water. The organic layers were dried over magnesium sulfate, filtered, and evaporated.

Nmr analysis showed the absence of peaks attributable to allyl groups at C-6 of the cyclohexadienones, indicating complete reaction of the starting dienones **4** and **5**. The relative yields of phenols and reduction products from the hydrogenation of compounds **4** and **5** were determined by the relative areas of the aromatic methyl absorptions due to the phenols and the allylic methyl absorptions due to the hydrogenated dienones **10** and **11**. The yield of phenol from hydrogenation of dienone **7** was determined by vpc analysis on a 6 ft × 0.25 in., 3% SE-30 on Chromosorb W column.

Isolation of Products of Hydrogenation. With the exception of the product from reduction of cyclohexadienone **9**, the reaction products from each hydrogenation, after work-up as described above, were dissolved in 10 ml of pentane and extracted with three 10-ml portions of Claisen alkali. The organic fractions were washed with water, dried, and evaporated to give the reduced cyclohexadienones. Pure samples of the previously unreported **10** and **11** were obtained by vpc on a 1 ft × 0.375 in., 30% SE-30 on Chromosorb W column.

The nmr spectrum of **6-isobutyl-4-*tert*-butyl-2,6-dimethylcyclohexa-2,4-dien-1-one (10)** in $CDCl_3$ showed a multiplet (1 H) at δ 7.0 (hydrogen at C-3), a doublet (1 H, $J = 2.5$ Hz) at δ 5.93 (hydrogen at C-5), a broad singlet (3 H) at δ 1.90 (methyl at C-2), singlets at δ 1.15 (9 H) and 1.08 (3 H) for the *tert*-butyl at C-4 and the methyl at C-6, and doublets (3 H, $J = 6$ Hz) at δ 0.76 and 0.88 (methyl groups on isobutyl side chain), as well as a multiplet (*ca.* 3 H) at δ 2.30–1.15 (methylene and methine of isobutyl group).

The nmr spectrum of **2,4,6-trimethyl-6-propylcyclohexa-2,4-dien-1-one (11)** in CCl_4 showed a multiplet (1 H) at δ 6.90 (hydrogen at C-3), a broad singlet (1 H) at δ 6.10 (hydrogen at C-5), a doublet (3 H, $J = 1.5$ Hz) at δ 1.99 (methyl at C-2), singlets (3 H each) at δ 1.93 and 1.11 (methyls at C-4 and C-6), and a multiplet (*ca.* 7 H) at δ 0.73–1.46 (propyl at C-6).

The neutral fraction from hydrogenation of dienone **7** showed a complex spectrum indicating that appreciable hydrogenation of double bonds in the ring had occurred. No pure product could be obtained from this mixture.

The aqueous layers from extraction with Claisen alkalie were acidified with 6 *N* hydrochloric acid and extracted with methylene chloride. The organic layers were washed with water, dried, and evaporated to give essentially pure phenols, which were identified by comparison with samples of known structure.

The hydrogenation product of dienone **9** was shown by vpc to contain a single product, which was identified by its nmr and ir spectrum as the known **2,6-di-*tert*-butyl-4-methyl-4-propylcyclohexa-2,5-dien-1-one.**[13]

Competitive Hydrogenolysis of Benzyl and 2-Methylallyl Groups. A solution of dienones **4** and **6** (3.0×10^{-4} mol of each) in 5 ml of methanol was hydrogenated as usual until *ca.* 20% of the starting materials had reacted. The mixture was filtered free of catalyst, the solvent was evaporated on a steam bath, and the residue was dissolved in 15 ml of pentane and extracted with Claisen alkali. The nmr spectrum of the neutral fraction showed it to consist largely of unreacted starting dienones. The alkaline fraction was acidified and extracted with methylene chloride. The methylene chloride layer was washed with water, dried over magnesium sulfate, and evaporated. The phenols obtained in this manner were analyzed by vpc on a 6 ft × 0.25 in., 5% SE-30 on Chromosorb W column at 170°. Comparison with synthetic mixtures showed the product to be 4-*tert*-butyl-2,6-dimethylphenol and 2,4,6-trimethylphenol in the molar ratio 1.5:1.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for a grant in support of this work.

Registry No.—**4**, 51869-07-9; **5**, 4278-92-6; **6**, 41388-92-5; **7**, 4278-95-9; **8**, 31040-77-4; **9**, 2756-79-8; **10**, 51869-08-0; **11**, 51869-09-1.

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Cis–Trans Isomerization of Allylic Radicals

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Received November 30, 1973

A series of cis and trans allylic halides has been reduced with triphenyltin hydride in a chain reaction which involves allylic radicals. Varying degrees of cis–trans isomerization of the intermediate allylic radicals have been observed and it has been shown that the variation is concentration dependent and also dependent on structure. Attempts to study allylic radicals where there is delocalization of the free electron onto CN, CO_2CH_3, and $CON(CH_3)_2$ by the same technique led to isomerization of starting material or product and thus no conclusion concerning the interconvertibility of the isomeric radicals could be reached. Chlorination of crotonitrile, isocrotonitrile, methyl crotonate, and methyl isocrotonate with *tert*-butyl hypochlorite led to varying amounts of cis–trans isomerization in the intermediate radicals as reflected by the composition of the chloro-substituted products. The factors which control these isomerizations are discussed.

In 1961 Walling and Thaler studied the chlorination of a variety of olefins by *tert*-butyl hypochlorite.[1] They found that in general cis and trans olefins gave cis and trans allylic chlorides, respectively. A notable exception was *cis*-4,4-dimethyl-2-pentene, which at 40° gave *trans*-1-chloro-4,4-dimethyl-2-pentene. It was suggested that the *tert*-butyl group destabilized the intermediate cis allylic radical by introducing steric effects which were not present in the other allylic radicals, and that the rate of conversion of the cis to trans allylic radical was thus enhanced.

Subsequently other workers have investigated the cis–trans isomerization of allylic radicals,[2] and isomerization has been observed under a variety of conditions.[2a-d] In the work being reported here cis and trans allylic radicals have

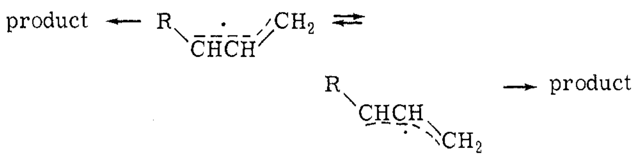
Table I
Composition of Products From Free-Radical Reduction of Allylic Chlorides by Triphenyltin Hydride at 80° in Cyclohexane

RCH=CHCH$_2$Cl	Concn,[a] *M*	Products, % Trans	Cis	1-Olefin
Trans (R = CH$_3$)	Neat	65	10	25
Trans (R = CH$_3$)	0.27	49	23	28
Trans (R = CH$_3$)	0.027	43	22	35
Trans (R = CH$_3$)	0.0135	41	23	36
88% cis, 12% trans (R = CH$_3$)	0.27	35	34	31
88% cis, 12% trans (R = CH$_3$)	0.027	41	25	34
88% cis, 12% trans (R = CH$_3$)	0.0135	41	24	35
Trans (R = C$_2$H$_5$)	0.027	55	17	28
Trans (R = C$_2$H$_5$)	0.0135	53	17	30
Cis (R = C$_2$H$_5$)	0.027	50	17	33
Cis (R = C$_2$H$_5$)	0.0135	53	18	29
Trans (R = *t*-C$_4$H$_9$)[b]	0.27	~90	0	~10
Cis (R = *t*-C$_4$H$_9$)[b]	0.27	~90	0	~10

[a] Concentrations of allylic chlorides and triphenyltin hydride were equivalent. [b] Purified *n*-octane was used as solvent for R = *t*-C$_4$H$_9$.

been generated by reduction of the isomeric chlorides with triphenyltin hydride under a variety of conditions[3] and by hydrogen abstraction with *tert*-butoxy radicals generated by decomposition of *tert*-butyl hypochlorite.

Under these conditions allylic radicals are generated and then consumed by attack on either triphenyltin hydride or *tert*-butyl hypochlorite. If the rate of interconversion of the isomeric radicals can compete with product formation, then isomerization will be found.



Results and Discussion

Reactions of Allylic Chlorides with Triphenyltin Hydride. Several allylic chlorides were allowed to react in a 1:1 mole ratio with triphenyltin hydride. The reactions were carried out in purified cyclohexane at 80° using azobisisobutyronitrile (AIBN) as initiator. For chlorides of the general structure RCH=CHCH$_2$Cl, the product compositions shown in Table I were obtained. In all experiments the purity of the allylic chloride was checked immediately before use by glpc. In the cases of the butenyl and pentenyl chlorides, experiments were performed using an excess of allylic chloride. The purity of the remaining starting material was checked after the reaction was complete. This was done to determine whether isomerization of the starting material occurred under the reaction conditions. In no case where an excess of pure cis or trans allylic chloride was used did isomerized chloride appear in the excess after the reaction was complete. In the case of the 88% cis, 12% trans mixture of butenyl chlorides the composition was observed to change to 76% cis, 24% trans. This change in composition can, on the basis of competition experiments, be attributed to the faster reaction of the cis butenyl chloride. The faster reaction of the cis isomer is probably due to a combination of steric and concentration effects.

For the results to be meaningful in terms of allylic radical isomerization, it is necessary to show that the products as well as the starting materials do not isomerize under the conditions of the reaction. Kuivila and Sommer[4] have shown that triphenyltin hydride will bring about isomerization of *cis*-2-butene on irradiation of neat samples with a 250-W lamp for 24 hr. They suggested that triphenyltin radical adds to the double bond to give a secondary radical. Loss of triphenyltin radical can give either *cis*- or *trans*-2-butene. In principle the secondary radical should be able to react with more triphenyltin hydride to give the addition product. In fact no evidence for addition of triphenyltin hydride to a nonterminal nonactivated double bond has been found. Kuivila and Sommer did find such an addition product from trimethyltin hydride.

The results of Kuivila and Sommer show that isomerization of 2-butenes, etc., by triphenyltin hydride can occur under extreme conditions. The conditions used in this work were much milder than theirs; however, a control experiment was deemed necessary and prudent. Such an experiment was performed by MacGregor at the inception of this work.[2a,5] MacGregor allowed an excess of a mixture of 87% neryl chloride (*cis*-1-chloro-2,7-dimethyl-2,6-octadiene) and 13% geranyl chloride (*trans*-1-chloro-3,7-dimethyl-2,6-octadiene) to react with triphenyltin hydride. After completion of the reaction, the mixture was analyzed for starting material and products. There was no change in the ratio of starting materials and the product ratio showed 87% cis and 13% trans olefin. It was thus concluded that isomerization by addition of triphenyltin radical and subsequent loss of triphenyltin radical does not occur under the conditions of these reactions. Isomerization in solution reactions was found in the neryl and geranyl systems and this was attributed to isomerization of intermediate allylic radicals.[2a] The results of these experiments and those of Kuivila and Sommers have led to the following conclusions: (1) product isomerization is not caused by reaction of product with radicals present in the reaction mixture, and (2) product is not consumed by addition of triphenyltin hydride. In this regard yields of products were not determined in this work; however, indications in the literature indicate that they are extremely high.[6]

The results in Table I show that interconversion and equilibration of allylic radicals is competitive with hydrogen transfer when triphenyltin hydride is the chain transfer agent. By varying the concentration of reactants the rate of the product-forming step, *i.e.*, attack on hydride, and hence the lifetime of the radical is varied. At sufficiently low concentrations the product-forming step slowed to a point where equilibrium between cis and trans radicals was established. As expected, the size of the group R had a profound effect on the position of equilibrium. Thus the amount of cis olefin at equilibrium decreases from R = CH$_3$ to R = *t*-C$_4$H$_9$.

The results of this study are in agreement with those of others[1,2a-d] and they serve to amplify the observation that cis–trans isomerization can compete with product-forming chain transfer reactions.

The observation of interconverting allylic radicals depends on the successful competition of rotation about a partial double bond with any process that quenches the radical. Providing that the barrier to rotation is not overwhelming, factors which prolong the lifetime of the radical can be manipulated to maximize the observed rotation. Since allylic radicals participating in a radical chain process are destroyed in a bimolecular chain transfer step, it is expected that the amount of unimolecular rotation would increase with dilution. Expressions for the rate constants involved in these processes have been derived by Golden.[2e] These lead to values of $\sim 10^{3.2}$ sec^{-1} for the rate constant for rotation, k_r, and $10^{3.4}$ M^{-1} sec^{-1} for the rate constant for hydrogen abstraction, k_a, at 80°, when the chain transfer agent is triphenyltin hydride. The ratio of the rate of rotation to abstraction (Λ) is therefore

$$\Lambda = \frac{k_r[R\cdot]}{k_a[R\cdot][Ph_3SnH]} = \frac{k_r}{k_a[Ph_3SnH]}$$

$$\Lambda = \frac{10^{3.2}}{10^{3.4}[Ph_3SnH]}$$

Golden's data indicate that rotation should compete with chain transfer at about 1 *M* triphenyltin hydride. Furthermore, each order of magnitude decrease in triphenyltin hydride concentration should lead to a corresponding order of magnitude increase in the amount of rotation over abstraction.

The results of this study qualitatively demonstrate this dilution effect. The amount of isomerization clearly is a function of concentration. Other workers[2c] have shown that butenyl radicals equilibrate readily in the gas phase where optimum conditions prevail.

Reaction of Triphenyltin Hydride with Allylic Chlorides of the Form $ClCH_2CH{=}CHZ$ where $Z = CO_2CH_3$, $CON(CH_3)_2$, and CN. The reactions of triphenyltin hydride with allylic chlorides in which the carbon–carbon double bond is conjugated with an electron-withdrawing group (Z) were studied in order to investigate the effect that such conjugation would have on the rate of isomerization of the allylic radicals. For each compound studied [$Z = CO_2CH_3$, $CON(CH_3)_2$, and CN] the same mixture of products was obtained regardless of concentration or geometry of the starting material. Isomerization of products and/or starting material would be expected to yield such results. Further investigation confirmed that isomerization of products occurs for $Z = CO_2CH_3$ and isomerization of starting material occurs for Z = CN. This was shown by performing the reactions in the presence of excess starting materials and in the presence of isomerically pure product followed by analysis of the reaction mixtures by glpc. Isomerization of starting material or products was not definitely shown for $Z = CON(CH_3)_2$; however, the absence of a concentration effect on product composition and the results from the other compounds strongly suggest that at least one of these isomerization processes is occurring.

The isomerization of starting materials and/or products probably occurs by reversible addition of triphenyltin radical to the carbon–carbon double bond. Such additions have been shown to ocur for conjugated alkenes,[1f] and are expected to be enhanced if the conjugating group is also electron withdrawing.[7]

***tert*-Butyl Hypochlorite Chlorination of Crotononitrile and Isocrotononitrile.** Allylic chlorination of crotononitrile (*trans*-2-butenonitrile) and isocrotonoitrile (*cis*-2-butenonitrile) by *tert*-butyl hypochlorite was performed at 25° employing irradiated AIBN as an initiator. Reactions were performed at varying concentrations in carbon tetrachloride. The data collected in Table II show a definite concentration dependence of the amounts of cis and trans monochlorination products. All reactions were performed in the presence of excess nitrile to prevent polychlorination. The excess nitrile was then analyzed after the reaction to determine whether isomerization had taken place during the reaction. In no case was isomerization observed. The stability of the products was investigated by irradiation of pure samples of the cis and trans chloronitriles in the presence of *tert*-butyl hypochlorite. Again, no isomerization was observed. The absence of the unconjugated isomeric 2-chloro-3-butenonitrile as a product in these reactions was noted and is consistent with the absence of the analogous bromo derivative in the radical bromination of crotononitrile and isocrotononitrile with *N*-bromosuccinimide.[8]

Table II
Allylic Chlorination of $CH_3CH{=}CHZ$ with *tert*-Butyl Hypochlorite at 25° in Carbon Tetrachloride

$CH_3CH{=}CHZ$	Concn of *t*-BuOCl, *M*	Products, % Trans	Cis
Trans (Z = CN)	Neat	80	20
Trans (Z = CN)	0.3	48	52
Trans (Z = CN)	0.03	46	54
Cis (Z = CN)	Neat	24	76
Cis (Z = CN)	0.3	35	65
Cis (Z = CN)	0.03	42	58
Trans ($Z = CO_2CH_3$)	Neat	95	5
Trans ($Z = CO_2CH_3$)	0.03	85	15
Cis ($Z = CO_2CH_3$)	Neat	37	63
Cis ($Z = CO_2CH_3$)	0.03	77	23

Miahle and Vessieri[9] have equilibrated the various isomeric chloronitriles under basic conditions in acetonitrile. They find at equilibrium that there are present 26% *cis*-4-chloro-2-butenonitrile, 55% *trans*-4-chloro-2-butenonitrile, 13% *cis*-4-chloro-3-butenonitrile, and 6% *trans*-4-chloro-3-butenonitrile. It is clear that the results obtained in this work are not due to formation of equilibrium mixtures of products by some isomerizing side reaction. It is not clear that the two 4-chloro-3-butenonitriles could be formed by free-radical isomerization of either *cis*- or *trans*-4-chloro-2-butenonitrile; however, free-radical isomerization of either of these would be expected to yield a mixture rich in *trans*-4-chloro-2-butenonitrile (*ca.* 2:1). The results of this work indicate a slight preference for the cis isomer under the most dilute conditions and thus it is safe to conclude that nonequilibrium mixtures of *cis*- and *trans*-4-chloro-2-butenonitrile were obtained.

Walling and Thaler[1] in their pioneering study found that most simple olefinic geometric isomers were chlorinated by *tert*-butyl hypochlorite with preservation of stereochemistry, the notable exception being *cis*-4,4-dimethyl-2-pentene . The conditions used in this work were very nearly the same as employed by Walling and Thaler. They employed neat reaction mixtures and 40° while the results for comparative purposes from this work are neat and 25°. The difference in their results and those obtained here can be attributed to at least two factors.

(1) The ability of the cyano group to accept the unpaired electron, contributor C, leads to less C-2–C-3 double-bond character in the hybrid relative to a nonsubstituted allylic radical. Lowering of the double-bond character lowers the activation energy for rotation and thus increases its rate.

$$\underset{A}{\cdot CH_2CH{=}CHC{\equiv}N} \longleftrightarrow \underset{B}{CH_2{=}CH\dot{C}HCN} \longleftrightarrow \underset{C}{CH_2{=}CHCH{=}C{=}N\cdot}$$

(2) Delocalization of the unpaired electron onto the nitrogen of the cyano group stabilizes the allylic radical relative to a nonsubstituted allylic radical. Such stabilization makes it less reactive toward the chain transfer reaction with *tert*-butyl hypochlorite, and therefore it has a longer lifetime than the unsubstituted allylic radicals. Such an extension of the lifetime allows rotation to compete more effectively with chain transfer.

***tert*-Butyl Hypochlorite Chlorination of Methyl Crotonate and Methyl Isocrotonate.** Allylic chlorination of methyl crotonate (methyl *trans*-2-butenoate) and methyl isocrotonate (methyl *cis*-2-butenoate) gave results (Table II) similar to those obtained in the previous case of the nitriles. The stabilities of the starting material and products were demonstrated as described for the nitriles.

Miahle and Vessiere[9] have equilibrated the various ethyl 4-chlorobutenoates with the following results: ethyl *cis*-4-chloro-2-butenoate, 4%; ethyl *trans*-4-chloro-2-butenoate, 71%; ethyl *cis*-4-chloro-3-butenoate, 16%; and ethyl *trans*-4-chloro-3-butenoate, 9%. The results obtained in this study indicate a preference for ethyl *trans*-4-chloro-2-butenoate when the reactions were conducted in solution. Whether a near-equilibrium mixture between the two isomers has been achieved cannot be stated definitely. It is quite obvious that such is not the case in the neat reactions. It seems safe to conclude that isomerization occurs in the allylic radicals. The alternative, some kind of adventitious catalysis of isomerization, would have to be more effective in dilute solution than it is in the neat solutions. It should be pointed out that the results with the nitriles and esters do not exclude addition of *tert*-butoxy radicals to the unsaturated system. If the intermediate radicals are captured faster than a *tert*-butoxy radical can be lost, then isomerization would not be observed. Alternatively, although unlikely, addition and loss of the *tert*-butoxy radical before rotation could occur in the intermediate radical would not lead to isomerization. Whether addition occurs in these systems is an interesting question; however, it has not been investigated in this study.

It should be noted that isomerization in the allylic radicals derived from crotononitrile, methyl crotonate, and their geometric isomers has been suggested previously from work on the bromination of the isomeric nitriles with *N*-bromosuccinimide (NBS).[10] In that study it was noted that the same mixture of cis and trans bromonitriles resulted from either cis or trans reactant. An alternate explanation for this observation, however, is that bromine caused isomerization of reactants and/or products by reversible addition of bromine atoms. The geometric integrity of the reactants and products was not reported.

Experimental Section

General. All boiling points and melting points are uncorrected. Unless otherwise indicated all infrared spectra were recorded using a Perkin-Elmer 137 spectrophotometer. Pmr spectra were recorded with a Varian A-60 with tetramethylsilane as internal standard. Unless otherwise indicated all glpc was performed with a Perkin-Elmer 801 instrument equipped with glass injection parts and a flame ionization detector.

Preparation of Allylic Chlorides. All of the allylic chlorides listed in Table I were prepared from their corresponding allylic alcohols by the procedure of Young, Sharman, and Winstein.[11]

A 24.9-g (0.210 mol) quantity of thionyl chloride was added over 2 hr to a stirred, ice–salt water cooled solution of 0.210 mol of the allylic alcohol and 38.5 g (0.210 mol) of tri-*n*-butylamine in 300 ml of absolute anhydrous ether. After the addition was complete, the reaction mixture was stirred at room temperature for 45 min. A low-pressure flash distillation was subsequently performed, and that material which distilled at 0.5 mm without heating above room temperature was collected in a Dry Ice–acetone cooled receiver. After the bulk of the solvent had been removed from the distillate by fractionation through a 25-cm glass helices packed column, a few drops of water and 2 g of anhydrous potassium carbonate were added to the residue. The mixture was then stirred overnight with a magnetic stirring apparatus. After a low-pressure flash distillation from the solid, the product was fractionated. For each chloride the following data were collected: *trans*-1-chloro-2-butene, yield 32%, bp 84–86° (lit.[11] bp 84°), significant ir (neat) bands at 1670 and 975 cm^{-1}, pmr δ 5.3–6.1 (m, 2) 3.94 (d, 2, J = 6.0 Hz), 1.65 (d, 3, J = 4.5 Hz); *cis*-1-chloro-2-butene,[12] yield 53%, bp 84–85° (lit.[11] bp 84°), significant ir bands at 1660 and 750 cm^{-1}, pmr δ 5.2–5.9 (m, 2), 3.98 (d, 2, J = 6.3 Hz), 1.65 (d, 2, J = 5.0 Hz); *trans*-1-chloro-2-pentene, yield 68%, bp 108–110° (lit.[13] bp 103–110°), significant ir bands at 1663 and 969 cm^{-1}, pmr δ 5.3–6.1 (m, 2), 3.97 (d, 2, J = 6.0 Hz), 1.8–2.3 (m, 2), 0.98 (t, 3, J = 7.3 Hz); *cis*-1-chloro-2-pentene, yield 56%, bp 51–51.5° (110 mm), significant ir bands at 1650 and 760 cm^{-1}, pmr δ 5.3–5.9 (m, 2), 4.05 (d, 2, J = 6.5 Hz), 1.8–2.4 (m, 2), 0.98 (t, 3, J = 7.5 Hz); *trans*-1-chloro-4,4-dimethyl-2-pentene, yield 63%, bp 60.0–60.5° (50 mm) [lit.[14] bp 59.0–59.5° (50 mm)], significant ir bands at 1664 and 975 cm^{-1}, pmr δ 5.2–6.0 (m, 2), 3.98 (d, 2, J = 5.0 Hz), 1.02 (s, 9); *cis*-1-chloro-4,4-dimethyl-2-pentene (87% cis), yield 48%, bp 60–61° (52 mm) [lit.[14] bp 58–59° (50 mm)], significant ir bands at 1650 and 775 cm^{-1}, pmr δ 5.1–5.7 (m, 2), 4.18 (d, 2, J = 6.4 Hz), 1.13 (s, 9). The isomeric purity of the allylic chlorides was checked by glpc under the following conditions: *cis*- and *trans*-1-chloro-2-butene, 10 ft × 0.125 in. o.d. 10% β,β'-thiodipropionitrile on 80–100 mesh Chromosorb G at 25°; *cis*- and *trans*-1-chloro-2-pentene, 6 ft × 0.125 in. o.d. Carbowax K20M on 80–100 mesh Chromosorb W at 25°; *cis*- and *trans*-1-chloro-4,4-dimethyl-2-pentene, 10 ft × 0.125 in. o.d. 10% β,β'-thiodipropionitrile on 80–100 mesh Chromosorb G at 50°.

Preparation of *cis*- and *trans*-Crotyl Alcohol. *trans*-Crotyl alcohol was prepared by lithium aluminum hydride reduction of crotonaldehyde using standard techniques. *cis*-Crotyl alcohol was prepared by the semihydrogenation of 2-butyn-1-ol in methanol using Lindlar's catalyst.[15]

Preparation of *trans*-2-Penten-1-ol. *trans*-2-Penten-1-ol was prepared by reduction of 2-pentyn-1-ol with sodium in liquid ammonia using standard techniques, yield 58%, bp 68° (38 mm) [lit.[16] bp 42.2° (7 mm)].

Preparation of *cis*-2-Penten-1-ol. *cis*-2-Penten-1-ol was prepared by semihydrogenation of 2-pentyn-1-ol using Lindlar's catalyst, yield 62%, bp 60–62° (30 mm) [lit.[16] bp 41.2° (7 mm)].

Preparation of *trans*-4,4-Dimethyl-2-penten-1-ol. *trans*-4,4-Dimethyl-2-penten-1-ol was prepared by reduction of 4,4-dimethyl-2-pentyn-1-ol with sodium in liquid ammonia according to the procedure used in preparing trans-2-penten-1-ol, yield 53%, bp 66.5–67.0° (16 mm) [lit.[14] bp 71.2–72.7° (20 mm)].

Preparation of *cis*-4,4-Dimethyl-2-penten-1-ol. *cis*-4,4-Dimethyl-2-penten-1-ol was prepared by the semihydrogenation of 4,4-dimethyl-2-pentyn-1-ol using 5% palladium on barium sulfate as catalyst, yield 57%, bp 73–74° (20 mm) [lit.[14] bp 73.5–74.0° (20 mm)].

Preparation of Triphenyltin Hydride. Lithium aluminum hydride (1.56 g, 0.041 mol) was placed in a 500-ml flask filled with nitrogen. Dry absolute ether (150 ml) was added slowly, with stirring, and the flask was cooled to 0°. Triphenyltin chloride (38.5 g, 0.1 mol) was added to the slurry all at once, and the mixture was stirred at 0° for 15 min. The mixture was then allowed to warm to room temperature and stirring was continued for 4 hr. The mixture was cooled to 0° and 100 ml of water was added slowly with vigorous stirring. The resulting layers were separated. The upper layer was washed twice with water and dried over anhydrous magnesium sulfate. The ether was removed using a rotary evaporator, and the liquid residue was dissolved in 250 ml of methanol at 0°. Some material which did not dissolve was separated in a separatory funnel. The methanol solution was cooled to −78°, and the resulting precipitate of triphenyltin hydride was collected in a Buchner funnel. The recrystallization was repeated and the solid was dried in an evacuated disiccator. This gave approximately 30 g (85%) of triphenyltin hydride, mp 26–27°.

Reaction of *cis*- and *trans*-1-Chloro-2-butene and *cis*- and *trans*-1-Chloro-2-pentene with Triphenyltin Hydride (0.0135 *M*). A 1-l., three-necked flask was fitted with a thermometer that was long enough to reach into the solution, a gas inlet adapter, and a reflux condenser with a narrow spiral path for the vapor. The top of the condenser was fitted with a gas inlet adapter which was connected to two small Dry Ice–acetone cooled traps in series. Approximately 1 ml of ether was placed in the first small trap. (This was omitted in the case of *cis*- and *trans*-1-chloro-2-pentene.)The entire apparatus was then purged with dry, oxygen-free nitrogen for 30 min. Cyclohexane (500 ml), which had been purified by stirring overnight with sulfuric acid and then for several hours with a mixture of sulfuric and nitric acids, washed, dried, and distilled, was then added to the flask. The cyclohexane was deoxygenated by refluxing it in a stream of nitrogen for 30 min and then cooling under a positive pressure of nitrogen. To the solvent was then added, in order, and into an emerging stream of nitrogen, 2.37 g (0.0675 mol) of triphenyltin hydride, 0.0675 mol of the appropriate allylic chloride, and 0.1025 g of azobisisobutyronitrile (AIBN). The flask was quickly closed and heated to a very gentle reflux. The mixture was stirred magnetically for 4 hr with no nitrogen flowing through the apparatus except for short periods of time at irregular intervals. At the end of the 4-hr period the water in the condenser was turned off and drained out. The vapors of cyclohexane were allowed to climb up the condenser until a few drops spilled over into the trap. At this point heating was stopped and the water in the condenser was turned on to force the vapors to recede. The combined material in the traps was analyzed by glpc as follows: butenes, 15 ft × 0.25 in. o.d. 20% 2,5-hexanedione on 35/80 Chromosorb P at 25°, He flow rate 30 ml/min, analysis was performed using an F and M 500 instrument; pentenes, 12 ft × 0.25 in. o.d. silver nitrate–ethylene glycol on 35/80 Chromosorb P at 25°, He flow rate 30 ml/min, analysis was performed using an F and M 500 instrument.

For experiments at other concentrations the same procedure was followed using an appropriate amount of solvent.

Reaction of *trans*-1-Chloro-2-butene with Triphenyltin Hydride (Neat). Triphenyltin hydride (2.37 g, 0.0067 mol) was placed in a 10-ml flask fitted with a reflux condenser and equipped with a 10/30 gas inlet joint which was connected *via* a stopcock to a nitrogen line. The top of the condenser was connected *via* a stopcock to a Dry Ice–acetone trap containing 1 ml of ether. *trans*-Crotyl chloride (0.608 g, 0.0067 mol) and AIBN (0.05 g) were added under nitrogen and the flask was placed in an oil bath held at 80°. Initiation was evidenced by a moderate evolution of nitrogen after a few minutes. The flask was allowed to remain in the bath for 4 hr, during which nitrogen was allowed to sweep through the apparatus at irregular intervals. After this the contents of the trap were analyzed by glpc as described above.

Reaction of *cis*- and *trans*-1-Chloro-4,4-dimethyl-2-pentene with Triphenyltin Hydride (0.27 *M*). Since the boiling points of the expected products are close to that of cyclohexane (bp 80°), it was found that isolation of the products was very difficult. A higher boiling solvent, *n*-octane (bp 125°), was therefore chosen as the reaction medium. The solvent was purified in a manner similar to that used for cyclohexane.

To a 100-ml, three-necked flask equipped as described above and purged with nitrogen was added 50 ml of purified *n*-octane. The *n*-octane was then deoxygenated by refluxing in a stream of nitrogen for 30 min and then cooling under a positive pressure of nitrogen. To the solvent was added in order, and into an emerging stream of nitrogen, 4.74 g (0.0135 mol) of triphenyltin hydride, 1.782 g of the appropriate chloride, and 0.164 g of AIBN. The mixture was stirred magnetically and heated by means of an oil bath so that the temperature of the contents was 80 ± 3° for 4 hr. At the end of this period the flask was cooled to room temperature, and any material in the condenser was rinsed into the flask with 5–10 ml of *n*-octane. The condenser was replaced by a narrow 30-cm Vigreux column fitted at the top with a short-path condenser leading to two Dry Ice–acetone cooled receivers in series. The flask was heated by means of a mantle to distil out the olefins. Distillation was continued until the temperature of the distillate rose above 120°. Examination of the second trap revealed no condensate and the distillate in the first trap was analyzed by glpc on a 50 ft × 0.125 in. o.d. column of SE-30 on Chromosorb at 25°. Analysis was performed using an F and M 700 instrument.

Preparation of Methyl γ-Chlorocrotonate. In a 250-ml, three-necked flask equipped with thermometer, gas inlet, condenser, and magnetic stirrer were placed 60 g (0.6 mol) of methyl crotonate and 21.6 g (0.2 mol) of *tert*-butyl hypochlorite. Dry oxygen-free nitrogen was bubbled through the methyl crotonate for 20 min before the hypochlorite was added. The flask was then irradiated for approximately 5.5 hr with a G.E. sun lamp. After this time the color of the *tert*-butyl hypochlorite was no longer evident. Fractionation of the mixture at reduced pressure on a spinning band column equipped with a Teflon band yielded the product: bp 65.5° (9 mm) [lit.[18] bp 80–81° (19 mm)]; significant ir bands at 980 and 1660 cm^{-1}; pmr δ 6.7–7.3 (m, 1), 6.15 (d, 1, J = 15.5 Hz), 4.25 (d, 2, J = 6.0 Hz), 3.75 (s, 3).

Preparation of Methyl γ-Chloroisocrotonate. 1,3-Dibromo-2-butanone was prepared according to a previously described method[19] and converted *via* Favorskii rearrangement to isocrotonic acid.[20] The crude isocrotonic acid was then esterified with dimethyl sulfate in the presence of base according to an established procedure.[21]

The methyl isocrotonate was then chlorinated with *tert*-butyl hypochlorite according to the procedure above for methyl crotonate. The product, methyl γ-chloroisocrotonate, was obtained in addition to significant amounts of other products. Fractional distillation on a spinning band column equipped with a Teflon band yielded the pure product: bp 59° (15 mm); significant ir bands at 825 and 1650 cm^{-1}; pmr δ 6.1–6.6 (m, 1), 5.9 (d, 1, J = 11.5 Hz), 4.7 (d, 2, J = 6.6 Hz), 3.7 (s, 3).

Preparation of γ-Chlorocrotononitrile and γ-Chloroisocrotononitrile. A commercial sample of crotononitrile which contained both the cis and trans isomers was fractionated on a spinning band column to give the pure cis isomer (bp 107°) and the pure trans isomer (bp 119°). Each isomer was then chlorinated in the same manner as methyl crotonate.

The resulting product, which contained both the cis and trans chloronitriles,[22] was fractionated to give the pure isomers: γ-chlorocrotononitrile, bp 71–72° (11 mm) [lit.[23] bp 71.0–71.2° (10 mm)], significant ir bands at 968, 1655, and 2250 cm^{-1}, pmr δ 6.6–7.1 (m, 1), 5.8 (d, 1, J = 16.0 Hz), 4.2 (d, 2, J = 5.7 Hz); γ-chloroisocrotononitrile, bp 54–56° (11 mm) [lit.[23] bp 55.1–55.3° (10 mm)], significant ir bands at 782, 1640, and 2250 cm^{-1}, pmr δ 6.4–6.9 (m, 1), 5.6 (d, 1, J = 11.0 Hz), 4.3 (d, 2, J = 7.8 Hz).

Preparation of γ-Chloro-*N*,*N*-dimethylcrotonamide. Methyl γ-bromocrotonate was prepared by allylic bromination of methyl crotonate using *N*-bromosuccinimide and hydrolyzed with aqueous sodium carbonate to give γ-hydroxycrotonic acid. Treatment of this with ethereal thionyl chloride afforded γ-chlorocrotonyl chloride, which was converted toγ-chloro-*N*,*N*-dimethylcroton amide by treatment with ethereal dimethylamine. The product showed the following properties: bp 84° (0.12 mm); significant ir bands at 975, 1610, and 1660 cm^{-1}; pmr δ 6.7 (m, 2), 4.3 (d, 2, J = 4.5 Hz), 3.0 (s, 6).

Reaction of Methyl γ-Chlorocrotonate and Methyl γ-Chloroisocrotonate with Triphenyltin Hydride at 80°. A. 0.027 *M* Solution. Cyclohexane (250 ml) was deoxygenated by refluxing in a stream of nitrogen for 30 min. The appropriate chloroester (0.905 g) was then added followed by 2.37 g of triphenyltin hydride and 0.1025 g of AIBN. The mixture was gently heated under reflux under nitrogen for 4 hr and then cooled to room temperature. Samples were taken from this solution and submitted directly to analysis by glpc on a 10 ft × 0.125 in. o.d. column of 10% β,β′-thiodipropionitrile on 80–100 mesh Chromosorb G at 60°.

B. Neat. Triphenyltin hydride (1.185 g), the appropriate chloro ester (0.453 g), and AIBN were mixed in a 10-ml flask fitted with a reflux condenser. The flask was flushed with nitrogen and then placed in a constant-temperature bath held at 80° for 4 hr. The top of the condenser was open to a nitrogen-filled balloon. After the 4-hr reaction time the flask was allowed to cool to room temperature, whereupon a solid mass formed. Cyclohexane (6–7 ml) was then added and the mixture was stirred magnetically until fine particles of solid were obtained. The supernatant liquid was then analyzed for products by glpc as described above.

Reaction of Methyl γ-Chlorocrotonate with Triphenyltin Hydride at 0°. A. 0.27 *M* Solution. Cyclohexane (12.5 ml), 1.185 g of triphenyltin hydride, 0.905 g of methyl γ-chlorocrotonate, and 0.082 g of AIBN were mixed in a nitrogen atmosphere in a 25-ml flask. A calcium chloride drying tube was attached and the flask was placed in a clear unsilvered Dewar flask which contained ice and water at 0°. The solution was irradiated with a G.E. sun lamp for 3 hr and then analyzed directly by glpc as described above.

B. Neat. Triphenyltin hydride (1.185 g), methyl γ-chlorocrotonate (0.500 g), and 0.042 g of AIBN were mixed under a nitrogen atmosphere in a pressure tube. The tube was closed and placed in a clear unsilvered Dewar flask which contained ice and water at 0°. The mixture was irradiated with a G.E. sun lamp for 3 hr. After this period the tube was opened and 6 ml of cyclohexane was added. A small magnetic stirring bar was added and the mixture was stirred until fine particles of solid were obtained. The supernatant liquid was then analyzed for products by glpc as described above.

Reaction of γ-Chlorocrotononitrile and γ-Chloroisocrotononitrile with Triphenyltin Hydride at 80°. γ-Chlorocrotononitrile and γ-chloroisocrotononitrile were allowed to react with triphenyltin hydride both neat and in solution in a manner analogous to that for methyl γ-chlorocrotonate. Glpc analysis of the products was performed on a 6 ft × 0.125 in. o.d. column of Carbowax K20M on 80–100 mesh Chromosorb W at 40°.

Reaction of γ-Chloro-*N*,*N*-dimethylcrotonamide with Triphenyltin Hydride at 80°. γ-Chloro-*N*,*N*-dimethylcrotonamide was allowed to react with triphenyltin hydride both neat and in solution in a manner analogous to that for methyl γ-chlorocrotonate. Glpc analysis of the products was performed on a 6 ft × 0.125 in. o.d. column of Carbowax K20M on 80–100 mesh Chromosorb W at 120°.

Reaction of *tert*-Butyl Hypochlorite with Crotononitrile and Isocrotononitrile at 25°. A. Solution (0.03 *M* in *tert*-Butyl Hypochlorite). A 250-ml Pyrex photolysis apparatus which was equipped with a water-cooled cold finger was filled with 250 ml of dry carbon tetrachloride. *tert*-Butyl hypochlorite (0.81 g, 0.0075 mol), crotononitrile or isocrotononitrile (1.68 g, 0.025 mol), and a small amount of AIBN were dissolved in the solvent under a nitrogen atmosphere. The apparatus was closed and irradiated with a G.E. sun lamp for up to 22.5 hr. Samples of the solution were then analyzed by glpc on a 6 × 0.125 in. o.d. column of Carbowax K20M on 80–100 mesh Chromosorb W at 95°.

For experiments at 0.3 M the same amounts of reactants were dissolved in 25 ml of solvent in a smaller apparatus.

B. Neat. Crotononitrile or isocrotononitrile (3.35 g, 0.05 mol) was placed in a Pyrex photolysis apparatus of appropriate size so that the cold finger reached into the liquid. To this was added 1.84 g (0.017 mol) of *tert*-butyl hypochlorite and a small amount of AIBN. The mixture was irradiated for up to 21 hr while being stirred magnetically and cooled by the cold finger. Samples of the mixture were then analyzed by glpc as described above.

Reaction of *tert*-Butyl Hypochlorite with Methyl Crotonate and Methyl Isocrotonate at 25°. Methyl crotonate and methyl isocrotonate were allowed to react with *tert*-butyl hypochlorite both neat and in solution in a manner analogous to that used for crotononitrile and isocrotononitrile. Glpc analysis of the products was performed on a 6 ft × 0.125 in. o.d. column of Carbowax K20M on 80–100 mesh Chromosorb W at 110°.

Acknowledgment. R. M. H. wishes to thank Johnson and Johnson, Inc., for Fellowship support of this research.

Registry No.—*trans*-1-Chloro-2-butene, 4894-61-5; *cis*-1-chloro-2-butene, 4628-21-1; *trans*-1-chloro-2-pentene, 6261-25-2; *cis*-1-chloro-2-pentene, 6261-19-4; *trans*-1-chloro-4,4-dimethyl-2-pentene, 19146-05-5; *cis*-1-chloro-4,4-dimethyl-2-pentene, 19146-06-6; triphenyltin hydride, 892-20-6; methyl γ-chlorocrotonate, 999-54-2; methyl crotonate, 623-43-8; *tert*-butyl hypochlorite, 507-40-4; methyl γ-chloroisocrotonate, 999-53-1; methyl isocrotonate, 4358-59-2; γ-chlorocrotononitrile, 7659-46-3; γ-chloroisocrotononitrile, 20592-22-7; *cis*-crotononitrile, 1190-76-7; *trans*-crotononitrile, 627-26-9; γ-chloro-*N*,*N*-dimethylcrotonamide, 51830-58-1; methyl γ-bromocrotonate, 6000-00-6.

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Three-Electron Oxidations. VII. The Pre-Steady-State Phase of the Chromic Acid Oxidation of Oxalic Acid[1,2]

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Received March 7, 1974

The study of the initial rates of formation of chromium(III) in the chromic acid oxidation of oxalic acid shows the absence of an induction period; this result is incompatible with any mechanism following the general scheme Cr(VI) → Cr(V) → Cr(III), according to which all chromium would pass through the chromium(V) state. In agreement with the previously proposed three-electron oxidation mechanism, the initial rate of formation of chromium(III) is never lower than one-half of the rate of reduction of chromium(VI). The initial rates of formation of chromium(III) as well as the maximum concentration of chromium(V) formed depend on both total chromic acid concentration and on the acidity. The results show that the $\cdot CO_2H$ radicals react predominantly with chromium(VI) to yield CO_2 and chromium(V) at high chromic acid concentrations and acidities, but undergo extensive bimolecular dimerization at low chromic acid concentrations and acidities.

In a recent paper from this laboratory[3] it was shown that during the chromic acid oxidation of oxalic acid, a long-lived chromium(V) intermediate is formed in rather large concentrations. The reaction can be described as having two distinct phases. The initial phase is characterized by a decrease in the concentration of chromium(VI) and a rapid buildup of the chromium(V) intermediate. During the second phase of the reaction, after the concentration of chromium(V) has reached its maximum, the concentrations of both chromium(V) and chromium(VI) decrease approximately in parallel, and a quasi-steady-state concentration of chromium(V) with respect to the concentration of chromium(VI) is established and maintained.

The purpose of this study was to obtain answers to two basic questions concerning the mechanism of reaction: (1) does all, or only a fraction, of the total chromium pass through the chromium(V) stage; (2) do all, or only a fraction of the free radicals undergo further oxidation?

The oxidation of oxalic acid takes place by two routes, namely, through a 1:1 and a 2:1 oxalic acid–chromic acid complex.[4] The mechanism for the second route, which (except for very low oxalic acid concentrations) is by far the