol, 63–64°; 4-chlorobenzenethiol, 117° (48 mm.). Stock solutions of maleic anhydride were made by dissolution in warm xylene and filtration to remove the insoluble maleic acid; very little acid was recovered. Triethylenediamine obtained from the Houdry Process Co. was used as received. Denatured 95% ethanol and analytical reagent grade silver nitrate were used without purification.

Preparation of S-Deuterio-1-butanethiol.—This thiol was prepared in 12% yield by the method of Hobden and co-workers.[18] The purity, 95–100% RSD, was established by infrared analysis; the S–H stretching frequency was shifted from 2566 to 1850 cm.$^{-1}$ with deuterium substitution. The corresponding shift found by Hobden for S-deuterio-1-ethanethiol was 2566 to 1863 cm.$^{-1}$.

Sample Kinetic Procedure and Analysis.—The reaction vessel was a 500-ml., three-necked, round-bottomed flask fitted with a mechanical stirrer, condenser, and a gas inlet tube for the introduction of nitrogen to prevent thiol oxidation, all immersed in a 30-l. water bath. The temperature was controlled to ±0.2° by a Thermo-o-watch regulator attached to a thermometer dipping into the reaction solution. To the reaction flask there was charged 3.0 g. of a 3% stock solution of maleic anhydride in xylene and 4.14 g. of a 2% stock solution of 1-butanethiol in xylene was added. To this solution 192.3 g. of xylene was added and the resulting solution was stirred rapidly under a nitrogen atmosphere for 30–60 min. to ensure temperature equilibration. The reaction was initiated by the addition of 0.2 ml. of a stock solution containing 5% triethylenediamine in xylene; prior to the addition of base to the reaction two 10-ml. aliquots of the stock solution were withdrawn for the zero time titers. Aliquots of the reaction solution were withdrawn at measured times for the thiol titer, and immediately quenched with an excess of concentrated sulfuric acid in 25 ml. of alcohol. Larger initial concentrations of reactants led to undesirably fast rates and to the development of color due to the competing maleic anhydride polymerization reaction.

The samples of the reaction solution (5 to 10 ml.) were transferred to 150-ml. beakers and diluted to 100 ml. with 95% alcohol; the extent of the reaction was determined by amperometric titration with standard silver nitrate solution.[19] The titration assembly consisted of a saturated calomel reference electrode and a rotating platinum indicator electrode (driven by a synchronous motor) connected in series to a galvanometer having a sensitivity of 0.22 ma. per millimeter. Accuracies of about 3% were achieved.

Data Treatment.—The initial rates of reaction with different initial concentrations of reactants dictated eq. 6 for the case of equal initial thiol and anhydride concentrations and eq. 7 for the

$$k = \frac{1}{(B)t}\left[\frac{1}{(RSH)} - \frac{1}{(RSH)_0}\right] \qquad (6)$$

case where $(RSH)_0 > (MA)_0$. MA refers to maleic anhydride,

$$k = \frac{2.3}{(B)t\{(RSH)_0 - (MA)_0\}} \log \frac{(MA)_0(RSH)}{(RSH)_0(MA)} \qquad (7)$$

B to triethylenediamine, and RSH to thiol. The average deviation in k was usually about 8% for any given run with 9 points, but the data for 16 runs showed a mean value of k_3 of 1.9×10^2 M^{-2} sec.$^{-1}$ with a standard deviation of the mean of ±0.05 and a value of 1.9 ± 0.1 with 95% confidence limits.

Acknowledgments.—Many of the titrations were performed by Mr. H. Yepez, the infrared measurements were done by Mr. O. Kinast and Dr. B. Katlafsky, and n.m.r. analyses were done by Dr. M. W. Dietrich.

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

Organic Sulfur Compounds. XIII.[1] Free-Radical Addition of Thiols to Phenylacetylene[2]

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RECEIVED AUGUST 20, 1963

Nucleophilic addition of thiols to acetylenes is well understood but little is known about the stereochemistry of the free-radical addition. In the present study, therefore, aromatic and aliphatic thiols and thiolacetic acid were added to phenylacetylene by a chain mechanism both in the absence and in the presence of ultraviolet light or hydroperoxide initiation. When equimolar amounts of reactants were mixed at ambient temperatures, mainly *trans* monoaddition occurred, yielding *cis*-1-substituted mercapto-2-phenylethenes. The apparent stereoselectivity of the reaction increased when an excess of phenylacetylene was used. The resulting *cis* adducts were readily isomerized by thiyl radicals to equilibrium mixtures consisting mainly of the *trans* isomer. The various *cis–trans* isomer mixtures were analyzed by a combination of the g.c. and n.m.r. techniques; n.m.r. and infrared spectra of the *cis* and *trans* adducts and their mixtures were systematically studied and led to general rules for the identification of the configuration of these adducts.

Introduction

As an extension of our studies of radical addition of thiols to mono-[4] and diolefins,[5–7] this paper describes the addition of thiols to phenylacetylene (phenylethyne). The work was undertaken primarily to elucidate the stereochemistry of the *cis* and/or *trans* monoadducts of such reactions.

(1) The previous paper of this series: *J. Org. Chem.*, **28**, 2355 (1963).

(2) Presented before the Organic Chemistry Division, 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

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(4) A. A. Oswald, *J. Org. Chem.*, **25**, 467 (1960).

(5) A. A. Oswald and F. Noel, *ibid.*, **26**, 3948 (1961).

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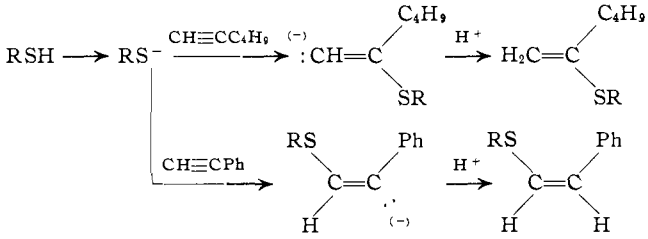
Nucleophilic (anionic) addition of thiols to acetylenes has been known for more than 60 years.[8] Reppe and co-workers[9] extensively studied the reaction with acetylene itself, while Truce and co-workers investigated the addition to monosubstituted acetylenes.

Truce established that the nucleophilic addition of thiols to acetylenes substituted with an electropositive or an electronegative group takes different courses.[10] For example, when starting with butylacetylene and phenylacetylene[11] the main reactions are



Generally, nucleophilic thiol–phenylacetylene additions yield exclusively the *cis*-1-substituted thiyl-2-phenylethenes.[12–15] So far the only known exception from this rule of *trans* addition is propiolic acid. Its sodium salt reacts with thiols to yield the *trans* product by a "*cis*-addition mechanism."

Free-radical addition of thiols to all monosubstituted acetylenes is expected to occur in an anti-Markownikoff manner. This should always yield 1,2-disubstituted ethylenes with the possibility of *cis* and/or *trans* isomers. However, little is known about the stereochemistry of such radical additions. In 1935, Kohler and Potter[16] added 4-toluenethiol without any catalyst to phenylacetylene. The reaction yielded about equal quantities of *cis*- and *trans*-1-*p*-tolylmercapto-2-phenylethene. Twenty-five years later, Truce and co-workers[15] have shown, by carrying out the same reaction in the presence of a peroxide catalyst, that the addition took place by a chain mechanism. However, it was impossible to decide whether the equal amounts of the two isomeric monoadducts are a result of the addition or of postisomerization, since both groups of authors had their reaction mixtures at about 80°. Indeed, Kohler and Potter[16] mention that the higher melting *cis* compound is slowly isomerized by distillation. In 1950, Smith and Davis, Jr.,[17] added benzenethiol to phenylacetylene at 0° without a catalyst, probably by a radical mechanism. By distillation *in vacuo*, which may have caused isomerization, they obtained 70% of a mixture of the liquid *cis* and *trans* monoadducts. On oxidation of this mixture 65% of a crystalline compound was obtained, which had the same melting point as the *trans* monoadduct synthesized in an unequivocal manner by Truce and co-workers.[18]

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(9) W. Reppe and co-workers, *Ann.*, **601**, 111 (1956).
(10) W. E. Truce and J. A. Simms, *J. Am. Chem. Soc.*, **78**, 2755 (1956).
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(15) W. E. Truce, H. G. Klein, and R. B. Kruse, *ibid.*, **83**, 4636 (1961).
(16) E. P. Kohler and H. Potter, *ibid.*, **57**, 1316 (1935).
(17) L. I. Smith and H. R. Davis, Jr., *J. Org. Chem.*, **15**, 824 (1950).
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Arens, Hermans, and Weiland[19] added ethanethiol to ethoxyacetylene by a radical mechanism to yield a mixture of *cis*- and *trans*-1-ethoxy-2-ethylmercaptoethene.

$$C_2H_5SH + HC{\equiv}C{-}OC_2H_5 \longrightarrow C_2H_5S{-}CH{=}CH{-}OC_2H_5$$

The isomer ratio was, however, not determined. Blomquist and Wolinsky[20] reacted ethanethiol with a series of acetylenic compounds under ultraviolet irradiation. However, in most cases they obtained only the corresponding diadducts as a result of the long irradiation period (2 weeks) and the excess of the ethanethiol used. Various other thiols have been added to acetylenic alcohols[21] and acids[22–24] by a radical mechanism. The ratio of the *cis* and *trans* monoadducts was, however, never determined. Thiolacetic acid was also added by a chain mechanism to various acetylenic compounds. This addition was first explored in Germany by Behringer during World War II.[25] The first paper on such radical additions was published by British researchers.[26] Several papers appeared later on the subject,[23,27,28] but the stereochemistry was not clarified.

The main objective of the present study was to determine whether thiol–phenylacetylene additions are stereospecific. Furthermore, the *cis–trans* isomerization of the resulting olefinic adducts was also examined. Simple aromatic and aliphatic thiols and thiolacetic acid were chosen as reagents. Because of the ease of postisomerization, the isomer ratios of the *cis* and *trans* monoadducts were determined at room temperature by nuclear magnetic resonance (n.m.r.)[29–31] and infrared spectroscopy.[31] In the case of aromatic thiol and thiolacetic acid adducts, the spectroscopical data were verified by the isolation of the pure, crystalline isomers; n.m.r. and infrared data of the more volatile, liquid aliphatic thiol adducts corresponded to the results of capillary gas chromatography (g.c.).

Results

Equimolar amounts of thiols were added to phenylacetylene by a radical mechanism without the formation of diadducts (Table I). Aromatic thiols (benzene-, 4-toluene-, 4-chlorobenzene-, 4-bromobenzene thiol) reacted readily at room temperatures without added catalysts. Aliphatic thiols—methane-, ethane-, *n*-butane thiol—reacted very slowly at ambient temperature in the absence of catalysis. Ultraviolet light irradiation and peroxide addition were effective in catalyzing the reaction. These facts indicate that the reaction proceeds by a chain mechanism. Heating of the reaction mixture to 80° also resulted in a fast monoaddition. Thiolacetic acid was found to react with

(19) J. F. Arens, A. C. Hermans, and J. H. S. Weiland, *Proc. Kon. Ned. Akad. Wetenschap.*, **B58**, 78 (1955).
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(27) L. W. C. Miles and L. N. Owen, *ibid.*, 817 (1952).
(28) H. Bader, *ibid.*, 116 (1956).
(29) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1951, Chapter 11.
(30) S. Alexander, *J. Chem. Phys.*, **28**, 358 (1958).
(31) W. E. Truce and B. Groten, *J. Org. Chem.*, **27**, 128 (1962).

phenylacetylene in a similar manner. As expected, its reactivity was somewhat lower than that of aromatic but much higher than that of aliphatic thiols. The main components of the adduct mixtures were, in all cases, the corresponding *cis*-1-substituted mercapto-2-phenylethenes (Table I). Some of the physical data and elemental analyses of the monoadducts obtained are shown in Table II.

TABLE I

ADDITION OF EQUIMOLAR AMOUNTS OF THIOLS TO PHENYLACETYLENES IN HEPTANE

Starting thiol	Reaction: Temp., °C.	Catalyst	Time, hr.	Conversion, %	*cis* adduct formed, %[a]: By n.m.r.	By g.c.
Benzenethiol	0	None	1	93	67	..
	0	Ultraviolet	2	99	54	..
4-Toluenethiol	0	None	1	97	73	..
Methanethiol[b]	0	Ultraviolet	3	14	81	84
	80	None	7	18	50	54
Ethanethiol	0	None	113	15	83	86
	0	Ultraviolet	5	28	80	80
	80	Ultraviolet	2	36	77	77
n-Butanethiol	0	None	3	27	..	..
	0	Ultraviolet	3	45	..	..
	0	Ultraviolet	8	66	75	72
	80	Ultraviolet	1	89	69	72
	0	Hydroperoxide[c]	3	32	..	..
	0	None	3	68	..	..
Thiolacetic acid	0	Ultraviolet	3	80	..	..
	0	None	16	89	..	..
	80	None	3	92	76	..
	0	Hydroperoxide[c]	3	90	..	..

[a] Was determined after several days standing at room temperature. [b] No solvent was used. [c] In the presence of 0.04 mole of cumene hydroperoxide/mole of thiol.

cluded from a n.m.r. investigation of the configuration of the olefinic aromatic thiol-propiolic acid adducts that values of these coupling constants supported the proposed geometrical configurations only when both isomers of each pair were available. It was therefore desirable to find other supporting correlations.

In most of our adducts, the vinyl protons of the geometric isomers showed simple and separated second-order splitting patterns, *i.e.*, AB quartets, arising from their different chemical shifts. The inner lines of these vinyl quartets were more intense than the outer ones because the difference in chemical shifts of the two vinyl protons in each isomer (δ_{AB} *cis* and δ_{AB} *trans*) is of comparable magnitude to their coupling constants ($J_{CH=CH}$ *cis* and $J_{CH=CH}$ *trans*).[32a] Representative spectra of the vinyl sulfide adducts of an aromatic and an aliphatic thiol and of the corresponding sulfones are shown in Fig. 1 and 2; n.m.r. parameters of all the synthesized thiol–phenylacetylene adducts and related compounds are given in Table VI in the Experimental part.

Correlations of the second-order splitting patterns of the vinyl protons showed that the mid-points of the *cis* protons appeared at a higher field and had a larger coupling constant than the *trans* protons.

Infrared.—Infrared absorption spectroscopy has been widely used as a method for the identification of the *cis* and *trans* monoadducts.[33] The thiol-phenylacetylene monoadducts are all 1,2-disubstituted ethylenes and, therefore, their configuration should be indicated

TABLE II

SOME PHYSICAL AND ANALYTICAL DATA OF THIOL–PHENYLACETYLENE ADDUCTS AND RELATED COMPOUNDS, R—SO_x—CH=CH—Ph

R	*x*	Summary formula	Yield,[a] %	B.p., °C. (mm.)[b] (m.p.)	*cis* isomer,[c] %	Calculated, %: C	H	S	Found, %: C	H	S
Phenyl	0	$C_{14}H_{12}S$	41	(44–46)[d]	100	79.15	5.72	15.13	78.96	5.75	15.11
	2	$C_{14}H_{12}O_2S$	69	(61–62)[d,e]	100	68.81	4.96	13.13	68.63	5.01	13.10
4-Chlorophenyl	0	$C_{14}H_{11}ClS$	52	63–66[d]	100	68.14	4.49	13.00	68.26	4.44	13.10
4-Bromophenyl	0	$C_{14}H_{11}BrS$	48	(74–76)[d]	100	57.74	3.81	11.01	57.63	4.01	11.00
Methyl	0	$C_9H_{10}S$	93	128–131 (4)	71	71.93	6.71	21.36	71.67	6.57	21.14
Ethyl	0	$C_{10}H_{12}S$	97	85–86 (1)	80	73.12	7.56	19.52	73.14	7.72	19.63
Butyl	0	$C_{12}H_{16}S$	95	113–115 (1)	78	76.53	6.43	17.04	76.27	6.61	17.22
	2	$C_{12}H_{16}O_2S$	45	(62–63)[e,f]	100	64.23	7.20	14.30	64.32	7.23	14.37
Acetyl	0	$C_{10}H_{10}OS$	51	(43–45)[f,g]	100	67.38	5.65	17.99	67.38	5.66	17.85

[a] On the basis of the reacted thiol. [b] Uncorrected. [c] Isomer mixtures were analyzed by capillary g.c. [d] Recrystallized from *n*-heptane. [e] Prepared by the oxidation of the corresponding sulfide with hydrogen peroxide in acetic acid. [f] Recrystallized from ethanol. [g] B.p. 103–104° at 1 mm.

The main products of the monoaddition of aromatic thiols, *cis*-1-arylmercapto-2-ethenes, could be easily separated by fractional crystallization from *n*-pentane or methanol. Similarly, *cis*-1-acetylmercapto-2-phenylethene, the main addition product of thiolacetic acid and phenylacetylene, can be readily crystallized from cold *n*-pentane. No attempt was made to separate by fractional distillation the isomeric liquid monoadducts derived from the aliphatic thiols and phenylacetylene. They could, however, be separated by capillary gas chromatography. The g.c. peaks were identified by semiquantitative determination of the individual isomers in various mixtures using nuclear magnetic resonance spectroscopy.

N.m.r.—The use of n.m.r. for configurational study is usually limited to unsymmetrical olefins.[29–31] The commonly applied method involves measurement of the spin–spin coupling constants between various protons on the double bond.[29,30] Truce and Groten[31] concluded by the wave length of their out of plane —CH= deformation vibrations.[33a] The examples of infrared spectra of pure *cis* and *trans* adducts and their mixtures in Fig. 3 show that the *trans* configuration can be readily recognized by a very strong absorption peak due to —CH= deformation vibration in the 10.4–10.7 μ region (Table VII). The *cis* adducts, however, exhibited no characteristic peaks which could be used to assign their configuration.

Isomers.—On comparison of the n.m.r. and g.c. data of Table I, it was obvious that the *cis* monoadducts have shorter retention times in the capillary column. The relative percentages of the *cis* and *trans* isomers as determined by the n.m.r. and the g.c. method have a

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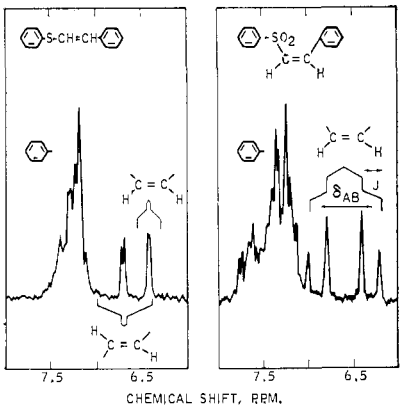


Fig. 1.—N.m.r. spectra of *cis*- and *trans*-phenylmercapto- and *cis*-phenylsulfonyl-2-phenylethene.

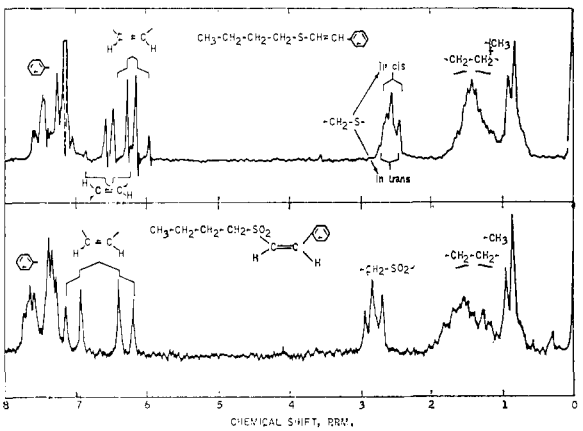


Fig. 2.—N.m.r. spectra of *cis*- and *trans*-1-*n*-butylmercapto- and *cis*-1-*n*-butylsulfonyl-2-phenylethene.

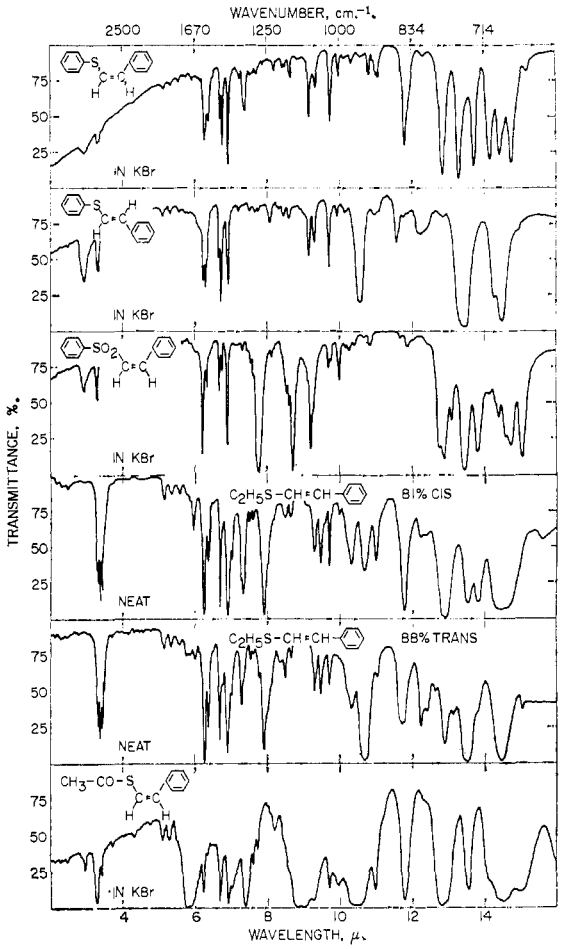


Fig. 3.—Infrared absorption spectra of *cis* and *trans* adducts of thiols and phenylacetylene.

maximum deviation of 4%. The g.c. method was not applicable to the aromatic thiol-phenylacetylene adducts because of their high boiling points. Their reported isomer ratios in the reaction mixtures are therefore exclusively based on the n.m.r. method.

It was found that *cis* and *trans* products are formed in a rather constant ratio at different temperatures if the other factors were kept the same (Table I). The *cis* adducts were always the predominant products though the aromatic thiol adducts showed a somewhat lower *cis*/*trans* ratio than the aliphatic ones.

The *cis*/*trans* ratio of the isolated mixtures remains rather constant with time on standing at room temperature. This indicates that at ambient temperatures thermal isomerization is not significant. Kohler and Potter[16] observed that the *cis* monoadduct of 4-toluenethiol and phenylacetylene was converted largely to the *trans* isomer during distillation. We have found that the *cis* adduct of 4-toluenethiol and phenylacetylene isomerizes on heating at 80° in *n*-heptane. Figure 4 shows that the isomerization is almost complete in a day at that temperature.

Distilled isomeric adducts of aliphatic thiols showed less tendency for thermal isomerization. The isomerization of all thiol and thiolacetic acid adducts (Table III) was, however, greatly enhanced by the addition of catalytic amounts of benzenethiol. In the presence of benzenethiol both ultraviolet irradiation and heating were very effective in isomerizing the *cis* adducts. During the isomerization very little of the benzenethiol disappeared from the mixture. Aliphatic thiols, such

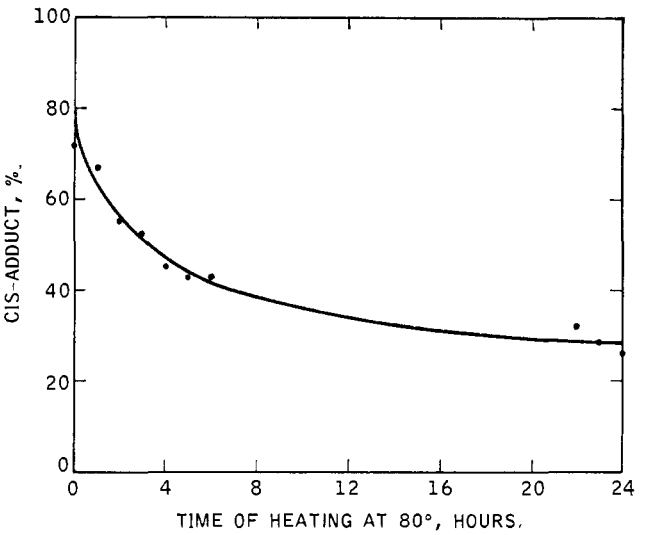


Fig. 4.—Isomerization of *cis*-2-*p*-tolylmercapto-1-phenylethene.

as ethanethiol and butanethiol, were relatively ineffective as isomerization catalysts under similar conditions. Thiolacetic acid, on the other hand, was about as effective as benzenethiol in catalyzing the isomerization.

It was apparent from the above experiments that thiols are effective postisomerization catalysts. Therefore, to avoid postisomerization during the addition, an excess of phenylacetylene was used. It was indeed found that a high excess of phenylacetylene over ben-

TABLE III

ISOMERIZATION OF *cis* ADDUCTS FROM THIOL–PHENYLACETYLENE REACTIONS BY VARIOUS THIOLS

Added thiol		Monoadduct		*cis* isomer, %						
				After ultraviolet irradiation[a]						
				0°, hr.					After heating	
					1	3	5		80° for 5 hr.	
Name	Concn., mole/l. (mole/mole)	Derived from	Concn. in heptane, mole/l.	Init. g.c. (n.m.r.)	G.c.	N.m.r.	N.m.r.	G.c.	N.m.r.	G.c.	N.m.r.
...	Nil	Benzenethiol	0.04	(100)	..	95	..	..	..	..	..
Benzenethiol	0.08	Benzenethiol	.04	(100)	..	45[b]	..	..	..	..	..
...	Nil	Ethanethiol	.4	79	75	..	..	..	..	80	78
Ethanethiol	0.004	Ethanethiol	.4	79	76	..	..	..	..	75	74
Benzenethiol	0.004	Ethanethiol	.4	79	19	..	..	..	..	18	20
...	Nil	Butanethiol	No solv.	77[c]	77	..	..	76	74	..	..
Butanethiol	(0.05)	Butanethiol	No solv.	77[c,d]	73	..	..	73	72	..	..
Benzenethiol	(0.05)	Butanethiol	No solv.	77[c,e]	53	..	..	31	34	..	..
...	Nil	Thiolacetic acid	No solv.	...	..	..	73[f]	..	..	..	..
Thiolacetic acid	(0.05)	Thiolacetic acid	No solv.	...	..	..	39[f]	..	..	..	..
Benzenethiol	(0.05)	Thiolacetic acid	No solv.	...	..	..	39[f]	..	..	..	..

[a] In a quartz test tube with stirring and ice–water cooling. [b] The benzenethiol catalyst was removed immediately after the irradiation by washing the solution with 5% aqueous sodium hydroxide solution. [c] Also determined after a few days standing without irradiation. [d] 73%. [e] 58%. [f] At 30°.

zenethiol resulted in the formation of a high *cis* content adduct mixture (Table IV).

TABLE IV

ADDITION OF BENZENETHIOL TO VARYING AMOUNTS OF PHENYLACETYLENE AT 0° WITH ULTRAVIOLET IRRADIATION FOR 2 HR.

Heptane solution of reactants, mole/l.		*cis* adducts, %
Benzenethiol	Phenylacetylene	by n.m.r.
0.05	1.1	>95
1.0	1.1	56
1.0	0.05	16

On examination of a number of thiols it was found that such a decrease of the thiol/phenylacetylene reactant ratio generally results in a high *cis* isomer content of the adduct (Table V *vs.* Table I).

TABLE V

STEREOSELECTIVE ADDITION OF THIOL (0.01 MOLE) TO AN EXCESS OF PHENYLACETYLENE (0.1 MOLE)

Added thiol	After ultraviolet irradiation at 0°, *cis* adduct, %			
	1 hr.	3 hr.	5 hr.	By n.m.r. 5 hr.
Methanethiol	87	..	84	..
Ethanethiol	88	85	85	..
n-Butanethiol	90	87	88	..
Thiolacetic acid	..	..	..	80
Benzenethiol	..	..	..	90
Toluenethiol	..	..	..	90

Discussion

The radical addition of various thiols to phenylacetylene in the liquid phase occurs by a predominantly *trans* mechanism and yields the thermodynamically less favored *cis*-vinylic sulfides. The over-all course of the addition of thiols to phenylacetylene is similar to that of hydrogen bromide[34]; both are stereoselective to the *cis* adducts.

The first propagation step of the addition of thiols by a chain mechanism is the addition of a thiyl radical to phenylacetylene. This could result in the formation of vinylic radicals having *cis* and/or *trans* configurations, which may be in equilibrium (Fig. 5). The relative instability of vinylic radicals seems to indicate that a linear sp-hybridized radical intermediate, incapable of geometric isomerism, is unlikely. The second propagation step is the abstraction of a hydrogen from the

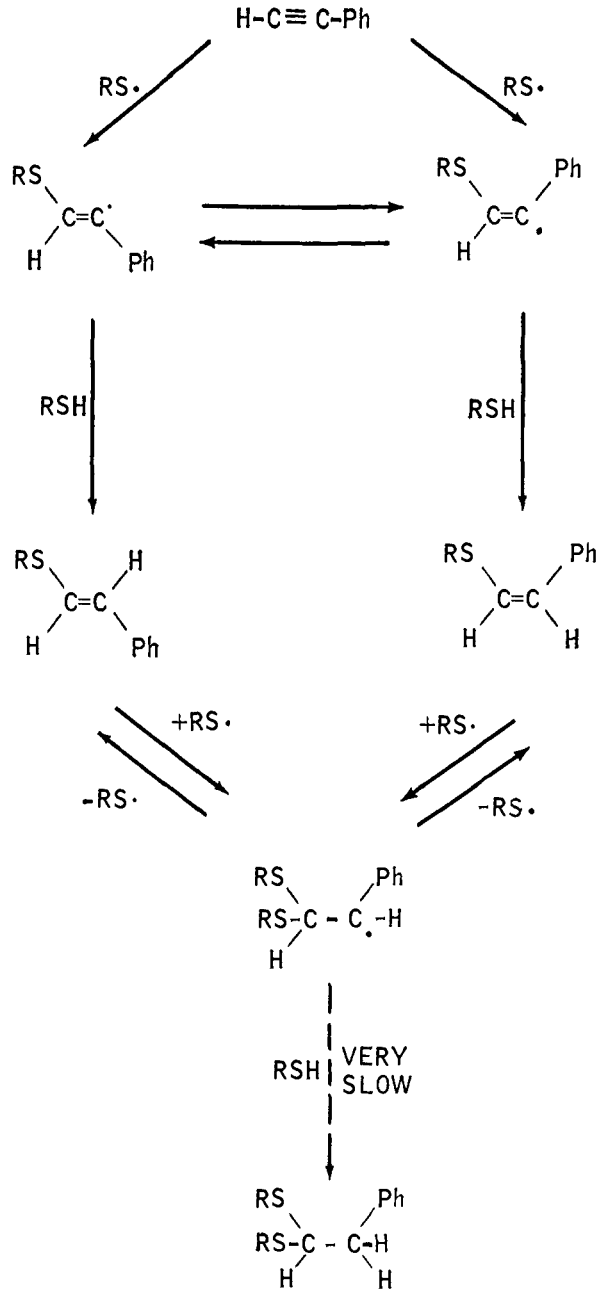


Figure 5.

(34) P. S. Skell and R. G. Allen, *J. Am. Chem. Soc.*, **80**, 5997 (1958).

thiol by the *cis*- or *trans*-vinylic radical. Reaction of the *cis* radical, of course, results in a vinylic product of *cis* configuration. Abstraction by the radical of *cis* configuration may be sterically assisted since the thiol can approach from the unhindered side.

The low *cis/trans* isomer ratio in the case of a thiol excess would normally indicate the primary formation of a *trans*-vinylic radical since the excess of thiols should result in a greater rate of hydrogen abstraction, and thus in a more effective trapping of the initial *trans* radical. The stereochemistry of the monoaddition of thiols to phenylacetylene is, however, complicated by the ready isomerization of the final products, vinylic sulfides. The *trans* monoadducts are, at least in part, formed by the postisomerization of the *cis* compounds. Such an isomerization is catalyzed by thiols on heating and ultraviolet irradiation. This indicates that thiyl radicals are the active catalytic agents. Their reversible addition to the monoadducts results in isomerization as shown in Fig. 5.

The catalysis of the isomerization of a monoadduct, *e.g.*, *cis*-1-phenylmercapto-2-phenylethene by benzenethiol, occurred with very little diadduct formation. It is believed that this is due to the high degree of stability, *i.e.*, low reactivity, of the benzylic radical formed on addition of the thiyl radical to the monoadduct. Steric factors may also effect the low rate of hydrogen abstraction from the thiol by this radical.

Aliphatic thiols are poorer isomerization catalysts than aromatic thiols under the same conditions (Table III) because it is more difficult to generate thiyl radicals from the aliphatic than from aromatic thiols.

It is interesting to compare the stereochemistry of thiol–phenylacetylene and thiol–olefin addition reactions.[35-39] Goering and co-workers had shown that the addition of benzenethiol to 1-chlorocyclohexene yielded predominantly the *cis* adduct, the product of kinetic control. The preferential formation of this isomer was explained by the stereoselective course of each of the two propagation steps. The addition of the benzenethiyl radical in the first step led to the formation of a radical intermediate leading to a *cis* adduct, rather than its conformer leading to a *trans* adduct. This was concluded from the fact that an increase in the mercaptan concentration caused an increase in stereoselectivity toward the *cis* adduct. This isomer distribution was thus dependent on the relative rates of the hydrogen abstraction reaction and the equilibration of the intermediate radical to the *trans* conformer. Since the reacting mercaptan can approach the radical in the *cis* conformation from the unhindered side, the higher rate of hydrogen abstraction was explained by steric assistance. With hydrogen bromide as the reactant, the *cis* adduct was the exclusive product.[34]

In the thiol–phenylacetylene additions, it was not possible to determine with similar experiments the *cis* or *trans* configuration of the primary vinylic radical because of the fast rate of isomerization of the *cis* monoadducts by excess thiol. These isomerizations will be discussed in a subsequent publication.

TABLE VI

PROTON NUCLEAR MAGNETIC RESONANCE SPECTRA OF THIOL–PHENYLACETYLENE ADDUCTS AND RELATED COMPOUNDS,[a] Ph—CH=CH—SO_xR—

Starting thiol	Compound: R	x	Parameters of structural units: AB quartet of vinyl protons, CH=CH: Chemical shift,[b] p.p.m.: Mid point: cis	Mid point: trans	$\delta_{trans-cis}$	δ_{AB}[c]: cis	δ_{AB}[c]: trans	Coupling constant $J_{CH=CH}$, c.p.s.: cis	Coupling constant $J_{CH=CH}$, c.p.s.: trans	Inner line separation,[d] c.p.s.: cis	Inner line separation,[d] c.p.s.: trans	R group signals (s, singlet; t, triplet; q, quartet; m, multiplet), chemical shift, p.p.m.[b]: Aryl: cis	Aryl: trans	Methyl: cis	Methyl: trans	Methylene: cis	Methylene: trans
Aromatic	Phenyl	0	6.42	6.63	0.21	0.08	0.12	10.0	17	1.2	1.5	m 7.0–7.8	m 7.0–7.8				
		2	6.63			.53		12.3		22.5		m 7.0–7.8					
	4-Tolyl	0	6.35	6.62	0.27	.09	0.15	10.3	15.6	1.0	4.2	m 6.8–7.4	m 6.8–7.4	s 2.25	s 2.25		
	4-Chlorophenyl	0	6.23	6.52	.29	.22	..	11.0	..	6.0	..	m 7.0–7.8	m 7.12				
	4-Bromophenyl	0	6.42	6.67	.25	.20	..	10.5	..	6.0	..	m 7.0–7.8	m 7.0–7.8				
Aliphatic	Methyl	0	6.13	6.44	.31	.32	0.46	11.2	15.5	11.3	17.5			s 2.02	s 2.04		
	Ethyl	0	6.24	6.56	.32	.33	.27	11.0	15.7	9.2	7.0			t 1.10[e]	t 1.15[e]		
	n-Butyl	0	6.21	6.52	.31	.25	.27	11.0	16.0	7.5	7.0			t 0.80[e]	t 0.85[e]	q 2.49[e]	q 2.58[e]
		2	6.69			.49		12.0		33.5				t 0.80[e]		m 1.1–1.7, t 2.55[f]	m 1.1–1.7, t 2.65[f]
Thiolacetic acid	Acetyl	0	6.82	6.94	0.12	.39	0.69	11.0	17.0	15.0	28.0			s 2.20	s 2.18	m 1.1–1.7, 2.76[f]	

[a] The n.m.r. spectra were recorded with a Varian Model A-60 proton resonance spectrometer. The liquid mixtures of isomeric adducts were run as such; the solids were in carbon tetrachloride solution. In all cases tetramethylsilane (TMS) was used as an internal standard. [b] Chemical shifts are given in parts per million downfield from TMS. [c] The computed difference of the chemical shifts of the two vinyl protons. [d] At 60 Mc. frequency. [e] J = 7 c.p.s. [f] Methylene group adjacent to sulfur, J = 7 c.p.s.

(35) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, Chapter 7, 1, 2. pp. 21–316.
(36) H. L. Goering and D. W. Larsen, *J. Am. Chem. Soc.*, **81**, 5937 (1959).
(37) H. L. Goering P. I. Abell, and B. F. Aycock, *ibid.*, **74**, 3588 (1952).
(38) H. L. Goering and L. L. Sims, *ibid.*, **77**, 3465 (1955).
(39) H. L. Goering, D. I. Relyea, and D. W. Larsen, *ibid.*, **78**, 348 (1956).

Experimental

Materials.—Phenylacetylene from Eastman was fractionated *in vacuo* before use. The thiols used were reagent grade chemicals. Thiolacetic acid from Matheson was redistilled before use.

Methods of Analyses.—Carbon and hydrogen were determined by the microcombustion technique. Sulfur analyses were obtained by the Parr method. The mercaptan concentrations of the reaction mixtures were determined by potentiometric titration with silver nitrate using a silver–glass electrode pair.

Capillary gas chromatographic separation of the isomers was carried out using a Barber–Coleman IDS Model LO chromatograph. A 50-ft. column coated with an *n*-tridecyl polyethylene glycol ether obtained from 30 moles of ethylene oxide per mole of *n*-tridecyl alcohol was used.

Addition of Thiols to Phenylacetylene.—A mixture of 0.1 mole of a thiol and 11.5 g. (0.11 mole) of phenylacetylene either in 100 ml. of *n*-heptane or without solvent was placed into a quartz reaction vessel (flask or tube) equipped with a magnetic stirrer. The reaction mixture was kept at the desired reaction temperature using a liquid bath. Some of the reactions were initiated by ultraviolet irradiation (from a medium pressure Hanovia utility lamp (115 v., 140 w., 60 c.) placed at 7 cm. distance from the quartz reaction vessel) or by an added hydroperoxide (4 mole %).

The reaction was followed by determining the decrease of the thiol concentration in the reaction mixture at intervals. After an arbitrary length of time the reaction was discontinued. The *cis/trans* isomer ratio of the aliphatic thiol–phenylacetylene reaction mixtures was determined directly by g.c. and n.m.r. The solutions of the aromatic thiol–phenylacetylene adducts were washed free of the starting thiol with 4% aqueous sodium hydroxide solution. This was necessary to avoid isomerization in solution by the catalytic amounts of the thiol left. In other cases, the solid products of aromatic thiol–phenylacetylene addition were dissolved in carbon tetrachloride just before n.m.r. analysis.

N.m.r.—The proton nuclear magnetic resonance spectra were recorded with a Varian Model A-60 proton resonance spectrometer. The liquid adducts were run as such, the solid adducts in carbon tetrachloride solution. It is noted, however, that on prolonged standing in solution the adducts may isomerize.

In both the *cis* and the*t rans* series of isomers, the midpoints of the quartets ("chemical shift, —CH=CH—") of the adducts derived from aliphatic thiols were at the highest field (Table VI). The adducts of aromatic thiols appeared at slightly lower field, and those of thiolacetic acid at the lowest. The *cis*-sulfone oxidation products also had their mid-points at a lower field than the corresponding *cis*-sulfide adducts.

The vinyl quartet mid-points occurred at a higher field for the *cis* than for the *trans* adducts. This is consistent with observations made by Curtin and co-workers[40] on isomeric stilbenes. The magnitude of this difference, $\delta_{trans\text{-}cis}$, is largest for the adducts of aliphatic thiols and smallest for the thiolacetic acid adducts.

The difference between the chemical shifts of the two vinylic protons, δ_{AB}, is due to the lack of symmetry of the molecule. In the case of our compounds, this value is usually smaller for the *cis* than for the corresponding *trans* compound. Exceptions are the *trans*-4-chloro- and 4-bromobenzenethiol adducts which showed no measurable chemical shift difference. Both the *cis* and the *trans* adducts of aliphatic thiols and especially those of thiolacetic acid have larger δ_{AB} values than those of aromatic thiols. The larger values for the former are apparently due to the increased molecular asymmetry and polarity arising from the absence of the second aromatic ring. For the same reason, the sulfones have much larger δ_{AB} values than the corresponding sulfides.

Coupling constants for *cis*-vinylic hydrogens, $J_{CH=CH}$, are consistently smaller than those for *trans*-hydrogens of the corresponding isomer.[15,29,30] In the case of our thiol–phenylacetylene adducts, the *cis* and *trans* isomers had typical $J_{CH=CH}$ values of about 11 and 17 c.p.s., respectively. The coupling constants of the *cis*-sulfones were about 12 c.p.s., slightly higher than those of the corresponding *cis*-sulfide adducts. (The coupling constants were determined directly as the separations in c.p.s. of the outer lines from the inner lines of the AB quartets.)

(40) D. Y. Curtin, H. Gruen, and B. A. Shoulders, *Chem. Ind.* (London), 1205 (1958).

TABLE VII

CHARACTERISTIC INFRARED ABSORPTION PEAKS OF THIOL–PHENYLACETYLENE ADDUCTS AND SOME RELATED COMPOUNDS, R—SO_x—CH=CH—Ph

Characteristic absorption peaks, mμ; vs, very strong; m, medium; w, weak; i, inflection

Compounds[a] R	x	Isomeric, % cis	trans	Olefinic C=C	Aromatic and alkane region: C skeletal	Aromatic and alkane region: C—H deformation vibrations	Fingerprint region	C—H deformation region: Aromatic and H C=C H	C—H deformation region: H C=C H
Phenyl	0[a]	100	...		6.25s, 6.3s, 6.4m	6.7m, 6.75s, 6.95vs, 7.4m	9.15m, 9.75m, 10w	10.8w	11.8s, 12.3vw, 12.85vs, 13.3vs, 13.7vs, 14.15s, 14.45s, 14.75vs
	0[a]	...	100		6.25s, 6.3s, 6.35m	6.7m, 6.75s, 6.95s	9.15m, 9.7m, 10w	*10.55vs*	11.6m, 12.25m, 13.5vs, 14.3s, 14.5vs
	2[a]	100	...		6.25vs, 6.35m	6.7m, 6.75w, 6.9s	7.7*vs*,[b] 8.7*vs*, 9.2s, 9.7w, 10m	10.8vw	11.9vw, 12.75s, 12.9vs, 13.1s, 13.45vs, 13.8s, 14.6s, 14.7s, 15.05vs
Tolyl	0[a]	100	...		6.2w, 6.3s, 6.4m	6.7s, 6.9s, 7.4m	9.15m, 9.8m, 10vw	10.8w	11.8s, 12.3vs, 12.9vs, 13.6s, 14.2s, 14.7s
Methyl	0	71	29	*6.0m*	6.25s, 6.35m	6.7vs, 6.9vs, 7.35s	7.6s, 9.3m, 9.7m, 10.2s	10.7s	11.85vs, 12.2m, 12.9vs, 13.6vs, 14.5vs
Ethyl	0	81	19	*6.0m*	6.25vs, 6.4m	6.7vs, 6.9vs, 7.31, 7.35s	7.9vs, 9.3m, 9.5m, 9.7m, 10.35m	10.7s	11.8vs, 12.25m, 12.95vs, 13.55s, 13.85s, 14.5vs
	0	12	88	*6.0w*	6.25vs, 6.35s	6.7s, 6.9vs, 7.3m, 7.35i	7.9vs, 9.3m, 9.5m, 9.7m, 10.35m	10.7vs	11.75s, 12.25s, 12.9s, 13.55vs, 13.85i, 14.5vs
Butyl	0	71	39	*6.0w*	6.25vs, 6.4m	6.7s, 6.85s, 6.9vs, 7.4s	7.9s, 8.2s, 9.1w, 9.3m, 9.7m, 10.0vw	10.7m	11.8s, 12.2w, 12.9vs, 13.55s, 14.5vs
	0	44	66	*6.0w*	6.25vs, 6.4m	6.7s, 6.85s, 6.9vs, 7.4m	7.9s, 8.2m, 9.1w, 9.3m, 9.7m, 10.0vw	*10.7s*	11.8s, 12.2m, 12.9vs, 13.55vs, 14.5vs
	2[a]	100	...		6.2s, 6.35w	6.7m, 6.8m, 6.9s, 7.65s	7.8*vs*,[b] 7.95*vs*, 8.9*vs*, 9.05s, 9.25m, 9.7vw, 9.9w	10.8m	11.9m, 12.5m, 12.9vs, 13.45s, 13.8s, 14.1vs, 14.6vs, 14.9vs
Acetyl	0	100	...	5.9vs[c]	6.2s, 6.35w	6.7s, 6.9s, 7.4vs	8.9*vs*, 9.3s, 9.7s, 10.0s	10.5vs	11.0s, 11.8s, 12.3i, 13.85s, 13.5s, 14.2i, 14.5vs, 15.1s
	0	39	61	5.9vs[c]	6.2s, 6.35w	6.7s, 6.9vs, 7.4vs	8.9*vs*, 9.3s, 9.7s, 10.0s	10.5vs	11.0m, 11.8m, 12.3w, 13.85s, 13.5vs, 14.5vs, 15.1m

[a] The spectra of the solid compounds were obtained in 0.5% KBr pellets. [b] Due to the sulfone group. [c] Carbonyl absorption.

As a reflection of the difference between the chemical shifts of the two vinyl protons, the inner line separation of the *cis* adducts was usually larger than that of the *trans* adducts. The aromatic adducts in general showed smaller values than the aliphatic ones. In the case of the *trans*-4-chloro- and 4-bromobenzenethiol adducts no inner line separation could be observed.

Infrared.—The infrared spectra were obtained using a Baird recording spectrophotometer. The out-of-plane —CH= deformation of the *trans*-benzenethiol adduct absorbed at 10.45 μ, the *trans*-alkyl mercaptan adducts at 10.7 μ. The vibrations of symmetrically disubstituted *trans*-ethylenes usually occurred at wave lengths between 10.2 and 10.4 μ.[33b] However, this absorption can be expected at a somewhat higher wave length in the case of our *trans* adducts since a higher wave length range, 10.5–11.2 μ, was also reported for bis(1,2-*p*-tolylmercapto)-ethenes.[31] Alkylmercaptoethenes also absorb at higher wavelengths, 10.9–11.2 μ.[41]

The out-of-plane —CH= deformation vibrations of the *cis* adducts cannot be assigned because of the interesting —CH= deformation vibrations of the aromatics and the uncertainty of the wave length at which the absorption of such *cis* deformation vibrations occur.[33e] However, it is apparent that the *cis* adducts have stronger absorption peaks than the *trans* adducts in the 12.75–15.2 μ region. The *trans* adducts usually show wide absorption peaks, the *cis* adducts sharper peaks. Although it is known that *cis*-disubstituted olefins show this absorption between 13.75 and 14.8 μ, little is certain about the effect of various substituents on the wave length of the absorption.

Another series of absorptions commonly employed for configurational information are the =C—H in-plane deformation vibrations. For *cis*- and *trans*-olefins, these appear near 7.1 and between 7.6 and 7.75 μ, respectively.[33c] It is apparent from Table VII that there is very little absorption in that region and that this absorption in our cases does not show relationship to the configuration of the compounds. It is interesting to note, however, that the *cis*- and *trans*-ethanethiol adducts show a definite difference in absorption at 7.30–7.35 μ. This absorption, however, is probably associated with the CH deformation of the methyl group.[33d] In general, the spectra of the corresponding *cis* and *trans* compounds are almost identical in the fingerprint region, between 7.5 and 10 μ. Similar observations were made by Truce and Groten[31] in a study of the infrared spectra of 4-tolylmercaptoethenes.

The C=C stretching frequency of the aliphatic thiol adducts apparently occurs at 6 μ. This is in the general range of the C=C stretching frequencies,[33e] although absorptions in the 6.4–6.6 μ region have been reported for mercaptoethenes.[31,41] As expected, on the basis of the effect of the symmetry of the molecule at the double bond,[33f] the *cis* adducts show C=C stretching absorptions of medium intensity. Neither the *cis* nor the *trans* isomers of the aromatic thiol adducts show any significant absorption at 6 μ. It is possible that the disappearance of the C=C stretching absorption in these compounds is connected with the increased molecular symmetry.

In the aromatic thiol adducts there are three absorption peaks in the 6.2–6.4 μ region due to aromatic C=C skeletal vibration,[33g] while the aliphatic thiol adducts show only two absorption peaks in that region. It is believed that the extra peak of the aromatic thiol adducts is due to the second aromatic group in the molecule.

Like their parent compounds *cis*-sulfone oxidation products of the corresponding sulfide adducts showed no characteristic peaks which could be used to assign their configuration. The presence of the sulfone group, however, could be readily recognized by the strong absorption at about 7.8 μ.[33h]

Acknowledgments.—The authors wish to acknowledge helpful discussions with D. N. Hall. They also thank T. J. Jermansen and A. M. Palmer for the valuable technical assistance, Miss M. J. Doolan and Mrs. M. C. Brooks for the g.c. analyses, and Mr. D. E. Bachert for recording the infrared spectra.

(41) H. J. Bonnstra and L. C. Rinzema, *Rec. trav. chim.*, **79**, 962 (1960).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE 39, MASS.]

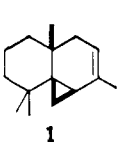
Photochemical Reactions. XIII.[1] A Total Synthesis of (±)-Thujopsene

BY G. BÜCHI AND J. D. WHITE[2]

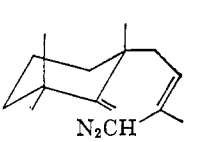
RECEIVED FEBRUARY 24, 1964

A total synthesis of (±)-thujopsene which corroborates the accepted structure is described.

The chemistry and structure of the sesquiterpene thujopsene has been the subject of considerable interest in recent years. The tricyclic hydrocarbon, which was isolated originally from the wood oil of Hiba,[3] has been found to occur widely in genera of the natural order Cupressaceae.[4] The structure of thujopsene (**1**) was first correctly deduced, in 1960, by Erdtman and Norin,[5] who assigned the relative stereochemistry shown.[6] The *cis* relationship of the angular methyl substituent and cyclopropane ring has subsequently been confirmed by a further degradative study[7] and by a stereospecific total synthesis of thujopsene.[8]



1



2

Although the formulation **1** for thujopsene rests secure, it was felt that the unusual tricyclic structure nevertheless constituted a legitimate target for further synthetic work. It was envisaged that decomposition of an intermediate such as **2** might afford a convenient synthesis of thujopsene by an intramolecular addition process, and efforts were therefore directed toward the acquisition of this intermediate.

β-Cyclogeraniol[9] was chosen as the starting point for the synthesis and was prepared from β-cyclocitral[10] by reduction with sodium borohydride. The vinyl ether **3** was obtained upon refluxing β-cyclogeraniol with an excess of ethyl vinyl ether in the presence of

(1) Part XII: J. G. Atkinson, D. E. Ayer, G. Büchi, and E. W. Robb' *J. Am. Chem. Soc.*, **85**, 2257 (1963).

(2) Cabot Solar Energy Fellow, 1962–1963; National Institutes of Health Predoctoral Fellow 1963–.

(3) M. Yano, *J. Soc. Chem. Ind. Japan*, **16**, 443 (1913); S. Uchida, *ibid.*, **31**, 501 (1928).

(4) H. Erdtman and B. R. Thomas, *Acta Chem. Scand.*, **12**, 267 (1958).

(5) H. Erdtman and T. Norin, *Chem. Ind.* (London), 622 (1960); T. Norin, *Acta Chem. Scand.*, **15**, 1676 (1961); S. Forsén and T. Norin, *ibid.*, **15**, 592 (1961).

(6) Two other groups arrived at the same gross structure for thujopsene: T. Nozoe, H. Takeshita, S. Ito, T. Ozeki, and S. Seto, *Chem. Pharm. Bull.* (Tokyo), **8**, 936 (1960), and K. Sisido, H. Nozaki, and T. Imagawa, *J. Org. Chem.*, **26**, 1964 (1961). Both, however, favored a *trans*-fused structure.

(7) T. Norin, *Acta Chem. Scand.*, **17**, 738 (1963).

(8) W. G. Dauben and A. C. Ashcraft, *J. Am. Chem. Soc.*, **85**, 3673 (1963).

(9) R. Kuhn and M Hoffer, *Ber.*, **67**, 357 (1934).

(10) Prepared from citral by cyclization (L. Colombi, A. Bosshard, H. Schinz, and C. F. Seidel, *Helv. Chim. Acta*, **34**, 265 (1951)) followed by base-catalyzed isomerization of the resulting mixture of α- and β-cyclocitrals (V. Prelog and H. Frick, *ibid.*, **31**, 417 (1948)). We are indebted to Chas. Pfizer and Co. for a generous supply of citral.