

m.p. 185–190° (depressed by the oxime). Recrystallization gave nitrile with a constant m.p. of 179.5–180°, which did not depress the m.p. of an authentic sample¹⁴ and had an identical infrared spectrum (absorption at 2222 cm.⁻¹).

(b) Procedure B.—The aldoxime (0.05 mole) and nickel acetate tetrahydrate (0.90 g., 3.6 mmoles, 7 mol. %) were stirred in 150 ml. of xylene at the reflux temperature for 5 hr., after which the mixture was filtered while hot, if solid was present. The mixture then was cooled and amide which crystallized was removed. More catalyst (0.45 g.) was added to the filtrate and heating with stirring was continued

(14) J. S. Meek and J. R. Dann, *J. Am. Chem. Soc.*, **77**, 6677 (1955).

for 10 hours (sometimes it was convenient to remove amide after 5 hr. of this period). The mixture then was concentrated to ca. 50 ml. and amide which separated was removed. The combined crops ("Crude amide") were recrystallized.

(c) Procedure C.—A mixture of 0.12 mole of aldoxime and 1.80 g. (7.2 mmoles, 6 mol. %) of nickel acetate tetrahydrate in 150 ml. of water was heated at the reflux temperature for 5 hr. Solid which appeared on cooling was removed; the filtrate was heated for 17 hr. more and then was concentrated in stages until further crops of amide seemed unlikely. All crops then were combined and recrystallized if necessary.

[CONTRIBUTION No. 2646 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIF., AND THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY CAMBRIDGE 39, MASS.]

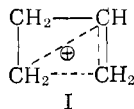
Small-Ring Compounds. XXXIII. A Study by Nuclear Magnetic Resonance of the Extent of Isotope-position Rearrangement in the Vapor-phase Photochlorination of *methyl*-¹³C-Cyclopropane¹

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RECEIVED DECEMBER 14, 1960

Vapor-phase photochlorination of *methyl*-¹³C-cyclopropane was found to yield cyclopropylcarbinyll-¹³C chloride and allyl-¹³C-carbinyll chloride. Within the experimental error of the analytical method (nuclear magnetic resonance spectroscopy), no other ¹³C-position isomers of the chlorides were formed.

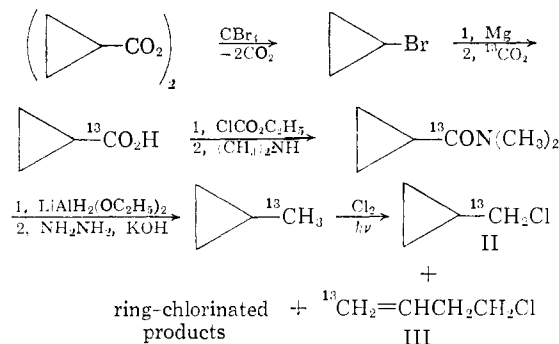
Very considerable isotope-position rearrangement attends carbonium ion-type reactions of isotopically labeled cyclopropylcarbinyll and cyclobutyl derivatives.³ These rearrangements seem best accounted for by assuming that rapidly equilibrating non-classical cationic intermediates are involved, such as I.^{3b-e}



It is of considerable theoretical and practical importance to know whether or not similar intermediates and rearrangements occur in the interconversion⁴ of cyclopropylcarbinyll and allylcarbinyll derivatives in reactions generally considered to proceed by way of free-radical and carbanion mechanisms. A typical free-radical reaction of interest in this connection is the vapor-phase photochlorination of methylcyclopropane, which yields roughly equal quantities of cyclopropylcarbinyll and allylcarbinyll chlorides along with lesser amounts of ring-chlorinated products.^{4a} Some preliminary results on the photochlorination of *methyl*-¹⁴C-cyclopropane⁵ indicated that the

cyclopropylcarbinyll and allylcarbinyll chlorides might have been formed with considerable shuffling of ¹⁴C. However, the work was very much hampered by the lack of a suitable method to locate ¹⁴C in cyclopropylcarbinyll chloride without incurring risk of additional isotope-position rearrangement. With the advent of n.m.r. spectroscopy, it has become possible to study isotope-position rearrangements in compounds of this type using ¹³C or ²H as tracers^{2c,4b} without need for chemical degradation. In the present study of the chlorination of methylcyclopropane, ¹³C was chosen as the tracer since the ²H might be expected to lead to large kinetic isotope effects on the chlorination reaction, which could seriously change the product ratios.

The reactions used and the results of this study follow.



The chlorination products were separated by preparative vapor-phase chromatography (v.p.c.) and the positions of the ¹³C determined by analysis of the effect of the ¹³C on the proton spectra (Fig. 1)

(5) Unpublished work by R. H. Mazur at the Massachusetts Institute of Technology, 1950–1951.

(1) Supported in part by the Office of Naval Research, the Petroleum Research Fund of the American Chemical Society, and the National Science Foundation. Grateful acknowledgment is hereby made to the donors of the Petroleum Research Fund.

(2) National Science Foundation Faculty Fellow, 1959–1960.

(3) (a) J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 3542 (1951); (b) R. H. Mazur, W. N. White, D. A. Semenov, C. C. Lee, M. S. Silver and J. D. Roberts, *ibid.*, **81**, 4390 (1959); (c) M. C. Caserio, W. H. Graham and J. D. Roberts, *Tetrahedron*, **11**, 171 (1960); (d) E. Renk and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 878 (1961); (e) E. F. Cox, M. C. Caserio, M. S. Silver and J. D. Roberts, *ibid.*, **83**, in press (1961).

(4) (a) J. D. Roberts and R. H. Mazur, *ibid.*, **73**, 2509 (1951); (b) M. S. Silver, P. R. Shafer, J. E. Nordlander, C. Ruchardt and J. D. Roberts, *ibid.*, **82**, 2646 (1960).

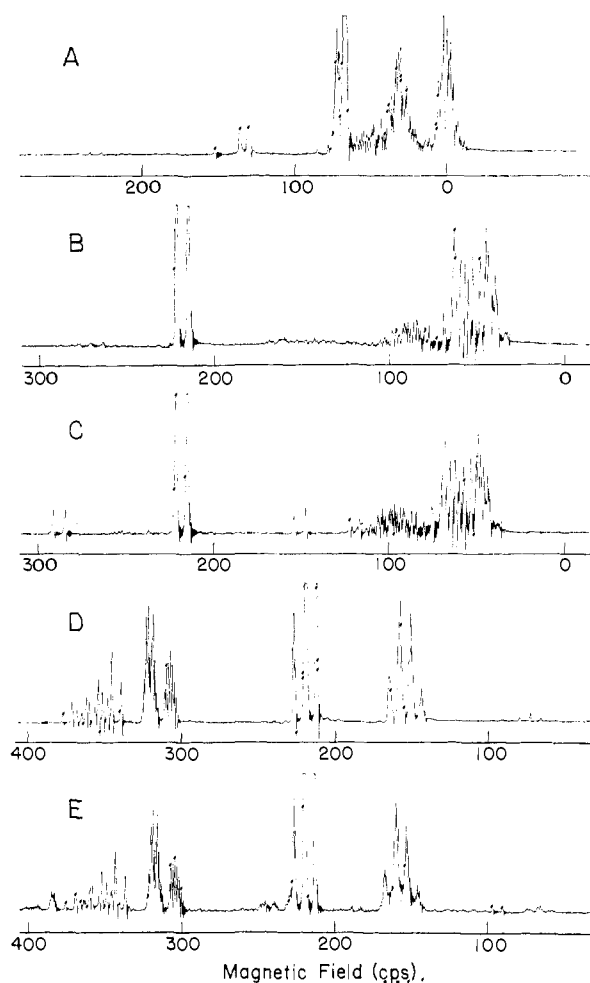


Fig. 1.—Nuclear magnetic resonance spectra at 60 Mc. with tetramethylsilane as external reference: A, methyl- ^{13}C -cyclopropane; B, cyclopropylcarbinyl chloride; C, cyclopropylcarbinyl- α - ^{13}C chloride from the chlorination of methyl- ^{13}C -cyclopropane; D, allylcarbinyl chloride; E, allylcarbinyl- γ - ^{13}C chloride from the chlorination of methyl- ^{13}C -cyclopropane (the weak resonances at 70–100 c.p.s. are due to contamination with a small amount of ring-chlorinated material and are not ^{13}C -satellites).

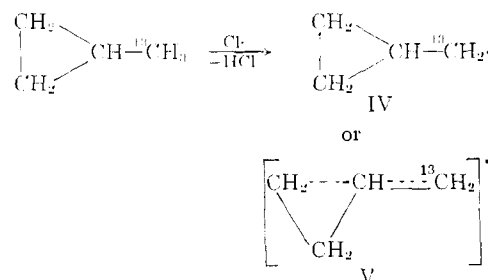
of the chlorides. The ^{13}C satellites⁶ shown by the proton spectra are those expected for the α -labeled chloride II and the γ -labeled chloride III. No evidence for other isotope-position isomers was found, although perhaps up to 5% might have gone undetected.

The lack of isotope-position rearrangement in this interconversion reaction and the conspicuous failure of cyclobutyl chloride to be formed³ argue against the intervention of a bicyclic, bridged radical with a structure analogous to I. This conclusion is in agreement with the predictions of simple molecular-orbital theory.⁷ At present, it is not possible to say whether or not the simple radical IV or a "homoallylic" radical V is formed by attack

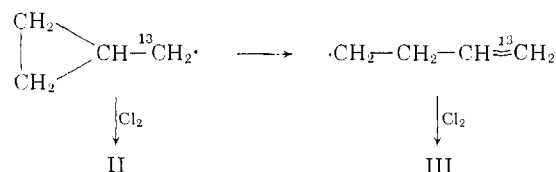
(6) A. D. Cohen, N. Sheppard and J. J. Turner, *Proc. Chem. Soc. (London)*, 118 (1958).

(7) (a) J. D. Roberts, Paper presented at the Sixteenth National Organic Chemistry Symposium, Seattle, Wash., June 15, 1959; (b) D. I. Schuster, Ph.D. Thesis, California Institute of Technology, 1960.

of a chlorine atom on a methyl hydrogen of methylcyclopropane.



The observed reaction products could result in the former case from ring opening of IV in competition with cyclopropylcarbinyl chloride formation. Thus



Alternatively, the radical could have the structure V and react with chlorine at either reactive end to give II and III. Further evidence on the nature of the radicals involved in this and related reactions will be presented in later papers.

Acknowledgments.—E. R. is indebted to Stiftung fuer Stipendien auf dem Gebiete der Chemie (Switzerland) for a grant in support of this work. Mr. Donald R. Davis rendered valuable help with the n.m.r. spectra.

Experimental

Cyclopropyl Bromide.⁸—A solution of 73 g. (0.22 mole) of carbon tetrabromide in 30 ml. of dry chlorobenzene in a three-necked flask, equipped with reflux condenser, dropping funnel and magnetic stirrer, was heated in an oil-bath at 130°. A solution of 10.0 g. (0.059 mole) of the peroxide of cyclopropanecarboxylic acid^{9a} in 30 ml. of chlorobenzene was then added over a 1-hour period at such a rate that smooth gas evolution took place. The resulting reaction mixture, combined with that from another run involving 63.4 g. of carbon tetrabromide and 15.8 g. of the peroxide, was distilled through a center-rod fractionating column and gave 15.8 g. (43%) of cyclopropyl bromide, b.p. 68–68.5°, with a purity higher than 99% as shown by v.p.c.

Cyclopropanecarboxylic-carboxyl- ^{13}C Acid.—Cyclopropyl bromide (6.0 g., 0.0496 mole) was converted to the Grignard reagent with 2.0 g. (0.083 mole) of magnesium turnings in 25 ml. of tetrahydrofuran and then carbonated in an evacuated system with carbon- ^{13}C dioxide generated from 8.5 g. (0.0427 mole) of barium carbonate- ^{13}C , containing 44.5% ^{13}C .⁹ The reaction mixture was decomposed with water, acidified with 4 N sulfuric acid, and, after combination with a second run of the same scale, continuously extracted with ether for 32 hr. The extract was concentrated at atmospheric pressure until the bath temperature reached 110°. Methylene chloride was added to the flask and the distillation continued until the distillate was clear. The residue distilled at 74–76° (8 mm.) and gave 6.1 g. (82% based on barium carbonate) of cyclopropanecarboxylic-carboxyl- ^{13}C acid.

N,N-Dimethylcyclopropanecarboxamide-carboxyl- ^{13}C .—To a stirred, ice-cooled solution of 10.0 g. (0.115 mole) of cyclopropanecarboxylic-carboxyl- ^{13}C acid and 10.0 g. of

(8) (a) H. Hart and D. P. Wyman, *J. Am. Chem. Soc.*, **81**, 4891 (1959); (b) J. D. Roberts and V. C. Chambers, *ibid.*, **73**, 3176 (1951).

(9) From Isomet Corporation, Palisade Park, New Jersey.

unlabeled acid in 200 ml. of dry chloroform was added 24.0 g. (0.238 mole) of triethylamine, followed by the addition of 24.0 g. (0.221 mole) of ethyl chlorocarbonate over a 10-min. period. The mixture was allowed to stand at room temperature for 1.5 hr. and then cooled in an ice-bath and about 40 ml. of anhydrous dimethylamine vaporized and bubbled in. After 17 hr. at room temperature, the greater part of the solvent was evaporated under reduced pressure, 20 ml. of water was added, and the aqueous phase was extracted six times with 50-ml. portions of chloroform. The combined chloroform extracts were dried over sodium sulfate and the solvent distilled at atmospheric pressure. The residue distilled at 102-105° (35 mm.) and gave 19.8 g. (75%) of *N,N*-dimethylcyclopropanecarboxamide-*carboxyl*-¹³C of a purity higher than 99%, as shown by v.p.c. Unlabeled carboxamide (1.5 g.) was added to the residue and distilled into the labeled material, giving a total of 21.1 g. of amide. The ¹³C content of the final product was calculated to be about 22%.

methyl-¹³C-Cyclopropane.—Lithium aluminum diethoxyhydride was prepared by adding a solution of 8.9 g. (0.10 mole) of ethyl acetate over a 1-hr. period to 100 ml. of a magnetically stirred, ice-cooled 1.0 *N* lithium aluminum hydride solution in ether. The resulting mixture was added to a stirred solution of 21.1 g. (0.186 mole) of *N,N*-dimethylcyclopropanecarboxamide-*carboxyl*-¹³C in 80 ml. of dry ether at 0° over 30 min. The mixture was stirred at room temperature for 30 min., then heated under reflux for 30 min., and finally ice-cooled and treated with 2 *N* sulfuric acid to decompose the aluminum complexes. The ether layer was separated and the aqueous suspension extracted eight times with 50-ml. portions of ether. The combined ether solutions were dried over sodium sulfate and concentrated by distilling the solvent through a 100-cm. Helipak column.¹⁰

The residue was cooled in ice, and 25 ml. of ethylene glycol and 20 ml. of 85% hydrazine hydrate were added. The mixture was allowed to stand at room temperature for 15 min., and a solution of 25 g. of potassium hydroxide in 125 ml. of ethylene glycol was then added. The flask was equipped with a magnetic stirring bar and connected to a 30-cm. semi-

(10) In a separate experiment it was found that 70% of cyclopropanecarboxaldehyde could be isolated from this concentrate as its semicarbazone; cf. H. C. Brown and A. Tsukamoto, *J. Am. Chem. Soc.*, **81**, 502 (1959).

micro column.¹¹ The mixture was stirred and heated in an oil-bath, the temperature of which was raised gradually to 160°. The distillate that collected to this point was discarded. A new receiver was then attached that was connected through a short reflux condenser to two traps cooled in Dry Ice-acetone. The bath temperature was raised over 30 min. up to 220° and kept at that temperature for 30 min. The liquid that condensed in the first trap was distilled through a calcium chloride tube into the second trap. Approximately 6 ml. of methyl-¹³C-cyclopropane was obtained, which was identified by its infrared spectrum. The n.m.r. spectrum of the product is shown in Fig. 1.

Photochlorination of methyl-¹³C-Cyclopropane.—Approximately 6 ml. of methyl-¹³C-cyclopropane was chlorinated in the apparatus described earlier.^{4a} The oil-bath surrounding the boiler was raised to 50° toward the end of the reaction, but there was still excess methylcyclopropane when the chlorination was stopped.¹² The chlorination products amounted to 4.0 g., which v.p.c. showed to be a complex mixture with cyclopropylcarbinyll-¹³C chloride and allylcarbinyll-¹³C chloride present in an approximate ratio of 65:35. No cyclobutyl chloride could be detected. Besides ring-chlorinated methylcyclopropane, considerable quantities of other products were present with longer retention times, probably polychlorinated products.

Cyclopropylcarbinyll and allylcarbinyll chlorides were separated from the crude chlorination product using a Perkin-Elmer vapor fractometer equipped with a preparative column A (diisodecyl phthalate) at 68° and employing helium as carrier gas at 5 p.s.i. About 0.35 ml. of allylcarbinyll-¹³C chloride and 0.6 ml. of cyclopropylcarbinyll-¹³C chloride were collected and sealed in n.m.r. tubes for analysis. The allylcarbinyll chloride so obtained was contaminated with perhaps 3% of *cis*- or *trans*-2-chloro-1-methylcyclopropane as evidenced by the slight high-field n.m.r. absorptions shown in Fig. 1.

(11) C. W. Gould, Jr., G. Holzman and C. Niemann, *Anal. Chem.*, **20**, 361 (1948).

(12) A marked decrease in yield of allylcarbinyll chloride was observed when attempts were made to complete the reaction, probably because of addition of chlorine to the double bond. Even when the reaction was not run to completion, v.p.c. showed that there were considerable variations in the ratio of the monochlorinated products in experiments at different chlorine flow rates.

[CONTRIBUTION FROM HICKRILL CHEMICAL RESEARCH LABORATORY, KATONAH, N. Y.]

Comparative Reactivity of Methylene, Carbomethoxycarbene and Bis-carboethoxycarbene toward the Saturated Carbon-Hydrogen Bond

BY W. VON E. DOERING¹ AND L. H. KNOX

RECEIVED NOVEMBER 4, 1960

The series of carbenes, CH₂, CHCOOCH₃ and C(COOC₂H₅)₂, reacts with the carbon-hydrogen bond with increasing discrimination in the sense 3° > 2° > 1°. The presence of carbalkoxy groups decreases the absolute reactivity of the carbene. The enhanced discrimination points to the contribution of polar structures in the transition state.

Insertion into the carbon-hydrogen bond is a novel reaction in the chemistry of carbenes. The firm establishment of a direct, single-step mechanism rests on labeling experiments in the reaction of the allylic carbon-hydrogen bond with methylene.² On the assumption that no intermediates are involved, the usual picture of a transition state incorporating the structural features of starting material and product is constructed.³⁻⁶ In such

(1) To whom inquiries may be directed: 1901-A Yale Station, New Haven, Conn.

(2) W. von E. Doering and H. Prinzbach, *Tetrahedron*, **6**, 24 (1959).

(3) J. Chanmugan and M. Burton, *J. Am. Chem. Soc.*, **78**, 509 (1956).

(4) W. von E. Doering and L. H. Knox, *ibid.*, **78**, 4947 (1956).

(5) P. S. Skell and R. C. Woodworth, *ibid.*, **78**, 4496 (1956).

(6) J. H. Knox and A. F. Trotman-Dickenson, *Chemistry & Industry*, 268 (1957).

a typically "no-mechanism" situation, where there are no catalysts to discuss, nor intermediates to define, the questions involve the hypothetical transition state. Has its geometry been correctly represented? Is it a useful working hypothesis by which to predict the effects of structural changes on rate?

In the insertion reaction the rates are so fast that structural changes make themselves felt as a change in degree of discrimination. Methylene itself reacts with the carbon-hydrogen bond without discrimination; that is, without being able to distinguish between different degrees of substitution.⁷ Analysis of the transition state along previous

(7) W. von E. Doering, R. G. Buttery, R. G. Laughlin and N. Chaudhuri, *J. Am. Chem. Soc.*, **78**, 3224 (1956).