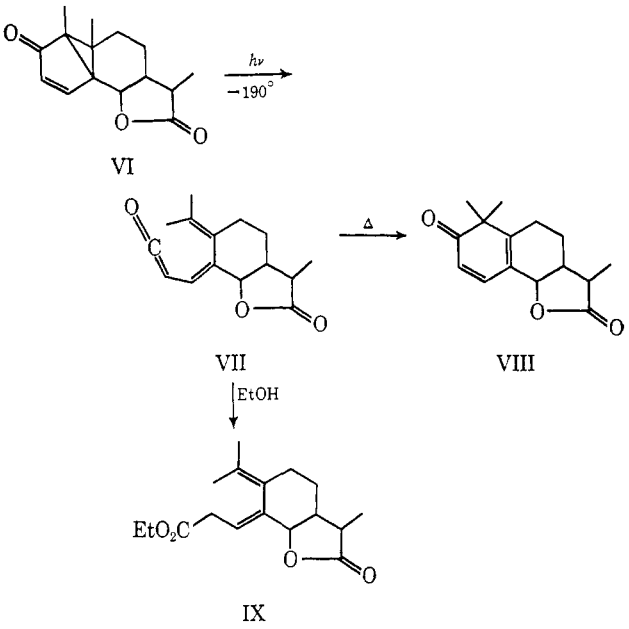
must be *cis*, and the 5,6 double bond is tentatively considered to be *trans* on the basis that this stereochemistry is most consistent with the facile cyclization of the diene ketene.[5] Thermal cyclizations of diene ketenes to 2,4-cyclohexadienones have been observed in other systems.[6-8]

There are two routes from umbellulone to thymol at low temperature, both involving ground-state intermediates. In the methanol-trapping experiments at $-190°$ comparable yields of ester and thymol are obtained. This result suggests that path A accounts for at least half of the thymol produced under these conditions. The fact that irradiation of umbellulone in methanol at room temperature gives no ester could mean either that diene ketene (V) cyclization to III is too fast at this temperature for nucleophilic attack by methanol to compete or that only path B is operative.

Irradiation of lumisantonin (VI) at room temperature gives a variety of products including VIII.[9-11] Irradiation of lumisantonin (VI) (crystalline or in an EPA glass) at $-190°$ gives a ketene (VII) as a primary photoproduct (Scheme II). It is possible that a trace of

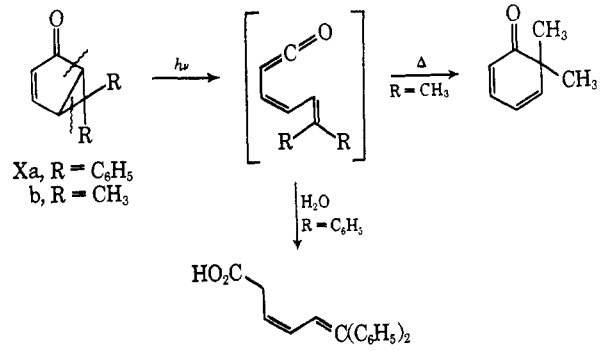
Scheme II



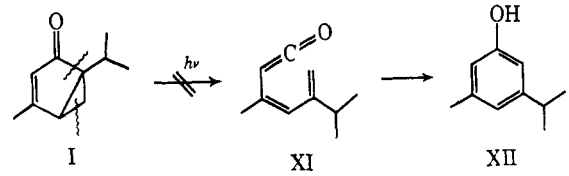
dienone VIII is produced as a primary product. We have observed also the blue species reported by Fisch and Richards,[10] but we have not been able to show conclusively that it goes thermally to dienone VIII. The ketene is assigned structure VII because on warming to room temperature it cyclizes to the dienone VIII. When lumisantonin (VI) is irradiated in an EPA glass at $-190°$ then warmed above $-160°$ the ketene absorption (2113 cm^{-1}) disappears with concurrent appearance of an absorption at 1738 cm^{-1} assigned to the carbonyl group of the ester IX. The sequence VI ($h\nu$) → VII (Δ) → VIII is an important but probably not unique path from VI to VIII.

Cyclization of ketenes V and VII is analogous to that reported in related systems.[6-8] The opening of the cyclopropane rings in I and VI, however, follows a different course from that observed in Xa[12] and Xb[7] (Scheme III). Cleavage of umbellulone in this fashion

Scheme III



would produce a diene ketene (XI) which should cyclize to *sym*-thymol (XII). *sym*-Thymol is not formed at room temperature[2] and could not be detected in any of our spectra.



The difference in the nature of the ring-opening process in I and VI as opposed to Xa,b may be due to differences in the position of substituents. Formation of ketenes V and VII from umbellulone and lumisantonin may involve a ketene–carbene mechanism as suggested by van Tamelen and coworkers.[13]

Acknowledgment. This investigation was supported by Public Health Service Grant GM 14305 from the National Institute of General Medical Sciences. A generous sample of umbellulone was provided by Professor James Wheeler.

(5) It is assumed that the stereochemistry of the double bonds is maintained in the addition of methanol. This has been shown to be true for related diene ketenes (P. M. Collins and H. Hart, *J. Chem. Soc. C*, 1197 (1967)).

(6) J. Griffiths and H. Hart, *J. Amer. Chem. Soc.*, **90**, 3297 (1968).

(7) J. S. Swenton, E. Saurborn, R. Srinivasan, and F. I. Sonntag, *ibid.*, **90**, 2990 (1968).

(8) J. D. Hobson, M. M. A. Holly, and J. R. Malpass, *Chem. Commun.*, 764 (1968).

(9) For a review of the photochemistry of santonin and related compounds see P. J. Kropp in "Organic Photochemistry," Vol. I, O. L. Chapman, Ed., Marcel Dekker, Inc., New York, N. Y., 1967, p 1.

(10) M. H. Fisch and J. H. Richards, *J. Amer. Chem. Soc.*, **90**, 1547, 1553 (1968); **85**, 3029 (1963).

(11) O. L. Chapman and L. F. Englert, *ibid.*, **85**, 3028 (1963).

(12) H. E. Zimmerman, R. Keese, J. Masielski, and J. S. Swenton, *ibid.*, **88**, 4895 (1966); H. E. Zimmerman and D. I. Schuster, *ibid.*, **84**, 4527 (1962).

(13) E. E. van Tamelen, S. H. Levin, G. Brenner, J. Wolinsky, and P. Aldrich, *ibid.*, **80**, 501 (1958); **81**, 1666 (1959).

(14) NASA Trainee, 1965–1968.

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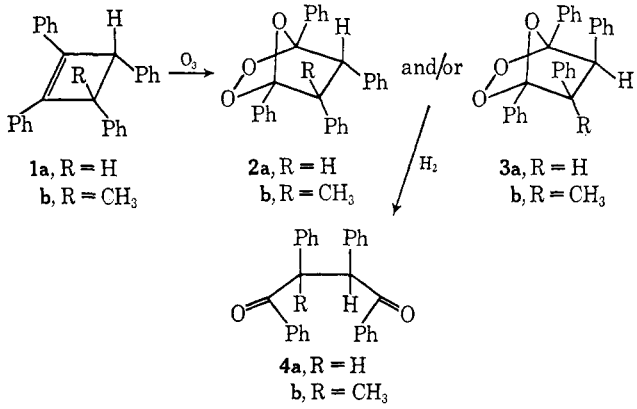
Steric Effects in the Ozonolysis of 1,2,3,4-Tetraphenylcyclobutenes

Sir:

The renewed interest in the mechanism of olefin ozonolysis has demonstrated that steric requirements of the olefinic substituents play an important role in determining product stereospecificity.[1,2] This has led to

proposals[1,2] for modification of the Criegee mechanism[3] and to the suggestion that ozonide formation from hindered *cis* olefins may be a concerted process proceeding stereospecifically from a σ complex to product.[1a,b] Our results on the ozonolysis of various 1,2,3,4-tetraphenylcyclobutenes offer some unusual examples of stereospecificity in ozonide formation (including the first example of *exo–endo* isomers), best rationalized by a mechanistic duality dictated by diverse steric considerations.

Ozonolysis of *cis*-1,2,3,4-tetraphenylcyclobutene[4] under our standard conditions (O_3, CH_2Cl_2, $-78°$) quantitatively[5] affords a single isomer (mp 163° dec, δ 4.81 (3 H, s)) which must possess either the *endo* (**2a**) or *exo* (**3a**) structure. The *trans*-cyclobutene[4] **5a** is also



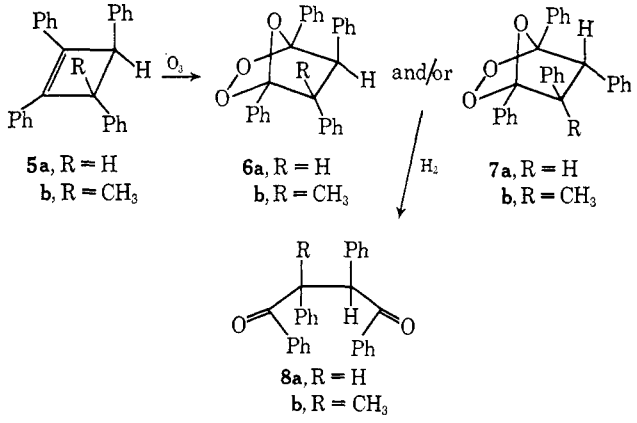
1a, R = H
b, R = CH_3

2a, R = H
b, R = CH_3

3a, R = H
b, R = CH_3

4a, R = H
b, R = CH_3

quantitatively converted to a single product, **6a** (mp 118–20° dec, AB quartet at δ 3.87 and 4.22 (2 H), J_{AB} = 5 Hz), though now the absence of isomers is dictated by product symmetry. Hydrogenation of **2a**/**3a** and **6a** (Pd on $CaCO_3$) gave the corresponding 1,4-diketones, *meso*- and *dl*-didesyl (**4a** and **8a**), identical with authentic[6] samples.



5a, R = H
b, R = CH_3

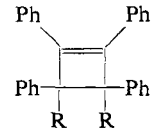
6a, R = H
b, R = CH_3

7a, R = H
b, R = CH_3

8a, R = H
b, R = CH_3

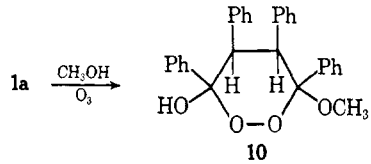
The *cis*- and *trans*-3-methyltetraphenylcyclobutenes (**1b** and **5b**)[7] also form crystalline ozonides quantitatively.[5] **5b** yields a single product, **6b** or **7b** (mp 118–20° dec, singlets at δ 0.83 (3 H) and 4.83 (1 H), which on hydrogenation gives the *threo* diketone **8b**, mp 105°. In contrast, *cis* isomer **1b** affords two isomeric ozonides, **2b** and **3b**: a compound melting with decomposition at 147° with methyl and cyclobutenyl singlets at δ 2.38 and 4.33, and an isomer melting with decomposition at 134° with singlets at δ 1.68 and 4.03. Both products are obtained in roughly equal amounts and the assumption that these are *endo* and *exo* isomers follows from the hydrogenation of each to the same *erythro* diketone **4b** of mp 150°.

A notable difference in reactivity is manifested by the α-tetrasubstituted cyclobutenes **9a–c**,[8] which do not react with ozone even at $-30°$. It appears from this result that at least one of the α-cyclobutenyl carbons must be monosubstituted for attack by ozone at the olefinic bond[9] and that initial C–O bond formation will occur at that side and face of the cyclobutene ring to which an H atom is attached.



9a, R = Br
b, R = Cl
c, R = CH_3

Equally important in its mechanistic implications is the observation that when ozonized in the presence of methanol (2.8 mmol of substrate, 0.3 mol of CH_2Cl_2, 3.2 mol of CH_3OH), **1a** is quantitatively converted to a new product, the cyclic peroxide[10] **10**, while **1b**, **5a**, and **5b** yield only the usual ozonides. Insofar as reaction with methanol discriminates between the presence or absence of a relatively stable dipolar intermediate,[11] these results suggest that such an intermediate is formed



10

only with **1a**.

To explain the stereospecificity and reaction with methanol of **1a**, we suggest (Scheme I) that formation of a primary ozonide (**11a**) occurs with ease by attack on its unhindered face. Rearrangement of **11a** yields the dipolar intermediate **11b**, which can transannularly

(1) (a) P. R. Story, R. W. Murray, and R. D. Youssefyeh, *J. Am. Chem. Soc.*, **88**, 3144 (1966); (b) R. W. Murray, R. D. Youssefyeh, and P. R. Story, *ibid.*, **89**, 2429 (1967); (c) P. R. Story, C. E. Bishop, J. R. Burgess, R. W. Murray, and R. D. Youssefyeh, *ibid.*, **90**, 1907 (1968).

(2) N. A. Bauld, J. A. Thompson, C. E. Hudson, and P. S. Bailey, *ibid.*, **90**, 1822 (1968).

(3) R. Criegee, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **18**, 111 (1957).

(4) H. H. Freedman, G. A. Doorakian, and V. R. Sandel, *J. Am. Chem. Soc.*, **87**, 3019 (1965).

(5) This refers to the crude product whose nmr spectrum corresponded to that of chromatographically purified product. All new compounds gave satisfactory analyses and spectral data. We are grateful to T. W. Shannon for mass spectral results.

(6) M. Pailer and U. Müller, *Monatsh.*, **79**, 615 (1948).

(7) G. A. Doorakian and H. H. Freedman, *J. Am. Chem. Soc.*, **90**, 3582 (1968). *trans* isomer **5b** is obtained from **1b** by epimerization with base.

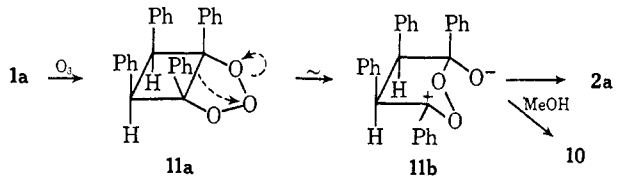
(8) **9a**: H. H. Freedman and G. A. Doorakian, *Tetrahedron*, **20**, 2181 (1964). **9b** and **9c** are obtained from **9a** by treatment with Cl_2 and CH_3MgBr, respectively.

(9) G. O. Schenck, W. Hartmann, and R. Steinmetz (*Ber.*, **96**, 498 (1963)) report that 1,2-dichloro-3,4-dimethyl-3,4-dicarboxycyclobutene is also unreactive toward ozone at $-60°$. However, generalization is inadvisable inasmuch as 3,4-dichlorotetramethylcyclobutene forms an ozonide (private communication from R. Criegee).

(10) The structure of **10**, mp 146°, follows from its nmr spectrum in THF-d_8: 20 phenyl protons at δ 6.8–7.5, three methoxyl protons at δ 3.32, hydroxyl proton at δ 6.51, and two coupled benzylic ring protons at δ 4.35 and 3.55 with J_{AB} = 7 Hz.

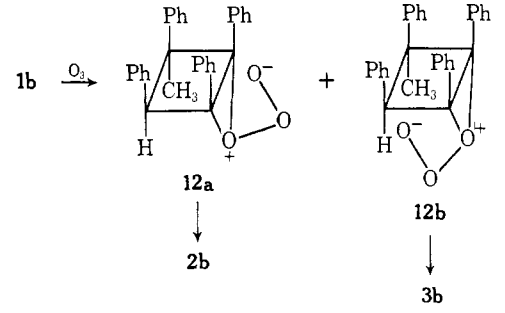
(11) *Cf.* (a) R. Criegee, *Ann.*, **583**, 1 (1953); (b) A. Rieche and M. Schultz, *Ber.*, **98**, 3623 (1965).

Scheme I

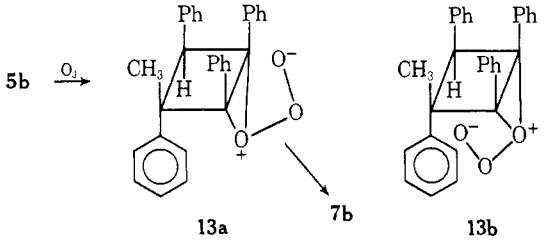


close to ozonide or be intercepted by methanol to form **10**. Scheme I requires that **2a** and not **3a** be produced.[12]

For the 3,4-trisubstituted cyclobutenes we propose that primary ozonide formation is sterically prohibited, and that attack takes place only at the olefinic carbon adjacent to and from the same side as the lone H to form



both σ complexes **12a** and **12b**. These, on concerted rearrangement,[1a,b] lead, respectively, to the *exo* and *endo* isomeric ozonides **2b** and **3b**. However, when a phenyl group is *cis* to the proton, as in **5b**, its preferred conformation is such that only **13a** can be produced, **13b** being sterically inaccessible. Accordingly, we predict that concerted rearrangement of the single σ complex produced from **5b** affords only **7b**.



(12) An X-ray structure determination of this compound is currently being carried out by F. P. Boer.

(13) Dow-Eastern Research Laboratory, Postdoctoral Research Fellow, 1967–1968.

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Received June 10, 1968

The Reaction of Trialkylboranes with Diazoacetone. A New Ketone Synthesis

Sir:

The interaction of trialkylboranes with nucleophiles (*i.e.*, ylides,[1] carbanions[2]) has been demonstrated to constitute an essential primary step in the elaboration of olefins to various homologated functionalized derivatives (alcohols,[1] esters,[1,2] amides,[1] α-haloesters,[2] dialkylacetic acid esters[2]). Based on this principle we find it possible to add to the already existing wealth of organoborane-based synthetic methods a new ketone synthesis.

We wish to report that the reaction of diazo ketones with organoboranes[3] (available from olefins *via* hydroboration), followed by treatment with alkaline hydrogen peroxide, or, more conveniently, alkaline hydrolysis in the absence of peroxide,[4] provides a convenient new method of homologating olefins to ketones (eq 1).

$$R_3B + CH_3COCHN_2 \xrightarrow{-N_2} \xrightarrow{\text{hydrolysis}} RCH_2COCH_3 \quad (1)$$

Yields[5] of ketones are in the range 36–89% for a variety of olefins (eq 2–6).

$$CH_3(CH_2)_2CH{=}CH_2 \xrightarrow{85\%} CH_3(CH_2)_3COCH_3 \quad (2)$$

$$CH_3(CH_2)_3CH{=}CH_2 \xrightarrow{89\%} CH_3(CH_2)_6COCH_3 \quad (3)$$

(4)

$$(CH_3)_2C{=}CH_2 \xrightarrow{56\%} (CH_3)_2CH(CH_2)_2COCH_3 \quad (5)$$

$$CH_3CH{=}CHCH_3 \xrightarrow{36\%} CH_3CH_2CH(CH_3)CH_2COCH_3 \quad (6)$$

Similarly, 1-pentene is converted to hexyl phenyl ketone and 1-hexene to heptyl phenyl ketone, each in 91% yield[5] (78% isolated yield), by treatment of the respective trialkylborane with diazoacetophenone followed by hydrolysis. The reaction of diazo ketones with trialkylboranes thus appears to be fairly general and complements the recent,[6b] elegant methyl ketone synthesis involving four-carbon homologation.

The procedure is simple. A solution of olefin in tetrahydrofuran is treated with sufficient diborane in tetrahydrofuran to ensure complete conversion to the corresponding trialkylborane.[7] An equimolar quantity of diazo ketone in tetrahydrofuran is added. In the case of a tri-*n*-alkylborane a mildly exothermic reaction ensues with immediate evolution of nitrogen, whereas the reaction with a more sterically hindered organoborane requires a reflux period.[8] After hydrolysis the ketone is conveniently isolated by extraction and distillation.

It is immediately apparent that the more hindered organoboranes[8] give the lowest yields of homologated product (eq 4–6). Attempts to increase the yields by employing a large excess of diazo ketone or by addition of copper or copper salts[9] were unsuccessful.

(1) (a) J. J. Tufariello and L. T. C. Lee, *J. Am. Chem. Soc.*, **88**, 4757 (1966); (b) J. J. Tufariello, L. T. C. Lee, and P. Wojtkowski, *ibid.*, **89**, 6804 (1967), and references cited therein.

(2) (a) H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **90**, 818 (1968); (b) *ibid.*, **90**, 1911 (1968).

(3) The reactions of diazoalkanes with boron compounds have recently been reviewed by C. E. H. Bawn and A. Ledwith, *Progr. Boron Chem.*, 1, 345 (1964).

(4) These conditions[1,2] simplify isolation of the desired ketone by avoiding oxidation of boron-bound alkyl groups of the intermediate α-boryl ketone to the unhomologated alcohol.

(5) Yields are by glpc analysis and are the average values of three independent runs. Here, as in other examples of organoborane homologative functionalizations,[1,2,6] only one of the alkyl groups of R_3B is constructively consumed.

(6) (a) M. W. Rathke and H. C. Brown, *J. Am. Chem. Soc.*, **89**, 2740 (1967); (b) A. Suzuki, A. Arase, H. Matsumoto, M. Itoh, H. C. Brown, M. M. Rogić, and M. W. Rathke, *ibid.*, **89**, 5708 (1967); (c) H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **89**, 5709 (1967); (d) H. C. Brown, R. A. Coleman, and M. W. Rathke, *ibid.*, **90**, 499 (1968).

(7) (a) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962; (b) G. Zweifel and H. C. Brown, *Org. Reactions*, **13**, 1 (1963).

(8) Six hours of reflux was required for reactions with boranes derived from 1,1- and 1,2-disubstituted olefins and 3 hr of reflux for tricyclopentylborane before nitrogen evolution ceased.

(9) An example of a reaction of a carbene with a trialkylborane is provided by the recent study of D. Seyferth and B. Prokai, *J. Am. Chem. Soc.*, **88**, 1834 (1966).