from the thermal isomerization of cis-1,2-dideuterio-cyclopropane and is similar to the product proportions obtained from the addition of methylene to ethylene at high pressures,[8] and suggests that the trimethylene species is an intermediate in these reactions.

(8) B. S. Rabinovitch, E. Tschuikow-Roux, and E. W. Schlag, *J. Am. Chem. Soc.*, 81, 1083 (1959).
(9) National Research Council of Canada Scholarship holder, 1964–1965.

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Ozonides from Aldehydic Zwitterions and Acetone

Sir:

Recent reports[1-3] have confirmed the implication of the Criegee mechanism of ozonolysis[4] that unsymmetrical olefins should give three ozonide pairs. The formation of two zwitterion and two carbonyl fragments requires the observed results when recombination occurs in a random fashion (*e.g.*, see Figure 1). Earlier reports[5] that only a single ozonide is formed under these conditions were regarded as consistent with the over-all mechanism provided that one invoked the operation of a cage mechanism which prevented exchange of zwitterion and carbonyl fragments. The presence and extent of a cage mechanism and its influence on ozonide distribution has been discussed by Loan, Murray, and Story.[3]

The nature of the zwitterion and carbonyl fragments also influences ozonide formation. Thus, while aldehydes react easily with aldehydic zwitterions[5] and can be used to demonstrate the presence of ketonic zwitterions[6] in trapping experiments, it has been reported that *simple ketones do not react with zwitterions.*[5,7,8] This last conclusion appears to be based on the reported failure of tetramethylethylene to give an ozonide upon treatment with ozone.[6] The presence of ketonic zwitterions in this last ozonolysis was confirmed by a trapping experiment with formaldehyde to give isobutylene ozonide.[6] The failure of tetramethylethylene to give an ozonide could be due, however, to the relative nonreactivity of acetone toward a *ketonic zwitterion.* There has been no clear evidence that simple ketones, such as acetone, will not react with *aldehydic zwitterions.* There are a number of reports of reactions of activated, that is, negatively substituted ketones, with zwitterions, to give ozonides.[9] Also, *intramolecular*

(1) O. S. Privett and E. C. Nickell, *J. Am. Oil Chemists' Soc.*, 41, 72 (1964).
(2) G. Riezebos, J. C. Grimmelikhuysen, and D. A. Van Dorp, *Rec. trav. chim.*, 82, 1234 (1963).
(3) L. D. Loan, R. W. Murray, and P. R. Story, *J. Am. Chem. Soc.*, 87, 737 (1965).
(4) For a thorough discussion of the mechanism of ozonolysis see P. S. Bailey, *Chem. Rev.*, 58, 925 (1958).
(5) R. Criegee, *Record Chem. Progr.* (Kresgee-Hooker Sci. Lib.), 18, 111 (1957).
(6) R. Criegee, G. Blust, and H. Zinke, *Chem. Ber.*, 87, 766 (1954).
(7) G. Lohaus, *Ann.*, 583, 6 (1953).
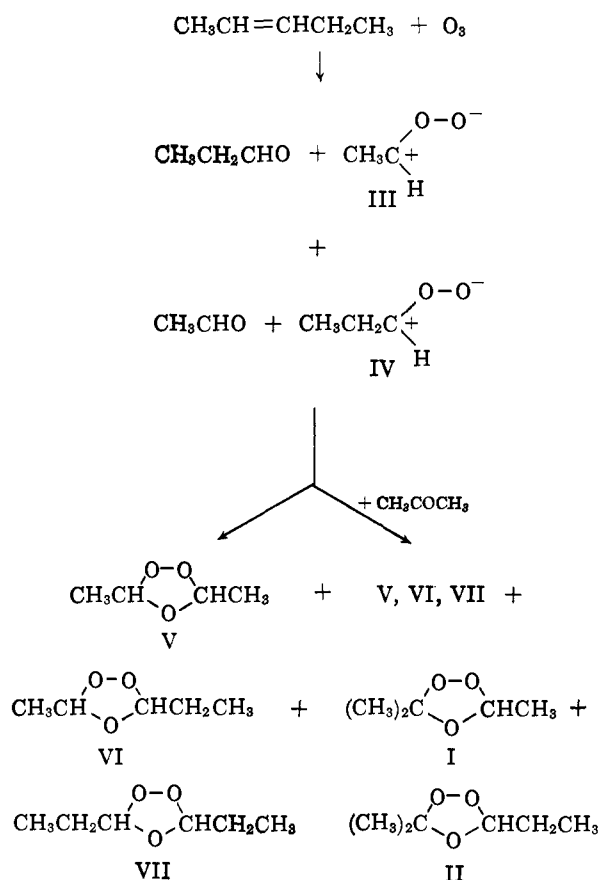(8) R. Huisgen, *Angew. Chem.*, 75, 604 (1963).

Figure 1.

reactions to give ozonides from simple ketones have been reported. For example, 1,2-dimethylcyclopentene gives a good yield of its normal ozonide.[10] These latter observations suggested to us that the long-standing view[5,9] that simple ketones do not react with zwitterions should be re-examined.

We wish to report the formation of ozonides from the reaction of acetone and aldehydic zwitterions. When pentene-2 is ozonized in the presence of excess acetone, the ozonides of 2-methylbutene-2 (I) and 2-methylpentene-2 (II) are produced, in addition to the previously reported[3] ozonides of butene-2, pentene-2, and hexene-3. It is proposed that ozonides I and II arise from the reaction of acetone with aldehydic zwitterions III and IV, respectively.

In a typical reaction 5 g. (71.4 mmoles) of pentene-2 in 50 g. of acetone was ozonized to 61.8% completion. The reaction mixture was analyzed by g.p.c. which showed the presence of two new peaks in addition to those previously shown to be due to the ozonides of butene-2, pentene-2, and hexene-3. The two new peaks were identified as the ozonides of 2-methylbutene-2 and 2-methylpentene-2 on the basis of chemical analysis (*Anal.* Found for I: C, 50.1; H, 7.99; O, 41.7.[11] Found for II: C, 54.5; H, 9.05; O, 36.4), infrared spectra (strong band at 1080–1110 cm.$^{-1}$, no OH or carbonyl), and n.m.r. spectra. The n.m.r.

(9) R. Criegee, S. S. Bath, and B. V. Bornhaupt, *Chem. Ber.*, 93, 2891 (1960).
(10) R. Criegee, P. de Bruyn, and G. Lohaus, *Ann.*, 583, 19 (1953).
(11) Because of the instability of the ozonide we were unable to obtain a completely satisfactory analysis. The analysis obtained is most consistent with the proposed structure, however.

spectrum of I had a quartet at 4.62,[12] a singlet at 8.51, and a doublet at 8.60, which partially overlapped the singlet. These absorptions are assigned to the methine, *gem*-dimethyl, and methyl protons, respectively, of 2-methylbutene-2 ozonide. The methyl:methine peak area ratio was 9.4:1. The spectrum of II has a triplet at 5.13, a multiplet at 8.56, a singlet at 8.83, and a triplet at 9.30. These are assigned to the methine, methylene, *gem*-dimethyl, and methyl protons, respectively, of 2-methylpentene-2 ozonide. The integrated areas were 1:8:3.16 for methine:*gem*-dimethyl plus methylene:methyl. Yields of the ozonides were 2.09, 2.22, 4.92, 2.0, and 2.06 mmoles, respectively, for the ozonides of butene-2, 2-methylbutene-2, pentene-2, 2-methylpentene-2, and hexene-3 (total yield of ozonides = 21.6%).

We are presently investigating the possibility of obtaining ozonides from the remaining unobserved zwitterion–carbonyl combination, that is, the reaction of ketonic zwitterions with simple ketones.

Acknowledgment. L. D. L. wishes to thank the Director of the Rubber and Plastics Research Association of Great Britain for a 1 year leave of absence, during which time this work was carried out.

(12) All n.m.r. results are reported as *τ*-values with tetramethylsilane as external standard.

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## An Elimination–Addition Route to Substituted Methylenecyclopropanes

Sir:

The observation that cyclopropenes are formed as intermediates in the base-induced β-elimination of halocyclopropanes[1] suggested a new, mechanistically simple approach to methylenecyclopropenes or, by the addition of appropriate nucleophiles, to certain interesting substituted methylenecyclopropanes.[2]

The reaction of 7,7-dichlorobicyclo[4.1.0]heptane (I) with potassium isopropoxide (1:5 mole ratio) in dimethyl sulfoxide (DMSO) at room temperature afforded a mixture of II and III in 0.7 and 72% yield, respectively. This ratio was found to be variable, almost at will, by changing the ratio of base to I. The proton at C-7 of II is observed in the n.m.r. spectrum at τ 6.76 ($J = 9.2$ c.p.s.). This coupling constant shows the two protons on the cyclopropane ring to be *cis*.[3,4] The *endo* C-7

(1) C. L. Osborn, T. C. Shields, B. A. Shoulders, J. F. Krause, H. V. Cortez, and P. D. Gardner, *J. Am. Chem. Soc.*, in press.
(2) For other approaches see R. F. Bleiholder and H. Shechter, *ibid.*, **86**, 5032 (1964), and references cited therein; A. S. Kende and P. T. Izzo, *ibid.*, **86**, 3587 (1964); P. S. Skell and L. D. Wescott, *ibid.*, **85**, 1023 (1963); A. C. Dey and M. C. Whiting, *Proc. Chem. Soc.*, 368 (1964); R. Breslow, J. Posner, and A. Krebs, *J. Am. Chem. Soc.*, **85**, 234 (1963); J. T. Gragson, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *ibid.*, **74**, 3344 (1952); W. M. Jones and R. S. Pyron, *ibid.*, **87**, 1608 (1965); A. S. Kende and P. T. Izzo, *ibid.*, **87**, 1609 (1965); W. M. Jones and R. S. Pyron, *Tetrahedron Letters*, 479 (1965). One example of an elimination–isomerization route to a methylenecyclopropane has been described by J. A. Carbon, W. B. Martin, and L. R. Swett, *J. Am. Chem. Soc.*, **80**, 1002 (1958).
(3) D. J. Patel, M. E. Howden, and J. D. Roberts, *ibid.*, **85**, 3218 (1963); K. B. Wiberg and B. J. Nist, *ibid.*, **85**, 2788 (1963).
(4) The methyls of the isopropyl group appear as two sets of doublets centered at *τ* 8.90 and 8.93 ($J = 6.5$ c.p.s.). A similar splitting pattern is observed in spectra of all isopropoxy compounds described. This

proton of III gives rise to a doublet centered at τ 9.6 ($J = 6.4$ c.p.s.). It is thus clear that potassium isopropoxide is playing the role of both base and nucleophile in this reaction. It is also apparent that the double bond of cyclopropenes, generated from dihalocyclopropanes by reaction with a strong base in the absence of a nucleophile, migrates to a position of greater stability outside of the three-membered ring[1] but that when a nucleophile is present a facile addition occurs.[5]
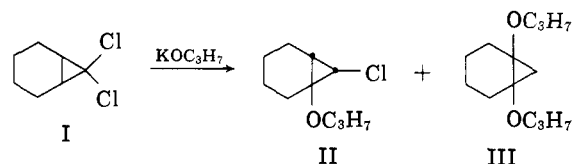
The reaction of *cis*-1,1-dichloro-2,3-dimethylcyclopropane (IV) with potassium isopropoxide (1:5) in DMSO at 30° afforded a mixture of V (31%) and VI (35%).[6] The n.m.r. spectrum of V exhibits multiplets at τ 4.45 and 4.62 for the two vinyl protons. The methyl signal appears as a singlet at τ 8.60.[4,7] The spectrum of VI possesses two multiplets (vinyl protons) at τ 4.44 and 4.56.[4,7] The proton on the ring carbon atom at which the isopropoxy group is attached gives
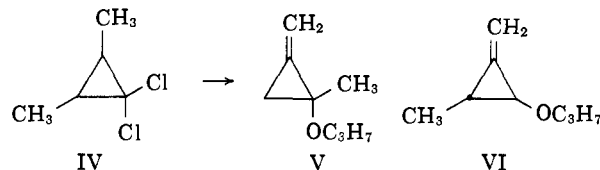
rise to a surprisingly sharp multiplet with half-width 4.5 c.p.s. This half-width suggests that the primary splitting due to coupling with the proton on the adjacent carbon has a small J value and that the two protons therefore bear a *trans* relationship.[3]

The observation that V and VI are the *only* products formed suggests that this reaction is sequentially quite different from the I → II + III conversion and that it very likely proceeds *via* 1-methyl-3-methylenecyclopropene. The relative amounts of V and VI formed reflect two opposing factors operative in the transition state. The relative stabilities of developing charge will favor V, but steric factors should favor VI. Thus, the two factors appear to be of nearly equal importance when the nucleophile is isopropoxide ion. It is noteworthy that the use of methoxide ion, a smaller nucleophile, afforded products analogous to V and VI in the ratio 2:1. It should also be noted that a sequence involving dehydrochlorination–addition–dehydrochlorination–double bond isomerization can be dismissed as it would, by analogy with the behavior of I, give only V as the product.[8]

increased multiplicity is undoubtedly a result of magnetic asymmetry at C-1. *Cf.* G. M. Whitesides, D. Holtz, and J. D. Roberts, *ibid.*, **86**, 2628 (1964), and references cited therein.
(5) The addition of *t*-butyl alcohol to ethyl 1-cyclopropenecarboxylate [K. B. Wiberg, R. K. Barnes, and J. Albin, *ibid.*, **79**, 4994 (1957)] was initially thought by us to be a formalistic Michael addition, but it now appears that the reaction is general for cyclopropenes.
(6) The mixture was flash distilled at 40°. Its subsequent separation and analysis was effected by preparative vapor–liquid chromatography using a 20-ft. cyanosilicone on Chromosorb P column at 70°. The use of higher temperatures induced partial rearrangement of VI. All compounds described gave satisfactory analytical and mass spectral data.
(7) Chemical shifts as well as multiplicities and relative areas of other signals are in agreement with the assigned structure.