The Reaction of Dimethyldioxirane with Alkynes[1]

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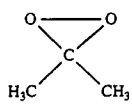
The reaction of dimethyldioxirane with several alkynes gives products which are conveniently rationalized by postulating the intermediacy of oxirenes and oxocarbenes. The latter serve as precursors to H atom or methyl group migration products, as well as to cyclopropane insertion products in some cases. Alkenes, derived from some of these carbene reactions, are partially converted to epoxides.

Introduction

While the literature contains an increasing number of reports[2] on the use of dioxiranes to epoxidize double bonds in a variety of molecular settings, comparatively little attention has been paid to the parallel reaction with triple bonds. In their seminal paper on the in situ generation of dioxiranes, Edwards, Curci et al.[3] describe the reaction of dimethyldioxirane, 1, with a single triply bonded



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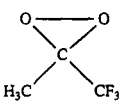

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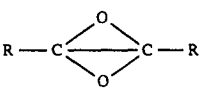

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compound, namely, phenylpropiolic acid. Some time ago we began a study of the reaction of 1 with a number of alkynes. During the course of our work, Curci, Tomaselli, et al.[4] have published a report describing their work on the reaction of 1 and methyl(trifluoromethyl)dioxirane, 2, with some acetylenes. None of the substrates chosen are common to these two efforts, however. Also, the chemistry observed is somewhat different and reflects the influence of substrate structure on the reaction course.

Results

Four alkynes were reacted with dimethyldioxirane in acetone solution at room temperature. Reactions were run with a 1:1 or 2:1 ratio of dioxirane to substrate. The results are shown in Table I. The reaction with 2-butyne (3) gave three products which were identified as 2-hydroxy-2-methyl-propanoic acid (4), 1-oxiranylethanone (5), and 2,2,5,5-tetramethyl-1,3-dioxolan-4-one (6). Compound 5 was present in trace amounts only. In a separate experiment it was shown that acid 4 does not react with acetone to give dioxolane 6. The reaction with 4,4-dimethyl-2-pentyne (7) gave six products which were isolated and characterized. One of these, 2-hydroxy-2,3,3-trimethylbutanoic acid (8), corresponds to acid 4 formed in the reaction of 2-butyne with 1. In the reaction with 7 the acid is not the major product as it was in the earlier case, however. The major product was identified as 1-(trimethyloxiranyl)ethanone (11). The next most abundant product was identified as 1-(2,2-dimethylcyclopropyl)-ethanone (10). Formed in smaller amounts were 4,4-dimethyl-1-penten-3-one (9), 3,4-dimethyl-3-penten-2-one (12), and 4,4-dimethyl-1,2-epoxy-pentan-3-one (13). As expected, the distribution between enone and epoxide products depended greatly on the amount of 1 used in the reaction since the epoxides are derived from the enones. The reaction of 1 with 2,2,5,5-tetramethyl-3-hexyne (14) was noticeably slower than the two previous reactions presumably due to steric hindrance from the *tert*-butyl groups. A similar steric effect had been observed earlier[5] by Baumstark and McCloskey in the reaction of 1 with hindered alkenes. The major product was identified as 2,2-dimethyl-1-(trimethyloxiranyl)-1-propanone (17). Two other products were formed, namely, 2,2-dimethylcyclopropyl *tert*-butyl ketone (15) and 2,2,4,5-tetramethyl-4-hexen-3-one (16). The reaction of 1-(trimethylsilyl)propyne (18) with 1 was also very slow. The major product of this reaction, obtained in 93% yield, was 2-hydroxy-2-(trimethylsilyl)propanoic acid (19). This product is analogous to acids 4 and 8 produced from the oxidations of alkynes 3 and 7, respectively. This reaction differed in a major way from the earlier ones. The reaction solution developed a pink color within 15 min of mixing the reagents. The color intensified as reaction proceeded, reaching a burgundy red color in 1 h. Suspecting formation of some kind of charge-transfer complex, we ran an ESR spectrum of the solution which proved to be negative. We repeated the reaction with the intent of isolating the material responsible for the intense color. After removal of acid 19 the reaction solution was concentrated and the resulting solution then used to isolate the colored material using preparative GLC. Spectroscopic data were obtained on this compound. These data permitted us to identify this material as 1-oxo-1-(trimethylsilyl)-2-propanone (20) based on a comparison with literature data.[6] Compound 20 was very light sensitive and began to lose its color while exposed to ambient lighting. Deliberate photolysis of 20 using a tungsten lamp led to its conversion to acid 19.

Discussion

The demonstrated ability of 1 to efficiently epoxidize unsaturated compounds under very mild conditions[2]

• Abstract published in *Advance ACS Abstracts*, August 15, 1993.

(1) Chemistry of Dioxiranes. 22. Part 21: Singh, M.; Murray, R. W. *J. Org. Chem.* **1992**, *57*, 4263.

(2) (a) Murray, R. W. *Chem. Rev.* **1989**, *89*, 1187. (b) Curci, R. In *Advances in Oxygenated Processes*; Baumstark, A. L., Ed.; JAI Press, Greenwich, CT, 1990; Vol. 2, Chapter 1. (c) Adam, W.; Hadjiarapoglou, L. P.; Curci, R. Mello, R. In Organic Peroxides; Ando, W., Ed.; J. Wiley and Sons: New York, 1992; Chapter 4. (d) Adam, W.; Curci, R.; Edwards, J. O. *Acc. Chem. Res.* **1989**, *22*, 205.

(3) Edwards, J. O.; Pater, R. H.; Curci, R.; DiFuria, F. *Photochem. Photobiol.* **1979**, *30*, 63.

(4) Curci, R.; Fiorentino, M.; Fusco, C.; Mello, R.; Ballistreri, F. P.; Failla, S.; Tomaselli, G.A. *Tetrahedron Lett.* **1992**, *33*, 7929.

(5) Baumstark, A. L.; McCloskey, C. J. *Tetrahedron Lett.* **1987**, *28*, 3311.

(6) (a) Reich, H. J.; Kelly, M. J. *J. Am. Chem. Soc.* **1982**, *104*, 1119. (b) Reich, H. J.; Kelly, M. J.; Olson, R. E.; Holtan, R. C. *Tetrahedron* **1983**, *39*, 960.

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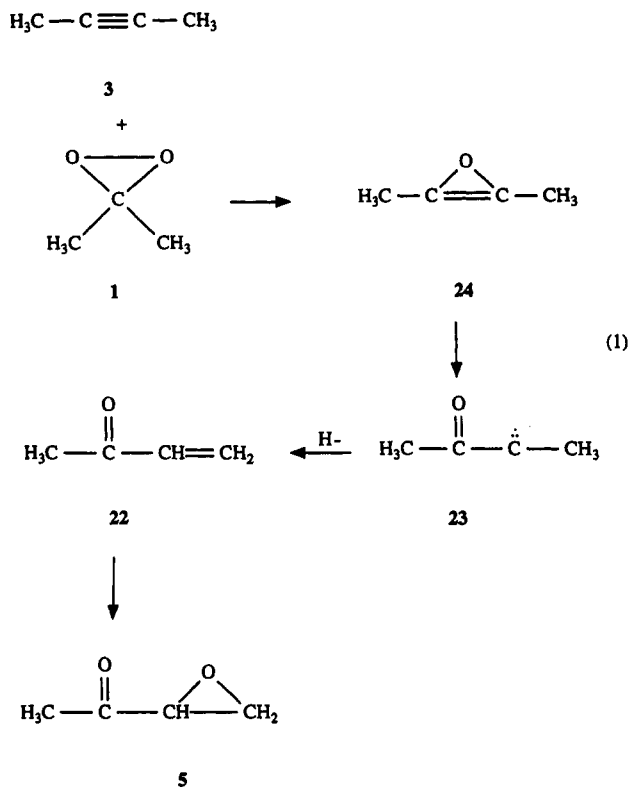
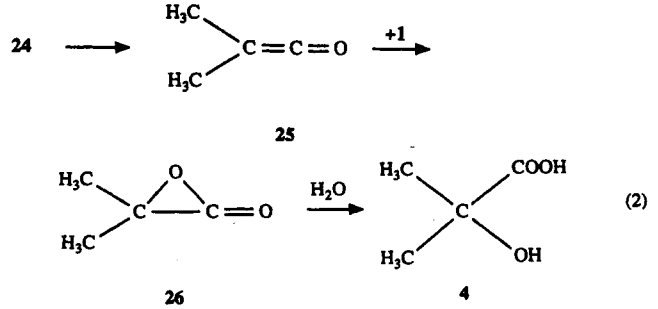
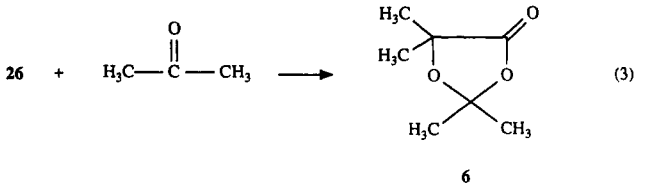


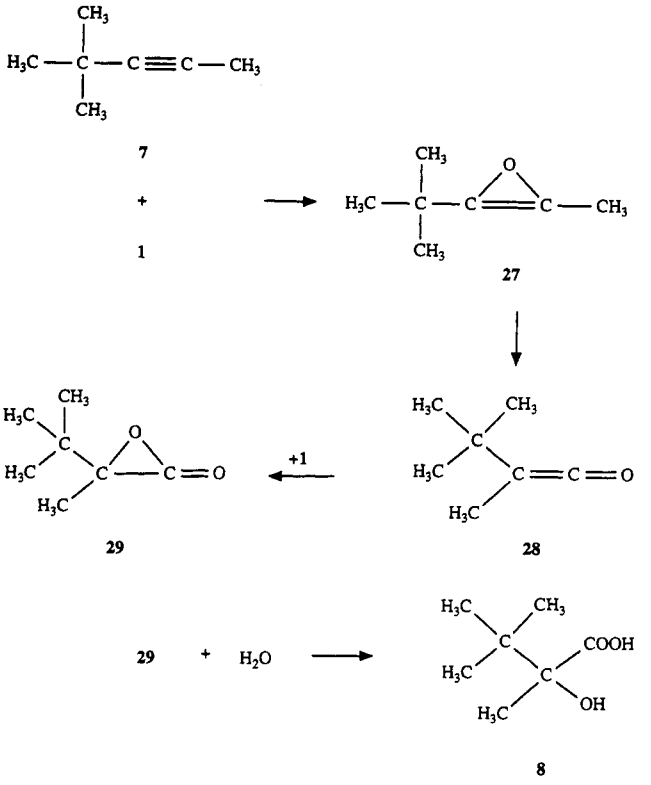
prompted us to study the reaction of 1 with suitable alkynes with the goal of obtaining the elusive dioxabicylobutanes, **21**. The reaction of 1 with four alkynes has led to a variety of products (Table I). The product structures indicate the presence of reaction paths that differ, in some cases, from those observed in the earlier work by Curci and co-workers.[4] These differences are most likely due to the different set of substituents used in this work. The products can be rationalized in most cases by comparing the results with those obtained[7-11] when similar alkynes are treated with peracids. Thus, the trace product **5** obtained from treatment of **3** with 1 presumably arises from epoxidation of alkene **22** which is a likely rearrangement product of carbene **23**. The latter intermediate has been postulated to be a rearrangement product of oxirene **24**, the expected product of the reaction of 1 with **3** (eq 1). The formation of acid **4** is somewhat unusual. In the earlier work[3] using in situ conditions and in the more recent work of Curci and co-workers[4] acids were obtained that were those expected from reaction of a precursor ketene with water. We suggest that the ketene, **25**, arising from rearrangement of oxirene **24** is reactive enough to undergo further reaction with 1, producing α-lactone **26** that gives **4** by reacting with adventitious water (eq 2). Dioxolane



6 is an unusual product whose presence can also be explainedby postulating the intermediacy of lactone **26**. The acid-catalyzed reaction of this lactone with acetone provides a reasonable route to the dioxolane (eq 3). We



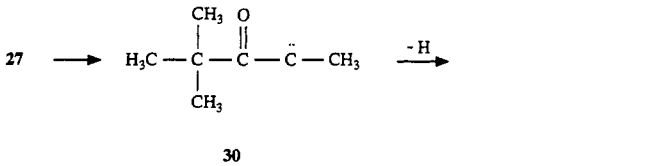
earlier reported[12] the conversion of an epoxide to a dioxolane via acid-catalyzed condensation with acetone. We have ruled out the alternative route to **6** involving reaction of acid **4** with acetone by storing **4** overnight with acetone and showing that no **6** is produced. The reaction of **7** with 1 was carried out at low temperature with monitoring of both ^1H and ^{13}C NMR spectra. No evidence for the formation of oxirene or dioxabicyclobutane intermediates was found. The reaction gave six products. One of these was acid **8** which presumably arises from reaction of the α-lactone, **29**, with water as in the case of **3**. The lactone derives from the reaction of ketene **28** with 1, and the ketene is seen as a rearrangement product of oxirene **27** as before (eq 4). The remaining five products can be



rationalized as arising from one of two oxocarbene intermediates, **30** and **31**, derived from oxirene **27**. Oxirene **30** would be expected to readily rearrange to alkene **9**,one of

(7) See, for example: Sawaki, Y. In *Organic Peroxides*; Ando, W., Ed.; J. Wiley and Sons: New York, 1992; p 433.
(8) McDonald, R. N.; Schwab, P. A. *J. Am. Chem. Soc.* **1964**, *86*, 4866.
(9) Stille, J. K.; Whitehurst, D. D.*J. Am. Chem. Soc.* **1964**, *86*, 4871.
(10) Ciabattoni, J.; Campbell, R. A.; Renner, C. A.; Concannon, P. W. *J. Am. Chem. Soc.***1970**, *92*, 3826.
(11) Lewars, E. G. *Chem. Rev.* **1983**, *83*, 519.
(12) Murray, R. W.; Ramachandran, V. *Photochem. Photobiol.* **1979**, *30*, 187.

the observed products. The latter would be epoxidized by 1 to give epoxide 13 (eq 5). Oxocarbene 31 could insert



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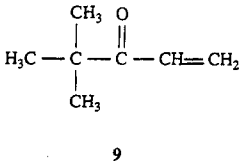

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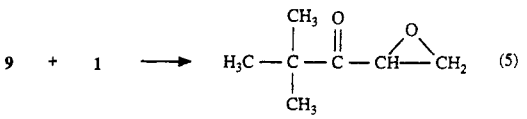

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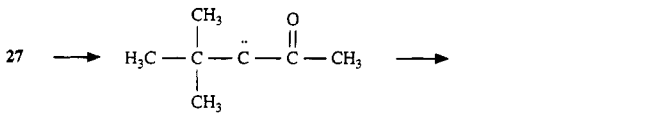
into a methyl group C–H bond to give cyclopropane product 10 (eq 6). Oxocarbene 31 could also undergo a



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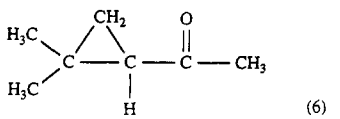

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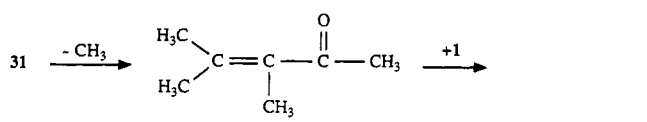
methyl group migration to give alkene 12. Epoxide product 13 is the expected product of the reaction of 1 with 12 (eq 7).



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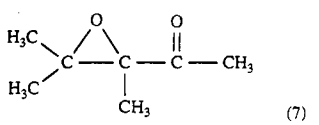

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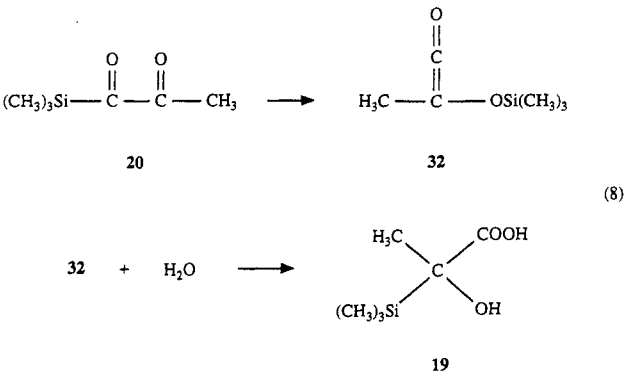
The reaction of alkyne 14 with 1 gave three products (Table I) in a total yield of 82%. These products are believed to be produced via mechanistic pathways which parallel those already described for 7. This reaction is sluggish and requires a much longer reaction time to achieve the results shown in the table. The reaction of the trimethylsilyl substituted alkyne 18 gave two products. One of these, acid 19, was major at 93% yield. As with 14 this reaction is also very slow. The reaction is also characterized by the immediate development of a pink color which becomes more intense as the reaction proceeds, finally becoming a deep wine red color.

The material responsible for the color was isolated by preparative GLC. A comparison of its UV–vis spectrum with that in the literature[5] for the dicarbonyl compound 20 led to its identity. This material is light sensitive and is slowly converted to acid 19. The photochemical rearrangement of 20 to siloxyketene 32 and the subsequent trapping of the ketene by alkene and aldehyde trapping agents has been reported.[13] Reaction of the ketene with water presumably leads to acid 19 under the conditions of our experiment (eq 8). The α-dicarbonyl product 20 is



20 32

(8)

19

similar to products obtained in the work of Curci et al.[4] These authors suggest that such products are produced *via* oxidation of an intermediate oxirene or an oxocarbene rearrangement product. An additional possibility involving an intermediate dioxabicyclobutane, 21, would also give 20. We have not been able to obtain any evidence for the presence of 21 however. On the other hand, products arising from an oxocarbene, such as seen in the other oxidations reported here, were also not observed.

Experimental Section

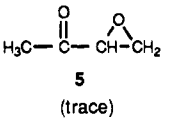
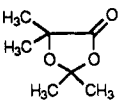
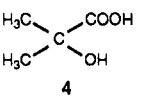
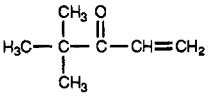
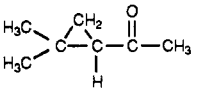
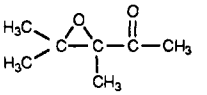
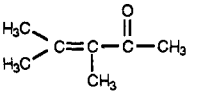
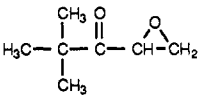
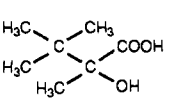
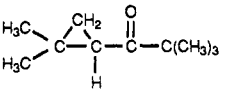
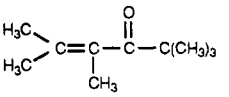
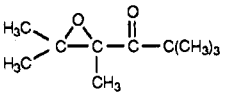
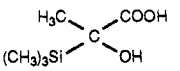
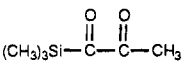
Materials. 2-Butyne (Aldrich), 4,4-dimethyl-2-pentyne, and 1-(trimethylsilyl)propyne (both from Lancaster Chemical) were of the highest purity and were used as such after verifying their purity by GLC. 2,2,5,5-Tetramethyl-3-hexyne (di-*tert*-butylacetylene) was obtained from Chem Samples Co. and was purified by preparative GLC. Acetone (Fisher reagent grade) was fractionally distilled over potassium carbonate. Oxone (DuPont), $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, was obtained from Aldrich and used as such. The dimethyldioxirane solution was prepared according to the literature procedure[14] and was assayed for dioxirane content using phenyl methyl sulfide and the GLC method.[14a]

General Procedure for the Reaction of 1 with Acetylenes. The reactions were carried out by addition of a solution of 1 in acetone to a stirred solution of the acetylene in acetone at room temperature. The progress of the reaction was monitored by GLC or GC–MS. The reactions with di-*tert*-butylacetylene and 1-(trimethylsilyl)propyne were slower and required longer reaction times to reach suitable conversions. Solvent was removed by fractional distillation. GLC analysis of the distillation fractions indicated that only minor amounts of the products were contained in these fractions. Products in the residue (5–10 mL) were separated and collected by preparative GLC. The collected products were reanalyzed to ensure purity. The products were characterized using ^1H and ^{13}C NMR, infrared spectroscopy, and mass spectrometry, and by comparison of their spectral and chromatographic properties with those of authentic samples or with literature values.

Reaction of 1 with 2-butyne (3). The general procedure was followed using a solution of 2-butyne (0.216 g, 3.986 mmol)

(13) Wright, B. B. *J. Am. Chem. Soc.* **1988**, *110*, 4456.
(14) (a) Murray, R. W.; Jeyaraman, R. J. *J. Org. Chem.* **1985**, *50*, 2847. (b) Adam, W.; Chan, Y.Y.; Cremer, D.; Scheutzow, D.; Schindler, M. *J. Org. Chem.* **1987**, *52*, 2800.

Table I. Products of the Reaction of Dimethyldioxirane with Alkynes[a]

alkyne	reactn time (h)	% conversn	products (% yield)[b]		
$H_3C-C\equiv C-CH_3$ **3**	20	100	 **5** (trace)	 **6** (3)	 **4** (42)
$H_3C-C\equiv C-C(CH_3)_3$ **7**	20	100	 **9** (6)	 **10** (18)	 **11** (40)
			 **12** (4)	 **13** (3)	 **8** (9)
$(CH_3)_3C-C\equiv C-C(CH_3)_3$ **14**	140	44	 **15** (17)	 **16** (14)	 **17** (51)
$H_3C-C\equiv C-Si(CH_3)_3$ **18**	140	50	 **19** (93)	 **20**	

[a] 1:alkyne ratio = 2:1 in all cases. [b] Based on alkyne reacted.

in 5 mL of acetone and 140 mL of an 0.06 M solution of **1** (8.4 mmol). GLC analysis of the solution after 20 h indicated the presence of three products in the ratio 10:15:75. After initial distillation to remove solvent the dark yellow residue (25 mL) was distilled *in vacuo* to give a colorless, crystalline solid. This solid was recrystallized from CH_2Cl_2/hexane to give colorless needles (0.174 g , 42%) of 2-hydroxy-2-methylpropanoic acid (**4**). Identification was made by comparing the mass spectral data for this compound with the literature data[15] and on the basis of the following data: mp 77–79 °C (sublimes) (lit.[16] mp 78–79 °C); ^{1}H NMR ($CDCl_3$) δ 1.50 (s, 6 H, $(CH_3)_2C$–), 6.3 (br s, OH and COOH); ^{13}C NMR ($CDCl_3$) δ 26.98 ($(CH_3)_2$–), 72.24 (>*C*(OH)COOH), 181.43 (–COOH); MS (EI, 70 eV) *m/z* 89 (M – CH_3, 5), 59 (100), 45 (7), 44 (4), 43 (53). Calcd for $C_4H_8O_3$: 104.10. The yellow distillate obtained above contained two products which were collected by preparative GLC. One of these products was obtained in trace amounts and was identified as 1-oxiranylethanone, **5**, by comparing its mass spectrum with that in the literature[15] and on the basis of the following data: ^{1}H NMR ($CDCl_3$) δ 2.06 (s, 3 H, CH_3C=O–), 2.90 (dd, J = 5.70, 2.47 Hz, 1 H, –CH_aH_b), 3.01 (dd, J = 5.67, 4.66 Hz, 1 H, –CH_aH_b), 3.40 (dd, J = 4.64, 2.47 Hz, 1 H, –C= OC*H*–); ^{13}C NMR ($CDCl_3$) δ 23.67 (CH_3C=O–), 45.78 (–CH_2–), 53.67 (–*C*=OCH–), 205.50 (–*C*=O–); MS (EI, 70 eV) *m/z* 87 (M + 1, 1), 86 (M^+, 17), 85 (13), 71 (18), 55 (7), 53 (1), 44 (3), 43 (100). Calcd for $C_4H_6O_2$: 86.09. The second product in the distillate was isolated as a colorless liquid and was identified as 2,2,5,5-tetramethyl-1,3-dioxolane-4-one,[17] **6** (18 mg, 3%), on the basis of the following data: IR (Neat, KBr) 2990, 2936, 1797 (vs, –OC=O), 1466, 1380, 1301, 1192, 1076, 1015, 931, 868, 838 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.48 (s, 6 H, $(CH_3)_2C<$ at C-4), 1.58 (s, 6 H, $(CH_3)_2C<$ at C-2); ^{13}C NMR ($CDCl_3$) δ 26.50 ($(CH_3)_2C<$ at C-5), 28.58 ($(CH_3)_2C<$ at C-2), 77.20 (C-5, $(CH_3)_2C<$), 109.30 (C-2), 175.73 (C-4, –OC=O); MS (EI, 70 eV) *m/z* 130 (1.3), 129 (M - CH_3, 22), 101 (20), 100 (8), 59 (81), 58 (39), 43 (100), (CI, methane) *m/z* 145 (M + H). Calcd for $C_7H_{12}O_3$: 144.17.

Reaction of 1 with 4,4-Dimethyl-2-pentyne (7). The general procedure was followed using 0.1076 g (1.119 mmol) of 4,4-dimethyl-2-pentyne in 2 mL of acetone and 34 mL (2.278 mmol) of 0.067 M dimethyldioxirane in acetone. GLC analysis indicated the presence of six products in the ratio 4:35:50:4:2:5 after 20 h of reaction. The solvent was fractionally distilled to give a colorless residue (10 mL). The residue was distilled *in vacuo* to give a solid material. This solid was recrystallized from CH_2Cl_2/hexane to give colorless needles of 2-hydroxy-2,3,3-trimethylbutanoic acid, **8** (0.015g, 9%), mp softening at 70 °C, 98–100 °C (lit.[18] mp 65–70 °C (softening), complete melting at 99–100 °C). The structure was established by comparing the IR spectrum with that in the literature[18] and the following data: IR (KBr) 3279 (br, OH), 2963, 1717 (C=O), 1472, 1372, 1272, 1219, 1149, 1118,1099, 1026, 941, 885, 768, 709 cm^{-1}; ^{1}H NMR ($CDCl_3$)δ1.03 (s, 9 H, $(CH_3)_3C$–), 1.44 (s, 3 H, CH_3–), 6.0 (br s, OH and COOH); ^{13}C NMR ($CDCl_3$) δ 20.63 (CH_3–), 25.30 ($(CH_3)_3C$–), 37.39 ($(CH_3)_3C$–), 79.40 (>*C*(OH)COOH), 181.32 (–COOH); MS (EI, 70 eV) *m/z* 147 (M + 1, 2), 146 (M^+, 14), 113 (10), 101 (54), 90 (100), 83 (27), 57 (79), 43 (34). Calcd for $C_7H_{14}O_3$: 146.18. The five products in the distillate (above) were collected by preparative GLC. One of these was identified as 4,4-dimethyl-1-penten-3-one,[19] **9** (7 mg, 6%), by comparing its properties with those of an authentic sample: ^{1}H NMR ($CDCl_3$) δ 1.17 (s, 9 H,$(CH_3)_3C$–), 5.66 (dd, J = 10.31, 2.14 Hz, 1 H, –CH=CH_aH_b), 6.35 (dd, J = 17.0, 2.1 Hz, 1 H, –CH=CH_aH_b), 6.81 (dd, J=16.95, 10.37 Hz, 1 H, –*C*H=CH_2); ^{13}C NMR ($CDCl_3$) δ 26.01 ($(CH_3)_3C$–), 42.98 ($(CH_3)_3C$–), 128.18 (=CH_2), 130.61 (–*C*H=), 204.02 (–C=O–); MS (EI, 70 eV) *m/z* 112 (M^+, 4), 84 (16), 70 (10), 69 (7), 57 (100), 56 (14), 55 (28), 41 (42). Calcd for $C_7H_{12}O$: 112.17. A major product was obtained as a colorless liquid (0.023 g, 18%) and was identified as 1-(2,2-dimethylcyclopropyl)ethanone, **10**, by com-

(15) Heller, S. R.; Milne, G. W. A. *EPA/NIH Mass Spectral Data Base*; U.S. Government Printing Office: Washington, D.C., 1978; Vol. 1.
(16) Vogl, O. *J. Org. Chem.* **1958**, *23*, 1488.
(17) Ruchardt, C.; Brinkmann, H. *Chem. Ber.* **1975**, *108*, 3224.
(18) Evans, R. J. D.; Landor, S. R. *J. Chem. Soc.* **1965**, 2553.
(19) Gras, J.-L. *Tetrahedron Lett.* **1978**, 2955.

paring its ^{1}H NMR spectrum with that in the literature[20] as well as on the basis of the following data: ^{1}H NMR ($CDCl_3$) δ 0.82 (dd, J = 7.55, 3.94 Hz, 1 H, –CH–), 1.09 (s, 3 H, CH_3), 1.20 (s, 3 H, CH_3), 1.24 (dd, J = 5.56, 3.96 Hz, 1 H, >CH_aH_b), 1.86 (dd, J = 7.50, 5.56 Hz, 1 H, >CH_aH_b), 2.24 (s, 3 H, CH_3 –C=O–); ^{13}C NMR ($CDCl_3$) δ 18.16 (CH_3), 23.26 (–CH_2–), 26.73 ((CH_3)$_2C$=), 27.36 (CH_3), 32.29 (CH_3C=O–), 35.72 (–CH–), 206.46 (CH_3C=O–); MS (EI, 70 eV) m/z 113 (M^+, 60), 98 (3), 97 (53), 79 (9), 69 (48), 55 (16), 43 (100), 41 (59). Calcd for $C_7H_{12}O$: 112.17. A second major product was also obtained as a colorless liquid (0.057 g, 40%) and was identified as 1-(trimethyloxiranyl)ethanone, **11**, by comparing its mass spectral data with those in the literature[15,21] and on the basis of the following data: IR (neat, KBr) 3000, 2968, 2933, 1712 (C=O), 1380, 1356, 1275, 1147, 1103, 979, 877, 818, 698, 649 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.24 (s, 3 H, CH_3–), 1.36 (s, 3 H, CH_3–), 1.45 (s, 3 H, CH_3–), 2.24 (s, 3 H, CH_3C=O–); ^{13}C NMR ($CDCl_3$) 15.53 (CH_3–), 20.45 (CH_3–), 21.19 (CH_3–), 27.23 (CH_3C=O), 62.50 ((CH_3)$_2C$<), 69.17 (>C<), 208.87 (CH_3C=O–); MS (EI, 70 eV) m/z 128 (M^+, 0.3), 113 (78), 86 (32), 71 (30), 57 (19), 53 (7), 43 (100), 41 (20). Calcd for $C_7H_{12}O_2$: 128.17. A fifth product was isolated as a colorless liquid (5 mg, 4%) and was identified as 3,4-dimethyl-3-penten-2-one, **12**, by comparing its ^{1}H NMR[21,22] and mass spectral data[15,22] with those in the literature and on the basis of the following data: ^{1}H NMR ($CDCl_3$) δ 1.75 (s, 3 H, CH_3–), 1.83 (s, 3 H, CH_3–), 1.86 (s, 3 H, CH_3–), 2.22 (s, 3 H, CH_3C=O); ^{13}C NMR ($CDCl_3$) δ 15.57 (CH_3–), 21.72 (CH_3–), 22.43 (CH_3–), 29.72 (CH_3C=O–), 131.29 ((CH_3)$_2C$<), 137.89 (>C(CH_3)C=OCH_3), 204.82 (CH_3C=O–); MS (EI, 70 eV) m/z 112 (M^+, 85), 97 (54), 69 (100), 67 (10), 53 (12), 43 (38), 41 (78). Calcd for $C_7H_{12}O$: 112.17. The sixth product was also isolated as a colorless liquid (5 mg, 3%) and was identified as 4,4-dimethyl-1,2-epoxypentan-3-one, **13**, on the basis of the following data: ^{1}H NMR ($CDCl_3$) δ 1.25 (s, 9 H, (CH_3)$_3$C–), 2.77 (dd, J = 6.83, 2.44 Hz, 1 H, OCHCH_aH_b), 2.95 (dd, J = 6.83, 4.43 Hz, 1 H, OCHCH_aH_b), 3.84 (dd, J = 4.48, 2.53 Hz, 1 H, –CH–); ^{13}C NMR ($CDCl_3$) δ 25.80 ((CH_3)$_3$C–), 43.84 (CH_3)$_3C$–), 47.62 (–CH_2), 48.81 (–CH–), 209.36 (–C=O–); MS (EI, 70 eV) m/z 128 (M^+, 8.4), 113 (5), 85 (7), 69 (6), 57 (100), 41 (36). Calcd for $C_7H_{12}O_2$: 128.17. An authentic sample of **13** was prepared by treating 4,4-dimethyl-1-penten-3-one with **1**. This material had the same spectral and chromatographic properties as **13**.

Reaction of 1 with 2,2,5,5-Tetramethyl-3-hexyne (Di-*tert*-butylacetylene) (14). The general procedure was used with a solution of di-*tert*-butylacetylene (0.222 g, 1.607 mmol) in 2 mL of acetone and 52 mL of a solution of **1** (0.062 M, 3.214 mmol). The combined solution was stirred with a magnetic stirrer and reaction progress followed by GLC. After 140 h 44% of the acetylene had reacted. The GLC analysis indicated the presence of three products in the ratio 11:16:73. After removal of solvent 5–10 mL of a colorless residue was obtained. These products were collected using preparative GLC. One of these products was isolated as a colorless liquid (0.018 g, 17%) and was identified as 1-(2,2-dimethylcyclopropyl) *tert*-butyl ketone, **15**, by comparing its properties with those in the literature[23] and on the basis of the following data: ^{1}H NMR ($CDCl_3$) δ 0.77 (dd, J = 7.51, 3.91 Hz, 1 H, –CH–), 0.99 (s, 3 H, CH_3), 1.15 (s, 9 H, (CH_3)$_3$C–), 1.20 (s, 3 H, CH_3), 1.25 (dd, J = 5.62, 3.96 Hz, 1 H, >CH_aH_b), 2.03 (dd, J = 7.51, 5.68 Hz, 1 H, >CH_aH_b); ^{13}C NMR ($CDCl_3$) δ 18.32 (CH_3), 22.04 (–CH_2–), 26.08 ((CH_3)$_2C$<), 26.39 (CH_3)$_3C$–), 27.05 (CH_3), 31.19 (–CH–), 43.91 (CH_3)$_3C$–), 212.66 (CH_3)$_3CC$=O–); MS (EI, 70 eV) m/z 154 (M^+, 18), 139 (4), 121 (1), 111 (2), 98 (7), 97 (100), 79 (4), 69 (14), 57 (22), 43 (6), 41 (23). Calcd for $C_{10}H_{18}O$: 154.24. The second product was also isolated as a colorless liquid (0.015 g, 14%) and was identified as 2,2,4,5-tetramethyl-4-hexen-3-one, **16**, by comparing its NMR[24] and mass spectral[25] data with those in the literature: ^{1}H NMR ($CDCl_3$) δ 1.18 (s, 9 H, (CH_3)$_3$C–), 1.57 (s, 3 H, CH_3–), 1.66 (s, 3 H, CH_3–), 1.76 (s, 3 H, CH_3–) (all methyl absorptions split at the top); ^{13}C NMR ($CDCl_3$) δ 16.45 (CH_3–), 19.16 (CH_3–), 22.54 ((CH_3)$_3$C–), 44.07 (CH_3)$_3C$–), 128.25 (>C<), 131.42 (>C<), 210.33 (CH_3)$_3CC$=O–); MS (EI, 70 eV) m/z 154 (M^+, 1), 111 (1), 98 (7), 97 (100), 96 (5), 69 (42), 67 (3), 57 (5), 53 (3), 41 (25). Calcd for $C_{10}H_{18}O$: 154.24. The third and major product was isolated as a colorless crystalline solid (0.061 g, 51%) and was identified as 2,2-dimethyl-1-(trimethyloxiranyl)-1-propanone, **17**, by comparing its ^{1}H NMR and mass spectral data with those in the literature:[21] colorless needles; mp 41–42 °C (lit.[21] mp 41–42 °C); ^{1}H NMR ($CDCl_3$) δ 1.21 (s, 3 H, CH_3–), 1.24 (s, 9 H, (CH_3)$_3$C–), 1.34 (s, 3 H, CH_3–), 1.47 (s, 3 H, CH_3–); ^{13}C NMR ($CDCl_3$) δ 17.79 (CH_3–), 20.32 (CH_3–), 22.39 (CH_3–), 27.08 ((CH_3)$_3$CC=O–), 44.53 (CH_3)$_3$CC=O–), 62.06 ((CH_3)$_2C$<), 69.85 (>C<), 214.12 (CH_3)$_3$CC=O–); MS (EI, 70 eV) m/z 170 (M^+, 1), 155 (14), 113 (5), 99 (3), 86 (18), 85 (14), 71 (19), 69 (7), 57 (100), 43 (37), 41 (26). Calcd for $C_{10}H_{18}O_2$: 170.24.

Reaction of 1 with 1-(Trimethylsilyl)propyne (18). The general procedure was used with 1-(trimethylsilyl)propyne (0.223 g, 1.98 mmol) in 2 mL of acetone. A solution of **1** in acetone (60 mL, 0.066 M, 3.976 mmol) was added and the combined solution stirred with a magnetic stirrer. A pink color developed within 15–20 min and became quite dark by 1.5 h. GLC analysis indicated a 50% conversion in 140 h. The solvent was removed to give a pale yellow residue (3–5 mL). This residue was dissolved in hexane and dried with Na_2SO_4 and the solvent removed on a rotary evaporator to give a colorless, crystalline solid. This solid was recrystallized from petroleum ether to give colorless needles, mp 102–104 °C (0.15 g, 93%). This solid was identified as 2-hydroxy-2-trimethylsilylpropanoic acid, **19**, on the basis of the following data. IR (KBr) 3438, 3369, 2960, 1718 (C=O), 1252, 1236, 1111, 1071, 870, 846, 775, 699, 626 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.13 (s, 9 H, (CH_3)$_3$Si–), 1.53 (s, 3 H, CH_3–), 5.5 (br s, OH and COOH); ^{13}C NMR ($CDCl_3$) δ –4.29 ((CH_3)$_3$Si–), 21.26 (CH_3–), 70.07 (>C(OH)COOH), 183.70 (–COOH); MS (EI, 70 eV) m/z 147 (M – CH_3 ,6), 146 (3), 145 (4), 129 (4), 119 (8), 117 (14), 101 (6), 91 (10), 77 (12), 75 (73), 73 (100), 72 (6), 55 (5), 47 (6), 45 (21), 43 (15). Calcd for $C_6H_{14}O_3Si$: 162.26. Anal. C, H.

A separate reaction was run in order to gain more information on the purple compound. The reaction was run at room temperature until a dark reddish purple solution was obtained. The reaction mixture was distilled *in vacuo* to give a colorless crystalline compound which was identified as **19** as before. The purple distillate was mixed with an equal volume of methylene chloride and concentrated on a rotary evaporator to give a dark reddish purple residue. A product was isolated from this residue as a purple liquid using preparative GLC. This material was identified as 1-oxo-1-(trimethylsilyl)-2-propanone, **20**, by comparing its spectral data with the literature values[6] and on the basis of the following data. UV–vis ($CDCl_3$) λ_{max} 534 nm; ^{1}H NMR ($CDCl_3$) δ 0.27 (s, 9 H, (CH_3)$_3$Si–), 2.17 (s, 3 H, CH_3–); ^{13}C NMR ($CDCl_3$) δ –2.71 ((CH_3)$_3$Si–), 21.52 (CH_3–), 199.15 (CH_3)$_3$SiC=O–), 235.73 (CH_3C=O–); MS (EI, 70 eV) m/z 116 (M – 28, 11), 101 (15), 73 (100), 72 (6), 59 (5), 58 (3), 43 (13); MS (CI, methane) m/z 145 (M + H), calcd for $C_6H_{12}O_2Si$: 144.24.

Photolysis of 20. It was observed that the intensity of the purple color of **20** decreased slowly in light. Monitoring of the solution with ^{1}H NMR indicated that the absorptions due to the acid, **19**, increased as the peaks due to the dione, **20**, decreased. The solution was then irradiated with a tungsten lamp for 2 min. After storage overnight the NMR of the solution indicated that the peaks due to **20** were absent and only those of the acid, **19**, remained.

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(20) Brown, H. C.; Peters, E. N.; Ravindranathan, M. *J. Am. Chem. Soc.* **1977**, *99*, 505.
(21) Kociensky, P. J.; Ciabattoni, J. J. *J. Org. Chem.* **1974**, *39*, 388.
(22) Tabushi, I.; Fujita, K.; Oda, R. *Tetrahedron Lett.* **1968**, 5455.
(23) Crandall, J. K.; Lin, L. C. *J. Am. Chem. Soc.* **1967**, *89*, 4526.
(24) Al-Jallo, H. N. A.; Arnold, B. J.; Rothwall, B. J.; Waight, E. S. *J. Chem. Soc. B* **1971**, 846.
(25) Crandall, J. K.; Conover, W. W., II. *J. Org. Chem.* **1978**, *43*, 1323.