where disubstitution at each terminal carbon may well give rise to slightly higher rotational barriers and lower frequency factors for rotation,[3] making $k_{\text{cyc}} > k_{\text{rot}}$.

The intermediate or set of intermediates formed in this reaction, however, *cannot* be only the same type as those produced from the 2,5-dimethylpyrazolines,[11] despite the superficial structural similarity, since the pyrazolines apparently produce diradicals which do undergo electrocyclic closure. Models indicate that decomposition of a pyrazoline is likely to directly produce the large central bond angle intermediate predicted[4b] to undergo such closure, while this intermediate may well be inaccessible starting from a cyclopropane.

Finally (assuming that optically active **2T** isolated from the kinetic experiments is formed by tertiary–tertiary rather than secondary–tertiary bond cleavage in (−)-**2C**[12]) our optical correlation indicates that rotation is not insuperably faster than cyclization, and that rotation of a methyl-substituted carbon about a single bond is slightly more rapid than rotation of an ethyl-substituted carbon.

Acknowledgments. We are grateful to Professor J. A. Berson for informing us of work, independently conceived and executed in his laboratories, on the pyrolysis of tetramethylcyclopropane-d_6, and for stimulating discussions following that. Financial support from the Arthur Amos Noyes Fund, the Petroleum Research Fund administered by the American Chemical Society (Grant 1053-G1), and a DuPont Young faculty grant is also gratefully acknowledged.

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(11) R. J. Crawford and A. Mishra, *J. Am. Chem. Soc.*, **88**, 3693 (1966). See also D. E. McGreer, N. W. K. Chiu, M. G. Vinje, and K. C. K. Wong, *Can. J. Chem.*, 43, 1407 (1965).

(12) This seems likely, based on strain considerations and the apparently general lowering of the activation energy for cyclopropane isomerizations by about 2.5–3 kcal per alkyl group. For good compilations of data, see ref 1d and 3.

(13) National Science Foundation Predoctoral Fellow, 1968–1969.

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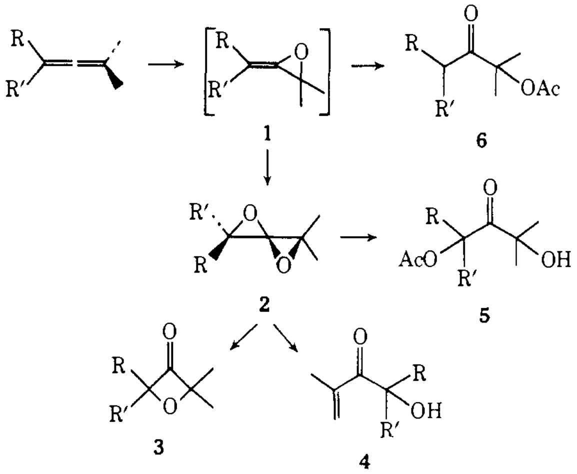
Allene Epoxidation. Isolation of a 1,4-Dioxaspiro[2.2]pentane Derivative

Sir:

We have recently postulated the existence of allene oxide **1a** and spiro dioxide **2a** as unisolated reactive intermediates in the peracid oxidation of tetramethylallene.[1] These species were invoked to provide a rational basis for the array of products (**3a**–**6a**) which was obtained from this reaction. Substantial supporting evidence for this proposal is herein presented by virtue of the isolation and characterization of 5-*t*-butyl-2,2-dimethyl-1,4-dioxaspiro[2.2]pentane (**2b**), an example of the unique spiro dioxide structure.[2] Thus, buffered peracetic acid oxidation[1] of 2,5,5-trimethyl-2,3-hexadiene[3,4] with 2 equiv of oxidant led to **2b** smoothly and in high yield. This material isomerized upon attempted glpc purification, but distillation through a spinning band column afforded a pure sample, bp 40° (2 mm). The homogeneity of this material was attested to by its well-resolved nmr spectrum: τ 6.63 (s, 1, epoxide proton), 8.54 (s, 3, CH_3), 8.56 (s, 3, CH_3), and 9.03 (s, 9, *t*-Bu). The chemical shift of the ring hydrogen is downfield about 0.5 ppm from those of simple epoxides,[5] undoubtedly owing to the effect of the neighboring oxide ring. The molecular formula of **2b** is assured by its elemental analysis (Found: C, 69.09; H, 10.18) and an accurate mass determination on the molecular ion in its mass spectrum (Found: *m/e* 156.1151).



a, R = R′ = CH_3
b, R = H; R′ = *t*-Bu

The mass spectrum (70 eV) showed important fragments at *m/e* (relative intensity) 156 (1), 128 (8), 113 (8), 100 (29), 98 (21), 83 (46), and 70 (100). The infrared spectrum was devoid of absorption in the hydroxyl and carbonyl regions but had a number of strong bands in the 8–14-μ region. A puzzling feature of the spectrum was the presence of a medium-intensity absorption at 6.10 μ. Interestingly, this band was absent in the Raman spectrum of **2b**.[6]

Treatment of spiro dioxide **2b** with hydrochloric acid in methylene chloride produced in good yield a 1:1 mixture of two isomeric compounds identified as oxetanone **3b** and unsaturated ketone **4b**. A variety of other acidic or thermal conditions including glpc readily effected this conversion. 4-*t*-Butyl-2,2-dimethyl-3-oxetanone (**3b**) shows: ir 5.50 μ; nmr τ 5.04 (s, 1, CH), 8.56 (s, 3, CH_3), 8.64 (s, 3, CH_3), and 9.02 (s, 9, *t*-Bu). 4-Hydroxy-2,5,5-trimethylhex-1-en-3-one

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(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) An early claim for this ring system has been shown to be incorrect by G. B. Hoey, D. O. Dean, and C. T. Lester, *ibid.*, 77, 391 (1955). A more recent assignment of this heterocyclic nucleus to the product from an allene epoxidation [V. I. Pansevich-Kolyada and Z. B. Idelchik, *J. Gen. Chem. USSR*, 24, 1601 (1954)] is based solely on rather poor analytical data. Our own experience leads us to severely doubt that a spiro dioxide derivative would have survived the conditions described.

(3) This allene was prepared from 2,4,4-trimethyl-2-pentene by conversion to the dibromocarbene adduct with bromoform–potassium *t*-butoxide and subsequent treatment of the adduct with methyllithium [L. Skattebøl, *J. Org. Chem.*, **31**, 2789 (1966)].

(4) All new compounds gave acceptable microanalytical data.

(5) For example, the methine proton in propylene oxide is found at *ca.* τ 7.1: NMR Spectra Catalog, Varian Associates, Palo Alto, Calif., 1962, Spectrum 32.

(6) This behavior appears to rule out the possibility that the absorption is C=C stretching. The nmr contraindicates the possibility of appreciable contamination by an impurity and, furthermore, the likely impurities are incompatible with the spectrum observed. The infrared band is not an overtone, but the possibility that it is an exceptionally strong combination band is not incompatible with the spectrum.

(**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).

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[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.

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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

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[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).