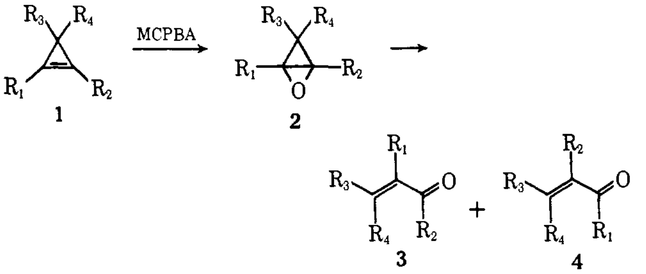
Communications to the Editor

The Peroxy Acid Oxidation of Hindered Cyclopropenes. Evidence for a Dual Pathway

Sir:

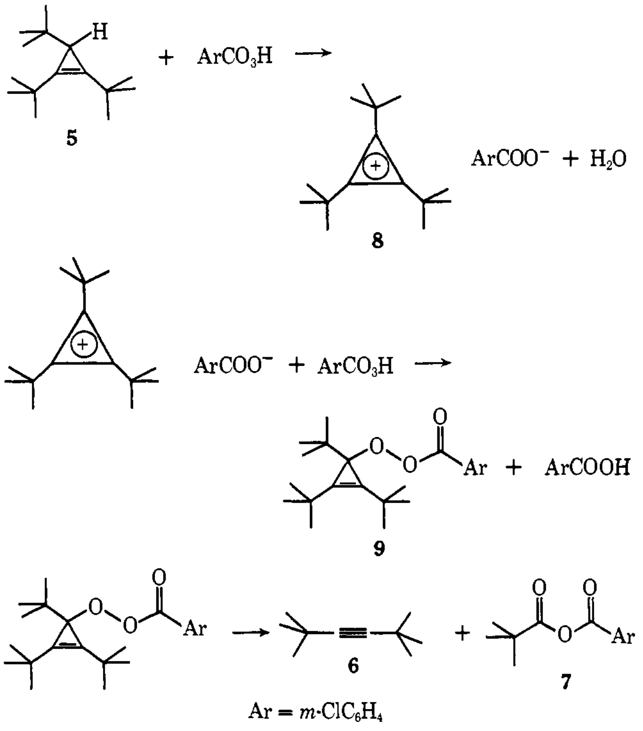
Recently we reported that unhindered cyclopropenes of type **1** ($R_1 \neq R_2$, $R_3 = R_4$) undergo oxidation with *m*-chloroperoxybenzoic acid (MCPBA) to afford two α,β-unsaturated carbonyl compounds **3** and **4**, probably *via* 2-oxabicyclo[1.1.0]butane intermediates **2**.[1,2]



We now wish to report a novel oxidative fragmentation reaction, unique to *hindered* cyclopropenes bearing a hydrogen at the 3 position, which occurs under similar conditions. Reaction of 1,2,3-tri-*tert*-butylcyclopropene (**5**)[3] with MCPBA in methylene chloride at room temperature afforded di-*tert*-butylacetylene (**6**) and mixed anhydride **7** as primary products.[4,5] No oxabicyclobutane or α,β-unsaturated ketone products derived from the epoxidation of **5** were detected.

1,2,3-Tri-*tert*-butyl-3-methylcyclopropene[3] and 1,2-di-*tert*-butyl-3-methyl-3-phenylcyclopropene[6] did not react with MCPBA under similar conditions, confirming our suspicion that the hydrogen in the 3 position was abstracted in the reaction. Conclusive evidence was provided by conducting the reaction of **5** with MCPBA in methylene chloride in the presence of perchloric acid. An nmr spectrum of the reaction mixture revealed a singlet at δ 1.58, corresponding to the tri-*tert*-butylcyclopropenyl cation **8**.[3] Furthermore, dilution of the reaction mixture with ether resulted in the precipitation of **8** as the perchlorate salt. The intermediacy of **8** was established by subjecting it (perchlorate salt) to the reaction conditions (MCPBA, sodium *m*-chlorobenzoate, CH_2Cl_2) which resulted in the formation of **6** and **7**.[7] Subsequent reaction of cation **8** with a second mole of MCPBA would be expected to afford peroxy ester **9**, the probable precursor of **6** and **7** (Scheme I). Peroxy ester **9** could not be isolated or detected by nmr spectroscopy (*vide infra*).

Scheme I. MCPBA Oxidation of **5**



Reaction of 1-phenyl-2,3-di-*tert*-butylcyclopropene (**10**)[8] with MCPBA in methylene chloride afforded α,β-unsaturated ketone **11** (55%), mp 74–76°, as well as acetylenes **6** and **14** (combined yield 45%) in the ratio of 1:3.5. The structure of **11** (exclusive of stereochemistry) was established on the basis of the following spectral data: ir (ν_{max}, CCl_4) 1665 cm^{-1}; uv (λ_{max}, 95% EtOH) 249 mμ (ϵ 12,100); nmr (CCl_4, δ) 0.92 (9 H, s), 1.07 (9 H, s), 5.53 (1 H, s), 7.25–7.60 (3 H, m), 7.80–8.05 (2 H, m); mass spectrum *m/e* 244, 105 (base peak).

The products derived from cyclopropene **10** are indicative of a dual oxidative pathway as illustrated in Scheme II. The proposed mechanism involves epoxidation of **10** to generate the intermediate oxabicyclobutane **13** which subsequently undergoes isomerization to afford α,β-unsaturated ketone **11**.[9] Alternatively, hydride abstraction from **10** by MCPBA generates cation **15**, which can be detected by nmr as the perchlorate salt (δ 1.67, s)[3] when the reaction is conducted in the presence of perchloric acid. Subsequent reaction of **15** with MCPBA generates peroxy esters **16** and **17** (in the ratio of 1:3.5) which decompose to afford the expected acetylene and anhydride products.[4] In an independent experiment, the reaction of **15** (perchlorate salt) with MCPBA and sodium *m*-chlorobenzoate in methylene chloride gave acetylenes **6** and **14** (in the expected ratio of 1:3.5) but not α,β-unsaturated ketone

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(1) J. Ciabattoni and P. J. Kocienski, *J. Amer. Chem. Soc.*, **91**, 6534 (1969).

(2) See also (a) L. E. Friedrich and R. A. Cormier, *J. Org. Chem.*, **35**, 450 (1970); (b) H. Prinzbach and U. Fischer, *Helv. Chim. Acta*, **50**, 1669 (1967).

(3) J. Ciabattoni and E. C. Nathan, III, *J. Amer. Chem. Soc.*, **91**, 4766 (1969).

(4) This oxidation requires 2 mol of MCPBA/mol of cyclopropene **5**. However, secondary products derived from MCPBA oxidation of di-*tert*-butylacetylene (**6**) were also observed. See J. Ciabattoni, R. A. Campbell, C. A. Renner, and P. W. Concannon, *ibid.*, **92**, 3826 (1970).

(5) The structures of all products unless otherwise indicated were established by vpc and/or spectral comparison with authentic samples.

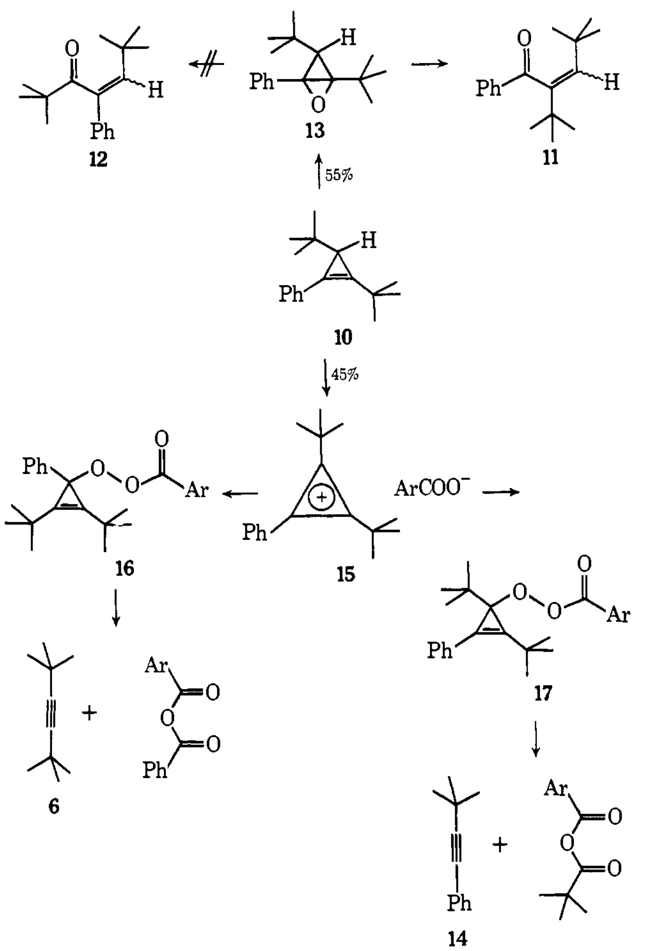
(6) Prepared by the reaction of phenyl di-*tert*-butylcyclopropenyl perchlorate[3] with methyllithium.

(7) The trimethyl- and triphenylcyclopropenyl cations also underwent this oxidative fragmentation reaction. Replacement of MCPBA with 90% hydrogen peroxide as the oxidant afforded analogous results.

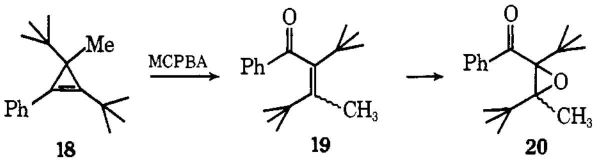
(8) Prepared by the reaction of phenyl di-*tert*-butylcyclopropenyl perchlorate with lithium aluminum hydride.

(9) The other possible isomeric α,β-unsaturated ketone **12** was not detected.

Scheme II. MCPBA Oxidation of **10**



11. These results support the intermediacy of peroxy esters **16** and **17** in the formation of acetylenes **6** and **14**, respectively, and exclude **16** as a possible precursor to **11** in the peroxy acid oxidation of **10**. In accordance with the proposed mechanism, oxidation of cyclopropene **18**[6] afforded only epoxy ketone **20**,[10] mp 123–124°, the structure of which (exclusive of stereochemistry) was established on the basis of the following spectral data: ir ($\nu_{\max}$ CCl_4) 1690 cm^{-1}; uv ($\lambda_{\max}$, 95% EtOH) 249 mμ (ϵ 11,600); nmr (CCl_4, δ) 0.83 (9 H, s), 1.00 (9 H, s), 1.57 (3 H, s), 7.20–7.45 (3 H, m), 7.70–7.95 (2 H, m); mass spectrum *m/e* 274, 105 (base peak).



The reaction of **5** with MCPBA was unaffected by the presence of the radical scavengers bromotrichloromethane or β,β-dichlorostyrene precluding a mechanism involving radical abstraction of hydrogen as a first step in the formation of the tri-*tert*-butylcyclopropenyl cation **8**. Thus the process appears to involve a direct transfer of hydride from the 3 position of the cyclopropene to the terminal electrophilic oxygen of MCPBA to generate a cyclopropenyl cation as the *m*-chlorobenzoate salt. To our knowledge this is the first example of the direct oxidation of a hydrocarbon to a carbonium ion by a peroxy acid.

The instability of peroxy esters **9**, **16**, and **17** is not surprising in view of the fact that the peroxide intermediates proposed in the oxidative decarbonylation of cyclopropenones[11] and cyclopropanones[12] with MCPBA and hydrogen peroxide, respectively, were not isolated under the reaction conditions. Furthermore, DePuy has observed that the related nitrite esters of cyclopropanols are extremely unstable, even at −50°.[13] The low activation energy for the decomposition of these three-membered ring nitrites and peroxides probably reflects (at least in part) a relief of ring strain in the transition state by partial ring opening as previously suggested.[13]

In theory, the decomposition of these peroxy esters may proceed *via* a radical, ionic, or concerted process.[14] If a radical or ionic mechanism is operative, it must be intramolecular (*i.e.*, radical cage or ion pair) since radical scavengers had no significant effect on the reaction of **5** with MCPBA and the reaction of **8** (perchlorate salt) with MCPBA in the presence of sodium acetate resulted in no incorporation of acetate into the anhydride product. Further mechanistic studies are in progress.

Acknowledgment. We are grateful to the Research Corporation for financial support of this research.

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(10) Epoxy ketone **20** undoubtedly arises from epoxidation of α,β-unsaturated ketone **19**.

(11) J. K. Crandall and W. W. Conover II, *Tetrahedron Lett.*, 583 (1971).

(12) J. E. Baldwin and J. H. I. Cardellia, *Chem. Commun.*, 588 (1968).

(13) C. H. DePuy, *Accounts Chem. Res.*, **1**, 33 (1968).

(14) For reviews of peroxide reactions see (a) D. Swern, Ed., "Organic Peroxides," Vol. 1, Wiley-Interscience, New York, N. Y., 1970; (b) Ya. K. Syrkin and I. I. Moiseev, *Russ. Chem. Rev.*, **29**, 193 (1960); (c) J. B. Lee and B. C. Uff, *Quart. Rev., Chem. Soc.*, **21**, 429 (1967).

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Received May 14, 1971

Transmission of π Interactions through σ Bonds in Tricyclo[4.4.2.0^{1,6}]dodeca-3,8-diene-11,12-dione and Its Tetrahydro Derivative

Sir:

The unusual spectral properties of the title compounds in the visible region have been reported and discussed by Bloomfield and Moser.[1] In an effort to investigate the electronic structure of these systems we have determined the molecular structure of the diene[2] and performed some molecular orbital calculations.[3] The results of these investigations lead to interesting conclusions regarding the nature of the π-electron system interactions involved.

The diene compound is found to crystallize in the monoclinic space group $P2_1/c$ with a = 7.438, b = 11.539, c = 12.935 Å, and β = 116.22°. There are four molecules per unit cell. The structure refined to a final R index of 0.065 for 1870 independent X-ray reflections.

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(1) J. J. Bloomfield and R. E. Moser, *J. Amer. Chem. Soc.*, 90, 5625 (1968).

(2) R. Fink, D. van der Helm, and S. C. Neely, Abstracts, American Crystallographic Association Meeting, March 1969, p 34.

(3) S. C. Neely, R. Fink, and D. van der Helm, Abstracts, Southeastern–Southwestern Regional Meeting of the American Chemical Society, Dec 1970, p 168.