Stereochemistry and Reactivities of Carbenoids from Benzal Chloride. Salt Effects in Carbenoid Reactions[1,2]

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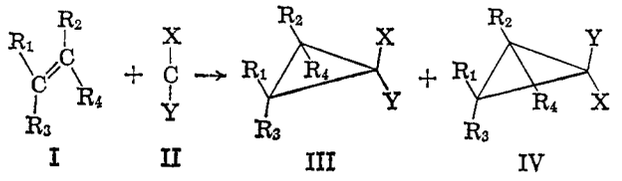
The configurations of cyclopropanes obtained from benzal chloride, potassium *t*-butoxide, and olefins have been determined. It was found that the reaction of benzal chloride, methyllithium, and olefins leads, in addition to 1-phenyl-1-chlorocyclopropanes, to varying proportions of 1-phenyl-1-methylcyclopropanes. Product ratios were shown to be strongly dependent on the nucleophilicities of olefin substrates and on the nature of halide ions present in solution. The results are explained in terms of a reaction scheme involving α,α-dichlorobenzyllithium as the key intermediate which may either lose lithium chloride, react with methyllithium, add to olefin, or react with halide ion. Competition among the various reagents for the intermediates qualitatively explains the product distribution.

Phenylchlorocarbene has been postulated as intermediate in reactions of benzal chloride with strong bases. Adducts of the hypothetical carbene to double bonds have been obtained by McElvain and Weyna using potassium *t*-butoxide,[4] and by Moss[5] using methyllithium as bases. Furthermore, the reaction has proved useful in the synthesis of various cyclopropenyl cations.[6] Our interest in this system originated in connection with the general problem of stereochemical preference of carbene additions. Unsymmetrically substituted methylene derivatives can add to olefins lacking both a center of symmetry and a symmetry plane coincident with the π-orbital plane, in two different ways to give a pair of epimeric cyclopropanes (I + II → III and IV). Since the stereochemistry of both chlorocarbene and phenylcarbene additions are known,[7-10] it appeared of interest to examine a system



containing both substituents. A second goal of this study was to determine whether cyclopropane formation from benzal chloride involves the intermediacy of a free carbene, or whether the reaction is better described by invoking a complexed methylene in which the formal valency of the central carbon atom is greater than two. The term carbenoid has previously been suggested to describe intermediates belonging in the latter category.[9]

Results

The reaction of benzal chloride with potassium *t*-butoxide in excess olefin gave 1-phenyl-1-chlorocyclopropanes in yields ranging from 50 to 90%. With low boiling olefins such as butenes the reaction was run in sealed tubes because attack of *t*-butoxide on benzal chloride is inconveniently slow at temperatures below 60°. The products were found to be stable under the conditions of their formation. Pairs of epimeric adducts were obtained from *cis*-2-butene, 2-methyl-2-butene, 1-butene, and cyclohexene. Separation of the isomers by gas–liquid partition chromatography (glpc) was only possible with the 1-butene adducts. Partial decomposition occurred on attempted glpc separations of the other isomer pairs. It was possible, however, to determine the isomer ratios by nuclear magnetic resonance (nmr) analysis of the product mixture. The configurations of the isomers will be designated by the prefix *syn* and *anti*, referring to the geometrical relationship between the phenyl substituent and the larger number of alkyl groups. Configurational assignments were carried out by nmr using a method which has proved to be very successful in the assignments of the corresponding phenylcyclopropanes.[9]

As has been shown in detail previously,[9] the magnetic shielding of methyl protons attached to a cyclopropane ring *cis* to a vicinal phenyl substituent is significantly larger than that of a corresponding *trans*-methyl group. Furthermore, on an absolute scale, the resonance signal of a *cis*-methyl group is shifted upfield from a position it would occur in a cyclopropane equally substituted but without a phenyl substituent. This observation is readily explained on the basis of conformational analysis combined with the well-known anisotropic long-range shielding effects associated with the phenyl ring system.[9,11,12] The chemical shifts of the methyl protons of various 1-phenyl-1-chlorocyclopropanes prepared in this study are listed in Table I. The difference in chemical shifts of the two methyl groups in 1-phenyl-1-chloro-2,2-dimethylcyclopropane is 0.67 ppm while the corresponding values for 1-phenyl-2,2-dimethylcyclopropane was found to be 0.43 ppm.[9] Introduction of a chlorine atom, therefore, appears to amplify the effect of the phenyl ring, which is in agree-

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(2) This paper is taken from the Ph.D. thesis submitted by J. J. C. to the Department of Chemistry, The University of Chicago, 1965.

(3) A. P. Sloan Foundation Fellow, 1962–1966.

(4) S. M. McElvain and P. L. Weyna, *J. Am. Chem. Soc.*, **81**, 2586 (1959).

(5) R. A. Moss, *J. Org. Chem.*, **27**, 2683 (1962).

(6) R. Breslow and H. W. Chang, *J. Am. Chem. Soc.*, **83**, 2367 (1961); R. Breslow, J. Lockhart, and H. W. Chang, *ibid.*, **83**, 2375 (1961); A. S. Kende, *ibid.*, **85**, 1882 (1963).

(7) G. L. Closs and L. E. Closs, *ibid.*, **82**, 5723 (1960).

(8) G. L. Closs, R. A. Moss, and J. J. Coyle, *ibid.*, **84**, 4985 (1962).

(9) G. L. Closs and R. A. Moss, *ibid.*, **86**, 4042 (1964).

(10) G. L. Closs and J. J. Coyle, *ibid.*, **87**, 4270 (1965).

(11) *Cf.* C. E. Johnson, Jr., and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

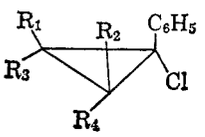
(12) G. L. Closs and H. B. Klinger, *J. Am. Chem. Soc.*, **87**, 3265 (1965).

(13) Comparison of the data in Table I with those of Table I in ref 9 shows that the chemical shift differences between *cis*- and *trans*-methyl groups in the various 1-phenyl-1-chlorocyclopropanes is approximately 1.6 times as large as the corresponding differences in the phenylcyclopropane series. This proportionality of relative chemical shifts in the two series supports the view that the anisotropy of the carbon–chlorine bond is responsible for the increased chemical shift differences in chlorophenylcyclopropanes and that the conformations of the phenyl rings are very similar in both series.

ment with theoretical predictions based on the magnetic anisotropy of the carbon–chlorine bond.[13] The difference of the chemical shifts of the *cis*- and *trans*-methyl groups in 1-phenyl-1-chlorotetramethylcyclopropane is reduced to 0.34 ppm. Conformational considerations provide an explanation for this observation. While the conformation with a minimum of nonbonded interactions for the dimethyl derivative is presumably the one in which the phenyl ring plane is normal to the plane described by C-1, C-2, and the *cis*-methyl carbon, minimization of nonbonded interactions in the tetramethyl derivative leads to a conformation in which a symmetry plane bisects both the phenyl and cyclopropane ring. These conformations place the *cis*-methyl group of the dimethyl derivative into the maximum shielding region of the phenyl ring, whereas the *cis*-methyl protons of the tetramethyl derivative are somewhat outside of the maximum diamagnetic zone. Similarly, the two epimeric 1-phenyl-1-chloro-*cis*-2,3-dimethylcyclopropanes show a difference of 0.3 ppm for the chemical shifts of their methyl protons, which have the same geometrical relationship as the *cis*- and *trans*-methyl groups in the tetramethyl derivative.

TABLE I

CHEMICAL SHIFTS OF METHYL PROTONS IN 1-PHENYL-1-CHLOROCYCLOPROPANES[a,b]



Starting olefin	R_1	R_2	R_3	R_4
2,3-Dimethyl-2-butene	8.97	8.97	8.63	8.63
2-Methyl-2-butene				
syn isomer	9.07	9.0 (m)	8.50	...
anti isomer	9.10	...	8.74	8.7 (m)
Isobutene	9.17	...	8.50	...
trans-2-Butene	9.2 (m)	...	...	8.6 (m)
cis-2-Butene				
syn isomer	9.1 (m)	9.1 (m)	...	...
anti isomer	...	...	8.8 (m)	8.8 (m)

[a] Measured in carbon tetrachloride solution with tetramethylsilane as internal reference; chemical shifts are in τ units. [b] When methyl proton signals occur as multiplets due to spin–spin splittings, the center of the signal is taken as the chemical shift. This is indicated by (m) following the chemical shift value.

On the basis of these arguments the stereochemistry of the geometrical isomers can be assigned as indicated in Table I. The strength of the arguments is considerably enhanced by the strict analogy of the chemical shift differences to those observed for the corresponding phenylcyclopropanes.[9] In the latter cases the configurational assignments were confirmed by independent methods such as equilibration of the isomers and independent stereospecific synthesis.

In Table II are listed the *anti/syn* isomer ratios of the cyclopropanes as obtained from additions to several olefins. It can be seen that formation of the *anti* isomers, in which the chlorine is located *cis* to the largest number of alkyl groups is favored. A similar observation was made by Hodgkins and co-workers who reported the same over-all stereochemical result in the addition of phenylchlorocarbene to cyclohexene.[14] Their configurational assignment was made on the basis of isomer distributions of 7-phenylnorcaranes obtained upon reduction of a mixture containing the isomeric phenylchloronorcaranes with a variety of reducing agents, assuming predominant retention of configuration of the phenyl group in the reduction process. This procedure, of course, required configurational assignment of the isomeric 7-phenylnorcaranes. The interpretation of the physical data of the 7-phenylnorcaranes, however, led to an assignment which did not agree with the general properties of *syn*- and *anti*-phenylalkylcyclopropanes as previously established in our laboratory.[9] Consequently, the configurations of the 7-phenylnorcaranes were investigated.

TABLE II

ISOMER RATIOS OF PHENYLCHLOROCYCLOPROPANES OBTAINED FROM THE REACTIONS OF BENZAL CHLORIDE, POTASSIUM *t*-BUTOXIDE, AND OLEFINS[a]

Olefin substrate	Ratio (*anti/syn*)
2-Methyl-2-butene	1.5
cis-2-Butene	3.0
Cyclohexene	2.0
1-Butene	1.7

[a] Reaction temperature held between 60 and 75°.

The reaction of benzal bromide with methyllithium in cyclohexene produced the two 7-phenylnorcaranes in a 3/1 ratio, and separation was easily accomplished by glpc.[15] The physical constants, relative glpc retention times, and spectral data of both isomers were in complete agreement with those reported. However, the predominantly formed isomer to which Hodgkins, *et al.*, have assigned the *anti* structure has in fact the *syn* configuration as is evident from the nmr and ultraviolet spectra and from equilibration experiments. Thus, the broad, unresolved multiplet originating from the methylene protons extends to a significantly higher field in the nmr spectrum of the major isomer (τ 8.0–9.5) than the corresponding signals of its epimer (τ 7.9–8.9). While the phenyl protons give a relatively narrow (half-width ~2 cps) signal in the spectrum of the former compound, a complex multiplet extends over 40 cps with its center displaced to higher field in the spectrum of the latter. As has been shown previously,[9,11] phenylcyclopropanes lacking a substituent *cis* to the phenyl ring show increased shielding of the *ortho* protons because the phenyl group can assume the conformation of maximum conjugation with the cyclopropane ring exposing the *ortho* protons fully to the shielding effect of the three-membered ring system. For steric reasons this conformation is very unfavorable in the *syn* isomer and the chemical shifts of *ortho*, *meta*, and *para* protons are very much alike. The ultraviolet spectrum bears out this relationship between conformation and conjugation by exhibiting an increase in intensity and batho-

(14) J. E. Hodgkins, J. D. Woodyard, and D. L. Stephenson, *J. Am. Chem. Soc.*, **86**, 4080 (1964).

(15) Photolysis of phenyldiazomethane in cyclohexene produces the isomeric phenylnorcaranes in a ratio of 1.1/1 in favor of the *syn* isomer.

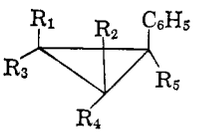
chromic shifts of the transitions of the minor isomer.[16] Finally, the most convincing evidence for the proposed new assignment is the almost complete conversion upon treatment with potassium *t*-butoxide in dimethyl sulfoxide of the predominantly formed into the minor isomer, while the latter remains almost unchanged under the same conditions. Since there can be little doubt that nonbonded interactions are significantly more severe in the *syn* structure, these experiments confirm the configurational assignment.

Configurational assignment of the two isomeric 7-phenyl-7-chloronorcaranes on the basis of their nmr spectra is more difficult because differences in the chemical shifts of the methylene protons in the two isomers are less distinct. Similarly, the chemical shifts of the *ortho* protons show a smaller dependence on the conformation than in 7-phenylnorcarane. The latter observation is predictable from consideration of the anisotropy of the carbon–chlorine bond, which counteracts the increased shielding resulting from the cyclopropane ring. Therefore, the assignment of the *anti* configuration to the predominant isomer must be regarded as tentative and is mostly supported by analogy to the reaction with *cis*-2-butene.[17]

An unusual result was obtained when excess methyllithium in ether was employed as base in the benzal chloride–olefin reaction. Not only were the expected 1-phenyl-1-chlorocyclopropanes isolated[5] but also substantial quantities of 1-phenyl-1-methylcyclopropanes. The latter products were separated and purified by glpc and identified by their characteristic nmr spectra, confirmatory infrared spectra, and elemental analysis. The influence of the phenyl ring on the chemical shifts of the vicinal alkyl groups was again used to make stereochemical assignments. The chemical shifts of the methyl groups of various 1-phenyl-1-methylcyclopropanes are listed in Table III. As side products, styrene and cumene were identified by comparison with authentic samples. The combined yields of cyclopropanes ranged from 65 to 90% while in no case more than 3% styrene or cumene was formed. Furthermore, it was found that the ratio of 1-phenyl-1-chlorocyclopropanes/1-phenyl-1-methylcyclopropanes was strongly dependent on the kind of halide ion present in the methyllithium solution. When methyllithium was prepared from methyl chloride and consequently contained chloride ion, the reaction mixture showed larger proportions of phenylchlorocyclopropanes, while this ratio was shifted in favor of the phenylmethyl derivative when iodide ion was present from the preparation of methyllithium from methyl iodide. Methyllithium solutions containing bromide ion gave intermediate results. The ratios of the two types of cyclopropanes were also found to be a function of the substitution pattern of the olefins employed as substrates. The more highly substituted olefins led to higher proportions of the phenylchloro derivatives. Table IV summarizes the product and isomer ratios obtained in these reactions.

TABLE III

CHEMICAL SHIFTS OF METHYL PROTONS IN 1-PHENYL-1-METHYLCYCLOLOPROPANES[a,b]

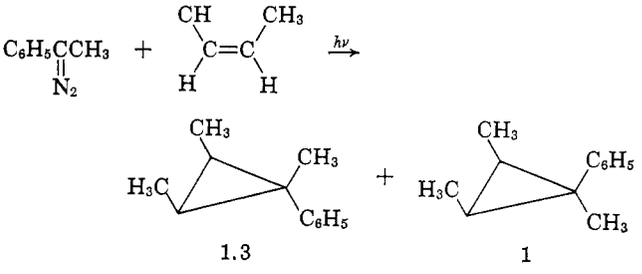


Starting olefin	R_1	R_2	R_3	R_4	R_5
2,3-Dimethyl-2-butene	9.09	9.09	8.85	8.85	8.77
Isobutene	9.28	...	8.62	...	8.72
trans-2-Butene	9.3 (m)	...	...	8.8 (m)	8.69
cis-2-Butene					
syn isomer	9.1 (m)	9.1 (m)	...	...	8.73
anti isomer	...	...	8.9 (m)	8.9 (m)	8.81

[a] Measured in carbon tetrachloride solution with tetramethylsilane as internal reference; chemical shifts are in τ units. [b] When methyl proton signals occur as multiplets due to spin–spin splittings, the center of the signal is taken as the chemical shift This is indicated by (m) following the chemical shift value.

The 1-phenyl-1-methylcyclopropanes were shown not to arise from a diplacement process by methyllithium on the 1-phenyl-1-chlorocyclopropanes by treating 1-phenyl-1-chloro-2,2-dimethylcyclopropane with methyllithium. No 1-phenyl-1,2,2-trimethylcyclopropane resulted.

Since the formation of 1-phenyl-1-methylcyclopropanes could conceivably result from the addition of phenylmethylcarbene to the olefin, it was of interest to generate this species independently by photolysis of 1-phenyldiazoethane. In the presence of isobutene this photolysis gave 42% 1-phenyl-1,2,2-trimethylcyclopropane together with 19% styrene. When *cis*-2-butene was used as substrate *syn*- and *anti*-1-phenyl-1-methyl-*cis*-2,3-dimethylcyclopropanes resulted in 34% yield with the *anti* isomer predominating 1.3/1.



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Discussion

The stereochemical aspects of carbenoid additions to olefins have been studied previously for chlorine and phenyl substituted methylenes.[7-10] It was found that both substituents are *syn* directing, resulting in predominant formation of the product with the larger number of alkyl groups *cis* to the substituent, when the carbenoid was produced by α elimination. It was also shown that the *syn*-directing power of the chlorine atom is somewhat larger than that of the phenyl group. The present study demonstrates (Table II) that the rela-

(16) Hodgkins and co-workers[14] also noticed the splitting of the phenyl resonances and the enhanced intensity and bathochromic shifts in the spectra of the minor isomer. However, they failed to recognize that the conformation of maximum electronic interactions between the two rings, as well as that of maximum shielding for the *ortho* protons, is the one in which the phenyl ring plane lies in the symmetry plane of the molecule and that this conformation is favored for the *anti* structure while being sterically unfavored in the *syn* isomer.

(17) Provided this assignment is correct, the assumption of configurational retention of the phenyl group in the dehalogenation does not hold for both isomers. It is possible to rationalize predominant formation of *syn*-phenylnorcarane from both phenylchloronorcaranes by assuming kinetically controlled protonation of the reduction intermediate to occur from the least hindered side of the molecule. The strong dependence of the isomer ratio obtained on the reduction conditions seems to support this view.[14]

TABLE IV

PRODUCT AND ISOMER RATIOS OBTAINED FROM REACTIONS OF BENZAL CHLORIDE, METHYLLITHIUM, AND OLEFINS IN THE PRESENCE OF DIFFERENT HALIDE IONS[a]

	Product ratios: 1-Methyl-/1-chlorophenylcyclopropane			Isomer ratios (*anti*/*syn*)[b]: 1-Methylphenylcyclopropane			1-Chlorophenylcyclopropane	
Olefin	Cl^-	Br^-	I^-	Cl^-	Br^-	I^-	Cl^-	Br^-
2,3-Dimethyl-2-butene	...	0.34	...					
2-Methyl-2-butene	...	0.46	...	...	0.71	...	...	1.6
Isobutene	0.23	0.35	1.42					
trans-2-Butene	...	2.0	...					
cis-2-Butene	...	2.1	...	...	0.43	...	...	3.0
1-Butene	0.72	4.2	>100	0.60	0.56	0.53	1.7	1.8

[a] Reaction temperature was held at $-40 \pm 2°$. [b] *syn* and *anti* refer to the geometrical relationship of the phenyl group and the largest number of alkyl groups.

tive directing powers of these substituents are maintained when they are both incorporated into the same system. The over-all stereochemical result is independent of the type of base used for the generation of the intermediate, although it must be pointed out that the isomer ratios observed in reactions with potassium *t*-butoxide are not strictly comparable with the ratios obtained with methyllithium because reaction temperatures differed by approximately 100°. The simple additivity of directive powers of carbenoid substituents, as observed in this system, lends support to the previously expressed hypothesis[9] that the stereochemical course is determined mainly by interactions between the olefin alkyl groups and the substituents on the carbenoid carbon, and that secondary steric effects originating from complexing of the activated state with halide ion or solvent molecules are of lesser importance. Since the steric course of the additions of monosubstituted carbenoids requires that the balance of substituent interactions leads to weak net attraction, London dispersion forces, and possibly charge-transfer interactions have been invoked to account for the experimental observations.[9] The present results are in agreement with this interpretation.

The nature and distribution of products obtained from the reaction of benzal chloride with methyllithium in the presence of olefins indicates a relatively complicated reaction sequence. The formation of 1-phenyl-1-methylcyclopropanes resembles an observation made by Katz and Garrat who isolated methylbicyclo-[6.1.0]nonatrienes from reactions of methyllithium with methylene chloride in the presence of cyclooctatetraene.[18] In analogy with the results obtained in this study the fraction of methyl substituted nonatriene was also found to be a function of the halide ions present. Although with the data at hand it is impossible to narrow the choice of conceivable mechanisms to only one, certain reaction paths can be shown to be more likely than others.

The initial step, that of hydrogen–metal interchange between benzal chloride and methyllithium is common to all probable mechanisms and results in the formation of α,α-dichlorobenzyllithium (V). That this intermediate is capable of independent existence at low temperature has recently been shown by Hoeg, *et al.*, who prepared V by halogen–metal interchange from benzotrichloride and *n*-butyllithium in tetrahydrofuran.[19] As indicated in Figure 1, four reactions can be visualized to occur on intermediate V: (1) unimolecular loss of lithium chloride giving phenylchlorocarbene (VI); (2) bimolecular reaction with olefin to give phenylchlorocyclopropane; (3) reaction with lithium halide to give a new α,α-dihalobenzyllithium (VII) (this reaction is of course degenerate when lithium chloride is the only halide present); (4) reaction with methyllithium to give 1-phenyl-1-chloroethyllithium (VIII), which ultimately is converted to 1-phenyl-1-methylcyclopropanes. Each of the new intermediates, VI and VII, can in turn undergo an equivalent set of reactions, namely cyclopropane formation, reaction with methyllithium, and reactions with halide ions resulting in interconversion of V, VI, and VII. While there is little difficulty in visualizing the detailed mechanisms of reaction V $\rightleftarrows$ VI, and VI $\rightleftarrows$ VII,[20] it is not so certain whether V can go to VII without the intermediacy of carbene VI. However, displacement by bromide ion on trichloromethyllithium has been observed at temperatures as low as $-100°$ where formation of dichlorocarbene is very slow.[21]

On the basis of the reaction scheme considered so far, it is obvious that the product ratio will increase in favor of phenylchlorocyclopropanes with increasing nucleophilicity of the olefin substrate. This trend, which is experimentally observed (Table IV), follows from the fact that all three intermediates, V, VI, and VII, are electrophilic species[22] and that the product ratios are determined by the relative rates of attack by olefin and by methyllithium on these intermediates. The scheme is also capable of accounting for the remarkable influence of halide ions on the product ratios. Naturally, the partition factor determining the rate of reaction with methyllithium relative to the rate of olefin addition will be different for each intermediate and the final product distribution will depend very much on this competition factor and on the relative steady-state concentrations of V, VI, and VII. The results listed in Table IV require that the partition factor increases in favor of the methyllithium reaction with increasing atomic weight of the halogen atom in the α,α-dihalobenzyllithium. This

(18) T. J. Katz and P. J. Garrat, *J. Am. Chem. Soc.*, **86**, 4876, 5194 (1964).

(19) D. F. Hoeg, D. I. Lusk, and A. L. Crumbliss, Abstracts, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, p 52p; *J. Am. Chem. Soc.*, **87**, 4147 (1965).

(20) J. Hine and A. M. Dowell, Jr., *ibid.*, **76**, 2688 (1954).

(21) W. T. Miller and D. M. Whalen, *ibid.*, **86**, 2089 (1964).

(22) *Cf.* W. Kirmse, *Angew. Chem.*, **77**, 1 (1965).

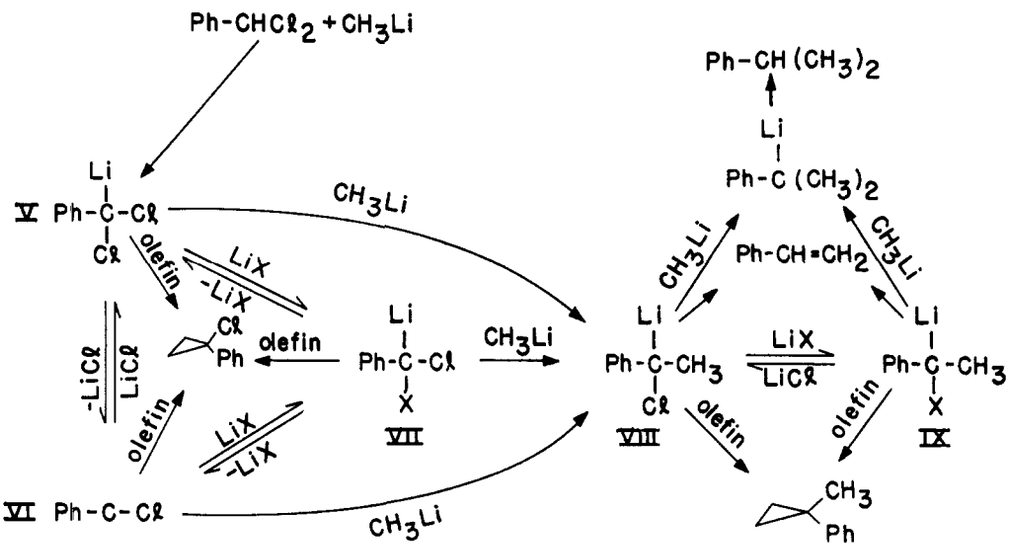

Figure 1.

trend is in line with the generally observed sequence of enhanced displacement rates of alkyl halides with increasing atomic weight of the halogen atom.

While the reaction scheme of Figure 1 is capable of explaining the product ratios, it is open to question whether *all* intermediates (V, VI, and VII) are necessary and to what extent the individual reactions are really taking place. As can be seen by inspection, the only intermediate which is superfluous is the carbene, although its intervention cannot be ruled out with the data at hand. It is, however, required that either V or VII or both should be able to react with methyllithium. If these intermediates are also able to add to the olefin, they should exhibit a difference in their reactivities which might reflect itself in the isomer ratios of cyclopropanes obtained. Table II shows that there is indeed a small variation in the isomer ratios of the adducts to 1-butene as the halide ion is varied. Unfortunately, the variation is barely outside of experimental error, and it is doubtful whether any significance can be attached to it. However, it has been shown previously[9,10,19,22] that α-halolithium compounds are able to add to olefins without going through free carbenes, and there is little doubt that carbenoids V and VII are also able to undergo this reaction. The only open question is that of the relative rates of loss of lithium halide on one hand and of reaction with olefin on the other. Since these rates can be expected to be strongly influenced by the nature of the substituents on the carbenoid carbon and by environmental changes, it is dangerous to extrapolate from one system to another.

The remaining products, 1-phenyl-1-methylcyclopropanes, styrene, and cumene, are easily seen to arise from intermediate VIII. In principle, VIII can be thought to undergo similar transformations as V, namely, conversion to IX with halide ion and loss of lithium halide to phenylmethylcarbene. The latter intermediate, however, seems to be of minor importance since its generation from 1-phenyldiazoethane in olefins leads to a significantly different product distribution, containing much more styrene, and giving a substantially different isomer ratio in its addition to *cis*-2-butene. However, it is interesting that both types of reactions give significant amounts of cyclopropanes although an intramolecular pathway, that of 1,2-hydride shift, is available. Normally, in carbenoid reaction this latter part is found to be almost the exclusive part.[23]

The results of this work together with those reported by Katz and Garrat[18] show that carbenoid reactions can be strongly influenced by seemingly unimportant changes in the reaction medium. Earlier work has shown that solvent composition is also capable of altering the reactivities of intermediates involved in α eliminations.[9] It appears, therefore, that just as much attention will have to be given to the nature of the reaction medium while comparing reactivities of various carbenoids, as is standard practice in carbonium ion chemistry.

Experimental Section

Melting points and boiling points are uncorrected. The nmr spectra were recorded on Varian A-60 and DP-60 spectrometers. Unless otherwise stated, the spectra were measured in carbon tetrachloride solution with tetramethylsilane as internal standard. Chemical shifts are reported in τ units, with the number in parenthesis indicating the number of protons causing the signal. The letter immediately following the parenthesis designates the multiplicity of the signal: s = singlet; d = doublet; t = triplet; m = unresolved multiplet.

Preparation of 1-Phenyl-1-chlorocyclopropanes. General Procedure Using Potassium *t*-Butoxide.—Olefin (50 ml) was condensed in a thick-walled Pyrex vessel (2.5-cm i.d., 60 cm long) and benzal chloride (8.05 g, 0.05 mole) and potassium *t*-butoxide (K and K Laboratories, 16.8 g, 0.15 mole) was added. After sealing the vessel the reaction mixture was agitated with a mechanical shaker and heated to 60–70° with a heating tape for 22 hr. The mixture was poured on ice and extracted with ether (75 ml). The ether extract was washed with water and dried over sodium sulfate. After removal of the solvent the product was distilled under reduced pressure. For determination of isomer ratios it was shown that vacuum distillation without column did not result in measurable fractionation.

With higher boiling olefins the reaction was carried out in a three-necked round-bottom flask employing a mechanical stirrer. Several experiments with shorter reaction times and excess-benzal chloride gave isomer ratios unchanged from those obtained under conditions stated above.

1-Phenyl-1-chlorotetramethylcyclopropane.—The previously reported chloride[6] was prepared as described above from 2,3-dimethyl-2-butene. After vacuum distillation (0.25 mm) the

(23) W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964, pp 47–64.

product solidified and was recrystallized from pentane (6.6 g, 63%): mp 65.5–66.5°; nmr, τ 2.77 (5) s, 8.63 (6) s, and 8.97 (6) s.

1-Phenyl-1-chlorotrimethylcyclopropane.—Use of 2-methyl-2-butene in a procedure identical with that described above gave a mixture of the geometrical isomers (8.45 g, 87%), bp 42–50° (0.15 mm).

Anal. Calcd for $C_{12}H_{15}Cl$: C, 74.03; H, 7.77; Cl, 18.21. Found: C, 73.90; H, 7.68; Cl, 18.03.

The predominantly formed isomer was obtained pure by glpc on a Carbowax 20M column followed by trapping in the conventional manner. The nmr spectrum of this isomer showed signals at τ 2.75 (5) s, 8.74 (7) s, and 9.19 (3) s. The minor isomer decomposed quantitatively on glpc. Its methyl resonances were determined from the nmr spectrum of the mixture and appeared at τ 8.50 (3) s, 9.0 (3) d, and 9.07 (3) s. Repeated integration of the nmr spectrum of the mixture yielded an isomer ratio of 1.5.

1-Phenyl-1-chloro-*trans*-2,3-dimethylcyclopropane.—Use of *trans*-2-butene in a procedure identical with that described above gave the adduct (5.4 g, 60%): bp 49–51° (0.25 mm); nmr, τ 2.75 (5) m, 8.6 (3) d, 8.8 (2) m, and 9.2 (3) d. Spacings of both doublets are 4.5 cps.

Anal. Calcd for $C_{11}H_{13}Cl$: C, 73.13; H, 7.25; Cl, 19.62. Found: C, 73.37; H, 7.36; Cl, 19.38.

1-Phenyl-1-chloro-*cis*-2,3-dimethylcyclopropane.—Use of *cis*-2-butene in an identical procedure gave a mixture of the geometrical isomers (6.25 g, 69%), bp 51–55° (0.3 mm).

Anal. Calcd for $C_{11}H_{13}Cl$: C, 73.13; H, 7.25; Cl, 19.62. Found: C, 73.37; H, 7.36; Cl, 19.38.

The nmr spectrum of the mixture showed multiplets centered at τ 2.63, 8.78, and 9.08. The relative intensities of the high-field/low-field signals was 8/5. The predominantly formed isomer was obtained in pure form by glpc of the mixture on Carbowax 20M at 120°. The minor isomer decomposed quantitatively under these conditions. The isomer ratio was determined by integration of the signals at 8.78 (*anti*) and 9.08 (*syn*) and was found to be 3.0 in favor of the *anti* isomer.

1-Phenyl-1-chloro-2,2-dimethylcyclopropane.—Use of isobutene in the procedure outlined above gave the previously described chloride[5] (8.0 g, 90%), bp 49–51° (0.3 mm). The nmr spectrum showed signals at τ 2.69 (5) m, 8.50 (3) s, 9.17 (3) s, and an AB quartet with chemical shifts of τ 8.69 and 8.93 and J = 6.0 cps.

1-Phenyl-1-chloro-2-ethylcyclopropane.—Use of 1-butene in the procedure outlined above gave a mixture of the geometrical isomers (4.9 g, 54%), bp 39–46° (0.2 mm).

Anal. Calcd for $C_{11}H_{13}Cl$: C, 73.13; H, 7.25; Cl, 19.62. Found: C, 73.08; H, 7.63; Cl, 19.27.

The isomers were separated by glpc on a Carbowax column operating at 110–120°. Quantitative analysis assuming idenictal thermoconductivity of the two isomers, gave a ratio of 1.7. The nmr spectrum of the major (*anti*) isomer gave signals at τ 2.72 (5) broad m and 8.1–9.1 (8) m. The positions of the signals in the spectrum of the minor (*syn*) isomer were at τ 2.68 (5) m and 8.8–9.2 (8) m.

7-Phenyl-7-chloronorcarane.[14]—Potassium *t*-butoxide (50 g, 0.45 mole) was added to cyclohexene (400 ml, 4 moles) which had been freshly distilled from sodium. The mixture was heated to reflux under vigorous stirring and benzal chloride (60 g, 0.373 mole) was added over a period of 90 min. The reaction mixture was stirred for an additional 6 hr before hydrolysis with ice water (500 ml). The organic layer was separated and washed until neutral, dried, and the excess cyclohexene was removed by distillation under reduced pressure. The remainder was distilled at 0.05 mm and the fraction boiling at 88–92° (46.7 g, 65%) was collected.

The nmr spectrum of the mixture showed it to be free of olefins: τ 2.6–2.9 (5) m, 8–9.5 (10) three broad, partially overlapping multiplets. Attempts to separate the stereoisomers by glpc under a variety of conditions resulted in decomposition. The predominantly formed isomer was obtained in pure form by adsorption chromatography on alumina. The isomer mixture (0.5 g) was dissolved in *n*-pentane (2 ml) and added to a column containing Woelm alumina, activity grade I (50 g). The column was eluted with *n*-pentane and the first fraction (0.233 g) was free of olefin as shown by nmr. Comparison of the nmr spectrum of this fraction [τ 2.7–2.9 (5) m, 7.9–8.35 (4) m, and 8.35–8.8 (6) m] with that of the mixture indicated the presence of one isomer only. Analysis of the nmr spectrum of the isomer mixture by integration of the multiplet between τ 8.9 and 9.4 (absent in the eluted isomer) indicated a ratio of 2/1 in favor of the isomer isolated and assigned the *anti* structure. Later fractions eluted from the column showed strong olefinic proton resonances and presumably originated from decomposition of the *syn* isomer.

Reaction of Benzal Chloride, Methyllithium, and Olefins. General Procedure. A. Preparation of the Methyllithium Solutions.—Methyllithium was prepared in ether from lithium wire (Lithium Corp. of America) and methyl chloride, methyl bromide or methyl iodide was added until little lithium remained. The reaction was maintained at reflux temperature using methyl chloride. With methyl bromide and methyl iodide the temperature was held between −20 and 0°. All operations were carried out under nitrogen. The methyllithium solutions were filtered into storage burets and kept under nitrogen atmosphere. Concentrations were determined by titration and ranged from 1.6 to 1.8 *M*.

B. Reaction with Benzal Chloride.—The appropriate olefin (1 mole) and benzal chloride (10.6 g, 0.066 mole) were placed in a flame-dried, 250-ml, three-necked flask, equipped with Dry Ice condenser, low-temperature thermometer, addition funnel, and magnetic stirrer and all operations were carried out under small positive nitrogen pressure. Methyllithium (0.10 mole) in ether was added over a period of 2.5 hr at −40°. After completion of the addition the reaction mixture was stirred for an additional hour, and then was poured onto ice. The product was washed with water and dried over sodium sulfate, and the excess olefin was allowed to distil. The ether and remaining olefin were removed under reduced pressure. The residue was distilled from flask to flask under vacuum.

Analysis of the reaction mixtures were carried out by glpc on a 3-ft Carbowax 20M column (20% on firebrick) operating at 120–150° with flow rates of 100–120 ml/min. The 1-phenyl-1-methylcyclopropanes were trapped from the glpc column for identification. In those cases where decomposition of the 1-phenyl-1-chlorocyclopropanes occurred under glpc conditions (see above) product analysis was carried by nmr by measuring the integrated intensities of selected peaks characteristic for each product. Product ratios and isomer ratios as obtained with the various methyllithium solutions are listed in Table IV. Yields as listed under the individul cyclopropanes are based on the amount of benzal chloride consumed, and are combined yields of both 1-phenyl-1-chloro- and 1-phenyl-1-methylcyclopropanes.

1-Phenyl-1,2,2,3,3-pentamethylcyclopropane.—Use of 2,3-dimethyl-2-butene and methyllithium prepared from methyl bromide in the procedure outlined above gave a 70% yield of cyclopropanes: nmr, τ 2.88 (5) s, 8.77 (3) s, 8.85 (6) s, and 9.09 (6) s.

Anal. Calcd for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 88.95; H, 10.80.

1-Phenyl-1,2,2,3-tetramethylcyclopropane.—Use of 2-methyl-2-butene and methyllithium prepared from methyl bromide in the procedure outlined above gave a 81% yield of cyclopropanes.

Anal. Calcd for $C_{13}H_{18}$: C, 89.59; H, 10.41. Found: C, 89.79; H, 10.34.

Separation of the epimeric pair of phenyltetramethylcyclopropanes could not be achieved under a variety of glpc conditions. The nmr spectra of the epimer mixture showed absorptions of the eight different methyl groups between 8.70 and 9.28. The singlet at τ 9.28 (3) was tentatively assigned to the C-2 methyl group *cis* to the phenyl ring in the *anti* isomer, and a singlet at τ 9.17 (3) to the C-2 methyl group *cis* to the phenyl group in the *syn* isomer. Integration of the two signals gave a value for the *anti*/*syn* ratio of 0.71.

1-Phenyl-1,2,2-trimethylcyclopropane.—Use of isobutene and methyllithium prepared from methyl chloride in the procedure outlined above gave a 78% yield of cyclopropanes. Methyllithium from methyl bromide gave 85% and methyllithium from methyl iodide gave 54%: nmr, τ 2.85 (5) s, 8.62 (3) s, 8.72 (3) s, 9.28 (3) s, AB quartet (2) at 9.13, and 9.60 (J = 4.3 cps).

Anal. Calcd for $C_{12}H_{16}$: C, 89.93; H, 10.07. Found: C, 89.90; H, 10.18.

1-Phenyl-1-methyl-*trans*-2,3-dimethylcyclopropane.—Use of *trans*-2-butene and methyllithium prepared from methyl bromide in the procedure outlined above gave a 58% yield of cyclopropanes: nmr, τ 2.84 (5) s, 8.69 (3) s, 8.8 (3) d (7 cps), 9.3 (3) d (7 cps), and 9.0–9.7 (2) m.

Anal. Calcd for $C_{12}H_{16}$: C, 89.93; H, 10.07. Found: C, 89.75; H, 10.20.

1-Phenyl-1-methyl-*cis*-2,3-dimethylcyclopropane.—Use of *cis*-2-butene and methyllithium prepared from methyl bromide in the procedure outlined above gave a 61% yield of cyclopropanes. Glpc separation and trapping gave *syn* and *anti* geometrical isomers: nmr, *syn* isomer, τ 2.81 (5) s, 8.73 (3) s, and 9.11 (8) broad s; *anti* isomer, τ 2.76 (5) broad s, 8.81 (3) s, and 8.93 (8) broad s.

Anal. Calcd for $C_{12}H_{16}$: C, 89.93; H, 10.07. Found: C, 89.82; H, 10.26.

1-Phenyl-1-methyl-2-ethylcyclopropane.—Use of 1-butene and methyllithium prepared from methyl chloride in the procedure outlined above gave a 43% yield of cyclopropanes. Methyllithium from methyl bromide gave 69% and methyllithium from methyl iodide gave 53%: nmr, *syn* isomer, τ 2.83 (5) broad s, 8.65 (3) s, and 9.0–9.4 (8) m; *anti* isomer, τ 2.86 (5) broad s, 8.63 (3) s, 8.3–9.3 (7) m, and 9.7 (1) m.

Treatment of 1-chloro-phenyl-2,2-dimethylcyclopropane with Methyllithium.—1-Chloro-1-phenyl-2,2-dimethylcyclopropane (1.81 g, 0.01 mole) dissolved in *n*-pentane (10 ml) was cooled to −10°. Methyllithium (0.01 mole) in ether (prepared from methyl bromide) was added to this solution and the mixture was kept at −10° for 5 hr. The reaction mixture was hydrolyzed, washed with water, and dried. Glpc analysis indicated that no detectable amounts of 1-phenyl-1,2,2-trimethylcyclopropane were formed under these conditons.

Photolysis of 1-Phenyldiazoethane in Isobutene.—1-Phenyldiazoethane was prepared by shaking a mixture of acetophenone hydrazone (4.5 g, 0.033 mole), yellow mercuric oxide (14.8 g, 0.068 mole), sodium sulfate (4.0 g), and 1 ml of a saturated solution of potassium hydroxide in ethanol and ethyl ether (50 ml) for 15 min. The resulting solution was filtered, washed with water, and titrated with benzoic acid (yield, 60%).

1-Phenyldiazoethane (1.3 g, 0.01 mole in ethyl ether (25 ml) was added to isobutene (75 ml) previously condensed in a 250-ml three-necked flask fitted with mechanical stirrer, Dry-Ice condenser, and a low-temperature thermometer. The mixture was then photolyzed at −40° over a a period of 8 hr using a General Electric photoflood, PH/RFL-2 500-w lamp. At the end of this period the remaining 1-phenyldiazoethane was destroyed by the addition of a solution of maleic anhydride (0.3 g, 0.003 mole) in ethyl ether (25 ml). Most of the olefin was allowed to distil, and the residue was washed with aqueous potassium hydroxide (5% solution), water, and dried over sodium sulfate. After flask-to-flask distillation under reduced pressure (1 mm) the products were subjected to glpc analysis on a 5-ft Carbowax 20M column operating at 140°. Styrene, 1-phenyl-1,2,2-trimethylcyclopropane, and a small amount of acetophenone were isolated by trapping and identified by comparison of nmr and infrared spectra with those of authentic samples. The yield based on consumed diazo compound was 41.5% of cyclopropane and 18.6% of styrene. Styrene was shown not to polymerize under the glpc conditions employed by calibration of known mixtures under identical conditions.

Photolysis of 1-Phenyldiazoethane in *cis*-2-Butene.—Employing an identical procedure with that described above but using *cis*-2-butene gave *syn*- and *anti*-1-phenyl-1-methyl-*cis*-2,3-dimethylcyclopropane (34%, *anti*/*syn* ratio, 1.3), and styrene (4.8%). Product identity was shown by comparison of glpc retention times and infrared spectra with those of authentic samples.

7-Phenylnorcarane. A. Photolysis of Phenyldiazomethane in Cyclohexane.—Phenyldiazomethane (1.00 g, 0.008 mole) was dissolved in freshly distilled cyclohexene (100 ml). Photolysis with a photoflood lamp was carried out at −30° as described above. After 7 hr of illumination the excess phenyldiazomethane was destroyed by the addition of excess maleic anhydride (1.0 g, 0.001 mole) in ether (100 ml). The reaction mixture was washed with aqueous potassium hydroxide (4%) and water, and dried over sodium sulfate. Most of the excess cyclohexene was removed by distillation over a 3-ft spiral column. To remove olefinic side products the residue was ozonized in methanol (100 ml) at −75°. After the ozonization was complete, 1-pentene (2.0 ml) was added at this temperature to destroy excess ozone. The ozonization mixture was allowed to warm to room temperature, and water (100 ml) was added. The product was extracted with ether and the solution was washed several times with sodium bisulfite solution. The ether was removed by distillation and the residue was subjected to glpc analysis on a 14-ft QF-1 column (20% on firebrick) operating at 155°. The isomeric 7-phenylnorcaranes were easily separable and were present in a ratio of 1.1/1. The isomer with the shorter retention time predominated. The isomers were individually trapped from the glpc column and identified by comparison of their infrared spectrum with the compounds prepared by α elimination from benzal bromide (see below). The yield of 7-phenylnorcaranes, based on phenyldiazomethane, was determined to be 34%.

B. Reaction of Benzal Bromide, Methyllithium, and Cyclohexene.—Following the general procedure of Closs and Moss[9] a solution of benzal bromide (25.0 g, 0.10 mole) in cyclohexene (82 g, 1 mole) was magnetically stirred and cooled to −30°. Methyllithium in ether (60 ml, 1.85 *M*) prepared from methyl bromide was added dropwise over a period of 2 hr. The reaction mixture was stirred for an additional hour at this temperature, hydrolyzed with ice–water, washed with water, and dried over sodium sulfate. The solvent was removed by distillation and the residue was fractionally distilled under reduced pressure. The fraction boiling between 60 and 105° (3 mm) was collected and analyzed by glpc on a 14-ft QF-1 column (20% on firebrick) operating at 155°. The two phenylnorcaranes were shown to be present in a ratio of 3/1, the isomer with the shorter retention time predominating. Yield based on benzal bromide was determined to be 21%. The two isomers were collected from the glpc column and the spectral properties were determined: nmr of predominating (*syn*) isomer, τ 2.74 (5) narrow multiplet of 2.0-cps half-width and 8.0–9.5 (11) very broad multiplet; minor (*anti*) isomer, 2.5–3.2 (5) m and 7.9–8.9 (11) very broad multiplet. Ultraviolet spectra in *n*-pentane follow: *syn* isomer, λ_{max} 217 mμ (ϵ 7490), 253 (ϵ 218), 260 (ϵ 250), and 266 (ϵ 193); *anti* isomer, λ_{max} 226 mμ (ϵ 10,800), 263 (ϵ 492), 269 (ϵ 625), and 276 (ϵ 570).

Base Equilibration of *syn*- and *anti*-7-Phenylnorcaranes.—A solution of the predominantly formed (*syn*) isomer of 7-phenylnorcarane (42 mg, 0.24 mmole) in dimethyl sulfoxide (1.0 ml, previously distilled from sodium hydride) and potassium *t*-butoxide (112 mg, 1.0 mmole) was sealed into an ampoule (2 ml) and was heated to 90° for 16 hr. The reaction mixture was hydrolyzed, extracted with pentane, and dried over sodium sulfate. Glpc analysis on a QF-1 column (20% on firebrick) operating at 155° indicated a better than 90% conversion to the minor isomer, *anti*-7-phenylnorcarane. For identification the compound was trapped from the glpc column and its infrared and nmr spectra were compared with those of authentic samples.

When the minor isomer, *syn*-7-phenylnorcarane (21 mg, 0.12 mmole), was treated in identical fashion, glpc analysis showed only one peak with the retention time of the starting material. Trapping and comparison of the infrared and nmr spectra identified this compound as unchanged starting material.

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