tions, the mono-complex of the [4.4]- and [6.6]-cycles failed to eliminate carbon monoxide to give compounds of structure VII. Such a reaction would involve rotation of the complexed benzene ring through 180° about the axis of the bonds extending from its 1,4-position. Such rotation is possible in [4.4]paracyclophane itself,[9] but the additional bulk of a chromium atom attached to one face of the benzene ring would provide considerable steric resistance to such a rotation in the [4.4]-system, and possibly even in the [6.6]-cycle.

Ultraviolet absorption spectral data for the complexes are recorded in Table I. These spectra exhibit a single $\lambda_{\max}$ in the region from 317 to 343 mμ. The open-chain compounds absorb at the shortest wave lengths (317-318), the larger paracyclophanes (m = 12, $m = n = 4$ and larger) at slightly longer, and the smaller paracyclophanes at the longest wave lengths. In general, the smaller the values of m and n, the greater the bathochromic shift, which reaches a maximum when $m = n = 2$. This effect is attributed to transannular electronic interactions as well as to distortions of the benzene rings from their normally planar configurations.

The infrared spectra of a few of the complexes were examined. Mono-complexes exhibit strong bands at 1876-1881 and 1963-1967 cm.$^{-1}$, and a weak band at 2900 cm.$^{-1}$ (chloroform solution), and an additional strong band at 1842-1856 cm.$^{-1}$ (potassium bromide disk). Bis-complexes have similar spectra, with an additional weak band at 3400 cm.$^{-1}$ (potassium bromide disk).

Experimental

General Procedure for Preparation of Paracyclophane and Model Tricarbonylchromium Complexes.—The hydrocarbon (0.001 mole) was dissolved in purified diethylene glycol dimethyl ether (10 ml.) and hexacarbonylchromium (0.0011 mole) was added. The solution was held at reflux for 3 hr. (bath temperature, 170–175°). Reagent which sublimed into the condenser was returned periodically to the solution with a glass rod. The solution was cooled, diluted with an equal volume of water, and filtered. The complex was separated from inorganic chromium by extraction of the solid with methylene chloride. In many cases filtration was not convenient, and the mixture was extracted several times with methylene chloride. The extract was evaporated under reduced pressure, and finally dried as a film on a rotatory drier at 0.05 mm. and 40–50° to remove diethylene glycol dimethyl ether.

The crude complex was dissolved in benzene or pentane–ether (3 to 1) and chromatographed on neutral, activity I alumina. Elution of the column with the same solvent removed first unchanged hydrocarbon, and then the mono-complex. In the two cases in which bis-complexes were formed, these were eluted with benzene–methanol (10 to 1). The complexes were recrystallized from the solvents indicated in Table I as rapidly as possible, and were stored at 0° or lower.

Use of 2 to 1 molar ratios of hexacarbonylchromium to hydrocarbon did not affect the character of product or yield to any extent. With [2.2.2]paracyclophane, a 4 to 1 molar ratio was used, but only the mono-complex could be isolated.

Pyrolysis of Paracyclophane Tricarbonylchromium Complexes.—The tricarbonylchromium complex of [4.4]paracyclophane (0.088 g.) was heated under nitrogen to 300° for 5 minutes and cooled. Chromatography on alumina of the residue yielded 0.024 g. of [4.4]paracyclophane, m.p. 145–146°, undepressed by admixture with an authentic sample. No other product was isolated. When heated to 180° under nitrogen for 5 minutes, the complex underwent no change and was recovered.

The tricarbonylchromium complex of [6.6]paracyclophane (0.040 g.) was heated to 180° under nitrogen for 5 minutes, cooled, and the residue was recrystallized from pentane to give 0.034 g. of starting material, m.p. 117–118°, undepressed by admixture with an authentic sample.

Similar pyrolyses of other complexes gave back either starting material or the parent hydrocarbon.

Attempted Decarbonylations of [4.4]Paracyclophane Tricarbonylchromium Complexes.—(a) A solution of 0.055 g. of complex and 0.050 g. of triphenylphosphine in 20 ml. of benzene was heated at reflux for 4 hours. The cooled solution was chromatographed on alumina to give 0.020 g. of unchanged complex and 0.010 g. of [4.4]paracyclophane.

(b) A mixture of complex (0.120 g.) and aluminum trichloride (0.039 g.) in 1 ml. of methylene chloride was cooled at 0° for 10 minutes. Ice was added to the solution, the layers were separated, and the aqueous extract was washed with methylene chloride. From the organic phase was isolated 0.018 g. of starting complex and 0.035 g. of [4.4]-paracyclophane.

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[9] D. J. Cram, R. J. Wechter and R. W. Kierstead, This Journal, **80**, 3126 (1958).

[Contribution from the George Herbert Jones Laboratory, the University of Chicago, Chicago 37, Ill.]

Carbenes from Alkyl Halides and Organolithium Compounds. I. Synthesis of Chlorocyclopropanes[1]

By Gerhard L. Closs and Liselotte E. Closs

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Alkyllithium compounds react with methylene chloride in the presence of olefins to form chlorocyclopropanes. This reaction is believed to proceed through the intermediate chlorocarbene. Seven alkyl-substituted chlorocyclopropanes have been prepared by this method. Configurations are assigned to the products by considerations of predictible non-bonded interactions in the transition states of the addition of chlorocarbene to the olefins. The configurations are confirmed by n.m.r. spectra.

Introduction

The chemistry of dihalocarbenes (dihalomethylenes) has been rather intensively investigated over the past decade. After Hine[2] demonstrated by kinetic methods that the alkaline hydrolysis of chloroform proceeds through dichloromethylene, many more reactions have been reported in which this intermediate has been postulated. Thus the reaction of haloforms with potassium *t*-butoxide leads to the formation of these divalent carbon species[3] as does the decarbalkoxylation of alkyl

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[1] Reported in part in a preliminary communication to the editor, G. L. Closs and L. E. Closs, This Journal, **81**, 4996 (1959).

[2] J. Hine, *ibid.*, **72**, 2438 (1950).

[3] W. v. E. Doering and A. K. Hoffmann, *ibid.*, **76**, 6162 (1954).

trichloroacetates[4] and decarboxylation of sodium trichloroacetate.[5] Recently the halogen–metal exchange reaction[6] of alkyllithium compounds with polyhalomethanes has been employed to generate dichloro- and dibromocarbene.[7] Dihalocarbenes as unstable molecules will undergo further reactions with suitable substrates in solution. Doering and Hoffmann demonstrated, in 1954, that dihalocarbenes add to olefins with formation of 1,1-dihalocyclopropanes.[3] In subsequent papers it was shown that dihalocarbenes react as electrophiles in these additions, and bond formation to both carbon atoms occurs simultaneously.[8–11] This reaction has been used as a convenient method to trap carbenes and has also served as a criterion for the intermediate formation of divalent carbon species.[4,5,7,12,13]

Methylene appears to be much more reactive than its dihalogen derivatives. Cyclopropane formation by *cis* addition of methylene to olefins does occur[11,14]; however, attack at carbon–hydrogen bonds yielding the corresponding homologous hydrocarbons is observed as a major side reaction. This insertion which dihalocarbenes do not undergo is a reaction of low discrimination and follows a nearly statistical pattern.[14] The difference in reactivity between dihalocarbene and methylene can be explained on the basis of resonance stabilization[8,15] of the former. However, the reactivity of the two species is not strictly comparable since dihalocarbenes are usually prepared by low-temperature base-catalyzed elimination methods whereas methylene is generated by photolytic reactions. It therefore seemed of interest to prepare monohalocarbenes and to study their reactivities and reactions. If halogen substitution on methylene stabilizes the molecule, monohalocarbenes should be more reactive in electrophilic additions than dihalocarbenes. Furthermore, monohalocarbenes promised to serve as synthetic tools leading to compounds otherwise difficult to prepare. It is the purpose of this paper to report the synthesis of monochlorocarbene and its addition to olefins, resulting in a convenient method for the preparation of chlorocyclopropanes.[16]

Chlorocyclopropane Synthesis.—Elimination of hydrogen chloride from methylene chloride appeared to be the most attractive route leading to the desired chlorocarbene. Two main difficulties could be foreseen. The removal of a proton from methylene chloride will be more difficult than from chloroform because of the diminished acidifying effect of two chlorine atoms *versus* three. Furthermore, an SN2 displacement reaction by the base on methylene chloride may be fast enough to compete successfully with the elimination.[17] Therefore a base of high basicity toward hydrogen but of low nucleophilicity toward a saturated carbon atom should be used in the attempted reaction. Alkyllithium compounds appeared to be promising reagents because they are known to be extremely strong bases, but do not displace halogen from saturated carbon atoms very readily. Olefins were chosen as trapping reagents because the resulting chlorocyclopropanes can be easily identified.

To test the suitability of alkyllithium compounds for the synthesis of carbenes, the formation of the known dichlorocarbene from chloroform was tried. When a solution of *n*-butyllithium was added to chloroform in cyclohexene at −70°, 7,7-dichlorobicyclo[4.1.0]heptane could be isolated in 19% yield.

The feasibility of the reaction having been demonstrated by this result, *n*-butyllithium was then added to a solution of methylene chloride and an excess of cyclohexene at −35 to −40°.[18,19] Immediate reaction took place as evidenced by the precipitation of lithium chloride. From the reaction mixture a compound $C_7H_{11}Cl$ was isolated in 31% yield and was shown to be 7-chloro-[4.1.0]bicycloheptane (I) by the following evidence: both infrared and nuclear magnetic resonance (n.m.r.) spectra provide no evidence for unsaturation. The presence of hydrogen stretching vibrations at 2990 and 3030 cm.$^{-1}$ suggested strongly a cyclopropane structure. On reduction with sodium and alcohol or, better, with sodium in liquid ammonia, compound I was converted to norcarane (II) in 82% yield. From the boiling behavior of I it was evident that more than one isomer has been produced. Vapor phase chromatography (v.p.c.) revealed the presence of two compounds in a ratio 3.2:1. The reduction to pure norcarane (II) in 82% yield and the absence of any other compound in the reduction mixture proves that the two compounds must be epimeric at the chlorine-bearing carbon atom.

Table I lists six other chlorocyclopropanes obtained from the appropriate olefins by the same method. The structures of these compounds are evident from their analyses and infrared[20] and n.m.r.

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(4) W. E. Parham and E. E. Schweizer, *J. Org. Chem.*, **24**, 1733 (1959).

(5) W. M. Wagner, *Proc. Chem. Soc.*, 229 (1959).

(6) For a general review on this reaction see: R. G. Jones and H. Gilman, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 339.

(7) W. T. Miller and Chung Sul Youn Kim, THIS JOURNAL, **81**, 5009 (1959).

(8) P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956).

(9) W. v. E. Doering and Wm. A. Henderson, Jr., *ibid.*, **80**, 5274 (1958).

(10) P. S. Skell and A. Y. Garner, *ibid.*, **78**, 3409 (1956).

(11) W. v. E. Doering and P. LaFlamme, *ibid.*, **78**, 5447 (1956).

(12) H. D. Hartzler, *ibid.*, **81**, 2024 (1959).

(13) R. M. Etter, H. S. Skovronek and P. S. Skell, *ibid.*, **81**, 1008 (1959); P. S. Skell and J. Klebe, *ibid.*, **82**, 247 (1960).

(14) W. v. E. Doering, R. G. Buttery, R. G. Laughlin and N. Chaudhuri, *ibid.*, **78**, 3224 (1956); W. v. E. Doering and H. Prinzbach, *Tetrahedron*, **6**, 24 (1959).

(15) J. Hine and S. J. Ehrenson, THIS JOURNAL, **80**, 824 (1958).

(16) After this work had been completed and published in part, M. E. Volpin, D. N. Kursanov and V. G. Dulova, *Tetrahedron*, **8**, 33 (1960), described the formation of monochlorocarbene from methylene chloride and potassium *t*-butoxide and its addition to benzene in poor yield.

(17) For the influence of halogen atoms on the SN2 reactivity of other halogen atoms attached to the same carbon atom see: J. Hine, C. H. Thomas and S. J. Ehrenson, THIS JOURNAL, **77**, 3886 (1955); J. Hine, S. J. Ehrenson and W. H. Brader, *ibid.*, **78**, 2282 (1956).

(18) Inverse addition produces only traces of I because of the reaction of chlorocarbene with butyllithium, favored under these conditions; G. L. Closs, in preparation.

(19) The reaction can be controlled better at these temperatures than at the originally reported −25°.[1]

(20) The allegedly characteristic band for cyclopropanes, near 1020 cm.$^{-1}$ (L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 29,

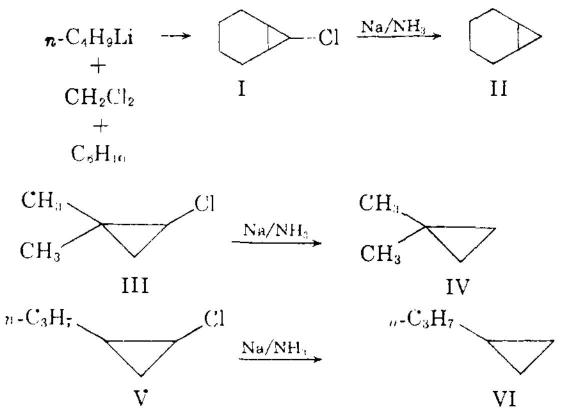
TABLE I

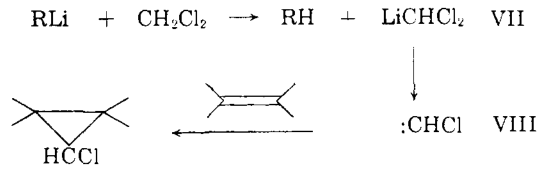
REACTIONS OF OLEFINS WITH METHYLENE CHLORIDE AND ALKYLLITHIUM COMPOUNDS[a]

Olefin	Product	Isomer ratio[b]	Yield, %
2,3-Dimethylbutene-2	1-Chloro-2,2,3,3-tetramethylcyclopropane		67
2-Methylbutene-2	1-Chloro-2,2,3-trimethylcyclopropane	1.6	50
Isobutylene	1-Chloro-2,2-dimethylcyclopropane		44 (50[c])
trans-Butene-2	1-Chloro-2,3-*trans*-dimethylcyclopropane		32 (40[d])
cis-Butene-2	1-Chloro-2,3-*cis*-dimethylcyclopropane	5.5	30
Cyclohexene	7-Chlorobicyclo[4.1.0]heptane	3.2	25 (31,[e] 48[f])
Pentene-1	1-Chloro-2-*n*-propylcyclopropane	3.4 (1.8[g])	10 (25[c])

[a] 3 moles of olefin and 2 moles of methylene chloride per mole of *n*-butyllithium at −35° to −40°. [b] Determined by v.p.c. assuming same thermoconductivity for both isomers. [c] Using methyllithium. [d] 5 moles of olefin. [e] 4 moles of olefin. [f] Methyllithium with 6 moles of olefin. [g] At 30°, using methyllithium.

spectra (*vide infra*). Yields increased with increasing number of alkyl substituents attached to the double bond. When methyllithium is substituted for butyllithium slightly higher yields are usually obtained and more convenient reaction temperatures are permissible (about 30°). Also, larger excesses of olefins produced increases in yields. To demonstrate the generality of the reduction method, 1-chloro-2,2-dimethylcyclopropane (III) and 1-chloro-2-*n*-propylcyclopropane (V) were both reduced with sodium and liquid ammonia in excellent yields to 1,1-dimethylcyclopropane (IV) and *n*-propylcyclopropane (VI), respectively. In the latter case again only one compound was obtained from a mixture of stereoisomeric chlorocyclopropanes.



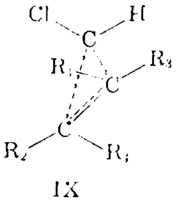


(1)

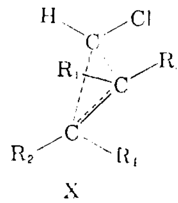
The formation of chlorocyclopropanes from methylene chloride, alkyllithium compounds and olefins provides strong evidence for the realization of reaction sequence 1. The existence of dichloromethyllithium (VII) as precursor to chlorocarbene (VIII) appears likely in view of the observed finite lifetime of trichloromethide ion.[2] Loss of chloride ion from VII can be expected to occur more slowly than from the corresponding trichloro derivative since further introduction of halogen atoms on the same carbon atom should accelerate dissociation.[21] Attempts to trap intermediate VII by carboxylation at −70° failed, indicating a relatively short lifetime for this species. The observed increase in yields of chlorocyclopropanes with increasing alkyl substitution of the olefin is indicative of electrophilic addition and supports the hypothesis of the intermediate existence of chlorocarbene. Careful analysis of the reaction mixture by v.p.c. gave no evidence for the formation of any products arising from insertion of the chlorocarbene into a carbon–hydrogen bond.

Steric Course of the Chlorocyclopropane Synthesis.—In line with expectations, the reaction of chlorocarbene with olefins was shown to result in pure *cis* addition. Thus, the cyclopropanes produced by additions to *cis*- and *trans*-butene-2 were uncontaminated by each other within the limits of detection of v.p.c. (<1%). *trans*-Butene-2 gave a single product only, whereas two isomers were obtained from *cis*-butene-2, a finding demonstrating the retention of the geometrical relationship of the methyl groups through addition. In all cases in which the olefin lacks a center of symmetry the two expected isomers have been found. The predominant isomer always had the higher boiling point as shown by fractional distillation and v.p.c. analysis of the fractions. They also showed the longer retention times in the vapor phase chromatograms. Although no complete separation of any pair of isomers has been carried out on a preparative scale, the ratios of the isomers were easily determined by v.p.c. and are listed in Table I.

Tentative assignments of configurations to the stereoisomeric products can be made on the basis of predictable non-bonded interactions in the transition states. The two possible transition states for the addition of chlorocarbene to an unsymmetrical olefin may be represented as in IX and X. Because the steric requirement of chlo-



IX



X

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proved to be unreliable in these compounds. A strong band between 1030 and 1010 cm.$^{-1}$ is found only in some of the compounds [entry 1, 4, 6 (one isomer only)]; the other compounds show bands in the vicinity, but outside of this region. For other examples of the unreliability of this band for identification of cyclopropane structures see, *e.g.*, C. F. H. Allen, T. J. Davis, W. J. Humphlett and D. W. Stewart, *J. Org. Chem.*, **22**, 1291 (1957).

(21) For the effect of halogen atoms on the SN1 reactivity of other halogen atoms attached to the same carbon atom see: J. Hine and D. E. Lee, THIS JOURNAL, **73**, 22 (1951).

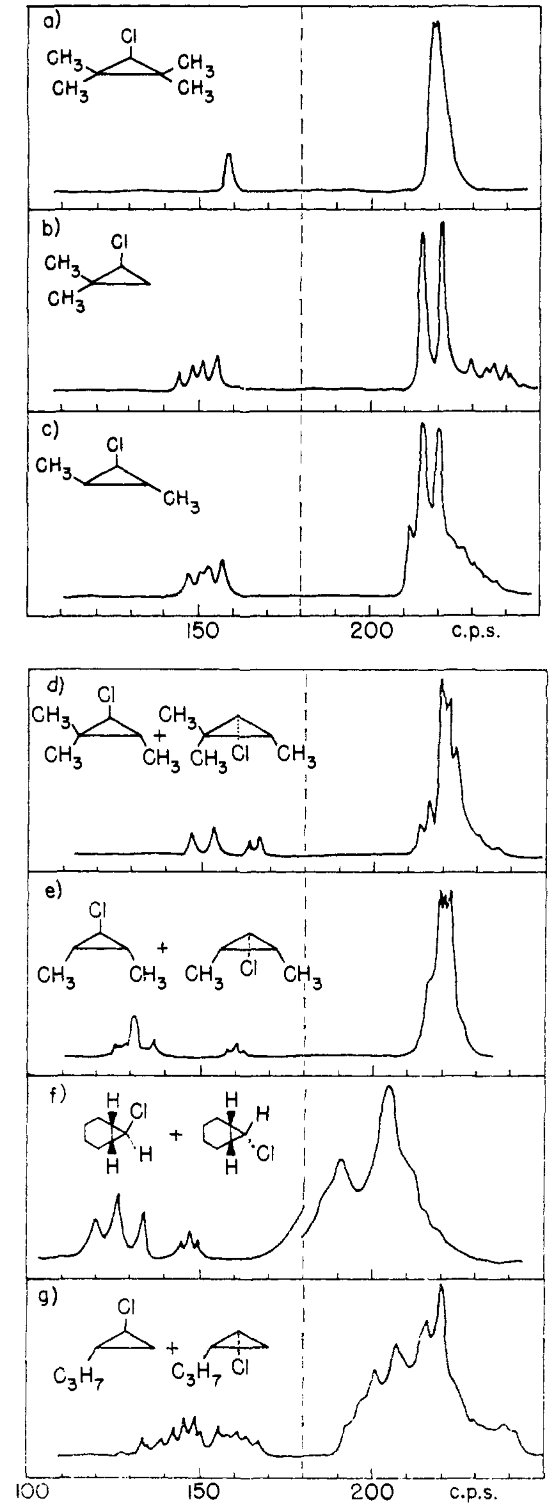

Fig. 1.—n.m.r. spectra of chlorocyclopropanes. The spectra were measured in 30% carbon tetrachloride solutions. Chemical shifts are relative to external benzene at 40 mc. Line intensities are enlarged twofold below 180 c.p.s. Isomer ratios in mixtures d–f are as reported in Table I; for g 1.6.

rine is large compared to hydrogen, non-bonded interactions between chlorine and the groups located on the same side of the incipient cyclopropane ring will mainly determine the difference in stabilities of the two transition states. If the combined steric requirements of R_1 and R_2 are smaller than those of R_3 and R_4, transition state IX will be more stable than X and the product resulting from it will predominate. The greater the difference in the steric requirements of the substituents on the separate sides of the double bond the larger will be the product ratio. From Table I it can be seen that this consideration predicts the observed results: *cis*-butene-2 gives the largest isomer ratio (5.5) which is caused by the difference in bulk of two methyl groups *versus* two hydrogen atoms. A smaller ratio (1.6) is observed for 2-methylbutene-2 in which the net difference in steric requirements on the separate sides of the double bond derives from one methyl group. The addition to pentene-1 results in an intermediate ratio (3.4), which is caused by the steric influence of an alkyl group somewhat larger than methyl. A relatively low ratio is found for the addition to cyclohexene (3.2) compared to the similarly substituted *cis*-butene-2 (5.5). It should be pointed out that the steric requirements of the substituents of the olefin are not the sole determining factor in the isomer ratio.

Steric factors being constant, a larger ratio will be observed for a less nucleophilic, slower-reacting olefin than for a highly reactive one. This may contribute to the relatively large ratio found for the addition to pentene-1, an olefin with low reactivity. Naturally, increase in reaction temperature decreases the isomer ratio as can be seen for the addition to pentene-1 at the two temperatures, −35° and 30°, resulting in the ratios 3.4 and 1.8, respectively.

From these considerations, the *trans configuration must be assigned to the predominant isomer*[22] (*trans* being used for the configuration in which chlorine is *trans* to the larger number of alkyl substituents on the cyclopropane ring). This assignment is strongly confirmed by the n.m.r. spectra of the isomeric mixtures.

N.m.r. Spectra.—Figure 1 shows the n.m.r. spectra of the chlorocyclopropanes; a–c are spectra of single compounds and d–g are of mixtures of the two isomers as obtained from the reaction. At high field are found the resonance lines of the alkyl protons partially overlapping with the resonances of the ring protons at carbon 2 and 3 which occur at still higher field. The chlorocyclopropanes having methyl groups directly attached to the ring show splitting patterns for these methyl protons to be expected for coupling with the adjacent ring protons. Considerable distortions in intensities of the components of the doublets can be observed due to the fact that the difference in chemical shift of the coupled protons approaches J. More useful information in regard to the stereochemistry can be obtained from the fine structure of the signal caused

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[22] If one applies the usually observed correlation of boiling point and dipole moment for rigid geometrical isomers (von Auwers–Skita rule) to the alkyl chlorocyclopropanes, one finds that the *trans* isomers should have the larger dipole moments. This is in line with expectations if one considers the cyclopropyl carbon the negative end of the cyclopropyl–alkyl bond moment, an assumption which seems justified because of the increased *s* character in the hybridization of the cyclopropyl carbon atom.

by the proton at carbon atom 1, which is less shielded because of the chlorine atom bonded to the same carbon. These signals are found between 120 and 170 c.p.s. (relative to external benzene, at 40 mc.). Chlorotetramethylcyclopropane (a) shows only one line in this region owing to the lack of any protons on the adjacent carbon atoms.[23] Both the 1-chloro-2,2-dimethylcyclopropane (b) and the 1-chloro-2,3-*trans*-dimethylcyclopropane (c) show splitting patterns as to be expected for an ABX system, where X is the proton at carbon atom 1, coupled differently to two non-equivalent ring protons at positions 2, and 2 and 3, respectively. Coupling constants for b were found to be 7 and 4 c.p.s. and for c 6.5 and 3.5 c.p.s.

Spin coupling constants for vicinal protons show a strong angular dependence with a maximum for bond angles of 180°.[24a] Whereas in six- and five-membered rings the *cis* protons in *eclipsed* conformations are more strongly coupled than the *trans* hydrogens,[25] the increased bond angle of the *trans* protons in four-membered rings increase their coupling to the point where both coupling constants are identical.[24b] In three-membered ring systems *trans* coupling should outweigh *cis* coupling, since further increase in bond angle between the vicinal *trans* protons will enhance the former and increased internuclear distance of the *cis*-hydrogens tends to weaken the latter.[24c]

On the basis of these considerations the *larger* coupling constants in b and c (7 and 6.5 c.p.s.) must be assigned to interactions between the proton at carbon atom 1 and the adjacent *trans* proton.[26,27] This assignment can be used to determine the stereochemistry of the isomers in the mixtures d to g; the spectrum of the mixture of the isomeric 1-chloro-2,2,3-trimethylcyclopropanes (d) shows two doublets between 147 and 167 c.p.s. That each doublet is caused by one isomer was confirmed by changing the ratio of the isomers by fractional distillation, which resulted in a proportional change in the integrated intensities of these signals. The more intense doublet at lower field (147, 153 c.p.s.) must originate from the isomer having the proton at position 3 *trans* to the proton at carbon atom 1 because its spacing is twice as large as that in the less intense doublet at 164 and 167 c.p.s. Similarly, spectra e and f show two triplets each, caused by the proton at position 1 coupled to two equivalent protons at carbon atoms 2 and 3. In both cases the more intense triplet, originating from the predominant isomer, is found at lower field and has the larger spacing (7 *versus* 3 c.p.s.), therefore again indicating a *trans* relationship of the coupled protons. The spectrum of the two isomeric 1-chloro-2-*n*-propylcyclopropanes is less conclusive because of the complicated splitting pattern (ABCX) for the signal from the proton at carbon atom 1. The multiplets of the two isomers are partially overlapping and the assignment of the lines to the isomers is ambiguous.

The n.m.r. spectra therefore give strong evidence that the predominant isomers formed in the reaction of chlorocarbene with unsymmetrical olefins have the *trans* configuration (*trans* used in the sense as defined above), thus confirming the conclusions drawn from the model for the transition state of the reaction.

Experimental

General.—All reactions were carried out under nitrogen. *n*-Butyllithium and methyllithium solutions were prepared by conventional procedures from the corresponding alkyl chloride or bromides in diethyl ether. The normalities of these reagents were kept between 1.2 and 1.6. Reagent grade methylene chloride was used without further purification. The purities of the olefins used is stated under the individual compounds. The final purifications of the chlorocyclopropanes were accompanied by fractionation over a 3-ft. column containing a tantalum spiral. Reflux to take-off ratios were kept at 20:1. The boiling points are uncorrected.

The v.p.c. chromatograms were obtained on a Fisher Gulf Partitioner equipped with integrator. A 12-ft. column was used, charged with 30% TCP on firebrick. The chromatograms were run at temperatures between 65 and 140° with helium flow rates between 50 and 90 ml./min.

The infrared spectra were recorded on a Perkin-Elmer model 21 spectrometer equipped with rock salt optics. The n.m.r. spectra were measured at 40 mc. with a Varian high-resolution spectrometer model V-4300 B with super-stabilizer. The compounds were measured without solvents. Chemical shifts were obtained by the usual side-band technique and are reported relative to benzene in an external annulus (Zimmerman tubes).

7,7-Dichlorobicyclo[4,1,0]heptane.—To a rapidly stirred solution of cyclohexene (25 g. 0.3 mole) and chloroform (24 g., 0.2 mole) was added *n*-butyllithium (0.1 mole) in diethyl ether at −70° over a period of 45 minutes. The reaction mixture was allowed to warm up to room temperature and hydrolyzed with ice-water. The organic layer was separated, dried and fractionated. The product was collected at 87–89°(15 mm.)(3.1 g., 0.019 mole, 19%). The infrared spectrum of the compound was compared with the spectrum of 7,7-dichlorobicyclo[4.1.0]heptane, prepared by a known method[3] and was found to be identical.

Preparation of Chlorocyclopropanes (General Procedures). a. Using *n*-Butyllithium.—The reaction is conveniently carried out in a three-neck flask equipped with stirrer, nitrogen inlet and addition funnel; 3 to 5 times the calculated amount of olefin and 2 molar excess of methylene chloride are to be used for maximum yields. The dropwise addition of *n*-butyllithium is carried out at −35 to −40° over a period of 60 to 90 minutes. Efficient stirring and slow addition are essential for good yields. The mixture is then hydrolyzed, the organic layer separated, washed and dried. The ether and excess olefin is distilled off and the product fractionated at a suitable pressure.

b. Using Methyllithium.—The procedure is equivalent to procedure a only higher temperatures are allowed for the addition of methyllithium. On reactions with low boiling olefins reflux temperature (Dry Ice condenser) gives good results whereas temperatures of 25 to 30° are desirable for higher boiling olefins. Products resulting from this method are usually purer than the compounds obtained by procedure a, because fewer impurities are introduced by methyllithium compared with butyllithium.

7-Chlorobicyclo[4.1.0]heptane.—Cyclohexene (33 g., 0.4 mole; peroxides removed and freshly distilled before use),

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(23) Coupling to protons more than one carbon atom removed appears to occur. The coupling is very weak, however, and the hyperfine structure cannot be resolved by the equipment used and appear as line-broadening effect.

(24) (a) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 194; (b) *e.g.*, β-propiolactone, see p. 146. (c) For the effect of internuclear distance in the coupling of *eclipsed cis* protons see: p. 195.

(25) Private communication, H. Conroy.

(26) The coupling constant for the *trans*-hydrogens in *trans*-tribenzoylcyclopropane was found to be 6.0 c.p.s., in good agreement with the values obtained for the chlorocyclopropanes. The n.m.r. spectrum of tribenzoylcyclopropane was reported by J. N. Shoolery, *Svensk Kem. Tidsr.*, **69**, 185 (1957). To obtain the coupling constant the spectrum of the substance has been remeasured.

(27) The larger coupling constant in the n.m.r. spectrum of styrene oxide has also been assigned to coupling between the *trans* ring protons; J. D. Roberts, "Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 48.

17 g. (0.2 mole) of methylene chloride and 0.1 mole of *n*-butyllithium gave 4.0 g. (0.031 mole, 31%) of 7-chlorobicyclo[4.1.0]heptane, b.p. 94–97° (70 mm.). Procedure b gave 6.3 g. (0.048 mole, 48%) of product from 49 g. (0.6 mole) of cyclohexene, 17 g. (0.2 mole) of methylene chloride and 0.1 mole of methyllithium at 25°.

Anal. Calcd. for $C_7H_{11}Cl$ (130.62): C, 64.36; H, 8.49; Cl, 27.14. Found: C, 64.28; H, 8.39; Cl, 26.94.

1-Chloro-2,2,3,3-tetramethylcyclopropane.—2,3-Dimethylbutene-2 (25 g., 0.3 mole, distilled immediately before use), 17 g. (0.2 mole) of methylene chloride and 0.1 mole of *n*-butyllithium gave 8.8 g. (0.067 mole, 67%) of 1-chloro-2,2,3,-3-tetramethylcyclopropane, b.p. 72.0 (105 mm.), n^{20}_{D} 1.4458.

Anal. Calcd. for $C_7H_{13}Cl$ (132.62): C, 63.39; H, 9.88; Cl, 26.73. Found: C, 63.22; H, 9.86; Cl, 26.50.

1-Chloro-2,2,3-trimethylcyclopropane.—2-Methylbutene-2 (21 g., 0.3 mole, Matheson Coleman and Bell, 99%, used without further purification), 17 g. of methylene chloride and 0.1 mole of *n*-butyllithium gave 5.9 g. (0.050 mole 50%) of 1-chloro-2,2,3-trimethylcyclopropane, b.p. 110–112°.

Anal. Calcd. for $C_6H_{11}Cl$ (118.61): C, 60.75; H, 9.35; Cl, 29.89. Found: C, 60.51; H, 9.29; Cl, 29.95.

1-Chloro-2,2-dimethylcyclopropane.—Isobutylene (17 g., 0.3 mole, Matheson "pure grade," used without further purification), 17 g. (0.2 mole) of methylene chloride and 0.1 mole of *n*-butyllithium gave 4.6 g. (0.044 mole, 44%) of 1-chloro-2,2-dimethylcyclopropane, b.p. 85.5°, n^{20}_{D} 1.4201. Procedure b gave 5.2 g. (0.050 mole, 50%) of product from 17 g. (0.3 mole) of isobutylene, 17 g. (0.2 mole) of methylene chloride and 0.1 mole methyllithium at reflux temperature.

Anal. Calcd. for C_5H_9Cl (104.58): C, 57.42; H, 8.68; Cl, 33.90. Found: C, 57.30; H, 8.77; Cl, 33.83.

1-Chloro-2,3-*trans*-dimethylcyclopropane.—*trans*-Butene-2 (17 g., 0.3 mole Philips Hydrocarbons, "research grade") 17 g. (0.2 mole) of methylene chloride and 0.1 mole of *n*-butyllithium gave 3.3 g. (0.032 mole, 32%) of 1-chloro-2,3-*trans*-dimethylcyclopropane, b.p. 91.3°, n^{20}_{D} 1.4286; 28 g. (0.5 mole) of *trans*-butene-2, 17 g. of methylene chloride and 0.1 mole of *n*-butyllithium gave 4.2 g. (0.040 mole, 40%) of product.

Anal. Calcd. for C_5H_9Cl (104.58): C, 57.42; H, 8.68; Cl, 33.90. Found: C, 57.13; H, 8.87; Cl, 33.84.

1-Chloro-2,3-*cis*-dimethylcyclopropane.—*cis*-Butene-2 (17 g., 0.3 mole; Philips Hydrocarbons, "pure grade," used without further purification), 17 g. (0.2 mole) of methylene chloride and 0.1 mole of *n*-butyllithium gave 3.1 g. (0.030 mole, 30%) of 1-chloro-2,3-*cis*-dimethylcyclopropane, b.p. 100–102°.

Anal. Calcd. for C_5H_9Cl (104.58): C, 57.42; H, 8.68; Cl, 33.90. Found: C, 57.75; H, 8.96; Cl, 33.30.

1-Chloro-*n*-propylcyclopropane.—Pentene-1 (42 g., 0.6 mole, Matheson, Coleman and Bell, "pure grade," distilled immediately before use), 34 g. (0.4 mole) of methylene chloride and 0.2 mole of methyllithium at 25–30° gave 5.9 g. (0.050 mole, 25%) of 1-chloro-*n*-propylcyclopropane, b.p. 124–127°. Procedure a gave 3.0 g. (0.025 mole, 10%) of product, b.p. 122–127°, from 52 g. (0.75 mole) of pentene-1, 42 g. (0.50 mole) of methylene chloride and 0.25 mole of *n*-butyllithium.

Anal. Calcd. for $C_6H_{11}Cl$ (118.61): C, 60.75; H, 9.35; Cl, 29.89. Found: C, 60.71; H, 9.20; Cl, 29.49.

Bicyclo[4.1.0]heptane. a. Reduction with Sodium and Methanol.—7-Chlorobicyclo[4.1.0]heptane (2.62 g., 20 mmoles) was dissolved in ether (20 ml.) and sodium (2.3 g., 100 mmoles) was added in small pieces. Then was added methanol (15 ml.) containing 5% water and the mixture was stirred at room temperature until all the sodium was dissolved (10 hours). The reaction mixture was washed with water, the organic layer separated and dried. The solvent was distilled off and the residue distilled. The product was collected at 116–118° (1.12 g., 12 mmoles, 60%). The infrared spectrum of the compound was compared with a spectrum of bicyclo[4.1.0]heptane obtained by an authentic procedure,[3] and was found to be identical. From the distillation residue unchanged starting material (0.65 g., 5 mmoles) was recovered.

B. Reduction with Sodium in Liquid Ammonia.—7-Chlorobicyclo[4.1.0]heptane (4.71 g., 36 mmoles) in ether (20 ml.) was added to sodium (2.0 g.) in ammonia (60 ml.). After 30 minutes stirring ammonium chloride (2.0 g.) was added and the ammonia allowed to evaporate. The residue was washed with ether several times and the combined organic washings were distilled over a short Vigreux column. The product was collected between 115.5 and 116° (2.95 g.), n^{20}_{D} 1.4552); v.p.c. analysis of the product showed it to be 96% pure (82% yield of pure bicyclo[4.1.0]heptane).

***n*-Propylcyclopropane.**—1-Chloro-2-*n*-propylcyclopropane (6.0 g., 51 mmoles) in ether (30 ml.) was added slowly to a solution of sodium (3.0 g.) in ammonia (100 ml.). The solution was stirred at the boiling point of ammonia for 30 minutes and then was neutralized with ammonium chloride (4 g.). The ammonia was distilled into a trap containing water. The distillation residue and the aqueous ammonia solution were both extracted with ether. The combined ether layers were washed, dried and the ether distilled off over a 3-ft. spiral column. The product was collected at 68–69°, n^{20}_{D} 1.3945 (3.7 g., 44 mmoles, 86%; reported[28] properties of *n*-propylcyclopropane: b.p. 68.5°, n^{18}_{D} 1.3957).

1,1-Dimethylcyclopropane.—1-Chloro-2,2-dimethylcyclopropane (7.3 g., 70 mmoles) was added to sodium (3.5 g.) in ammonia (100 ml.). After stirring for 30 minutes the solution was neutralized with ammonium chloride (5 g.) and allowed to warm up. The escaping gas containing ammonia and the product was swept with nitrogen through a series of 3 traps. The first two traps were filled with water and dilute sulfuric acid, respectively; the third trap was cooled to −70° to collect the product. The product was obtained by distillation from the third trap *into a cooled receiver* (4.3 g., 61 mmoles, 87%); b.p. 20°, n^{15}_{D} 1.3705; reported b.p.[29] 21°, n^{17}_{D} 1.3687.

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