phosphine in 10 mL of tetrahydrofuran was stirred under argon at room temperature for 15 min and then cooled to 0 °C. A solution of dimethyl sodiomalonate (from 0.0093 g (0.070 mmol, 2 equiv) of dimethyl malonate and 0.0017 g (0.070 mmol, 2 equiv) of sodium hydride) was added via syringe in one portion. The mixture was allowed to warm to room temperature and stirred overnight. The reaction mixture was partitioned between water and diethyl ether. The aqueous layer was extracted twice with diethyl ether, and the combined organic layer was washed with saturated aqueous sodium chloride solution. The organic layer was dried ($MgSO_4$), filtered, and evaporated under reduced pressure. Chromatographic purification (1-mm silica gel chromatotron plate, 3:1 hexane/ethyl acetate followed by preparative thin-layer chromatography, 3:1 hexane/ethyl acetate) gave 0.012 g (56%) of **14** as a clear oil: ^{1}H NMR ($CDCl_3$) δ 1.35 (s, 3 H, CH_3), 1.36 (s, 3 H, CH_3), 1.90 (s, 3 H, $-NHCOCH_3$), 2.34 (s, 3 H, tosyl CH_3), ABX system, δ_A 3.19, δ_B 3.39, δ_X 4.85 (J_{AX} = 8.3 Hz, J_{BX} = 5.3 Hz, J_{AB} = 15.5 Hz, $-CH_2CH-$), 3.48 (s, 1 H, $-CH(COOCH_3)_2$), 3.69 (s, 6 H, $-CH(COOCH_3)_2$), 3.70 (s, 3 H, $-COOCH_3$), 6.09 (d, 1 H, J = 7.8 Hz, $-NHCOCH_3$), 6.28 (d, 1 H, J = 15.8 Hz, indole $-CH=CH-$), 6.92 (d, 1 H, J = 15.8 Hz, indole $-CH=CH-$), 7.15-7.30 (m, 4 H, ArH), 7.41 (s, 1 H, indole 2*H*), 7.72 (d, 2 H, J = 8.2 Hz, ArH), 7.77 (d, 1 H, J = 7.5 Hz, indole 7*H*); IR (neat) 3300 (NH), 1745 ($COOCH_3$), 1735 ($COOCH_3$), 1645 ($NHCOCH_3$) cm^{-1}. Anal. Calcd for $C_{31}H_{36}N_2O_9S$: C, 60.77; H, 5.92; N, 4.57; S, 5.23. Found: C, 60.65; H, 6.19; N, 4.29; S, 5.41.

Acknowledgment. Support for this research under Grant 2RO1 GM26178-06 from the National Institutes of General Medical Sciences (PHS) is gratefully acknowledged. High-field NMR spectra were obtained in the Colorado State University Regional NMR Center, funded by National Sciences Foundation Grant CHE 78-18581.

Epoxidation of 3,6-Di-*tert*-butyl-2,2,7,7-tetramethyl-3,4,5-octatriene. Isolation of a Stable Methylenecyclopropanone

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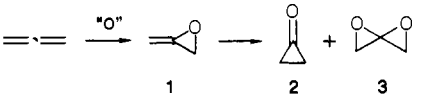
Abstract: The oxidation of 3,6-di-*tert*-butyl-2,2,7,7-tetramethyl-3,4,5-octatriene (**4**) with *m*-chloroperbenzoic acid gave the methylenecyclopropanone derivative **5** as the major product, along with the methyleneoxetanone **6** and *m*-chlorobenzoate **7**. Low-temperature ^{1}H and ^{13}C NMR studies indicate the formation of an unstable precursor to the observed products which is assigned the cumulene oxide structure **11**.

The peracid oxidation of allenes has been demonstrated to involve allene oxides (methyleneoxiranes, **1**) and cyclopropanones (**2**), as well as spirodioxides (**3**) derived from the further epoxidation of **1**.[1,2] While these species are normally reactive intermediates that evolve into stable products under the reaction conditions, examples of each have been isolated and characterized in instances where bulky substituents serve to stabilize these fragile molecules.[1] We have recently begun to extend our epoxidation studies to higher cumulenes[3] and report herein our initial results concerning the peracid oxidation of the highly hindered cumulene 3,6-di-*tert*-butyl-2,2,7,7-tetramethyl-3,4,5-octatriene (**4**).[4,5]

Reaction of **4** with 1.3 equiv of *m*-chloroperbenzoic acid (MCPBA) in CH_2Cl_2 at 0 °C with the exclusion of light gave a mixture of three products that were isolated by chromatography over silica gel, again with protection from light. These products are assigned structures **5** (84% yield), **6** (8%), and **7** (2%) on the basis of spectroscopic and chemical characterization.

Scheme I



Methylenecyclopropanone **5**[5] is a dark yellow solid, mp 56-57 °C, which analyzes for $C_{20}H_{36}O$ and shows an M + 1 peak at *m/e* 293 in its chemical-ionization mass spectrum (CH_4). Its IR spectrum (Nujol) shows a strong, high-frequency carbonyl band at 1785 cm^{-1}, as well as a strong band at 1585 cm^{-1} for the carbon-carbon double bond.[6] The 300-MHz proton NMR spectrum ($CDCl_3$) reveals sharp singlets at δ 1.14, 1.31, and 1.43 in a 2:1:1 ratio. The UV spectrum (2,2,4-trimethylpentane) manifests an unusually long wavelength $n \rightarrow \pi^*$ absorption at 435 nm (ϵ 91) in addition to a relatively weak $\pi \rightarrow \pi^*$ band at 260 nm (ϵ 6640).[6] Finally, the 75.4-MHz ^{13}C NMR spectrum ($CDCl_3$) of **5**, including a proton-coupled experiment, is fully consistent with this formulation: δ 30.9 (q), 31.3 (q), 32.2 (q), 37.3 (s), 38.5 (s), 42.5 (s), 53.9 (s), 121.4 (s), 164.5 (s), 208.4 (s).

Methylenecyclopropanone **5** is light-sensitive, decomposing essentially quantitatively to tetra-*tert*-butylallene (**8**)[8] merely upon exposure to sunlight for a few minutes.[7] A similar conversion to **8** was provoked by preparative GC of **5** with the injector port at 250 °C. Nonetheless, **5** was remarkably stable to a variety of

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(4) Hartzler, H. D. *J. Am. Chem. Soc.* **1971**, *93*, 4527-4531.

(5) This work was first presented at the 192nd National Meeting of the American Chemical Society, Anaheim, CA; September 7-12, 1986. Subsequently, a report of the isolation of several hindered methylenecyclopropanones from the epoxidation of 1,2,3-cumulenes appeared: Ando, W.; Hayakawa, H.; Tokitoh, N. *Tetrahedron Lett.* **1986**, *27*, 6357-6360.

(6) Simple cyclopropanones normally show carbonyl frequencies in the range 1815-1825 cm^{-1} and weak UV absorption in the 330-350-nm region.[7]

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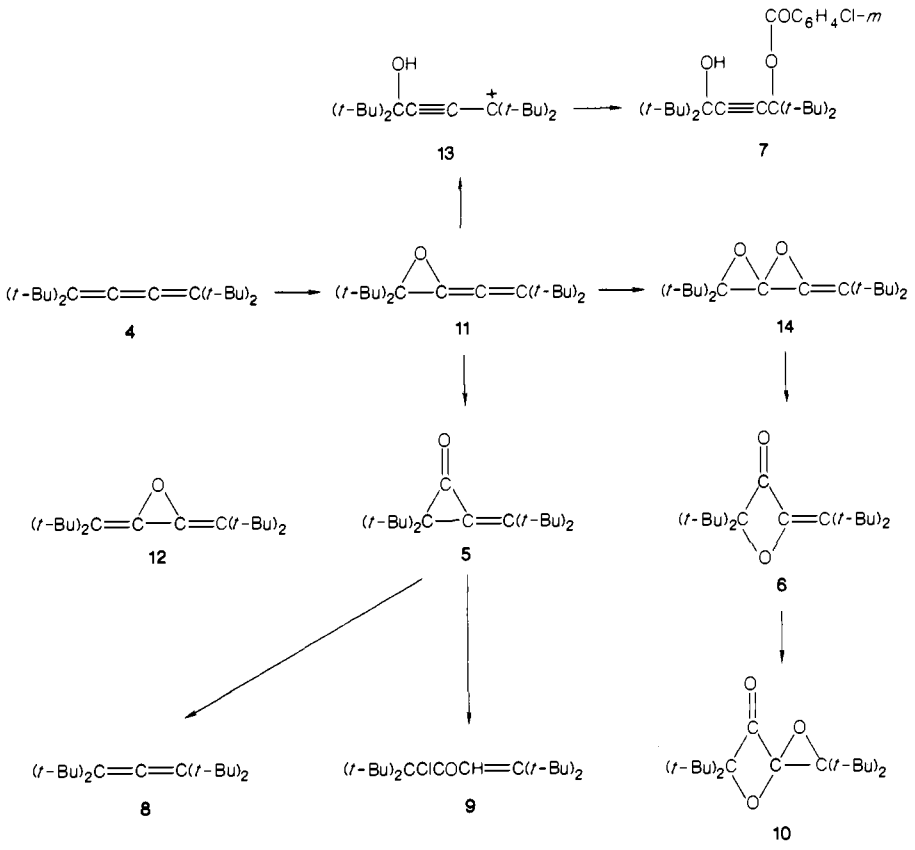
Scheme II



chemical reagents, including MCPBA, methanolic sodium methoxide, and acetic acid. Reaction with an excess of concentrated HCl in CH_2Cl_2 did, however, effect a clean conversion to chloro ketone **9** in 87% yield.[9]

The second epoxidation product, methyleneoxetanone **6**, is a white solid (mp 46–47 °C) which analyzes for $C_{20}H_{36}O_2$ and shows the following: IR (Nujol) 1780, 1560 cm^{-1}; UV (2,2,4-trimethylpentane) 292 (ϵ 4860), 345 (ϵ 95) nm; ^1H NMR ($CDCl_3$) δ 1.13 (s, 18), 1.30 (s, 9), 1.40 (s, 9); ^{13}C NMR ($CDCl_3$) δ 28.3 (q), 30.9 (q), 32.5 (q), 32.7 (s), 37.2 (s), 38.4 (s), 109.1 (s), 136.5 (s), 161.2 (s), 193.2 (s); mass spectrum, *m/e* (relative intensity) 308 (7), 251 (14), 196 (19), 195 (62), 181 (11), 167 (14), 151 (37), 139 (64), 111 (35), 97 (100). Passing **6** through a vacuum pyrolysis system at 450 °C resulted in partial conversion to di-*tert*-butylketene (IR 2100 cm^{-1}; ^1H NMR δ 1.20).[10]

The third epoxidation product, *m*-chlorobenzoate **7**, was identified by comparison with an authentic sample prepared by acylation of the corresponding diol.[4]

Reaction of cumulene **4** with 5 equiv of MCPBA at −30 °C gave **5** (37%), **6** (13%), **7** (4%), and a new compound **10** (42%). Epoxy ketone **10** was also obtained by treatment of **6** with MCPBA.

The results implicate an intermediate cumulene oxide such as **11** or **12** as the initial product in the peracid oxidations of **4**. Indeed, an ^1H NMR experiment conducted by monitoring a reaction in the temperature range −50 to +40 °C clearly established the clean formation of a new reactive species which readily isomerized to methylenecyclopropanone **5**. This intermediate shows equivalent singlets at δ 1.15 and 1.22, consistent with either structure **11** or **12**. Evidence in support of the less symmetrical structure **11** was provided by a low-temperature ^{13}C NMR spectrum which showed a total of eight signals (δ 29.2, 32.5, 37.6, 38.6, 81.1, 118.3, 144.0, and 170.9) that are attributed to the intermediate. The last chemical-shift value is assigned to the sp-hybridized carbon of **11**. This is significantly shielded relative to the corresponding carbon of simple allenic compounds,[11] but the combined shielding influences of heavy substitution on the allene, conjugation with the oxygen,[12] and the strained-ring effect[13] provide a satisfactory rationalization of this chemical shift.

Thus, epoxide **11** is visualized as the immediate precursor of structurally rearranged methylenecyclopropanone **5** by an isomerization similar to the **1** → **2** conversion.[1] Alternatively, protonation of epoxide **11**, followed by cleavage of the other carbon–oxygen bond, would generate the stabilized propargyl cation **13**, which is a logical precursor of the *m*-chlorobenzoate **7** that is formed as a minor product in the oxidation of cumulene **4**. The formation of methyleneoxetanone **6** is hypothesized to proceed through an intermediate diepoxide, most probably **14**, which is derived from competitive oxidation of the cumulene oxide **11**. The shifting of the product distribution toward **6** and epoxy ketone **10** when the reaction is performed with an excess of MCPBA at −30 °C is fully consistent with this explanation. The proposed transformation of **14** to **6** finds analogy in the well-documented rearrangements of spirodioxides of type **3** to 3-oxetanones.[1] However, the low-temperature NMR experiments gave no indication of the accumulation of a second unstable intermediate. Consequently, if **14** actually intervenes on the way to **6**, its rearrangement must be extremely facile under the reaction conditions. We are continuing to explore the novel oxidation chemstry of higher cumulenes.

Experimental Section

Epoxidation of 3,6-Di-*tert*-butyl-2,2,7,7-tetramethyl-3,4,5-octatriene (4) with MCPBA. To a solution of 4.0 g (15 mmol) of **4**[4] in 100 mL of CH_2Cl_2 under nitrogen at 0 °C was added 3.5 g (20 mmol) of *m*-chloroperbenzoic acid (MCPBA) in 120 mL of CH_2Cl_2 in the absence of light. After 3 h the mixture was allowed to warm to room temperature and stirred overnight. A few drops of tetramethylethylene were added to eliminate excess peracid and the mixture was washed twice with sat-

(9) Ketone **9** decomposed to 3,6-di-*tert*-butyl-2,3,7,7-tetramethyl-1,5-octadien-4-one upon attempted purification by GC.

(10) Newman, M. S.; Arkell, A.; Fukunaga, T. *J. Am. Chem. Soc.* **1960**, *82*, 2498–2501.

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(12) Steur, R.; van Dongen, J. P. C. M.; de Bie, M. J. A.; Drenth, W.; de Haan, J. W.; van de Ven, L. J. M. *Tetrahedron Lett.* **1971**, *36*, 3307–3310.

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urated $NaHCO_3$ solution and dried ($MgSO_4$). The solvent was removed to give 4.5 g of a yellow solid, mp 53–55 °C. TLC analysis indicated one major component. Chromatography over silica gel with hexane as the eluent afforded three fractions.

The second fraction consisted of 3.0 g (71%) of a yellow solid assigned structure **5**: mp 56–57 °C; IR (Nujol) 1785, 1585, 1390, 1355 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.14 (s, 18), 1.31 (s, 9), 1.43 (s, 9); ^{13}C NMR ($CDCl_3$) δ 208.4 (s), 164.5 (s), 121.4 (s), 53.9 (s), 42.5 (s), 38.5 (s), 37.3 (s), 32.2 (q), 31.3 (q), 30.9 (q); UV (2,2,4-trimethylpentane) λ 260 nm (ϵ 6640), 435 nm (ϵ 91); chemical-ionization mass spectrum (CH_4), *m/e* (relative intensity) 293 (4), 276 (0.5), 237 (3), 236 (4), 220 (3), 219 (5), 180 (8), 179 (57), 163 (8), 151 (16), 139 (20), 57 (100).

Anal. Calcd for $C_{20}H_{36}O$: C, 82.12; H, 12.41. Found: C, 81.7; H, 12.2.

The first fraction was rechromatographed (silica gel–hexane) to give 390 mg (9%) of **5** and 340 mg (8%) of a white solid identified as **6**: mp 46–47 °C; IR (Nujol) 1780, 1560, 1390, 1360 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.13 (s, 18), 1.30 (s, 9), 1.40 (s, 9); ^{13}C NMR ($CDCl_3$) δ 193.2 (s), 161.2 (s), 136.5 (s), 109.1 (s), 38.4 (s), 37.2 (s), 32.7 (s), 32.5 (q), 30.9 (q), 28.3 (q); UV (2,2,4-trimethylpentane) λ 292 nm (ϵ 4860), λ 345 nm (ϵ 95); mass spectrum, *m/e* (relative intensity) 308 (7), 251 (14), 196 (19), 195 (62), 181 (11), 167 (14), 151 (37), 139 (64), 111 (35), 97 (100).

Anal. Calcd for $C_{20}H_{36}O_2$: C, 77.87; H, 11.76. Found: C, 77.8; H, 12.1.

The third fraction was rechromatographed to give 162 mg (4%) of pure **5** and 113 mg (2%) of a white solid assigned by comparison with an authentic sample as **7**: mp 112–114 °C; IR (CCl_4) 3630, 3550, 3070, 1730, 1575, 1480, 1395, 1370 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.23 (s, 18), 1.30 (s, 18), 2.55 (s, 1), 7.38 (t, 1), 7.51 (d, 1), 7.89 (d, 1), 7.98 (d, 1); ^{13}C NMR ($CDCl_3$) δ 162.8 (s), 134.5 (d), 133.6 (d), 132.5 (d), 129.7 (s), 129.6 (s), 127.6 (d), 94.7 (s), 91.6 (s), 83.4 (s), 81.8 (s), 44.0 (s), 41.7 (s), 29.3 (q), 29.0 (q).

Anal. Calcd for $C_{27}H_{41}O_3Cl$: C, 72.24; H, 9.14; Cl, 7.92. Found: C, 72.3; H, 8.9; Cl, 8.1.

Epoxidation of 4 with an Excess of MCPBA. To a solution of 276 mg (1 mmol) of **4** in 25 mL of CH_2Cl_2 at −30 °C under nitrogen and in the absence of light was added 862 mg (5 mmol) of MCPBA in 5 mL of CH_2Cl_2. After the mixture was stirred for 3 days at this temperature a few drops of tetramethylethylene were added and the reaction mixture was washed twice with saturated $NaHCO_3$ solution and dried ($MgSO_4$). Removal of the solvent gave 318 mg of a yellow solid. Chromatography over silica gel with hexane as eluent gave 109 mg (37%) of **5**, 39 mg (13%) of **6**, 19 mg (4%) of **7**, and 137 mg (42%) of a white solid identified as **10**: mp 52–53 °C; IR (CCl_4) 1820, 1485, 1395, 1370 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.13 (s, 9), 1.17 (s, 9), 1.18 (s, 9), 1.28 (s, 9); ^{13}C NMR ($CDCl_3$) δ 205.6 (s), 109.3 (s), 106.9 (s), 81.2 (s), 39.2 (s), 38.9 (s), 38.5 (s), 37.5 (s), 30.1 (q), 29.8 (q), 29.7 (q), 28.3 (q); mass spectrum, *m/e* (relative intensity) 309 (0.3), 253 (1), 212 (4), 197 (21), 183 (6), 154 (11), 139 (100), 111 (53), 97 (45).

Anal. Calcd for $C_{20}H_{36}O_3$: C, 74.03; H, 11.18. Found: C, 74.0; H, 10.9.

Reaction of 5 with Concentrated HCl. To a stirred solution of 153 mg (0.52 mmol) of **5** in 10 mL of CH_2Cl_2 was added 5 mL of concentrated HCl. After 10 min, the yellow color of **5** had disappeared. The organic layer was separated and dried ($MgSO_4$). Removal of the solvent gave 176 mg of a yellow liquid which was chromatographed (silica gel; hexane–ether 9:1) to give 150 mg (87%) of a light yellow solid identified as 3-chloro-3,6-di-*tert*-butyl-2,2,7,7-tetramethyloct-5-en-4-one (**9**): mp 35–37 °C; IR (neat) 1685, 1570, 1490, 1385, 1370 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.26 (s, 18), 1.28 (s, 9), 1.39 (s, 9), 7.17 (s, 1); UV (2,2,4-trimethylpentane) λ 255 nm (ϵ 12950), shoulder λ 294 nm (ϵ 1500); ^{13}C NMR ($CDCl_3$) δ 200.6 (s), 174.0 (s), 124.7 (d), 97.0 (s), 43.6 (s), 41.7 (s), 38.6 (s), 31.6 (q), 31.5 (q), 30.6 (q); chemical-ionization mass spectrum (NH_4), *m/e* (relative intensity) 329 (0.1), 293 (0.1), 292 (0.2), 278 (0.1), 235 (2), 168 (9), 167 (76), 139 (8), 111 (40), 83 (43), 57 (100). Negative ion spectrum $[MH]^-$: 329.261 (calcd 329.2613).

An attempt to purify **9** by preparative GC (8-ft × 0.25-in. column of 20% Carbowax on Chromosorb P) resulted in almost complete transformation to a new compound identified as 3,6-di-*tert*-butyl-2,3,7,7-tetramethyl-1,5-octadien-4-one: IR (neat) 3095, 1695, 1630, 1595, 1395, 1380, 1365, 1220, 1005, 900 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.11 (s, 1), 5.16 (m, 1), 4.87 (m, 1), 1.84 (s, 3), 1.33 (s, 9), 1.31 (s, 3), 1.20 (s, 9), 1.06 (s, 9); UV (2,2,4-trimethylpentane) λ 243 nm (ϵ 10000), shoulder 298 nm (ϵ 840); ^{13}C NMR ($CDCl_3$) δ 208.5 (s), 166.2 (s), 145.9 (s), 125.7 (d), 116.0 (t), 61.17 (s), 40.1 (s), 38.1 (s), 36.3 (s), 32.5 (q), 31.7 (q), 27.65 (q), 23.7 (q), 19.4 (q). Negative ion spectrum $[MH]^-$: 293.284 (calcd 293.2846).

Photolysis of 5. A solution of 38 mg of **5** in $CDCl_3$ in an NMR tube was exposed to the sunlight. After a few minutes the yellow color had disappeared. NMR analysis showed only a singlet at 1.20 ppm. Removal of the solvent gave 33 mg (97%) of a white solid identified as tetra-*tert*-butylallene (**8**): mp 41–42 °C (lit.[8] mp 41–42 °C); IR (CCl_4) 1920, 1475, 1385, 1360 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20 (s); ^{13}C NMR ($CDCl_3$) 199.0 (s), 118.8 (s), 35.4 (s), 32.4 (q); mass spectrum, *m/e* (relative intensity) 264 (4), 208 (6), 152 (15), 151 (82), 109 (20), 95 (28), 57 (100).

Table I. Percent of Observed Products

temp, °C	4	11	5	6	7
−50	57	43			
−25	55	45			
−10	50	50			
0	35	59	6		
10	20	62	16	2	
25	6	14	69	10	
40	3		82	15	traces

Pyrolysis of 5. A solution of 100 mg of **5** in a small amount of hexane was passed through a preparative GC DEGS column at 170 °C with the injector port at 250 °C. The only significant product was 83 mg (90%) of **8**.

Reaction of 5 with MCPBA. To 30 mg (0.1 mmol) of **5** in 5 mL of CH_2Cl_2 was added 86 mg (0.5 mmol) of MCPBA. After 5 days no transformation of the starting material was observed by TLC and NMR analysis.

Reaction of 5 with Sodium Methoxide. To 30 mg (0.10 mmol) of **5** was added a sodium methoxide solution prepared by adding 150 mg of NaH to 10 mL of methanol. After refluxing for 18 h the mixture was poured into water and extracted with ether. The extract was dried ($MgSO_4$) and concentrated. TLC and NMR analysis showed only recovered starting material. A solution of 27 mg of **5** in a similar amount of methanolic sodium methoxide was sealed in a glass tube and heated in a steam bath for 5 days. After a similar workup, NMR analysis showed only starting material.

Reaction of 5 with Methanol. A solution of 10 mg of **5** in 2 mL of CH_3OH was stirred at room temperature for 4 days. After this time TLC and NMR analysis showed only methanol and unreacted starting material.

Reaction of 5 with Acetic Acid. To a solution of 15 mg of **5** in CH_2Cl_2 in an NMR tube was added a few drops of CH_3COOH. After 3 h TLC and NMR analysis showed unchanged starting material.

Pyrolysis of 6. A 22-mg sample of **6** was passed through a vacuum pyrolysis system at 450 °C. GC analysis of the crude product showed 70% of **6** and 20% of a compound identified as di-*tert*-butylketene:[10] IR (neat) 2100 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20 (s).

Reaction of 6 with MCPBA. To a 21-mg sample of **6** in an NMR tube was added 5 equiv of MCPBA. After a few hours NMR analysis showed complete transformation to **10**. To the crude product was added 3 drops of tetramethylethylene and the reaction mixture was washed twice with saturated $NaHCO_3$ solution and dried ($MgSO_4$). Removal of solvent gave 18 mg (81%) of pure **10**.

Acetylenic Ester 7. A mixture of 0.5 g (1.6 mmol) of 3,6-di-*tert*-butyl-2,2,7,7-tetramethyloct-4-yn-3,6-diol[4] in 5 mL of hexane and 3 mL of dry THF was cooled to −78 °C under nitrogen in a 15-mL, two-necked, round-bottom flask equipped with a rubber septum. *n*-Butyllithium (1.0 mL of 1.6 M solution in hexane, 1.6 mmol) was added dropwise. After the mixture was stirred for 5 min, 0.28 g (1.6 mmol) of *m*-chlorobenzoyl chloride was added slowly. The mixture was allowed to warm to room temperature, stirred overnight, quenched with water, and extracted twice with hexane. The extracts were dried ($MgSO_4$) and concentrated. Chromatography of the crude product over silica gel (hexane-ether 9:1) gave, in addition to unidentified products, 383 mg (53%) of **7** whose spectral characteristics were identical with those of the product arising from the epoxidation of cumulene **4**.

^1H NMR Experiment: Epoxidation of 4 with 1.4 equiv of MCPBA. To an NMR sample of 4 mg of **4** in $CDCl_3$ was added, at −30 °C, 3.5 mg (1.4 equiv) of MCPBA. The reaction mixture was allowed to stand at −50 °C for 2 days prior to data accumulation. Spectra were recorded upon increasing the temperature incrementally from −50 to 40 °C. Relative amounts of the observed products as determined by NMR integration at different temperatures are given in Table I.

^1H NMR Experiment: Epoxidation of 4 with 5 equiv of MCPBA. To 4 mg of **4** in $CDCl_3$ in an NMR tube was added, at −30 °C, 12.5 mg (5 equiv) of MCPBA. The reaction mixture was allowed to stand at −30 °C for 2 h before data accumulation. Spectra were recorded upon increasing the temperature from −30 to 25 °C. Relative amounts of the observed product at different temperatures are given in Table II.

^{13}C NMR Experiment: Epoxidation of 4 with 1.3 equiv of MCPBA. To an NMR sample of 70 mg (0.25 mmol) of **4** in $CDCl_3$ at −30 °C was

Table II. Percent of Observed Products

temp, °C	4	11	5	6	7	10
−30	44	56				
−20	27	73				
−10	12	70	7	11		
0		59	17	23	≤1	
10		40	22	37	≤1	
20		8	35	45	≤1	12
25 (1 h)			39	47	≤1	13

added 57 mg (0.33 mmol) of MCPBA. The reaction mixture was allowed to stand at −40 °C for 3 h before data accumulation. In addition to small peaks for **4**, MCPBA, and *m*-chlorobenzoic acid, the following signals were attributed to **11**: ^{13}C NMR ($CDCl_3$) δ 170.9, 144.0, 118.3, 81.1, 38.6, 37.6, 32.5, and 29.2.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. G.E.S. received fellowship support from the Fundacion Gran Marical de Ayacucho and the Instituto Universitario de Tecnologia-Cumana, Venezuela. J.K.C. thanks the Fulbright Commission for a travel grant and Professor J. Levisailles and l'Universite Pierre et Marie Curie, Paris, for support during the preparation of this article for publication. Departmental equipment grants aided in the purchase of the Nicolet 360 NMR (CHE-81-05004), the Varian 300 NMR (PHS-SID-RR-1882-01), and the Kratos GC/MS 80 (CHE-81-11957) instruments used in this work.

Registry No. **4**, 33512-45-7; **5**, 108263-91-8; **6**, 108296-88-4; **7**, 108296-89-5; **8**, 83720-82-5; **9**, 108296-90-8; **10**, 108296-91-9; **11**, 108296-92-0; 3,6-di-*tert*-butyl-2,3,7,7-tetramethyl-1,5-octadien-4-one, 108296-93-1; di-*tert*-butylketene, 19824-34-1; 3,6-di-*tert*-butyl-2,2,7,7-tetramethyloct-4-yn-3,6-diol, 33420-20-1.

Absolute Rate and Philicity Studies of Methoxyphenylcarbene. An Extended Range for Carbenic Ambiphilicity

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Received November 20, 1986

Abstract: Methoxyphenylcarbene (MeOCPh) was generated by photolysis (−10 °C) or thermolysis (25, 45 °C) of 3-methoxy-3-phenyldiazirine and added to six alkenes, affording the corresponding cyclopropanes. The substrates and their relative reactivities toward thermally generated MeOCPh at 25 °C were trimethylethylene (3.4), isobutene (10.6), *trans*-butene (1.00), 1-hexene (0.74), methyl acrylate (172), and acrylonitrile (445). Absolute addition rates were studied by laser flash photolysis, following the disappearance of MeOCPh at 290 nm. Laser flash photolysis gave no evidence for the participation of methoxyphenyldiazomethane. MeOCPh is an ambiphile with an extraordinarily strong nucleophilic component. An ab initio molecular orbital study of MeOCPh gave geometries and frontier orbital energies for the cis and trans conformers of the carbene. *trans*-MeOCPh is predicted to be ambiphilic, whereas its cis conformer is predicted to be nucleophilic in additions to the above alkenes. The very high-lying HOMO of MeOCPh is responsible for its unexpectedly pronounced nucleophilic properties.

During the past decade, several principal themes have emerged in the study of singlet carbenes that reflect a desire to more precisely quantitate and categorize the reactivity of these species toward alkenes. These themes include (1) the use of linear free energy relations and selectivity studies to define the "philicity" of the carbene;[1,2] (2) application of ab initio molecular orbital methods to calculate the carbene's HOMO and LUMO energy levels which, together with frontier molecular orbital concepts, lead to an a priori prediction of philicity;[2,3] (3) laser flash photolytic measurement of absolute rate constants and activation parameters for carbene/alkene additions;[4-6] (4) increased recognition of the role of activation entropy in determining the rates of these reactions;[6-8] and (5) development of the halodiazirine exchange reactions that make available a variety of convenient new carbene precursors.[9,10]

Four of these five themes now converge in a study of methoxyphenylcarbene (MeOCPh), the precursor of which, methoxyphenyldiazirine, was the first to be prepared by diazirine exchange.[9] Although MeOCPh is anticipated by empirical criteria to be electrophilic toward alkenes (its *calculated* selectivity index,[1,2] $m_{CXY} = 1.34$, is within the currently defined "electrophilic region" of the carbene selectivity spectrum[1c,2]), ab initio calculations (see below) afford HOMO and LUMO orbital energies that lead to predictions of ambiphilicity for *trans*-MeOCPh and nucleophilicity for *cis*-MeOCPh. The conflict between these expectations stimulated the present experimental study, and the results now lead us to redefine the "border" between electrophilic and ambiphilic carbenes. Moreover, absolute rate constants were estimated for the additions of MeOCPh to electron-deficient alkenes. The resulting combination of theoretical calculations, product-based relative rate constants, and intermediate-based absolute rate

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