

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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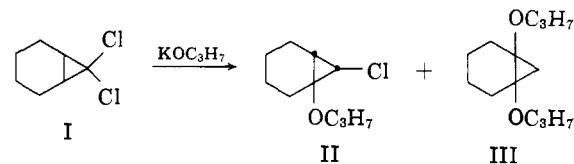
An Elimination-Addition Route to Substituted Methylene-cyclopropanes

Sir:

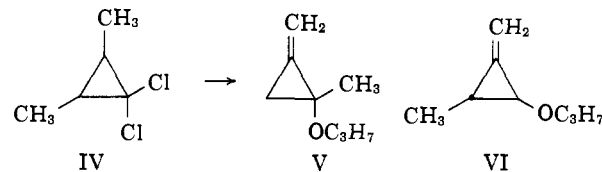
The observation that cyclopropenes are formed as intermediates in the base-induced β -elimination of halocyclopropanes¹ suggested a new, mechanistically simple approach to methylenecyclopropenes or, by the addition of appropriate nucleophiles, to certain interesting substituted methylenecyclopropenes.²

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

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 ring¹ 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 $I \rightarrow II + III$ 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.

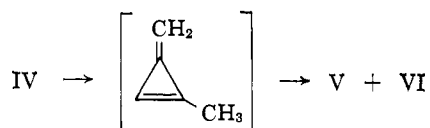
(7) Chemical shifts as well as multiplicities and relative areas of other signals are in agreement with the assigned structure.

(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.

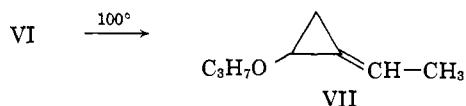
(2) For other approaches see R. F. Bleiholder and H. Shechter, *ibid.*, 86, 5032 (1964), and references cited therein; A. S. Kende and P. T. Izzo, *ibid.*, 86, 3587 (1964); P. S. Skell and L. D. Wescott, *ibid.*, 85, 1023 (1963); A. C. Dey and M. C. Whiting, *Proc. Chem. Soc.*, 368 (1964); R. Breslow, 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).

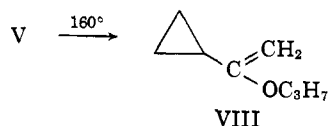
(4) The methyls of the isopropyl group appear as two sets of doublets centered at τ 8.90 and 8.93 ($J = 6.5$ c.p.s.). A similar splitting pattern is observed in spectra of all isopropoxy compounds described. This



The isomerization of VI proceeds smoothly below 100° to give VII as a mixture of *syn* and *anti* isomers.^{4,7,9}



The rearrangement of V requires temperatures of the order of 160° and affords a single product (VIII, 95%) *via* a transient intermediate detectable by vapor-liquid chromatography. The n.m.r. spectrum of VIII exhibits two sets of doublets centered at τ 6.13 and 6.32



($J = 1.9$ c.p.s., terminal methylene, two protons).⁷

The elimination-addition sequences described have been extended to several other substituted dichlorocyclopropanes with similar results. Nucleophiles examined thus far include isopropoxide ion, methoxide ion, and methylmercaptide ion. These studies as well as details regarding the thermal rearrangement of substituted methylenecyclopropanes will be described in the full paper.

(8) Another mechanism which warrants consideration is that involving initial formation of 1,3-dimethyl-3-isopropoxycyclopropane followed by an $\text{S}_{\text{N}}2'$ attack by isopropoxide and rearrangement to VI. Although the product ratios observed (methoxide *vs.* isopropoxide) are not in the order expected for such a sequence, it cannot be unequivocally ruled out on the basis of these data.

(9) This type of rearrangement has been studied with other methylenecyclopropanes at much higher temperatures: E. F. Ullman and W. J. Fanshaw, *J. Am. Chem. Soc.*, **83**, 2379 (1961); J. P. Chesick, *ibid.*, **85**, 2720 (1963).

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Zeeman Effect of the Nuclear Quadrupole Resonance of Chlorine-35 in 3,5- and 2,6-Dichloropyridine

Sir:

Working on single crystals of 3,5- and 2,6-dichloropyridine, we determined the so-called "zero-splitting" cones¹ corresponding to the C-Cl bonds and the asymmetry parameters of the relative electric field gradients at the chlorine nuclei: $\eta = (V_{XX} - V_{YY})/V_{ZZ}$.² The value of η often depends largely on the extent of π -bond character between the Cl atom and the atom to which it is bonded.

The measurements were made by using a super-regenerative spectrometer and a magnetic field generated by a coil capable of orienting around a vertical and a

(1) T. H. Das and P. L. Hahn, "Solid State Physics," Supplement 1, "Nuclear Quadrupole Resonance Spectroscopy," Academic Press Inc., New York, N. Y., 1958.

(2) We follow the Das-Hahn convention: $|V_{XX}| < |V_{YY}| < |V_{ZZ}|$.

horizontal axis, according to a technique which has been already described.³

The cones were first referred to a laboratory reference system, x, y, z (in the origin of which there was the crystal). Their principal axes, X, Y, Z , were then determined by calculating their eulerian angles with respect to the former system. From these, we determined the angles between the two C-Cl bonds existing in each of these molecules. The working temperature was $26 \pm 1^\circ$.

Some common features of these two substances are listed. In the single crystal there appear to be only two C-Cl directions. This means that the molecules lie in the crystal all parallel to the same plane and with the same direction, N-C₄. The X axes of the two cones are substantially parallel: the small angles resulting are probably within the limits of the experimental error in the orientation of the X and Y axes (about 2°). The two C-Cl bonds are then coplanar (or "quasi"-coplanar) and probably lie in the plane of the ring, while the X axes are perpendicular to it. Other results are collected in Table I.

Table I

	Dichloropyridine	
	3,5-	2,6-
Frequency, ^a Mc.p.s.	34.773	33.850
η	0.086 ± 0.002	0.118 ± 0.002
Angle between the two C-Cl bonds	$122^\circ 23' \pm 10'$	$113^\circ 50' \pm 10'$

^a Frequency measurements were made with a BC 221 frequency meter.

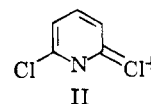
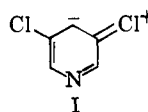
The directions of the C-Cl bonds were assumed, as usual, to be coincident with the directions of the Z axes of the zero-splitting cones. The obtained angles are slightly smaller than those given for the corresponding C-H directions in pyridine⁴: $124^\circ 8'$ and $114^\circ 46'$ for the 3,5- and 2,6-positions, respectively.

If we make the calculation concerning the double bond and the ionic character of the C-Cl bonds according to the approximate theory of C. H. Townes and B. P. Dailey,¹ we obtain the results shown in Table II

Table II

	Dichloropyridine	
	3,5-	2,6-
Double-bond character, %	3.72	5.05
Ionic character, %	18.3	19.3

The strong relative change of the π -bond character is probably due to the greater weight of the resonance structures of type II with respect to that of the structures of type I.



(3) (a) P. Bucci, P. Cecchi, and E. Scrocco, *Ric. Sci.*, **34** (IIA), 129 (1964); (b) P. Bucci and P. Cecchi, *ibid.*, **34** (IIA), 543 (1964).

(4) B. Bak, L. Hansen, and J. Rastrup-Andersen, *J. Chem. Phys.*, **22**, 2013 (1954).