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The Radical Addition and Telomerisation of Conjugated Dienes

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Reactions are reviewed involving the radical addition and telomerisation of conjugated dienes with halogeno-derivatives of aliphatic hydrocarbons, thiols, sulphonyl chlorides, stannanes, t-butyl hypochlorite, chlorine, and hydrogen bromide. The mechanisms are examined of reactions occurring under the influence of the usual radical-generating initiators, and also of redox systems based on salts of metals of variable valency, peculiarities of the reaction of the growing chain in the allyl radical caused by its low reactivity. A considerable part of the paper deals with problems of the structural and steric isomerism of the addition products, the kinetics of the reactions under consideration, and the reactions of several analogues of conjugated dienes. A list of 86 references is included.

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I. INTRODUCTION

An unsaturated isoprenoid chain with regularly arranged methyl groups constitutes the basis of the structure of very important naturally occurring compounds, such as the carotenoids, vitamin A, the terpenes, natural rubber, side-chains of ubiquinones, and vitamins K and E. Its cyclisation yields cyclic mono-, di-, and tri-terpenes, and also their structural analogues, on which the structure of the steroid hormones, steroidal alkaloids, and several other natural compounds is based.

Considerable progress has been made during recent years in studying the biogenesis of natural isoprenoids, in identifying the intermediate compounds which form building blocks in their biosynthesis. However, much still remains obscure in understanding the processes of formation of unsaturated isoprenoid chains with their rigorous steric and structural specificity[1].

The reactions of the radical addition and telomerisation of conjugated dienes, leading to isoprenoids or their close analogues, have several specific features. The low activity and hence great selectivity of the growing allyl radical, the structural and steric isomerism of the telomers are of interest for the theory of free-radical reactions. Furthermore, investigations on the free-radical isomerisation and cyclisation of unsaturated compounds, in particular telomers of conjugated dienes, may open up a route to the synthesis of cyclic analogues of natural compounds.

The present review may be of interest to research workers concerned with the chemistry of free-radicals and to those dealing with the synthesis of natural compounds.

II. MECHANISM OF RADICAL REACTIONS OF CONJUGATED DIENES

In 1936 Kharasch et al.[2] discovered that peroxides influence the relative proportions of the isomeric bromobutenes formed by the reaction of buta-1,3-diene with hydrogen bromide. They therefore suggested a free-radical mechanism for the formation of the 1,4-isomer, which has since been confirmed many times. In the case of radical reactions of conjugated dienes the Kharasch mechanism can be represented by the general scheme

$$AX + R_i\cdot \rightarrow A\cdot + R_iX \quad \text{initiation} \qquad (1)$$

or

$$AX \xrightarrow{h\nu} A\cdot + X\cdot$$

$$\left.\begin{array}{l} A\cdot + \text{Diene} \rightarrow A(\text{Tel})\cdot \\ A(\text{Tel})\cdot + (n-1)\ \text{Diene} \rightarrow A(\text{Tel})_n\cdot \end{array}\right\} \text{chain growth} \qquad (2a),\ (2b)$$

$$A(\text{Tel})_n\cdot + AX \rightarrow A(\text{Tel})_nX + A\cdot \quad \text{chain transfer} \qquad (3)$$

$$\left.\begin{array}{l} 2A\cdot \rightarrow \text{Products} \\ A(\text{Tel})_n\cdot + A(\text{Tel})_m\cdot \rightarrow \text{Products} \end{array}\right\} \text{chain termination} \qquad (4)$$

Here R_i is an initiator radical, AX a molecule of the compound (telogen) which adds to the diene. Addition of more than one diene molecule to the telogen radical A· leads to formation of a telomeric radical $A(Tel)_n$. and then to telomeric products $A(Tel)_nX$.

A fundamental difference between this mechanism and the mechanism of radical telomerisation of alkenes and unconjugated dienes is that in the present case the telomeric radical is allyl, which is relatively unreactive. Therefore the dissociation energy of the A–X bond and the

heat of reaction of the chain transfer (3) play a decisive part in effecting a chain mechanism. If the dissociation energy D(A–X) is relatively high, and the heat of reaction ΔH of stage (3) negative, reaction becomes impossible (at ordinary temperatures) owing to the low activity of the radical $A(Tel)_n^{\cdot}$.

Table 1 gives tentative values of D(A–X) and ΔH for the reactions of dienes $CH_2:CRCH:CH_2$ (R = H, CH_3) with several halogenated compounds. Since in this case addition should take place mainly at the 1,4-positions (Table 2), it was assumed in the calculations that

$$D\,(ACH_2CR{=}CHCH_2{-}X) \approx D\,(CH_2{=}CHCH_2{-}X).$$

In conformity with these calculations, investigation of the reactions of isoprene with the compounds listed in Table 1 has shown[4] that, in the presence of benzoyl peroxide or azoisobutyronitrile in glass ampoules, or also on ultraviolet irradiation at 20–100°C, only bromotrichloromethane reacts, the chain-transfer stage being least endothermic (almost thermoneutral) for this compound.

Table 1. Energy of dissociation of bonds D(A–X) and heat of reaction of chain transfer ΔH for the addition of halogenated alkanes to conjugated dienes.

A–X	D(A–X)(Ref.3), kcal mole^{-1}	$D(ACH_2CR:CHCH_2{-}X)$ (Ref.3), kcal mole^{-1}	ΔH, kcal mole^{-1}
CCl_3—Br	49,5±3	47,5±2	−2±3
CCl_3—Cl	67	60,4±3	−7±3
C_2H_5—I	51	34,1±1,5	−17±1,5
CCl_3—H	90±3	77	13±2

An important variation of the Kharasch mechanism is the scheme of radical telomerisation of dienes initiated by redox systems based on salts of metals of variable valency. In this case the metal salts are involved in the stages not only of initiation but also of chain transfer. For example, carbon tetrachloride reacts readily with buta-1,3-diene[5,6] and isoprene[4] if the iron(III) chloride–diethylamine hydrochloride-benzoin system is used as initiator. It is supposed[6] that initiation and chain transfer take place by means of the following reactions (with butadiene):

$$FeCl_2 + CCl_4 \rightleftarrows FeCl_3 + CCl_3\cdot \qquad (5)$$

$$CCl_3(C_4H_6)_n\cdot + FeCl_3 \rightleftarrows CCl_3(C_4H_6)_nCl + FeCl_2\,. \qquad (6)$$

Both reactions are probably reversible. Since $D(FeCl_2{-}Cl)$ = 50 kcal mole^{-1},[3] the heat of reaction (6) is $\Delta H \simeq +10$ kcal mole^{-1}: i.e. iron(III) chloride is a considerably more effective chain carrier than is carbon tetrachloride.

Another possible explanation of the action of redox systems is that the solvents used for homogenising the reaction mixture with redox initiation probably also take part in the reaction. Very reactive intermediate compounds ("mediators") can then be formed, which are efficient chain carriers. This mechanism was suggested[7] for the initiation by iron salts of the telomerisation of ethylene with carbon tetrachloride in propan-2-ol, it being assumed that the mediator is the chlorocarbinol $(CH_3)_2CCl(OH)$.

III. REACTIONS INVOLVING FISSION OF C–X BONDS (X = H, Hal) IN THE TELOGEN MOLECULE

In contrast to unconjugated dienes and alkenes, conjugated dienes react with great difficulty by a free-radical mechanism with compounds where chain transfer involves the C–X bond (X = H, Hal). This is explained by the relatively high dissociation energies of the bonds and the low activity of the telomeric allyl radical. The most detailed study has been made of the reactions of bromotrichloromethane, which reacts readily with buta-1,3-diene[8–12,14], isoprene[4,13], 2,3-dimethylbuta-1,3-diene[13], 2-t-butylbuta-1,3-diene[15,16], 1,1,3-trifluorobuta-1,3-diene[17], cyclopentadiene[18], and cyclohexa-1,3-diene[18]. Peroxides and exposure to visible light, ultraviolet radiation, X-rays, and γ-rays have been used to initiate these reactions. Thermal initiation is also possible. The main reaction product was the telomer $CCl_3(Tel)Br$ (n_1) with a chain length $n = 1$. In several cases products of high molecular weight were formed[9,11–13], the content of these compounds increasing with the duration of the reaction. This suggests that the telomer n_1 reacts in stages:

$$CCl_3(Tel)\,Br + CCl_3\cdot \rightarrow CCl_3Br + CCl_3(Tel)\cdot \qquad (7)$$

$$CCl_3(Tel)\cdot + Diene \rightarrow CCl_3(Tel)_2\cdot \xrightarrow{CCl_3Br} CCl_3(Tel)_2Br + CCl_3\cdot \qquad (8)$$

not in conformity with Eqn. (2b).

Isoprene reacts similarly with carbon tetrabromide (under the influence of γ-rays[19]), and butadiene with ethyl tribromoacetate (on ultraviolet irradiation[20]), with pentadecafluoro-1-iodoheptane (in the presence of azoisobutyronitrile[21] and on heating[22]), and with carbon tetrabromide (in the presence of potassium peroxodisulphate[23]). The addition of trichloroiodomethane to perfluorobutadiene under the influence of ultraviolet radiation has been described in the patent literature[24,25]. The reactivity of these telogens is close to that of bromotrichloromethane.

Telomerisation of carbon tetrachloride with buta-1,3-diene[26,27] and piperylene[27] in the presence of benzoyl peroxide, and that of chloroform with butadiene[29] in the presence of acetyl peroxide, have also been reported. The reactions with carbon tetrachloride were conducted only in steel autoclaves[26]. As mentioned in Section II, the allyl radical is unable to react at ordinary temperature with the C–Cl bond in carbon tetrachloride. The above results[26,27] therefore, are probably explained by the presence in the steel autoclaves of catalytic quantities of iron salts, which form redox initiator systems.

In the reaction of butadiene with chloroform[28] a large amount of initiator was used (molar ratio of acetyl peroxide to butadiene 1 : 2). The authors state that only the telomer n_2 was obtained, isomeric composition (45% 1,4-1,4-, 45% 1,2-1,2-, and 10% 1,4-1,2-isomers) being inconsistent with a radical reaction mechanism. Perhaps a side-reaction involving acetyl peroxide took place in this case.

An American patent[29] has described the reaction between chloroform and perfluorobutadiene in the presence of trichloroacetyl peroxide, but the structure of the reaction products was not determined.

The use of redox systems based on salts of metals of variable valency has recently enabled addition and telomerisation reactions to be accomplished between conjugated dienes and unreactive telogens. It has already been mentioned that carbon tetrachloride reacts with buta-1,3-diene[5,6] and isoprene[4] at 100–140°C under the influence of redox systems based on iron and copper salts. In the reaction with butadiene the telomer n_2 was isolated[6] as

Table 2. Content of isomers in products of addition (n_1) to conjugated dienes.

Telogen	R^a	Reaction temp., °C	Initiator	Telogen radical	Content of isomers in n_1, %			Ref.
					1,4-	4,1-	1,2-	
1	2	3	4	5	6	7	8	9
1. Reactions with butadiene $CH_2^1=CH^2-CH^3=CH_2^4$								
CCl_3Br	4	50—60	uv[b]	$CCl_3\cdot$	75±10		25±10	8
CCl_3Br	1	20	X-rays	$CCl_3\cdot$	96.3 (*trans*)			12
$C_2H_5OCOCBr_3$	4	20	uv	$C_2H_5OCOCBr_2\cdot$	≈100 (*trans*)			20
$(CH_3)_2SnH_2$	1	25—50	uv	$(CH_3)_2HSn\cdot$	≈100 (*trans*)			39
$(C_2H_5)_2SnH$	0.5	40—70	ABN[c]	$(C_2H_5)_2Sn\cdot$	78±80 (*trans*)		20—22	41
(iso-$C_4H_9)_2SnHCl$	0.5	40—70	ABN	(iso-$C_4H_9)_2ClSn\cdot$	80—84 (*trans*)		16—20	41
$(C_4H_9)_2NCl$		—5—+15	d	$(C_4H_9)_2\overset{+}{N}H\cdot$	≈100 (*trans*)			45
CH_3SH	1	20	uv	$CH_3S\cdot$	96 (*trans*)		3	52
C_2H_5SH	1	20	uv	$C_2H_5S\cdot$	90 (*trans*)		4	52
C_2H_5SH	1	70	ABN	$C_2H_5S\cdot$	99 (80% *trans*, 20% *cis*)		1[e]	53
C_6H_5SH	1	20	uv	$C_6H_5S\cdot$	99 (*trans*)		1	52
CH_3COSH	1	20	uv	$CH_3COS\cdot$	98 (*trans*)		2	52
SF_3Cl	2.6	100	—				≈45	64,65
$(CH_3)_3COCl$		0	visible light	$(CH_3)_3CO\cdot$	74 (*trans*)		26	48
Cl_2		—9	uv	$Cl\cdot$	77[f] (*trans*)		23	69
HBr		—12	BP[g] ascaridole	$Br\cdot$	77±81		19—23[h]	2
$(C_5H_{11}COO)_2^i$ $Cu(OCOCH_3)_2$		26—50	—	$CH_3(CH_2)_4\cdot$	10—12 (*trans*)		88—90	70
$(CH_2=CHCH_2CH_2COO)_2$ $Cu(OCOCH_3)_2$		57	—	$CH_2=CHCH_2CH_2\cdot$	14 (*trans*)		86	70
 =O, H_2O_2 CH_3OH, $CuSO_4$		0	—	$CH_3OOC(CH_2)_5\cdot$	23,2 (*trans*)		76,8	71
(cyclo-$C_6H_7COO)_2$ $Cu(OCOCH_3)_2$		26	—	(cyclo-$C_6H_7\cdot$	11 (*trans*)		89	70
$(CH_3)_2COOH$ $FeCl_3$, $CuCl_2$		0	—	$(CH_3)_2CO\cdot$	65 (*trans*)		35	48
$(CH_3)_3COOCOCH_3$ $Cu(OCOCH_3)_2$		0	—	$(CH_3)_3CO\cdot$	18—27 (*trans*)		73—82	48
CH_3COOK (electrolysis)		20	—	$CH_3\cdot$	≈78[k] (*trans*)		≈22	72
2. Reactions with isoprene $CH_2^1=C^2(CH_3)-CH^3=CH_2^4$								
CCl_3Br	1.3	25—40	X-rays	$CCl_3\cdot$	71.9	26.1	0.5—1.5[l]	13
$(C_2H_5)_2SnH$	0.5	65—70	ABN	$(C_2H_5)_2Sn\cdot$		81—82(?)[m]		41
$(C_4H_9)_2SnHCl$	0.5	40—70	ABN	$(C_4H_9)_2SnCl\cdot$		67—68 (?)		41
(iso-$C_4H_9)_2SnHCl$	0.5	40—70	ABN	(iso-$C_4H_9)_2SnCl\cdot$		76—77(?)		41
CH_3SH	1	20	uv	$CH_3S\cdot$	76	22		52
C_2H_5SH	1	20	uv	$C_2H_5S\cdot$	75	25		52
C_6H_5SH	1	20	uv	$C_6H_5S\cdot$	97.5	2.5		52
CH_3COSH	1	20	uv	$CH_3COS\cdot$	89	10		52
 =O, H_2O_2[i] CH_3OH, $CuSO_4$		0	—	$CH_3OOC(CH_2)_5\cdot$	17.5		82.5	71
$(CH_3)_2COOCOC_6H_5$ CuBr		60—70	—	$(CH_3)_2CO\cdot$	n			48
CH_3COOK (electrolysis)		20	—	$CH_3\cdot$	o			72
3. Reactions with *trans*-piperylene $CH_3^1-CH^2=CH^3-CH^4=CH_2$								
CH_3SH (75% conversion)	0.5	25	uv	$CH_3S\cdot$	49.5 (*trans*-) 4.4 (*cis*)	17.1	27.1 (*trans*-) 1.9 (*cis*)	60
CH_3SH (90% conversion)	0.5	25	uv	$CH_3S\cdot$	48.8 (*trans*-) 4.9 (*cis*)	14.6	29.3 (*trans*-) 2.4 (*cis*)	60
C_6H_5SH	0.5	25	uv	$C_6H_5S\cdot$	36.9 (*trans*-) 3.4 (*cis*)	6.2	51.4 (*trans*-) 2.1 (*cis*)	60

Table 2 (cont'd).

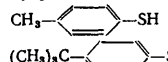
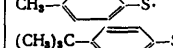
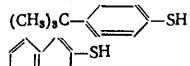
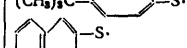
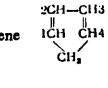
Telogen	R^a	Reaction temp., °C	Initiator	Telogen radical	Content of isomers in n_1, %			Ref.
					1,4-	4,1-	1,2	
1	2	3	4	5	6	7	8	9
4. Reactions with *cis*-piperylene $CH_2^1=CH\overset{3}{CH}=\overset{4}{CH}CH_3^2$								
CH_3SH (81% conversion)	0.5	25	uv	$CH_3S\cdot$	58.4 (*trans*-) 1.6 (*cis*)	21,1	5.9 (*trans*-) 13.0 (*cis*)	0
CH_3SH (96% conversion)	0.5	25	uv	$CH_3S\cdot$	47.8 (*trans*-) 3.2 (*cis*)	21,6	13.4 (*trans*-) 14.0 (*cis*)	60
C_6H_5SH	0.5	25	uv	$C_6H_5S\cdot$	56.8 (*trans*-) 0.0 (*cis*)	4,3	3.2 (*trans*-) 29.5 (*cis*)	60
$(C_2H_5)_3SnH^p$	0.5	40—70	ABN	$(C_2H_5)_3Sn\cdot$	60—66		34—40	41
(cyclo- $C_6H_{11})_3SnH$	0.5	40—70	ABN	(cyclo-$C_6H_{11})_3Sn\cdot$	53—55		45—47	41
$(C_6H_5)_3SnH$	0.5	40—70	ABN	$(C_6H_5)_3Sn\cdot$	40—45		55—60	41
$(C_4H_9)_3SnHCl$	0.5	40—70	ABN	$(C_4H_9)_3SnCl\cdot$	55—57		43—45	41
(iso- $C_4H_9)_3SnHCl$	0.5	40—70	ABN	(iso- $C_4H_9)_3SnCl\cdot$	56—57		43—44	41
5. Reactions with 2,3-dimethylbuta-1,3-diene $CH_2^1=C(CH_3)^2C(CH_3)^3=CH_2^4$								
CCl_3Br	1	25—40	X-Rays	$CCl_3\cdot$	≈100			13
$(C_2H_5)_3SnH$	0.5	40—70	ABN	$(C_2H_5)_3Sn\cdot$	66—70		30—34	41
$(C_4H_9)_3SnH$	0.5	40—70	ABN	$(C_4H_9)_3Sn\cdot$	68—72		28—32	41
(iso- $C_4H_9)_3SnH$	0.5	40—70	ABN	(iso- $C_4H_9)_3Sn\cdot$	81—83		17—19	41
(cyclo-$C_6H_{11})_3SnH$	0.5	40—70	ABN	(cyclo- $C_6H_{11})_3Sn\cdot$	68—70		30—32	41
$(C_6H_5)_3SnH$	0.5	40—70	ABN	$(C_6H_5)_3Sn\cdot$	>90		<10	41
$(C_4H_9)_2SnHCl$	0.5	40—70	ABN	$(C_4H_9)_2SnCl\cdot$	62—63		37—38	41
(iso- $C_4H_9)_2SnHCl$	0.5	40—70	ABN	(iso-$C_4H_9)_2SnCl\cdot$	72—73		27—28	41
$(C_4H_9)_2SnH_2$	0.5	40—70	ABN	$(C_4H_9)_2SnH\cdot$	69—71		29—31	41
CH_3SH	1	20	uv	$CH_3S\cdot$	97		2.5	52
C_2H_5SH	1	20	uv	$C_2H_5S\cdot$	96		3	52
C_6H_5SH	1	20	uv	$C_6H_5S\cdot$	98		1	25
CH_3COSH	1	20	—	$CH_3COS\cdot$	99		1	52
	1	20	—		99			52
6. Reactions with 2,4-dimethylhexa-2,4-diene $(CH_3)_2C^1=C^2H\overset{3}{C}H=C^4(CH_3)_2$								
CH_3SH	1	20	uv	$CH_3S\cdot$	25 (*trans*-)		75	61
C_2H_5SH	1	20	uv	$C_2H_5S\cdot$	32 (*trans*-)		68	61
C_6H_5SH	1	95	—	$C_6H_5S\cdot$	24 (*trans*-)		76	61
	1	95	—		16 (*trans*-)		84	61
	1	95	—		15 (*trans*-)		85	61
	1	95	—		8 (*trans*-)		92	61
7. Reactions with 2-t-butylbuta-1,3-diene $CH_2^1=\overset{2}{C}(C(CH_3)_3)-\overset{3}{CH}=\overset{4}{CH_2}$								
CCl_3Br	2	56	visible light	$CCl_3\cdot$	50	50		16
C_6H_5SH	2	56	ditto	$C_6H_5S\cdot$	≈100			16
8. Reactions with 2-chlorobuta-1,3-diene $CH_2^1=\overset{2}{C}Cl\overset{3}{C}H=\overset{4}{CH_2}$								
CH_3SH	1	20	uv	$CH_3S\cdot$	75	25		52
C_2H_5SH	1	20	uv	$C_2H_5S\cdot$	72	28		52
C_6H_5SH	1	20	uv	$C_6H_5S\cdot$	95	5		52
CH_3COSH	1	20	uv	$CH_3COS\cdot$	86	13		52
9. Reactions with 1,1,2-trifluorobuta-1,3-diene $\overset{1}{C}F_2=\overset{2}{C}F\overset{3}{C}H=\overset{4}{C}H_2$								
CCl_3Br	5	20	visible light	$CCl_3\cdot$	≈100			17
10. Reactions with cyclopentadiene 								
$(C_2H_5)_3SnH$	0.5	40—70	ABN	$(C_2H_5)_3Sn\cdot$	84—89		11—16	41
$(C_6H_5)_3SnH$	0.5	40—70	ABN	$(C_6H_5)_3Sn\cdot$	>90		<10	41
$(C_4H_9)_2SnHCl$	0.5	40—70	ABN	$(C_4H_9)_2SnCl\cdot$	94—96		4—6	41
(iso- $C_4H_9)_2SnHCl$	0.5	40—70	ABN	(iso- $C_4H_9)_2SnCl\cdot$	93—95		5—7	41
C_6H_5SH	1	20	—	$C_6H_5S\cdot$	58		42	41
	1	20	—		56		44	41

Table 2 (cont'd).

Telogen	R^a	Reaction temp., °C	Initiator	Telogen radical	Content of isomers in n_1, %			Ref.
					1,4-	4,1-	1,2-	
1	2	3	4	5	6	7	8	9
11. Reactions with cyclohexa-1,3-diene								
$(C_6H_5)_3SnH$	0,5	40—70	ABN	$(C_6H_5)_3Sn\cdot$	39—42		58—61	41
C_6H_5SH	1	20	—	$C_6H_5S\cdot$	57		43	61
HS—C$_6$H$_4$—SH	1	20	—	HS—C$_6$H$_4$—S·	56		44	62
12. Reactions with cyclo-octa-1,3-diene								
C_6H_5SH	1	20	—	$C_6H_5\cdot$	85		15	62
HS—C$_6$H$_4$—SH	1	20	—	HS—C$_6$H$_4$—S·	83		17	62
13. Reactions with 1,2-dimethylenecyclohexane								
H_3C—C$_6$H$_4$—SH	1	70—100	—	H_3C—C$_6$H$_4$—S·	≈100			63
14. Reactions with 3-methylenecyclohexene								
H_3C—C$_6$H$_4$—SH	1	70—100	—	H_3C—C$_6$H$_4$—S·	≈100			63
15. Reactions with 2,3-dimethylenebicyclo[2,2,1]heptane								
HS—C$_6$H$_4$—SH	1	20	—	HS—C$_6$H$_4$—S·	98		2	63

[a] Initial telogen : diene molar ratio.
[b] uv = ultraviolet irradiation.
[c] ABN = azoisobutyronitrile.
[d] Reaction conducted in strongly acid medium (H_2SO_4).
[e] 2,1-Isomer, $CH_3CH(SC_2H_5)CH:CH_2$.
[f] 1.5% of the *cis*-1,4-isomer may be present.
[g] BP = benzoyl peroxide.
[h] 2,1-Isomer, $CH_3CHBrCH:CH_2$.
[i] Reaction of peroxides with dienes in the presence of iron and copper salts.
[k] Ratio of 1,4- and 1,2-isomers determined from quantity of *trans*-hex-3-ene and 3-methylpent-1-ene formed by recombination of $CH_3C_4H_6^{\cdot}$ and $CH_3^{\cdot}$ radicals.
[l] Unidentified isomers.
[m] In the opinion of the authors the reaction products contain only 4,1- and 4,3-isomers.
[n] 1,2- and 4,3-Isomers.
[o] In the opinion of the authors, the *cis*-1,4-isomer. (See Section VII for the unreliability with which the configuration of addition products to isoprene can be identified.)
[p] Reaction with a mixture of *cis*- and *trans*-piperylene.

well as n_1. Chloroform reacts under similar conditions with butadiene[5,30,31], with the formation mainly of 1,5,5-trichloropent-2-ene:

$$CHCl_3 + CH_2{=}CHCH{=}CH_2 \xrightarrow{(FeCl_3,CuCl_2)} CHCl_2CH_2CH{=}CHCH_2Cl \qquad (9)$$

i.e. chloroform reacts with cleavage of the C–Cl bond. This confirms that chain transfer involves the metal salt ("ligand" transfer) or "carrier"[7], since chain transfer involving chloroform is accompanied predominantly by cleavage of a C–H bond[32].

When solutions of iron(II) chloride in acetonitrile are used, buta-1,3-diene reacts at 90–120°C with mono-, di-, and tri-chloroacetonitrile, allyl chloride, and 1,3-dichloropropene, isoprene with dibromoacetonitrile, chloroprene with but-2-enyl chloride and dichloroacetonitrile, and 2,3-dimethylbuta-1,3-diene with dibromoacetonitrile and trichloroacetonitrile[33]. In all cases the main product of the reaction was the telomer n_1. The reactions were accompanied by cleavage of C–Cl and C–Br bonds in the telogen molecules.

IV. REACTIONS INVOLVING FISSION OF Si–X, Sn–X, N–X, P–X, O–X, S–X, Cl–X, and Br–X BONDS (X = H, Hal) IN THE TELOGEN MOLECULE

1. Compounds of Group IV Elements (other than Carbon)

Trichlorosilane reacts with buta-1,3-diene at 300°C to form 1-trichlorosilylbut-2-ene [34], but in the presence of azo-compounds at 65–115°C readily hydrolysable telomers having $n = 7–8$ are obtained [35]. Trichlorosilane probably reacts similarly with perfluorobutadiene [36]. According to Steele et al. [37] the dissociation energy of the $Cl_3Si–H$ bond is 93 ± 4 kcal mole^{-1}, so that the chain-transfer stage should be strongly endothermic ($\Delta H \simeq -16$ kcal mole^{-1}). It has already been pointed out (Section II) that, with such a value for the heat of reaction of the chain-transfer stage, the addition of organic compounds to conjugated dienes is not very probable. It must be borne in mind, however, that the dissociation energies of bonds in organoelementary compounds have not been determined too reliably (see below). The dissociation energy of the Sn–H bond in organotin hydrides is relatively small (~50 kcal mole^{-1}) [38], and therefore alkyl- and aryl-stannanes (dimethyl-, trimethyl-, triethyl-, tricyclohexyl-, dibutyl-, triphenyl-, and di-isobutyl-stannanes) add easily to buta-1,3-diene [39,41] isoprene [41], piperylene [40,41], 2,3-dimethylbuta-1,3-diene [41], cyclopentadiene [41], and cyclohexa-1,3-diene [41] on heating, on exposure to ultraviolet radiation, and in the presence of azoisobutyronitrile, e.g.

$$(C_2H_5)_3SnH + CH_2{=}CHCH{=}CH_2 \rightarrow (C_2H_5)_3SnC_4H_7\,. \qquad (10)$$

2. Compounds of Group V Elements

It has been reported in the patent literature that the telomerisation of buta-1,3-diene with ammonia can take place under the influence of γ-rays [42]. Telomers of general formula $NH_2[C_4H_6]_nH$ are obtained, where $n = 6, 7$. Since the dissociation energy of the N–H bond in ammonia is 103 kcal mole^{-1}, [43] the heat of reaction of the chain transfer (3) is $\Delta H \simeq -26$ kcal mole^{-1}. Therefore a radical chain reaction mechanism is improbable in this case.

Nitrogen compounds containing reactive N–Hal bonds may be expected to react by a free-radical mechanism. In fact, nitryl chloride NO_2Cl [44] and dialkylchloramines [45] add readily to buta-1,3-diene with cleavage of the C–Cl bond. However, a radical mechanism has been suggested only for the reaction with dialkylchloramines, the radicals being assumed to react in the protonated form (radical-cations). The addition of aliphatic azo-compounds to conjugated dienes undoubtedly occurs by a radical mechanism [46]. For example, azoisobutyronitrile reacts with butadiene at 75°C to form telomers having $n_{av} = 2–5$:

$$NC(CH_3)_2C{-}N{=}N{-}C(CH_3)_2CN \rightarrow 2(CH_3)_2CCN + N_2 \qquad (11)$$

$$2(CH_3)_2\dot{C}CN + nC_4H_6 \rightarrow NC(CH_3)_2C(C_4H_6)_nC(CH_3)_2CN\cdot \qquad (12)$$

The chain-transfer stage (3) is probably absent from this reaction, the telomers being formed by the recombination of growing radicals.

Only one example of the addition of phosphines to conjugated dienes is known: dibutylphosphine reacts with buta-1,3-diene in the presence of azoisobutyronitrile to form the telomers n_1 and n_2. [47]

3. Compounds of Group VI Elements

According to Kochi [48] t-butyl hypochlorite adds to buta-1,3-diene under the influence of ultraviolet radiation:

$$(CH_3)_3COCl + C_4H_6 \rightarrow (CH_3)_3COC_4H_6Cl\,. \qquad (13)$$

This reaction is the sole example of a radical chain addition to conjugated dienes with rupture of the O–X bond in the chain-transfer stage†.

Besides bromotrichloromethane, thiols mostly take part in free-radical addition reactions of dienes. Published values of D(RS–H) are 88 at 75 kcal mole^{-1} for methanethiol and benzenethiol [43]. It can therefore be expected that only thiophenol will react relatively easily, since in this case the heat of reaction of stage (3) is $\Delta H = +2$ kcal mole^{-1}. However, aliphatic thiols, for which $\Delta H \simeq -(10–11)$ kcal mole^{-1}, react quite well with conjugated dienes. It seems to us that the difference in reactivity between thiols and derivatives of aliphatic hydrocarbons (carbon tetrachloride, chloroform, etc.) may be apparent, since the above values of D(S–H) are not very reliable, and according to Refs. 49 and 50, for example, $D(CH_3S–H) = 83.1$ kcal mole^{-1}. Therefore further discussion of the energetics of chain transfer in the reactions of thiols will be possible only after values for the dissociation energies of the bonds involved have been refined.

The reactions of aliphatic thiols, thiophenol, thioacetic acid, β-thionaphthol, etc. have been described with buta-1,3-diene [52–59], isoprene [52,58], piperylene [52,60], 2,3-dimethylbuta-1,3-diene [52], 2-t-butylbuta-1,3-diene [16], 2,5-dimethylhexa-2,4-diene [61], chloroprene [52], cyclopentadiene [62], cyclohexa-1,3-diene [62], cyclo-octa-1,3-diene [62], 2,3-dimethylenebicyclo[2,2,1]heptane [62], 1,2-dimethylenecyclohexane [63], and 3-methylenecyclohexene [63]. Although the formation of telomers of high molecular weight was observed in several cases, the main products of the reaction were adducts of chain length $n = 1$.

In the absence of an initiator, sulphur chloride pentafluoride readily adds to buta-1,3-diene at 100°C: [64,65]

$$SF_5Cl + CH_2{=}CHCH{=}CH_2 \rightarrow SF_5C_4H_6Cl\,. \qquad (14)$$

Similarly, alkane- and arene-sulphonyl chlorides react with conjugated dienes with cleavage of the S–Cl bond. In these compounds, however, the dissociation energy of the bond is probably quite high, and addition occurs only in redox systems based on salts of metals of variable valency. In these reactions, therefore, a "ligand" chain-transfer mechanism involving the metal salt should be operative (Section III), e.g. [66]

$$CH_3SO_2Cl + Cu^{1+} \rightarrow CH_3SO_2\cdot + Cu^{2+}Cl \qquad (15)$$

$$CH_3SO_2\cdot + CH_2{=}CHCH{=}CH_2 \rightarrow CH_3SO_2C_4H_6\cdot \qquad (16a)$$

$$CH_3SO_2C_4H_6\cdot + Cu^{2+}Cl \rightarrow CH_3SO_2C_4H_6Cl + Cu^{1+}. \qquad (16b)$$

With the use of solutions of copper(II) chloride in acetonitrile (with or without the addition of diethylamine hydrochloride) or in dichloromethane at 70–100°C, buta-1,3-diene and isoprene react with benzenesulphonyl, benzene-*m*-disulphonyl, *p*-chlorobenzenesulphonyl, and toluene-*p*-sulphonyl chlorides [66–68].

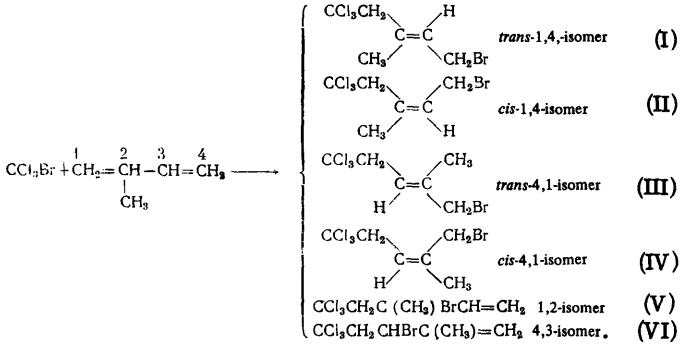
†The addition of peroxides ROOR and hydroperoxides ROOH [48,51] to dienes has a radical chain mechanism. However, instead of the chain transfer (3), the radicals here undergo oxidation by metal salts (Section V).

4. Compounds of Group VII Elements

Although the addition of halogens and hydrogen halides to conjugated dienes is well known, the free-radical character of the reaction has been demonstrated only in a few cases. As already mentioned (Section II), a radical mechanism was first suggested[2] actually for the reaction of hydrogen bromide with butadiene in the presence of peroxides. Even in this case, however, it is not possible to suppress ionic addition completely. In 1966 Poutsma showed[69] that the chlorination of buta-1,3-diene in the dark at −9°C in the absence of oxygen takes place mainly by a free-radical mechanism, although this reaction had previously been regarded as a classical example of electrophilic addition. The radical nature of the reaction was proved by the formation of chlorocyclohexane on the addition to the reaction mixture of cyclohexane, which does not undergo ionic chlorination. In the presence of oxygen—which inhibits the free-radical reaction—the quantity of chlorocyclohexane in the reaction products dropped sharply. On irradiation radical chlorination took place even in solvents. The reaction resulted in the adduct ClC_4H_6Cl, and the formation of higher telomers and tetrachloroalkanes was also noted. A free-radical mechanism is evidently possible also in the reactions of dienes with hydrogen chloride, bromine, and in other similar cases.

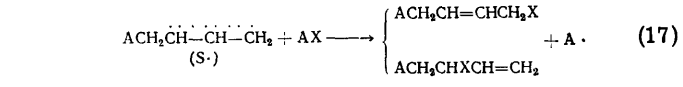
V. STRUCTURAL ISOMERISM OF TELOMERS. COMPETITION BETWEEN 1,2- AND 1,4-ADDITION

Even with the chain length $n = 1$ telomerisation products of conjugated dienes constitute a complicated mixture of both structural isomers and stereoisomers. As example a scheme is given below for formation of the n_1 telomer from bromotrichloromethane and isoprene (an unsymmetrical diene):



The possible reaction products are not exhausted by the six compounds given above, but the remaining compounds (2,1- and 3,4-isomers) are hardly formed at all, since free radicals attack mainly the terminal carbon atoms of the diene molecule. In the case of symmetrical dienes (buta-1,3-diene, 2,3-dimethylbuta-1,3-diene, etc.) the number of isomers diminishes to three (I, II, and V).

From the scheme for the chain-transfer reaction



(17)

which is mainly responsible for the ratio of 1,4- and 1,2-isomers (I and V) produced, it is seen that the relative quantities of these isomers should be determined by the dual reactivity of the allyl radical (S·), and hence should depend on the structure of the diene and the telogen. This radical S· exists predominantly in the form of the secondary radical, which is further stabilised by hyperconjugation of the unpaired electron with the ACH_2 group.

The relative proportions of 1,4- and 1,2-isomers found experimentally are given in Table 2. (It should be noted that reliable quantitative determination of the ratio (I) : (V), and also of other stereoisomers and structural isomers, has become possible only during recent years as a consequence of the development of methods of high-efficiency gas–liquid chromatography and nuclear magnetic resonance spectroscopy. Therefore papers and patents[5,6,10,11,21,22,26,33] which noted the formation only of 1,4-isomers—without the requisite careful analysis—require further checking, and are not included in Table 2.) It is seen from Table 2 that, even in the reactions of the same diene (e.g. buta-1,3-diene, which has been studied in greatest detail), the ratio (I) : (V) varies within wide limits (from ~ 100 : 0 to 10 : 90) depending on the nature of the telogen. This ratio is evidently determined mainly by the rate of reaction (17). The greater the rate of this reaction (i.e. the weaker the A–X bond which is cleaved and the greater the heat of reaction of chain transfer), the more probable is reaction of the more stabilised and consequently less active secondary radical S·, and hence the larger the amount of the 1,2-isomer formed. Thus among the products of reactions for which $\Delta H_{17} \leqslant 0$ (bromotrichloromethane, ethyl tribromoacetate, thiols, dialkylchloramines) the content of the 1,4-isomer is close to 100%, whereas when $\Delta H > 0$ (alkylstannanes, chlorine, and probably t-butyl hypochlorite) it is 75–80%.

Chain transfer is probably accomplished with still greater ease in the catalytic addition of peroxides[48,70]. In these reactions transfer of an electron by scheme (6) i.e. the redox reaction between the free radical and an ion of the metal of variable valency, takes place instead of the "ligand" chain transfer. For example, the following mechanism has been suggested[48] for the addition of acetyl t-butyl peroxide to buta-1, 3-diene in the presence of copper acetate:

$$(CH_3)_3COOCOCH_3 + Cu^{1+} \rightarrow (CH_3)_3CO\cdot + Cu^{2+}OCOCH_3 \quad (18)$$

$$(CH_3)_3CO\cdot + C_4H_6 \rightarrow (CH_3)_3COC_4H_6\cdot \quad (19)$$

$$(CH_3)_3COC_4H_6\cdot + Cu^{2+}OCOCH_3 \rightarrow (CH_3)_3COC_4H_6OCOCH_3 + Cu^{1+}. \quad (20)$$

Although the heat of reaction (20) is unknown, it is probably quite high, since the content of the 1,4-isomer falls to 10–30% (Table 2). "Ligand" chain transfer involving metal salts probably occurs at a lower rate, and therefore, in the addition of t-butyl hydroperoxide to butadiene in the presence of iron and copper halides, the content of the 1,4-isomer in the mixture of reaction products is 65%.[48]

The addition of the electrochemically generated methyl radical to buta-1,3-diene has been reported[72]. The ratio of 1,4- and 1,2-isomers is then 78 : 22, but in this case the ratio may be determined to a considerable extent by adsorption of radicals on the electrode.

The above reactions were conducted at temperatures between −10° and +100°C. Available data do not enable the dependence of the ratio of 1,4- and 1,2-isomers on the reaction temperature to be assessed, although rise in temperature must be expected to increase the content of the 1,2-isomer, which is formed by reaction of the less active secondary radical.

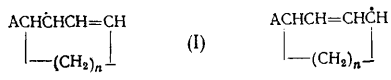
The structure of the diene also can influence the ratio of 1,4- and 1,2-isomers. Addition to isoprene produces an isomeric ratio (1,4 + 4,1) : 1, 2 which is close to the

corresponding ratio with butadiene (Table 2). In the reactions of *cis*- and *trans*-piperylene, both 1,2- and 1,4-isomers are formed from secondary radicals $ACH_2\dot{C}HCH:CHCH_3$ and $ACH_2CH:C\dot{H}CHCH_3$, and therefore products of the reactions of thiols and stannanes with both isomeric piperylenes contain increased amounts of the 1,2-isomers in comparison with the reaction products obtained with buta-1,3-diene[60]. Moreover, the 4,1-isomer is formed, but the 4,3-isomer is absent. This result was to be expected, since the former isomer is produced from a primary radical, and the latter from a secondary radical. The ratio of 1,2- and 1,4-isomers in the reaction products of bromotrichloromethane, stannanes, and thiols with 2,3-dimethylbuta-1,3-diene[13,41,52] and with buta-1,3-diene changes little on passing from one diene to the other.

In the reactions of 2,5-dimethylhexa-2,4-diene[61], however, the 1,2-isomer becomes the main product (68–92% of the total composition of the telomer n_1), since formation of the 1,4-isomer involves the still less active tertiary radical $AC(CH_3)_2CH:C\dot{H}C(CH_3)_2$.

1,2-Isomers are absent among products of the addition of bromotrichloromethane and butanethiol to 2-t-butylbuta-1,3-diene[16].

The addition of a telogen radical to cyclic conjugated dienes yields only secondary radicals (I) and (II)



(I)



(II)

so that in these cases formation of 1,4- and 1,2-isomers should be about equally probable. The quantities of 1,4- and 1,2-isomers found experimentally vary respectively within the limits 40–90% and 10–60% (Table 2). The reaction products obtained from conjugated methylenecycloalkenes (3-methylenecyclohexene, 1,2-dimethylenecyclohexane, 2,3-dimethylenebicyclo[2,2,1]heptane[63]) comprise almost entirely 1,4-isomers, since the radicals leading to 1,2-isomers are tertiary.

VI. STRUCTURAL ISOMERISM OF TELOMERS. COMPETITION BETWEEN 1,4- AND 4,1-ADDITION

Structural 1,4–4,1-isomerism is possible for the products of addition to unsymmetrical dienes, the relative content of the two isomers depending on the nature and position of the substituent in the diene molecule. If the substituent is attached to a quaternary carbon atom, the radical from which the 1,4-isomer is formed is secondary, i.e. more stable. Furthermore, in this case steric hindrance to attack by the free radical on the substituted end of the diene molecule is possible. Both effects tend to prevent formation of 4,1-isomers, and therefore the content of 1,4-isomers in the products from *cis*- and *trans*-piperylenes with thiols[60] exceeds by factors of 3–10 the content of the 4,1-isomers.

The influence of substituents in position 2 of a conjugated diene on the distribution of 1,4- and 4,1-isomers is more complicated. Both radicals ($ACH_2CY:CHCH_2^{\cdot}$ and $ACH_2CH:CYCH_2^{\cdot}$) responsible for formation of the corresponding isomers are primary, and their reactivity can be differentiated only by means of an indirect (polar, resonance, or steric) effect of the substituent Y. Results obtained for additions to isoprene show (Table 2) that the introduction of a methyl group into a diene molecule leads to the formation mainly of 1,4-isomers‡. The predominance of 1,4-isomers in this case is probably explained by greater stabilisation of the radical $ACH_2C(CH_3):CHCH_2^{\cdot}$ than of $ACH_2CH:C(CH_3)CH_2^{\cdot}$, by hyperconjugation of the unpaired electron with the methyl group. The polar effect of the methyl group can probably be neglected. This is seen from the example of the reactions of bromotrichloromethane and thiols with isoprene, 2-t-butylbuta-1,3-diene, and chloroprene: reaction of bromotrichloromethane with isoprene yields 71.9% of the 1,4-isomer and 26.1% of the 4,1-isomer[13], but in the reaction with 2-t-butylbuta-1,3-diene 50% of each isomer is formed[16]. Thus, although the polar effect of the t-butyl group exceeds that of the methyl group (the Taft constant $\sigma^*_{(CH_3)_3C} = -0.300$ [73]), the absence of α-hydrogen atoms makes the group almost incapable of hyperconjugation with the unpaired electron, so that it does not influence the distribution of 1,4- and 4,1-isomers resulting from attack by the trichloromethyl radical. On the other hand, the distribution of 1,4- and 4,1-isomers in the addition products of thiols to chloroprene[52] is the same as in reactions with isoprene[52], although such a strongly electronegative substituent as chlorine ($\sigma^*_{Cl} = 2.9$ [73]) should have more strongly prevented attack by the electrophilic radicals RS$^{\cdot}$ in position 1 than in position 4. The predominance of the 1,4-isomer in this case is probably explained by stabilisation of the corresponding radical by hyperconjugation with the chlorine atom.

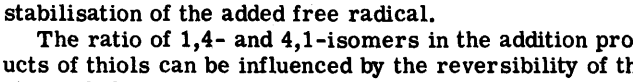
As already remarked, the ratio of 1,4- and 1,2-isomers is determined primarily by the molecular structure of the conjugated diene and the rate of chain transfer. However, 1,4—4,1-isomerism of addition products is probably influenced to a considerable extent also by the nature of the attacking free radical. A radical containing polar substituents will obviously add to the diene in such a way that unfavourable interactions with polar substituents of the diene will be minimised. In the reaction of bromotrichloromethane with 1,1,2-trifluorobuta-1,3-diene, for example, the trichloromethyl radical adds to the diene only at the fourth carbon atom, which then leads to formation of the 1,4-isomer $BrCF_2CF:CHCH_2CCl_3^{\cdot}$:

Stabilisation of a telogen radical increases its selectivity, so that the less active a free radical the greater the probability of formation of a more stabilised radical by reaction with a diene. It is therefore likely that the difference in reactivity between free radicals explains the diminished content of the 4,1-isomer in the reactions of isoprene with the radicals $CCl_3^{\cdot}$ [13] and $CH_3OOC[CH_2]_5^{\cdot}$ [71] respectively. The influence of the nature of the telogen radical can be traced most clearly in the reactions of isoprene with thiols as example. Reaction of isoprene with ethanethiol, as in the case of bromotrichloromethane, yields 75% of the 1,4-isomer and 25% of the 4,1-isomer[52]. In the reactions with thioacetic acid and thiophenol, however, the content of the 4,1-isomer falls to 10% and 2.5% respectively[52]. The reason for this change in the ratio of the isomers is evidently increased stabilisation and hence diminished reactivity of the free radicals in the sequence $C_2H_5S^{\cdot}$, $CH_3COS^{\cdot}$, $C_6H_5S^{\cdot}$. Thus determination of the relative rates of addition to the first and the last carbon atom of an

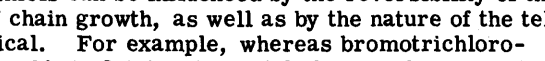
‡An exception is Neumann and Sommer's paper[41], in which it is stated, on the basis of an analysis of the infrared spectra, that predominantly 4,1-isomers are formed by the reaction of alkylstannanes with isoprene. In our opinion, however, this assertion, which contradicts the results of other investigations, requires further confirmation.

unsymmetrical diene can be used to estimate the resonance stabilisation of the added free radical.

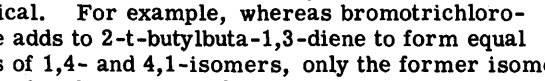
The ratio of 1,4- and 4,1-isomers in the addition products of thiols can be influenced by the reversibility of the stage of chain growth, as well as by the nature of the telogen radical. For example, whereas bromotrichloromethane adds to 2-t-butylbuta-1,3-diene to form equal amounts of 1,4- and 4,1-isomers, only the former isomer is obtained with butanethiol[16]. The authors explain this anomaly by the reversibility of the addition of thiyl radicals to the diene:



(21)



(22a)

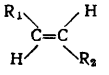


(22b)

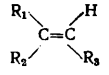
The probability of the formation of radicals (A) and (B) on the addition of $C_4H_9S^{\cdot}$ is the same as in the case of the trichloromethyl radical, but if, owing to steric hindrance due to screening of the reaction centre by the t-butyl group, the rate of chain transfer (22b) is considerably lower than the rate of reaction (21), the 4,1-isomer will be almost completely absent. It is interesting that, if the suggested mechanism is correct, the ratio of 1,4- and 4,1-isomers for analogous reactions should depend on the thiol : diene ratio, since the rate of reaction (22b) depends on the thiol concentration, whereas the rate of reaction (21) is independent thereof.

VII. STEREOISOMERISM OF TELOMERS

As already mentioned (Section V), stereoisomerism (*cis–trans*) is possible in the reaction products of 1,4- and 4,1-addition. In most of the work, unfortunately, the spatial configuration of the telomers has been determined only by infrared spectroscopy without separation of the isomers. Infrared spectra enable the presence only of a *trans*-isomer having two substituents adjacent to the double bond



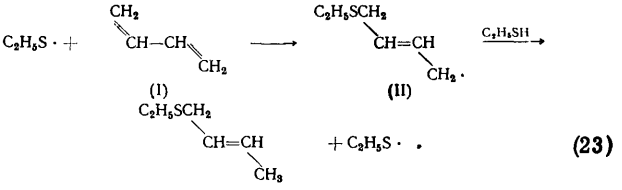
to be established reliably (frequency of deformation vibration of C–H bond 965 cm^{-1}), whereas the absorption frequency of the corresponding *cis*-isomer (728–675 cm^{-1}) is not characteristic[74]. Determination of the steric configuration of compounds containing three substituents adjacent to the double bond



is probably impossible from the infrared spectra, so that there are hardly any data on the *cis–trans*-isomerism of addition products to conjugated dienes containing substituents attached to the second carbon atom.

Most authors consider that radical 1,4-addition to buta-1,3-diene yields only the *trans*-isomer (Table 2). Although relatively small amounts of the *cis*-isomer might be formed and remain undetected for the reason indicated above, the predominant formation of the *trans*-isomer can evidently be accepted as proved. For example, Poutsma[69] showed by gas–liquid chromatography that the 1,4-isomer formed by reaction of chlorine with buta-1,3-diene was identical with the known *trans*-isomer, while the *cis*-isomer was absent from the mixture of reaction products. In contrast to the results obtained by most other authors, Jacobs and Illingworth[53] found that ethanethiol reacts with butadiene in the presence of azoisobutyronitrile at 70°C to form a mixture of addition products comprising 80% of the *trans*-isomer and 20% of the *cis*-isomer. However, the products of the same reaction under the influence of ultraviolet radiation at 20°C contain not more than 6% of the *cis*-isomer[52].

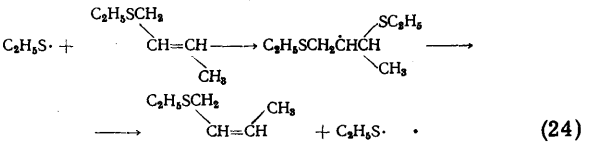
The configuration of telomers is evidently determined by the steric structure of the diene[60] and the possibility of isomerisation of the resulting addition product. At ordinary temperatures buta-1,3-diene occurs mainly (> 96%) in the more stable transoid conformation (I).[75] If, therefore, the initial conformation of the diene molecule is preserved during addition of the telogen radical and the subsequent chain-transfer reaction, the resulting telomer will have the *trans*-configuration:



(23)

With rise in temperature the content of butadiene in the *cis*-conformation increases, and the probability of change in the spatial conformation of the radical (II) also increases, which should lead to an increase in the yield of the *cis*-1,4-isomer. In fact, raising the temperature from 0° to 100°C in the radical polymerisation of butadiene leads to an increase in the *cis*-units in the polymer from 12% to 35%.[76]

Conducting the reaction at a low temperature and excluding the effect of metallic walls of the reaction vessel enable thermal and catalytic isomerisation of the products to be avoided. However, the presence of free thiyl radicals, as well as bromine and iodine atoms, in the reaction medium may cause isomerisation of the telomers as a consequence of the ability of these radicals to add reversibly at a double bond:



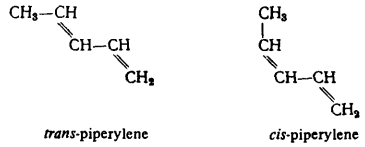
(24)

Therefore the increase in the yield of the *cis*-product of the addition of ethanethiol to butadiene with rise in reaction temperature from 20° [52] to 70°C [53] can be explained both by increase in the relative content of butadiene in the cisoid conformation and by isomerisation of the *trans*-isomer by thiyl radicals.

As in the case of buta-1,3-diene, the interaction of thiols with 2,5-dimethylhexa-2,4-diene[61] involves predominant formation of the *trans*-1,4-isomer compared with the *cis*-1,4-isomer.

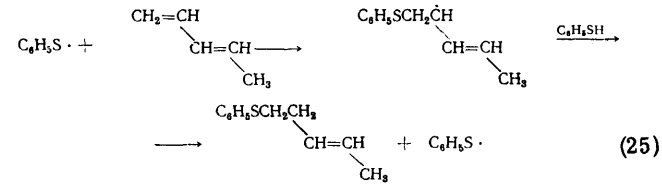
A detailed study has been made[60] of the stereoisomerism of addition products of thiols with *cis*- and *trans*-piperylene, when it was assumed that, as with buta-1,3-diene,

both isomers of piperylene exist in the more stable transoid conformation:

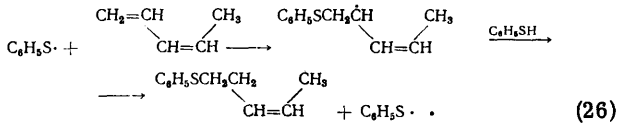


trans-piperylene *cis*-piperylene

Therefore the 1,4-isomers of the addition products, independently of the spatial structure of the initial diene, had the *trans*-configuration. Investigation of the isomerism of the 1,2-addition products enabled the dependence of the steric structure of the radical on the structure of the telogen (thiol) to be determined. It was found that 1,2-isomers of the reaction products with thiophenol were formed from radicals which preserved the configuration of the diene: i.e. *trans*-piperylene yielded mainly the *trans*-1,2-isomer, whereas *cis*-piperylene gave the *cis*-1,2-isomer:



(25)



(26)

When thiophenol was replaced by aliphatic thiols, the stereospecificity of 1,2-addition dropped sharply. Thus the reaction of *cis*-piperylene with methanethiol (at 96% conversion of the latter) led to the formation of 14% of *cis*- and 13.4% of *trans*-1,2-isomers. The loss of stereospecificity is explained by a decrease in the rate of chain transfer via methanethiol molecules (in comparison with benzenethiol), and hence an increase in the lifetime of the free allyl radical, this in turn increasing the probability of change in its steric configuration.

The principal factors influencing the relative proportions of structural isomers and stereoisomers in the mixture of reaction products from conjugated dienes can be summarised as—(1) the structure of the dienes, (2) the structure of the telogens, (3) stabilisation of the telomeric (allyl) radical, (4) the polar effect of the reaction, (5) the temperature of the reaction, (6) the relative rates of forward and reverse reactions in the addition of the telogen radical to the diene, and (7) isomerisation of the reaction products.

VIII. KINETIC INVESTIGATIONS

Few kinetic data are available on the free-radical addition and telomerisation of conjugated dienes. Investigations have been made of the kinetics of the radical addition of ethyl tribromoacetate to butadiene[20] and of bromotrichloromethane to butadiene, isoprene, and 2,3-dimethylbuta-1,3-diene[12,13]. It was found that the reaction velocity was independent of the diene concentration but increased with the concentration of the telogen. These data suggest that even at high telogen : diene ratios the rate-determining stage of the reaction is chain transfer. With a bromotrichloromethane : diene ratio of 3 the reaction velocity is approximately proportional to the square root of the rate of initiation, and in the case of ethyl tribromoacetate to the rate of initiation to the power 0.83. Thus with bromotrichloromethane chain termination is bimolecular, whereas with ethyl tribromoacetate termination is possible also by a unimolecular mechanism. The overall activation energies for the reactions of bromotrichloromethane with butadiene, isoprene, and dimethylbutadiene are respectively 5.45, 3.96, and 3.09 kcal mole^{-1}.

Chain-transfer constants have been determined for the telomerisation of buta-1,3-diene with aliphatic thiols[77,78]. The values obtained (at 0–60°C) lie in the range from 3–6 (for tertiary thiols) to 15–25 (for primary thiols). Sivertz and his coworkers[79] used the rotating sector method to determine the chain-transfer rate constant for the telomerisation of isoprene with butanethiol (93 M^{-1} s^{-1} at 25°C).

Table 3. Ratio of rate constants for the addition of free radicals to butadiene and to ethylene.

Radical	Temp., °C	$\frac{k_{Bu}}{k_{Et}}$	Ref.
CH_3[b]	25	94	80
CH_3[b]	65	53	81
CH_3[c]	65	43	8
CCl_3[c]	50—60	18[a]	82
CF_3[c]	65	11.6	80

[a] Compared with the rate of addition to oct-1-ene.
[b] In the gas phase.
[c] In the liquid phase.

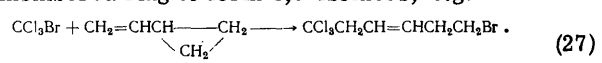
The addition of several free radicals to buta-1,3-diene in both gaseous and liquid phases has been investigated. Table 3 shows that the rate constants for addition of free radicals to butadiene are considerably higher than to ethylene, which is undoubtedly explained by resonance stabilisation of the allyl radical formed. Because of the high rate constants for addition of the radicals, the rate-determining stage in telomerisation and addition to conjugated dienes is chain transfer.

IX. ANALOGUES OF CONJUGATED DIENES

The free-radical additions of thiols to conjugated alkenynes—butenyne, 2-methylbutenyne, etc.—investigated by Sulimov and Petrov[83] are of considerable interest. These workers found that, of the six possible structural isomers in the reaction of thiols with butenyne, only four—e.g. (I) $CH_3SCH_2CH_2C:CH$ (39%), (II) $CH_3SCH_2CH:C:CH_2$ (40%), (III) $CH_2:C(SCH_3)CH:CH_2$ (18%), and (IV) $CH_3SCH::CHCH:CH_2$ (3%)—were formed. (The mixtures of isomers were analysed by gas–liquid chromatography and also by infrared and nuclear magnetic resonance spectroscopy.) The results show that thiyl radicals attack the butenyne molecule mainly at the double bond, the 1,2- and 1,4-isomers (I) and (II) being formed in roughly equal quantities. It is noteworthy that in this case the radical

$CH_3SCH_2CH:C:CH^{\bullet}$, from which the 1,4-isomer is formed, is not allylic, and is probably considerably less stabilised than is the secondary radical $CH_3SCH_2\dot{C}HC:CH$. The reactions of butenyne with benzenethiol, and of substituted butenynes with ethanethiol and butanethiol, yield only two isomers, corresponding to (I) and (II).

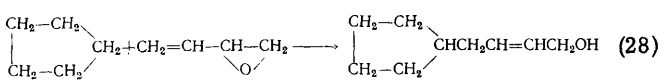
Compounds in which a double bond can be conjugated with a three-membered ring can also be regarded as analogues of conjugated dienes. Work has been done on the addition and telomerisation of vinylcyclopropane [84,86], isopropenylcyclopropane [85], and also their oxygen-containing derivatives [86] and butadiene monoxide [84] with bromotrichloromethane, carbon tetrachloride, thiols, propan-2-ol, and cycloalkanes in the presence of benzoyl peroxide and under the influence of radiation. Vinylcyclopropane and isopropenylcyclopropane reacted with cleavage of the three-membered ring to form 1,5-isomers, e.g.



$$CCl_3Br + CH_2{=}CHCH\!\!<\!\!\begin{matrix}CH_2\\ CH_2\end{matrix}\!\!> \longrightarrow CCl_3CH_2CH{=}CHCH_2CH_2Br \quad (27)$$

An exception was provided by the reaction with thiols, which, depending on the structure of the vinylcyclopropane derivatives, produced, owing to their high reactivity, a mixture of rearranged and unrearranged (without ring cleavage) products or even one of the possible isomers [85,86].

A study of the three-dimensional structure of the reaction products of vinylcyclopropane with bromotrichloromethane showed [84] that the 1,5-isomer is an equilibrium mixture of *cis*- and *trans*-forms. The establishment of equilibrium was proved by the fact that additions of iodine and methanethiol do not affect the proportions of the stereoisomers. On the other hand, since 1,5-isomers formed from butadiene monoxide with cycloalkanes and isopropyl alcohol in conformity with the scheme



$$\begin{matrix}CH_2{-}CH_2\\ |\quad\quad\\ CH_2{-}CH_2\end{matrix}\!\!>CH_2 + CH_2{=}CH{-}CH{-}CH_2 \longrightarrow \begin{matrix}CH_2{-}CH_2\\ |\quad\quad\\ CH_2{-}CH_2\end{matrix}\!\!>CHCH_2CH{=}CHCH_2OH \quad (28)$$

have the *trans*-structure, it was considered that the reaction of bromotrichloromethane with cyclopropane at first also yields exclusively (or predominantly), the *trans*-isomers, which only then are converted, under the influence of bromine atoms, into an equilibrium mixture of the two isomers. (Bromine atoms are formed from bromotrichloromethane at the stage of initiation by ultraviolet radiation.) In conformity with this, the telomers formed by the reaction of cyclohexane with vinylcyclopropane (in which no atoms or free radicals capable of reacting reversibly with a double bond are present) are probably *trans*-isomers [84].

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