ring in *cis*-butene saturated with deuteriotrifluoroacetic acid. The cyclopropane product when isolated was found to contain negligible amounts of deuterium (<1%).

To show that there is no preequilibrium and exchange of deuterium of the acid and the diazo compound, phenyldiazomethane was treated with an excess of deuteriotrifluoroacetic acid in pentane solution. The benzyl trifluoroacetate was isolated and was found to contain no dideuterated product. Olefins were found not to react with the deuterated acids under the reaction conditions.[32]

Acknowledgment. We thank the National Science Foundation (Grant GP 4214) for support. One of us (S. H. G.) thanks the Uniroyal Foundation for a fellowship.

Registry No.—5-*p*-Chlorophenylpent-2-enyl trifluoroacetate, 51157-78-9; 5-*p*-chlorophenyl-3-pent-1-enyl trifluoroacetate, 51157-79-0.

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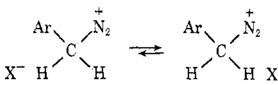

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Allene Epoxidation. The Isolation of Reactive Intermediates from Hindered Allenes[1a]

Jack K. Crandall,*[1b] Woodrow W. Conover,[1c] Joyce B. Komin, and Warren H. Machleder

Contribution No. 2348 from the Department of Chemistry, Indiana University, Bloomington, Indiana 47401

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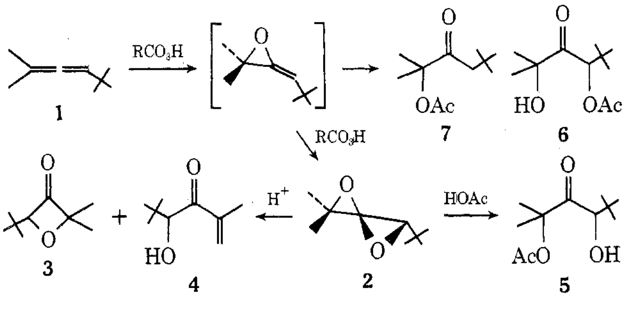
The peracid oxidation of several highly hindered allenes has resulted in the isolation of allene oxides and 1,4-dioxaspiro[2.2]pentanes (spiro dioxides), and the chemistry of these sequentially formed products has been explored. Allene **1** yields spiro dioxide **2**, which readily isomerizes to oxetanone **3** and unsaturated ketone **4**. The addition of acetic acid to **2** gives **5**. Allene **8** yields labile allene oxide **19**, which spontaneously isomerizes to cyclopropanone **11**. Remarkably stable **11** is photochemically or thermally decarbonylated to **12**. Sodium methoxide cleaves **11** to **13** and **14**; acid treatment gives rearranged ketones **15** and **16**. In the presence of excess oxidant, **8** is transformed to oxetanone **22** and oxacyclopentanone **23**, presumably *via* a transient spiro dioxide intermediate. Allene **25** leads to stable allene oxide **26**, which is converted to its geometric isomer **28** by irradiation or heating. Thermolysis converts either **26** or **28** to **29** and **30**. Rearrangement of **26** to **29** is also effected by BF_3. Further peracid oxidation of **26** gives dioxidation products **27**, **31**, and **32** *via* labile spiro dioxide **33**. Allene **36** gives allene oxide **37** and dioxidation products **39** and **40**. Acid or heat transforms **36** to ketone **38**. Ozone converts allene **8** to cyclopropanone **11** and also effects the oxidation of allene **25** to spiro dioxide **33**.

Recent work on the epoxidation of allenes has provided a reasonably detailed understanding of this rather complex reaction.[2-4] Several interesting species have been implicated as reactive intermediates in this process, including allene oxides, cyclopropanones, and 1,4-dioxaspiro[2.2]pentanes. In the present study, the oxidation of several sterically hindered allenes has been explored in an attempt to isolate examples of these proposed intermediates. Steric stabilization has been previously utilized in a number of instances as an aid in the isolation of reactive small-ring heterocycles.[5]

The reaction of 1,1-dimethyl-3-*tert*-butylallene[6] (**1**) with 2 equiv of peracetic acid smoothly generated 5-*tert*-butyl-2,2-dimethyl-1,4-dioxaspiro[2.2]pentane[7] (**2**) in high yield.[8] Although it was very sensitive to handling, pure **2** could be obtained by distillation under reduced pressure. The nmr of **2** shows a *tert*-butyl signal, two methyls, and a unique proton at δ 3.37. As expected the ir displays a number of intense bands in the 8–14-μ region. In addition, there is an unusual band of moderate intensity at 6.10 μ, which is Raman inactive and inappropriately situated to be an overtone. Although the origin of this anomalous band remains unclear, the other spectral data and the chemical conversions of **2** secure the assigned structure. Attempts to purify **2** by glpc served only to transform it into a mixture of 4-*tert*-butyl-2,2-dimethyloxetan-3-one (**3**) and 4-hydroxy-2,5,5-trimethylhex-1-en-3-one (**4**), unambiguously identified by their characteristic spectral data (see Experimental Section). A similar conversion was effected with a catalytic amount of concentrated HCl. The reaction of spiro dioxide **2** with acetic acid also yielded **3** and **4** along with minor quantities of a material assigned as 2-acetoxy-4-hydroxy-2,5,5-trimethyl-3-hexanone (**5**). This structure is preferred over alternative **6** because of the better agreement between anticipated[9] and experimental values for the δ 5.43 methine proton signal in the nmr, and the absence of an important fragment in its mass spectrum corresponding to the loss of acetic acid.

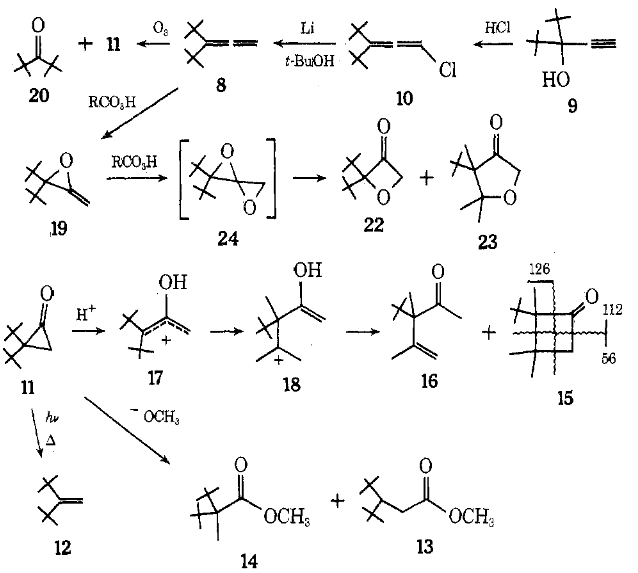
An attempt to isolate an allene oxide intermediate by the slow addition of 1 equiv of peracetic acid to a solution of **1** in CH_2Cl_2 led only to a product mixture consisting of unreacted allene, spiro dioxide **2**, and a small amount of 2-acetoxy-2,5,5-trimethyl-3-hexanone (**7**). Clearly, the second epoxidation is much faster than the first step and the only monooxidation product observed is acetoxy ketone **7**. Nonetheless, isolation of the spiro dioxide effectively demonstrates that an allene oxide intervenes in the reaction. The allene oxide structure in Chart I is preferred over the alternatives on the basis of analogy (*vide infra*). Furthermore, the reactions of spiro dioxide **2** are in full agreement with those suggested in our earlier studies for hypothesized reactive intermediates of this type.[2,3] Products **4** and **5** can be rationalized by straightforward acid-catalyzed mechanisms; oxetanone **3** may have arisen in this fashion also, although a purely thermal rearrangement is a second possibility.

Chart I



The epoxidation of 1,1-di-*tert*-butylallene (**8**) was examined next.[10] The addition of lithium acetylide to di-*tert*-butyl ketone formed propargyl alcohol **9**, which was transformed to chloroallene **10** by reaction with concentrated HCl. Conversion of **10** to allene **8** was effected by lithium and *tert*-butyl alcohol in THF. This reaction proceeds cleanly without further reduction of the allene product.

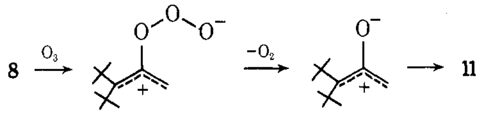
Chart II



Allene **8** reacted with 2 equiv of peracetic acid in CH_2Cl_2 to yield 2,2-di-*tert*-butylcyclopropanone (**11**) as the only product. The cyclopropanone is a stable, waxy solid with characteristic spectroscopic properties:[11] ir 5.48 μ; uv 345 nm (ϵ 52). Interestingly, the nmr spectrum of **11** is not altered by the addition of methanol. Apparently, steric forces prevent the hemiketal formation which is characteristic of less congested cyclopropanones.[11] Consistent with this reluctance to undergo carbonyl addition, cyclopropanone **11** was also resistant to oxidative decarbonylation[3,12] by either *p*-nitroperbenzoic acid (PNPBA) or basic hydrogen peroxide. However, **11** was subject to other typical cyclopropanone reactions, albeit sluggishly.[11] Thus, pyrolysis at 600° cleanly converted **11** to 1,1-di-*tert*-butylethylene (**12**). Irradiation into the n-π^* absorption band also effected this transformation. Favorskii cleavage of **11** with sodium methoxide proceeded slowly to give a 75:25 ratio of methyl β,β-di-*tert*-butylpropionate (**13**) and methyl α,α-di-*tert*-butylpropionate (**14**). Curiously, the more congested ring bond is preferentially broken, whereas the alternate cleavage process generates a better incipient carbanionic center.[13] Prolonged exposure of cyclopropanone **11** to acetic acid yielded a mixture of 2-*tert*-butyl-2,3,3-trimethylcyclobutanone (**15**) and 3-*tert*-butyl-3,4-dimethylpent-4-en-2-one (**16**). Structure **15** is secured by a 5.65-μ ir absorption and odd-electron fragments at *m/e* 126, 112, and 56 in the 10-eV mass spectrum. These ions correspond to the indicated fragmentation of the molecular ion of **15** and establish its substitution pattern.[14] The formation of these acid-catalyzed products can be explained by the sequence of events illustrated in Chart II. Thus, protonation and ring opening of cyclopropanone **11** gives hydroxyallyl cation **17**, which undergoes methyl migration to yield tertiary cation **18**, the immediate precursor of **15** (by intramolecular alkylation) and **16** (by loss of a proton and tautomerization).

The unanticipated production of cyclopropanone **11** in the epoxidation of allene **8** is best understood in terms of the initial formation of allene oxide **19**, which subsequently isomerizes to **11** under the reaction conditions. Corroboration for this hypothesis was obtained by oxidizing allene **8** with *p*-nitroperbenzoic acid (PNPBA) at −30°. Under these conditions a 20:80 mixture of starting material and allene oxide **19** was formed. The nmr of **19** shows doublets at δ 3.97 and 4.16[15] (J = 3 Hz) in addition to a single *tert*-butyl signal. Its ir shows bands at 5.61 and 10.7 μ appropriate for the double-bond stretching[16] and CH out-of-plane bending[17] modes of the terminal methylene group. These data demonstrate that epoxidation has occurred at the substituted double bond of **8.** Allene oxide **19** was stable in CCl_4 solution for several hours at room temperature. However, the addition of several drops of methanol triggered a rapid rearrangement to cyclopropanone **11.** These results are consistent with those of Camp and Greene, who earlier isolated an allene oxide from 1,3-di-*tert*-butylallene and showed that it underwent a facile, complete isomerization to the corresponding cyclopropanone.[4]

In certain instances, ozone has been found to transfer oxygen to hindered olefins, giving epoxides[18] instead of the usual oxidative cleavage products. Consequently the reaction of O_3 with allene **8** was examined.[19,20] Thus, reaction of **8** with 1.2 equiv of O_3 in CH_2Cl_2 at −78° gave cyclopropanone **11** as the major product along with cleavage products di-*tert*-butyl ketone and paraformaldehyde. No intermediates accumulated in this reaction as demonstrated by low-temperature nmr monitoring. It is consequently unlikely that allene oxide **19** is an intermediate in this particular transformation, since it should have been stable toward isomerization to **11** at −78°. An alternative mechanism involves electrophilic attack of O_3 at the central allenic carbon of **8** to give dipolar intermediate **21.** The loss of O_2 from **21** generates the open zwitterionic form of **11** as indicated below. Ring closure of this species leads directly to cyclopropanone **11** without the intervention of allene oxide **19.** Interestingly, ozonolysis of 1,3-di-*tert*-butylallene under similar conditions gives only pivaldehyde, the oxidative cleavage product.



21

The oxidation of allene **8** with excess PNPBA yielded di-*tert*-butyl ketone,[21] cyclopropanone **11**, 2,2-di-*tert*-butyloxetan-3-one (**22**), and 4,5,5-trimethyl-4-*tert*-butyloxacyclopentan-3-one (**23**). The latter two materials are probably derived from spiro dioxide **24**, the diepoxidation product of **8.** The ozonolysis of allene oxide **19** also gave a mixture of these four products, indicating that spiro dioxide **24** can also be generated in this fashion.

Tri-*tert*-butylallene (**25**) was synthesized from di-*tert*-butyl ketone and *tert*-butylacetylene by a sequence similar to that utilized for **8.** Treatment of **25** with an excess of *m*-chloroperbenzoic acid (MCPBA) in CH_2Cl_2 produced the *E* allene oxide **26** and 2,2,4-tri-*tert*-butyloxetan-3-one (**27**) in a 90:10 ratio.[22] The nmr of **26** exhibits a vinylic proton singlet at relatively high field (δ 4.56) in addition to a closely spaced pair of *tert*-butyl singlets at δ 1.06. The exocyclic double bond is shown by a sharp ir band at 5.60 μ. Peracid attack clearly takes place at the more substituted double bond. The assigned stereochemistry presumes peracid approach from the sterically least hindered side of this double bond (away from the *tert*-butyl substituent on the monosubstituted sp^2 carbon).

A number of experiments designed to isomerize allene oxide **26** to the corresponding cyclopropanone were unsuccessful, presumably owing to the steric destabilization of the latter, which would possess eclipsed vicinal *tert*-butyl substituents.[23] This effect is apparently large enough to completely reverse the strong preference for the cyclopropanone over its allene oxide isomer that was noted with the two di-*tert*-butyl systems described above. Thus irradiation of a hexane solution of **26** through quartz with a high-pressure mercury arc generates a 30:70 mixture of **26** and an isomeric compound assigned as *Z* allene oxide **28.** The nmr of **28** shows its olefinic proton as a singlet at δ 4.25[24] and its ir exhibits a 5.59-μ band. The substantially shorter glpc retention time of **28** relative to that of **26** on a Carbowax 20M column supports the stereochemical assignments, since the basic oxygen atom of **28** should be more sterically shielded than that of **26.** The photochemical cis–trans isomerization of simple double bonds is well documented[25] and a similar process most likely obtains in the present instance. Flow pyrolysis of **26** at 350° leads to *Z* isomer **28**, 2,3,6,6-tetramethyl-3-*tert*-butylhept-1-en-4-one (**29**), and 2,3,3-trimethyl-2,4-di-*tert*-butylcyclobutanone (**30**). A similar pyrolysis of isomer **28** also yields **29** and **30.** Allene oxide **26** was unaffected by either sodium methoxide or potassium *tert*-butoxide, but prolonged exposure to BF_3 in ether prompted rearrangement to ketone **29.** This transformation presumably occurs *via* an intermediate oxyallyl cation in a process similar to the related conversions of cyclopropanone **11.** It appears likely that the thermal conversions of **26** and **28** to ketones **29** and **30** also proceed by acid-catalyzed mechanisms. It is conceivable that the allene oxide is isomerized to the corresponding cyclopropanone prior to the formation of the observed products in these reactions, but there is no evidence requiring this embellishment.

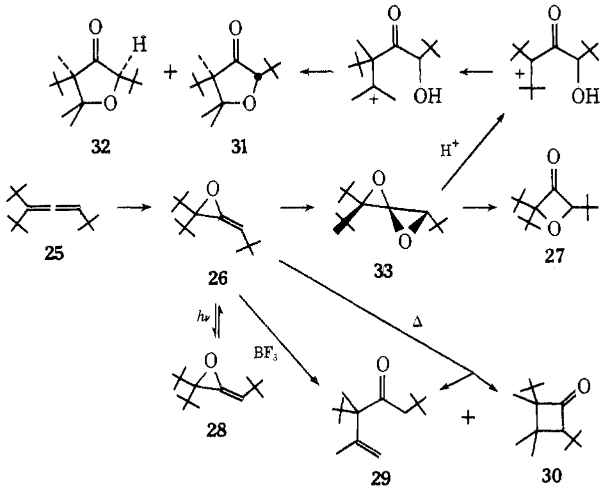
The treatment of allene **25** with 3 equiv of PNPBA gives *trans*- and *cis*-2,4-di-*tert*-butyl-4,5,5-trimethyloxacyclopentan-3-one (**31** and **32**) in addition to allene oxide **26** and oxetanone **27.** The stereochemical assignments indicated for the oxacyclopentanones are based on their behavior to methanolic sodium methoxide, which caused no change in a pure sample of **31**, but converted **32** to **31.** Consequently, **32** is the thermodynamically less stable isomer with cis *tert*-butyl groups. Oxetanone **27** does not appear to be the precursor of these products, since it was stable to prolonged exposure to acetic acid in refluxing CH_2Cl_2.

The reaction of allene **25** with 2 equiv of O_3 at −78° gave a 6:94 ratio of di-*tert*-butyl ketone and 2,5,5-tri-*tert*-butyl-1,4-dioxaspiro[2.2]pentane (**33**).[19] Spiro dioxide **33** displays a 6.40-μ ir band and a δ 3.05 nmr singlet for one proton in addition to three separate *tert*-butyl signals. However, after standing for 3 days the nmr indicated complete rearrangement to oxetanone **27.** Reaction of spiro dioxide **33** with a trace of *p*-nitrobenzoic acid produced an 80:20 mixture of oxetanone **27** and oxacyclopentanone **31.** The use of trifluoromethanesulfonic acid gave only oxacyclopentanones **31** and **32** in a 60:40 ratio. Reaction of allene oxide **26** with 1 equiv of PNPBA also led to a mixture of oxetanone **27** and oxacyclopentanone **31.** These experiments establish spiro dioxide **33** as the key intermediate leading to the dioxidized products in the reaction of allene **25** with peracids. A plausible route to the oxacyclopentanones is outlined in Chart III. The observation that increasing the acid strength of the reaction medium for the rearrangement of the spiro dioxide increases these materials at the expense of the oxetanone product suggests that the latter arises by a noncatalyzed thermal pathway.

Reaction of allene **25** with only 1 equiv of O_3 gave a 47:7:46 mixture of **25, 26,** and **33.** Allene oxide **26** was converted separately to spiro dioxide **33** by 1 equiv of O_3. These results confirm that the spiro dioxide is formed by sequential reaction of the allene with two molecules of O_3, the second step being much faster than the first.

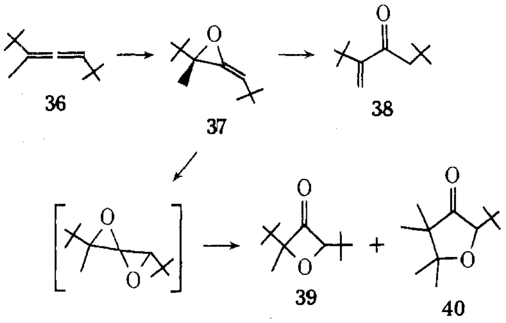
Finally, 1,3-di-*tert*-butyl-1-methylallene (**36**) was examined in an attempt to achieve a system with a more balanced equilibrium between allene oxide and cyclopropanone isomers. Allene **36** was obtained from *tert*-butylacetylene and pinacolone by the same sequence as utilized

Chart III



for **8**. Oxidation of **36** with 1 equiv of PNPBA resulted in a 46:6:36:12 mixture of allene oxide **37**, 2-*tert*-butyl-5,5-dimethylhex-1-en-3-one (**38**), 2,4-di-*tert*-butyl-2-methyloxetan-3-one (**39**), and 2-*tert*-butyl-4,4,5,5-tetramethyloxacyclopentan-3-one (**40**) (Chart IV). Allene oxide **37** shows a 5.60-μ ir band and a δ 4.55 olefinic proton in its nmr in addition to a methyl and two *tert*-butyl singlets. Pyrolysis of allene oxide **37** at 250° resulted in partial conversion to ketone **38**. The addition of a trace of trifluoromethanesulfonic acid to **37** also provoked this isomerization. No reaction was observed upon irradiation in the case of allene oxide **37**. Thus, allene oxide **37** also manifests a reluctance to isomerize to the corresponding cyclopropanone.

Chart IV



Experimental Section

General. Nmr spectra were recorded for CCl_4 solutions on Varian HR-220 and A-60 spectrometers. Ir spectra of neat samples or CCl_4 solutions were recorded on a Perkin-Elmer 137 Infracord spectrophotometer. Mass spectra (70 eV) were obtained on Varian MAT CH-7 and AEI MS-9 mass spectrometers. Commercial *m*-chloroperbenzoic acid (MCPBA) was recrystallized from CH_2Cl_2 to give material of greater than 98% purity;[26] *p*-nitroperbenzoic acid (PNBPA) (>97% purity) was used as obtained. Gas chromatography (glpc) was performed on Aerograph A600 and A700 instruments. Analyses were performed by Midwest Microlab, Inc., and Schwarzkopf Microanalytical Laboratory. Anhydrous $MgSO_4$ was routinely used as a drying agent.

Peracetic Acid Solutions. Acetic acid was removed from commercial 40% peracetic acid by adding dropwise to a cold slurry of excess anhydrous Na_2CO_3 in CH_2Cl_2. After stirring at 0° for 45 min, the solid salts were removed by suction filtration and the peracid was used immediately. Nmr analysis indicated about a 95:5 mixture of peracetic and acetic acids. Analysis indicated that the amount of peracetic acid was undiminished by this process. In the following experiments the indicated amount of 40% peracetic acid was treated by this process prior to reaction with the allenes.

1,1-Dimethyl-3-*tert*-butylallene (1). Allene **1** was synthesized by the method of Skattebøl.[27] The spectra were identical with those recorded.[6]

Reaction of 1 with Excess Peracetic Acid. To a slurry of 8.0 g of **1** and 40 g of Na_2CO_3 in 100 ml of CH_2Cl_2 was slowly added 24.7 g of peracetic acid. After stirring at 25° for 70 hr, the inorganic salts were removed by filtration and the solvent was removed. The crude product (10.3 g) was shown by nmr to be essentially a single component. Spinning-band distillation afforded pure **2**: bp 40° (2 mm); ir 6.10, 8.10, 10.5, 10.9, 12.3, and 13.3 μ; nmr δ 3.37 (s, 1), 1.46 (s, 3), 1.44 (s, 3), and 0.97 (s, 9); mass spectrum *m/e* (rel intensity) 156 (1), 128 (8), 113 (8), 100 (29), 98 (21), 83 (46), and 70 (100).

Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 69.1; H, 10.2.

When spiro dioxide **2** was submitted to preparative glpc, a 50:50 mixture of **3** and **4** was obtained. Compound **3** showed ir 5.50 μ; nmr δ 4.96 (s, 1), 1.44 (s, 3), 1.36 (s, 3), and 0.98 (s, 9); mass spectrum *m/e* (rel intensity) 128 (12), 83 (66), and 70 (100).

Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 69.1; H, 10.3.

Ketone **4** showed ir 2.8, 5.98, and 6.13 μ; nmr δ 5.83, 5.76, (m, 2), 4.44 (s, 1), 3.08 (s, 1), 1.89 (m, 3), and 0.88 (s, 9); mass spectrum *m/e* (rel intensity) 156 (2), 100 (48), 87 (65), 70 (60), 69 (66), and 57 (100).

Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 69.0; H, 10.5.

Reaction of 2 with Hydrochloric Acid. Stirring **2** in the presence of a small amount of concentrated HCl for 3 hr gave a 50:50 mixture of **3** and **4**.

Reaction of 2 with Acetic Acid. To a 1.3-g sample of **2** in 15 ml of CH_2Cl_2 was added 1.0 g of glacial acetic acid. An exothermic reaction occurred after which stirring was continued for 5 hr. After the addition of excess Na_2CO_3, the reaction mixture was filtered and the solvent was removed. The products consisted of **3** (35%), **4** (59%), and **5** (6%): ir 2.8, 5.74, 5.81, and 8.0 μ; nmr δ 5.43 (s, 1), 3.18 (s, 1), 2.05 (s, 3), 1.33 (s, 3), 1.26 (s, 3), and 1.00 (s, 9); mass spectrum *m/e* (rel intensity) 173 (2), 156 (2), 98 (11), 87 (7), 83 (35), 70 (5), 59 (35), 57 (18) and 43 (100).

Anal. Calcd for $C_{11}H_{20}O_4$: C, 61.09; H, 9.32. Found: C, 60.9; H, 9.5.

Epoxidation of 1 with 1 Equiv of Peracid. To an ice-cold slurry of 10.0 g of allene and 40 g of Na_2CO_3 in 150 ml of CH_2Cl_2 was added 15.3 g of peracetic acid over a period of 6 hr. After stirring for 22 hr, the reaction mixture was filtered and the solvent was removed. Nmr and glpc analysis indicated that 50% of unreacted **1** was present in addition to 42% of **2** and 8% of **7**: ir 5.74, 5.79, and 8.0 μ; nmr δ 2.29 (s, 2), 1.97 (s, 3), 1.39 (s, 6), and 1.01 (s, 9).

Anal. Calcd for $C_{11}H_{20}O_3$: C, 65.97; H, 10.07. Found: C, 65.7; H, 10.1.

3-*tert*-Butyl-4,4-dimethylpent-1-yn-3-ol (9). A suspension of 2 g of Li wire in 100 ml of benzene was stirred under a nitrogen blanket in a 500-ml, three-necked flask, equipped with a condenser, dropping funnel, and mechanical stirrer. Ethylenediamine (18 g) was added dropwise over 1 hr and the mixture was heated to reflux and stirred for 3 hr. The reaction was cooled to 25° and acetylene was bubbled in for 30 min. Di-*tert*-butyl ketone (22 g) was added dropwise and stirring was continued for 18 hr. The reaction was quenched with 100 ml of water and stirred for 1 hr. The mixture was extracted with ether, and the extracts were combined, dried, and concentrated to yield 26 g (99%) of **9**:[28] ir 2.85, 3.05, 6.75, 9.20, 9.50, and 10.0 μ; nmr δ 2.35 (s, 1), 2.22 (s, 1), and 1.10 (s, 18).

1-Chloro-3,3-di-*tert*-butylallene (10). Alcohol **9** (10.0 g) was added to an ice-cold slurry of 6.7 g of $CaCl_2$ and 0.1 g of hydroquinone in 30 ml of concentrated HCl. After stirring for 6 hr, the reaction mixture was extracted with pentane. The extract was washed with saturated Na_2CO_3 and dried. Removal of the solvent and distillation gave 9.2 g (83%) of **10**:[29] bp 88–94° (26 mm); ir 5.17 and 13.6 μ; nmr δ 5.73 (s, 1) and 1.22 (s, 18); mass spectrum *m/e* (rel intensity) 188 (0.3), 186 (1.1), and 57 (100).

1,1-Di-*tert*-butylallene (8). A mixture of 8.3 g of **10**, 8.7 g of *t*-BuOH, and 2.4 g of Li wire in 60 ml of THF was refluxed for 4 hr. The crude product was poured onto ice and extracted with pentane. After drying and solvent removal, distillation gave 5.4 g (81%) of **8**: bp 155–157°; ir 5.19 and 12.0 μ; nmr δ 4.55 (s, 2) and 1.18 (s, 18); mass spectrum (10 eV) *m/e* (rel intensity) 152 (79), 137 (92), 96 (35), and 57 (100).

Anal. Calcd for $C_{11}H_{20}$: C, 86.76; H, 13.24. Found: C, 86.4; H, 13.1.

Reaction of 8 with Peracetic Acid. A 0.3-g sample of **8** was stirred for 26 hr at 25° with 0.8 g of peracetic acid in 10 ml of CH_2Cl_2 and 0.8 g of Na_2CO_3. Excess peracid was destroyed by addition of 2-methyl-2-butene. The inorganic salts were removed by filtration and the solvent was removed to yield 0.3 g of crude product. This material was collected by glpc using a freshly prepared 5-ft column of 15% Carbowax 20M on Chromosorb W with the entire glpc system maintained below 110°. Cyclopropanone **11** showed mp 41–43°; ir 5.48 and 10.5 μ; nmr δ 1.44 (s, 2), 1.10 (s, 18); uv max (hexane) 345 nm (ϵ 52); mass spectrum m/e (rel intensity) 168 (0.4), 126 (25), 112 (24), 111 (55), 97 (75), 69 (53), and 57 (100); exact mass 168.151 (calcd for $C_{11}H_{20}O$, 168.1514).

Attempted purification of **11** on a number of other glpc columns as well as column chromatography (silica gel, 5% ether–hexane) resulted in partial conversion to **15.**

Reaction of 11 with MeOH. To an nmr sample of **11** ($\sim$10 mg) in CCl_4 was added 300 mg of MeOH. After 20 min no change had occurred in the nmr spectrum and a drop of 1 *N* HCl was added. Upon standing at 25° for 20 hr, nmr analysis indicated that most of the **11** was still present. There was no evidence for hemiketal formation. The only observable change was partial conversion to **15.**

Pyrolysis of 11. Pyrolyses were carried out by vacuum transfer of material through a Sargent tube furnace using a 28 × 1.2 cm quartz tube packed with quartz chips. The product was collected in a Dry Ice–acetone bath. Pyrolysis of 48 mg of **11** at 600° (0.04 mm) required 3.5 hr and gave a 75% yield of di-*tert*-butylethylene: ir 6.18 and 11.1 μ; nmr δ 4.93 (s, 2) and 1.21 (s, 18). Pyrolysis of a 47-mg sample of **11** at 400° (0.04 mm) gave a 66% yield of the same product.

Photolysis of 11. A 0.5-g sample of **11** in 3 ml of pentane was photolyzed with 3100-Å light in a Rayonet photochemical reactor for 19 hr. Removal of the solvent gave 0.4 g of crude product. Glpc indicated only 1,1-di-*tert*-butylethylene.

Reaction of 11 with Sodium Methoxide. A solution of sodium methoxide was prepared by adding 1.0 g of sodium to 30 ml of MeOH. The resulting solution was added to 1.0 g of **11** in 30 ml of MeOH. After refluxing for 46 hr, the reaction mixture was poured into water, extracted with pentane, and dried. The solvent was removed to give 0.8 g of crude product. Glpc analysis indicated two products in a 75:25 ratio. The major component was identified as **13:** ir 5.73 μ; nmr δ 3.57 (s, 3), 2.18 (d, 2, J = 5 Hz), 1.82 (t, 1, J = 5 Hz), and 0.96 (s, 18); mass spectrum m/e (rel intensity) 185 (1), 169 (6), 145 (23), 144 (18), 129 (26), 123 (11), 97 (19), 87 (93), 69 (30), and 57 (100).

Anal. Calcd for $C_{12}H_{24}O_2$: C, 71.95; H, 12.08. Found: C, 71.7; H, 12.2.

The minor component was identified as **14:** ir 5.80 μ; nmr δ 3.64 (s, 3), 1.22 (s, 3), and 1.11 (s, 18); mass spectrum m/e (rel intensity) 169 (0.4), 145 (3), 144 (27), 129 (100), 97 (7), 73 (14), 69 (13), and 57 (81). This was compared with an authentic sample prepared by diazomethane esterification of the corresponding acid.[30]

Reaction of 11 with Acetic Acid. A 0.5-g sample of **11** was stirred in 5 ml of CH_2Cl_2 containing 1.0 g of glacial acetic acid for 72 hr at 25°. Glpc indicated that half of the **11** had been converted to two new products. The crude product was resubmitted to the reaction conditions for 6 days, at which point one-third of the **11** remained. The CH_2Cl_2 was removed and replaced with chloroform. After 78 hr in refluxing chloroform, ir indicated only trace amounts of **11.** Two products in a 84:16 ratio were isolated by glpc. The major component was identified as **15:** mp 80–81°; ir 5.65 μ; nmr δ 2.61 (AB quartet, 2, $\Delta\nu$ = 28 Hz, J = 17 Hz), 1.44 (s, 3), 1.24 (s, 3), 1.18 (s, 3), and 1.04 (s, 9); mass spectrum m/e (rel intensity) 168 (1), 126 (40), 112 (28), 111 (78), 97 (100), 69 (62), and 57 (50); (10 eV) 126 (100), 112 (41), and 56 (11).

Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.8; H, 12.0.

The minor component was identified as **16:** ir 5.86, 6.13, and 11.1 μ; nmr δ 5.04, 4.64 (m, 2 total), 1.90 (s, 3), 1.75 (m, 3), 1.24 (s, 3), and 0.96 (s, 9); exact mass, 168.152 (calcd for $C_{11}H_{20}O$, 168.1514).

Reaction of 11 with PNPBA. A 100-mg sample of **8** in CH_2Cl_2 was ozonized to produce an 84:16 mixture of **11** and **20.** This mixture was stirred at 25° for 24 hr with 3 equiv of PNPBA. Glpc and ir analysis showed no change in the mixture.

Reaction of 8 with PNPBA. A 100-mg sample of **8** was stirred at −30° for 2 hr with 1.23 g of PNPBA in 15 ml of CH_2Cl_2. The solution was filtered, the solvent was removed, and the residue was dissolved in CCl_4 and carefully filtered to remove *p*-nitrobenzoic acid. Nmr showed a 20:80 mixture of **8** and **19:** ir 5.61 and 10.7 μ; nmr (220 MHz) δ 1.10 (s, 18), 3.97 (d, 1, J = 3 Hz), 4.16 (d, 1, J = 3 Hz). The nmr sample of **8** and **19** in CCl_4 showed no change after standing for 3.5 hr at 25°. Examination of the nmr spectrum 3 hr after addition of 10 drops of MeOH showed only **8** and **11.**

A 1-g sample of **8** was stirred at 25° for 24 hr with 3 equiv of PNPBA in 75 ml of CH_2Cl_2. The solution was filtered and the solvent was removed. The product was dissolved in CCl_4 and filtered to remove *p*-nitrobenzoic acid. Glpc analysis indicated four products present in a 9:38:26:27 ratio which were identified as **20, 11, 22,** and **23.** Compound **22** showed ir 5.51, 9.44, and 10.4 μ; nmr δ 1.04 (s, 18) and 4.85 (s, 2); mass spectrum m/e (rel intensity) 142 (15), 141 (7), 139 (7), 128 (44), 111 (19), 109 (14), 99 (26), 85 (9), 69 (5), and 57 (100).

Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.70; H, 10.94. Found: C, 71.5; H, 11.0.

Compound **23** showed mp 85–87°; ir 5.71, 8.01, and 9.39 μ; nmr δ 1.04 (s, 12), 1.21 (s, 3), 1.38 (s, 3), 3.77 (AB quartet, 2, $\Delta\nu$ = 24 Hz, J = 18 Hz); mass spectrum m/e (rel intensity) 184 (31), 169 (63), 113 (49), 111 (49), 97 (10), 84 (100), 83 (41), 69 (42), 67 (13), 57 (73), 55 (32), 52 (13), and 43 (11); exact mass, 184.146 (calcd for $C_{11}H_{20}O_2$, 184.1463).

Ozonolysis of 8. A 41-mg sample of **15** in 2 ml of CH_2Cl_2 was cooled to −78° and 1.2 equiv of O_3 from a Welsbach generator was bubbled in at 0.33 ml/min as a 3–5% stream in oxygen. The solution was warmed to 25°. Glpc analysis indicated a 62:27:16 ratio of **20, 11,** and paraformaldehyde. A similar reaction run at −110° in Freon-12 was transferred while still cold to a precooled nmr tube. Spectra run at −100, −80, −60, −40, −20, and 0° indicated that the only change taking place was trimerization of formaldehyde.

Reaction of 1,3-Di-*tert*-butylallene with O_3. The addition of 1.5 equiv of O_3 to 20 mg of 1,3-di-*tert*-butylallene in CH_2Cl_2 at −78° and warming to 25° gave 71% pivaldehyde. A similar reaction in Freon-12 followed by low-temperature nmr indicated only pivaldehyde.

Ozonolysis of 19. A 150-mg sample of **8** was treated with 1 equiv of PNPBA as above to yield 66% of **19** by nmr integration in a mixture of other known compounds. The mixture was dissolved in Freon-11 and cooled to −78° and 1 equiv of O_3 was bubbled in. The resulting blue solution was warmed to 25° and N_2 was passed through to remove excess ozone. The nmr integral showed a 19:19:44:18 mixture of **23, 22, 20,** and **11.**

2,2,6,6-Tetramethyl-5-*tert*-butylhept-3-yn-5-ol. A suspension of 1.3 g of Li dispersion in 50 ml of benzene was stirred in a 250-ml three-necked flask fitted with a dropping funnel, condenser, magnetic stirrer, and gas inlet tube. A static argon atmosphere was maintained throughout the reaction. Ethylenediamine (11 g) was slowly added at room temperature. An exothermic reaction occurred and stirring was continued for 45 min, after which the reaction mixture was heated to reflux for 2 hr. After cooling to 45°, 15 g of *tert*-butylacetylene was added slowly and the reaction mixture was stirred for 4.5 hr. Di-*tert*-butyl ketone (26 g) was added and stirring was continued for 18 hr. The reaction was quenched with water, and the organic layer was separated, dried, and concentrated. The crude semisolid product was suction filtered to give 24 g (67%) of white, crystalline material. A pure sample of the propargyl alcohol was obtained by glpc: mp 60–61°; ir 2.85, 4.51, and 10.3 μ; nmr δ 1.53 (s, 1), 1.23 (s, 9), and 1.12 (s, 18).

Anal. Calcd for $C_{15}H_{28}O$: C, 80.29; H, 12.58. Found: C, 80.4; H, 12.6.

1-Chloro-1,3,3-tri-*tert*-butylallene. A mixture of 5.0 g of tri-*tert*-butylpropargyl alcohol, 2.5 g of $CaCl_2$, 0.02 g of hydroquinone, 10 ml of concentrated HCl, and 5 ml of hexane was stirred in an ice bath. After several hours, the reaction mixture was warmed to 43° and stirred for an additional 12 hr. The reaction mixture was diluted with hexane, and the aqueous layer was discarded. The organic layer was washed with saturated Na_2CO_3 solution, dried, and concentrated to give 5.3 g (92%) of crude product. Glpc showed a single component. A pure sample of the chloroallene was obtained by glpc: ir 5.13, 10.8, 12.6, and 14.9 μ; nmr δ 1.21 (s, 18) and 1.15 (s, 9).

Anal. Calcd for $C_{15}H_{27}Cl$: C, 74.19; H, 11.21; Cl, 14.60. Found: C, 74.4; H, 11.1; Cl, 14.7.

1,1,3-Tri-*tert*-butylallene (25). A suspension of 4.0 g of the tri-*tert*-butylchloroallene, 1.2 g of lithium, and 4.3 g of *t*-BuOH in 30 ml of THF was refluxed for 5.5 hr. The reaction mixture was allowed to cool to room temperature and filtered through glass wool to remove excess lithium. The solution was poured over 100 g of ice and the aqueous layer was extracted with hexane and dried. Distillation afforded pure **25** (2.7 g, 74%): bp 100–108° (28 mm); ir 5.14 and 12.5 μ; nmr δ 4.94 (s, 1), 1.17 (s, 18), and 1.02 (s, 9); mass spectrum m/e (rel intensity) 208 (8), 152 (5), 137 (18), 109 (7), 108 (8), 95 (7), and 57 (100).

Epoxidation of 25 with MCPBA. A slurry of 3.0 g of **25,** 3.5 g

(2 equiv) of MCPBA, and 3 g of Na_2CO_3 in 70 ml of CH_2Cl_2 was refluxed for 10 hr. The inorganic salts were removed by filtration and the solvent was removed to give 3.0 g of crude product. Glpc analysis indicated a 10:1 ratio of two products. The major component was identified as **26**: ir 5.60 μ; nmr (220 MHz) δ 4.56 (s, 1), 1.063 (s, 9), and 1.055 (s, 18); mass spectrum *m/e* (rel intensity) 224 (1), 168 (3), 154 (13), 126 (31), 111 (100), 97 (31), 83 (25), and 57 (83).

Anal. Calcd for $C_{15}H_{28}O$: C, 80.29; H, 12.58. Found: C, 80.2; H, 12.4.

The minor component was isolated by glpc and identified as **27**: ir 5.56 μ; nmr δ 4.76 (s, 1), 1.16 (s, 9), 1.12 (s, 9), and 1.02 (s, 9); mass spectrum *m/e* (rel intensity) 240 (trace), 184 (4), 154 (9), 139 (36), 127 (4), 111 (30), 98 (6), 85 (29), 83 (33), 69 (10), and 57 (100).

Anal. Calcd for $C_{15}H_{28}O_2$: C, 74.95; H, 11.74. Found: C, 74.9; H, 11.7.

Photolysis of 26. Photolysis was carried out with a Hanovia high-pressure mercury arc in a quartz apparatus. An 85-mg sample of **26** as a 1% solution in hexane was photolyzed for 20 hr. Glpc showed a 50:50 mixture of **26** and **28**. Photolysis was continued for 26 hr more, after which time the ratio was 30:70. Compound **28** showed ir 5.58, 7.95, 8.35, 12.9, and 13.4 μ; nmr δ 4.28 (s, 1), 1.10 (s, 9), and 1.06 (s, 18); mass spectrum *m/e* (rel intensity) 224 (2), 209 (3), 168 (4), 167 (5), 153 (41), 127 (12), 126 (88), 112 (57), 111 (62), 98 (12), 97 (87), 84 (14), 83 (95), 69 (100), and 57 (92); exact mass, 224.212 (calcd for $C_{15}H_{28}O$, 224.2140).

Treatment of 26 with Base. A 22-mg sample of **26** was stirred for 24 hr at 25° with 2 ml of 0.2 *N* *t*-BuOK in *t*-BuOH. The solution was poured into water and extracted with ether. The extract was washed with water and dried and the solvent was removed. Glpc showed only starting material.

A 25-mg sample of **26** was refluxed for 24 hr in 2 ml of 1.3 *N* NaOMe in MeOH. The reaction was worked up as before to yield only **26**.

Reaction of 26 with BF_3. A 100-mg sample of **26** was stirred with 2 drops of boron trifluoride etherate in 4 ml of anhydrous ether for 10 days at 25°. The crude mixture was washed successively with NH_4OH solution and water, dried, and concentrated. Glpc and nmr indicated only one significant product, which was isolated by glpc and identified as **29**: ir 3.22, 5.84, 6.13, and 11.0 μ; nmr δ 5.07 (m, 1), 4.68 (m, 1), 2.18 (s, 2), 1.77 (m, 3), 1.24 (s, 3), 0.97 (s, 9), and 0.93 (s, 9); mass spectrum *m/e* (rel intensity) 224 (2), 168 (40), 153 (7), 125 (23), 111 (13), 99 (60), 97 (40), 83 (23), 71 (43), 69 (40), and 57 (100); exact mass, 224.212 (calcd for $C_{15}H_{28}O$, 224.2140).

Pyrolysis of 26. Allene oxide **26** (30 mg) was transferred under vacuum (0.1 mm) through a 15-cm tube filled with quartz chips heated to 350°. Glpc showed a 5:12:39:43 ratio of **28**, **26**, **29**, and **30**. Compound **28** was identified by its glpc retention time. Compound **30** showed ir 5.68 and 11.56 μ; nmr δ 1.01 (s, 3), 1.02 (s, 9), 1.07 (s, 9), 1.22 (s, 3), 1.52 (s, 3), and 2.99 (s, 1); mass spectrum *m/e* (rel intensity) 224 (2), 126 (73), 112 (62), 111 (100), 97 (96), 83 (23), 69 (27), 57 (73), and 55 (42); exact mass, 224.215 (calcd for $C_{15}H_{28}O$, 224.2140).

Pyrolysis of 28. An 11.5-mg sample of **28** was pyrolyzed in a vacuum flow system as above. Glpc and nmr analysis showed a 75:25 ratio of **30** and **29**.

Oxidation of 25 with PNPBA. Allene **25** (1.05 g) was stirred at 25° for 24 hr with 1.2 equiv of PNPBA in 200 ml of CH_2Cl_2. The solution was filtered and the solvent was removed. Glpc indicated five products in a 5:24:41:20:11 ratio which were isolated by glpc and identified as **20**, **26**, **27**, **31**, and **32**.

Product **31** showed ir 5.73, 6.78, 8.02, 9.30, 9.43, 11.5, and 12.0 μ; nmr δ 0.94 (s, 9), 1.04 (s, 12), 1.29 (s, 3), 1.37 (s, 3), and 3.31 (s, 1); (benzene-d_6) δ 0.97 (s, 3), 1.00 (s, 9), 1.10 (s, 9), 1.17 (s, 6), and 3.37 (s, 1); mass spectrum *m/e* (rel intensity) 240 (9), 183 (42), 127 (66), 126 (45), 112 (36), 111 (100), 97 (91), 84 (43), 70 (23), 69 (43), and 57 (98); exact mass, 240.209 (calcd for $C_{15}H_{28}O_2$, 240.2089).

Compound **32** gave ir 5.75, 6.81, 8.04, 9.42, 9.87, and 11.82 μ; nmr δ 0.96 (s, 9), 1.06 (s, 9), 1.17 (s, 3), 1.30 (s, 3), 1.34 (s, 3), and 3.65 (s, 1); mass spectrum *m/e* (rel intensity) 240 (4), 183 (29), 152 (4), 127 (64), 126 (46), 111 (100), 98 (9), 97 (64), 84 (34), 71 (47), 69 (61), and 57 (100); exact mass, 240.209 (calcd for $C_{15}H_{28}O_2$, 240.2089).

Allene **25** (1.05 g) was treated with 3 equiv of PNPBA in 300 ml of CH_2Cl_2 at 25° for 24 hr. The reaction mixture was poured into 10% $Na_2S_2O_3$ solution and extracted with hexane. The extract was concentrated and analyzed by glpc. Four products in a 6:67:21:6 ratio were identified as **26**, **27**, **31**, and **32**.

Reaction of 31 with NaOMe–MeOH. A 35-mg sample of **31** was stirred for 2 hr at 60° with 4 ml of 1.3 *N* NaOMe in MeOH. The mixture was poured into water, extracted with ether, dried, and concentrated. Glpc showed quantitative recovery of **31**.

Reaction of 32 with NaOMe–MeOH. An 11-mg sample of **32** was stirred at 60° for 5 hr with 2 ml of 1.3 *N* NaOMe in MeOH. Work-up as before and glpc showed complete conversion of **32** to **31**.

Reaction of 27 with HOAc. A 120-mg sample of **27** was stirred at 40° for 60 hr with 1 ml of HOAc in 5 ml of CH_2Cl_2. The mixture was poured into water, neutralized with $NaHCO_3$, and extracted with ether. The solvent was dried and removed to yield 112 mg of pure **27**.

Reaction of 25 with O_3. **25** (100 mg) in 1 ml of $CFCl_3$ was cooled to −78° and 1 equiv of O_3 was bubbled into the solution. The solution was warmed to room temperature and analyzed by glpc to show **25**, **26**, and **27** in a 49:5:41 ratio.

The nmr of the crude reaction mixture showed singlets at δ 4.94, 4.59, and 3.05 indicating **25** (47%), **26** (7%), and **33** (46%). The ir of the reaction mixture displayed no carbonyl absorption. Glpc collection gave **25**, **26**, and **27**.

A similar reaction using 2 equiv of O_3 gave a sample whose nmr at −78 and 25° were similar, the only apparent difference being considerable line broadening at −78°. The spectrum at 25° displayed singlets at δ 3.05, 1.21, 1.17, 1.12, and 1.04 in a 1:1:9:9:9 ratio. After the sample had stood for 3 days, the spectrum showed singlets at δ 4.85, 1.21, 1.16, 1.12, and 1.02 in a 1:1:9:9:9 ratio. The ir of the initial sample displayed no carbonyl absorption: 6.40, 6.8, 7.2, 7.35, 10.3, 11.0, and 11.9 μ. The ir of the final sample was identical with that of **27**. Glpc indicated a 97:3 mixture of **27** and **20**.

Reaction as above with 2 equiv of O_3 followed by the addition of 1 ml of MeOH precooled to −78°, warming to room temperature, and solvent removal gave a 97% yield of **27**.

Reaction of 33 with Acid. Allene **25** (40 mg) in Freon-11 was treated at −78° with excess ozone. The nmr showed a 24:60:16 ratio of **25**, **33**, and **27**. This mixture was stirred with 250 mg of *p*-nitrobenzoic acid in CH_2Cl_2 at 25° for 25 hr. After filtration and solvent removal, nmr and glpc indicated an 87:13 ratio of **27** and **31**.

A 28-mg sample of **25** ozonized at −78° showed only **33** by nmr analysis. Addition of 1 drop of trifluoromethanesulfonic acid produced a 60:40 mixture of **31** and **32** by nmr and glpc.

Reaction of 26 with O_3. To 12 mg of **26** in 1 ml of ether at −78° was added 1 equiv of O_3. After warming to room temperature, glpc showed only **27**. The nmr of the crude reaction mixture was identical with that of **33**.

Oxidation of 26 with PNPBA. A 40-mg sample of **26** was stirred with 1 equiv of PNPBA in 5 ml of CH_2Cl_2 for 23 hr. The solution was filtered and the solvent was removed. Glpc showed an 80:20 mixture of **27** and **31**.

2,2,5,6,6-Pentamethylhept-3-yn-5-ol (34). In a 500-ml three necked flask equipped with a mechanical stirrer, gas inlet, condenser, and dropping funnel was placed 1.5 g of Li wire and 50 ml of benzene under a nitrogen blanket. Ethylenediamine (11 g) was added dropwise and the mixture was stirred at reflux for 2 hr. The reaction was cooled to 40° and 15 g of *tert*-butylacetylene was added dropwise over 45 min. The resulting solution was stirred 5 hr before 18.5 g of pinacolone was added dropwise. After the mixture was stirred for an additional 18 hr, the reaction was quenched by the addition of water; the mixture was extracted with ether, and the combined extracts were dried and concentrated to yield 24 g (73%) of crude **34**. A pure sample of **34** was obtained by glpc: ir 2.85, 4.50, 11.0, and 12.7 μ; nmr δ 0.96 (s, 9), 1.19 (s, 9), 1.25 (s, 3), and 1.52 (s, 1); mass spectrum *m/e* (rel intensity) 167 (1), 126 (9), 125 (89), 69 (7), 57 (26), 55 (16), and 43 (100).

Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 79.1; H, 12.2.

1-Chloro-1,3-di-*tert*-butyl-3-methylallene (35). A mixture of 15 g of $CaCl_2$, 60 ml of concentrated HCl, 0.2 g of hydroquinone, and 24 g of crude **34** in 35 ml of hexane was stirred in an ice bath for 1 hr and then at 40° for 18 hr. The layers were separated, and the aqueous layer was extracted with hexane. The combined extracts were dried and concentrated to yield 21 g (80%) of crude **35**. Pure **35** was obtained by glpc: ir 5.14, 10.9, and 11.6 μ; nmr δ 1.06 (s, 9), 1.10 (s, 9), and 1.75 (s, 3); mass spectrum *m/e* (rel intensity) 202 (3), 200 (7), 165 (3), 164 (2), 57 (100), and 41 (18).

Anal. Calcd for $C_{12}H_{21}Cl$: C, 71.80: H, 10.54. Found: C, 72.0; H, 10.6.

1,3-Di-*tert*-butyl-1-methylallene (36). A mixture of 25 g of *tert*-butyl alcohol, 150 ml of dry THF, and 7 g of Li wire cut into small pieces was stirred at 40° while 21 g of crude **35** was added rapidly until a vigorous reaction started and then dropwise. The reaction was refluxed for 5 hr, filtered to remove excess Li, and poured over ice. The mixture was extracted with hexane, and the combined organic layers were dried and concentrated. Distillation gave pure **36:** bp 59–60° (15 mm); ir 5.14, 9.04, and 12.8 μ; nmr δ 0.99 (s, 9), 1.02 (s, 9), 1.66 (d, 3, J = 3.5 Hz), and 4.90 (quartet, 1, J = 3.5 Hz); mass spectrum m/e (rel intensity) 166 (11), 151 (5), 110 (6), 109 (12), 95 (18), and 57 (100).

Anal. Calcd for $C_{12}H_{22}$: C, 86.67; H, 13.33. Found: C, 87.0; H, 13.1.

Peracid Oxidation of 36. A 100-mg sample of **36** was stirred at 25° for 18 hr with 1.10 g of PNPBA in 50 ml of CH_2Cl_2. The reaction mixture was filtered and the solvent was removed from the filtrate. Glpc showed a 46:6:36:12 mixture of **37**, **38**, **39**, and **40**. Allene oxide **37** showed ir 5.60, 8.62, 8.91, 9.2, and 10.1 μ; nmr δ 0.97 (s, 9), 1.07 (s, 9), 1.40 (s, 3), and 4.55 (s, 1); mass spectrum m/e (rel intensity) 182 (1), 167 (5), 127 (14), 111 (19), 97 (13), 85 (13), 84 (100), 69 (68), and 57 (30).

Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 79.0; H, 12.2.

Ketone **38** showed ir 5.95, 6.85, 9.7, 9.9, and 10.7 μ; nmr 0.99 (s, 9), 1.13 (s, 9), 2.43 (s, 2), 5.53 (s, 1), and 5.55 (s, 1); mass spectrum m/e (rel intensity) 182 (11), 167 (40), 126 (6), 112 (9), 111 (100), 84 (9), 83 (56), 69 (6), and 57 (45).

Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 79.1; H, 12.2.

Oxetanone **39** showed ir 5.55, 10.3, and 11.3 μ; nmr δ 0.99 (s, 18), 1.43 (s, 3), and 4.77 (s, 1); mass spectrum m/e (rel intensity) 198 (6), 170 (7), 155 (10), 142 (18), 112 (17), 111 (19), 100 (23), 98 (27), 97 (44), 85 (42), 84 (93), 83 (91), 69 (100), and 57 (67).

Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.6; H, 11.3.

Oxacyclopentanone **40** showed ir 5.70, 9.4, and 9.8 μ; nmr δ 0.88 (s, 3), 0.92 (s, 3), 0.97 (s, 9), 1.11 (s, 3), 1.20 (s, 3), and 3.34 (s, 1); mass spectrum m/e (rel intensity) 198 (7), 142 (32), 127 (14), 97 (14), 85 (20), 84 (100), 83 (13), 70 (33), 69 (90), 57 (60), and 55 (30); exact mass, 198.161 (calcd for $C_{12}H_{22}O_2$, 198.1620).

Oxidation of 100 mg of **36** with 3 equiv of PNPBA under identical conditions gave a 6:2:75:17 mixture of **37**, **38**, **39**, and **40**.

Two other minor products from this oxidation were isolated by glpc and identified as pinacolone and 2-*tert*-butyl-5,5-dimethyl-4-hydroxyhex-1-en-3-one: ir 2.90, 5.99, 7.75, and 10.7 μ; nmr δ 0.87 (s, 9), 1.20 (s, 9), 3.14 (m, 1), 4.36 (m, 1), 5.80 (br s, 1), and 5.82 (br s, 1); mass spectrum m/e (rel intensity) 198 (1), 142 (25), 141 (14), 127 (16), 112 (67), 111 (75), 97 (39), 87 (44), 84 (50), 83 (69), 69 (86), and 57 (100); exact mass, 198.160 (calcd for $C_{12}H_{22}O_2$, 198.1620).

Pyrolysis of 37. An 8.3-mg sample of **37** was pyrolyzed in a vacuum flow system at 250° to yield a 37:63 mixture of **37** and **38** by glpc and nmr.

Photolysis of 37. A 22-mg sample of **37** in 2 ml of pentane was irradiated through quartz with a 450-W high-pressure Hanovia lamp. Glpc and nmr showed only **37**.

Reaction of 37 with Acid. To a 20-mg sample of **37** in CCl_4 in an nmr tube was added 1 drop of trifluoromethanesulfonic acid. Nmr analysis showed only **38**.

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Registry No.—**1**, 21020-30-9; **2**, 21590-00-1; **3**, 21502-98-7; **4**, 23116-55-4; **5**, 51211-83-7; **7**, 21503-00-4; **8**, 22585-31-5; **9**, 33420-19-8; **10**, 16487-16-4; **11**, 21400-16-8; **13**, 21400-17-9; **14**, 51211-84-8; **15**, 21400-18-0; **16**, 51211-85-9; **19**, 51211-86-0; **20**, 815-24-7; **22**, 51211-87-1; **23**, 51211-88-2; **25**, 42066-38-6; **26**, 26000-19-1; **27**, 24294-51-7; **28**, 51211-89-3; **29**, 51211-90-6; **30**, 51211-91-7; **31**, 51211-92-8; **32**, 51271-03-5; **33**, 51262-43-2; **34**, 36187-02-7; **35**, 51211-93-9; **36**, 51211-94-0; **37**, 51211-95-1; **38**, 35373-22-9; **39**, 51211-96-2; **40**, 51211-97-3; ethylenediamine, 107-15-3; di-*tert*-butylethylene, 22808-06-6; 1,3-di-*tert*-butylallene, 42066-39-7; 2,2,6,6-tetramethyl-5-*tert*-butylhept-3-yn-5-ol, 36187-03-8; 1-chloro-1,3,3-tri-*tert*-butylallene, 37892-65-2; *tert*-butylacetylene, 917-92-0; 2-*tert*-butyl-5,5-dimethyl-4-hydroxyhex-1-en-3-one, 51211-98-4.

References and Notes

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