ing a single residence on the catalyst is much larger on palladium than on platinum.

Experimental

Cycloalkenes.—The preparations and purifications of all of the cycloalkenes except $\Delta^{1,9}$-octalin have been described earlier.[2] $\Delta^{1,9}$-Octalin was prepared as follows: the mixture of isomeric 1-decalols, obtained in 75% yield from 1-naphthol in acetic acid over reduced platinum oxide at 3–4 atmospheres of hydrogen, was oxidized by reverse addition of chromic acid[11] to give 92% of 1-decalone, b.p. 125–130° at 23 mm., n^{27}D 1.4848. This product was reduced with sodium in absolute ethanol[12] to give 75% of *trans-trans*-1-decalol, m.p. 58–60°. The acetate distilled at 117–118° at 10 mm., n^{24}D 1.4706. Pyrolysis of the acetate at 516° furnished 91% of octalins composed of 56% $\Delta^{1,9}$-octalin and 44% $\Delta^{1,2}$-*trans*-octalin. This mixture was hydrogenated in acetic acid with Adams catalyst at 40 p.s.i. until 70% of the theoretical hydrogen has been adsorbed. Chromatography

(11) A. S. Hussey and R. H. Baker, *J. Org. Chem.*, **26**, 1434 (1960).
(12) W. G. Dauben, *et al.*, *J. Am. Chem. Soc.*, **76**, 4420 (1954).

on silica, using petroleum hexane as eluent, furnished $\Delta^{1,9}$-octalin in the trailing fractions, b.p. 99° at 45 mm. This contained less than 0.5% $\Delta^{9,10}$-octalin as indicated by analysis through a 6-foot column of saturated silver nitrate–triethylene glycol on 60–80 mesh fire brick.

Hydrogenation and Analysis.—The cycloalkenes were hydrogenated in purified glacial acetic acid, or ethyl alcohol, in a micro-hydrogenation apparatus as described earlier.[2] Analyses of the product mixtures were by vapor–liquid partition chromatography as before.[2] Part hydrogenations were interrupted at 25 to 50% uptake of theoretical hydrogen.

Catalysts.—Three different samples of commercial palladium-on-charcoal (10%)[13] and palladium-on-barium sulfate (5%)[14] were used in these studies. The latter catalyst appeared to furnish a slightly lesser amount (*ca.* 2%) of the more stable of the two isomers (see footnotes *b*, *c*, *d*, Table I).

(13) The American Platinum Works, Newark, N. J.
(14) R. Mozingo, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 685.

Positive Halogen Compounds. III. Allylic Chlorination with *t*-Butyl Hypochlorite. The Stereochemistry of Allylic Radicals[1]
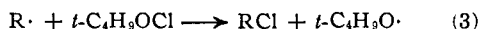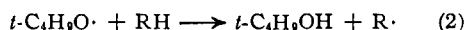
BY CHEVES WALLING AND WARREN THALER

A variety of olefins have been shown to react with *t*-butyl hypochlorite by a photoinduced radical chain process to give good yields of allylic chlorides. Relative reactivities of allylic C–H bonds have been shown to lie in the order primary < secondary < tertiary with further differentiation in each class. A small amount of addition to give β-chloroalkyl *t*-butyl ethers accompanies substitution, and the factors determining the competition are discussed. It is shown that substitution products arising without double-bond shift retain their *cis-trans* stereochemistry, so that *allylic radicals are configurationally stable in this reaction.* The stereochemistry of substitution products which have undergone allylic rearrangement also has been elucidated and is explained in terms of olefin conformation at the moment of reaction. The ratio of allylic isomers from a given allylic radical favors the more substituted olefin, although less so when it is necessarily a *cis* isomer.

Previous work in this Laboratory has shown that *t*-butyl hypochlorite is an efficient free radical chlorinating agent for a variety of hydrocarbons and derivatives.[2] The over-all reaction is effected in non-polar solvents using light or free radical

$$t\text{-C}_4\text{H}_9\text{OCl} + \text{RH} \longrightarrow t\text{-C}_4\text{H}_9\text{OH} + \text{RCl} \quad (1)$$

sources as initiators, and proceeds *via* the radical chain sequence

$$t\text{-C}_4\text{H}_9\text{O}\cdot + \text{RH} \longrightarrow t\text{-C}_4\text{H}_9\text{OH} + \text{R}\cdot \quad (2)$$

$$\text{R}\cdot + t\text{-C}_4\text{H}_9\text{OCl} \longrightarrow \text{RCl} + t\text{-C}_4\text{H}_9\text{O}\cdot \quad (3)$$

Preliminary experiments indicating that the reaction of cyclohexene under these conditions gives 3-chlorocyclohexene in high yield[3] suggested the utility of *t*-butyl hypochlorite as an allylic halogenating agent. This paper describes a study of such allylic halogenations, showing that allylic substitution rather than addition is indeed the preferred reaction of *t*-butoxy radicals with many olefins, and also that allylic radicals may retain their *cis* or *trans* stereochemistry during the reaction.

(2) C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6108, 6113 (1960).
(3) B. B. Jacknow, unpublished work.

Results

Reactions of *t*-butyl hypochlorite with a variety of olefins were carried out in sealed evacuated tubes employing in general 10–20-fold excesses of olefin in order to avoid possible polychlorination and using an incandescent light for photoinitiation. Whenever possible, products were separated and analyzed by gas–liquid chromatography (g.l.c.). Details for particular systems are given in the Experimental Part.

Butenes.—Results on the chlorination of the four isomeric butenes are listed in Table I and

TABLE I

CHLORINATION OF BUTENES WITH *t*-BUTYL HYPOCHLORITE

Butene	T, °C.	Composition of allylic chlorides, %		% Addition product[d]
		1-Chloro-2-butene	3-Chloro-1-butene	
trans-2-	−78.5	83.1 ± 0.2[a]	16.9 ± 0.2	Trace
Butene	40	73.2 ± .3[a]	26.8 ± .3	3–4
cis-2-	−78.5	65.0 ± .0[b]	35.0 ± .0	16.4 ± 0.2
Butene	40	63.2 ± 1.1[b]	36.8 ± 1.1	16.9 ± 0.9
1-Butene	−78.5	73.9 ± 0.1[c]	26.1 ± 0.1	Trace
	40	69.1 ± 0.3[c]	30.9 ± 0.3	3.3
Isobu-	−78.5	Methallyl chloride		11.8 ± 0.1
tylene	40			17.1 ± 0.9

[a] Solely *trans* isomer. [b] Solely *cis* isomer. [c] Mixed *cis* and *trans*, 65 + 5% *trans* at 40°. [d] For structure, see text.

show allylic chlorides to be the major product in every case. The radical chain nature of the re-

TABLE II

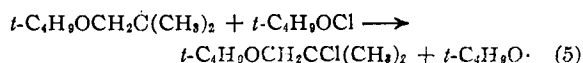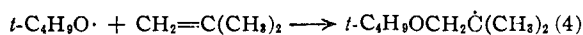PERCENTAGE COMPOSITION OF ALLYLIC CHLORIDES FROM *t*-BUTYL HYPOCHLORITE CHLORINATION OF *n*-PENTENES

Pentene	T, °C.	3-Chloro-1-pentene	1-Chloro-2-pentene		4-Chloro-2-pentene	
			trans	*cis*	*trans*	*cis*
trans-2-Pentene	−78.5	3.5 ± 0.1	12.4 ± 0.6	None	76.1 ± 0.3	7.9 ± 0.5
	0	5.4	15.6	None	69.2	9.8
	40	6.8 ± 0.2	17.2 ± 0.3	None	65.3 ± 0.3	10.7 ± 0.3
	100	9.3	18.9	None	61.9	9.9
cis-2-Pentene	−78.5	7.2 ± 0.1	None	9.9 ± 0.3	57.3 ± 0.1	25.7 ± 0.3
	0	8.5	None	14.5	44.0	33.0
	40	9.7 ± 0.1	None	15.9 ± 0.2	43.4 ± 0.1	33.0
	100[a]					
1-Pentene	−78.5	31.6[b]	54.8	13.6		
	40	41.2 ± 0.1[b]	43.6 ± 0.2	15.2 ± 0.2		

[a] No complete analysis of products, but 1-chloro-2-pentenes approximately 3:1 *cis:trans*. [b] Contains some 4-chloro-1-pentene.

action under our conditions was demonstrated by storing reaction tubes in the dark. After times longer than those required for complete reaction under irradiation no fading of the yellow color of *t*-butyl hypochlorite was noted, and no chlorination products could be detected. Examination of recovered olefin from irradiated systems after reaction also showed no isomerization of 1- to 2-butene, or *cis-trans* isomerization of 2-butene.

Besides the demonstration of allylic chlorination as the chief reaction between *t*-butyl hypochlorite and the butenes, the most interesting feature of Table I is the variation in the ratios of 1-chloro-2-butene to 3-chloro-1-butene and of *cis*- to *trans*-1-chloro-2-butene formed from 1-butene and *cis*- and *trans*-2-butene. This finding is quite incompatible with the idea that all three olefins yield a common allylic radical, and is discussed further below.

The materials listed as addition products in Table I represent small quantities of higher-boiling fractions obtained from the reaction products. That from isobutylene analyzed as a monochlorinated dibutyl ether, had an infrared spectrum consistent with such a structure, and apparently contained a tertiary chlorine as it reacted instantly with AgNO₃. These properties are consistent with 1-*t*-butoxy-2-chloro-2-methylpropane, the expected product from the chain sequence

$$t\text{-}C_4H_9O\cdot + CH_2{=}C(CH_3)_2 \longrightarrow t\text{-}C_4H_9OCH_2\dot{C}(CH_3)_2 \quad (4)$$

$$t\text{-}C_4H_9OCH_2\dot{C}(CH_3)_2 + t\text{-}C_4H_9OCl \longrightarrow$$
$$t\text{-}C_4H_9OCH_2CCl(CH_3)_2 + t\text{-}C_4H_9O\cdot \quad (5)$$

The product from *cis*-2-butene also had an analysis and infrared spectrum consistent with a monochlorodibutyl ether, but g.l.c. analysis showed two peaks of equal size, presumably the *threo* and *erythro* isomers of 2-*t*-butoxy-3-chlorobutane. The product from *trans*-2-butene again gave equal peaks of the same retention times, while that from 1-butene gave a single peak, considered to be 1-*t*-butoxy-2-chlorobutane, but not examined further because of the small amount available.

Pentenes.—Chlorination of the isomeric straight chain pentenes yielded primarily allylic chlorides with only minor amounts of addition products. The latter were not investigated in detail, but in the *cis*-2-pentene system appeared as four small resolved peaks on g.l.c. analysis, amounting to approximately 10 mole % of the total product

and presumably representing the two possible *threo-erythro* isomer pairs.

The compositions of the allylic halides are listed in Table II. In these systems *cis-trans* isomers were clearly resolved by g.l.c., and isomer distributions again vary significantly depending upon the pentene used.

Results of chlorination of the isomeric methylbutenes appear in Table III. Here identification of the individual allylic chlorides was not directly possible by infrared spectra of products collected from individual g.l.c. peaks as in other systems. The methods and arguments used are given in the Experimental section, and we are reasonably confident of the assignments given. Again, allylic substitution is the chief reaction observed, and the small amounts of addition products were not investigated further.

TABLE III

CHLORINATION OF METHYLBUTENES AT 40°

Olefin	Composition of allylic chlorides, %	% addition
3-Methyl-1-butene	1-Chloro-3-methyl-2-butene, 83.2 ± 0.9	2.6
	3-Chloro-2-methyl-1-butene, 16.8 ± 0.9	
2-Methyl-1-butene	2-Methyl-3-chloro-1-butene, 30.1 ± 0.4	6.1
	2-Chloromethyl-1-butene, 22.8 ± 0.3	
	1-Chloro-2-methyl-2-butene A,[a] 26.8 ± 0.1	
	1-Chloro-2-methyl-2-butene B,[a] 20.3	
2-Methyl-2-butene	3-Chloro-3-methyl-1-butene, 4.8 ± 0.1	5.6
	2-Methyl-3-chloro-1-butene, 23.3 ± 0.3	
	1-Chloro-2-methyl-2-butene A,[a] 14.2 ± 0.3	
	1-Chloro-2-methyl-2-butene B,[a] 57.7 ± 0.7[b]	
	1-Chloro-3-methyl-2-butene	

[a] *cis-trans* isomers (unidentified). [b] Not resolved.

No reaction was observed between *t*-butyl hypochlorite and 3-methyl-1-butene in the dark, indicating the absence of any competing polar reaction. With 2-methyl-1-butene at −78°, reaction was complete in 1 hr. with irradiation, but incomplete after 5 days in the dark. However, samples mixed at −78° and then immediately injected into the g.l.c. apparatus showed appreciable chlorination products which however did not increase in quantity if reaction mixtures were kept for longer times at −78° in the dark. Further, the product distribution under these conditions differed markedly from those of irradiated systems, particularly in the absence of 2-methyl-3-chloro-1-butene, the one product which would *not* be anticipated from an electrophilic process. Finally, samples held at 40° in the dark for two hours and then irradiated,

or stored in the dark until complete reaction, gave products identical with initially irradiated samples. All these results, and similar observations with 2-methyl-2-butene, lead us to the conclusion that here, too, the chlorination is a radical chain process, but that, when hypochlorite–olefin mixtures are injected into the g.l.c. apparatus, some non-radical substitution may occur, presumably catalyzed by metals or metal salts present.

Other Olefins.—Chlorination of the isomeric 4,4-dimethylpentenes yielded the mixtures of allylic halides given in Table IV, and again showed significant differences for different starting materials. Examination of unreacted olefin also indicated no isomerization.

TABLE IV

COMPOSITION OF ALLYLIC CHLORIDES FROM 4,4-DIMETHYL-PENTENES

Pentene	T, °C.	1-Chloro-4,4-dimethyl-2-pentene		3-Chloro-4,4-di-methyl-1-pentene
		trans	*cis*	
trans-4,4-Dimethyl-2-	−78.5	93.5 ± 0.2	None	6.5 ± 0.2
	40	88.9 ± 0.1	None	11.1 ± .1
cis-4,4-Dimethyl-2-	−78.5	None	76.3 ± 0.1	23.7 ± .1
	40	38.9 ± 4.6	41.1 ± 4.6	20.0
4,4-Dimethyl-1-	−78.5	94.0 ± 0.2		6.0 ± 0.2
	40	87.8 ± 0.2		12.2 ± 0.2

Chlorinations of cyclohexene and cyclopentene both occurred readily and gave the allylic chlorides as sole detectable products. The chlorination of styrene also was investigated as a case in which allylic substitution is impossible. Styrene and *t*-butyl hypochlorite react violently on mixing, although the reaction shows an induction period when oxygen is present. However, if the hypochlorite is added slowly in the presence of oxygen, holding the temperature just below boiling, a 40% yield of 1:1 addition product may be obtained. When a dilute solution of styrene and *t*-butyl hypochlorite was degassed and stored at 0°, reaction was incomplete in the dark in 24 hr., but went to completion in 30 min. on irradiation. Distillation of the irradiated mixture gave a 72% yield of material analyzing as a 1:1 addition product, and giving an immediate precipitate with AgNO₃, indicating the reaction anticipated from a radical

$$t\text{-}C_4H_9OCl + CH_2\text{=}CHC_6H_5 \longrightarrow$$
$$t\text{-}C_4H_9OCH_2CHClC_6H_5 \quad (6)$$

addition process. Since the products of all three reactions had identical infrared spectra and indices of refraction, we conclude that there is no serious competition from a polar addition.

Competitive Experiments.—In order to determine the relative reactivities of allylic hydrogens in different olefins toward chlorination, a number of competitive reactions were carried out, and followed either by determining the relative rates of hydrocarbon disappearance or appearance of chlorinated products. Results were calculated using the usual equation

$$\log (A_0/A)/\log (B_0/B) = k_A/k_B \quad (7)$$

where k_A/k_B represents the ratio of rate constants for attack by the halogenating agent (here the *t*-butoxy radical) on hydrocarbons A and B, respectively. Reaction mixtures were analyzed by g.l.c., using an internal standard in those cases where

hydrocarbon disappearance was followed[4] and results are given in Table V.

TABLE V

COMPETITIVE CHLORINATIONS WITH *t*-BUTYL HYPOCHLORITE (40°)

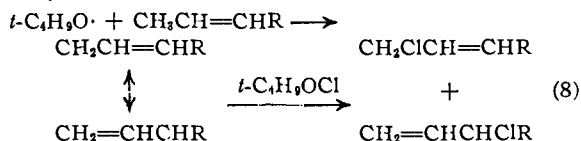| A	B	Internal standard	k_A/k_B
3-Methyl-1-butene	*trans*-2-Butene	CF₂ClCF₂Cl	1.48 ± 0.08
Cyclohexene	Cyclohexane	C₇F₃Cl₄[c]	8.46 ± .74
Styrene	Ethylbenzene	C₃F₃Cl₄[c]	1.65 ± .05
trans-2-Pentene	*trans*-2-Butene	CF₂ClCF₂Cl	2.18 ± .10
Cyclohexane	Cyclopentane	CF₂ClCFCl₂	1.31
trans-2-Pentene	Cyclopentane	CF₂ClCFCl₂	1.87 ± 0.06
Cyclopentene	Cyclohexene	CF₂ClCFCl₂	1.04 ± .04
trans-2-Butene	Isobutylene	[a]	1.67 ± .04
cis-2-Butene	Isobutylene	[a]	1.77 ± .04
trans-2-Butene	*n*-Butane[b]	[a]	2.41 ± .04
cis-2-Butene	*n*-Butane[b]	[a]	2.66 ± .04
1-Butene	*n*-Butane[b]	[a]	2.57 ± .01

[a] k_A/k_B determined from ratio of chlorinated products. [b] On basis of *sec*-butyl chloride formed, so reactivity is relative to secondary hydrogens only. [c] Genetron-112 (Allied Chemicals—General Chemicals Div.) a mixture of isomers which, however, are not resolved in our g.l.c. analysis.

Discussion

The results just presented provide information on three aspects of *t*-butyl hypochlorite chlorination: the stereochemistry of allylic radicals, the relation between structure and reactivity of olefins both in regard to the allylic substitution and its competition with addition, and the positional isomer distribution arising from the reaction of the intermediate allylic radicals with *t*-butyl hypochlorite. These points are considered in order below.
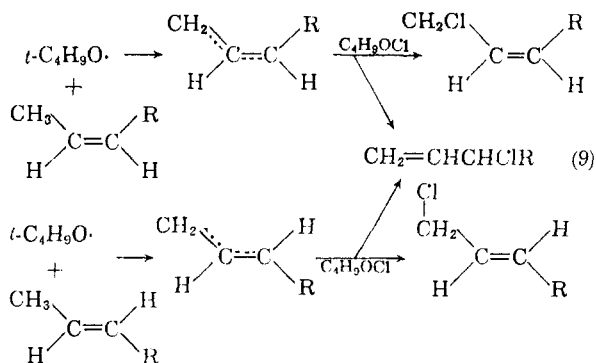
Stereochemistry of Allylic Radicals.—The simplest entry into the problem of the stereochemistry of allylic substitution by *t*-butyl hypochlorite is through a consideration of the products arising from *t*-butoxy radical attack on the C₁-hydrogens of 2-olefins. Here, since no question of stereochemistry arises in the 3-chloro-1-olefin fraction of the

$$t\text{-}C_4H_9O\cdot + CH_3CH\text{=}CHR \longrightarrow$$

$$CH_2CH\text{=}CHR \qquad\qquad CH_2ClCH\text{=}CHR$$

$$\updownarrow \qquad \xrightarrow{\quad t\text{-}C_4H_9OCl \quad} \qquad + \qquad (8)$$

$$CH_2\text{=}CHCHR \qquad\qquad CH_2\text{=}CHCHClR$$

product arising from double bond migration, attention may be concentrated on the 1-chloro-2-olefin product where the double bond retains its position. From Table I it is evident that *complete retention of cis-trans stereochemistry* is observed with the 2-butenes. Similar results are obtained with the 2-pentenes at 40° and below (Table II) and with the 4,4-dimethyl-2-pentenes at −78° (Table IV). Such results are clearly inconsistent with the assumption of a common intermediate radical arising from the isomeric *cis*- and *trans*-olefins, and seem most easily explained on the assumption that *cis*- and *trans*-allylic radicals are able to retain their stereochemistry until they react with t-butyl hypochlorite to yield the observed products, (9).

While the stereochemical results supply the strongest evidence for this conclusion, it may be

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

$$t\text{-}C_4H_9O\cdot \; + \; \underset{H}{\overset{CH_3}{>}}C=C\underset{H}{\overset{R}{<}} \longrightarrow \underset{H}{\overset{CH_2}{>}}C\cdots C\underset{H}{\overset{R}{<}} \xrightarrow{C_4H_9OCl} \underset{H}{\overset{CH_2Cl}{>}}C=C\underset{H}{\overset{R}{<}}$$

$$CH_2=CHCHClR \qquad (9)$$

$$t\text{-}C_4H_9O\cdot \; + \; \underset{H}{\overset{CH_3}{>}}C=C\underset{R}{\overset{H}{<}} \longrightarrow \underset{H}{\overset{CH_2}{>}}C\cdots C\underset{R}{\overset{H}{<}} \xrightarrow{C_4H_9OCl} \underset{H}{\overset{CH_2}{>}}C=C\underset{R}{\overset{H}{<}}$$

$$\underset{Cl}{\overset{\mid}{CH_2}}$$

noted that the cis- and trans-olefins also yield significantly different ratios of 1-chloro-2-olefin and 3-chloro-1-olefin products, consistent with two *different* radicals in the product-determining step.

The idea that a large barrier to free rotation must exist in allylic radicals is consistent with their large resonance energy (approximately 25 kcal./mole), which requires a planar confirmation for its full development.[5] Actually, the barrier may not be as large as might be anticipated, for we see that, with increasingly bulky groups in 9, the cis-allylic radical is sufficiently destabilized so that rotation can occur at higher temperatures. Thus cis-2-pentene gives some trans-product at 100°, while cis-4,4-dimethyl-2-pentene gives a stereochemically clean reaction only at −78°. In any case, the situation may be contrasted with the properties of non-allylic radicals. As in most other cases[6] we find that our cis- and trans-olefins give identical mixtures of threo- and erythro-chloroethers in that portion of the product which arises from addition. Further, there is no evidence that reversibility of addition accounts for the failure of the allylic substitution to remain completely stereospecific at higher temperatures, since no cis–trans isomerization of unreacted olefin could be detected, even in the case of cis-4,4-dimethyl-2-pentene.
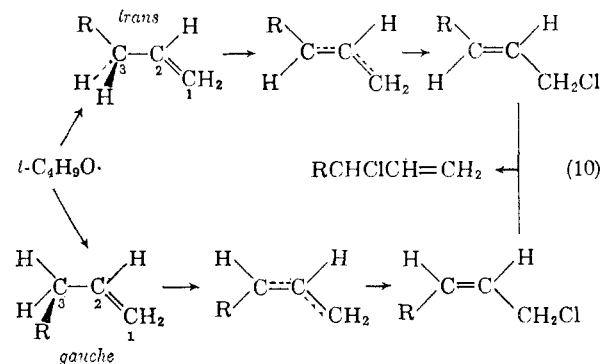
An alternate formulation of our stereospecific allylic substitutions would be a polymolecular process in which the t-butoxy radical reacts with an olefin–t-butyl hypochlorite complex which immediately goes to product plus a new t-butoxy radical without any existence of a "free" allylic radical. Although the only direct evidence against such a scheme is the general observation that relative reactivities of different olefins are apparently concentration independent and only slightly temperature dependent, we regard such a scheme as very unlikely. Goering and Sims have made a careful and unsuccessful search for evidence for such phenomena to explain the trans stereochemistry of HBr addition to 1-substituted cyclohexenes,[7] where the tendency to form such complexes would seem to be much more likely.

(5) C. Walling. "Free Radicals in Solution." John Wiley and Sons, Inc., New York, N. Y., 1957, Ch. 2.

(6) The only case where *addition* reactions to cis- and *trans*-olefins clearly give different stereoisomeric products is in low temperature reactions with HBr. *Cf.* H. L. Goering and D. W. Larsen, *J. Am. Chem. Soc.*, **81**, 5937 (1959); P. S. Skell and R. C. Allen, *ibid.*, **81**, 5383 (1959).

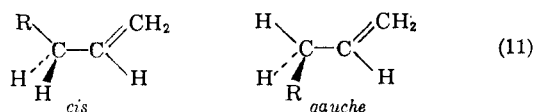(7) H. L. Goering and L. L. Sims, *ibid.*, **77**, 3465 (1955).

The chlorination of 1-olefins permits examination of the stereochemical consequences of double bond shifts during allylic substitution. If it is granted that allylic radicals once formed can retain their stereochemistry, the stereochemistry of the 1-chloro-2-olefins produced must reflect the composition of the allylic radicals formed at the instant of attack on the olefin by the t-butoxy radical. We suggest that this, in turn, is determined by the conformational distribution of the olefin at the moment of reaction, since we are dealing with an extremely rapid low-activation energy process[2] which might be expected to occur by a path involving only very small nuclear displacements. Assuming a staggered conformation of the groups on C_3, and the double bond about C_2–C_3, *trans*- and *gauche*- conformations are possible. Radical

$$\underset{H\;\;H}{\overset{R\quad H}{>}}\overset{trans}{\underset{3}{C}-\underset{2}{C}}\overset{}{\underset{1}{CH_2}} \longrightarrow \underset{H}{\overset{R}{>}}C=C\overset{H}{\underset{CH_2}{<}} \longrightarrow \underset{H}{\overset{R}{>}}C=C\overset{H}{\underset{CH_2Cl}{<}}$$

$$t\text{-}C_4H_9O\cdot \qquad\qquad RCHClCH=CH_2 \longleftarrow \qquad (10)$$

$$\underset{H\;\;R}{\overset{H\quad H}{>}}\overset{}{\underset{3}{C}-\underset{2}{C}}\overset{}{\underset{1}{CH_2}} \longrightarrow \underset{R}{\overset{H}{>}}C\cdots C\overset{H}{\underset{CH_2}{<}} \longrightarrow \underset{R}{\overset{H}{>}}C=C\overset{H}{\underset{CH_2Cl}{<}}$$

gauche

attack on the *trans* form should give rise to the *trans*-allylic radical with a minimum of nuclear displacements, and accordingly to a *trans* product, while the *gauche*-structure gives the cis-radical and cis products.

Although there are two equivalent *gauche* structures so it is statistically favored, it becomes increasingly sterically hindered as –R increases in size, and the *trans* structure should be the one of lower energy. Our results are certainly consistent with this picture. For R = methyl (1-butene) the resulting chloroölefin is 65% *trans* with R = ethyl (1-pentene); R = t-butyl (4,4-dimethyl-1-pentene) products are, respectively, 75% and 100% *trans*.

Alternatively, it is possible that potential minima exist for olefin conformations about C_2–C_3 where $CH_2=$ is eclipsed.[8] Here the situation is less clear-

$$\underset{H\;\;H}{\overset{R\quad CH_2}{>}}\overset{}{C-C}\overset{}{\underset{H}{<}} \qquad \underset{H\;\;R}{\overset{H\quad CH_2}{>}}\overset{}{C-C}\overset{}{\underset{H}{<}} \qquad (11)$$

$$\text{cis} \qquad\qquad\qquad \text{gauche}$$

cut, but it seems evident that the cis-allylic radical would arise more readily from the cis conformation, which again would suffer from increasing intergroup repulsion as the size of R is increased.

The same arguments can be applied to non-terminal olefins where the products resulting from double bond shifts have distinguishable cis-trans stereochemistry. Radical attack on C_4 of cis-2-

(8) Studies of microwave spectra indicate such eclipsing in propylene; D. R. Herschbach and L. C. Krishner, *J. Chem. Phys.*, **28**, 728 (1958).

pentene can give rise to two stereoisomeric allylic radicals, *cis-cis* and *cis-trans*, depending upon olefin confirmation, while attack on C_4 of *trans*-2-pentene can give *cis-trans* or *trans-trans*

$$(12)$$
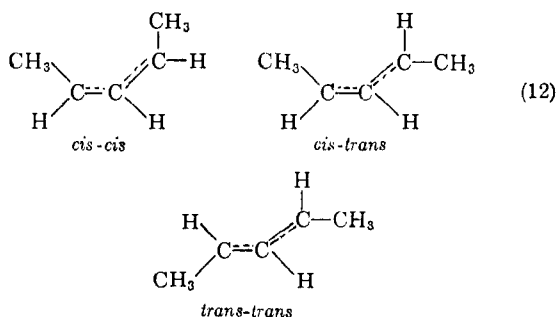
Since *cis-cis* gives rise only to *cis* product and *trans-trans* to *trans* product, while *cis-trans* can give either, it would be predicted that neither olefin would yield a single stereoisomer of 4-chloro-2-pentene, but that more of the *trans* isomer would result from *trans*-2-pentene than from *cis*-2-pentene. From Table II, the *trans/cis* ratios at 40° are 6.1 and 1.31, respectively, both increasing slightly at lower temperatures. Inspection of models indicates that both the *cis-cis* radical and the olefin conformations from which it would arise are highly hindered. If it is assumed, accordingly, that no *cis-cis*-allylic radical is actually formed from *cis*-2-pentene, we may calculate from the above ratios that the allylic radicals from *trans*-2-pentene are actually 34% *cis-trans* and 66% *trans-trans*. This compares well with the stereochemistry observed with 1-butene as it should, since in *trans*-2-pentene C_1 is well removed from the point of radical attack on C_4.

Presumably these same arguments and conclusions can be extended to other free radical allylic substitutions, providing the following criteria are met. First, reaction of the intermediate allylic radical to yield a non-radical product must be sufficiently rapid to compete with isomerization. As we have seen, even the very fast reactions of allylic radicals with *t*-butyl hypochlorite do not always achieve this condition. Second, there must not be a competing reversible addition, leading to olefin isomerization before or after the substitution step.

Although allylic bromination with N-bromosuccinimide has been studied extensively, most workers have ignored the stereochemistry of the products, or have not employed systems where the stereochemistry would be significant.[9] Further, there is real danger that our second criterion would not be obeyed. Small quantities of bromine atoms (traces of which, at least, probably are formed in most NBS reactions[10]) are extraordinarily effective in bringing about both *cis-trans* isomeriza-

tion of olefins, and allylic rearrangement of allylic bromides.[11]

Autoxidation reactions provide a better test, since the reaction of the intermediate allylic radicals with oxygen is extremely rapid,[12] and there is no evidence at present for a reversible addition step. Swern has reported that the hydroperoxides from methyl oleate have predominantly the *trans* configuration.[13] In our interpretation, *trans*-hydroperoxide would only be found in that portion of the product in which a double bond shift had occurred, and it would be interesting to carry out such a study on a molecule where it would be simpler to make a really complete product analysis.

Radical additions to 1,3-dienes present a very similar stereochemical situation, since the relative initial amounts of *cis* and *trans* intermediate radical must depend upon the conformation of the diene molecule. Simple radical additions to butadiene give chiefly 1,4-products, but their stereochemistry has not been reported. The polymerization of butadiene has been studied in detail, and gives approximately 80% 1,4-addition over a considerable temperature range. The *cis* content of the polymer, however, increases strikingly with temperature.[14] Chain propagation here is a relatively slow reaction, so it cannot be said unequivocally whether this is a consequence of isomerization of an initially *trans* radical, or a change in the distribution of conformers in the butadiene.

Relative Reactivities.—The results of the competitive experiments in Table V may be combined with our results on isomer distributions in Tables I–IV and the data reported earlier[2] to calculate relative reactivities per hydrogen for a number of olefins. Results are listed in Table VI, taking a primary hydrogen of *n*-butane as standard (and using a redetermined ratio of secondary/primary hydrogen reactivity in *n*-butane of 12.1).

Considering first the reactivities of various allylic hydrogens, in non-cyclic molecules they fall clearly in the sequence primary < secondary < tertiary, paralleling both expected bond-dissociation energies and electron availability at the reaction site.[2] Within this sequence a further differentiation is apparent. Secondary allylic hydrogens which on reaction give rise to an allylic radical in which the odd electron is delocalized between two secondary carbons are more easily attacked than those giving allylic radicals delocalized between a secondary and a primary carbon. This order corresponds to the expected stability of the allylic radicals and is also observed in a comparison of various types of primary allylic C–H's. Allylic hydrogens in cyclic systems, cyclopentene and cyclohexene, also appear to be abnormally reactive. No comparable increase in reactivity is observed in the cycloparaffins, and, while we have no unequivocal explanation, the result may arise from the fact that in going from

(9) 1-Octene, however, is reported to give 17% 3-bromo-1-octene, 39% *cis*-1-bromo-2-octene and 44% *trans*-1-bromo-2-octene; L. Bateman and J. I. Cunneen, *J. Chem. Soc.*, 941 (1950).

(10) The possibility that NBS reactions proceed entirely through bromine atoms has been suggested by J. Adam, P. A. Gosselain and P. Goldfinger, *Nature*, 171, 704 (1953), and the argument recently espoused by B. P. McGrath and J. M. Tedder, *Proc. Chem. Soc.*, 80 (1961). Evidence on this question from this Laboratory will be published elsewhere.

(11) Reference 5, pp. 302–305.

(12) A. A. Miller and F. R. Mayo, *J. Am. Chem. Soc.*, 78, 1017 (1956), estimate the rate constant for reaction of styrene radicals with oxygen as 3 × 10⁷ at 50°.

(13) D. Swern, *et al.*, *ibid.*, 75, 3135 (1953).

(14) For a summary of data, *cf.* F. E. Condon, *J. Polymer Sci.*, 11, 139 (1953).

TABLE VI

RELATIVE REACTIVITIES OF ALLYLIC HYDROGENS IN t-BUTYL HYPOCHLORITE CHLORINATION AT 40° (RESULTS CALCULATED PER HYDROGEN)

Cyclopentene (allylic H)	383
Cyclohexene (allylic H)	368
3-Methyl-1-butene (t-allylic)	176
trans-2-Pentene (sec-allylic)	94.4
cis-2-Pentane (sec-allylic)	92.1
Cumene (benzyl H)	68.9[a]
1-Butene (sec-allylic)	61.1
2,3-Dimethylbutene (t-H)	42.4
Ethylbenzene (benzyl H)	32.1[a]
cis-2-Butene (p-allylic)	21.1
trans-2-Butene (p-allylic)	19.9
Cyclohexane	15.1
Cyclopentane	13.9
n-Butane (sec-hydrogen)	12.1
Isobutylene (p-allylic)	11.9
Toluene	10.1[a]
t-Butylbenzene	1.06[2]
n-Butene (p-hydrogen)	1.00
2,3-Dimethylbutane (p-hydrogen)	0.95

reactants to allylic radicals in open-chain systems there is an entropy loss in freezing the stereochemistry of planar allylic radical. In a cyclic molecule the system is already largely frozen.

Table VII summarizes all of these conclusions, and compares reactivities of primary, secondary and tertiary paraffinic, benzyl and allylic hydrogens using averaged values from Table VI. From the preparative point of view, while t-butyl hypochlorite gives almost quantitative allylic halogenation of simple molecules, it is evident that complex molecules with many secondary or tertiary C–H bonds will give a mixture of products. Accordingly, in such cases N-bromosuccinimide and analogous N-bromoamides probably are preferable reagents for allylic halogenation.

A small increase in selectivity may be achieved by working at lower temperatures. In trans-2-pentene (Table II) the ratio of attack on C_4 to C_1 increases from 2.54 at 100° to 5.27 at −78.[7] Since we are dealing with the competition between very fast, low activation energy processes, large temperature effects are hardly to be anticipated, and the actual activation energy difference is only 522 cal. A similar difference of 526 cal. can be calculated for cis-2-pentene.

TABLE VII

SUMMARY OF REACTIVITIES OF C–H BONDS IN t-BUTYL HYPOCHLORITE CHLORINATION AT 40°

	Paraffinic	Benzylic	Allylic[a]
Primary	1.0	10	12 (p,p)
			20 (p,s)
Secondary	12.2	32	61 (s,p)
			93 (s,s)
			375 (cyclic)
Tertiary	44	69	176 (t-p)

[a] p,p refers to reaction leading to an allylic radical in which the odd electron is delocalized between two primary carbons, s,p between a primary and secondary carbon, etc.

The relative rates of the competing addition reactions can also be calculated from Tables I–V

and are summarized in Table VIII relative to attack on the primary C–H of n-butane. The sequence 1-butene, 3-methyl-1-butene < isobutylene < styrene is the expected one observed with a variety of radical additions, and parallels both electron supply in the olefin and resonance stabilization of the resulting radical. The greater reactivity of cis-2-butene compared with the trans isomer presumably arises from relief of steric strain in going from cis-olefin to transition state. This appears to be a rather general phenomenon in radical additions to cis-trans pairs in which the development of resonance stabilization in the transition state does not suffer from steric inhibition in the cis isomer.[16]

TABLE VIII

RELATIVE RATES OF t-BUTOXY RADICAL ADDITION TO OLEFINS AT 40° (REACTIVITY TOWARD PRIMARY C–H OF n-BUTANE = 1)

Styrene	105	3-Methyl-1-butene	4.7
cis-2-Butene	25.9	trans-2-Butene	4.4
Isobutylene	14.6	1-Butene	4.2

The magnitude of the difference is surprisingly large, but it is paralleled by the notable difference in yields of addition products observed in cis- and trans-2-pentene ($\sim$10% and <2%). Finally, our data do not show the usual lowering of reactivity of non-terminal olefins ascribable to steric hindrance, since even trans-2-butene is as reactive as 1-butene. In the carbon radical additions involved in copolymerization this difference is generally at least 10-fold,[16] although it is not as large in ·CCl$_3$[17] or RS·[4] additions.

Allylic Isomer Ratios.—The relative yields of the two allylic chlorides (ignoring cis-trans isomers) derived from a given allylic radical are of particular interest since, in our systems, the chlorides are perfectly stable and accordingly truly kinetically controlled products. Our results are summarized in Table IX in terms of ratios of 1-chloro-2-olefin

TABLE IX

RATIO OF 1-CHLORO-2-OLEFIN TO 3-CHLORO-1-OLEFIN IN t-BUTYL HYPOCHLORITE CHLORINATION (AT 40° UNLESS INDICATED)

Olefin	Ratio	Olefin	Ratio
1-Butene	2.24	3-Methyl-1-butene	4.94
trans-2-Butene	2.73	2-Methyl-1-butene	1.56
	4.90[a]	4,4-Dimethyl-1-	7.19
cis-2-Butene	1.72	pentene	15.7[a]
	1.85[a]	trans-4,4-Dimethyl-	7.99
trans-2-Pentene	2.51	2-pentene	14.4[a]
	3.51[a]	cis-4,4-Dimethyl-	4.00
cis-2-Pentene	1.63	2-pentene	3.22[a]
	1.37[a]		

[a] At −78.5°.

to 3-chloro-1-olefin products, the former being the major product in every case. Three factors might be expected to contribute to the relative energies of the two transition states determining product ratios: (1) Odd electron distribution in the radical:

(15) P. M. Lewis and P. R. Mayo, J. Am. Chem. Soc., 70, 1533 (1948).

(16) P. R. Mayo and C. Walling, Chem. Revs., 46, 191 (1950).

(17) M. S. Kharasch and M. Sage, J. Org. Chem., 14, 537 (1949).

Since the stabilizing effect of an alkyl group on a double bond is approximately 2 kcal. (from heats of hydrogenation) and on a radical approximately 4 kcal. (from bond dissociation energies), this should favor the 3-chloro-1-olefin product. (2) Steric hindrance which should favor reaction at C_1 to give 1-chloro-2-olefin. (3) Stability of the product: equilibration of allylic isomers generally gives chiefly the more highly substituted olefin, again favoring the 1-chloro-2-olefin product.

Our results are consistent with a predominant role of items 2 and 3, and the larger ratios with 3-methyl-1-butene and particularly 4,4-dimethyl-1-pentene indicate that steric effects are important. Ratios for *trans*-olefins are larger than for *cis*-, which might be expected since the 1-chloro-2-olefin formed from the *cis*-olefin is necessarily the higher energy *cis* form. Incidentally, the ratio obtained from 1-butene is, within experimental error, that expected from the ratio of *cis*- and *trans*-allylic radicals present as indicated by the ratio of *cis*- to *trans*-1-chloro-2-butene in the product.

Finally, we may note that the ratios increase at lower temperatures. Interestingly, the effect is considerably larger for *trans* radicals than for *cis*. While this can be expressed in terms of entropy and energy factors, we see no obvious explanation.

Experimental

Materials.—Olefins and other hydrocarbons were commercial pure or research grade materials, unless otherwise noted. The 4,4-dimethyl-2-pentenes and *trans*-2-pentene were American Petroleum Institute standard samples. 4,-4-Dimethyl-1-pentene was prepared from *t*-butyl magnesium chloride and allyl bromide as described by Whitmore and Homeyer.[18] *cis*-2-Pentene was a sample which had been prepared in 1939.[19] Purity of all reactants was checked by g.l.c. before use. *t*-Butyl hypochlorite was prepared by the method of Teeter and Bell[20] and handled as previously described.[3]

Allylic Halogenations.—*t*-Butyl hypochlorite (usually 0.5 to 2.5 millimoles) and approximately a 10–20-fold excess of olefin were degassed and sealed in small Pyrex tubes, placed in a thermostat, and irradiated with an incandescent lamp for at least 30 min. after the yellow color of the hypochlorite had disappeared. With this amount of excess olefin, no polychlorination products could be detected. Analyses were carried out by g.l.c. using Perkin–Elmer "A" (diisodecyl phthalate) or "C" (silicone) 2-meter columns at 25 lb. helium pressure unless indicated. Each experiment was analyzed 3–5 times and results (which agreed within 1–3%) averaged, assuming peak areas proportional to concentrations for the allylic isomers involved. Compositions given in Tables I–IV represent means of triplicate (40°) or duplicate or triplicate (other temperatures) experiments, and experimental errors given are deviations of individual experiments from those means. Significant details for individual systems are given below.

Butenes.—1-Chloro-2-butene and 3-chloro-1-butene were resolved on a C column at 27° and had the same retention time as authentic samples. Products from large runs were collected (using an Apiezon column), gave immediate precipitates with AgNO₃, and were identified by gas phase infrared spectra. The *cis* and *trans* isomers of 1-chloro-2-butene could not be resolved, but those from *cis*- and *trans*-2-butene had infrared spectra identical with those reported for *cis*- and *trans*-1-chloro-2-butene, respectively.[21] The product from 1-butene was estimated as 65 ± 5% *trans*

from its infrared spectrum. Analysis of reaction mixtures from each of the butenes at 21° using A and C columns in series (which separate the butenes in the order 1-butene, *trans*-2-butene, *cis*-2-butene) showed no isomerization of unreacted olefin.

Gas–liquid chromatographic analysis on the C column at 82° showed two high-boiling products from the 2-butenes. Those from *cis*-2-butene were collected, gave no precipitate with AgNO₃ in 3 min., and showed an ether band in the infrared at 9.2 μ. They were considered to be the *threo* and *erythro* addition products. *Anal.* Calcd. for C₈H₁₇-OCl: C, 58.34; H, 10.41; Cl, 21.53. Found: C, 58.55; H, 10.20; Cl, 21.42. The product from 1-butene gave a single high-boiling peak, but in too small quantity for characterization.

Isobutylene gave two products with markedly different retention times. The more volatile one had the same retention properties as methallyl chloride. The second was collected, showed a strong ether band in the infrared, and gave an immediate precipitate with AgNO₃ so it was considered to be 1-*t*-butoxy-2-chloro-2-methylpropane, n^{25}D 1.4132. *Anal.* Found: C, 58.53; H, 10.65; Cl, 21.72.

Pentenes.—Gas–liquid chromatographic analysis of the product from 1-pentene at 59° using the A column showed three peaks at 14.6, 26.0 and 27.6 min. Combined *anal.* Calcd. for C₅H₉Cl: C, 57.46; H, 8.68; Cl, 33.93. Found: C, 57.56; H, 8.58; Cl, 33.80. The 14.6-min. peak was collected and gave an immediate precipitate with AgNO₃. Since it showed infrared bands at 10.1 and 10.75 μ it was identified as 3-chloro-1-pentene (probably contaminated with some 4-chloro-1-pentene.) The other two peaks were collected and also gave an immediate precipitate with AgNO₃. They showed a strong infrared band at 10.35 μ and a moderate band at 13.0 μ indicating predominantly *trans*-olefin containing some *cis*. From their relative sizes, the g.l.c. peak at 26.0 min. was thus identified as *cis*-1-chloro-2-pentene and that at 27.6 as *trans*-1-chloro-2-pentene. No higher-boiling products could be detected by gas–liquid chromatographic analysis at 128° or 157°. Gas–liquid chromatographic analysis of the products from *trans*-2-pentene under the same conditions showed four peaks at 14.6 min. (3-chloro-1-pentene), 17.0, 19.0 and 27.6 min. (*trans*-1-chloro-2-pentene). The 17.0- and 19.0-min. peaks were collected together and showed strong *trans*- and weak *cis*-olefin bands in the infrared. From the relative peak heights, the 17.0-min. peak was assigned to *cis*-4-chloro-2-pentene, and the 19.0-min. peak to its *trans* isomer. The products from *cis*-2-pentene also showed four peaks, but at 14.6 (3-chloro-1-pentene), 17.0 (cis-4-chloro-2-pentene), 19.0 (*trans*-4-chloro-2-pentene) and 26.0 min. (*cis*-1-chloro-2-pentene). The 17.0- and 19.0-min. peaks were now of comparable size, and, collected together, showed a stronger *cis*-olefin band in the infrared, confirming the previous assignment. Gas–liquid chromatographic analysis of products from both *cis*- and *trans*-2-pentene at 128° (A column) showed four small peaks of longer retention time. These represented approximately 10% of the product from *cis*-2-pentene, but only traces from *trans*-2-pentene. They were not investigated further, but assumed to be the four possible isomeric addition products.

Methylbutenes.—Six isomeric allylic chlorides are possible from the three methylbutenes investigated. Their structures and retention times from gas–liquid chromatographic analysis (C column, 53°) are listed in Table X, and actual assignment was worked out as follows. Chlo-

TABLE X

RELATIVE RETENTION TIMES (MIN.) OF METHYLBUTENE CHLORINATION PRODUCTS (C COLUMN, 53°)

Butene		
3-Chloro-3-methyl-1-	I	6.6
2-Methyl-3-chloro-1-	II	0.0
2-Chloromethyl-1-	III	13.4
1-Chloro-2-methyl-2-	IVA	16.0
1-Chloro-2-methyl-2-	IVB	18.0
1-Chloro-2-methyl-2-	V	18.0

rination of 3-methyl-1-butene might be expected to give two allylic chlorides, I and V. Gas–liquid chromatographic analysis showed peaks at 6.6 and 18.0 min. The major

(18) F. C. Whitmore and A. H. Homeyer, *J. Am. Chem. Soc.*, **55**, 4555 (1933).

(19) M. S. Kharasch, C. Walling and F. R. Mayo, *ibid.*, **61**, 1559 (1939).

(20) H. M. Teeter and E. W. Bell, *Org. Syntheses*, **32**, 20 (1952).

(21) C. F. Hatch and S. S. Nesbitt, *J. Am. Chem. Soc.*, **72**, 727 (1950).

peak at 18.0 min. was collected. It gave an immediate precipitate with AgNO₃, showed a strong infrared band at 11.9 μ (trisubstituted olefin) and had n^{25}D 1.4477. *Anal.* C, 57.60; H, 8.72; Cl, 32.78. Calcd. for C₅H₉Cl: C, 57.47; H, 8.64; Cl, 33.90. It was accordingly identified as V, and the structure I assigned to the 6.6-min. product. Chlorination of 2-methyl-1-butene could give four allylic chlorides, II. III, IVA and IVB, none identical with I or V, and gas–liquid chromatographic analysis indeed gave four peaks at 10.0, 13.4, 16.0 and 18.0 min., the last appearing at the same time as V. Analysis at 109° also indicated addition product, considered to be 1-*t*-butoxy-2-chloro-2-methylbutane.

Chlorination of 2-methyl-2-butene, in turn, can give five allylic chlorides, I, II, IVA, IVB and V. Gas–liquid chromatographic analysis showed four peaks at 6.6 (I), 10.0, 16.0 and 18.0 min. (V plus another isomer). Since the 13.4-min. peak was absent, but present in the 2-methyl-1-butene product, it was thus identified as III. The 10.0-min. peak was collected and gave an infrared band at 11.05 μ (disubstituted terminal olefin) but no bands at 12 μ (trisubstituted olefin). It was accordingly assigned structure II. The 16.0- and 18.0-min. peaks were collected and showed an infrared doublet at 11.9 and 12.1 μ (trisubstituted olefins) indicating that they contained the *cis-trans* isomers IVA and IVB together with V. Analysis at 111° also showed a higher-boiling product, believed to be 3-*t*-butoxy-3-chloro-2-methylbutane.

4,4-Dimethylpentenes.—Analysis of the reaction products from 4,4-dimethyl-1-pentene (C column, 58°) showed product peaks at 18.0 and 24.0 min. The major peak at 24.0 min. was collected and showed a strong infrared band at 10.3 μ indicating *trans*-1-chloro-4,4-dimethyl-2-pentene, n^{25}D 1.4404. The combined peaks were isolated by fractional distillation of a larger run; b.p. 29–32° (9 mm.). *Anal.* Calcd. for C₇H₁₃Cl: C, 63.40; H, 9.88; Cl, 26.72. Found: C, 63.34; H, 9.71; Cl, 27.12. Analysis of the products from *cis-* and *trans*-4,4-dimethyl-2-pentene also showed product peaks at 18.0 and 24.0 min. The 24-min. peak from the *trans*-olefin had an index of refraction and infrared spectrum identical with that from the 1-olefin. However, that from the *cis*-olefin showed both *cis* and *trans* bands in the infrared. When the chlorination was carried out at −78°, only *cis*-olefin could be detected. This low-temperature product was collected and analyzed. It gave an immediate precipitate with AgNO₃, n^{25}D 1.4441. *Anal.* Found: C, 63.86; H, 9.79; Cl, 27.12. It was subsequently found that the *cis* and *trans* products could be partially resolved on a 10-ft. polysuccinate column at 110°. Reaction

products from each olefin were examined in this manner and the absence of *cis*-allylic chloride from 4,4-dimethyl-1-pentene and *trans*-4,4-dimethyl-2-pentene confirmed. The starting olefins were cleanly separated on a C column at 24°, and the lack of any isomerization demonstrated.

Reaction of Styrene with *t*-Butyl Hypochlorite.—Styrene (20.8 g., 0.2 mole) was placed in an erlenmeyer flask and a few drops of *t*-butyl hypochlorite added. As soon as the yellow color was discharged 10.8 g. (0.1 mole) of hypochlorite was added slowly keeping the mixture just below its boiling point. Distillation gave a 40% yield of product, b.p. 105° (44 mm), n^{25}D 1.5017. The infrared spectra showed a strong ether doublet at 9.0–9.2 μ. Redistillation gave a center cut, n^{25}D 1.5009, with the same infrared spectrum. *Anal.* Calcd. for C₁₂H₁₇CCl: C, 67.75; H, 8.06; Cl, 16.67. Found: C, 68.27; H, 8.27; Cl, 17.03. Since the product gave an immediate precipitate with AgNO₃ (indicating benzylic chlorine) it was considered to be 1-phenyl-1-chloro-2-*t*-butoxyethane. When a similar experiment was carried out adding the hypochlorite all at once and bubbling oxygen through the system, it showed a long induction period and then reacted very violently. The product had an infrared spectrum similar to the first product.

Two samples containing 0.1 mole of styrene. 0.05 mole of hypochlorite and 20 cc. of CF₂ClCH₂Cl were degassed and stored at 0°, one illuminated by an incandescent lamp and the other in the dark. Reaction in the irradiated sample was complete in 30 min., and gave a product with the same infrared spectrum and other properties as the preparation above. The other still contained much hypochlorite after 24 hours.

Competitive Reactions by Product Analysis.—Approximately 2.45 cc. of each of two hydrocarbons were mixed in a 10-cc. reaction tube and a sample withdrawn for accurate gas–liquid chromatographic analysis. *t*-Butyl hypochlorite (0.25 cc.) was added and the tubes degassed, sealed, and irradiated at 40°. The products were then analyzed by gas–liquid chromatography essentially as described above and relative reactivities calculated as in our previous papers.[2]

Competitive Reactions by Reactant Analysis.—Small samples (0.25 cc.) of two hydrocarbons and the internal standard were mixed and a sample withdrawn for gas–liquid chromatographic analysis. Hypochlorite (0.1 cc.) was added, the tubes degassed, sealed and irradiated. Comparison of peak heights before and after reaction then was used to calculate relative reactivities as previously described.[2,4]

Calculated Isotope Effects for Reactions of Lyonium Ion in Mixtures of Light and Heavy Water[1⁻3]

BY C. GARDNER SWAIN AND EDWARD R. THORNTON

Relative nucleophilicities of D₂O, HDO and H₂O are calculated. Equations relating isotope effect to atom fraction of deuterium in the solvent are derived for reactions of L₃O⁺ in water at 25° *via* (1) SL⁺, (2) S--LO⁺L₂ or L₂O⁺SL, and (3) L₂O⁺L---*SL* transition states, where L is H or D in any combination, S is any substrate and L*S* is any substrate with exchangeable L. Curves are shown for the three types for k_D/k_H values of 3, 2, 1, 0.73 and 1/₃.

The Gross equation (1) for the dependence of isotope effect on atom fraction of deuterium in the solvent for reactions of L₃O⁺ with substrates S in water solution at 25° proceeding *via* SL⁺ transition states (L = H or D) was derived in a previous

paper.[2] It applies also to transition states involving water [S--L--OL₂]⁺ or [L₂O--SL]⁺ (L = H or D in any combination) for the extremes of these transition states which have the same charge on this oxygen as in a water molecule. A second equation (2), derived below, applies to the opposite extremes of these transition states, those with the same positive charge on this oxygen as in a lyonium ion. A third equation (3) will be derived for nearly complete attack of water in the special case where the water is removing a proton or deuteron which is in equilibrium with the solvent,

(1) Supported in part by the National Institutes of Health through Research Grant RG-3711(C6) and by a postdoctoral fellowship to E. R. T. from the Division of General Medical Sciences. U. S. Public Health Service.

(2) Paper II in this series by C. G. Swain, R. F. W. Bader and E. R. Thornton. *Tetrahedron.* **10,** 200 (1960).

(3) Previous paper III in this series by C. G. Swain, A. D. Ketley and R. F. W. Bader, *J. Am. Chem. Soc.,* **81,** 2353 (1959).