result from some unusual solvent interaction associated with the highly fluorinated substituent. The perfluoroisopropyl group also showed a decreased σ value when determined from the pK_a of benzoic acids in this solvent system; actually the σ_m of the perfluoroisopropyl group calculated from the pK_a of the benzoic acid in 50% ethanol–water had previously been noted to be low compared to parameters determined by other methods.[9] Whether this solvent interaction effect involves the un-ionized or ionized form is not clear at this point.

In conclusion, the pentafluorophenyl group is electron withdrawing inductively, but much weaker than the trifluoromethyl group or single halogen atoms.[17] The interaction between the p electrons of the five fluorines and the π system obviously greatly disturbs the electron distribution in the phenyl ring so that it no longer behaves as a typical aromatic system. Many of the unusual properties of perfluoroaromatic compounds, particularly perfluorophenylorganometallic, cannot be simply ascribed to a strong electron-withdrawing effect of the pentafluorophenyl ring but rather to the unusual π system that results from p–π interactions.

Acknowledgments. We wish to acknowledge with thanks the special assistance received from Mrs. Joan Hogan on pK_a measurements, Miss Ellen Wallace for ultraviolet measurements, Mr. Louis Walther for nmr calibrations, and Mr. Ed Wonchoba and Dr. Allan Cairncross on synthesis.

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[17] A similar conclusion has been reached by C. A. Tolman [*J. Amer. Chem. Soc.*, **92**, 2953 (1970)] from a spectroscopic study of the electron donor–acceptor properties of phosphorus ligands.

Stereochemistry of Addition Reactions of Allenes. III. Free-Radical Reactions of 2,3-Pentadiene and 2-Pentyne with *t*-Butyl Hypochlorite

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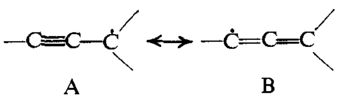
Contribution from the Department of Chemistry, University of California, Irvine, California 92664. *Received December 31, 1969*

Abstract: Free-radical chlorination of 2,3-pentadiene with *t*-butyl hypochlorite has been found to give substitution products that may be formally considered as arising from both allylic and allenic hydrogen abstraction. Allenic abstraction led to formation of 4-chloro-2-pentyne which was also formed in the related chlorination of 2-pentyne. No 2-chloro-2,3-pentadiene was detected in the products from either hydrocarbon. Also, optically active 2,3-pentadiene gave racemic 4-chloro-2-pentyne. These results are discussed in terms of the radical intermediates involved, particularly with respect to the hybrid nature of the 2,3-pentadienyl radical. Competitive chlorination of 2,3-pentadiene and 2-pentyne indicates that the order of reactivity of hydrogen toward *t*-butoxy radicals is allenic ~ propargylic > allylic. Addition products were also formed in the chlorination of 2,3-pentadiene and were identified as *cis*- and *trans*-3,4-dichloro-2-pentene and *cis*- and *trans*-3-*t*-butoxy-4-chloro-2-pentene. Chlorination of optically active 2,3-pentadiene produced racemic adducts, which suggests the intervention of symmetrical resonance-stabilized allylic intermediates. Addition products were the major products of chlorination of 2,3-pentadiene and 2-pentyne in ether solution which reactions were observed to proceed by spontaneous initiation. The major product of reaction with either hydrocarbon as solvent was 4-chloro-2-pentyne. The effects of solvation of *t*-butoxy radicals in determining product distribution and the question of spontaneous initiation are briefly discussed.

Free-radical reactions of certain allenes and isomeric acetylenes and their derivatives can in principle lead to the formation of common resonance-stabilized radical intermediates which may be considered as hybrids of propargylic and allenic structures, A and B.



A B

The physical and chemical evidence pertaining to the hybrid nature of propargylic free radicals and the factors influencing the distribution of propargylic and allenic products obtained with various atom transfer agents have been carefully reviewed by Fantazier and Poutsma.[4] In summary, the relative energies of the two possible transition states and hence the product distribution for reactions at the two nonequivalent termini of propargylic radicals appear to depend in part on the relative thermodynamic stabilities of the derived products and in part on the relative spin densities at the two reacting termini. Steric effects may also play a role but their importance is difficult to evaluate.

In the case of photoinduced halogenation of allenes and acetylenes with chlorine and with *t*-butyl hypohalites, the major substitution products are propargylic halides even when the haloallene is known to be the more stable isomer. Reactions of this type therefore exhibit kinetic control and reflect a greater contribution of the propargylic structure A to the intermediate

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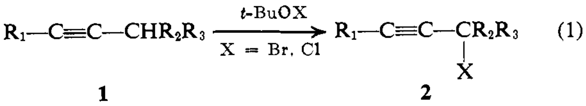
[1] N.D.E.A. Fellow, 1967–present.

[2] The authors wish to gratefully acknowledge the support of this work by the donors of the Petroleum Research Fund of the American Chemical Society (PRF 2357-A1,4).

[3] Part II: W. S. Linn, W. L. Waters, and M. C. Caserio, *J. Amer. Chem. Soc.*, **92**, 4018 (1970).

[4] R. M. Fantazier and M. L. Poutsma, *ibid.*, **90**, 5490 (1968).

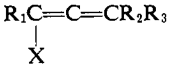
hybrid free radical. For example, Walling and coworkers[5] demonstrated that chlorination of acetylenes **1** with *t*-butyl hypochlorite and hypobromite led to substitution products having the propargyl structure **2** (eq 1). Haloallenes **3** were not obtained. Similarly,



$$R_1{-}C{\equiv}C{-}CHR_2R_3 \xrightarrow[X\,=\,Br,\,Cl]{t\text{-BuOX}} R_1{-}C{\equiv}C{-}\underset{X}{C}R_2R_3 \quad (1)$$

1 **2**

$R_1 = CH_3$; $R_2 = R_3 = H$
$R_1 = C_6H_5$; $R_2 = R_3 = CH_3$
$R_1 = C_6H_5$; $R_2 = R_3 = H$
$R_1 = C_6H_5$; $R_2 = H$; $R_3 = CH_3$



$$R_1\underset{X}{C}{=}C{=}CR_2R_3$$

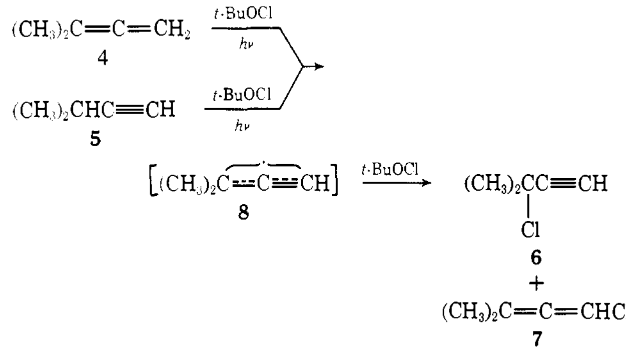
3 (not formed)

Caserio and Pratt[6] reported that propargyl chloride was the sole substitution product formed in the chlorination of both propyne and 1,2-propadiene with *t*-butyl hypochlorite.

$$CH_3C{\equiv}CH \xrightarrow[h\nu]{t\text{-BuOCl}} ClCH_2C{\equiv}CH \xleftarrow[h\nu]{t\text{-BuOCl}} CH_2{=}C{=}CH_2$$

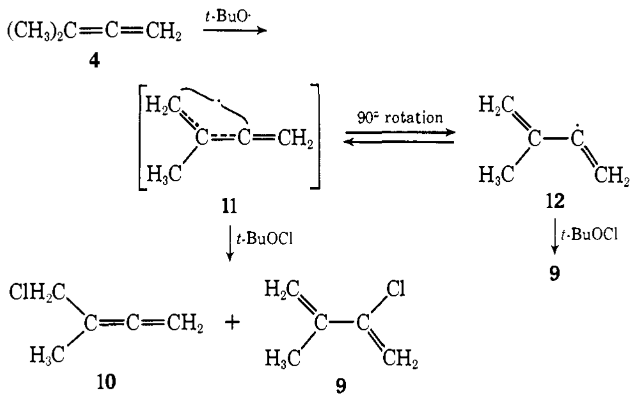
Perhaps the most unequivocal evidence that the same hybrid radical is formed from acetylene and allene precursors comes from the recent work of Poutsma[7] on the photoinduced chlorination of 3-methyl-1,2-butadiene (**4**) and 3-methyl-1-butyne (**5**) with *t*-butyl hypochlorite. The *same* mixture of propargylic and allenic chlorides, **6** and **7**, in the ratio of 1.7:1 was formed from *both* hydrocarbons, as demanded by the intervention of a common hybrid radical **8** (Scheme I).[7a]

Scheme I



Poutsma also found that nearly 40% of the reaction products from the chlorination of **4** were derived from allylic hydrogen abstraction giving rise to 2-chloro-3-methyl-1,3-butadiene (**9**) (38%) and 4-chloro-3-methyl-1,2-butadiene (**10**) (2%). These products reflect the ambident character of the methyleneallyl radical **11** and suggest that the odd electron spin density is concentrated at the sp-hybridized carbon. Intervention of a dienyl radical **12** formed from **11** by a bond rotation of 90° cannot be rigorously excluded, however, and some of the product **9** may possibly arise from **12** (Scheme II).

Scheme II

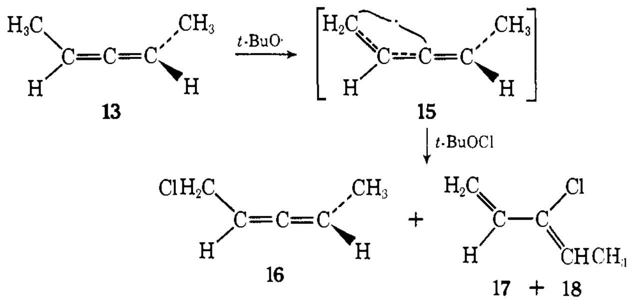


The present work describes the photochlorination of 2,3-pentadiene (**13**) and 2-pentyne (**14**) with *t*-butyl hypochlorite.

$CH_3CH{=}C{=}CHCH_3$ **13** $CH_3CH_2C{\equiv}CCH_3$ **14**

This work was initially undertaken to evaluate the relative reactivities of allylic, allenic, and propargylic hydrogens toward abstraction by *t*-butoxy radicals and to further study the ambident character of allylic and propargylic radical intermediates from the distribution of substitution products obtained. We also hoped to probe the stereochemistry of the radical intermediates involved by employing optically active 2,3-pentadiene as substrate. Thus, we planned to determine the stereochemical integrity of the allylic radical **15** by the preservation or loss of dissymmetry in the allenic product **16**, if such were formed (Scheme III).

Scheme III



The results of this study are described forthwith. They proved to be relevant concerning the natures of the allylic and propargylic radicals involved in the component free-radical *substitution* reactions, as well as the natures of the radical intermediates involved in free-radical *addition* reactions. Thus, the chlorination of 2,3-pentadiene led to unexpectedly large amounts of addition products which proved to be informative as to the types of free radicals formed in the addition process.

Results

Reaction of *t*-butyl hypochlorite with a tenfold excess of 2,3-pentadiene as a 40% solution in ether was

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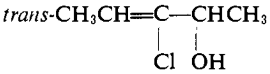
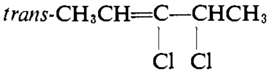
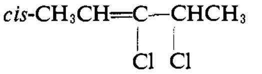
(5) C. Walling, L. Heaton, and D. D. Tanner, *J. Amer. Chem. Soc.*, 87, 1715 (1965).

(6) M. C. Caserio and R. E. Pratt, *Tetrahedron Lett.*, 91 (1967).

(7) M. L. Poutsma, *ibid.*, 2925 (1969).

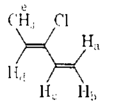
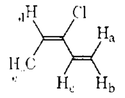
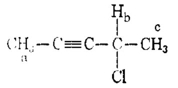
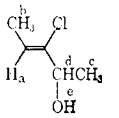
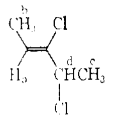
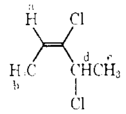
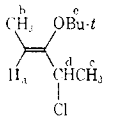
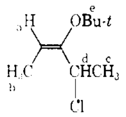
(7a) NOTE ADDED IN PROOF. A recent paper reports the esr of free radicals from a number of acetylenes and allenes [J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, 92, 4110 (1970)]. The authors' findings are pertinent to the present study and may be summarized as follows: (a) the same paramagnetic species $C_3H_3\cdot$ is generated by hydrogen atom abstraction from methylacetylene and allene with *t*-butoxy radicals; other isomeric allene–acetylene pairs give identical radicals (*e.g.*, **8** from **4** and **5**); (b) radicals generated by abstraction of allylic hydrogen atoms of methyl-substituted allenes give esr hyperfine splittings that are more consistent with the alkylene allyl structure than with the localized dienyl structure (*e.g.*, **11** rather than **12**); (c) the reactivities of allenic and propargylic hydrogens toward abstraction by *t*-BuO· are comparable; allenic hydrogens are more reactive than allylic hydrogens, and the secondary propargylic hydrogens of 2-pentyne are more reactive than the primary propargylic hydrogens, which in fact were not abstracted by *t*-BuO· at −93°.

Table I. Product Distribution in the Reaction of 2,3-Pentadiene with *t*-Butyl Hypochlorite

Compound	No.	Reaction products obtained in ether,[a,b] % L[c]	D[d]	Reaction products obtained in neat **13**,[b] % L[c]	D[d]
trans-$CH_3CH{=}CClCH{=}CH_2$	**17**	13.9	13.5	12.2	12.4
cis-$CH_3CH{=}CClCH{=}CH_2$	**18**	19.0	17.4	17.2	12.9
$CH_3C{\equiv}CCHClCH_3$	**19**	4.5	9.9	44.4	41.1
 *trans*-$CH_3CH{=}\underset{Cl}{C}{-}\underset{OH}{C}HCH_3$	**20**	4.5	9.2	Trace	2.5
 *trans*-$CH_3CH{=}\underset{Cl}{C}{-}\underset{Cl}{C}HCH_3$	**21**	22.3	18.2	6.1	7.3
 *cis*-$CH_3CH{=}\underset{Cl}{C}{-}\underset{Cl}{C}HCH_3$	**22**	7.5	7.1	6.8	11.0
trans-$CH_3CH{=}C(t\text{-}BuO){-}C(Cl)HCH_3$	**23**	24.0	21.4	7.8	10.0
cis-$CH_3CH{=}C(t\text{-}BuO){-}C(Cl)HCH_3$	**24**	4.2	3.3	1.0	2.8

[a] An ~40% solution of **13** in ether was used. [b] A 10:1 mol ratio of **13** to *t*-BuOCl was used. [c] Per cent composition of product mixture in light-induced reaction. [d] Per cent composition of product mixture in dark reaction.

Table II. Nmr Spectral Parameters of Products of Reaction of 2,3-Pentadiene with *t*-Butyl Hypochlorite[a]

Compd	No.	δ_a	δ_b	δ_c	δ_d	δ_e	*J*, Hz
	**17**[c]	5.6	5.10	6.37	5.85 (q)	1.79 (d)	$J_{de} = 7.4$ $J_{bc} = 10.6$ $J_{ac} = 17.0$
	**18**[c]	5.6	5.25	6.65	5.81 (q)	1.84 (d)	$J_{de} = 7.6$ $J_{bc} = 10.5$ $J_{ac} = 16.6$
	**19**	1.84 (d)	4.61 (m)	1.68 (d)			$J_{ab} = 2.3$ $J_{bc} = 6.8$
	**20**	5.82 (q)	1.73 (d)	1.34 (d)	4.32 (q)	3.47 (s)[b]	$J_{ab} = 6.6$ $J_{cd} = 6.3$ $J_{ad} = 0.7$ $J_{bd} = 0.7$
	**21**	5.93 (q)	1.75 (d)	1.65 (d)	4.67 (q)		$J_{ab} = 6.7$ $J_{cd} = 6.6$ $J_{ad} = 0.4$
	**22**	5.74 (q)	1.75 (d)	1.63 (d)	5.10 (q)		$J_{ab} = 7.2$ $J_{cd} = 6.5$ $J_{ad} = 0.3$
	**23**	5.84 (q)	1.70 (d)	1.25 (d)	4.08 (q)	1.18 (s)	$J_{ab} = 6.7$ $J_{cd} = 6.4$ $J_{ad} = 0.9$
	**24**	5.57 (q)	1.74 (d)	1.24 (d)	4.50 (q)	1.20 (s)	$J_{ab} = 7.3$ $J_{cd} = 6.4$

[a] Chemical shifts are reported in parts per million downfield from internal TMS; spectra were recorded as 25% solutions in $CDCl_3$. [b] Chemical shift is concentration dependent. [c] The nmr spectra for **17** and **18** are very complex and a complete analysis to obtain all the spectral parameters was not made.

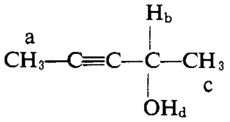
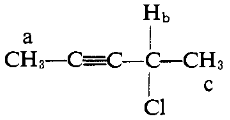
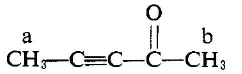
conducted at room temperature in sealed Pyrex ampoules. The mixture was irradiated for 30 min with incandescent light. The reaction products included *t*-butyl alcohol, small amounts of methyl chloride and acetone, and eight products derived from 2,3-pentadiene detected by glpc. Each of these eight products was isolated by preparative glpc and identified from its nmr and ir spectra. The structures assigned to these eight products and the per cent composition of the overall product mixture are listed in Table I. The nmr spectral parameters of the products are summarized in Table II. A more detailed discussion of the structural assignments based on nmr evidence is given in the Experimental Section. The orientation shown for the

Table III. Product Distribution in the Reaction of 2-Pentyne with *t*-Butyl Hypochlorite

Compd	No.	Reaction products obtained in ether,[a,b] % L[c]	D[d]	Reaction products obtained in neat **14**,[b] % L[c]	D[d]
$CH_3C\equiv CCH(OH)CH_3$	**26**	0.7	Trace	5.0	
$CH_3C\equiv CCHClCH_3$	**19**	23.6	26.1	58.0	82
$CH_3C\equiv CC(=O)CH_3$	**27**	2.8		12.0	
$CH_3CCl=CClCH_2CH_3$	**28**	51.8	56.9	4.0	
$CH_3CH_2C\equiv CCH_2Cl$	**29**	11.6	5.9	16.0	12
Higher mol wt products		9.5	11.0	4.0	Trace

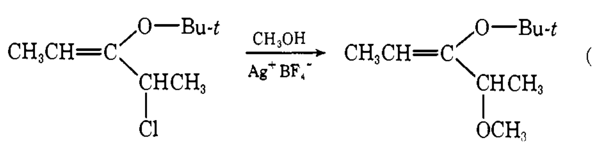
[a] An ~40% solution of **14** in ether was used. [b] A 10:1 mol ratio of **14** to *t*-BuOCl was used. [c] Per cent compostion of product mixture in light-induced reaction. [d] Per cent composition of product mixture in dark reaction.

Table IV. Spectral Parameters of Products from Reaction of 2-Pentyne with *t*-Butyl Hypochlorite[a]

Compd	No.	δ_a	δ_b	δ_c	δ_d	*J*, Hz
 $\overset{a}{CH_3}—C\equiv C—\overset{H_b}{\underset{OH_d}{C}}—\underset{c}{CH_3}$	**26**	1.81 (d)	4.46 (m)	1.40 (d)	2.63 (s)[b]	$J_{ab} = 2.1$ $J_{bc} = 6.5$
 $\overset{a}{CH_3}—C\equiv C—\overset{H_b}{\underset{Cl}{C}}—\underset{c}{CH_3}$	**19**	1.84 (d)	4.61 (m)	1.68 (d)		$J_{ab} = 2.3$ $J_{bc} = 6.8$
 $\overset{a}{CH_3}—C\equiv C—\overset{O}{\overset{\|}{C}}—\overset{b}{CH_3}$	**27**	2.00 or 2.27 (s)	2.27 or 2.00 (s)			
$\overset{a}{CH_3}CCl=CCl\overset{b}{CH_2}\overset{c}{CH_3}$	**28**	2.19 (t)	2.55 (q)	1.10 (t)		$J_{ab} = <1$ $J_{bc} = 7.6$
$\underset{a}{CH_3}\underset{b}{CH_2}C\equiv C\underset{c}{CH_2}Cl$	**29**	1.13 (t)	2.23 (m)	4.11 (t)		$J_{ab} = 7.3$ $J_{bc} = 2.3$ $J_{ac} = 0.7$

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

adduct **23** was established chemically by its facile silver-catalyzed methanolysis to the corresponding methyl ether **25**, showing that the chlorine of **23** must be allylic rather than vinylic (eq 2).



$$CH_3CH=C\begin{smallmatrix}O—Bu\text{-}t\\ CHCH_3\\ |\\ Cl\end{smallmatrix} \xrightarrow[Ag^+BF_4^-]{CH_3OH} CH_3CH=C\begin{smallmatrix}O—Bu\text{-}t\\ CHCH_3\\ |\\ OCH_3\end{smallmatrix} \quad (2)$$

23 **25**

The dark reaction of **13** with *t*-butyl hypochlorite in ether solution was also investigated and gave, after 1.5 hr, the *same* distribution and overall yield as observed in the light-initiated reaction. This result suggests that reaction is spontaneously initiated[5] and this point is discussed in more detail later. Overall, the *major* products obtained from **13** in ether solution were the adducts **21–24** (58%) whereas the substitution products **17–19** amounted to about 38% of the product mixture of which only 4.5% may be attributed to allenic hydrogen abstraction to give 4-chloro-2-pentyne (**19**). When, however, the light-induced chlorination of **13** was carried out in the *absence* of ether, a striking change in the product distribution was observed. The major products were substitution products (**17–19**, 75%) with formation of only 21% of the adducts **21–24**. The single product formed in the highest yield (44.5%) was the allenic abstraction product **19**. The corresponding dark reaction of neat **13** produced the same product distribution as in the light-induced reaction, indicating that spontaneous initiation occurs whether ether is present or not.

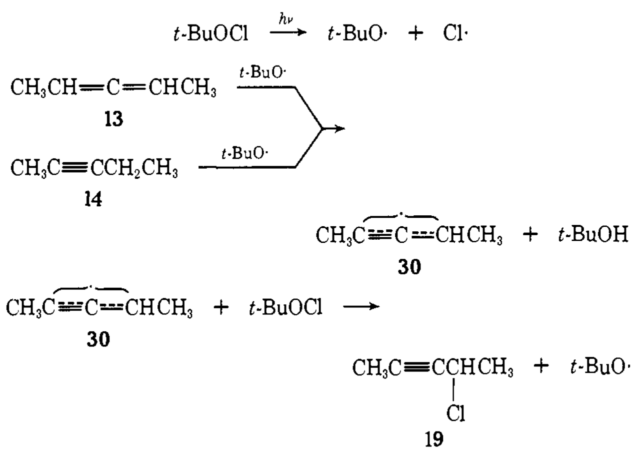
The comparable light-induced reaction of neat 2-pentyne with *t*-butyl hypochlorite using a tenfold excess of the hydrocarbon produced five major products which were isolated by preparative glpc and identified on the basis of their respective nmr and ir spectra. These products and their distributions are listed in Table III and their spectral parameters are summarized in Table IV. Further discussion of the structural assignments may be found in the Experimental Section. The dominant course of reaction was that of substitution to give the propargylic chlorides **19** and **29**. Only 4% of the dichloro adduct **28** was obtained and no products of addition of *t*-butyl hypochlorite were observed. The corresponding dark reaction of 2-pentyne with *t*-butyl hypochlorite was extremely slow. After 2 days, the only products formed were the propargylic chlorides **19** and **29**, and the yields were much reduced relative to those in the light-induced reaction. A substantial change in the product distribution was observed, however, in the chlorination of 2-pentyne in ether solution. Both the light-induced and dark reactions gave essentially the same product distributions in which the major product was the dichloro adduct **28**.

Chlorination of optically active 2,3-pentadiene, $[\alpha]^{25}D$ −13.2° (*c* 21, ether), was carried out as described for the racemic material in ether solution. The product distribution was essentially the same as that reported in Table I for racemic **13** in ether. The major products capable of optical activity, **19**, **21**, and **23**, were isolated by preparative glpc. All three products, namely, the propargylic chloride **19**, the *trans*-dichloro adduct **21**, and the *trans-t*-butoxychloro adduct **23**, had *no* observable optical activity. In contrast, however, the recovered unreacted allene (**13**) had lost none of its initial activity. Since it was difficult to exclude the possibility that the products **19**, **21**, and **23** may have racemized under the conditions of separation by glpc, a different approach was used. Reaction of **13**, $[\alpha]^{25}\text{D}$ $-21.6°$ (c 32, ether), with t-butyl hypochlorite was carried out in ether as before; excess allene was recovered and the residual oily reaction mixture flash distilled at low pressure. The optical rotation of the recovered allene was $[\alpha]^{25}\text{D}$ $-20.6°$ (c 29, ether) while the rotation of the products in the mixture was essentially zero. Barring an extraordinary coincidence of mutual cancellation of optical rotations, we conclude that optically active **13** leads to racemic substitution product **19** and racemic addition products **21** and **23**.

Discussion

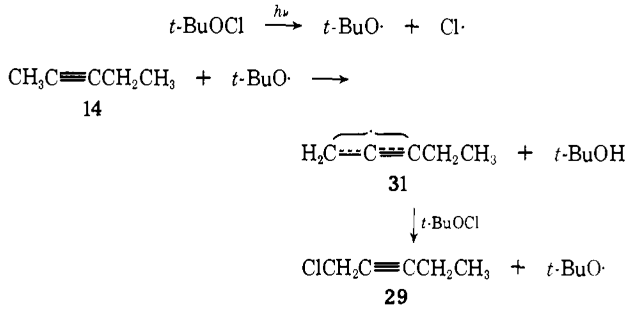
Substitution Reactions. A striking feature of the product distribution obtained in the reaction of 2,3-pentadiene with t-butyl hypochlorite (Table I) is the relatively minor amount of allenic abstraction product present, 4-chloro-2-pentyne (**19**; 4.5%), in the reaction mixture produced in ether solution and the relatively major amount of **19** (44%) formed in the neat hydrocarbon. Likewise, **19** is the major reaction product (58%) in the reaction of neat 2-pentyne with t-butyl hypochlorite (Table III), but the yield of **19** is much reduced in reactions of **14** in ether solution. The important point, however, is that both **13** and **14** yield the propargylic chloride **19** with no detectable amount of the isomeric chloroallene, 2-chloro-2,3-pentadiene. This result is consistent with the formation of the hybrid radical **30** by the reaction sequence of Scheme IV. The finding that racemic **19** was obtained from the reaction of optically active **13** is also consistent with the intervention of a symmetrical radical precursor such as **30**.

Scheme IV



The absence of 2-chloro-2,3-pentadiene in the products agrees with the related findings of Walling and coworkers[5] who observed that chlorination of 2-butyne gave only 1-chloro-2-butyne (eq 1), and with the work of Fantazier and Poutsma[4] who found that chlorine abstraction of 1-chloro-2-butyne with tri-n-butyltinhydride led to a 25:1 ratio of 2-butyne to 1,2-butadiene. Evidently, substitution of methyl groups at the sp terminus of propargylic radicals markedly favors atom abstraction at the sp^2 or propargylic terminus. Further evidence of this is apparent in the formation of 1-chloro-2-pentyne (**29**) from **14**. This product is presumably formed by the reaction sequence of Scheme V in which abstraction of the 1-propargyl hydrogen of **14** occurs in the first propagation step to give the hybrid radical **31** which subsequently reacts at the *unsubstituted* terminus to give **29**. No 3-chloro-1,2-pentadiene corresponding to abstraction of chlorine at the sp terminus was observed.

Scheme V



The fact that there is a small but distinct preference for abstraction of hydrogen at the 4 position relative to the 1 position of **14** (Table III) is a clear indication that alkyl substitution stabilizes propargylic radicals (*i.e.*, **30** is more stable than **31**—the relative reactivity of hydrogen at C-4 *vs.* C-1 being 6.2 ± 0.6 based on an average of five runs) but the reasons why *both* these radicals undergo further atom abstraction so preponderantly at the propargylic position are not obvious. The most attractive explanation is that propargylic products are formed as the result of two complementary factors, one being the substantial spin density at the propargylic position and the other being the greater stability of the propargylic product *vs.* the allenic products.[8]

A second interesting feature about the chlorination of 2,3-pentadiene is the formation of *trans*- and *cis*-3-chloro-1,3-pentadienes **17** and **18** in significant amounts (Table I). These products may be viewed as formed from the ethyleneallyl radical **32** derived from **13** by abstraction of *allylic* hydrogen (Scheme VI). If this is so, we must conclude that the ratio of allylic to allenic abstraction is strongly solvent dependent since this ratio changes by a factor of 10 on changing the solvent composition from hydrocarbon to a mixture of ether and hydrocarbon. Furthermore, if **17** and **18** are derived from **32**, then chlorine atom abstraction occurs exclusively at the sp-hybridized carbon since none of the anticipated 1-chloro-2,3-pentadiene (**16**) was detected. There is more than a superficial resemblance between the allylic radical **32** and the propargylic radical **31** since both have reacting termini that may be formulated as sp^2 and sp hybridized, yet one reacts exclusively at the sp^2-hybridized terminus (**31**) while the other appears to react exclusively at the sp-hybridized terminus (**32**).

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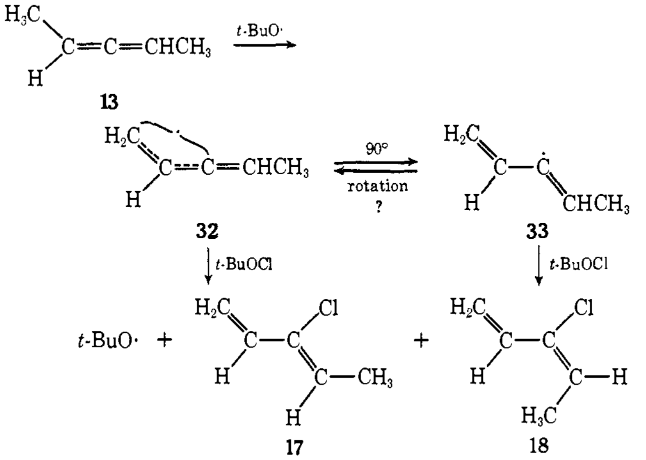
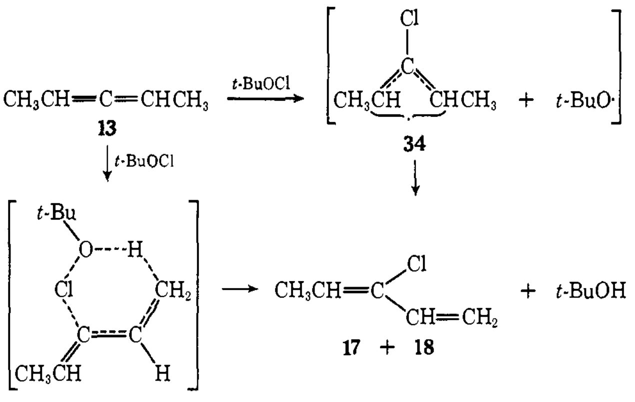
(8) The relative thermodynamic stabilities of the isomeric chlorides **19** and 2-chloro-2,3-pentadiene, **29**, and 3-chloro-1,2-pentadiene are not known. While the rearrangement of primary and secondary 3-halo-1-alkynes to 1-haloallenes is well documented, the corresponding rearrangement of 1- and 4-halo-2-alkynes to the 4- or 2-haloallenes has not to our knowledge been reported. This may indicate that 1- and 4-halo-2-alkynes are more stable than the isomeric haloallenes (*cf.* T. L. Jacobs and W. F. Brill, *J. Amer. Chem. Soc.*, **75**, 1314 (1953); T. L. Jacobs and W. L. Petty, *J. Org. Chem.*, **28**, 1360 (1963). Thermodynamic data for hydrocarbons show that 1,3-disubstituted allenes are significantly less stable than the corresponding isomeric internal acetylenes (*cf.* W. R. Moore and H. R. Ward, *J. Amer. Chem. Soc.*, **85**, 86 (1963); T. L. Jacobs, R. I. Akawie, and R. G. Cooper, *ibid.*, **73**, 1273 (1951)).

Scheme VI



Scheme VII



Admittedly, the two radicals differ in hybridization at the central atom, but this difference does not suggest that the radicals should therefore have very different spin density distributions. One possible explanation for the observed difference in behavior is that the product distribution obtained from the allylic species **32** is *not* controlled by the spin density distribution in the radical but is determined largely by the relative stabilities of the possible products. Formation of the conjugated dienes to the exclusion of **16** then appears reasonable. It should be noted, however, that this view may be oversimplified since the transition state for chlorine-atom abstraction at the sp terminus of **32** does not appear to closely resemble the conjugated dienes since it is twisted 90° out-of-plane from that expected for the normal *s-cis* and *s-trans* conformations of **17** and **18**.

A second explanation for the formation of **17** and **18** may be that the radical precursor is a localized radical **33** formed from **32** by a 90° bond rotation (Scheme VI). This explanation is unattractive for several reasons. Theoretical calculations of the extended Hückel type predict that radicals of type **32** should be more stable than **33**.[7a,9] Also, Walling and Thaler[10] have shown that chlorine abstraction by allylic radicals is faster than rotation about the allylic bond. We had in fact planned to determine whether or not bond rotation in the allylic radical **32** could take place by measuring the preservation or loss of dissymmetry in the allene **16** obtained from optically active **13**, but since **16** was not formed, our plans were foiled.

There is yet a third, eminently reasonable explanation for the formation of the dienes **17** and **18**. This involves a mechanism of *addition* of a chlorine atom to the central allenic carbon of **13** to give the allylic radical **34** and a *t*-butoxy radical (Scheme VII). Hydrogen abstraction, presumably within the radical cage, would then give the dienes **17** and **18**. Alternatively, the reaction may be a concerted homolysis. This mechanism is plausible for the reason that the allylic radical **34** may be formed in the overall reaction as evidenced by the production of 3,4-dichloro-2-pentenes, **21** and **22**, which is discussed later in the paper. Also, Bumgardner and McDaniel[11] have obtained evidence that photodifluoramination of allene gives the substitution product $HC{\equiv}CCH_2NF_2$ by way of an addition–elimination sequence rather than by hydrogen abstraction. A further point in favor of the mechanism of Scheme VII is the observation that the ratio of substitution products **17** and **18** to **19** formed in the chlorination of **13** is profoundly affected by the presence of ether (Table I). If the substitution products are all formed by way of hydrogen abstraction reactions in a conventional radical-chain mechanism, it is difficult to explain why the presence of ether should greatly change the relative reactivities of allylic *vs.* allenic hydrogen toward *t*-butoxy radicals. Admittedly, solvent effects are known to change the distribution of hydrogen abstraction products, but they are rather small.[12a] More specifically, Walling and Mintz[12b] have shown that the chlorination of a mixture of cyclohexane and 2,3-dimethylbutane with *t*-butyl hypochlorite in the presence of ether is spontaneously initiated and also involves chlorination of ether, but the relative reactivities of the two hydrocarbons and the product distributions obtained agree with those found in the normal photoinduced reaction in the absence of ether. In the present case of chlorination of 2,3-pentadiene, the main effect of ether in the reaction mixture is to increase the amount of addition products **21–24** at the expense of the propargylic chloride **19**. This suggests that **19** is formed by a chain reaction (Scheme IV) that becomes kinetically short in the presence of ether. The fact that the proportion of dienes **17** and **18** is the same with ether as without suggests that a different mechanism may be involved in their formation from that giving rise to **19**. This is speculative, however, and our evidence is insufficient to allow for any firm conclusions at this time. Whatever the respective mechanisms are that lead to the substitution products, **17**, **18**, and **19**, it is important to note that the ratio of propargylic product to chloro dienes formed in the absence of ether approaches 6:4. This ratio is in excellent agreement with that obtained by Poutsma[7] in the related chlorination of 3-methyl-1,2-butadiene under comparable conditions and verifies his findings that, under the stated conditions, allenic hydrogens are more reactive than allylic hydrogens toward substitution with *t*-butyl hypochlorite. In terms of atom abstraction, this represents a relative reactivity of *allenic vs. allylic hydrogen* of 4.5.

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[9] R. M. Kopchik and J. A. Kampmeier, *J. Amer. Chem. Soc.*, **90**, 6733 (1968).

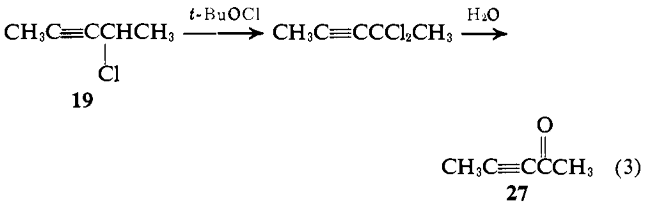
[10] C. Walling and W. Thaler, *ibid.*, **83**, 3877 (1961).

[11] C. L. Bumgardner and K. G. McDaniel, *ibid.*, **91**, 1032 (1969).

[12] (a) C. Walling and P. J. Wagner, *ibid.*, **86**, 3368 (1964); (b) C. Walling and M. J. Mintz, *ibid.*, **89**, 1515 (1967).

To assess the reactivities of allylic and allenic hydrogen relative to propargylic hydrogen, *t*-butyl hypochlorite was allowed to compete for a large excess of an equimolar mixture of 2,3-pentadiene and 2-pentyne. From the relative amounts of substitution products formed (see Experimental Section), the relative reactivities of *allenic vs. propargylic methylene hydrogen* were estimated as 0.77 ± 0.18, *allenic vs. propargylic methyl hydrogen* as 4.7 ± 0.6, *allylic vs. propargylic methylene hydrogen* as 0.10 ± 0.01, and *allylic vs. propargylic methyl hydrogen* as 0.63. From these data, the estimated value for the relative reactivity of allenic *vs.* allylic hydrogen of **13** is 7.6 ± 2 which may be compared to the value of 4.5 determined by direct experiment (Table I). The agreement is not impressive but is probably within the limits of experimental uncertainty. It is interesting to note that the methylene hydrogens of **14** and the allenic hydrogens of **13** have similar reactivities. This substantiates earlier findings that abstractions of propargylic and allenic hydrogen to give the same ambident radical occur at comparable rates.[6,7] Of equal interest is the observation that allylic hydrogens of **13** appear to be only slightly less reactive than propargylic methyl hydrogens of **14** although they are tenfold less reactive than the methylene hydrogens of **14**.[7a]

Before concluding the discussion of the substitution reactions of **13** and **14**, some mention should be made of the origin of the minor products **20**, **26**, and **27**. Formation of 3-pentyn-2-one (**27**) could occur by further chlorination of **19** to give 4,4-dichloro-2-pentyne followed by hydrolysis, which may be expected to be rapid (eq 3). This explanation seems unlikely, however, since 3-pentyn-2-one should then be formed in the chlorination of 2,3-pentadiene, but was not detected. Alternatively, both the ketone **27** and the alcohol **26** could be formed by autoxidation of the parent hydrocarbon **14** either during the reaction if traces of oxygen were present or during subsequent work-up. Similarly, formation of **20** from 2,3-pentadiene could result from the trapping of the intermediate radical **34** with traces of oxygen present followed by decomposition of the derived hydroperoxide during or subsequent to reaction. Formation of the alcohols **20** and **26** by hydrolysis of the related chlorides **21** and **19** may be ruled out for the reasons that precautions were taken to exclude moisture and attempts to hydrolyze the chlorides under conditions comparable to the chlorination reactions did not lead to alcohols.

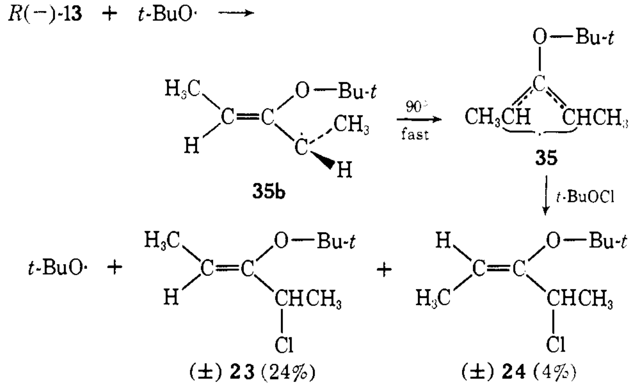


$$\underset{\mathbf{19}}{\mathrm{CH_3C{\equiv}C\underset{\displaystyle Cl}{\underset{|}{C}}HCH_3}} \xrightarrow{t\text{-BuOCl}} \mathrm{CH_3C{\equiv}CCCl_2CH_3} \xrightarrow{\mathrm{H_2O}} \underset{\mathbf{27}}{\mathrm{CH_3C{\equiv}C\overset{\displaystyle O}{\overset{\|}{C}}CH_3}} \qquad (3)$$

Addition Reactions. The major path in the reaction of 2,3-pentadiene with *t*-butyl hypochlorite in ether is one of addition to give *trans*- and *cis*-3,4-dichloro-2-pentenes, **21** and **22**, and *trans*- and *cis*-3-*t*-butoxy-4-chloro-2-pentenes, **23** and **24**. Some 60% of the overall product mixture consists of these monoadducts (Table I). Furthermore, the distribution of addition products is the same in the light-induced reaction as in the dark reaction. Similarly, the major product in the light and dark reactions of 2-pentyne in ether is the dichloro adduct **28**.

The addition of hypochlorites to alkenes is a well-known reaction[13] and the free-radical nature of the reaction has been demonstrated by Walling and Thaler[10] for the light-induced reaction of *t*-butyl hypochlorite with butenes. The addition of *t*-butyl hypochlorite to **13** is accordingly formulated in Scheme VIII as a free-radical chain addition reaction in which the chain-transfer *t*-butoxy radical attacks the *central* allenic carbon to give the symmetrical, resonance-stabilized radical intermediate **35**; subsequent chlorine atom abstraction leads to the observed products, **23** and **24**. The intervention of a symmetrical radical intermediate **35** is implied by the observation that optically active **13** gave racemic adduct **23**. Thus, if the dissymmetric radical **35b** is initially formed, it must rotate 90° to the symmetrical species **35** *faster* than it undergoes chlorine-atom abstraction to give products (Scheme VIII). This is in contrast to representative electrophilic addition reactions of **13** which have been shown to proceed by way of dissymmetric allylic cations.[3,14] Electrophilic addition of *t*-butyl hypochlorite to **13** is conceivable but may be ruled out in the present case on the basis of the observed orientation. Attack of positive halogen is known to occur exclusively at the central allenic carbon of **13**[14] which would lead to the opposite orientation from that observed.

Scheme VIII



The orientation of radical addition of *t*-butyl hypochlorite to **13** reflects that initial attack occurs at the central allenic carbon by the *t*-butoxy radical. This is consistent with previous work on the orientation of radical addition wherein methyl-substituted allenes react preferentially, if not exclusively, by central attack.[15,16] Similar conclusions as to the nature of the allylic radical intermediates involved have been made based on product distributions.[16]

The recovery of unreacted **13** of unchanged optical purity in the light-induced hypochlorite reaction necessarily means that formation of **35** is essentially irreversible.[17] It also means that *radical attack at the*

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[13] For a review, see M. Anbar and D. Ginsburg, *Chem. Rev.*, **54**, 925 (1956), especially pp 929–933.

[14] W. L. Waters, W. S. Linn, and M. C. Caserio, *J. Amer. Chem. Soc.*, **90**, 6741 (1968).

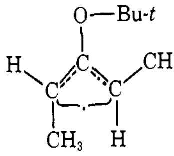
[15] T. L. Jacobs and G. E. Illingsworth, Jr., *J. Org. Chem.*, **28**, 2692 (1963).

[16] (a) H. G. Kuivila, W. Rahman, and R. H. Fish, *J. Amer. Chem. Soc.*, **87**, 2835 (1965); (b) R. Y. Tien and P. I. Abell, *J. Org. Chem.*, **35**, 956 (1970).

[17] The free-radical addition of HBr and thiols to allene has been

terminal allenic position occurs to a negligible extent since no products of this orientation were observed and reversible addition at the terminal position would be expected to lead to racemic **13**.

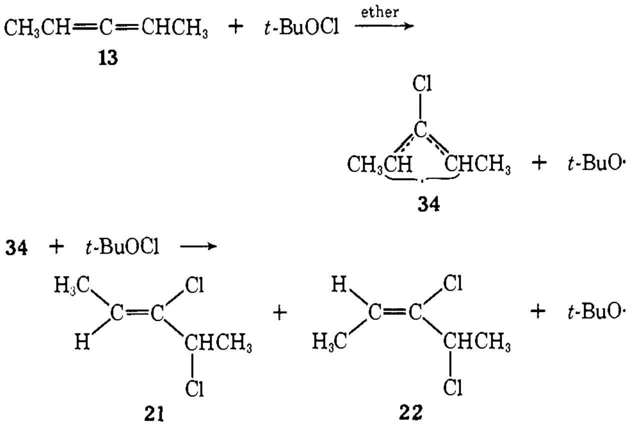
Reasons for the preponderance of the *trans*-isomer **23** over the *cis*-isomer **24** are not obvious, although models do show that the *trans* isomer may be more stable since nonbonded interactions would appear to be more severe between *cis*-methyl and chloroethyl groups than between *cis*-methyl and *t*-butoxy groups. The fact that the *cis* isomer is formed at all suggests that the radical leading to products can exist at least in part in the conformation **35a**. Reaction of **35a** with *t*-BuOCl would give the *cis* isomer at one terminus and the *trans* isomer at the other.



35a

There remains the problem of accounting for the formation of the dichloro adducts **21**, **22**, and **28** in the reactions of **13** and **14** with *t*-butyl hypochlorite. An explanation is also required of the change in product distribution in reactions of **13** and **14** with and without ether present. Walling and coworkers[5] observed that substantial amounts of dichloro adducts were formed in the reaction of neat 2-butyne with *t*-butyl hypochlorite and they attributed this to a "spontaneous" initiation process involving the hypochlorite and the alkyne whereby homolysis of the hypochlorite is made energetically feasible by concomitant carbon–chlorine bond formation. Since 2,3-pentadiene resembles 2-butyne in that it reacts rapidly with *t*-butyl hypochlorite whether or not the reaction mixture is irradiated, spontaneous initiation is probably occurring here also. We accordingly represent the formation of **21** and **22** by the homolysis reactions of Scheme IX which involve atom transfer to the central allenic carbon to give **34** followed by a second atom transfer at allylic carbon to give the products.

Scheme IX



However, the totally unexpected increase in the amount of dichloride formation when ether is present is more difficult to explain. Some 30% of the products derived from 2,3-pentadiene are dichloro adducts while 52–57% dichloro adduct is formed from 2-pentyne in ether. Walling and Mintz[12b] have shown that *t*-butyl hypochlorite reacts spontaneously, even explosively, with ether to produce α-chloroethyl ethyl ether. They have also shown that the reaction of saturated hydrocarbons in ether solution can be controlled at low temperatures and proceeds normally. The present reactions of **13** and **14** with hypochlorite in ether cannot, however, be regarded as normal since the product distributions are drastically changed over those obtained in the neat hydrocarbons. If the dichlorides are produced by the molecule-assisted homolysis of the type shown in Scheme IX, then equivalent amounts of chain termination products should be formed, but the nature of these remains obscure—although formation of a small amount of resinous material was observed. In one experiment specifically designed to determine material balance in the chlorination of **13** in ether, 86% of the starting hypochlorite was accounted for in the products **17–24**. Furthermore, the moles of *t*-butyl alcohol formed agreed well with the moles of substitution products **17–19** and dichloro adducts obtained assuming that 2 mol of *t*-butyl alcohol are formed for every mole of dichloro adduct (see Experimental Section).

The presence of molecular chlorine may be implicated in the formation of dichlorides in ether solution since α-chloroethyl ethyl ether, which could be formed initially,[12b] is known to resinify above 0° with probable loss of HCl.[18] Any HCl formed would react with *t*-butyl hypochlorite to produce molecular chlorine which could then add to the hydrocarbon. Careful analysis of the crude reaction mixtures in ether failed to reveal any products of ether chlorination other than varying amounts of white resinous material. The choice of ether as a solvent in radical reactions is usually to be avoided, but it was dictated in the present work by the fact that our method of resolution of **13** utilizes boron trifluoride etherate; the ether present is recovered along with partially resolved **13** from which it cannot easily be separated.

Whatever the origin of the dichlorides, it is important to note that *racemic* **21** was isolated from the reaction of *R*-(−)-**13** with *t*-butyl hypochlorite in ether. We conclude, therefore, that the precursor to **21** is a symmetrical intermediate. If a dissymmetric intermediate is formed initially by virtue of the dissymmetry inherent in the parent allene, rotation to a symmetrical intermediate occurs faster than reaction to give the observed product.

As previously mentioned, the amount of *t*-butyl hypochlorite adducts **23** and **24** formed from 2,3-pentadiene is markedly increased at the expense of the substitution product **19** in ether solution (Table I). The importance of solvation in determining the fate of *t*-butoxy radicals has been amply demonstrated by Walling and Wagner[12] who found that the ratio of β scission to hydrogen abstraction (eq 4 and 5) increases

carefully investigated by Heiba and Haag. These workers found that radical addition at the central carbon produces allylic radicals irreversibly whereas addition to the terminal carbon is reversible: E. I. Heiba, *J. Org. Chem.*, 31, 776 (1966); E. I. Heiba and W. O. Haag, *ibid.*, 31, 3814 (1966). Similarly, addition of HBr to methyl-substituted allenes, including 2,3-pentadiene, has been shown to proceed *via* irreversible attack at the central carbon. See ref 16b.

(18) O. Grummitt, E. P. Budewitz, and C. C. Chudd, "Organic Syntheses," Coll. Vol. IV, Wiley, New York, N. Y., 1963, p 748.

$$(CH_3)_3CO\cdot \longrightarrow CH_3\cdot + (CH_3)_2C{=}O \qquad (4)$$

$$(CH_3)_3CO\cdot + RH \longrightarrow (CH_3)_3COH + R\cdot \qquad (5)$$

significantly with increasing polarity and polarizability of the solvent. The present results show that ether produces a substantial increase in the ratio of addition to substitution products. Solvation effects in the transition states for the two types of reaction may therefore be different. Hydrogen-abstraction reactions of solvated alkoxy radicals require desolvation in the transition state[12] which would explain the reduced yields of **19** in ether. In contrast, our results would indicate that *addition* reactions of alkoxy radicals may not require desolvation of the forming radical and in fact may be stabilized by ether solvation. While admittedly speculative, this explanation of the dominance of addition products **23** and **24** in the chlorination of **13** is quite reasonable and merits further investigation.

Experimental Section

All nmr spectra were recorded with a Varian Associates A-56/60 spectrometer. Optical rotation measurements were taken with a Zeiss polarimeter reading to 0.01°. Gas chromatographic analyses and collections employed a Varian series 200 gas chromatograph with 20 ft × $^3/_8$ in. aluminum column packed with 20% DC-550 fluid on Chromosorb W (AW, DMCS, 45-60). A flow rate of about 150 cc/min was used; the column temperature was maintained isothermally at 85 or 125° as described below.

The *t*-butyl hypochlorite used was prepared according to the procedure described by Teeter and Bell.[19] Racemic 2,3-pentadiene was prepared in 50% yield from the reaction of *cis*- and *trans*-1,1-dibromo-2,3-dimethylcyclopropane[20] with methyllithium according to the method of Skattebøl.[21] The crude reaction mixture was flash distilled and then fractionally distilled through a 1-m spinning band column at a 20:1 reflux ratio to afford an approximately 50% solution of 2,3-pentadiene in ether, bp 36–45°. This sample was used without further enrichment. Samples of 2,3-pentadiene (98% pure) were also purchased from Chemical Procurement Lab., New York, N. Y. Racemic 2,3-pentadiene was partially resolved by the method described previously.[3,14] Samples of 2-pentyne (99% pure) were purchased from Chemical Procurement Lab., New York, N. Y., and were used without further purification.

Light-Initiated Reaction of 2,3-Pentadiene with *t*-Butyl Hypochlorite. A 9.6-g sample of 48% (w/w by glpc) solution of (±)-**13** (4.6 g, 67.7 mmol) in ether was mixed with 0.65 g (6.0 mmol) of *t*-butyl hypochlorite at −78° in a 12-cc Pyrex ampoule. The ampoule was sealed under nitrogen and irradiated at room temperature for 30 min with light from a 100-W unfrosted incandescent bulb positioned about 6 in. from the wall of the ampoule—the entire set-up being wrapped in aluminum foil. Ether and unreacted hydrocarbon (bp 35–40°) were removed by distillation through a 20-cm Vigreux column. The residual yellow oil was analyzed by glpc (column conditions given above) at 85° for 0–30 min and 125° for 30–60 min. During the first isothermal range, products **17–19** were eluted while during the second, **20–24** were eluted; no higher molecular weight products were evident. Using successive 200-μl injections, enough of each fraction was collected for spectral analysis and characterization. The product distribution obtained is listed in Table I.

The reaction of *R*-(−)-**13** with *t*-butyl hypochlorite in ether was carried out as described for (±)-**13** using 8.5 g of 48% (w/w by glpc) ethereal *R*-(−)-**13** having $[\alpha]^{26}\text{D}$ −13.2 ± 0.2° (*c* 21, ether). The excess allene was recovered and found to have $[\alpha]^{26}\text{D}$ −13.2 ± 0.2° (*c* 15, ether). About 120 mg of **19**, 210 mg of **21**, and 160 mg of **23** were isolated by preparative glpc and their respective rotations taken in chloroform using a 1 mm × 1 dm polarimeter tube. Each sample showed $[\alpha]^{26}\text{D}$ 0.00 ± 0.02° (*c* 24–42, $CHCl_3$). In a separate experiment, 6.80 g (44 mmol) of *R*-(−)-**13** as a 44% solution in ether, $[\alpha]^{25}\text{D}$ −21.6 ± 0.2° (*c* 32, ether), was allowed to react with 0.70 g (6.4 mmol) of *t*-butyl hypochlorite as previously described. Some unreacted allene was recovered by distillation and had $[\alpha]^{25}\text{D}$ −20.6 ± 0.2° (*c* 29, ether). The residual products were flash distilled at about 1 mm and a temperature below 90° to give 0.9 g of a colorless oil. Analysis by glpc showed that 40% of **13** was present, and the product distribution was the same as obtained with racemic **13**. The observed rotation of the distilled reaction mixture was $\alpha_{\text{obsd}} = -2.32°$ (neat), and this residual rotation was accounted for solely from the amount of allene remaining in the mixture. Thus, products **19** and **21–24**, which are capable of optical activity, were totally racemic.

Reaction of neat 2,3-pentadiene (6.25 g, 91.7 mmol) with *t*-butyl hypochlorite (1.00 g, 9.17 mmol) was carried out as described for reactions in ether solution. After irradiation for 1 hr, 2.13 g of a yellow oil was isolated and analyzed by glpc. The products included *t*-butyl alcohol, acetone, and methyl chloride, as well as the products listed in Table I.

Dark Reaction of 2,3-Pentadiene with *t*-Butyl Hypochlorite in Ether. This reaction was carried out essentially as described for the light-induced reaction except that a blackened Pyrex ampoule was used. A 5.2-g sample of a 30% (w/w by glpc) solution of **13** (23 mmol) in ether was sealed with 0.6 g (5.5 mmol) of *t*-butyl hypochlorite. After 1.5 hr at room temperature the ampoule was opened and found to contain no unreacted hypochlorite. The product mixture was worked up as before to give 0.9 g of products which, by glpc analysis, showed the same product distribution as in the light-induced reaction (Table I). The dark reaction of neat **13** with *t*-butyl hypochlorite was carried out similarly.

Light-Initiated Reaction of 2-Pentyne with *t*-Butyl Hypochlorite. A mixture of neat 2-pentyne (4.25 g, 62.5 mmol) and *t*-butyl hypochlorite (0.78 g, 7.2 mmol) was sealed in a 10-cc Pyrex ampoule at −78°. The ampoule was irradiated for 1 hr at room temperature as described for **13**. Unreacted 2-pentyne (3.7 g, 98% of theoretical) was removed by distillation through a 20-cm Vigreux column. No unreacted *t*-butyl hypochlorite remained and only traces of acetone and methyl chloride were detected. The residual yellow oil was analyzed by glpc isothermally at 85°. After 40 min, products **19** and **26–29** were eluted. Using successive 200-μl injections, enough of each product was isolated for spectral analysis and characterization. The product distribution is listed in Table III. The related reaction of **14** as a 40% solution in ether was also carried out.

Dark Reaction of 2-Pentyne with *t*-Butyl Hypochlorite. A mixture of 2-pentyne (4.3 g, 63.2 mmol) and *t*-butyl hypochlorite (0.75 g, 6.9 mmol) was sealed in a darkened ampoule and allowed to remain at room temperature for 48 hr; the reaction mixture was worked up as before. About 4.1 g of material was distilled and found by glpc to contain 3.1 g of unreacted **14**, 0.33 g of *t*-butyl hypochlorite, 0.15 g of acetone, and 0.51 g of methyl chloride, corresponding to about 20% consumption of *t*-butyl hypochlorite. The major products were a 7:3 mixture of **19** and **29** (Table III). The related reaction of **14** as a 40% solution in ether was also carried out.

Competitive Chlorination of 2,3-Pentadiene and 2-Pentyne. A mixture of 3.59 g (52.8 mmol) of **13** and 3.59 g (52.8 mmol) of **14** was sealed under nitrogen at −70° in an ampoule with 0.59 g (5.44 mmol) of *t*-butyl hypochlorite. After irradiation for 30 min the color due to the hypochlorite had disappeared. The ampoule was opened and the contents analyzed by glpc for the relative amounts of substitution products present (*i.e.*, **17**, **18**, **19**, **26**, **27**, and **29**). If x mol of substitution products derived from hydrogen abstraction at C-4 of **14** are present (*i.e.*, x mol of **19**, **26**, and **27**), and if y mol of **19** are formed from **13**, z mol of **29** from **14**, and ω mol of **17** and **18** from **13**, then the relative amounts of substitution products are $(x + y):z:\omega$ and were measured as 567:78:98. From these data and the known reactivity of propargylic hydrogens of **14** (*i.e.*, $x/z = 4.1 \pm 0.4$) the following relative reactivities were calculated: $CH_3CH{=}C{=}CHCH_5/CH_3CH_2C{\equiv}CCH_3 = y/x = 0.77 \pm 0.18$; $CH_3CH{=}C{=}CHCH_3/CH_3CH_2C{\equiv}CCH_3 = 3y/2z = 4.7 \pm 0.6$; $CH_3CH{=}C{=}CHCH_3/CH_3CH_2C{\equiv}CCH_3 = 2\omega/6x = 0.10 \pm 0.01$; $CH_3CH{=}C{=}CHCH_3/CH_3CH_2C{\equiv}CCH_3 = 3\omega/6z = 0.63$.

Material Balance Determination in Chlorination of 2,3-Pentadiene in Ether. A mixture of 4.25 g (62.5 mmol) of **13** in 3.80 g of ether was sealed under nitrogen at −70° in an ampoule with 0.85 g (7.18 mmol) of *t*-butyl hypochlorite. After irradiation for 30 min and removal of volatiles as before (7.57 g, 30–50°), a product fraction of 1.18 g was obtained by flash distillation (30–50° at 5 mm). A resinous material, 0.14 g, could not be distilled.

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[19] H. M. Teeter and E. W. Bell, "Organic Syntheses," Coll. Vol. IV, Wiley, New York, N. Y., 1963, p 125.

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

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

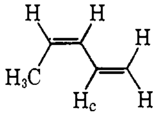
The moles of *t*-butyl alcohol and chlorinated products present in both fractions were estimated by glpc (isothermal ranges of 25, 85, 125°), assuming relative peak areas to be proportional to relative weight per cents. The results shown in Table V were obtained.

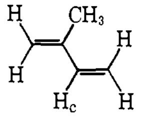
Table V

Component	Mass, g	mmol
Initial *t*-BuOCl	0.85	7.18
t-BuOH	0.48	6.51
cis- and *trans*-$CH_3CH{=}C(Cl)CH{=}CH_2$	0.18	1.73
$CH_3{-}C{\equiv}C{-}\underset{Cl}{C}HCH_3$	0.04	0.40
cis- and *trans*-$CH_3CH{=}\underset{Cl}{C}{-}\underset{Cl}{C}HCH_3$	0.28	2.03
cis- and *trans*-$CH_3CH{=}\underset{t\text{-}BuO}{C}{-}\underset{Cl}{C}HCH_3$	0.12	0.69

Silver-Assisted Methanolysis of *trans*-3-*t*-Butoxy-4-chloro-2-pentene. To about 200 mg of **23** (collected in a capillary tube by preparative glpc) was added methanolic silver tetrafluoroborate. Silver chloride precipitated. The mixture was centrifuged and the supernatant analyzed by nmr. The spectrum showed, besides the resonances due to methanol, a one-proton vinyl quartet at 6.07 ppm, a one-proton allylic quartet at 4.6 ppm, a three-proton singlet at 3.30 ppm, two sets of methyl doublets centered at 1.78 and 1.40 ppm, and a nine-proton singlet at 1.23 ppm. This spectrum is entirely consistent with the structure assigned to the product as 3-*t*-butoxy-4-methoxy-2-pentene.

Spectroscopic Identification of Reaction Products. Configuration was assigned to the 3-chloro-1,3-pentadienes **17** and **18** by the first-order generation of the fine structure for the H_d resonance of each compound (*cf.* Table II) using butadiene as the model for the magnitude of the long-range couplings.[22] The observed fine structure for each isomer was thereby closely reproduced. The assignment was corroborated by comparison of the chemical shifts of the H_c resonances of **17** and **18** with related compounds, namely *cis*-piperylene for which H_c has $\delta = 6.58$ ppm[23] and 2-methylbutadiene for which H_c has $\delta = 6.35$ ppm.[23] The marked dependence of ν_c on geometry has been shown to be quite general in conjugated alkadienes and thus diagnostic of *cis–trans* geometry in such systems.[24]





The configurations of **21** and **22** were assigned by analogy with the closely related *trans*- and *cis*-3,4-dibromo-2-pentenes whose nmr spectra have been reported.[14] Thus, on going from *trans*- to *cis*-3,4-dibromo-2-pentene, the vinylic proton resonance shifts *upfield* by 0.22 ppm while the allylic proton resonance shifts *downfield* by 0.33 ppm. Similarly, on going from **21** to **22**, the vinylic proton resonance shifts 0.19 ppm upfield and the allylic proton resonance shifts 0.43 ppm downfield (*cf.* Table II). Accordingly, **21** and **22** were assigned the *trans* and *cis* configurations, respectively.

The configurations of **23** (νC=C 1670 cm^{-1}) and **24** were assigned by the same analogy to *trans*- and *cis*-3,4-dibromo-2-pentenes used to characterize **21** and **22**. Thus, on going from **23** to **24**, the vinylic proton shifts upfield by 0.27 ppm while the allylic proton shifts downfield by 0.42 ppm. Accordingly, **23** and **24** were assigned the *trans* and *cis* configurations, respectively. The assigned geometry is consistent with the fact that allylic coupling (J_{ad} in Table II) is observed in **23** but not in **24**. In general, such couplings are larger for systems in which the vinyl and allyl protons are in a cisoid relationship (*trans* isomer) than in a transoid one (*cis* isomer).[25] This behavior is likewise observed for the dichlorides since allylic coupling in **21** is slightly larger than in **22** (Table II).

The structure of **20** was established by its nmr spectrum which showed a broadened, concentration-dependent singlet at 3.0–3.5 ppm. Strong O—H absorption bands were also evident at 3600 and 3420 cm^{-1} as well as C=C stretch at 1661 cm^{-1} in the infrared spectrum of **20**. That **20** was actually a 9:1 mixture of *trans* and *cis* isomers was strongly suggested by the presence of nmr resonances identical in pattern with the major ones but chemically shifted and integrating in the ratio of 1:9 minor to major product. The assignment of the major product as *trans* is consistent with the observation that the *trans* adducts generally predominate in this system. Also, the major vinylic resonance exhibited a larger allylic coupling than that of the minor product.

The structure of **19** was unambiguously established from its nmr spectrum. The 13-line fine structure of the resonance ascribed to the propargylic proton could be generated by a first-order analysis using the coupling constants determined from the methyl region.

Compound **26** was characterized by the similarity of its nmr spectrum to **19** and by the concentration-dependent broad singlet at about 2.5 ppm (*cf.* Table IV).

The ketone **27** was identified by comparison of its nmr[26] and infrared[27] spectra with those reported in the literature. The infrared spectrum of **27** showed νC≡C at 2220 and 2280 cm^{-1}, and νC=O at 1680 cm^{-1}.

The geometry about the double bond in **28** was not established.

The structure of **29** was unambiguously assigned on the basis of its nmr spectrum (Table IV) and its infrared spectrum (νC≡C 2248 cm^{-1}).

Acknowledgment. The authors would like to express their appreciation for the helpful comments received from the referees in their evaluation of this work.

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[22] R. T. Hobgood, Jr., and J. H. Goldstein, *J. Mol. Spectrosc.*, **12**, 76 (1964).

[23] D. F. Koster and A. Danti, *J. Phys. Chem.*, **69**, 486 (1965).

[24] C. G. Cardenas, *Tetrahedron Lett.*, 4013 (1969).

[25] E. D. Becker, "High Resolution Nmr," Academic Press, New York, N. Y., 1969, p 97.

[26] L. B. Sokolov and A. A. Petrov, *J. Org. Chem. USSR*, **2**, 994 (1966).

[27] M. Fontaine, J. Chauvelier, and P. Barchewitz, *Bull. Soc. Chim. Fr.*, 2145 (1962).