tion of the chlorosilane can be calculated from the following equation

$$\frac{[\alpha]_D \text{ MW moles}}{100} + \frac{[\alpha]_D' \text{ MW}' \text{ moles}'}{100} = \phi \text{ moles}''$$

where $[\alpha]_D$ = specific rotation of the remaining (+)-R_3Si^*H, MW = molecular weight of R_3Si^*H, moles = moles of R_3Si^*H remaining after reaction, $[\alpha]_D'$ = specific rotation of (−)-R_3Si^*Cl, MW′ = molecular weight of R_3Si^*Cl, moles′ = moles of R_3Si^*Cl formed in reaction, ϕ = molecular rotation of reaction mixture = (observed rotation) (ml)/(path length, dm) (moles″) (100), and moles″ = total moles of reactant.

Therefore, from the gross molecular rotation of the reaction mixture and an $[\alpha]_D$ of +35.0° for R_3Si^*H, the specific rotation of the formed (−)-R_3Si^*Cl can be calculated. The amount of silane remaining (moles) and the amount of chlorosilane formed (moles′) can be obtained from glpc or nmr analysis.

Reaction of (+)-α-Naphthylphenylmethylsilane and CCl_4.—In a 25-ml round-bottom flask equipped with a reflux condenser and a nitrogen inlet tube were placed 2.0 g (0.008 mol) of (+)-α-naphthylphenylmethylsilane, $[\alpha]_D$ +35.0°, and 0.19 g (0.0008 mol) of benzoyl peroxide in 8 ml of carbon tetrachloride. The resulting solution was refluxed for 14 hr under nitrogen. The reaction mixture was transferred quantitatively to a polarimeter tube and a rotation was taken. Calculations yielded ϕ = −6.60° (c 6.6, CCl_4). The solvent was removed, the remaining oil was taken up in cyclohexane, and a known quantity of phenanthrene was added [TCF = phenanthrene/R_3SiH = 1.05 (weight basis), phenanthrene/R_3SiCl = 1.42, R_3SiH/R_3SiCl = 1.34]. The solution was analyzed by glpc and 0.18 g of R_3Si^*H and 2.1 g of R_3Si^*Cl were found to be present. Calculation using the equation previously described yielded $[\alpha]_D$ −5.5° for the chlorosilane produced. Nmr, ir, and glpc analyses were consistent with the assigned structures.

Reaction of (+)-α-Naphthylphenylmethylsilane with 50% Carbon Tetrachloride and 50% Cyclohexane.—In a 25-ml round-bottom flask equipped with a reflux condenser and a nitrogen inlet tube were placed 2.0 g (0.008 mol) of (+)-R_3Si^*H, $[\alpha]_D$ +35.0°, and 0.19 g (0.0008 mol) of benzoyl peroxide in 4 ml of carbon tetrachloride and 4 ml of cyclohexane. The solution was refluxed for 14 hr under nitrogen. Following the procedure described above yielded ϕ = −1.34° (c 6.6, CCl_4) for the molecular rotation of the reaction mixture and $[\alpha]_D$ −3.84 for the R_3Si^*Cl formed (0.21 g of R_3Si^*H remaining and 2.0 g of R_3Si^*Cl formed).

Reaction of (+)-α-Naphthylphenylmethylsilane with 33% Carbon Tetrachloride and 67% Cyclohexane.—In a 25-ml round-bottom flask equipped with a reflux condenser and a nitrogen inlet tube were placed 2.0 g (0.008 mol) of (+)-R_3Si^*H, $[\alpha]_D$ +35.0°, 0.19 g (0.0008 mol) of benzoyl peroxide in 2.6 ml of carbon tetrachloride, and 5.4 ml of cyclohexane, and the solution was refluxed for 14 hr under nitrogen. The procedure described previously yielded ϕ = +17.2° (c 6.6, CCl_4) for the molecular rotation of the reaction mixture and $[\alpha]_D$ −2.78° for the R_3Si^*Cl formed (0.54 g of R_3Si^*H remaining and 1.8 g of R_3Si^*Cl formed).

Reaction of α-Naphthylphenylmethyldeuteriosilane and Carbon Tetrachloride.—In a 25-ml round-bottom flask were placed 1.1000 g (4.42 mmol) of R_3SiD and 0.1000 g (0.414 mmol) of benzoyl peroxide in 5 ml of carbon tetrachloride. The solution was refluxed for 11 hr under nitrogen. The volatile material was removed under vacuum and trapped in a flask cooled by a Dry Ice–acetone bath. The chloroform formed was isolated by preparative glpc and a mass spectrum was taken. The results indicated that 98% of the hydrogen in the chloroform was deuterium.

Reaction of α-Naphthylphenylmethyldeuteriosilane and Cyclohexane.—In a 25-ml round-bottom flask were placed 0.3000 g (1.2 mmol) of α-naphthylphenylmethyldeuteriosilane and 0.0300 g (0.124 mmol) of benzoyl peroxide in 4 ml of cyclohexane and the solution was refluxed for 17 hr under nitrogen. Infrared examination of the reaction mixture indicated that no R_3SiH formed.

Reaction of α-Naphthylphenylmethyldeuteriosilane, Chloroform, Toluene, Benzene, and 1,3,5-Trimethylbenzene.—In a manner analogous to that described above, R_3SiD and benzoyl peroxide were treated with $CHCl_3$, PhMe, PhH, and $PhMe_3$. Infrared analysis indicated that no R_3SiH formed in any of the reactions.

Registry No.—**1**, 1025-08-7; **1**-Cl, 960-82-7; **2**, 1770-59-8; **2**-Cl, 15942-84-4; **3**, 36358-49-3; **3**-Cl, 36358-50-6; **4**, 36411-23-1; **4**-Cl, 36358-51-7; **5**, 15726-86-0; **5**-Cl, 15942-85-5; carbon tetrachloride, 56-23-5.

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Stereochemistry of Addition Reactions of Allenes. VI. Orientation and Stereochemistry of Radical Addition

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Products of radical addition of *p*-toluenesulfonyl iodide, $ArSO_2I$, to various allenes (propadiene, 1,2-butadiene, 3-methyl-1,2-butadiene, 2,3-pentadiene, 2-methyl-2,3-pentadiene, and 1,2-cyclononadiene) have been identified. Each allene except propadiene gave an allylic iodide by way of central attack on the allenic system by arylsulfonyl radicals. Evidence supporting the intervention of symmetrical allylic radicals was obtained from a study of the addition of $ArSO_2I$ to optically active 2,3-pentadiene and 1,2-cyclononadiene. Radical addition of halomethanes, CF_3I, CH_3I, and CCl_3Br, to 2,3-pentadiene gave products of terminal attack by CX_3 radicals (X = F, H, Cl) accompanied by 41–49% central attack in the case of CCl_3Br. The stereospecificity of addition of $BrCCl_3$ to (+)-2,3-pentadiene was found to be almost negligible, indicating that the products are formed from symmetrical allylic radicals and configurationally unstable vinylic radicals. The factors that influence the orientation of radical addition to allenes are discussed.

Radical-chain additions to allenes are presumed to involve radical intermediates of allylic structure by way of initial attack at the central allenic carbon, and of vinylic structure by attack at the terminal carbons. The degree to which radicals of either structure are involved depends on the structure of the starting allene, the nature of the attacking radicals, and the reaction conditions.[3] Nevertheless, orientation data for the addition of various radical reagents to propadiene do not reveal any obvious correlation between the nature of the attacking radical and its regioselectivity. For example, under kinetic control, where reversibility

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[2] Part V: L. R. Byrd and M. C. Caserio, *J. Amer. Chem. Soc.*, **93**, 5758 (1971).

[3] (a) M. C. Caserio in "Selective Organic Transformations," Vol. 1, B. S. Thyagarajan, Ed., Wiley-Interscience, New York, N. Y., 1970, p 239. (b) For a thoughtful review on structure and reactivity in free-radical chemistry, see C. Ruchardt, *Angew. Chem., Int. Ed. Engl.*, **9**, 830 (1970).

TABLE I

SELECTIVITY IN RADICAL ADDITIONS TO PROPADIENE AND 2,3-PENTADIENE

Reagent	Attacking radical	$CH_2=C=CH_2$ Terminal attack[a]	$CH_2=C=CH_2$ Central attack[a]	$CH_2=C=CH_2$ Ref	$CH_3CH=C=CHCH_3$ Terminal attack[a]	$CH_3CH=C=CHCH_3$ Central attack[a]	$CH_3CH=C=CHCH_3$ Ref
HBr[b]	$Br\cdot$		100	9	6	94	6
HBr[c]	$Br\cdot$	66	33	4			
SF_6[d]	^{18}F	~50	~50	8			
N_2F_4	$F\cdot$		100	10			
PH_3	$H_2P\cdot$		100	11			
$(CH_3)_3SnH$	$(CH_3)_3Sn\cdot$	55	45	5		100	5
C_6H_5SH	$C_6H_5S\cdot$	75	25	6			
p-$CH_3C_6H_4SO_2I$	*p*-$CH_3C_6H_4SO_2\cdot$	100		12		100	*e*
$(CH_3)_3COCl$	$(CH_3)_3CO\cdot$					100	17
CF_3I	$F_3C\cdot$	100		7	100		*e*
CCl_3Br	$Cl_3C\cdot$	100		6	59	41	*e*
CH_3I	$H_3C\cdot$	100		7	100		*e*

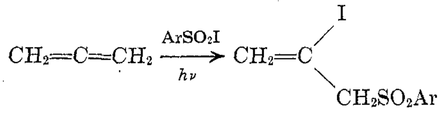
[a] Per cent distribution, statistical correction not included. [b] Gas phase. [c] Liquid phase under conditions of kinetic control. [d] Gas-phase reaction of ^{18}F from $^{19}F(n,2n)$ in excess SF_6. Moderated by SF_6 at τ 3500, the intermediate radicals were scavenged by HI. [e] Present work.

of initial attack is not a factor, fluorine atoms, bromine atoms (in the liquid phase),[4] trimethyltin,[5] and benzenethiyl radicals[6] are relatively nonselective (*cf.* Table I[4-12]). In contrast, radicals of the type $CX_3\cdot$ are highly selective and attack the terminal carbons exclusively, regardless of the nature of X (F, Cl, or H).[6-8]

Studies of radical additions to substituted allenes are more limited, but the results of HBr,[9] thiol,[13] and trimethyltin hydride[5] additions to methylated allenes indicate a strong preference for central radical attack with increasing methyl substitution. The origin of this effect is not entirely clear, although it must certainly be related to the steric and electronic influence of methyl substituents on the reactivity of the central over the terminal positions provided that attack at either site is irreversible. Of special interest, however, is the question of whether the reactivity of the central carbon is enhanced by formation of resonance-stabilized allylic intermediates or whether these intermediates are actually nonplanar localized radicals. To investigate this question, we have chosen to study radical addition to optically active allenes using reagents that can in principle lead to asymmetric adducts. Induction of activity in the products would provide evidence for the intervention of dissymmetric radicals, whereas formation of racemic adducts would suggest that products were formed from planar delocalized allyl radicals. The allenes chosen for this work were 2,3-pentadiene and 1,2-cyclononadiene, both of which are readily available and easily resolved. Unfortunately, a study of the addition of HBr, thiols, and tin hydrides to these allenes is unsuited to our objectives since the adducts are achiral. We therefore studied the radical addition of *p*-toluenesulfonyl iodide (tosyl iodide) and, since little information was available on the orientation of addition of this reagent, we extended the study to include symmetrical allenes. We have also investigated the radical additions of CF_3I, CCl_3Br, and CH_3I to 2,3-pentadiene and related allenes, the results of which are pertinent to the overall question of orientation.

Results

Addition of Tosyl Iodide.—The allenes studied included propadiene, 1,2-butadiene, 3-methyl-1,2-butadiene, 2,3-pentadiene, 2-methyl-2,3-pentadiene, and 1,2-cyclononadiene. A twofold molar excess of allenic hydrocarbon to freshly prepared tosyl iodide in ether or pentane was irradiated in a sealed, thick-walled Pyrex cylinder with a 200-W heat lamp until reaction was complete, which typically required 20 min. Comparable reaction mixtures maintained in the dark were unreactive over a period of at least 6 hr with the exception of 1,2-cyclononadiene, which underwent spontaneous reaction as low as 0°. The monoadducts formed were isolated as crystalline solids in nearly quantitative yields. Apart from the *tert*-allylic iodide **6** obtained from 2-methyl-2,3-pentadiene, the adducts were stable to the reaction conditions; however, isolation of **6** within minutes of reaction was necessary to prevent its resinification. The structure of each adduct was established from its nmr spectrum (Table II) and from the structure of the products obtained on solvolysis of the adduct in methanolic silver tetrafluoroborate (Table III). The tosyl iodide reactions were remarkably straightforward and selective in that only one crystalline monoadduct was obtained from each allene. Consistent with the previously reported results of Truce and Wolf,[12] propadiene was the only allene that produced a vinylic iodide **1** (eq 1) and



$$CH_2=C=CH_2 \xrightarrow[h\nu]{ArSO_2I} CH_2=C(I)CH_2SO_2Ar \qquad (1)$$

a minor by-product identified as the disulfone **2**. As expected, **1** was unreactive toward methanolic silver tetrafluoroborate.

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(9) (a) P. I. Abell and R. S. Anderson, *Tetrahedron Lett.*, 3727 (1964); (b) R. Y. Tien and P. I. Abell, *J. Org. Chem.*, **35**, 956 (1970).

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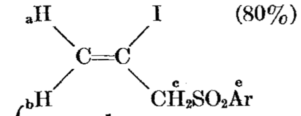
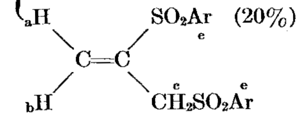
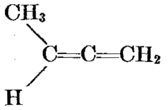
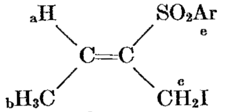
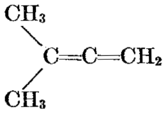
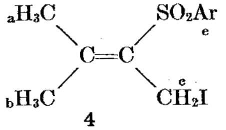
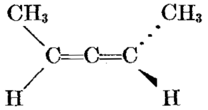
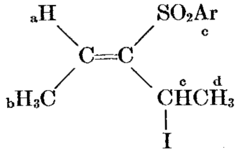
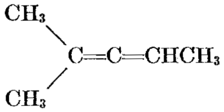
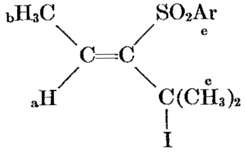
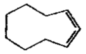
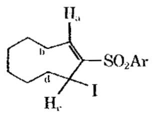
(13) T. L. Jacobs and G. E. Illingworth, Jr., *J. Org. Chem.*, **28**, 2692 (1963).

TABLE II

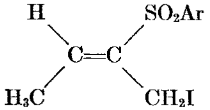
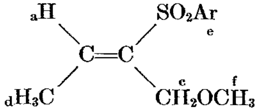
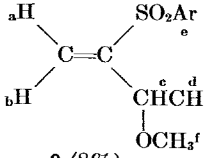
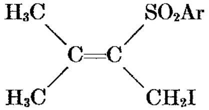
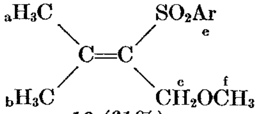
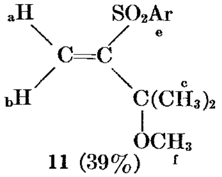
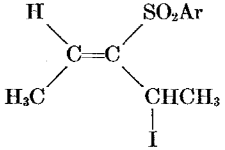
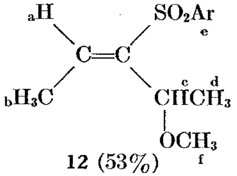
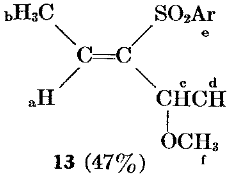
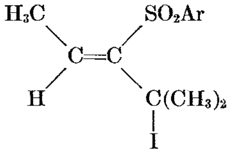
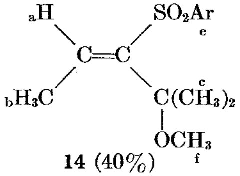
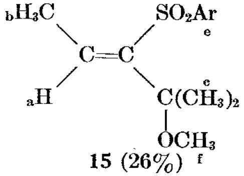
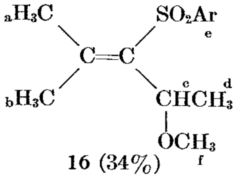
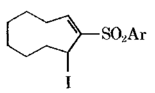
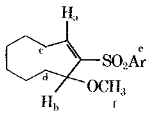
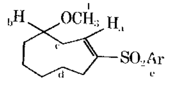
PRODUCT DISTRIBUTION IN ADDITION OF TOSYL IODIDE TO ALLENES. NMR SPECTRAL PARAMETERS OF ADDUCTS^{a-e}

Allene	Compd	Mp, °C^d	Yield, %	δ_a	δ_b	δ_c	δ_d	δ_e	J, Hz
$CH_2=C=CH_2$	 (80%) 1	74–76	64^e	6.12 (m)	5.91 (d)	4.08 (d)		7.05–7.75 (m)	ab = 1.9 ac = 0.9
	 (20%) 2	152–153		6.48 (d)	6.33 (m)	3.95 (d)		7.0–7.6 (m)	ab = 1.1 bc = 1.0
	 3	104–106	73^e	7.12 (q)	1.74 (d)	3.97 (s)		7.1–7.9 (m)	ab = 7.1
	 4	77–80	73^e	2.02 (s)	1.84 (s)	4.33 (s)		7.1–8.0 (m)	
	 5	110–112 dec	82^e	7.14 (q)	1.90 (d)	4.98 (q)	1.87 (d)	7.2–7.8 (m)	ab = 7.5 cd = 7.4 ac = 0.5
	 6	f	99^f	5.78 (q)	2.03 (d)	2.01 (d)		7.2–7.8 (m)	ab = 7.5 ac = 1.8
	 7	104–106 dec	80^e	7.15 (dd)	2.0–3.2 (m)	5.0 (dd)	1.8 (m)	7.2–7.9 (m)	ab = 11, 5 ac = 1.3 cd = 11, 5

[a] Ar = C_6H_4-p-CH_3. [b] Chemical shifts are reported in parts per million downfield from internal TMS; spectra were recorded as 25% solutions in $CDCl_3$. [c] δ_e refers to phenyl protons; $\delta_{p\text{-}CH_3}$ = 2.43 for all adducts. [d] Melting points were taken after one recrystallization from 95% ethanol. [e] Crude yield, prior to recrystallization, was practically quantitative. [f] This figure represents a crude yield; the adduct decomposed before the melting point could be determined.

Table III

Product Distribution in Silver-Assisted Methanolysis of Allene–Tosyl Iodide Adducts. NMR Spectral Parameters of Products[a, b]

Adduct	Methanolysis products	No.	δ_a	δ_b	δ_c	δ_d	δ_e	δ_f	J, Hz
 3	 8 (92%)	8	7.15 (q)	1.88 (d)	4.14 (s)		7.1–7.9 (m)	2.98 (s)	ab = 7.1
	 9 (8%)	9	6.37 (s)	5.97 (s)	3.51 (q)	2.32 (d)	7.1–7.9 (m)	2.86 (s)	cd = 6.5
 4	 10 (61%)	10	2.07 (s)	1.91 (s)	4.26 (s)		7.1–7.9 (m)	3.21 (s)	
	 11 (39%)	11	6.38 (s)	6.02 (s)	1.38 (s)		7.1–7.9 (m)	2.75 (s)	ab = 0
 5	 12 (53%)	12	7.10 (q)	1.90 (d)	4.12 (q)	1.29 (d)	7.2–7.8 (m)	2.78 (s)	ab = 7.4 ac = 0.7 cd = 6.4
	 13 (47%)	13	6.43 (q)	2.15 (d)	4.12 (q)	1.29 (d)	7.2–7.8 (m)	2.92 (s)	ab = 7.4 ac = 0.7 cd = 6.4 bc = 0.7
 6	 14 (40%)	14	7.27 (q)	2.31 (d)	1.48 or 1.36(s)		7.1–7.9 (m)	2.95 (s)	ab = 7.6
	 15 (26%)	15	2.38 or 2.08 (s)	2.08 or 2.38 (s)	4.48 (q)	1.38 (d)	7.1–7.9 (m)	2.93 (s)	cd = 6.7
	 16 (34%)	16	6.67 (q)	2.12 (d)	1.36 or 1.48 (s)		7.1–7.9 (m)	2.97 (s)	ab = 7.8
 7	 17 (72%)	17	7.18 (dd)	4.25 (m)	2.0–2.5 (m)	1.1–2.0 (m)	7.2–7.9 (m)	2.86 (s)	ac = 7, 12
	 18 (28%)	18	7.12 (dd)	2.6–3.2	2.0–3.3 (m)	1.1–2.2 (m)	7.2–7.9 (m)	3.23 (s)	ac = 7, 12

[a] Ar = C_6H_4-*p*-CH_3. [b] Chemical shifts are reported from internal TMS; spectra were recorded as 25% solutions in $CDCl_3$; δ_e refers to phenyl protons; $\delta_{p\text{-}CH_3}$ = 2.42 for all products.

In contrast, the substituted allenes gave only allylic iodides **3**–**7** (Table II). Solvolysis of these adducts occurred readily in methanolic silver tetrafluoroborate and was accompanied by allylic rearrangement, geometric isomerization, and, in the case of 1,2-cyclononadiene, transannular hydride shifts. The structure and nmr spectral parameters of the solvolysis products **8**–**18** are summarized in Table III. Whereas 2,3-pentadiene has been reported to react with tosyl iodide to give an adduct of the opposite orientation to that reported here,[13] the spectral parameters and chemical behavior of **5** leave no doubt that the adduct we obtained from 2,3-pentadiene is 4-iodo-3-tosyl-2-pentene (**5**).

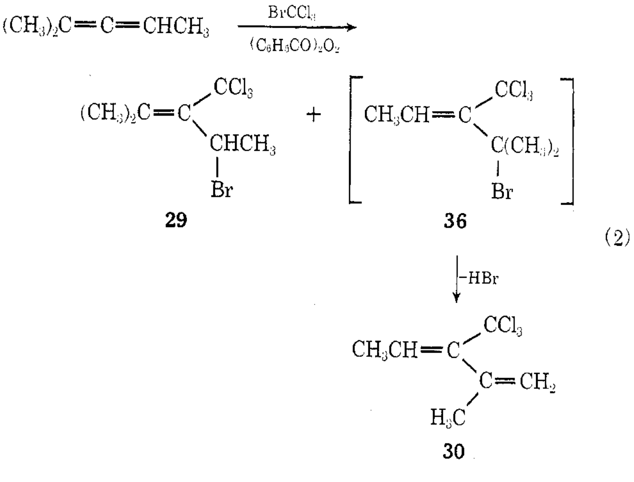
Addition of tosyl iodide to partially resolved (*S*)-(+)-2,3-pentadiene having a specific rotation of $[\alpha]^{28}\mathrm{D}$ 23.20 ± 0.05° (*c* 30, ether) gave *cis*-4-iodo-3-tosyl-2-pentene (**5**), which showed *no observable activity* either before or after purification by recrystallization. The recovered unreacted 2,3-pentadiene showed only a small loss in initial optical activity, $[\alpha]^{28}\mathrm{D}$ 21.61 ± 0.05° (*c* 27, ether). Addition of tosyl iodide to partially resolved (*S*)-(−)-1,2-cyclononadiene with $[\alpha]^{28}\mathrm{D}$ $-23.30 + 0.05°$ (neat) gave *cis*-3-iodo-2-tosylcyclononene (**7**), which like adduct **5** from (+)-2,3-pentadiene, had no measurable activity. However, the recovered unreacted 1,2-cyclononadiene had, after distillation, lost most of its observed rotation and in fact showed a slight positive rotation, $[\alpha]^{28}\mathrm{D}$ 0.46 ± 0.05° (neat).

Addition of Iodomethane.—Reaction mixtures comprised of a twofold excess of CH_3I to allene (2,3-pentadiene or 2-methyl-2,3-pentadiene) were irradiated in sealed, degassed quartz test tubes using a low-pressure mercury vapor lamp as the light source. Typically, 12 hr of irradiation brought about a 45% conversion of the allene to a complex mixture of products of which some 23% consisted of 1:1 adducts; these were isolated from the crude reaction mixtures by flash distillation followed by preparative glpc. Their structures were established by nmr and infrared spectroscopy and from the fact that they were *inert* to methanolic $AgBF_4$. The pertinent structural data are summarized in Table IV, from which it may be noted that the only isolable 1:1 adducts of iodomethane addition to 2,3-pentadiene and 2-methyl-2,3-pentadiene are vinylic iodides, **19**–**22**. This result, however, does not exclude the possibility that allylic iodides may be formed, since they would be expected photolyze under the reaction conditions. Attempts to analyze the complex mixture of higher molecular weight products were unsuccessful and we can comment only that their spectral properties (nmr, ir) are incompatible with diadducts or telomers derived in any simple fashion from monoadducts of either orientation.

Addition of Iodotrifluoromethane to 2,3-Pentadiene.—A twofold molar excess of CF_3I was condensed in 2,3-pentadiene; the mixture was degassed and sealed in a thick-walled Pyrex tube and irradiated for 24 hr using a medium-pressure mercury vapor uv lamp. About 60% of the allene was consumed to produce a complex mixture of products of which some 44% corresponded to monoadducts. Isolation of three compounds from the monoadduct fraction was achieved by preparative glpc. Structure was assigned on the basis of ^1H and ^{19}F nmr spectra (Table IV), infrared spectra, and lack of reactivity toward methanolic $AgBF_4$. Thus, the monoadduct fraction consisted of 9.4% *trans*-3-iodo-2-pentene (**23**), 70.3% *trans*-3-iodo-4-trifluoromethyl-2-pentene (**24**), and 20.3% *cis*-3-iodo-4-trifluoromethyl-2-pentene (**25**). Formation of the minor product **23** presumably occurs by attack of iodine atoms followed by hydrogen abstraction. The major products are CF_3I adducts with iodine at the vinylic position. As with methyl iodide addition, the absence of allylic iodides does not necessarily exclude their formation, since they may not be photostable. Unfortunately, the secondary products of higher molecular weight were not identified owing to the complexity of the mixture.

Addition of Bromotrichloromethane.—2,3-Pentadiene, 2-methyl-2,3-pentadiene, and 1,2-cyclononadiene reacted cleanly and in high yield (~70%) with bromotrichloromethane at reflux temperatures using benzoyl peroxide as the initiator. Reaction was generally complete within 2 hr. The adducts were isolated by distillation and characterized by their nmr, mass, and ir spectra and their reactivity toward $AgBF_4$ (Tables IV and V). 2,3-Pentadiene gave a mixture of 59% vinylic bromides **26** and **27** and 41% allylic bromide **28**. Using partially resolved (*S*)-(+)-2,3-pentadiene having $[\alpha]^{25}\mathrm{D}$ 23.42 ± 0.05° (*c* 38, ether), a mixture of 51% **26** and **27** and 49% **28** was isolated which showed a low specific rotation of $[\alpha]^{24}\mathrm{D}$ −0.33 ± 0.05 (neat). Significantly, the recovered unreacted allene had lost essentially *none* of its optical activity, $[\alpha]^{24}\mathrm{D}$ 23.3 ± 0.1° (*c* 26, ether).

Addition of $BrCCl_3$ to 1,2-cyclononadiene gave a single monoadduct, identified as *cis*-3-bromo-2-trichloromethylcyclononene (**31**). Addition to 2-methyl-2,3-pentadiene gave the allylic bromide **29** and the diene **30**. The latter possibly forms by way of the alyllic precursor **36** by loss of HBr (eq 2).



Solvolysis of allylic bromides from the addition of $BrCCl_3$ to the three allenes studied gave a complex mixture of products from the adduct of 1,2-cyclononadiene, a mixture of *dl* and meso diethers **32** and **33** from the adduct of 2,3-pentadiene **28**, and an allylic ether **34** and diene **35** from the adduct of 2-methyl-2,3-pentadiene (Table V). Solvolysis of **28** evidently occurs at both the bromoallylic and chloroallylic sites

TABLE IV
PRODUCT DISTRIBUTION IN ADDITION OF CX_3Y TO ALLENES. NMR SPECTRAL PARAMETERS OF ADDUCTS

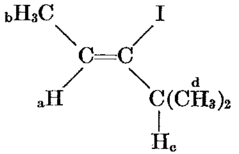
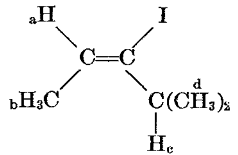
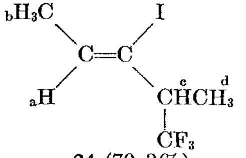
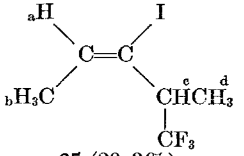
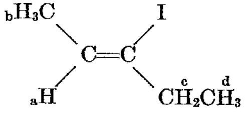
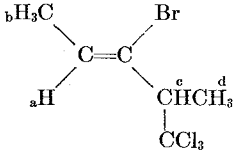
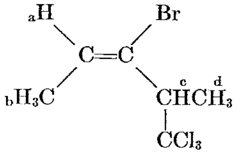
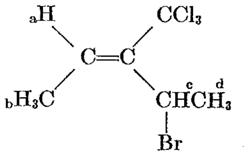
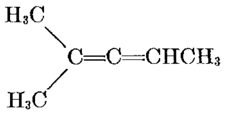
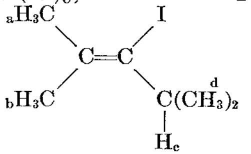
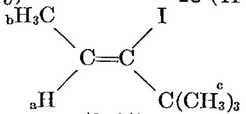
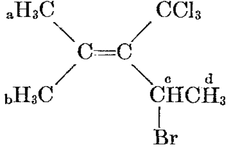
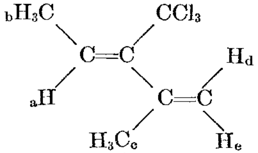
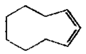
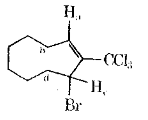
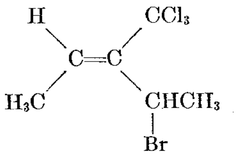
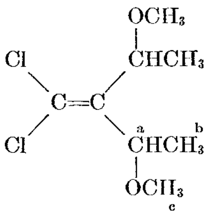
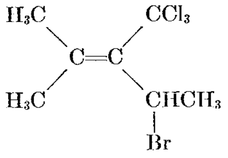
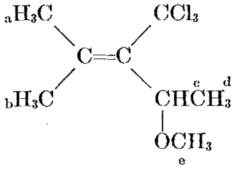
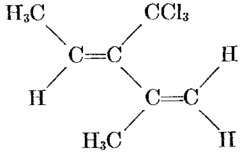
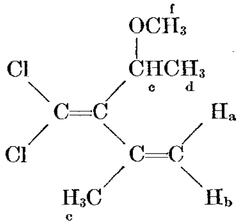
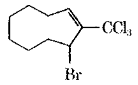
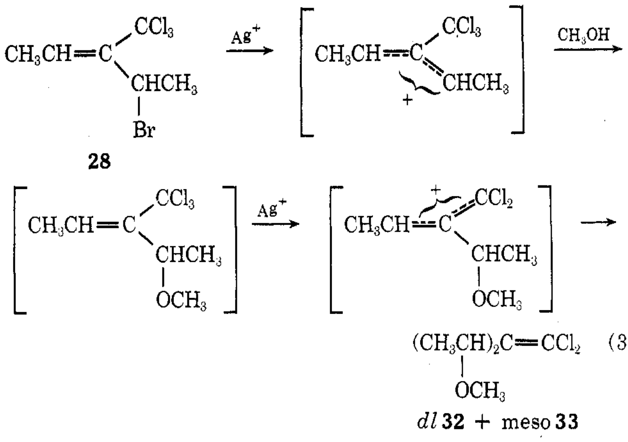
Allene	Adding reagent	Products	No.	δ_a	δ_b	δ_c	δ_d	δ_e	*J*, Hz
$CH_3CH{=}C{=}CHCH_3$	CH_3I	 **19** (75%)	**19**	5.66 (q)	1.70 (d)	1.8–2.6 (m)	1.03 (d)		ab = 6.6 cd = 6.6 ac = 0.9 bc = 0.4
		 **20** (25%)	**20**	6.17 (q)	1.66 (d)	1.8–2.6 (m)	1.03 (d)		ab = 7.4 cd = 6.6 ac = 0.4
	CF_3I	 **24** (70.3%)	**24**	6.01 (q)	1.80 (d)	3.05 (d)	1.30 (d)		ab = 6.4 cd = 7.0 ce = 8.8
		 **25** (20.3%)	**25**	6.70 (q)	1.74 (d)	3.15 (m)	1.26 (d)		ab = 7.3 cd = 7.0 ce = 8.8
		 **23** (9.4%)	**23**	5.59 (q)	1.73 (d)	2.50 (q)	1.08 (t)		ac = 1.3 ab = 6.4 bc = 1.3
	$BrCCl_3$	 **27** (47%)	**27**	6.18 (q)	1.79(d)	3.50 (q)	1.56 (d)		ab = 6.7 ac = 0.5 cd = 6.8
		 **26** (12%)	**26**	6.27 (q)	1.77 (d)	3.77 (q)	1.52 (s)		ab = 7.5 cd = 6.6
		 **28** (41%)	**28**	6.65 (q)	1.98 (d)	5.07 (q)	2.07 (d)		ab = 7.6 ac = 2.0 cd = 7.4
 $(H_3C)_2C{=}C{=}CHCH_3$	CH_3I	 **21** (72%)	**21**	1.86 or 1.92(s)	1.92 or 1.86(s)	2.37 (m)	0.93 (d)		cd = 6.5
		 **22** (28%)	**22**	5.60 (q)	1.75 (d)	1.18 (s)			ab = 6.5
	$BrCCl_3$	 **29**	**29**	1.90 or 1.92 (a)	1.92 or 1.90 (s)	4.80 (q)	1.75 (d)		cd = 6.8
		 **30**	**30**	4.98 (q)	1.75 (d)	3.37 (s)	5.72 or 5.88 (s)	5.88 or 5.72 (s)	ab = 6.8 ec = de = 1.0
	$BrCCl_3$	 31 (100%)	**31**	6.70 (dd)	2.0–3.3 (m)	5.02 (dd)	1.1–2.0 (m)		ab = 7, 12 cd = 6, 11 ac = 2.0

TABLE V
STRUCTURE AND SPECTRAL PARAMETERS OF METHANOLYSIS PRODUCTS OF ALLENE–CX_3Y ADDUCTS[a]

Adduct	Methanolysis product	δ_a	δ_b	δ_c	δ_d	δ_e	δ_f	J, Hz
 **28**	 **32** (50%) *dl* **33** (50%) meso	4.22 or 4.30 (q)	1.32 or 1.28 (d)	3.18 or 3.22 (s)				ab = 6.7 or 6.9
 **29**	 **34**	1.91 or 1.93 (s)	1.93 or 1.91 (s)	3.97 (q)	1.16 (d)	3.20 (s)		cd = 6.4
 **30**	 **35**	5.40 or 5.55 (s)	5.55 or 5.40 (s)	4.12 (q)	1.16 (d)	3.37 (d)	3.20 (s)	cd = 6.4
 31	Complex mixture							

[a] Chemical shifts are reported in parts per million downfield from internal TMS; spectra were recorded as 25% solutions in $CDCl_3$.

(eq 3). Likewise, solvolysis of the diene occurs at the trichloromethyl group.

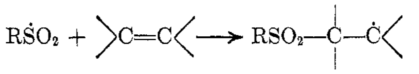


(3)

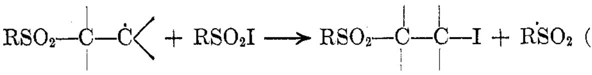
Discussion

Addition of Tosyl Iodide.—The addition of sulfonyl halides RSO_2X to alkenes is considered to be a radical-chain process in which a sulfonyl radical RSO_2 is the chain-carrying agent.[14,15] The propagation steps for $X = I$ are shown in eq 4 and 5. The observed orientation of tosyl iodide addition to allenes (Table II) demonstrates the selectivity of tosyl radicals for transfer to the *terminal* positions of propadiene and to the *central* position of all the methyl analogs, including 1,2-cyclononadiene.[16] Allylic radicals are therefore implicated as intermediates in additions to methylallenes, and the question arises as to whether these radicals are nonplanar localized radicals or planar delocalized radicals. The results of addition to (*S*)-(+)-2,3-pentadiene are important in this respect. The observed formation of *racemic* adduct **5** from (+)-2,3-pentadiene and the recovery of unreacted allene of essentially retained optical purity implies that tosyl radicals attack the central carbon of 2,3-pentadiene *irreversibly* to give planar allylic intermediates **37**. If bridged or localized radicals **38** are initially formed, they must necessarily lose their dissymmetry by a 90° bond rotation to give **37** faster than they can abstract iodine atoms from tosyl iodide (eq 6). This result parallels our earlier finding that *tert*-butoxy radicals and possibly chlorine atoms attack the central carbon of 2,3-pentadiene irreversibly to give allylic intermediates which lead to racemic adducts.[17] Irreversibility of radical addition to the central carbon is also consistent with the kinetic schemes deduced for HBr[4,9] and thiol[6a] additions to allenes. It has been shown for HBr additions that the hydrogen-abstraction step is rate determining.[9]

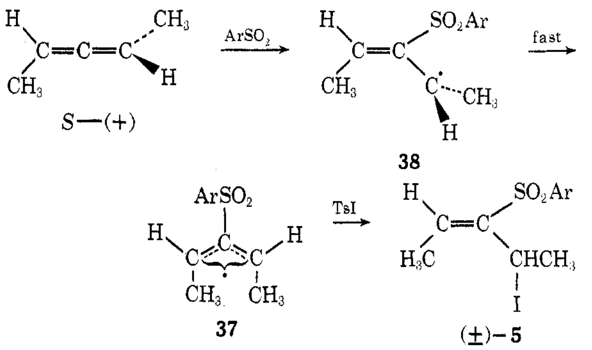
$$RSO_2X \xrightarrow{h\nu \text{ or heat}} R\dot{S}O_2 + \dot{I}$$



$$R\dot{S}O_2 + \rangle C{=}C\langle \longrightarrow RSO_2{-}\overset{|}{\underset{|}{C}}{-}\dot{C}\langle \qquad (4)$$



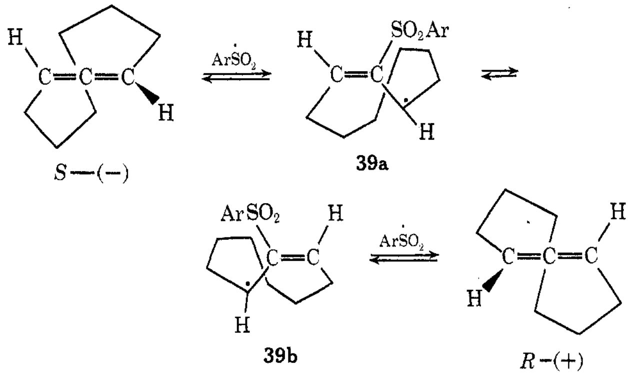
$$RSO_2{-}\overset{|}{\underset{|}{C}}{-}\dot{C}\langle + RSO_2I \longrightarrow RSO_2{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}I + R\dot{S}O_2 \qquad (5)$$



(6)

Terminal attack by tosyl radicals cannot be significant for 2,3-pentadiene, since products of this orientation were not observed and a rapid reversible attack is improbable for the reason that racemization of the allene during reaction is negligible. In contrast, a small amount of reversible terminal addition of bromine atoms to 2,3-pentadiene has been noted.[9]

Addition of tosyl iodide to (*S*)-(−)-1,2-cyclononadiene is interesting in several respects. The reaction is spontaneously initiated and both the recovered unreacted allene and the monoadduct **7** are essentially racemic. Racemization of the allene may mean that central attack by tosyl radicals is reversible in this case. Molecular models suggest that a coplanar allylic system within a nine-membered carbocycle may be less comfortable than a nonplanar system owing to torsional strain and unfavorable nonbonded interactions. A nonplanar chiral radical **39** lacks the 10 kcal of allylic resonance stabilization[18] and could conceivably be formed reversibly in a nearly thermoneutral process. Furthermore, rapid conformational interconversion of **39a** with its mirror image **39b** would lead to the recovery of a racemic adduct and racemic allene, as observed.



The behavior of 1,2-cyclononadiene in radical additions is also interesting when compared with polar additions. A major product in the ionic addition of bromine to 1,2-cyclononadiene is 1,4-dibromocyclononene arising by way of a 1,5-transannular hydride shift.[2] However, no products related to 1,5-transannular hydrogen-atom transfers were observed in the radical addition of either tosyl iodide or bromotrichloromethane to 1,2-cyclononadiene. Evidently, internal hydrogen abstraction in **39** cannot compete effectively with abstraction of a halogen atom (Br or I) from an external reagent.

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(14) M. Asscher and D. Vofsi, *J. Chem. Soc.*, 4962 (1964); S. J. Cristo and D. I. Davis, *J. Org. Chem.*, **29**, 1282 (1964).

(15) W. E. Truce and G. C. Wolf, *ibid.*, **36**, 1727 (1971).

(16) Truce and Wolf (ref 12 and 15) have also observed that tosyl iodide addition to phenylallene gives the adduct of central attack by $ArSO_2$, *i.e.*, $C_6H_5CH{=}C(SO_2Ar)CH_2I$.

(17) L. R. Byrd and M. C. Caserio, *J. Amer. Chem. Soc.*, **92**, 5422 (1970).

(18) D. M. Golden, N. A. Gac, and S. W. Benson, *ibid.*, **91**, 2136 (1969).

Another noteworthy aspect of tosyl iodide addition to allenes is the selectivity of product formation. Whereas central attack by a tosyl radical could in principle lead to a mixture of isomeric allylic iodides, only one isomer is actually formed. Selectivity of this kind has also been observed in the addition of tosyl iodide to alkynes, giving a single 1:1 adduct by way of anti (trans) addition.[15] In the present case, the tosyl radical is evidently selective in its *direction* of approach as well as in its locus of attack, since either a cis or a trans adduct is formed but not both (Table II). Also, the intermediate allylic radicals react selectively in the atom-abstraction step to transfer iodine in all cases except one to the least substituted allylic terminus to form the product having the most highly substituted double bond (Table II). The one apparent exception is **6**, the adduct of 2-methyl-2,3-pentadiene, which is formed by iodine transfer to the most highly substituted allylic terminus. While it is entirely possible that product stability controls the observed selectivity in product formation, this cannot be established with certainty from the present data. In contrast, radical reagents such as HBr,[9] thiols,[10] and tin hydride[5] are less selective in the atom-transfer step of radical additions to allenes than is tosyl iodide, although the most stable of the possible adducts formed from these reagents are the major products.

Addition of Halomethanes.—The products of addition of iodomethane, iodotrifluoromethane, and bromotrichloromethane to 2,3-pentadiene show that carbon radicals $CH_3\cdot$, $CF_3\cdot$, and $CCl_3\cdot$ attack the terminal allenic carbons. Even in the case of 2-methyl-2,3-pentadiene, the only observable monoadducts reflect terminal attack by methyl radicals (Table IV). This is in distinct contrast to the behavior of tosyl iodide, which in every case except that for propadiene gave adducts of central attack by tosyl radicals. Bromotrichloromethane is apparently less selective than either CH_3I or CF_3I, since adducts of central attack by $CCl_3\cdot$ were isolated from additions to 2,3-pentadiene, 2-methyl-2,3-pentadiene, and 1,2-cyclononadiene. The question of orientation is discussed further below.

Orientation of Addition.—The orientation data obtained in the present study (Tables II and IV) together with pertinent data taken from the literature is summarized collectively in Table I with respect to propadiene and 2,3-pentadiene. The most consistent feature is the high selectivity for central attack on 2,3-pentadiene by $Br\cdot$, $RO\cdot$, $RS\cdot$, $R_3Sn\cdot$, and RSO_2. Radicals of the type $\cdot CX_3$ ($X = H, F, Cl$) are exceptional in showing a relatively high reactivity toward the terminal carbons of both propadiene and 2,3-pentadiene. Another general observation is the increase in reactivity of the central over the terminal positions with increasing methyl substitution, although this is less evident in the behavior of either $CH_3\cdot$ or $CF_3\cdot$ radicals.

Factors that have been considered as influential in determining the orientation in kinetically controlled radical additions to allenes include the electron distribution in the starting allene,[19] polarity of the attacking radicals,[20] steric effects, and the relative stabilities of the allylic and vinylic radicals formed. If the ground-state electron distribution in the allene were of singular importance, products of terminal attack should dominate.[19] Likewise, electrophilic radicals (*e.g.*, $CF_3\cdot$, $Br\cdot$) should show a preference for terminal attack over so-called nucleophilic radicals (*e.g.*, $CH_3\cdot$, $R_3Sn\cdot$), but this is not supported by the data. Steric factors may be expected to favor central attack. In fact, changes in the orientation of addition of the halomethanes can reasonably be ascribed to steric effects. Whereas the carbon radicals $CF_3\cdot$, $CH_3\cdot$, and CCl_3 attack only the terminal position of propadiene, they behave differently toward the methyl-substituted allenes. Thus, the more highly substituted the allene and the larger the attacking radical ($CCl_3\cdot$), the greater the amount of adduct formed by way of central attack (Table IV).

The extent to which the transition states leading to allylic and vinylic radicals are influenced by electronic factors is more difficult to evaluate. Our data clearly imply that planar allylic radicals are involved in the product-forming step of the central-attack pathway, but this does not exclude the possibility that the transition state for central attack has a twisted rather than a planar allylic configuration. In fact, the *lack* of selectivity exhibited by some radicals toward propadiene (Table I) requires that, in these cases at least, the two possible transition states must be closely balanced in energy, which suggests that the 10 kcal of resonance stabilization to be gained by the allylic system on achievement of coplanarity is *not* felt in the transition state for central attack. Other factors that may influence transition-state energies include hyperconjugation effects of terminal methyl groups and the higher strength of the bond forming between the attacking radical and the central carbon relative to the terminal carbon. These effects would both favor central radical attack, particularly in methyl-substituted allenes. On reflection then, it is somewhat surprising that methyl and trifluoromethyl radicals behave differently from all of the other radicals studied thus far in that they selectively attack the terminal positions of propadiene and its methyl analogs. The reasons for this seemingly anomalous behavior are not obvious and further discussion does not seem warranted at this time.

Stereospecificity in $BrCCl_3$ Addition.—The products obtained from bromotrichloromethane and (+)-2,3-pentadiene determine that $CCl_3\cdot$ radicals attack both terminal and central carbons. Recovery of unreacted (+)-2,3-pentadiene of *retained* optical purity assures that attack of $CCl_3\cdot$ at either site is essentially irreversible. The products, however, showed a small net rotation of $[\alpha]^{24}D$ $-0.33°$ which may reasonably be ascribed to the adducts of terminal attack, **26** and **27**. That is, if the allylic bromide **28** is assumed to be racemic, the small residual activity in the products may be related to the stereospecificity of terminal attack, which is evidently low. Racemic or nearly racemic products are to be expected if the attacking radical is nonselective as to which side of the double bond it attacks (path a or b, Scheme I). Accepting this, the 80:20 mixture of racemic **27** and **26** may then be ex-

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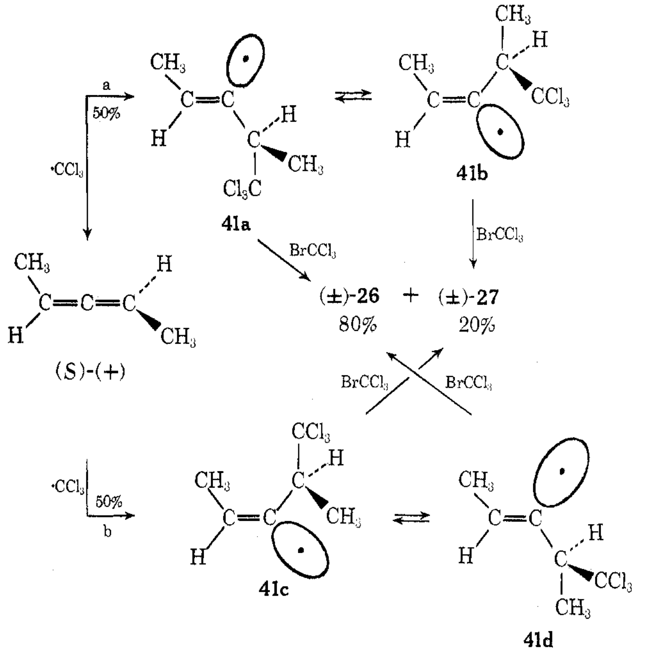
(19) Molecular orbital CNDO/2 calculations indicate that the charge density in propadiene and methyl analogs is greatest at the terminal carbons. This is supported by ^{13}C nmr data, which show the central carbons to be appreciably deshielded relative to the terminal carbons (J. K. Crandall, S. A. Sojka, and W. W. Conover, Indiana University, seminar presented at the International Symposium on Acetylenes, Allenes, and Cumulenes, University of Nottinham, July 1971).

(20) A. P. Stefani, L. Herk, and H. Szwarc, *J. Amer. Chem. Soc.*, **83**, 4732 (1961).

SCHEME I



plained in terms of initially formed vinyl radicals which rapidly equilibrate with their geometric isomers.[21] This is consistent with independent studies on α-alkylvinyl radicals, which in general appear to be configurationally unstable.[22,23] Thus, atom transfer to enantiomers **41a** and **41d** occurs 80% of the time to give (±)-**26** and to enantiomers **41b** and **41c** 20% of the time (apparently for steric reasons) to give (±)-**27** (Scheme I).

Experimental Section

All the allenes used in this study were obtained from Matheson or Chemical Samples except for 2-methyl-2,3-pentadiene and 1,2-cyclononadiene. The former was prepared in 60% yield from 1,1-dibromo-2,2,3-trimethylcyclopropane[24] according to the method of Skattebøl;[25] 1,2-cyclononadiene was obtained in 87% yield from *cis*-9,9-dibromobicyclo[6.1.0]nonane by the method of Skattebøl and Solomon.[26] Partial resolution of 2,3-pentadiene and 1,2-cyclononadiene was achieved by the method described earlier.[2]

p-Toluenesulfonyl (tosyl) iodide was prepared (freshly before each use) in 90% yield from sodium *p*-toluenesulfinate dihydrate (Eastman, practical grade) and iodine according to a published procedure.[27] Methyl iodide (Mallinckrodt) and trifluoromethyl iodide (PCR, Inc.,) were analyzed by glpc (>99% pure) and used without treatment. Bromotrichloromethane (Aldrich) was distilled under nitrogen from molecular sieves prior to use.

Addition of Tosyl Iodide.—A typical procedure is given below for 3-methyl-1,2-butadiene. About 10.35 g (36.8 mmol) of tosyl iodide was dissolved in ~50 ml of anhydrous pentane in a 150-ml Fischer-Porter Pyrex high-pressure cylinder equipped with valves and pressure gauge. About 7.0 g (103 mmol) of 3-methyl-1,2-butadiene was weighed into the vessel and sufficient ether was added to ensure homogeneity. The resulting light orange solution was degassed, then irradiated for 30 min with a 250-W heat lamp positioned about 6 in. away. The color gradually faded to a pale yellow, at which time reaction was complete. The vessel was cooled to −78° to cause precipitation of the crystalline adduct. The cylinder was vented at room temperature, solvent and unreacted allene were decanted, and the product was blown dry with nitrogen. One recrystallization from 95% ethanol afforded 9.42 g (26.9 mmol, 73% based on tosyl iodide) of pale yellow crystals, mp 77–80°. Characterization of this and related adducts was based on ir, nmr (Table II), and solvolysis data (Table III). Configuration (cis or trans) was based on the observation that vinylic protons of vinyl sulfones are markedly deshielded (7.0–7.3 ppm) when cis to the sulfonyl group.[28]

Reaction with (*S*)-(+)-2,3-pentadiene was carried out as for the racemic material except that 15.0 g of a 42% (w/w) solution (6.3 g, 93 mmol) of partially resolved 2,3-pentadiene, $[\alpha]^{28}\text{D}$ 23.20 ± 0.05° (*c* 30, ether), and 5.82 g (20.6 mmol) of tosyl iodide were used. After the solution was heated for 30 min with the lamp, the ethereal solution of 2,3-pentadiene was decanted and distilled (6.1 g of a 38% solution in ether) and showed $[\alpha]^{28}\text{D}$ 21.61 ± 0.05° (*c* 27, ether). The crude adduct (7.0 g, 98%) showed no observable activity.

Reaction with (*S*)-(−)-1,2-cyclononadiene (10.0 g, 80 mmol), $[\alpha]^{28}\text{D}$ −23.20 ± 0.05° (neat), and 11.28 g (40 mmol) of tosyl iodide in ether was spontaneous and exothermic. The supernatant was dried ($MgSO_4$) and distilled to give 2.8 g of 1,2-cyclononadiene, bp 63–65° (11 mm), $[\alpha]^{28}\text{D}$ 0.46 ± 0.05° (neat). This residual rotation was attributed to a small amount of (+)-α-pinene carried over from the partial resolution. The crude adduct (13.8 g, 85%) showed no observable activity.

Silver-Assisted Methanolysis of the Tosyl Iodide Adducts.—An identical procedure was followed in the methanolysis of each of the adducts. A typical procedure for a particular adduct follows. To a solution of 3.50 g (10.0 mmol) of 3-tosyl-4-iodo-2-methyl-2-butene (**4**) in 50 ml of anhydrous methanol and 20 ml of $CHCl_3$ was added a solution of 2.05 g (13 mmol) of $AgBF_4$ in 25 ml of anhydrous methanol. Yellow silver iodide precipitated quantitatively and exothermically. The solution was filtered, 150 ml of ether was added, and the solution was washed successively with 50-ml portions of 10% aqueous $NaHSO_4$ (twice) and distilled water (five times). The solution was dried for 3 hr over anhydrous magnesium sulfate and filtered, and the solvent was removed at reduced pressure. The yield of colorless, viscous oil was 2.50 g (9.8 mmol), 98% of theory based on starting adduct. Analysis by nmr was straightforward (Table III) and revealed a mixture of 3-tosyl-4-methoxy-2-methyl-2-butene (**10**) (61%) and 2-tosyl-3-methoxy-3-methyl-1-butene (**11**) (39%). Product percentages in this and all other methanolyses were determined directly by nmr integration.

Addition of Methyl Iodide.—A 6-in. quartz test tube was charged with a solution of 2.5 g (36.7 mmol) of (±)-2,3-pentadiene in 10.43 g (73.4 mmol) of methyl iodide. The solution was degassed and the tube was sealed at liquid nitrogen temperatures. The tube was suspended in a 150-ml quartz well containing iced water. The well itself was supported within the center of four parallel low-pressure mercury resonance lamps, 90% of the output being 253.7 nm (Ultraviolet Products, Inc.). After irradiation for 10 hr, the tube was opened at −78°. Unreacted methyl iodide and (±)-2,3-pentadiene were distilled away at atmospheric pressure and the residual material was distilled at 25° (5 mm) to give a volatile fraction constituting 23% of the total product mixture. Two 1:1 adducts were isolated from this fraction by preparative glpc in the ratio of 75:25. The major adduct was identified from its nmr spectrum (Table IV) as *trans*-3-iodo-4-methyl-2-pentene (**19**) and the minor adduct as the cis isomer **20**. Geometry was assigned from the fact that a vinylic proton cis to halogen is deshielded relative to a corresponding trans proton.[29] (*Cf.* the spectra of CF_3I adducts **23**, **24**, and **25**.) The chemical shift of the methine heptet in both **19** and **20** is the same as that reported for a very similar compound, 2-iodo-3-methyl-1-butene.[30] Repetition of the above experiment in the presence of 0.95 g (12.2 mmol) of benzene as internal standard showed that 44% of the allene was consumed in

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[21] Linear vinylic radicals **41** would also accommodate the results.

[22] O. Simamura in "Topics in Stereochemistry," Vol. 4, N. L. Allinger and E. L. Eliel, Ed., Wiley-Interscience, New York, N. Y., 1969.

[23] (a) L. A. Singer and N. P. Kong, *Tetrahedron Lett.*, 2089 (1966); *J. Amer. Chem. Soc.*, **88**, 5213 (1966); (b) J. A. Kampmeier and R. M. Fantazier, *ibid.*, **88**, 1959 (1966).

[24] W. von E. Doering and A. K. Hoffmann, *J. Amer. Chem. Soc.*, **76**, 6162 (1954).

[25] L. Skattebøl, *Acta Chem. Scand.*, **17**, 1683 (1963).

[26] L. Skattebøl and S. Soloman, *Org. Syn.*, **49**, 35 (1969).

[27] F. C. Whitmore and N. Thurman, *J. Amer. Chem. Soc.*, **45**, 1068 (1923).

[28] J. Uliana, D. Brundage, and M. C. Caserio, unpublished results, University of California, Irvine.

[29] R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," 2nd ed, Wiley, New York, N. Y., 1967, p 138.

[30] S. A. Sherrod and R. G. Bergman, *J. Amer. Chem. Soc.*, **93**, 1925 (1971).

10 hr. The 1:1 adducts produced were completely inert to $AgBF_4$ in methanol.

Addition of methyl iodide to 2-methyl-2,3-pentadiene was carried out similarly. Glpc analysis revealed a very complex product mixture of which 26% corresponded to 1:1 adducts. These were isolated and identified as 3-iodo-2,4-dimethyl-2-pentene (**21**) (72%; ir 1624, 1374, and 1385 cm^{-1}) and *trans*-3-iodo-4,4-dimethyl-2-pentene (**22**) (28%; ir 3030, 1625 and 1362 cm^{-1}). The trans geometry for **22** was assigned by comparison of the chemical shift of the vinyl proton to that of **19**. Both **21** and **22** were inert to $AgBF_4$ in methanol.

Addition of Trifluoromethyl Iodide.—A 150-ml Fischer-Porter Pyrex high-pressure cylinder equipped with inlet and bleed valves and pressure gauge was charged with 3.0 g (44.1 mmol) of (±)-2,3-pentadiene. The tube was cooled to −78° and evacuated, and 15.2 (77.4 mmol) of trifluoromethyl iodide was condensed into the cylinder. The solution was degassed and then irradiated at 25° for 24 hr using a Hanovia medium-pressure mercury vapor uv utility lamp. The excess CF_3I was vented and the unreacted allene was distilled away at atmospheric pressure (1.2 g, 40%). The slightly pink residue was taken up in 50 ml of ether and washed successively with 50-ml portions of 10% aqueous $Na_2S_2O_3$ (twice) and distilled water (twice). The colorless ethereal solution was dried over anhydrous $MgSO_4$ and filtered, and the ether was removed by rotary evaporation at 100 mm. The residual liquid was flash distilled at 25–40° (0.5 mm) to give 4.32 g of a colorless, fruity-smelling liquid, trapped at −78°, and about 2.3 g of a dark resinous material which could not be distilled. Analysis by glpc revealed a very complex mixture of products, including three major volatile products comprising about 44% of the total. The 1:1 adduct fraction was isolated virtually free from higher molecular weight products by flash distillation at room temperature (10 mm). The three suspected 1:1 adducts were isolated by preparative glpc. The most volatile and least abundant product (9%) was identified as *trans*-3-iodo-2-pentene (**23**). Geometry was assigned by comparison of δ_a, δ_b, and J_{ab} with those of similar compounds **19** and **22** (Table IV). The compound was inert to methanolic $AgBF_4$; ir 1638 cm^{-1} (C=C), 200–450 cm^{-1} (C–I). Its ^{19}F nmr spectrum was transparent within the range accessible by the spectrometer. The major adduct (70% of mixture of 1:1 adducts) was characterized as *trans*-3-iodo-4-trifluoromethyl-2-pentene (**24**) on the basis of its ^1H and ^{19}F nmr and ir spectra. Geometry was assigned by analogy to the cis–trans vinyl iodide isomers previously characterized (*cf.* **19**, **22**, **23**, Table IV). Orientation was confirmed by the inertness to methanolic $AgBF_4$ and also by the magnitude of J_{HF}. The value of 8.8 Hz (Table IV) derived from the ^{19}F doublet is entirely consistent with a vicinal H–F interaction but incompatible with an H–F interaction through three carbon atoms.[31] Its ir spectrum showed 1630 (C=C), 1130, 1175, 1255 (C–F), 900, 955, 1000 cm^{-1} (=CH bend). The minor 1:1 adduct was similarly characterized as *cis*-3-iodo-4-trifluoromethyl-2-pentene (**25**). Its ir spectrum showed 1620 (C=C), 1120, 1165, 1255 (C–F), 900, 955, 955 cm^{-1} (=CH bend). Several of the higher molecular weight products were isolated by preparative glpc and examined by ^1H and ^{19}F nmr spectroscopy. The spectra were very complex and in no case could they be correlated to 1:1 adducts of opposite orientation, 2:1 adducts of either orientation, or secondary photoproducts derived in any simple fashion from the observed 1:1 adducts.

Addition of Bromotrichloromethane to (±)-2,3-Pentadiene.—A 100-ml round-bottom flask equipped with thermometer, reflux condenser, and magnetic stirrer was charged with 10.0 g (0.147 mol) of (±)-2,3-pentadiene, 50.0 g (0.253 mol) of bromotrichloromethane, and 0.57 g (0.0024 mol) of benzoyl peroxide. The mixture was stirred at room temperature until solution of the peroxide was complete, then gradually heated to 80°, whereupon gentle reflux began. The reaction mixture was refluxed for 2.5 hr, during which time the temperature of reflux reached 95°. Unreacted hydrocarbon and bromotrichloromethane were removed by flash distillation at 25–40° (1 mm). The residual sweet-smelling liquid was distilled *in vacuo* at 0.5 mm to give three fractions: (1) 56–60°, 4.50 g; (2) 60–65°, 10.4 g; (3) 65–68°, 21 g. Each of the fractions showed clearly by nmr a mixture of three 1:1 adducts, and so were combined. Isolated yield of product oil is 61% based on starting allene.

The orientation of two of the adducts was assigned as **26** and **27** by reason of their inertness toward methanolic silver tetrafluoroborate. Their nmr spectra, in particular the chemical shifts of their methine quartets (δ_c 3.50, 3.77, Table IV) are compatible with allylic CX_3 (*cf.* **24**, **25**, Table V) but incompatible with allylic Br (*cf.* **28**, **31**, Table IV). By analogy to **24**, **25** and **19**, **20**, trans geometry was assigned to the major terminal attack adduct **27** (47%) and cis to the minor isomer **26** (12%).

Addition of $BrCCl_3$ to 2-methyl-2,3-pentadiene was carried out similarly; 12.06 g (0.147 mol) of hydrocarbon, 50.00 g (0.253 mol) of $BrCCl_3$, and 1.0 g (0.0041 mol) of benzoyl peroxide were refluxed (80–85°) for 2 hr. After distillation to remove unreacted materials, the mixture was distilled *in vacuo*. The major fraction (18.50 g), bp 80–88° (0.1 mm), corresponded to compounds **29** and **30** (Table IV). The structures assigned are supported by the structures of the methanolysis products (Table V) and from their mass spectra: **29** showed *m/e* 278, 280, 282, 284 in the ratio of 1:2:1.3:0.3 and corresponds to M^+ containing the elements $BrCl_3$; **30** showed *m/e* 198, 200, and 202 in the ratio 1:1:0.3 for M^+ containing three chlorines.[32]

Reaction of $BrCCl_3$ with 1,2-cyclononadiene in the mole ratio of 2:1 gave a quantitative conversion to adduct **31** after 2 hr at 75° in the presence of benzoyl peroxide.

Silver-Assisted Methanolysis of Halomethane Adducts.—Reactions were carried out essentially as described previously for the tosyl iodide adducts. The structures assigned the products are shown in Table V along with the nmr data. Compounds **19**–**27** failed to react, consistent with the absence of allylic halogen. The mass spectrum of the product obtained from **28** showed *m/e* 180, 182, 184 in the ratio of 65:41:7, corresponding to M^+ containing two chlorines. The fragmentation on electron impact and the nmr spectrum support the assigned structures as **32** and **33** corresponding to solvolysis of allylic chlorine and bromine. Solvolysis of **29** gave **34** (*m/e* 230, 232, 234 in ratio 1:1:0.3), and **30** gave **35** for which no parent molecular ion was observed in its mass spectrum. Solvolysis of **31** gave a complex mixture which could not be analyzed satisfactorily.

Registry No.—**1**, 35890-15-4; **2**, 35925-44-1; **3**, 35890-16-5; **4**, 35890-17-6; **5**, 35890-18-7; **6**, 35890-19-8; **7**, 35890-20-1; **8**, 35890-21-2; **9**, 35890-22-3; **10**, 35890-23-4; **11**, 35890-24-5; **12**, 35890-25-6; **13**, 35890-26-7; **14**, 35890-27-8; **15**, 35890-28-9; **16**, 35890-29-0; **17**, 35890-30-3; **18**, 35895-34-2; **19**, 35895-35-3; **20**, 35895-36-4; **21**, 35895-37-5; **22**, 35895-38-6; **23**, 35895-39-7; **24**, 35895-40-0; **25**, 35895-41-1; **26**, 35895-42-2; **27**, 35895-43-3; **28**, 35895-44-4; **29**, 35895-45-5; **30**, 35895-46-6; **31**, 35895-47-7; **32**, 35895-48-8; **33**, 35895-49-9; **34**, 35895-50-2; **35**, 35925-45-2; propadiene, 463-49-0; 1,2-butadiene, 590-19-2; 3-methyl-1,2-butadiene, 598-25-4; 2,3-pentadiene, 591-96-8; 2-methyl-2,3-pentadiene, 3043-33-2; 1,2-cyclononadiene, 1123-11-1.

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[32] J. H. Beynon, R. A. Saunders, and A. E. Williams, "The Mass Spectra of Organic Molecules," Elsevier, Amsterdam, 1968, p 376.