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Carbenes from Alkyl Halides and Organolithium Compounds. II.[1] The Reactivity of Chlorocarbene in its Addition to Olefins

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Chlorocarbene, generated from methylene chloride and *n*-butyllithium, has been allowed to react with pairs of olefins of different nucleophilicity. The reaction mixtures were analyzed quantitatively by v.p.c. and the relative rates of the additions have been determined. The results show that chlorocarbene is a less discriminating species than dichlorocarbene, indicating a smaller degree of internal stabilization in the monochloro derivative of methylene.

The formation of chlorocyclopropanes from methylene chloride, olefins and alkyllithium compounds[1] constitutes strong evidence for the existence of chlorocarbene in this reaction. Information about its reactivity relative to other known derivatives of divalent carbon appears to be of interest and will contribute to establish correlations of the stabilizing influence of substituents on the electron deficient carbon. Qualitatively it can be expected that the stability of chlorocarbene will be intermediate between methylene and dichlorocarbene.

The fact that no carbon–hydrogen insertion products have been detected in the reaction of chlorocarbene with olefins[1] indicates a less reactive molecule than methylene which reacts to a substantial degree *via* this path.[2] Addition to olefins under formation of cyclopropane derivatives appears to be a reaction which most carbenes undergo readily. Divalent carbon species are therefore conveniently compared by measuring their reactivities in this addition reaction. Thus Skell[3] and Doering[4] studied the relative rates of additions of a number of carbenes to various olefins. The magnitude of the spread of the relative rates for a given set of olefins serves as a convenient measure of the ability to discriminate, a property directly related to the internal stabilization of the carbene. This paper is concerned with the determination of the reactivity of chlorocarbene as evaluated by competitive reaction with seven olefins, and with the comparision of the results with those obtained by Doering and Skell for dihalocarbenes.

Results

The relative rates of the addition of chlorocarbene to olefins can be determined by the usually employed competition method in which the carbene is allowed to react with pairs of olefins. Relative rate constants for this process are given by eq. 1

$$k/k_0 = P/P_0 \times O_0/O \qquad (1)$$

(P = mole fraction of product, O = mole fraction of olefin). This equation can be applied only if the olefins are present in large excess, and if it can be shown that the product ratio is not changed by consecutive reactions.

To establish whether the second condition is satisfied, a known mixture of chlorocyclopropanes (1-chloro-2,2,3,3-tetramethylcyclopropane, 1-chloro-2,3-*trans*-dimethylcyclopropane, 1-chloro-2,2-dimethylcyclopropane and 1-chloro-2,2,3-trimethylcyclopropane) was treated in pentane and methylene chloride with *n*-butyllithium under conditions similar to those adopted for the competition experiments. The mixture was analyzed by vapor phase chromatography (v.p.c.) and the chlorocyclopropanes were found in almost unchanged ratios.

The competition runs were carried out between −35 and −40° with a tenfold excess of olefin and a twofold excess of methylene chloride, using *n*-butyllithium to generate the carbene. The crude reaction mixtures were analyzed by v.p.c. and the relative rates were obtained from expression 1. Since five of the olefins were measured in competition with isobutylene the rate for the addition to this olefin was set equal to one and served as standard relative to which the other rates are reported.[5] The results are listed in Table I. The errors introduced by the simplifications in eq. 1 are rather small in view of the excess olefin employed, and with the experimentally observed differences in rate do not exceed 5%. The internal consistency of the method is demonstrated by two double measurements: 2-methylbutene-2 and pentene-1 were both allowed to compete with *trans*-butene-2. The values obtained were adjusted to isobutylene as standard and agree well with the results derived from the competitive experiments with isobutylene.[6] For analytical reasons cyclohexene could not be compared directly with isobutylene and the relative rate for its reaction with chlorocarbene was obtained by competition with *cis*-butene-2.

Four of the olefins used in the competition runs are capable of forming two isomeric chlorocyclopropanes because of the lack of symmetry with respect to the double bond. Two rate constants can therefore be obtained for each such olefin if both isomers are analyzed separately. In the preceding paper it has been demonstrated that the *trans* isomer is the predominant product of the addition reaction of the olefins examined (*trans* indicating a *trans* relationship of the chlorine atom with the *larger* number of alkyl groups). In order to make these rate constants comparable with the values obtained for the addition to sym-

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(1) Part I of this series: G. L. Closs and L. E. Closs, THIS JOURNAL, **82**, 5723 (1960).

(2) W. v. E. Doering, R. G. Buttery, R. G. Laughlin and N. Chaudhuri, *ibid.*, **78**, 3224 (1956).

(3) (a) P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956); (b) P. S. Skell and R. M. Etter, *Chemistry & Industry*, 624 (1938).

(4) W. v. E. Doering and W. A. Henderson, Jr., THIS JOURNAL, **80**, 5274 (1958).

(5) The most frequently used standard for relative rates of additions to olefins, cyclohexene,[4] is not particularly well suited to serve as reference in this reaction because two stereoisomers are produced on the addition of chlorocarbene to this olefin.

(6) The extreme close agreement for the two double measurements must be regarded as fortuitous because the combined experimental and systematical errors are in the order of 10%.

TABLE I

RELATIVE RATES OF ADDITION OF CHLOROCARBENE AND DICHLOROCARBENE TO OLEFINS

Olefin	I $(k/k_0)_{\mathrm{CHCl}}$	II	II log $(k/k_0)_{\mathrm{corr.\ CHCl}}$	III log $(k/k_0)^{a}_{\mathrm{CCl_2}}$
2,3-Dimethylbutene-2	2.81		0.45	0.81
2-Methylbutene-2	1.78 (1.76)[b]	*cis*	.14	.45
		trans	.34	
Isobutylene	1.00		.00	.00
trans-Pentene-2				− .59
trans-Butene-2	0.45		− .35	
cis-Pentene-2				− .71
cis-Butene-2	.91	*cis*	− .55	
		trans	.19	
Cyclohexene	.60[c]	*cis*	− .55	− .92
		trans	− .04	
Pentene-1	.23 (0.24)[b]	*cis*	−1.00	
		trans	−0.45	−1.78

[a] These data are taken from Doering and Henderson.[4] [b] Measured in competition with *trans*-butene-2. [c] Measured in competition with *cis*-butene-2.

metrical olefins, a statistical correction factor of 2 has to be applied. The logarithms of these corrected relative rate constants are listed in Table I, column II.

Discussion

On evaluating the table one finds that higher rates are observed with increased substitution of the double bond. This behavior is clearly that to be expected for an *electrophilic* species in an addition reaction and indicates some fraction of a positive charge on the olefin carbon atoms in the transition state.[7] This finding may be regarded as additional evidence for the carbene mechanism of this reaction. One tertiary and one primary carbon in the olefin was found to be more favorable for the addition than two secondary sites (isobutylene *vs.* *trans*-butene-2), in close analogy to the behavior of the dihalocarbenes.

A steric factor is clearly operative as can be seen from the different rates of formation of the two possible isomers from unsymmetrical olefins. Increasing substitution of the double bond leads to larger steric hindrance in the transition state and partially offsets the accelerating effect these substituents exert by increasing the electron density on the olefinic carbon atoms. In no case, however, is the steric retardation of a larger magnitude than the electronic acceleration. Thus, the above-mentioned sequence for electrophilic addition is preserved.

For reasons set forth in the introduction a comparison of the reactivities of chloro- *versus* dichlorocarbene is of interest. The data reported by Doering and Henderson[4] for the relative rates for the addition of dichlorocarbene to olefins are summarized in Table I, column III. The values have been adjusted to isobutylene as standard. It can be seen that the over-all difference in relative rates for the addition of chlorocarbene to the selected olefins is much smaller than for dichlorocarbene. The reaction of chlorocarbene with 2,3-dimethylbutene-2 is 28 times faster than the reaction with pentene-1 leading to the *cis* product. The corresponding ratio for dichlorocarbene is 390.

To establish an exact relationship between the two carbenes, a quantitiative assessment of the importance of steric effects in the determination of relative reactivity would be required. Thus, dichlorocarbene with two chlorine atoms causing non-bonded interactions in the transition state will be more susceptible to steric retardation than the smaller chlorocarbene. To minimize the uncertainties introduced by steric effects, the relative rates for the addition of dichlorocarbene should be compared with the rates of formation of the *cis*-chlorocyclopropanes. If chlorine–alkyl repulsions are considered as the main contributing factor and chlorine–hydrogen and hydrogen–hydrogen interactions are neglected, there will be similar steric effects operating for both carbenes in the addition to pentene-1 and cyclohexene. The transition states for the addition of chlorocarbene to isobutylene and 2-methylbutene-2 have one less such interaction than the corresponding transition states for dichlorocarbene. The most serious influence of steric effects is expected for the addition to 2,3-dimethylbutene-2. In this case, two chlorine–methyl interactions for chlorocarbene *versus* four for the dichloro derivative contribute to the destabilization of the transition state.

The different reactivities of the two carbenes are perhaps demonstrated best by plotting the logarithms of the relative rates, proportional to $\Delta\Delta F^{\ddagger}$, for chlorocarbene against those for dichlorocarbene. When the "*cis*" relative rates for chlorocarbene are compared to the data for dichlorocarbene in this manner, the deviations from a hypothetical line are not unreasonably large, particularly since no strict compensation has been made for steric effects. The slope of the line $d \log (k/k_0)_{\mathrm{CHCl}}/d \log (k/k_0)_{\mathrm{CCl_2}}$ is significantly smaller than one (about 0.5), showing that *chlorocarbene is a less discriminating species than dichlorocarbene.* This finding is in full agreement with the expectation that one chlorine atom has a smaller stabilizing influence on the two-valent carbon atom than two. It should be pointed out that the relative rates for the additions were measured at different temperatures for the two carbenes (−15° for CCl_2 and −35° for CHCl),[8] and an appropriate adjustment is required for a more precise comparison. This would result in a further reduction of the slope because any rise in temperature will tend to reduce the selectivity of the carbene. Similarly, a better compensation for steric factors would increase the reactivity ratio of the two carbenes because the selectivity of the bulkier dichloro derivative would be even larger if steric hindrance in the transition state could be reduced to the same level as observed for the addition of chlorocarbene.

The available data[4] allow no unambiguous conclusions to be drawn as to the stability of dibromocarbene in comparison with chlorocarbene. The

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[7] The increase in yield of chlorocyclopropanes with increasing substitution of the double bond[1] already indicated an electrophilic addition to the olefin. Here, the olefin competes with the organolithium reagent for the carbene.

[8] The competition reactions for chlorocarbene could not be carried out at the same temperature as reported for the reactions of dichlorocarbene, because the addition of *n*-butyllithium to the olefin–methylene chloride mixture is difficult to control at −15°.

difference of the steric requirements of the two carbenes is too large to be neglected and accounts for the failure to obtain a linear relationship of the logarithms of the relative rates in olefin additions. The same observation was made by Doering on comparing dibromo- with dichlorocarbene.[4]

Experimental

Materials.—The chlorocyclopropanes used for standardization of the vapor phase chromatograph were synthesized following the procedures described in the preceding paper.[1] Cyclohexene (Eastman Kodak Co., white label), 2,3-dimethylbutene-2, 2-methylbutene-2 (Matheson, Coleman and Bell, 99%) and pentene-1 (Matheson, Coleman and Bell, 99%) were purified before use by fractional distillation. Isobutylene (Matheson, "pure grade"), *cis*-butene-2 (Philips Hydrocarbons, "pure grade") and *trans*-butene-2 (Philips Hydrocarbons, "research grade") were used without further purification. *n*-Butyllithium was prepared by standard procedure from butyl bromide and lithium in diethyl ether. Methylene chloride ("reagent grade") was used unpurified.

Vapor Phase Chromatograms.—Vapor phase chromatograms were carried out with a Fisher–Gulf Partitioner equipped with integrator. The separations were effected by the use of a 12-ft. column charged with TCP on firebrick. Suitable temperatures were determined for each separation (50 to 140°), and helium flow rates of 60 to 80 ml./min. gave satisfactory resolution. The sensitivity of the detector cell for each product was determined by chromatographing known mixtures of the chlorocyclopropanes and determination of the peak area. Two such runs with different ratios of chlorocyclopropanes have been carried out for each pair of products.

Test for Product Stability.—A mixture of chlorocyclopropanes of the following composition was prepared: 1-chloro-2,2,3,3-tetramethylcyclopropane (I), 5.02 mmoles; 1-chloro-2,2,3-trimethylcyclopropane (II) (both isomers), 4.85 mmoles; 1-chloro-2,2-dimethylcyclopropane (III), 4.81 mmoles; 1-chloro-2,3-*trans*-dimethylcyclopropane (IV), 5.29 mmoles. The mixture was dissolved in pentane (30 ml.) and methylene chloride (8.4 g.). To this solution was added over a period of 30 minutes *n*-butyllithium (50 mmoles) at −35°. The reaction mixture was washed with water and analyzed by v.p.c. The ratios of chlorocyclopropanes were found to be 1.06 (I):1.05 (II):1.00 (III):1.05 (IV) (*vs.* 1.04:1.01:1.00:1.10 for the composition of the starting mixture).

Competition Runs.—The competition runs were carried out in a three-neck flask equipped with stirrer, addition funnel and nitrogen inlet tube. Both olefins (0.25 mole of each) and methylene chloride (0.1 mole) were added and cooled to −35°. To this solution was added *n*-butyllithium (0.05 mole) over a period of 30 minutes. The temperature was kept between −35 and −40°. After addition was complete the reaction mixture was washed with water, dried and analyzed by v.p.c.; *trans*/*cis* isomer ratios were found to be: 1-chloro-2,2,3-trimethylcyclopropane, 1.6; 1-chloro-2,3-*cis*-dimethylcyclopropane, 5.5; 7-chlorobicyclo[4.1.0]heptane, 3.2; 1-chloro-2-*n*-propylcyclopropane, 3.4.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF MICHIGAN, ANN ARBOR, MICH.]

The Alleged Role of Nitroxyl in Certain Reactions of Aldehydes and Alkyl Halides[1]

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The reaction of primary alkyl halides with Piloty's acid ($C_6H_5SO_2NHOH$) or Angeli's salt ($Na_2N_2O_3$), reported by Angeli to give aldoximes, has been shown to proceed by alkylation of the benzenesulfonhydroxamate or nitrohydroxamate ion, respectively, rather than by alkylation of nitroxyl, HNO, which these compounds generate. Sodium nitrosyl does not convert alkyl halides to oximes, nor does it convert aldehydes to hydroxamic acids (Angeli–Rimini aldehyde test). The rate of breakdown of Angeli's salt to nitrite and nitroxyl has been found to follow first-order kinetics, and to be unaffected by a change in solvent from water to ethanol, but it is markedly retarded by sodium hydroxide. Alkaline nitration of cyclohexylhydroxylamine gives cyclohexanone oxime through the unstable N-cyclohexylnitrohydroxamate anion. The O-acetyl and O-tetrahydropyranyl derivatives of Piloty's acid can be alkylated efficiently on the nitrogen to give isolable products, which can be converted to aldoximes by hydrolytic cleavage of the blocking group and treatment with base. By the various methods mentioned benzyl and 2,4,6-trimethylbenzyl chlorides and ethyl and hydrocinnamyl iodides have been converted to the corresponding oximes.

Introduction

The substance nitroxyl, HNO (or its hydrate, $HN(OH)_2$) has had a long history as a hypothetical intermediate in various reactions, but has nevertheless been consigned to obscurity by being completely ignored by numbers of otherwise comprehensive treatises on inorganic chemistry. Latimer and Hildebrand[3] provide a notable exception to this. Although nitroxyl itself has not been isolated (it has, however, been trapped in a frozen argon matrix[4]), its sodium salt, NaNO, has been known for many years from its direct formation from sodium and nitric oxide.[5] The principal interest in nitroxyl, however, has been in its role as an intermediate in various reactions in which hyponitrite or nitrous oxide is formed from substances containing only a single nitrogen atom. These reactions have been correlated by the assumption that a characteristic reaction of nitroxyl is dimerization to hyponitrous acid, which in turn readily decomposes to nitrous oxide (eq. 1).

$$2HNO \longrightarrow HON{=}NOH \longrightarrow N_2O + H_2O \quad (1)$$

Recently, renewed attention has been given to nitroxyl as a species that can be eliminated from organic molecules. Examples are the nitrosative degradation of tertiary amines[6] (eq. 2) and the Nef reaction[7,8] (eq. 3). The latter reaction when ap-

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(1) Presented at the 135th National Meeting of the American Chemical Society, Boston, Mass., April, 1959. From the doctoral thesis of G. E. Hein, 1959.

(2) National Science Foundation Predoctoral Fellow.

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(8) M. F. Hawthorne, *ibid.*, **79**, 3471 (1957).