(**4b**) has: ir 2.8, 5.98, and 6.13 μ; nmr τ 4.17, 4.24 (m, 2 total, $C{=}CH_2$), 5.56 (s, 1, CH), 6.92 (s, 1, OH), 8.11 (m, 3, CH_3), and 9.12 (s, 9, *t*-Bu). In the presence of acetic acid **2b** leads to **3b** (35%), **4b** (59%), and 4-acetoxy-2-hydroxy-2,5,5-trimethyl-3-hexanone (**5b**, 6%): ir 2.8, 5.74, 5.81, and 8.0 μ; nmr τ 4.57 (s, 1, CHOAc), 6.82 (s, 1, OH), 7.95 (s, 3, OAc), 8.67 (s, 3, CH_3), 8.74 (s, 3, CH_3), and 9.00 (s, 9, *t*-Bu).[7]

Reaction of the allene with 1 equiv of peracid was also examined in an attempt to isolate the first intermediate, allene oxide **1b**. However, even when the peracid solution was added slowly to the allene solution, the product consisted of unreacted allene (50%), spiro dioxide **2b** (40%), and 2-acetoxy-2,5,5-trimethyl-3-hexanone (**6b**, 8%): ir 5.74, 5.79, and 8.0 μ; nmr τ 7.71 (s, 2, CH_2), 8.03 (s, 3, OAc), 8.61 (s, 6, CH_3), and 8.99 (s, 9, *t*-Bu).

The above studies fully support our earlier contention[1] that **2a** was an intermediate in the conversion of tetramethylallene to its dioxidation products **3a**, **4a**, and **5a**, since isolated **2b** independently yields an analogous series of transformation products. Furthermore, isolation of **2b** provides the best evidence to date for the real existence of allene oxide intermediates, since only this species appears to be a reasonable precursor for **2b** and its homologs. In the reaction utilizing equivalent amounts of allene and oxidant, a small proportion of **1b** is evidently trapped by acetic acid to give **6b**, in competition with attack by a second molecule of peracid. However, the addition of acetic acid to both **1b** and **2b** is much suppressed relative to the corresponding tetramethylallene intermediates, probably because of the steric influence of the *t*-butyl group.

The illustrated stereochemistry of **1b** and **2b** is assigned on the assumption that peracid attacks the more heavily substituted double bond from the direction remote from the *t*-butyl side chain. The importance of substituents on the rate of olefin epoxidation is well established,[8] and our qualitative observations with a series of allenes suggest that alkyl substituents similarly enhance the reactivity of cumulative double bonds. Support for reaction at the disubstituted double bond is available by the formation of **6b** if it is assumed that this product is generated directly from the allene oxide intermediate.[9] Examination of models reveals that the *t*-butyl group substantially shields one side of this olefinic unit. The stereochemistry of **1b** necessarily determines that of **2b**.

It is apparent that allene oxide **1b** reacts with peracid much faster than the allene itself. The reactivity of **1b** can be attributed to the resonance interaction of the substituent oxygen atom which increases the nucleophilicity of the double bond in **1b**. Analogy is available in the very facile reaction of enol ethers with peracid.[10] This conclusion suggests that special circumstances will be required in order to isolate an intact allene oxide from peracid oxidation of an allene. The results of one approach to this problem are discussed in the accompanying communication.[11]

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. The mass spectrometer was purchased with a National Science Foundation equipment grant (GP 5234).

---

[7] The magnetic nonequivalency of the methyl groups undoubtedly is a result of the proximate asymmetric center in **5b**: R. H. Bible, "Interpretation of NMR Spectra," Plenum Press, New York, N. Y., 1965, p 75.

[8] D. Swern, *Org. Reactions*, 7, 380 (1953).

[9] The possibility that **6b** is formed by the reaction of acetic acid with a cyclopropanone intermediate derived from an allene oxide by isomerization cannot be excluded.

[10] C. L. Stevens and J. Tazuma, *J. Amer. Chem. Soc.*, **76**, 715 (1954).

[11] J. K. Crandall and W. H. Machleder, *ibid.*, **90**, 7347 (1968).

[12] (a) Alfred P. Sloan Research Fellow, 1968–1970; (b) National Science Foundation Summer Undergraduate Research Participant, 1967.

J. K. Crandall,[12a] W. H. Machleder, M. J. Thomas[12b]
Contribution No. 1616, Department of Chemistry
Indiana University, Bloomington, Indiana 47401

Received August 14, 1968

Allene Epoxidation. Isolation of a Cyclopropanone

Sir:

In continuing our synthetic efforts[1,2] directed toward the isolation of a representative allene oxide (*e.g.*, **1**), we have examined the peracid oxidation of 1,1-di-*t*-butylallene[3] with the idea that allene oxide **1** might possess a measure of kinetic stability owing to the shielding effect of the bulky *t*-butyl substituents.[6] However, the sole product obtained from buffered peracetic acid treatment of this allene with 1 equiv of oxidant in methylene chloride[1] was the exceptionally stable cyclopropanone **2**. 2,2-Di-*t*-butylcyclopropanone is a waxy solid, mp 41–43°, with distinctive infrared absorption at 5.48 ($C{=}O$) and 10.5 μ and nmr bands as sharp singlets at τ 8.56 and 8.90 (1:9). The ultraviolet spectrum (hexane) shows a maximum at 345 nm (ϵ 52). These rather distinctive spectral characteristics are in excellent agreement with those reported for other cyclopropanones.[6,7] The mass spectrum of **2** displays important fragments at *m/e* (relative intensity): (70 eV) 168 (0.4), 126 (25), 112 (24), 111 (55), 97 (75), 69 (53), and 57 (100); (10 eV) 168 (3), 153 (2), 140 (2), 126 (100), 112 (78), 111 (31), 97 (45), 85 (11), 84 (23), 57 (30), and 56 (29). An accurate mass determination on the molecular ion (found, 168.1514) confirmed the molecular formula. This cyclopropanone possesses substantial stability which allows it to be manipulated without any special precautions to exclude air or hydroxylic solvents, and it could even be purified by preparative glpc on a freshly prepared 5-ft column of 15% Carbowax 20M on Chromosorb W when the entire glpc system was maintained below 110°. The nmr of **2** does not change

---

[1] J. K. Crandall and W. H. Machleder, *Tetrahedron Lett.*, 6037 (1966); J. K. Crandall and W. H. Machleder, *J. Amer. Chem. Soc.*, **90**, 7292 (1968).

[2] J. K. Crandall, W. H. Machleder, and M. J. Thomas, *ibid.*, **90**, 7346 (1968).

[3] Lithium and *t*-butyl alcohol reduction[4] of 1-chloro-3,3-di-*t*-butylallene[5] gave the desired allene in good yield: bp 155–157°; ir, 5.19 and 12.0 μ; nmr, τ 5.45 (s, 2) and 8.82 (s, 18). All new compounds described in the text have been characterized by acceptable microanalysis or accurate mass determination of the molecular ion by mass spectrometry.

[4] L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," John Wiley & Sons, Inc., New York, N. Y., 1967, pp 604–606.

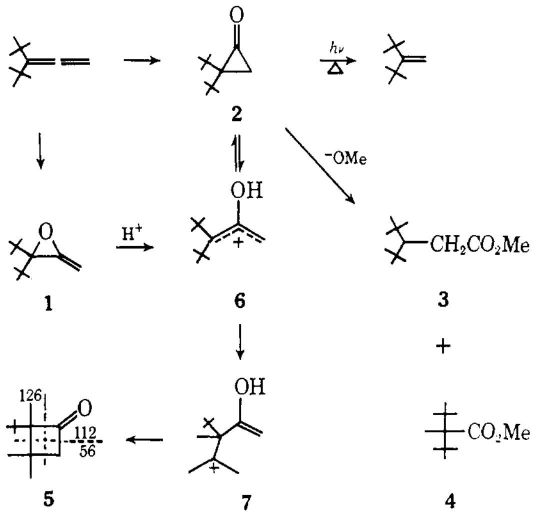
[5] Y. R. Bhatia, P. D. Landor, and S. R. Landor, *J. Chem. Soc.*, 24 (1959).

[6] J. F. Pazos and F. D. Greene, *J. Amer. Chem. Soc.*, **89**, 1030 (1967).

[7] N. J. Turro and W. B. Hammond, *ibid.*, **87**, 2774 (1965); W. B. Hammond and N. J. Turro, *ibid.*, **88**, 2880 (1966); N. J. Turro and W. B. Hammond, *ibid.*, **88**, 3672 (1966).

in the presence of excess methanol, which appears to indicate that hemiketal formation is much less favorable than with other cyclopropanones.[6,7]

Several chemical transformations serve to bolster the physical evidence for structure **2**. Either photolysis at 3100 Å in pentane solution or pyrolysis at 600° in a vacuum flow unit converted **2** to 1,1-di-*t*-butylethylene[8,9] as the only major product. Two days at reflux in 0.7 *M* methanolic sodium methoxide was required to drive the Favorskii cleavage to completion. Surprisingly, bond breakage at both sides of the carbonyl group occurred to produce a 3:1 mixture of methyl β,β-di-*t*-butylpropionate (**3**) and methyl α,α-di-*t*-butylpropionate (**4**). Ester **3** shows: ir 5.73 μ; nmr τ 6.43 (s, 3, CO_2CH_3), 7.81 (d, 2, $J = 5$ Hz, $CH_2CO_2CH_3$), 8.18 (t, 1, $J = 5$ Hz, CH), and 9.04 (s, 18, *t*-Bu). Ester **4** has: ir 5.80 μ; nmr τ 6.36 (s, 3, CO_2CH_3), 8.78 (s, 3, CH_3), and 8.89 (s, 18, *t*-Bu), and was identical with an authentic sample prepared from the corresponding acid.[10]



On the basis of carbanion stabilities a predominance of **4** would be expected from this reaction, in contrast to experiment. Apparently relief of steric strain in the transition state is of major importance, and this favors cleavage of the more congested bond of the tetrahedral intermediate derived from **2** to yield ester **3** as the predominant product.

A variety of acidic conditions promote a slow transformation of cyclopropanone **2** to an isomeric material assigned structure **5**. Thus, after 3 days in the presence of 6 equiv of acetic acid at reflux in chloroform all but a trace of **2** is converted to **5**.[11] Peracid oxidation of the starting allene without the prior removal of acetic acid and the small amount of sulfuric acid present in commercial peracetic acid leads directly to **5**. 2-*t*-Butyl-2,3,3-trimethylcyclobutanone (**5**) shows: mp 80–81°; ir (CCl_4) 5.65 μ; nmr τ 7.39 (AB quartet, 2, $\Delta\nu = 28$ Hz, $J = 17$ Hz, CH_2CO), 8.56 (s, 3, CH_3), 8.76 (s, 3, CH_3), 8.82 (s, 3, CH_3), and 8.96 (s, 9, *t*-Bu); mass spectrum (70 eV) *m/e* (rel intensity) 168.1514 (1) 126 (40), 112 (28), 111 (78), 97 (100), 69 (62), and 57 (50). At 10 eV the only significant fragments were odd-electron ions at *m/e* 126 (100), 112 (41), and 56 (11), which substantiate the assigned substitution pattern of **5** over positional isomers.[12] The isomerization of **2** to **5** is viewed as proceeding *via* the hydroxyallyl cation **6** which is formed by protonation of **2** and subsequent ring opening. This process is probably reversible, and **5** is derived from 1,2 methyl migration in **6** and recyclization of the resulting carbonium ion **7** to the cyclobutanone.

The results of this study supply important information concerning one of the significant questions which initially motivated our studies of allene epoxidation, namely the possibility of allene oxide–cyclopropanone interconversion. The most straightforward description of the peracid oxidation of 1,1-di-*t*-butylallene is that allene oxide **1** is formed initially as a real intermediate.[13] This species serves as a precursor for the observed cyclopropanone, probably in an acid-catalyzed isomerization proceeding through intermediate **6**. The isolation of a spiro dioxide in the preceding paper[2] argues strongly in favor of an intermediate allene oxide as opposed to electrophilic attack of OH^+ (or its equivalent) at the central allenic carbon to give **6** directly. It is interesting to note that, even with excess peracid, diepoxidation was not competitive with cyclopropanone formation, since the latter was still the only product. Assuming that the above interpretation is correct, the equilibrium between **1** and **2** lies far on the side of the cyclopropanone. All of the physical data available[14] on other cyclopropanones gives no indication of detectable amounts of allene oxide isomers. We continue our efforts to elaborate on the chemistry of allene oxides.[14a]

Acknowledgment. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. The mass spectrometer was purchased with a National Science Foundation equipment grant (GP 5234). Finally, the assistance of Mr. A. C. Clark in obtaining the mass spectral data and Mr. S. J. Nance for

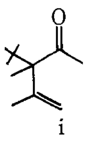
---

(8) N. J. Turro, P. A. Leermakers, H. R. Wilson, D. C. Neckers, G. W. Byers, and G. F. Vesky, *J. Amer. Chem. Soc.*, **87**, 2613 (1965).

(9) V. J. Shiner, Jr., and G. F. Meier, *J. Org. Chem.* **31**, 137 (1966).

(10) M. S. Newman and A. Leegwater, *ibid.*, **33**, 2144 (1968). We thank Professor Newman for generously supplying a sample of α,α-di-*t*-butylpropionic acid.

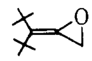
(11) A minor product (~10%) has also been isolated which is tentatively identified as 2,3-dimethyl-3-*t*-butylpent-1-en-4-one (i): ir 5.85, 6.13, and 11.1 μ (doublet); nmr, τ 4.96, 5.36 (m, 2 total, $C{=}CH_2$), 8.10 (s, 3, $RCOCH_3$), 8.25 (m, 3, $C{=}CCH_3$), 8.76 (s, 3, CH_3), and 9.04 (s, 9, *t*-butyl).



i

(12) H. Audier, J. M. Conia, M. Fétizon, and J. Goré, *Bull. Chem. Soc. Fr.*, 787 (1967).

(13) The experimental evidence does not allow distinction between **1** and the isomeric allene oxide ii as the hypothetical precursor of **2**. However, models indicate that both double bonds in the allene are shielded substantially by the *t*-butyl substituent and therefore epoxidation at the more substituted double bond appears likely.



ii

(14) J. M. Pochan, J. E. Baldwin, and W. H. Flygare, *J. Amer. Chem. Soc.*, **90**, 1072 (1968); L. K. Montgomery and J. Coetzer, unpublished results.

(14a) Note Added in Proof. Camp and Greene [R. L. Camp and F. D. Greene, *J. Amer. Chem. Soc.*, **90**, 7349 (1968)] have recently isolated an intact allene oxide and demonstrated its conversion to the related cyclopropanone. This observation provides strong confirmation for the pathway to **2** proposed above. We thank Professor Greene for informing us of his results prior to publication.

able assistance with certain preparative aspects of this work is also acknowledged.

[15] Alfred P. Sloan Research Fellow, 1968–1970.

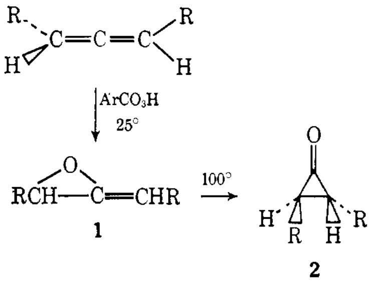
J. K. Crandall,[15] W. H. Machleder
Contribution No. 1617, Department of Chemistry
Indiana University, Bloomington, Indiana 47401
Received August 14, 1968

1,3-Di-*t*-butylallene Oxide. Isolation and Isomerization to *trans*-2,3-Di-*t*-butylcyclopropanone

Sir:

We wish to report the preparation and characterization of an allene oxide, a type of species which has been suggested as an intermediate, but which has hitherto eluded isolation.[1]

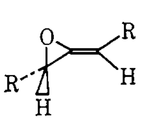
Reaction of excess 1,3-di-*t*-butylallene with *m*-chloroperbenzoic acid in hexane followed by removal of the *m*-chlorobenzoic acid by filtration and bulb-to-bulb distillation of the filtrate gave a distillate showing one major and three minor peaks, all of retention time longer than the allene by glpc (SE 30 on Chromosorb W). Collection of the major peak afforded a colorless liquid to which is assigned the allene oxide structure **1** on the basis of the following evidence: nmr (CCl_4) δ 0.98 (s, 9 H), 1.08 (s, 9 H), 3.25 (s, 1 H), 4.82 (s, 1 H); ir (CCl_4) 2960 (s), 2900 (s), 2860 (s), 1795 (m, broad), 1475 (s), 1465 (s), 1395 (m), 1365 (s), 1260 (w), 1200 (m), 1125 (m), 1085 (s), 980 (s), 940 (m), 930 (m), 920 (m), 870 (m), 710 (m) cm^{-1}; mass spectrum at 80 eV: *m/e* (relative intensity), 168 (4.3), 140 (8.6), 126 (20.7), 125 (29.3), 109 (8.6), 97 (27.6), 83 (81), 70 (84.5), 69 (89.7), 57 (100). The mass spectrum of the compound is similar to that of *trans*-2,3-di-*t*-butylcyclopropanone (**2**),[2] differing principally in the relative intensity of several ions. The glpc retention time of **1** on SE 30 is also the same as that of **2**. However, the infrared, nmr, and ultraviolet spectra of **1** collected from glpc showed that **2** was not present. Upon heating to 100°, the allene oxide **1** does isomerize to the cyclopropanone **2** (time for 50% isomerization, ~5 hr), identical ir and uv spectra with those of an authentic sample.



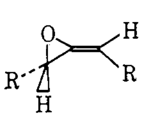
(1)

R = *t*-butyl

Two epoxides of 1,3-di-*t*-butylallene are possible, **1a** and **1b**. The simplicity of the nmr spectrum of **1** is suggestive that it is a single species.

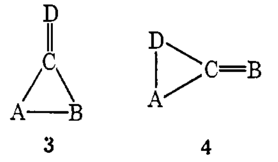


1a



1b

The type of small-ring isomerism depicted in eq 2 (**3**–**5**)[3] is known in the all-carbon system[4] and has been suggested in some examples containing heteroatoms.[5] The results of the present study provide an example of eq 2 in a heterocyclic system in which both isomers (**1** and **2**) are isolable species and establish that the cyclopropanone form is the more stable of the two in this case.[6]



(2)

---

[1] See J. K. Crandall and W. H. Machleder, *Tetrahedron Lett.*, 6037 (1966), and references cited therein. See also, J. K. Crandall and W. H. Machleder, *J. Amer. Chem. Soc.*, **90**, 7347 (1968). We wish to thank Professor Crandall for sending us a copy of his paper prior to publication.

[2] J. F. Pazos and F. D. Greene, *ibid.*, **89**, 1030 (1967).

[3] For **3**, **4**, and **5**, the appropriate number of substituents are assumed to be attached to A, B, and D, corresponding to the usual valence states of these atoms.

[4] J. P. Chesick, *J. Amer. Chem. Soc.*, **85**, 2720 (1963); E. F. Ullman and W. J. Fanshawe, *ibid.*, **83**, 2379 (1961), and references cited therein.

[5] J. A. Deyrup and R. B. Greenwald, *Tetrahedron Lett.*, 5091 (1966); I. Lengyell and J. C. Sheehan, *Angew. Chem.*, **80**, 27 (1968); F. D. Greene and J. F. Pazos, *J. Org. Chem.*, in press.

[6] The asymmetry present in the 1,3-di-*t*-butylallene oxide–*trans*-2,3-di-*t*-butylcyclopropanone system should permit a detailed examination of the stereochemistry of these interconversions on which we hope to report at a future date.

Ronald L. Camp, Frederick D. Greene
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139
Received September 9, 1968

The Benzoate Sector Rule, a Method for Determining the Absolute Configurations of Cyclic Secondary Alcohols

Sir:

Brewster's benzoate rule,[1] which covers Freudenberg's phthalate rule[2] and Mills' rule,[3] is widely employed to determine the absolute configurations of cyclic secondary alcohols.[4,5] However, it is not applicable to certain types of compounds, such as those in which the carbinyl carbon is flanked by two methylene groups (entry 4 in Table I) and those in which one of the carbons adjacent to the carbinyl carbon is the bulkier and also more polar (Figure 1).[6]

We have found that the strong Cotton effect of benzoates due to $\pi \rightarrow \pi^*$ intramolecular charge-transfer transition[7] at *ca.* 225 mμ permits predictions of the

---

[1] J. H. Brewster, *Tetrahedron*, **13**, 106 (1961); see also J. H. Brewster, *J. Am. Chem. Soc.*, **81**, 5475, 5483, 5493 (1959).

[2] K. Freudenberg, "Stereochemie," Deuticke, Leipzig, 1933, p 696.

[3] J. A. Mills, *J. Chem. Soc.*, 4976 (1952).

[4] See the following for a slightly extended application of the benzoate rule: M. Miyamoto, K. Morita, Y. Kawamatsu, Y. Kawashima, and K. Nakanishi, *Tetrahedron*, **23**, 411 (1967).

[5] See the following for alcohol derivatives which give rise to Cotton effects: P. Crabbé, "Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1965, Chapter 11.

[6] See footnote 28 in K. Nakanishi, M. Ohashi, M. Tada, and Y. Yamada, *Tetrahedron*, **21**, 1231 (1965).

[7] N. Harada and K. Nakanishi, *J. Am. Chem. Soc.*, **90**, 7351 (1968).