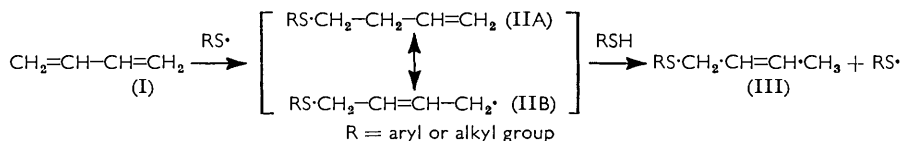


902. *The Reaction of Some cis-Dienes with Aromatic Thiols*

By J. A. CLAISSE and D. I. DAVIES

The reaction of aromatic thiols with (i) cyclopentadiene, (ii) cyclohexa-1,3-diene, (iii) cyclo-octa-1,3-diene, and (iv) 2,3-dimethylenebicyclo[2,2,1]-heptane has been investigated. The ratio of 1,2- to 1,4-addition is reported, together with relative reactivities of the dienes toward reaction with thiophenol, and the significance of the results discussed.

OSWALD, GRIESBAUM, THALER, and HUDSON¹ studied the free-radical addition of simple aliphatic and aromatic thiols to open-chain 1,3-dienes, and obtained chiefly the 1,4-*trans*-mono-adducts. Taking butadiene (I) as example they envisaged the reaction as proceeding *via* the intermediate resonance-stabilised allylic radical (II) to give product (III).



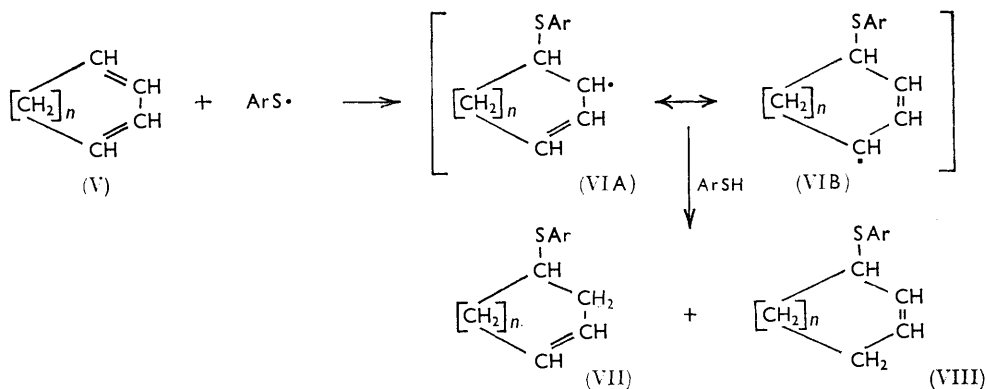
They rationalised their results in which reaction apparently takes place at the less stable primary radical canonical structure (IIB) of the resonance-stabilised intermediate (II) on the grounds that abstraction of hydrogen from the thiol is a step of significant activation energy, so that the transition state leading to the most highly substituted olefin (III) is of lower energy and is consequently more favoured than the transition state leading to the less highly substituted olefin $\text{ArS}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}=\text{CH}_2$ (IV). In addition, they considered

¹ A. A. Oswald, K. Griesbaum, W. A. Thaler, and B. E. Hudson, *J. Amer. Chem. Soc.*, 1962, **84**, 3897.

that the formation of the thermodynamically more stable product (III) is sterically favoured.

Our work has been concerned with the addition of aromatic thiols to some *cis*-dienes, since we considered that the determination of the ratio of 1,2- to 1,4-addition product and of the relative reactivities of the dienes would provide evidence for the relative importance of steric factors in controlling both 1,2- versus 1,4-addition, and the rate at which reaction occurs, and might provide an example in which 1,4-addition of thiol to diene was not so predominant as in the examples studied by Oswald.¹ We have studied some cyclic (cyclopentadiene, cyclohexa-1,3-diene, cyclo-octa-1,3-diene) and semicyclic (2,3-dimethylenebicyclo[2,2,1]heptane) dienes in which the diene system is *perforce cis*. The only previous work on *cis*-dienes of which we are aware is that of Posner,² who obtained 1,3-dibenzenesulphonylcyclopentane by the addition of thiophenol to cyclopentadiene and subsequent oxidation of the addition product, and also of Cristol and Nagpal,³ who obtained solely the 1,4-addition product from *p*-thiocresol and 1,2-dimethylenecyclohexane.

The reaction of an aromatic thiol with a cyclic *cis*-diene may be written as shown.

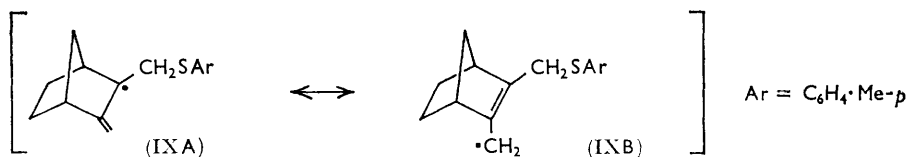


The reaction of 2,3-dimethylenebicyclo[2,2,1]heptane is similar, the intermediate allylic radical being (IX). The ratio of 1,2- to 1,4-addition product in the reaction of thiophenol and *p*-thiocresol with the *cis*-dienes is given in Table 1.

TABLE 1

The ratio of 1,2- to 1,4-addition product formed in reaction of dienes with aromatic thiols

Diene	Thiophenol addition		<i>p</i> -Thiocresol addition	
	1,2 (%)	1,4 (%)	1,2 (%)	1,4 (%)
(i) Cyclopentadiene	42	58	44	56
(ii) Cyclohexa-1,3-diene	43	57	44	56
(iii) Cyclo-octa-1,3-diene	15	85	17	83
(iv) 2,3-Dimethylenebicyclo[2,2,1]heptane ...			2	98

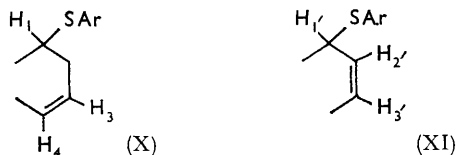


In general, separation of the 1,2- from the 1,4-addition product could not be achieved by gas-liquid chromatography, but the presence of the two isomers in the product was

¹ T. Posner, *Ber.*, 1905, **38**, 646.

³ S. J. Cristol and K. L. Nagpal, *J. Org. Chem.*, 1961, **26**, 365.

demonstrated by the presence in the nuclear magnetic resonance spectrum of signals due to the systems (X) and (XI) found in the 1,2- and 1,4-addition products, respectively.



H-1 occurs at higher field than H-1', and H-3 and H-4 at higher field than H-2' and H-3'. Use of the peak area integrals in the spectra allowed the relative amounts of 1,2- and 1,4-addition product to be estimated. Table 2 gives the τ -values for olefinic protons, and protons on carbon α to sulphur observed in 1,2- and 1,4-adducts.

TABLE 2

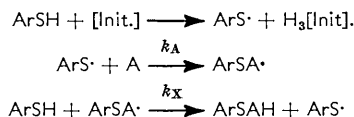
Diene	Thiol	1,2-Adduct		1,4-Adduct	
		Olefinic H	S-CH	Olefinic H	S-CH
(i)	Thiophenol	4.42	6.25	4.28	5.85
(ii)	"	4.40	6.73	4.24	6.20
(iii)	"	4.54	6.75	4.41	5.91
(i)	<i>p</i> -Thiocresol	4.42	6.30	4.30	5.90
(ii)	"	4.42	6.80	4.28	6.30
(iii)	"	4.45	6.75	4.36	5.90
(iv)	"			—	6.53

The assignments for the 1,4-addition product of *p*-thiocresol and cyclohexa-1,3-diene were confirmed by synthesis of the product from 3-bromocyclohexene and sodium *p*-thiocresoxide.

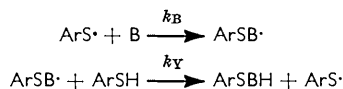
Considering the three cyclic *cis*-dienes, the two possible product olefins in each case are similarly substituted and hence of comparable thermodynamic stability; similarly, the two major canonical structures of the resonance-stabilised allylic radical intermediate are secondary radicals, and hence of comparable stability. Thus, steric factors should largely control the product ratio. For cyclopentadiene and cyclohexa-1,3-diene steric factors in the reaction of the intermediate allylic radical with the thiol are small but lead to a small preference for 1,4- over 1,2-addition as reflected in the observed results. In cyclo-octa-1,3-diene the importance of steric factors in controlling 1,2- versus 1,4-addition is magnified. This is readily observed if the two products are taken as models for the transition states leading to their formation when markedly increased non-bonded interactions are found in the 1,2- as compared with the 1,4-addition product. This accounts for the marked preference for 1,4-addition observed experimentally. With 2,3-dimethylenecyclo-[2,2,1]heptane, just as Cristol and Nagpal³ found for 1,2-dimethylenecyclohexane, virtually exclusive 1,4-addition occurs. In both examples the relative stability of the two possible product olefins and steric factors combine to make 1,4-addition very much favoured over 1,2-addition and accounts for chain transfer taking place at the primary rather than the tertiary radical component of the allylic radical. Thus, our results on cyclic and semi-cyclic *cis*-dienes are consistent with the basic principles laid down by Oswald¹ based on his experiments with open-chain dienes. Thus, to predict the ratio of 1,2- to 1,4-addition the thermodynamic stability of resultant products and steric factors in the chain-transfer step leading to their formation must be taken into account.

The rate of reaction of a thiol with a diene should depend on (a) steric factors, and (b) comparative stability of attacking thiyl radical and intermediate allylic radical. Measurement of absolute rates would be very difficult owing to the very fast reaction, and thus relative rates were obtained by mixing a standard olefin (oct-1-ene or norbornene)

and a diene with thiophenol (sufficient for <50% reaction), and estimating by gas-liquid chromatography the amount of olefin and diene remaining after reaction had proceeded for 1 hr. Choice of standard olefin was governed by ease of gas-chromatographic separation of standard olefin and diene, and also the magnitude of their difference in reactivity. In the addition of an aromatic thiol to an olefin A an initiator [Init.] starts the reaction, which then proceeds as follows:



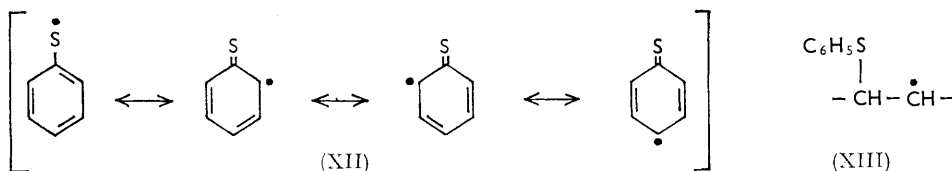
Similarly for the diene B:



In a reaction where an olefin A and a diene B compete for an aromatic thiol, if $[A_0]$ and $[A]$, and $[B_0]$ and $[B]$, are the initial and final concentrations, respectively, of olefin and diene, then

$$\log([A_0]/[A])/\log([B_0]/[B]) = k_A/k_B$$

provided $k_A \ll k_X$ and $k_B \ll k_Y$, *i.e.*, the rate-controlling step must be the addition of thiyl radical to olefin or diene and not chain transfer between intermediate radical and thiol. The aromatic thiyl radical is resonance-stabilised as shown in the scheme (XII) to a greater extent than the intermediate radicals (XIII) and (VI) formed when it reacts with an olefin



and a diene, and thus attack of the aromatic thiyl radical on olefin or diene should be the rate-controlling step. The results of our experiments are given in Table 3 and should be considered as approximate, since the large amount of heat generated in the very fast reaction makes adequate control of temperature impossible.

TABLE 3
Relative rate ratios for the reaction of *cis*-dienes with thiophenol

Olefin or diene	Determined rate ratios		Rate ratios calculated rel. to oct-1-ene
	Rel. to oct-1-ene	Rel. to bicyclo[2,2,1]hept-2-ene	
Oct-1-ene	1.0		1.0
Cyclo-octa-1,3-diene	2.9		2.9
Bicyclo[2,2,1]hept-2-ene	97	1.0	97
Cyclopentadiene		2.04	198
Cyclohexa-1,3-diene		26	2520
2,3-Dimethylenebicyclo[2,2,1]heptane		31.7	3078

Since the intermediate radical (XIII) formed by reaction of a thiyl radical with a simple olefin like oct-1-ene is less stable than the allylic radical (VI) formed by reaction with a diene, the energy barrier for formation of radical (XIII) will be greater than for formation of radical (VI). Thus, an increased reactivity of dienes over simple olefins like oct-1-ene is to be expected. Among the *cis*-dienes themselves a tremendous difference in reactivity was observed. *cis*-Cyclo-octa-1,3-diene is the least reactive and models indicate that in the conformation for minimal non-bonded interactions the diene system is not planar and

consequently conjugation in the ground state of the molecule is less efficient than in a planar diene system. Thus, the thiol radical is attacking a system in some respects similar to one having isolated double bonds. For ready resonance-stabilisation of the intermediate allylic radical, coplanarity of the allylic system is required, but as this sets up increasing strain and non-bonded interactions the stability of the intermediate allylic radical is reduced. This latter factor is largely responsible for a high energy barrier to formation of the allylic radical. Cyclopentadiene is very much more reactive than cyclo-octa-1,3-diene, which may be accounted for by the planarity and hence ready resonance-stabilisation of the intermediate allylic radical which lowers the energy barrier to formation of the allylic radical leading to an increased rate of reaction. In cyclohexa-1,3-diene this factor applies even more strongly, since the diene system and intermediate allylic radical are less strained in a six-membered than in a five-membered ring system. This further lowers the energy barrier to formation of the intermediate allylic radical and accounts for cyclohexa-1,3-diene being 13 times more reactive than cyclopentadiene.

2,3-Dimethylenebicyclo[2,2,1]heptane is also very reactive, and this may be due in part to efficient resonance-stabilisation of the intermediate allylic radical (IX) which has a tertiary radical canonical structure (IXA). However, since bicyclo[2,2,1]hept-2-ene is very reactive for an olefin, part of the high reactivity of this diene may be due to properties inherent in this strained bridged polycyclic system.

The relative reactivities of cyclopentadiene and cyclohexadiene compared with oct-1-ene and bicyclo[2,2,1]hept-2-ene towards reaction with trichloromethyl radicals were measured by Kharasch and Friedlander⁴ and are given in Table 4.

TABLE 4
Relative reactivities of various olefins and dienes towards reaction with free trichloromethyl radicals⁴

Unsatd. compound	Rate relative to oct-1-ene	Unsatd. compound	Rate relative to oct-1-ene
Oct-1-ene	1.0	Cyclopentadiene	4.5
Bicyclo[2,2,1]hept-2-ene	4.2	Cyclohexa-1,3-diene	4.0

Trichloromethyl radicals are very bulky, which renders attack on an unsaturated system difficult on steric grounds. This steric hindrance to attack will vary little between olefins and dienes and will be an important contributor to the energy barrier to formation of the intermediate allylic radical. In our results in which steric hindrance to attack is much reduced, the relative stabilities of reacting diene and intermediate allylic radical will be the major factors determining the energy barrier for formation of the intermediate allylic radical, and hence our results give a better representation of the relative reactivities towards free-radical attack.

EXPERIMENTAL

Nuclear magnetic resonance spectra were obtained on a Perkin-Elmer R10 instrument operating at 60 Mc./sec.

Dienes and Olefins.—Cyclopentadiene was prepared by cracking dicyclopentadiene at 160° and collecting the distillate, b. p. 45°, in a cooled receiver; cyclohexa-1,3-diene was prepared by the method of Hammond and Warkentin;⁵ cyclo-octa-1,3-diene was a gift from the Columbian Carbon Company; 2,3-dimethylenebicyclo[2,2,1]heptane was prepared by the method of Bowe, Miller, Rose, and Wood.⁶ Bicyclo[2,2,1]hept-2-ene (Aldrich) and oct-1-ene (L. Light & Co.) were purified by distillation prior to use.

Addition Reactions of Dienes.—Equimolar amounts of diene and thiol were mixed at room temperature when an exothermic reaction rapidly ensued. After 1 hr., when considerable reaction had occurred, the product was distilled under high vacuum. The reaction is not

⁴ M. S. Kharasch and H. N. Friedlander, *J. Org. Chem.*, 1949, **14**, 239.

⁵ G. S. Hammond and J. Warkentin, *J. Amer. Chem. Soc.*, 1961, **83**, 2554.

⁶ M. A. P. Bowe, R. G. J. Miller, J. B. Rose, and D. G. M. Wood, *J.*, 1960, 1541.

reversible and products are not interconverted under these conditions, and when 3-*p*-thiocresylcyclohex-1-ene was mixed with sufficient *p*-thiocresol for 50% reaction, after 1 hr. unchanged 3-*p*-thiocresylcyclohex-1-ene was recovered, and no 4-*p*-thiocresylcyclohex-1-ene was detected. The properties of the products are given in Table 5.

TABLE 5
Properties of 1:1 addition products of a diene and an aromatic thiol

Diene	Thiol	Re-action time (hr.)	B. p./mm. of 1:1 adduct mixture	Yield of mixture (%)	Ref. index	Formula	Analysis			
							Found (%)		Reqd. (%)	
						C	H	C	H	
(i)	Thiophenol	1	78°/0.4	32	n_D^{23} 1.5880	C ₁₁ H ₁₂ S	74.7	7.1	74.9	6.85
(i)	<i>p</i> -Thiocresol	1	88—90°/0.4	41	n_D^{20} 1.5800	C ₁₂ H ₁₄ S	76.3	7.65	75.75	7.4
(ii)	Thiophenol	1	93°/0.65	80	n_D^{17} 1.5904	C ₁₂ H ₁₄ S	75.6	7.25	75.75	7.4
(ii)	<i>p</i> -Thiocresol	1	107°/0.5	71.5	$n_D^{17.5}$ 1.5810	C ₁₃ H ₁₆ S	76.35	7.7	76.45	7.9
(iii)	Thiophenol	1	118°/0.6	23	n_D^{25} 1.5809	C ₁₄ H ₁₈ S	77.25	8.0	77.05	8.3
(iii)	<i>p</i> -Thiocresol	1	128°/0.7	23	n_D^9 1.5819	C ₁₅ H ₂₀ S	77.6	8.85	77.5	8.7
(iv)	<i>p</i> -Thiocresol	1	147—150°/2.2	74	n_D^{18} 1.5732	C ₁₆ H ₂₀ S	78.6	8.35	78.65	8.25

3-*p*-Thiocresylcyclohex-1-ene was prepared by the method of Bardwell and Kern⁷ from 3-bromocyclohex-1-ene⁸ and sodium *p*-thiocresoxide.

Free-radical Nature of the Reactions.—In the addition of aromatic thiols to the *cis*-dienes under investigation, catalytic quantities of peroxides accelerated the rate of reaction, but had no effect on the nature and proportions of the products formed.

Competitive Reactions.—The standard olefins and dienes employed were freshly distilled prior to use. Approximately equimolar quantities of standard olefin and diene were used, the exact quantities being estimated by gas-liquid chromatography using a Griffin Density

TABLE 6
Initial and final concentration of diene and standard olefin

Standard olefin and diene pairs	*[A ₀] or [B ₀]	[A] or [B]	log $\frac{[A_0]}{[A]}$ or log $\frac{[B_0]}{[B]}$	$\frac{k_A}{k_B}$
Cyclo-octa-1,3-diene	1.3180	1.1568	0.0566	} 2.84
Oct-1-ene	0.8526	0.8143	0.0199	
Bicyclo[2,2,1]hept-2-ene	1.2280	0.1572	0.8927	} 97.0
Oct-1-ene	1.0500	1.028	0.0092	
Cyclo-octa-1,3-diene	1.1022	1.0840	0.0112	} 32.9
Bicyclo[2,2,1]hept-2-ene	1.4958	0.6418	0.3676	
Cyclopentadiene	0.6661	0.3684	0.2572	} 2.04
Bicyclo[2,2,1]hept-2-ene	1.2280	0.9178	0.1262	
2,3-Dimethylenebicyclo[2,2,1]heptane ...	2.2740	0.3496	0.8133	} 31.7
Bicyclo[2,2,1]hept-2-ene	1.7122	1.6135	0.0257	
Cyclohexa-1,3-diene	0.6007	0.3992	0.1775	} 26.0
Bicyclo[2,2,1]hept-2-ene	0.9069	0.8928	0.0068	

* Concentrations relative to marker 1.0000.

Balance and a 2-m. column at 100° packed with 30% 2-ethylhexyl sebacate on Celite (80—100 mesh), and thiophenol added (sufficient for less than 50% reaction). After 1 hr. the standard olefin and diene concentrations were again estimated by gas-liquid chromatography. Table 6 reports the measurements made.

We thank Professor D. H. Hey, F.R.S. and Dr. C. W. Rees for their help and interest, and Columbian Carbide Company for a gift of cyclo-octa-1,3-diene. One of us (J. A. C.) thanks the D.S.I.R. for the award of a Maintenance Grant.

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⁷ F. G. Bardwell and R. J. Kern, *J. Amer. Chem. Soc.*, 1955, **77**, 1141.

⁸ K. Ziegler, A. Späth, E. Schaaf, W. Schumann, and E. Winkelmann, *Annalen*, 1942, **551**, 80.