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

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

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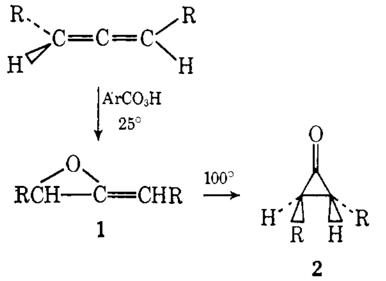
1,3-Di-*t*-butylallene Oxide. Isolation and Isomerization to *trans*-2,3-Di-*t*-butylcyclopropanone

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]

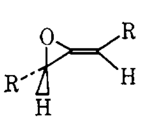
Reaction of excess 1,3-di-*t*-butylallene with *m*-chloroperbenzoic acid in hexane followed by removal of the *m*-chlorobenzoic acid by filtration and bulb-to-bulb distillation of the filtrate gave a distillate showing one major and three minor peaks, all of retention time longer than the allene by glpc (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, $\sim$5 hr), identical ir and uv spectra with those of an authentic sample.



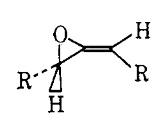
(1)

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.

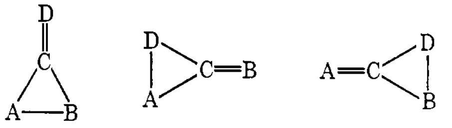


1a



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]



3 **4** **5**

(2)

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[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.

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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

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[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).