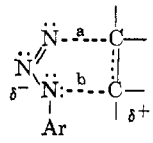
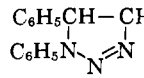


IV

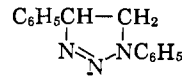
state approximated by IV. In IV bond formation at a has progressed to a greater extent than at b; consequently, the development of partial charge is as indicated. Rate enhancement by electron-withdrawing substituents is then attributable to the stabilization of partial negative charge on the α-nitrogen in the transition state.

The unsatisfactory fit of the p-NO_2 substituent (using σ^0) in the Hammett plots (Figures 1–3) suggests the development of considerable negative charge. This substituent appears to stabilize the transition state in an "exceptional" manner, by a direct resonance interaction. To place the p-NO_2 substituent on the Hammett line (25°) would require a σ-value of +0.93, considerably larger than the σ^0-value (+0.73) though less than the older $\sigma^-_{p\text{-}NO_2}$(+1.27).[25]

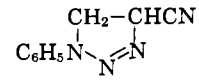
Our interpretation of the aryl azide–norbornene addition finds confirmation in orientational results obtained by others working with different systems. Thus Buckley has shown that phenyl azide adds stereospecifically to styrene to produce triazoline V, rather than VI.[7a] In



V



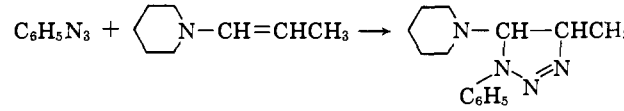
VI



VII

terms of a transition state corresponding to IV, it is clear that the phenyl group (formerly of styrene) is favorably situated for the stabilization of partial positive charge only in the transition state leading to V. Similarly, the structure of the phenyl azide–acrylonitrile adduct[7d] VII is explicable when consideration is given to the inductive effect of the nitrile group. The partial positive charge developed in transition is better accommodated on the β- than the α-carbon.

Munk and Kim[11] and others[12,13] have found that phenyl azide adds to enamines in a highly stereospecific manner. The specificity, in this case, presumably results from the conjugative stabilization imparted by the enamino nitrogen to the partial positive charge in the favored transition state.



In common with other 1,3-dipolar additions, it seems likely that the addition of aryl azides to olefins occurs *via* an essentially concerted process, involving a transition state in which charge is partially developed. Furthermore, from the available evidence it appears that (in transition) bond formation from the *terminal* azido nitrogen to the olefinic carbon is more complete than bond formation from the α-azido nitrogen to the other carbon. The consequent charge imbalance (as detected by substituent and orientational effects) suggests an initial electrophilic attack by the terminal nitrogen. However, the actual charge distribution in the transition state may well be quite sensitive to the structures of the particular azide–olefin pair undergoing reaction. In view of the relatively few systems studied, a thorough generalization regarding the azide–olefin reaction is not justified at this time.

Acknowledgment. The authors gratefully acknowledge the assistance of Professor J. E. Finholt, and the financial support of the National Institutes of Health, Grant CA 07183-01.

The Stereochemistry of Free-Radical Addition to Dienes. The Addition and Cooxidation of Thiols with Piperylene[1]

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Contribution from the Central Basic Research Laboratory, Esso Research and Engineering Company, Linden, New Jersey. *Received September 2, 1964*

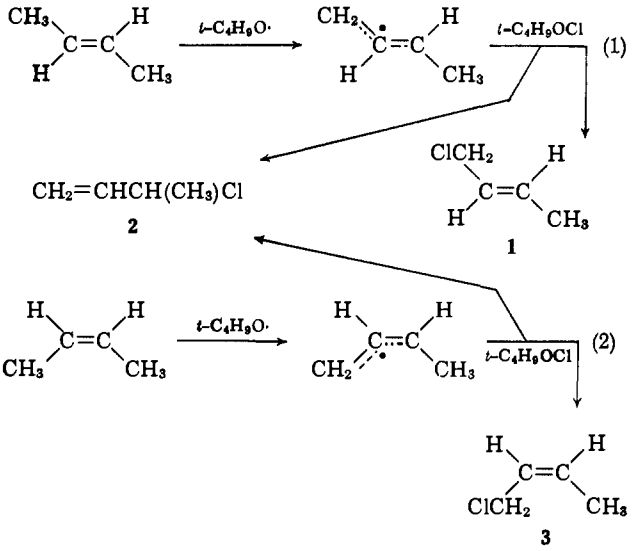
The stereochemical course of the addition and cooxidation reactions of thiols with cis- and trans-1,3-pentadiene (piperylene) was examined. Aromatic thiol gave 1,2-adducts with better than 90% retention of configuration while the formation of 1,2-adducts from aliphatic thiols showed a relatively low degree of retention of configuration. The reaction of thiols with cis- and trans-piperylene in the presence of oxygen (cooxidation) led to the formation of allylic alcohols. The 1,2-adduct alcohols were formed with complete retention of geometry. The 1,4-addition and cooxidation products were almost entirely trans. The geometry of 1,2-reaction products was used to measure the degree of retention of configuration of the allylic radical intermediates. In those instances where the allylic radicals retained their configuration, the geometry of the 1,4-reaction product obtained was related to the conformation of the reacting diene.

Introduction

The *abstraction* of a hydrogen atom from the allylic position of olefins results in the formation of allylic free radicals. The allylic free radicals produced in this fashion, during the *t*-butyl hypochlorite chlorination of olefins, were capable to maintaining their stereochemi-

(1) Presented in part at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1962.
(2) Esso Research Center, Linden, N. J.

cal integrity throughout the time interval necessary for further reaction with the hypochlorite.[3] Thus *trans*-2-butene gave *trans*-1-chloro-2-butene (**1**) while *cis*-2-butene gave 1-chloro-2-butene (**3**) which was completely *cis*.

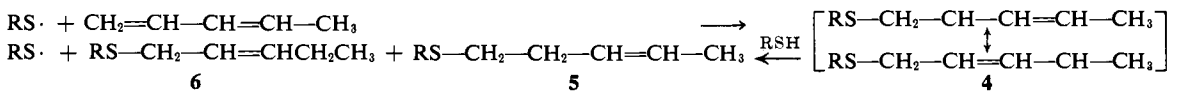


The *addition* of a free radical to a diene also produces allylic radicals, $X\cdot + CH_2{=}CH{-}CH{=}CHR \rightarrow XCH_2{-}CH{=}CH{-}CHR$, and similarly can result in the formation of several products which are structural isomers. The relation between the structure of allylic free radicals and the isomer distribution of the products (ignoring *cis–trans* isomers) derived therefrom, has also been the object of recent scrutiny[3,4]; the isomer distributions from different reactions were attributed to activation energy differences between the second chain propagation step involving the allylic radicals.

The stereochemistry of the addition of free radicals to conjugated dienes has, however, received little attention. Most of the information on this subject deals with butadiene polymerization, a rather nonstereospecific process, and the stereochemistry of the 1,4-polymer units.[5,6] The present investigation of the stereochemistry of free-radical addition to a conjugated diene was undertaken in order to obtain additional information concerning the properties of allylic free radicals, and radical addition (and polymerization) reactions of dienes in general.

Results

Piperylene (1,3-pentadiene) is the simplest conjugated diene which displays *cis–trans* isomerism. The free-radical addition of different thiols to a commercial *cis–trans* piperylene mixture[4b] demonstrated that the major products were the 1,2- (**5**) and 1,4-adducts (**6**), formed from the attack of thiyl radical at C-1 of piperylene (eq. 3). Only minor products [4,3- (**8**) and 4,1- (**9**)] resulted from attack at C-4 (eq. 4). The enhanced attack at C-1 over C-4 was attributed to the greater stability of the transition state for the formation of the disecondary allylic radicals (**4**) relative to that of the primary–secondary radicals (**7**). The formation of both the 1,2- and 1,4-adducts in similar quantities from **4** was also anticipated since both the reactive positions of the allylic radical intermediate (**4**) were secondary. Thus it was felt that the radical addition of thiols to the pure *cis* and *trans* isomers of piperylene would provide a suitable model reaction for an examination of the stereochemistry of the simultaneous 1,2- and 1,4-addition processes.



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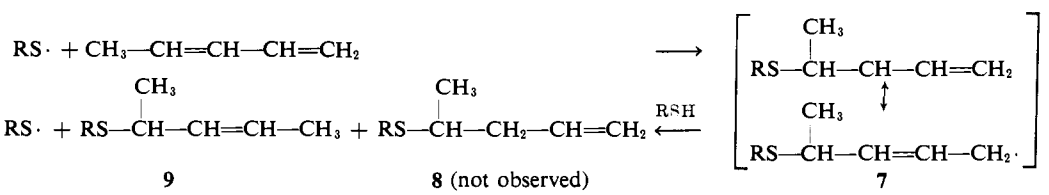


(4)

The reaction of thiols with dienes in the presence of oxygen (cooxidation reaction) also involves the addition of a thiyl radical to the diene to give allylic radical intermediates. However, these allylic radicals now combine with oxygen to form peroxy radicals which in turn remove a hydrogen atom from the thiol to give a hydroperoxide and regenerate the thiyl radical.[4a,c] In the presence of catalytic quantities of amine the hydroperoxide is immediately reduced by excess thiol to an allylic alcohol. Thus the same allylic intermediates (**4** and **7**) resulting from the addition of thiyl radical to piperylene would be involved in both the thiol addition and cooxidation reactions. Analogously, the 1,2- and 1,4-cooxidations with piperylene (eq. 5) should give both 1,2- (**10**) and 1,4-cooxidation products (**11**) while smaller amounts of the 4,3- (**12**) and 4,1-cooxidation products (**13**) might result from the less favorable attack at C-4 of piperylene (eq. 6).

A general scheme for the stereochemistry of the addition of free radicals to *trans*- and *cis*-piperylene is depicted in Figures 1 and 2, respectively. Specifically, in the case of thiol addition X = RS and Y = H, whereas X = RS and Y = O_2 for the cooxidation reaction. Subsequent reactions of the peroxy radical with thiol in the presence of an amine catalyst result first in

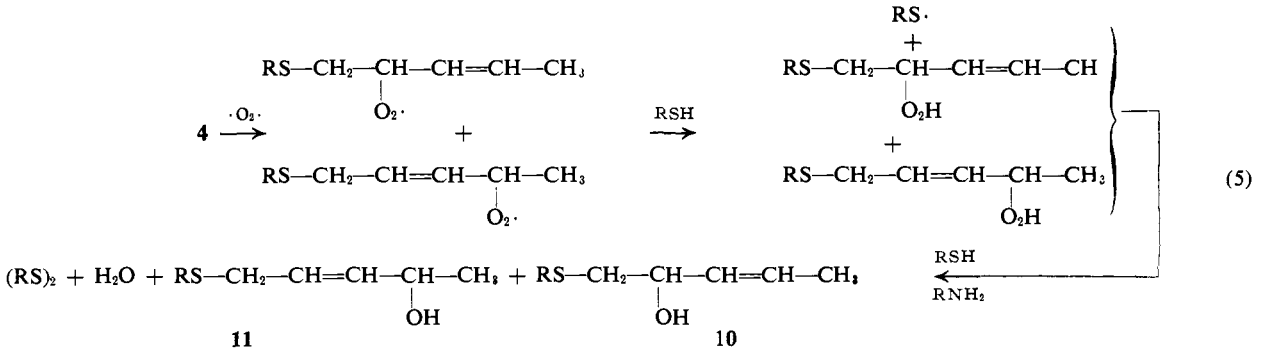
(3) C. Walling and W. Thaler, *J. Am. Chem. Soc.*, **83**, 3877 (1961).

(4) (a) A. A. Oswald, B. E. Hudson, Jr., G. Rodgers, and F. Noel, *J. Org. Chem.*, **27**, 2439 (1962); (b) A. A. Oswald, K. Griesbaum, W. A. Thaler, and B. E. Hudson, Jr., *J. Am. Chem. Soc.*, 84, 3897 (1962); (c) A. A. Oswald, K. Griesbaum, and B. E. Hudson, Jr., *J. Org. Chem.*, **28**, 2355 (1963); (d) H. R. Gersmann, H. J. W. Nieuwenhuis, and A. F. Bickel, *Tetrahedron Letters*, **21**, 1383 (1963).

(5) J. Condon *J. Polymer Sci.*, **11**, 139 (1953).

(6) An interesting example involving allylic diradicals demonstrates that the allylic diradical intermediates in the cycloaddition of 1,1-dichloro-2,2-difluoroethylene can maintain their stereochemistry during the time interval required for the coupling of the unpaired electrons.[7]

(7) P. D. Bartlett, L. K. Montgomery, and B. Seidel, *J. Am. Chem. Soc.*, **86**, 616 (1964); L. K. Montgomery, K. Schueller, and P. D. Bartlett, *ibid.*, **86**, 622 (1964).



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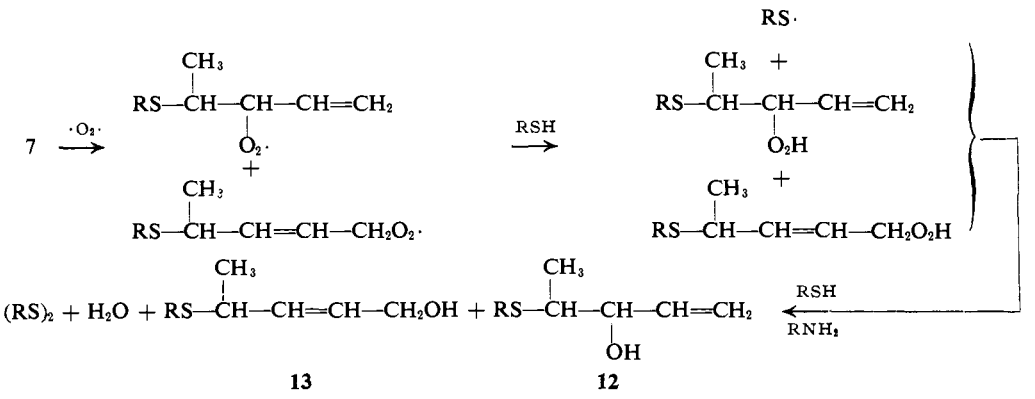


(6)

the formation of hydroperoxide (Y = OOH) and then alcohol (Y = OH) as the final product.

The validity of these schemes is dependent upon the assumptions that the products are not isomerized after their formation, and that the dienes do not undergo isomerization prior to reaction with the attacking radical (RS·).

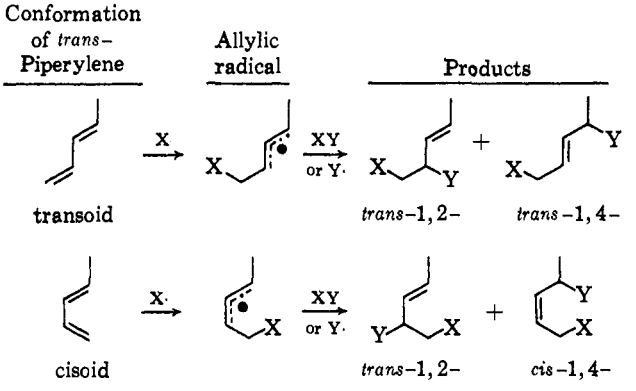


Figure 1. Stereochemical scheme for the addition of radicals to *trans*-piperylene.

If these assumptions are valid, then *the stereochemical configuration of the 1,2-products would serve as a direct measure of the retention of configuration of the intermediate allylic radicals, while the stereochemistry of the 1,4-products would be determined by the rotational conformation of the reacting diene.* Therefore, if the intermediate allylic radicals do not isomerize, then *trans*-piperylene would give 1,2-product which would be exclusively *trans* (Figure 1) while *cis*-piperylene would give 1,2-product with a completely *cis* configuration (Figure 2). If it was demonstrated in this fashion that these intermediate radicals did indeed maintain their configuration, then the geometry of the 1,4-products should be the same as that of the rotational conformation of piperylene which was attacked by thiyl radical. The cisoid and transoid conformations, which have all p-orbitals coplanar, thereby permitting maximum overlap, are the two most stable rotational forms of both *cis*- and *trans*-piperylene. The formation of the *cis*-1,4-product from the cisoid conformation and the *trans*-1,4-product from the transoid conformation, regardless of the *cis* or *trans* structure of the reacting piperylene, is also depicted in Figures 1 and 2.

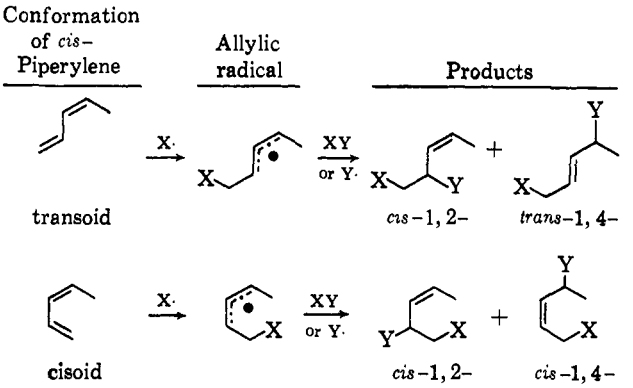


Figure 2. Stereochemical scheme for the addition of radicals to *cis*-piperylene.

Cooxidation. By adding benzenethiol dropwise to a methanol solution containing double the required stoichiometric quantity of piperylene, it was possible to maintain an O_2-saturated solution, and a 97% yield of allylic alcohols could be isolated after removal of most of the phenyl disulfide by filtration of the cold alcohol solution. The cooxidation of benzenethiol with *cis*- and *trans*-piperylene (Table I) gave predominately the

Table I. Isomer Distribution of Products from the Cooxidation of Benzenethiol with *cis*- and *trans*-Piperylene, %

	Derived from attack on C-1[a]				Derived from attack on C-4	
	1,2-Products		1,4-Products		4,3-Products	4,1-Products
	trans (**14**)	*cis* (**16**)	*trans* (**15**)	*cis* (**19**)	(**17**)	(**18**)
trans-Piperylene	32.8	...[b]	63.1	...	2.7	1.4
cis-Piperylene	...	28.2	66.0	...	3.7	2.1

[a] Piperylene $\overset{1}{CH_2}=\overset{2}{CH}-\overset{3}{CH}=\overset{4}{CH}-\overset{5}{CH_3}$ (1,3-pentadiene). [b] Indicates none detectable by capillary v.p.c. analysis.

products resulting from the attack of thiyl radical at C-1 (~95%). Examination of the stereochemistry of the 1,2-reaction products revealed that their formation had been completely (>99%) stereospecific. *cis*-Piperylene gave *cis*-1,2-product (**16**) while *trans*-piperylene gave *trans*-1,2-product (**14**). The 1,4-products (**15**) appeared to be entirely *trans*, although the presence of small quantities of the *cis*-1,4-product isomer could not be ruled out completely due to the tailing of the capillary v.p.c. peaks to a small extent. Acetate esters prepared from the reaction product mixtures showed essentially identical isomeric product distributions with the corresponding allylic alcohols, according to n.m.r. and v.p.c. analysis.

$PhSCH(CH_3)CHOHCH{=}CH_2$
17

$PhSCH(CH_3)CH{=}CHCH_2OH$
18

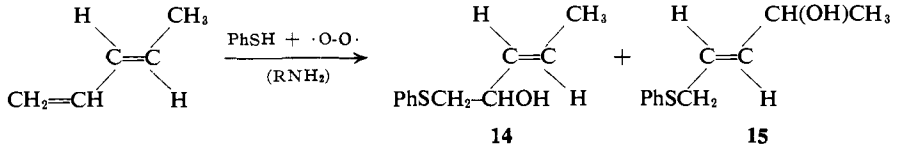
$PhSCHC{=}CCH(OH)CH_3$ (H H)
19

Examination of the unreacted piperylene from cooxidation reactions with pure *cis*- and *trans*-piperylene revealed that no isomerization of excess diene had occurred. This observation coupled with the stereospecific formation of cooxidation products indicated a rapid combination of the allylic radical intermediate with the oxygen diradical and suggested that the addition of thiyl radical to diene in the presence of oxygen was an irreversible process. The relative rate of reaction of benzenethiyl radical with *cis*- and *trans*-piperylene could, therefore, be measured by competitively cooxidizing the two isomers and determining their relative rate of disappearance by v.p.c. The determination revealed that the benzenethiyl radical adds to both isomers at essentially the same rate (k_{cis}/k_{trans} for piperylene = 0.94 ± 0.04).

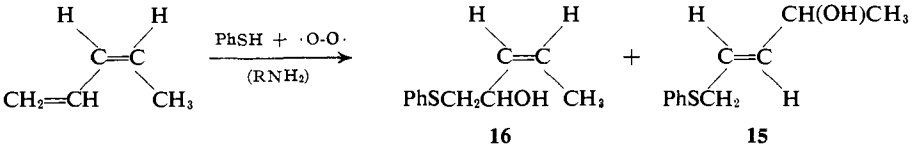
The cooxidation of piperylene with methanethiol and ethanethiol gave sizable quantities of carbonyl-containing material along with the expected cooxidation products. This introduced the possibility of changes in the initial isomer distribution of the cooxidation products. For this reason the stereochemical course of the cooxidation of aliphatic thiols with piperylene was not investigated. The n.m.r. parameters for these cooxidation products along with those of benzenethiol are presented in Table VI.

Addition of Aromatic Thiols. The addition of benzenethiol to *cis*- and *trans*-piperylene proceeds smoothly in the dark at 25°. The use of a free-radical initiator such as hydroperoxide or ultraviolet radiation increased the rate of the addition. The reaction, regardless of initiator, resulted in the formation of 1:1 adducts which could be isolated in better than 95% yield.

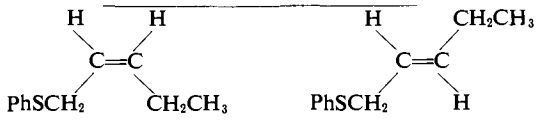
The reaction of benzenethiol with a onefold excess of piperylene (Table III) both with and without added initiator gave principally (~95%) the products resulting from the attack of the thiyl radical at C-1 of piperylene. The 1,2-adduct from *cis*-piperylene was about 92% *cis* (**20**) while the 1,2-adduct from *trans*-piperylene was 96% *trans* (**21**). The 1,4-adduct was 92% *trans* (**23**) from *cis*-piperylene (8% *cis* (**22**)) and essentially pure *trans* (**23**) (99+ %) from *trans*-piperylene.



14 **15** (7)

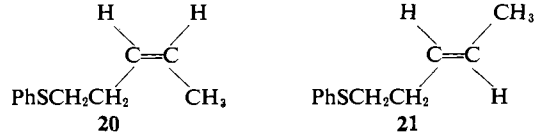


16 **15** (8)



22 *cis* **23** *trans*

1,4-adduct



20 *cis* **21** *trans*

1,2-adduct

$PhSCH(CH_3)CH{=}CHCH_3$
24
4,1-adduct

The high retention of configuration exhibited by these 1,2-addition products demonstrated that these allylic radicals were relatively stable and did not readily interconvert during the time interval necessary for the abstraction of a hydrogen atom from the aromatic thiol.

Examination of unreacted excess piperylene after the thiol had been consumed revealed, much to our surprise, that considerable isomerization of diene had occurred.

The unreacted starting piperylene was almost 40% *trans*-piperylene when initially pure *cis*-piperylene was used, and up to 10% *cis*-piperylene from the reaction with *trans*-piperylene.

Runs using benzenethiol with *cis*- and *trans*-piperylene mixtures, in which the initial ratio of *cis*- and *trans*-diene was varied (Table II), gave *cis*/*trans* ratios for the 1,2-adducts which corresponded reasonably with those of the initial piperylene mixtures. This result is consistent with the equal reactivity of both *cis*- and *trans*-piperylene towards benzenethiyl radical as determined by competitive cooxidation. There also was some indication from these runs that piperylene isomerized to a greater extent when the reaction was carried to a higher degree of thiol conversion.

Table II. Reaction of Benzenethiol with *cis*- and *trans*-Piperylene Mixtures at 25°[a]

cis-Piperylene,[b] % Before reaction	*cis*-Piperylene,[b] % After reaction	Conversion of thiol, %	1,2-Adduct that is *cis*, %
100	97.8	14	92.0
100	78.8	86	94.8
97.0	94.5	22	93.2
85.6	85.7	30	83.7
81.1	79.8	18	81.7
76.9	68.8	25	76.6
77.0	50.7	91	68.5
51.6	52.7	23	52.0
51.3	35.7	85	51.8
25.7	24.0	18	28.1
25.6	14.0	86	30.0
16.4	12.5	89	17.0
0 (100% *trans*)	3.8	92	2.1

[a] All reaction mixtures initially contained 2 moles of piperylene to 1 mole of benzenethiol. [b] Portion of total piperylene that is *cis*.

Periodic sampling of reaction of benzenethiol with pure *cis*- or *trans*-piperylene (Figure 3) revealed that the *cis*/*trans* ratio for the 1,2-adduct was essentially invariant with time, and indeed the entire isomer distribution of the adducts was independent of the degree of conversion of the thiol (Table III); however, piperylene isomerization was found to increase with increasing thiol conversion.

A graphic representation (Figure 3) of the change of configuration of unreacted piperylene and of 1,2-adduct formed as a function of the degree of reaction provides an answer as to how benzenethiol addition to *cis*-piperylene proceeds with better than 90% retention of configuration while the remaining piperylene was isomerized to the extent of 40%. The results in Figure 3 showed that the vast majority of product was formed before much isomerization of piperylene occurred, the degree of piperylene isomerization increasing markedly as the thiol concentration approached zero. Since benzenethiyl radical adds to both *cis*- and *trans*-piperylene at the same rate, a calculation was made, based on this piperylene isomerization curve, which predicted that when all the thiol was reacted the 1,2-product from *cis*-piperylene would be at most 12% *trans*. This is in good agreement with our experimental value of 92.5% *cis* and 7.5% *trans*. Similar observations were made for the reaction of *trans*-piperylene except here the extent of conversion to *cis*-piperylene is

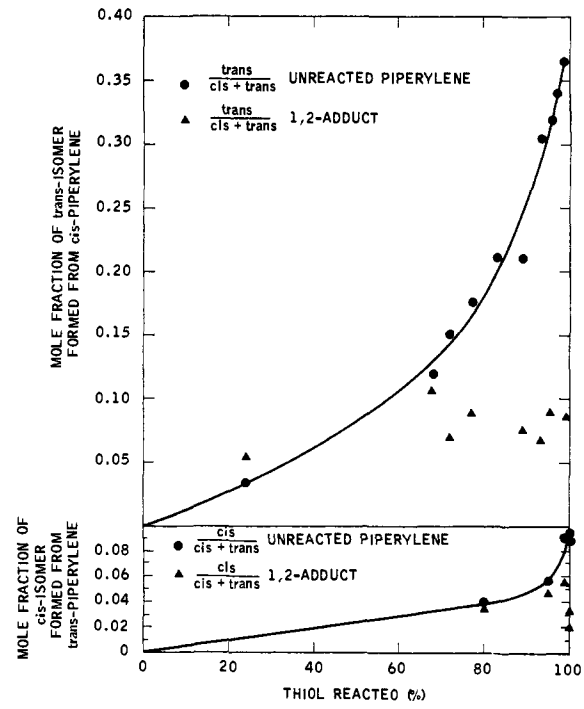
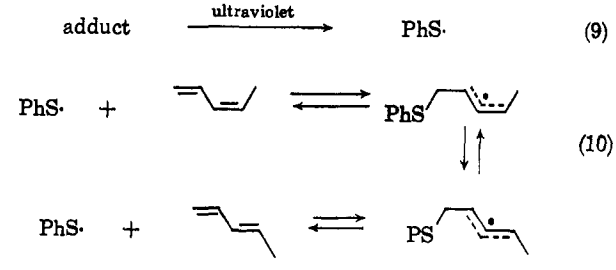


Figure 3. Formation of 1,2-addition products and the isomerization of excess piperylene as a function of thiol conversion.

small since it is limited by the thermodynamic values of 15% *cis*- 85% *trans*-piperylene at equilibrium.

The photoinitiated reaction of benzenethiol with piperylene also gave some remarkable results. The 1,2-products from both *cis*- and *trans*-piperylene were formed with a high degree of stereospecificity yet the recovered excess diene was found to be completely equilibrated (85% *trans*- and 15% *cis*-piperylene from either initially pure piperylene isomer). This apparent anomaly was reconciled by demonstrating that although ultraviolet irradiation of piperylene alone had no effect piperylene was readily isomerized to an equilibrium mixture of the *cis*- and *trans*-diene when some benzenethiol–piperylene adduct was dissolved in the pure piperylene isomer and the solution was irradiated. These same solutions did not show any piperylene isomerization upon heating for prolonged periods.

The formation of thermodynamic equ ibrium mixture made an interpretation involving the adduct as a photosensitizer for the isomerization of piperylene unlikely.[8] An explanation involving photolysis of a very small amount of the adduct (eq. 9) to produce



benzenethiyl radical (PhS·) appears more plausible. In the absence of benzenethiol, no chain-transfer reaction can readily occur to consume the allylic radicals which are formed when this benzenethiyl radical adds

(8) G. S. Hammond, *J. Am. Chem. Soc.*, **83**, 2396 (1961).

Table III. Reaction of Benzenethiol with *cis*- and *trans*-Piperylene at 25°[a]

	1,2-Adduct, % in *cis* configuration	1,4-Adduct, % in *trans* configuration	Isomer distribution, %[b]				
			1,2-Adduct		1,4-Adduct		4,1-Adduct
			cis (**20**)	*trans* (**21**)	*cis* (**22**)	*trans* (**23**)	(**24**)
cis-Piperylene	92.5	99.9	29.5 ± 1.6	3.2 ± 0.5	...	56.8 ± 2.0	4.3 ± 0.4
trans-Piperylene	3.9	91.6	2.1 ± 0.5	51.4 ± 0.1	3.4 ± 0.2	36.9 ± 0.2	6.2 ± 0.4

[a] Two moles of piperylene to 1 mole of thiol. [b] Isomer distributions are the mean values (together with deviation from the mean) sampled periodically as thiol concentration diminished from 100 to 0% (Figure 3).

Table IV. Isomer Distribution of Products from the Addition of Methanethiol to *cis*- and *trans*-Piperylene at 25°[a]

	Thiol reacted, %	1,2-Isomer that is *cis*, %	Isomer distribution				
			1,2-Products		1,4-Products		4,1-Product
			trans	*cis*	*trans*	*cis*	
trans-Piperylene	75	6.6	27.1	1.9	49.5	4.4	17.1
	90	7.6	29.3	2.4	48.8	4.9	14.6
cis-Piperylene	81	68.8	5.9	13.0	58.4	1.6	21.1
	96[b]	51.1	13.4	14.0	47.8	3.2	21.6

[a] Initial piperylene/thiol (mole) = 2. [b] Accompanied by the formation of 12% *trans*-piperylene.

to the diene. Instead the radicals are long lived and have an opportunity to rotate, thereby establishing a route for equilibration of the diene (eq. 10).

Indeed, when examining the ultraviolet-initiated benzenethiol addition, if irradiation was discontinued just before the thiol was completely consumed, the results were then similar to the thermally and peroxide initiated reactions.

The possibility of direct somerization of the adducts by reversible addition of thiyl radical to the olefinic bond[9] of these adducts was also a consideration. Competitive thiol addition reactions between olefins and piperylene as well as adduct and piperylene showed that the thiyl radical did not attack the monoolefin bond when the more reactive diene was present.

Addition of Aliphatic Thiol. In contrast to the photoinitiated reaction using benzenethiol, which was complete in 2 hr. (25°), the photoinitiated reactions of methane and ethanethiol were very sluggish and had to be irradiated for about 10 days to achieve 75–80% conversion. The yields of 1:1 adduct based on thiol consumed were comparatively poor. About a 60% yield of 1:1 adduct was isolated along with higher boiling telomeric products. V.p.c. analysis of the unreacted excess diene (100% excess present initially), when compared with determinations of thiol by titration, confirmed that more piperylene than thiol was used on a mole-to-mole basis.

The addition of aliphatic thiol to piperylene did not cause isomerization of the unreacted excess piperylene (a small amount of isomerization could be observed only when the reaction was irradiated for exceedingly long periods (3 weeks) such that thiol was almost completely consumed).

Despite the apparent advantage stemming from the freedom from isomerization of the piperylene, aliphatic thiol addition (Table IV) was not characterized by the high degree of stereospecificity observed with aromatic thiol. The observation of some preference for *cis* 1,2-adduct from *cis*-piperylene and *trans* 1,2-adduct from *trans*-piperylene suggests that while the intermediate allylic radicals undergo considerable isomerization under these conditions they are still not interconverting freely. For if this were so, the same distribution of isomeric products would be obtained from both *cis*- and *trans*-diene.

The results which have been obtained with aliphatic thiol are consistent with a situation in which the intermediate allylic radical is longer lived and has an opportunity to interconvert by rotation or to add again to another mole of diene (giving telomer) before it abstracts a hydrogen atom from the aliphatic thiol.

Identification of Products. Vapor phase chromatographic analysis using packed columns (Carbowax 20M) revealed the same three peaks from the addition of benzenethiol to either *cis*- or *trans*-piperylene; however, the relative amounts of these three components was different. Elemental analysis confirmed that they were isomeric 1:1 addition products.

The two major products were freed from the third component by distillation, and the mixture was hydrogenated (diimide reduction) to give a single product which was shown to be identical with phenyl *n*-pentyl sulfide synthesized independently.

$$\begin{array}{l} \mathrm{PhSCH_2CH_2CH{=}CHCH_3} + \mathrm{PhSCH_2CH{=}CHCH_2CH} \\ \qquad\qquad\qquad\qquad \downarrow \mathrm{HN{=}NH} \\ \qquad\qquad\qquad\qquad \mathrm{PhSCH_2CH_2CH_2CH_2CH_3} \\ \qquad\qquad\qquad\qquad \uparrow \text{ultraviolet} \\ \mathrm{PhSH} + \mathrm{CH_2{=}CHCH_2CH_2CH_3} \end{array}$$

The infrared spectra of each of the reaction product mixtures showed strong absorption at 10.4 μ attributable to *trans*-olefin. The *cis*-olefin absorption region was obscured by the phenyl substitutents. Infrared spectra revealed no trace of any terminal double bonds.

Nuclear magnetic resonance spectra of the isomeric adducts from *cis*- or *trans*-piperylene indicated that both reactions gave a mixture of 4,1-, 1,2-, and 1,4-adducts in different proportions. It did not, however, indicate the *cis* or *trans* character of their double bonds. The absence of any n.m.r. absorption attributable to $=CH_2$ protons together with the infrared evidence indicates that no 4,3-adduct was formed. The n.m.r. parameters of these adducts obtained from a commerical

(9) C. Walling and W. Helmreich, *J. Am. Chem. Soc.*, **81**, 1144 (1959).

mixture of *cis*- and *trans*-piperylene were presented elsewhere.[4b]

Assignments of v.p.c. peaks were made by distilling the reaction mixtures into arbitrary fractions containing different proportions of the three isomers and comparing the v.p.c. analysis with the quantitative estimate of isomer composition made independently by n.m.r. (Table V).

Table V. Comparison between N.m.r. and V.p.c. Analyses of Isomeric Mixtures of Benzenethiol–Piperylene Adducts

Isomer type	Thiol adducts of *trans*-Piperylene, Isomer, %		Thiol adducts of *cis*-Piperylene, Isomer, %		V.p.c. peak no.
	N.m.r.	V.p.c.	N.m.r.	V.p.c.	
	First distillate fraction				
1,2	40	44	20	23	3
1,4	50	46	60	60	2
4,1	10	10	20	17	1
	Second distillate fraction				
1;2	60	59	40	38	3
1,4	40	41	55	59	2
4,1	0	0	5	3	1
	Total reaction mixture				
1,2	..	54	..	39	3
1,4	..	40	..	57	2
4,1	..	6	..	4	1

The 1,2- and 1,4-adducts were resolved analytically into their respective *cis* and *trans* isomers by the use of a 200-ft. capillary v.p.c. column (Surfonic TD 300). Both *cis*- and *trans*-piperylene gave essentially *trans* 1,4-adduct; however, their 1,2-adducts were quite different. *cis*-Piperylene gave essentially a *cis* 1,2-adduct peak along a small *trans* 1,2-adduct peak; *trans*-piperylene showed the reverse.

The 1,2- and 1,4-adducts were separated by fractionation through a $^1/_8$-in. coated tubular v.p.c. column (Surfonic N 300). The separated products were checked by capillary v.p.c. to ensure that no change had occurred during fractionation (although packed v.p.c. columns gave no isomerization between 1,2- and 1,4-adducts, fractionations using these columns resulted in *cis–trans* isomerization of the components). Infrared spectra of the resolved 1,2- and 1,4-adducts substantiated our *cis–trans* assignments to the capillary v.p.c. peaks. The 1,2-adduct from *trans*-piperylene showed a very strong *trans*-olefin absorption at 10.4 μ; however, this absorption was practically absent from the 1,2-adduct from *cis*-piperylene. Both 1,4-adducts showed strong *trans* absorptions.

Similar procedures were used to assign structures to the capillary v.p.c. peaks obtained from the other addition and cooxidation reactions of piperylene which were examined. N.m.r. (Table VI) indicated that the two major components of the cooxidation mixtures were the 1,2- and the 1,4-cooxidation products. The 1,2-cooxidation product could be recognized by a downfield shift of the methyl signal while the 1,4-product was characterized by the downfield shift of the methylene signal. The 4,3-alcohol, although a minor component, could be identified readily by its terminal vinyl group. In contrast, the 4,1-alcohol had an internal vinyl multiplet and a methyl doublet shifted downfield. Acetate ester derivatives were prepared from the cooxidation products to help confirm these assignments.

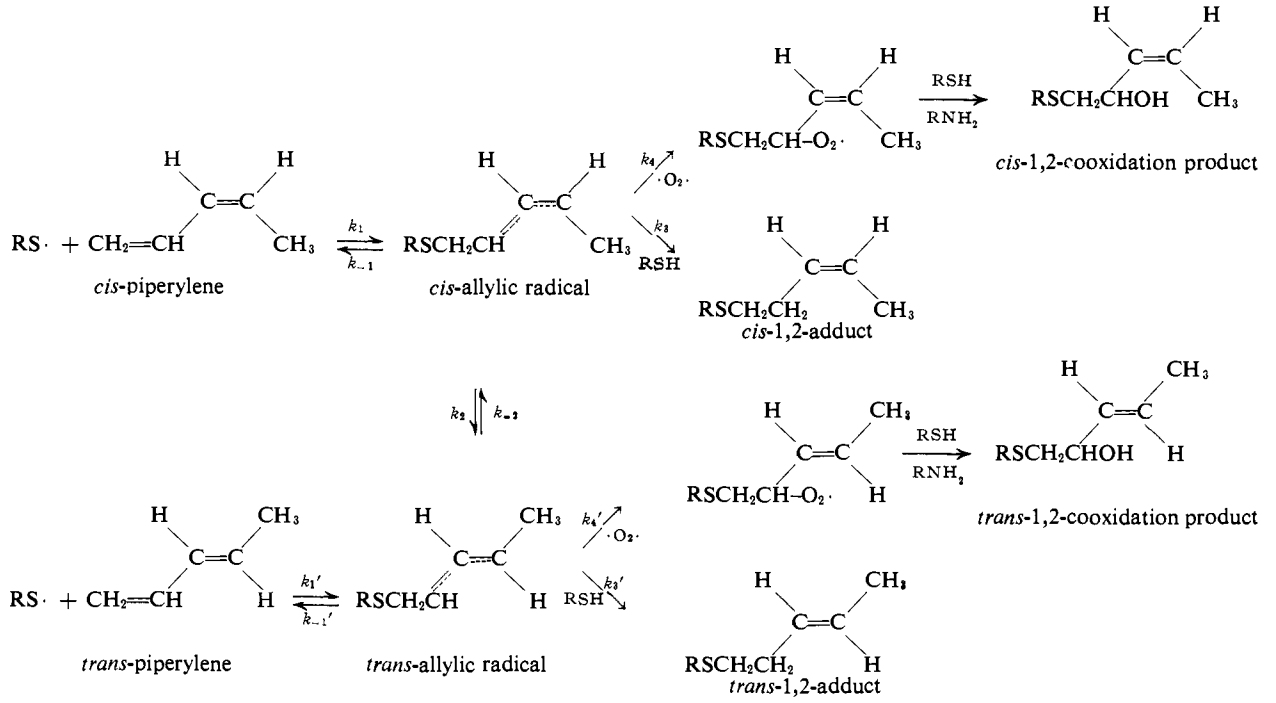
Table VI. Proton Nuclear Magnetic Resonance Spectra of Thiol–Piperylene Cooxidation Products

Product	Structural unit	Chemical shifts of structural units, p.p.m.[a] Starting thiol: Benzene	Methane	Ethane
1,2	RS—	7.0–7.5 m	2.05 s	1.20 t[b] 2.35 q[b]
	—CH_2—	2.95 d[b]	2.47 d[b]	2.50 d[b]
	—CH—	4.1 m	4.05 d	4.15 m
	(—OH)	3.7 s[c]	3.7 s[c]	3.7 s[c]
	—CH=	5.5 m[d]	5.5 m[d]	5.45 m[d]
	=CH—	5.5 m[d]	5.5 m[d]	5.45 m[d]
	—CH_3	1.53 d[e]	1.65 d[e]	1.65 d[e]
1,4	RS—	7.0–7.5 m	1.92 s	1.20 t[b] 2.35 q[b]
	—CH_2—	3.40 d[f]	2.97 d[f]	3.05 d[f]
	—CH=	5.5 m[d]	5.45 m[d]	5.45 m[d]
	=CH	5.5 m[d]	5.5 m[d]	5.45 m[d]
	—CH—	4.10 m[d]	4.10 m	4.05 m
	(—OH)	3.7 m[c]	3.70 s	4.15 s
	—CH_3	1.07 d[g]	1.18 d[g]	1.18 d[g]
4,3	RS—	7.0–7.5 m		
	—CH—	m[h]		
	(—CH_3)	1.23 d[b]		
	—CH—	m[h]		
	(OH)	3.70 s[c]		
	—CH=	m[i]		
	=CH_2	5.40 m[i]		
4,1	RS—	7.0–7.5 m		
	—CH—	m[h]		
	(—CH_3)	1.31 d[b]		
	—CH=	5.5 m[d]		
	=CH—	5.5 m[d]		
	—CH_2—	d[h]		
	—OH	3.7 s[c]		

[a] Downfield from tetramethylsilane, internal standard: s, singlet; d, doublet; t, triplet; q, quartet; and m, multiplet. [b] J = 7 c.p.s. [c] Approximate for solutions in CCl_4; OH peak appears at about 4.2 p.p.m. in the absence of diluent. [d] Internal vinyl multiplet only partially resolved, width 20–30 c.p.s. [e] J = 5 c.p.s. [f] Apparent coupling constant, J = 5 c.p.s. [g] J = 6 c.p.s. [h] Indistinct; may lie in the 3.7–4.7-p.p.m. region. [i] One peak of terminal vinyl ABC pattern can be distinguished adjacent to the internal vinyl multiplet.

Discussion

The addition and cooxidation of *benzenethiol* with *cis*- and *trans*-piperylene appear to be highly specific reactions. The 1,2-adducts and adduct alcohols which are produced essentially retain the same geometry as the dienes from which they are derived. These results suggest that different intermediate allylic radicals, which maintain their steric configuration, are involved in these reactions of *trans*- and *cis*-piperylene. The cooxidation with benzenethiol has been found to proceed without any isomerization of reacting diene, while the addition of benzenethiol causes significant *cis–trans* isomerization of piperylene. This isomerization of the parent diene has little effect on the stereochemistry of the products. The explanation for this has been suggested by the result of continuously sampled runs as well as reactions of mixtures of the two isomeric dienes with benzenethiol. The data obtained in these experiments revealed that most of the isomerization occurs in the latter portion of the reaction, increasing sharply as the thiol concentration approaches zero. Although *cis*- and *trans*-piperylene react with benzenethiol at essentially identical rates, the addition product which is formed after significant isomerization has occurred makes but a small contri-



bution to the total product already present, and for this reason does not affect the configuration of the total product significantly.

The addition of aliphatic thiol occurs without isomerization of the reacting piperylenes; nevertheless, the products formed show little retention of configuration. The differences in the stereochemistry of the 1,2-products observed between aromatic and aliphatic thiols, and between addition and cooxidation reactions, can be rationalized by the following scheme which depicts potential reaction paths for the more stable transoid conformations of *cis*- and *trans*-piperylene. The primary contribution of the more stable transoid conformation to the total structure of each piperylene isomer is reflected in the preponderance of *trans*-1,4-products from both *cis*- and *trans*-piperylene.

The interconversion of the intermediate allylic radicals which are produced in these reactions should be a function of their lifetime. If these radicals are not consumed rapidly, they then have an opportunity to rotate, and in this manner the stereospecificity of the reaction can be destroyed. Aromatic thiols possess a weak sulfur–hydrogen bond compared to aliphatic thiols because the thiyl radical resulting from the scission of the former bond can be strongly stabilized by resonance with the phenyl ring. As a result, the abstraction of a hydrogen from methanethiol (R = CH_3) should be more difficult than a similar abstraction from benzenethiol (R = Ph). Since $k_3(PhSH) > k_3(CH_3SH)$ more isomerization of the intermediate allylic radical should be possible with aliphatic thiol and is indeed observed with methanethiol. The very slow over-all rate of the methanethiol addition coupled with the observance of telomer formation in this reaction serve to substantiate this.

As a consequence of the differences in stability of the aromatic and aliphatic thiyl radicals, the addition of PhS· to piperylene would be expected to be more reversible than the addition of CH_3S· [k_{-1}(R = Ph) > k_{-1}(R = CH_3)]. If such a reversible addition occurred many times for each abstraction step [$k_{-1} >> k_3$·(PhSH)], the smallest amount of rotation of the intermediate allylic radical would cause significant isomerization of the remaining piperylene, regardless of the fact that the dissociation of each allylic radical back into diene occurred stereospecifically.[10] The observation that benzenethiol addition leads to isomerization of diene, while methanethiol addition does not, lends support to the theory that the benzenethiol addition to diene involves a reversible thiol radical addition while methanethiol addition does not. The finding that CH_3S· addition to diene is essentially irreversible while the addition to olefin has been shown to be highly reversible can be attributed to the greater stability of the allylic radical intermediate.

The observation that the preferential coupling of the intermediate allylic radical and oxygen, a process which presumably requires lower activation energy ($k_4 >> k_3$) than abstraction of hydrogen from thiol, eliminates any isomerization of diene and gives 1,2-adducts with complete retention of configuration further supports this over-all scheme. Apparently the reaction of the intermediate allylic radical with oxygen is a very rapid step ($k_4 > k_{-1} >> k_3$), a not too surprising observation in the light of the numerous examples of the scavenging action of oxygen on radicals.

Direct isomerization of the olefinic products by thiyl radicals[9] does not appear to be a factor in these reactions, presumably because the attack of these radicals on diene (which is always in excess) to give an allylic radical is preferred to the production of alkyl radical by attack on olefin.

The 1,4-adducts from the addition of benzenethiol to piperylene are mainly of the *trans* configuration. Investigation of the conformational distribution of dienes such as butadiene[11] has shown that the transoid con-

(10) The reversible addition of thiyl radical to C-4 of piperylene could also contribute to the isomerization of the diene; however, the very small extent to which attack at this position has been observed makes such a scheme less attractive.

(11) J. G. Aston and G. Szasz, *J. Chem. Phys.*, 14, 67 (1946).

formation predominates (4% cisoid conformation at 25°). Therefore, it is not surprising that reactions which involve retention of configuration by the intermediate allylic radical also produce essentially *trans* 1,4-adduct.

It is of interest to note that while benzenethiol addition to *cis*-piperylene consistently gave no *cis* 1,4-adduct, *trans*-piperylene gave 1,4-adduct which was about 6–7% *cis*. Examination of models of these dienes reveals that *trans*-piperylene can exist in cisoid and transoid conformations similar to butadiene, while the cisoid conformation of *cis*-piperylene is highly hindered, and in all likelihood contributes nothing to the total structure of the molecule. The failure of the *cis* isomer of piperylene to undergo Diels–Alder reaction,[12] a process which should involve the cisoid conformation, gives additional evidence for the absence of contributing cisoid conformation of *cis*-piperylene. Thus the production of some *cis* 1,4-adduct from *trans*-piperylene, while no *cis* 1,4-isomer is formed from *cis*-piperylene, tends to support the suggestion that the configuration of the products of 1,4-addition to dienes is related to the conformational distribution of the reacting diene, provided the intermediate allylic radicals which are produced maintain their geometry and undergo no interconversion.

The lact of direct correlation between the structure of the product and the conformational distribution of the diene observed in the free-radical polymerization of butadiene (*e.g.*, 4% cisoid butadiene conformation at 25° gives 25% *cis* 1,4-polymer at 25°) can perhaps be attributed to the isomerization of the intermediate allylic radicals which are produced here. The observations that higher temperatures, which would increase the rate of isomerization of allylic radicals as well as increase the relative stability of the *cis* radical, gave increasing amounts of *cis* polymer is consistent with this interpretation.

Experimental

Materials. *cis*-Piperylene was isolated from Enjay commerical piperylene by the method of Frank, Emmick, and Johnson.[12] The piperylene prepared in this manner contained 67% *cis*-piperylene, 33% cyclopentene, and was free from *trans*-piperylene. 99.9+% pure *cis*-piperylene was prepared from this mixture by the method of Craig[13] using a cuprous ammonium chloride treatment. *trans*-Piperylene specially prepared by the Columbia Organic Chemicals Co. contained 98% *trans*-piperylene, 2% cyclopentene, and was free from *cis*-piperylene. Research grade (99+% pure) cyclopentene was obtained from Phillips Petroleum Co. Benzenethiol was obtained from the Matheson Coleman and Bell and was distilled under nitrogen before use. Methanethiol was purchased from the Matheson Co., Inc., and was condensed into reaction vessels directly from the cylinder. Ethenethiol, Eastman reagent grade, was used without further purification.

Methods. N.m.r. analysis was performed on a Varian A-60 spectrometer. Infrared spectra were obtained with a Baird Model No. 4-55 spectrophotometer, V.p.c. analysis of piperylenes and cyclopentene were made with a Perkin-Elmer Model D vapor fractometer using a 2-m. "E" column (2,4-dimethylsulfolane). Analysis of structural isomers of thiol–piperylene adducts were made on an F and M Model No. 500 temperature programmed v.p.c. instrument using a 10-ft. column, packed with 20% Carbowax 20M on Chromosorb P. Analytical resolution of thiol–piperylene adducts into their respective *cis* and *trans* isomers was accomplished using a Barber Coleman Model No. 20 capillary v.p.c. unit equipped with a 200-ft., 0.01-in. i.d. column coated with Surfonic TD 300 (a tridecyl alcohol–ethylene oxide adduct). Fractionation of 1,2- from 1,4-adducts to obtain samples for infrared analysis was accomplished using the F and M instrument equipped with a 250-ft., $^1/_8$-in. o.d. open tubular column coated with Surfonic N.D. 300 (nonyl alcohol–ethylene oxide adduct). The benzenethiol addition was analyzed at 175°, and the methanethiol addition products were analyzed at 78°. The benzenethiol cooxidation products were analyzed using a Surfonic T.D. 300 coated 50-ft., 0.01-in. i.d. column at 175°.

Thermally initiated addition reactions were carried out in sealed tubes, which had been evacuated, flushed with nitrogen, and placed in a thermostated bath. Photochemically initiated addition reactions were carried out in similarly degassed quartz tubes and were irradiated with a Hanovia 100-w. utility lamp equipped with a Vycor heat filter and placed about 7 cm. from the vessel. Photoinitiated additions of benzenethiol could be carried out in Pyrex tubes just as readily. The details of the cooxidation procedures are described below.

Addition of Benzenethiol to Piperylene. In typical preparative-scale run, 110 g. (1 mole) of benzenethiol and 136 g. (2 mole) of piperylene were irradiated overnight at 25°. Potentiometric titration of thiol with $AgNO_3$ showed that 100% reaction had occurred. A small sample was withdrawn and unreacted piperylene was removed for analysis by bulb-to-bulb vacuum distillation into a liquid nitrogen cooled trap. The piperylene obtained in this manner was analyzed by v.p.c. and the adducts by capillary v.p.c.

Similar reactions using a 2:1 mixture of piperylene and cyclopentene instead of piperylene only gave identical results. The cyclopentene did not undergo any reaction in the presence of the highly reactive diene. The absence of any cyclopentene–benzenethiol adduct was verified by the absence of any v.p.c. peak corresponding to that obtained from a sample of this material prepared by the reaction of benzenethiol and pure cyclopentene.

Cyclopentene could therefore be used as an internal standard for v.p.c. analysis where necessary. It offered the advantage of codistilling with piperylene without any changes in relative concentration.

The product was isolated from the reaction mixture by distillation, b.p. 87–93° (1 mm.), $n^{20}D$ 1.5581, 168 g. (95% yield). *Anal.* Calcd. for 1:1 adduct: C, 74.13; H, 7.92; S, 17.95. Found: C, 73.99; H, 8.36; S, 18.40.

Diimide Reduction of Benzenethiol–Piperylene Adducts. The adduct, 8.9 g. (0.05 mole), b.p. 92–93° (1 mm.), $n^{20}D$ 1.5592, fractionated from the previously described reaction mixtures and containing approximately equal quantities of 1,4- and 1,2-adduct free

(12) R. L. Frank, R. D. Emmick, and R. S. Johnson, *J. Am. Chem. Soc.*, **69**, 2313 (1947).
(13) D. Craig, *ibid.*, **65**, 1006 (1943).

from 4,1-adduct according to v.p.c., and 18.5 g. (0.1 mole) of *p*-toluenesulfonylhydrazine[14] in 100 g. of diglyme were refluxed for 1.5 hr. (160°) under nitrogen and allowed to stand overnight. The reaction mixture was filtered and diglyme was removed at reduced pressure. The brown residual material was dissolved in 100 ml. of *n*-pentane which was filtered and washed seven times with 25-ml. portions of distilled water. The pentane solution was dried over $MgSO_4$, the pentane was removed, and the remaining yellow oil was distilled, b.p. 99–100° (0.8 mm.), 4.28 g. (48% yield). The pot residue was a dark viscous material which was not volatile and could not be made to distill. This distillate had an identical refractive index, $n^{20}D$ 1.5394, with a sample of phenyl *n*-pentyl sulfide prepared by the addition of benzenethiol to 1-pentene. The infrared and n.m.r. spectra of the two were indistinguishable and v.p.c. analysis showed the complete disappearance of the 1,2- and 1,4-adduct peaks and the appearance of a single new peak whose retention time was identical with that of the authentic sample. *Anal.* Calcd. for phenyl *n*-pentyl sulfide: C, 73.30; H, 8.95; S, 17.75. Found: C, 73.42; H, 9.01; S, 17.95.

Continuously Sampled Runs. In a typical run 27.2 g. (0.4 mole) of *cis*-piperylene, 14.1 g. (0.2 mole) of cyclopentene, and 22.0 g. (0.2 mole) of benzenethiol were placed in a flask equipped with a nitrogen inlet, mercury bubbler outlet, and a dual stopcock sampler which permitted samples to be withdrawn without admitting air to the system. The flask was cooled in a Dry Ice bath, purged with nitrogen for 1 hr., and then placed in a thermostated bath at 25°.

Samples were withdrawn periodically. A portion was titrated potentiometrically with $AgNO_3$ solution to follow the disappearance of thiol. A second portion was used to obtain the unreacted piperylene–cyclopentene mixtures. This was accomplished by bulb-to-bulb distillation of these highly volatile materials into a liquid nitrogen trap at about 20 mm. The material collected in this manner was free from adduct and unreacted thiol, and could be analyzed by v.p.c. to follow the disappearance and/or isomerization of the piperylene. The remaining portion of sample was washed free of thiol with 5% sodium hydroxide solution, dried over magnesium sulfate, filtered, and analyzed by capillary v.p.c.

Reaction of cis–trans-Piperylene Mixtures. A total of 4 ml. of piperylene with the *cis* and *trans* isomers in their desired proportions was placed in a reaction tube along with 2 ml. of cyclopentene. A few microliters of this mixture was withdrawn for v.p.c. analysis and 2.13 g. of benzenethiol was added. Two 0.2-ml. samples of this mixture were titrated and the tube was degassed, sealed, and placed in a thermostated bath at 25° for the desired time.

The tube was then opened and 0.2-ml. samples were titrated to determine the amount of the thiol consumed. The piperylene–cyclopentene volatiles were removed in the manner described in the previous section and were analyzed by v.p.c. to determine the extent of piperylene isomerization and the amount of piperylene consumed. The remaining reaction mixture was washed free of thiol and the adduct was analyzed by capillary v.p.c.

(14) R. S. Dewey and E. E. van Tamelen, *J. Am. Chem. Soc.*, **83**, 3729 (1961).

Addition of Methanethiol to Piperylene. In a typical run 12.0 g. (0.25 mole) of methanethiol and 34.0 g. (0.5 mole) of *trans*-piperylene were placed in a quartz tube which was evacuated, sealed, and irradiated at 25° for 19 days. At the end of this time, thiol concentration was determined by potentiometric titration of an aliquot (90% conversion). A sample was taken and piperylene was removed by a bulb-to-bulb distillation *in vacuo* and collected in a liquid nitrogen trap. Both the piperylene and the residual product were washed free of unreacted thiol with 5% NaOH and were analyzed by v.p.c. The reaction mixture was distilled and fractionated into lower cuts containing 1:1 adduct, 19.5 g. (67% yield), b.p. 58–63.5° (37 mm.), $n^{20}D$ 1.4738, and higher cuts, b.p. 108 (11 mm.)–59° (0.1 mm.), $n^{20}D$ 1.4827–1.4866, containing telomeric material. *Anal.* Calcd. for the fraction containing 1:1 adducts: C, 62.04; H, 10.41; S, 27.55. Found: C, 62.35; H, 10.76; S, 27.43.

Cooxidation of Benzenethiol and Piperylene. In a typical experiment 45.4 g. (0.666 mole) of *cis*-piperylene and 7.31 g. (0.1 mole) of *t*-butylamine dissolved in 450 ml. of methanol were placed in a 1-l. flask equipped with an efficient reflux condenser, magnetic stirrer, thermometer, gas inlet tube, and dropping funnel. The gas inlet and the outlet tubes from the condenser were equipped with bubble counters. An ice bath was placed around the reaction flask and the oxygen flow was adjusted such that the gas left the reaction mixture at the rate of one bubble every 10–15 sec. Benzenethiol (110 g., 1.0 mole) was added dropwise over a period of about 5 hr. The temperature was maintained at 0–2° for a total of 11.5 hr. (75% reaction by titration). The O_2 bubbling was continued for a total of 24 hr. and the reactants were permitted to come to room temperature overnight.

Titration with silver nitrate at the end of this time showed that only trace quantities of thiol were present. The reaction mixture was cooled to −78° and the crystalline precipitate formed was filtered by suction and then washed with a small quantity of cold methanol and dried to yield 70.4 g. (96.8%) of diphenyl disulfide, m.p. 57.5–59°. Unreacted excess piperylene was isolated by distillation both before and after filtration of disulfide. V.p.c. showed no difference in the isomer composition resulting from work-up.

The methanol solution was concentrated and the residual product was then pumped out for 5 hr. at room temperature (0.5 mm.) to remove any traces of solvent. The yield of unpurified alcohol was 62.3 g. (96.5%). This material was analyzed on a 50-ft. capillary v.p.c. column and was shown to be free of any thiol addition product. The cooxidation product was distilled and cut into arbitrary fractions, b.p. 98–114° (0.05 mm.), $n^{20}D$ 1.5735–1.5825 (92% total yield). The compositions of these fractions were analyzed by v.p.c. and n.m.r., and the comparison was used for structural assignments of isomers. The 1,2-isomer produced in this experiment (with *cis*-piperylene) was also shown to have a different v.p.c. retention time from that of the 1,2-isomer formed in the *trans*-piperylene–benzenethiol cooxidation.

Cooxidation of aliphatic thiols was carried out in a similar fashion. Table VI gives the n.m.r. parameters of thiol–piperylene cooxidation products.

Competition reactions using mixtures of *cis*- and

trans-piperylene along with cyclopentene as an internal standard were carried out in much the same manner described here except that a closed system arrangement was used in order to avoid any changes in diene concentration due to evaporation caused by the bubbling of gas through the system. The oxygen pressure was maintained by repressuring a reservoir whenever it became necessary. Samples were withdrawn periodically diluted with an excess of a 5% NaOH solution to remove methanol and thiol. The oil which came to the top was subjected to a bulb-to-bulb vacuum distillation to isolate the mixtures of piperylene and cyclopentene which were then analyzed by v.p.c.

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Reactions of Enol Ethers with Carbenes. V. Rearrangements of Dihalocyclopropanes Derived from Six-, Seven-, and Eight-Membered Cyclic Enol Ethers[1]

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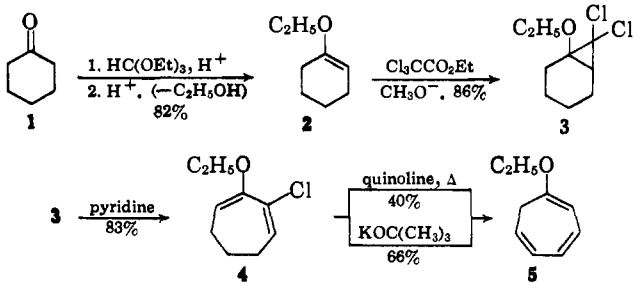
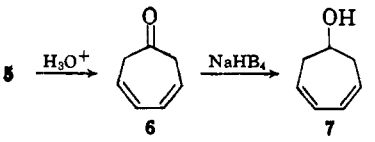
1,1-Dihalocyclopropanes have been prepared from enol ethers derived from cyclohexanone, cycloheptanone, and cyclooctanone. The product derived from cyclohexanone affords 1-ethoxy-1,3,5-cycloheptatriene (**5**) *in 55% over-all yield by a two-step process involving pyridine with subsequent reaction of the intermediate chlorodiene* **4** *with potassium t-butoxide, or in 37% yield by a one-step process involving quinoline. Cyclopropanes derived from the larger ring enol ethers do not react with hot pyridine, but give products with hot quinoline formed by transannular reactions. Other reactions of products and intermediates are discussed.*

The conversion of cyclohexanone to 1-ethoxycycloheptatriene (**5**), by a process involving reaction of the intermediate **3** with hot quinoline, was described in a preliminary communication.[3] This reaction scheme



was subsequently extended,[4] as we had suggested, to the synthesis of tropone and β-tropolone by employing cyclic enol ethers containing an additional double bond. In this paper we wish to present details of these and related reactions, and describe certain transformations of the reaction products and intermediates.

The reaction of 1-ethoxy-7,7-dichlorobicyclo[4.1.0]-heptane (**3**) with hot quinoline produced 1-ethoxycycloheptatriene (**5**) in 38% yield. The triene **5** was characterized by its conversion in low yield to a solid adduct with N-phenylmaleimide, by oxidation with selenious acid to a mixture containing tropone (~38% yield),



and by hydrolysis to 3,5-cycloheptadienone (**6**, 91% yield). The 3,5-cycloheptadienone was, in turn, identified by its conversion to the known adduct with N-phenylmaleimide, and by its reduction to 3,5-cycloheptadien-1-ol (**7**) and to cycloheptanone. The positions of the double bonds in 1-ethoxy-1,3,5-cycloheptatriene[5] (**5**) were evident from the n.m.r. spectrum; of the four possible position isomers, only **5** would show the observed doublet for the ring methylene protons.

The cyclopropane **3** did not react with alcoholic silver nitrate at room temperature or with hot methanolic sodium methoxide, but gave a complex mixture containing 1-ethoxy-1,3,5-cyclohepatriene (**5**, 3.3% yield) and *o*-methylphenetole (24% yield) upon reaction with potassium *t*-butoxide in dimethyl sulfoxide.[6] When 1-ethoxy-7,7-dichlorobicyclo[4.1.0]heptane (**3**) was treated with boiling pyridine the intermediate 2-

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(2) In part from the Ph.D. Thesis of James R. Throckmorton, The University of Minnesota, 1964.

(3) W. E. Parham, R. W. Soeder, and R. M. Dodson, *J. Am. Chem. Soc.*, **84**, 1755 (1962).

(4) A. J. Birch and J. M. H. Graves, *Proc. Chem. Soc.*, 282 (1962).

(5) E. Weth and A. S. Dreiding [*ibid.*, 59 (1964)] have shown that thermal equilibration of the methoxycycloheptatrienes leads predominantly to the formation of 1-methoxy-1,3,5-cycloheptatriene.

(6) Formation of *o*-methylphenetole may be rationalized as shown