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OXIDATION OF 1,2,3-BUTATRIENES: A FACILE FORMATION OF METHYLENECYCLOPROPANONES AND THEIR SUBSEQUENT PHOTODECARBONYLATION

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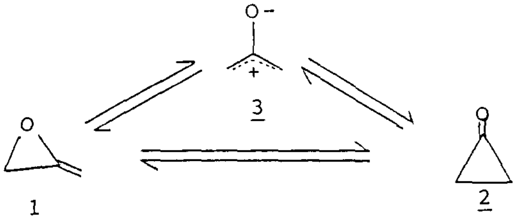
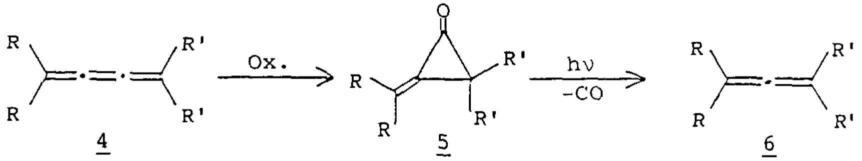
Summary: A peracid oxidation of some sterically hindered 1,2,3-butatrienes (4) using an alkaline biphasic solvent system was examined, and the resulted methylenecyclopropanones (5) were readily photodecarbonylated to give the corresponding allenes (6) in good yields.

Although the oxidation of allenes has been investigated extensively from a viewpoint of generating a valence tautomeric triad with an allene oxide (1), cyclopropanone (2), and oxyallyl (3),[1] the oxidation of 1,2,3-butatrienes has not been fully investigated because of the instability of the reaction products.



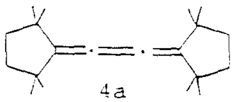
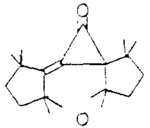
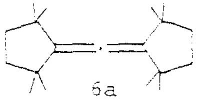
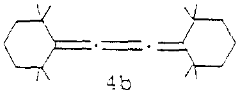
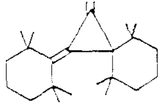
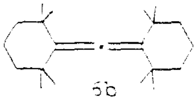
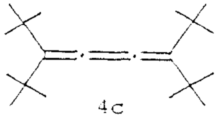
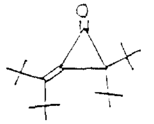
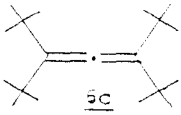
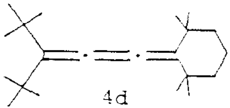
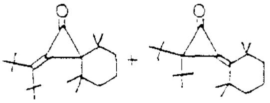
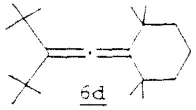
In this paper, we wish to report the first example of the peracid oxidation of sterically hindered 1,2,3-butatrienes (4) leading to the corresponding methylenecyclopropanones (5), and a subsequent photodecarbonylation of 5 resulting a facile formation of the hindered allenes (6), the decarbonylation products.



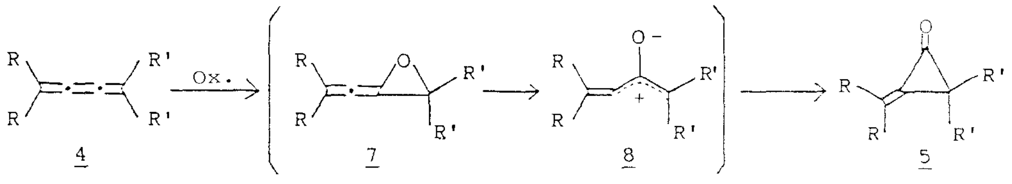
The oxidation of butatrienes (4) by m-chloroperbenzoic acid (mCPBA) was achieved very easily and effectively using the alkaline biphasic solvent system.[2] For example, 4a was treated with an equimolar amount of mCPBA in CH_2Cl_2-$NaHCO_3$ solvent system to give the corresponding methylenecyclopropanone

(5a) in 81% yield as a yellow oil.[3] The results with the other butatrienes are listed in Table 1. In the case of unsymmetric butatriene (4d), the peracid oxidation gave the mixture of two regioisomeric methylenecyclopropanones (5d) and (5d') in 81% yield.[4]

Table 1. The transformation of 4 into 6 via 5.[5]

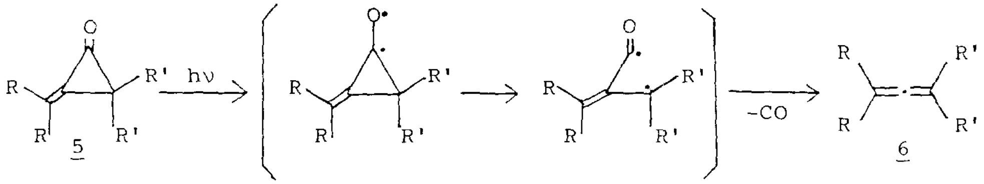
Butatruenes 4	Methylenecyclopropanones 5		Allenes 6	
 4a	 5a	81%	 6a	81%
 4b	 5b	97%	 6b	98%
 4c	 5c	89%	 6c	77%
 4d	 5d (3 : 1)5d'	81%	 6d	73%

By analogy to the rearrangement of allene oxide (1) into cyclopropanone (2),[1,6-8] the formation of the methylenecyclopropanones (5) was interpreted with the intermediacy of the initially formed epoxides (7) followed by the ring transformation via the oxyallyl intermediates (8). However, in spite of the presence of the bulky substituents the unsaturated epoxide (7) was not stable enough to isolate in contrast to the allene oxide (1).[1,6-8] As for the regiochemistry, the initial epoxidation of 4 seems to occur not at the central π-bond but at the terminal π-bond, considering the facts that the analogous nucleophilic species such as diazomethane[9] and dichlorocarbene[10,11] attack butatrienes at the terminal π-bonds.



For the decarbonylation reaction of the methylenecyclopropanones (5), 5a (90 mg, 0.33 mmol) was irradiated in 1.8 ml of benzene by a 400 W medium pressure mercury lamp through a phenanthrene filter solution (1.4 g/250 ml of methanol) under cooling with water. In a few minutes the original yellow color of the solution disappeared and the ^{1}H-NMR spectrum of the mixture showed a quantitative conversion of 5a into the decarbonylated allene (6a). The isolation by the column chromatography on silica gel afforded 6a in 81% yield (69.5 mg) as a colorless oil. The results obtained using the other methylenecyclopropanones (5) as a substrate are summarized in Table 1.

The fact that the photoreaction of the methylenecyclopropanone (5b), which has two UV absorption maxima in hexane at 423(log $\varepsilon \approx 3.06$, $n\rightarrow\pi^*$) and 260 nm (log $\varepsilon \approx 5.08$, $\pi\rightarrow\pi^*$), was accomplished by the $n\rightarrow\pi^*$ excitation using phenanthrene filter (>365 nm) suggests that the photodecarbonylation of 5 proceeded through the Norrish Type I cleavage[12]) of the cyclopropanone ring.



In view of the facility of this conversion and the ready availability of either symmetrical or unsymmetrical butatrienes as a substrate, the present sequence provides a new conversion method for the preparation of sterically hindered allenes.

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2. W. K. Anderson and T. Veysoglu, J. Org. Chem., 38, 2267 (1973).
3. When the oxidation of 4 was carried out as usual with mCPBA in CH_2Cl_2, the reaction gave a very complex mixture and low yield of products, probably due to the low stability of the reaction intermediates towards the coexisting m-chlorobenzoic acid. For example, in the case of 4a, 5a was obtained only in 12% yield by usual peracid oxidation.
4. Although 5d and 5d' could not be separated by column chromatography, the mixture of them gave satisfactory spectral data by ^{1}H-NMR, ^{13}C-NMR, IR, and MS specra. In ^{13}C-NMR spectrum two carbonyl carbons were observed and the ratio of 5d to 5d' was 3:1.
5. 5a: ^{1}H-NMR(CCl_4); δ 0.92(6H, s), 1.13(6H, s), 1.17(6H, s), 1.27(6H, s), and 1.67-1.79(8H, m), ^{13}C-NMR($CDCl_3$); δ 59.6(s), 109.6(s), 174.1(s), and 204.2(s), IR(neat); 1780(C=O) and 1620(C=C) cm^{-1}, MS; m/e 288(M^+, 3%), 260(19), 245(23), and 69(100), exact mass; m/e 288.2481(Calcd for $C_{20}H_{32}O$, m/e 288.2453).

   5b: ^{1}H-NMR($CDCl_3$); δ 0.93(6H, s), 1.16(6H, s), 1.25(6H, s), 1.43(6H, s), and 1.58-1.68(12H, m), ^{13}C-NMR($CDCl_3$); δ 52.8(s), 128.3(s), 165.1(s), and 208.2(s), IR(neat); 1780(C=O) and 1575(C=C) cm^{-1}, MS; m/e 316(M^+, 13%), 288(43), 273(76), and 69(100), exact mass; m/e 316.2768(Calcd for $C_{22}H_{36}O$, m/e 316.2766).

5c: ^{1}H-NMR(CDCl$_3$); δ 1.13(18H, s), 1.30(9H, s), and 1.42(9H, s), ^{13}C-NMR(CDCl$_3$); δ 54.1(s), 121.5(s), 164.3(s), and 208.2(s), IR(neat); 1780 (C=O) and 1580(C=C) cm^{-1}, MS; m/e 292(M^{+}, 5%), 264(6), 235(10), and 57 (100), exact mass; m/e 292.2754(Calcd for $C_{20}H_{36}O$, m/e 292.2765).

6a: ^{1}H-NMR(CDCl$_3$); δ 1.12(24H, s) and 1.63(8H, s), ^{13}C-NMR(CDCl$_3$); 30.9 (s), 39.5(t x 2), 47.0(s), 130.5(s), and 188.5(s), MS; m/e 260(M^{+}, 98%) and 245(100), exact mass; m/e 260.2478(Calcd for $C_{19}H_{32}$, m/e 260.2503).

6b: ^{1}H-NMR(CDCl$_3$); δ 1.10(24H, s) and 1.13-1.59(12H, m), ^{13}C-NMR(CDCl$_3$); δ 31.2(q), 34.1(s), 118.1(S), and 194.7(s), mp 58-59°C (lit. mp 59°C$^{13)}$), MS; m/e 288(M^{+}, 69%) and 273(100), exact mass; m/e 288.2829(Calcd for $C_{21}H_{36}$, m/e 288.2817).

6c: ^{1}H-NMR(CDCl$_3$); δ 1.19(36H, s), ^{13}C-NMR(CDCl$_3$); δ 32.5(q), 35.4(s), 118.8(s), and 199.0(s), MS; m/e 264(M^{+}, 10%), 207(1), 151(20), and 57(100), exact mass; m/e 264.2806(Calcd for $C_{19}H_{36}$, m/e 264.2816).

6d: ^{1}H-NMR(CDCl$_3$); δ 1.10(12H, s), 1.19(18H, s), and 1.33-1.52(6H, m), ^{13}C-NMR(CDCl$_3$); δ 30.9(q), 32.5(q), 34.2(S), 41.4(S), 116.4(s), 120.5(S), and 196.7(S), MS; m/e 276(M^{+}, 10%), 219(7), 151(42), and 57(100), exact mass; m/e 276.2835(Calcd for $C_{20}H_{36}$, m/e 276.2817).

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