As unstable intermediates, ion pairs of course can serve in many of the roles historically played by dissociated ions. In particular their relative instabilities should make them relatively unselective in their subsequent reactions, thus accounting for the diversity of products and reactions modes frequently observed under solvolytic conditions. Among the reactions which might reasonably be expected of an unstable ion pair (other than return to covalent starting material) are (1) attack by nucleophile (solvent and/or external nucleophile) to give substitution product,[5] (2) attack by base and/or solvent to give olefin,[23] (3) further charge separation to a solvent-separated ion pair,[20] (4) oxygen scrambling in, *e.g.*, sulfonates and *p*-nitrobenzoates,[24] (5) racemization,[25] and (6) rearrangement *via* neighboring group intervention.

The first five of these reactions have been documented; the sixth, rearrangements, and the related phenomenon of anchimeric assistance may well follow upon the initial formation of an unrearranged ion pair. The

$$\begin{tikzcd}
\mathrm{RX} \arrow[r, shift left, "k_1"] & \mathrm{R^+X^-} \arrow[l, shift left, "k_{-1}"] \arrow[r, "\text{rearrangement}"] & \mathrm{R'^+X^-} \arrow[d] \\
 & & \text{products}
\end{tikzcd}$$

rate enhancements generally associated with anchimeric assistance, then, may result from an increased rate of rearrangement of the ion pair, competitive with k_{-1}, rather than from any enhancement of its rate of formation from covalent starting material.

Finally we return to the question of the role of ion pairs, if any, in the reactions of primary and methyl systems. One's *a priori* thinking about ion-pair stabilities, of course, is inevitably conditioned by his knowledge of the literature of dissociated carbonium ions. If in fact the parallel is complete it is difficult to credit the suggestion that ion pairs intervene in the substitution reactions of these precursors of notoriously unstable carbonium ions.

It then follows either (1) that primary and methyl compounds choose an alternate mechanism (traditional SN2?) of substitution, bypassing the unstable ion pair, or (2) that the ion pairs derived from primary and methyl substrates do not in fact parallel, at least quantitatively, in stability the corresponding dissociated carbonium ions; the energy differences are attenuated.

The latter alternative seems to us, at least aesthetically, the more satisfying, and one can make a quite reasonable argument in its defense. In particular because of the nature of the electrostatic stabilization in an ion pair the positive charge in the alkyl moiety should resist dispersal by any mechanism away from the negative counteranion. Thus the usual mechanisms of charge dispersal, generally considered to be of great importance in stabilizing dissociated carbonium ions, such as polarization and resonance, may be of considerably lesser importance with the corresponding ion pairs.

If this be the case it follows that ion pairs should be less sensitive to substituent effects than are the corresponding dissociated carbonium ions and makes credible the suggestion that even primary and methyl systems undergo substitution reactions *via* the ion-pair mechanism. Definitive experiments are under way.

solvent molecule of a solvent-separated ion pair might be expected to take place with retention, thus providing an alternative explanation to nonclassical bonding for the frequently observed examples of retention.

(23) R. A. Sneen and H. M. Robbins, *J. Am. Chem. Soc.*, **91**, 3100 (1969).

(24) H. L. Goering and R. W. Thies, *ibid.*, **90**, 2967, 2968 (1968).

(25) S. Winstein, M. Hojo, and S. Smith, *Tetrahedron Letters*, 12 (1960).

Dichlorocarbene, Free or Complexed? Relative Reactivities of Free CCl_2

P. S. Skell and M. S. Cholod

Contribution from the Department of Chemistry,
The Pennsylvania State University, University Park, Pennsylvania 16802.
Received May 9, 1969

Abstract: High-temperature pyrolysis of $CHCl_3$ or CCl_4 produces CCl_2. Dichlorocarbene molecules issuing from a 1500° furnace zone into a high vacuum chamber experience collisionless flight to the wall. Wescott demonstrated that this free CCl_2 reacts stereospecifically with *cis-* and *trans-*2-butene when it is cocondensed with the cold olefin. Since the graphite furnace provides a surface for spin equilibration, it was concluded that the ground state of CCl_2 is singlet. This same technique has been employed to determine the relative reactivities of olefins in reaction with this variety of CCl_2. Dichlorocarbene intermediates generated from MCX_3 in similar media[18] show the same relative reactivities, suggesting that free CCl_2 is the active reagent in dichlorocyclopropanation of olefins.

The direct observation of carbenes by optical and electron spin resonance spectroscopies leaves little doubt regarding the independent existence of these species.[1] However, in the usual chemical experiments it is not apparent that the free carbenes are intermediates. It is conceivable that excited states of diazo compounds and ketenes eliminate nitrogen or carbon monoxide as they react with substrates. Further, carbenes may form complexes with ligands which can transfer the carbene moiety directly to an olefin.

(1) R. A. Bernheim, R. J. Kempf, J. V. Gramas, and P. S. Skell, *J. Chem. Phys.*, **43**, 196 (1965); D. E. Milligan and M. E. Jacox, *ibid.*, **47**, 703 (1967); L. Andrews, *Tetrahedron Letters*, 1968; A. M. Trozzolo, *Accounts Chem. Res.*, **1**, 529 (1968), footnote 7.

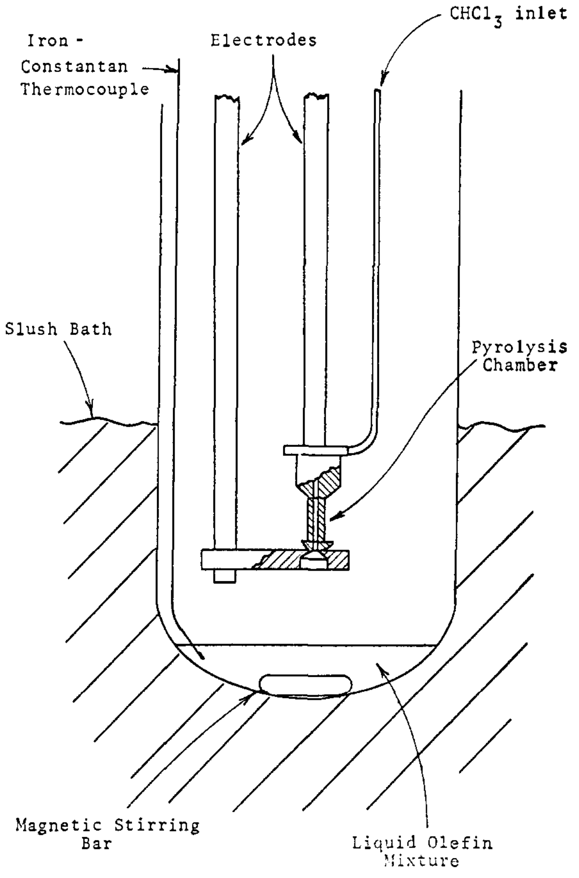

Figure 1. Reactor chamber.

Two different intermediates are formed in uncatalyzed and copper-catalyzed thermal decompositions of ethyl diazoacetate, the two intermediates exhibiting different *exo*/*endo* ratios for addition to cyclohexene.[2] Also the species from the uncatalyzed, but not the catalyzed, decompositions inserts into carbon–hydrogen bonds.[3] These differences have been attributed to the free carbene intermediate and a copper–carbene complex.[2,4,5]

α-Elimination reactions were first though to proceed through free carbene intermediates, but later it was recognized that organometallic intermediates could be the cyclopropanating reagent. This was the thesis of a lecture[6] illustrated by the behavior of carbethoxycarbene, above, and CH_2 from a variety of sources[7] (photolysis and pyrolysis of diazomethane, copper-catalyzed decomposition of diazomethane, $CH_2I_2 + Zn$,[8] $CH_3Cl + NaC_6H_5$: the use of first two systems result in addition to olefins and insertions, the remainder only additions). At this same symposium G. L. Closs discussed the α elimination of α-aryl alkyl halides, raising the possibility that carbenoids rather than free carbenes were intermediates.

Chlorocarbene[10] from thermolysis of chlorodiazomethane adds to double bonds and inserts into the C–H bonds; CHCl generated by α elimination (CH_2Cl_2 + RLi) adds to double bonds but does not insert into C–H bonds. Olefin reactivities toward CHCl from $CHClN_2$ and α eliminations were different as were the *syn*/*anti* ratios of the chlorocyclopropane products. The intermediate from α elimination (carbenoid) is distinctly different from the presumably free carbene produced from the diazo compound.

Kinetic evidence had been presented for the occurrence of a free CCl_2 intermediate in the basic hydrolysis of chloroform,[11,12] but these results cannot be extrapolated to include the olefin addition reaction. The majority of methods employed for generating CCl_2 involve intermediates of the type MCX_3, in some cases stable isolable species.[13–16] Considerable controversy centers about the reaction intermediate of dichlorocyclopropanation: is it free CCl_2, or does the reagent transfer CCl_2 directly to the olefin; if the latter, what are the properties of free CCl_2?

Wescott and Skell[17] reported on the chemistry of unambiguously free dichlorocarbene derived from high-vacuum chloroform pyrolyses. This free dichlorocarbene was generated under spin relaxing conditions: stereospecific *cis* additions to olefins were observed when this CCl_2 was trapped by olefins in condensed phase. An extension of this work is presented here. The relative rates of addition to olefins of free dichlorocarbene and the species derived from α elimination reactions[18] are compared.

Results

Free CCl_2 was generated by the pyrolysis of chloroform ($T \sim 1400$ °K) in a high-vacuum system (Figure 1) providing for molecular flow of the pyrolysate to the wall. The substances leaving the pyrolysis chamber (Figure 2) experienced a 10^{-5}-sec free flight before encountering the stirred solution of olefins in paraffin hydrocarbon solvent. By using appropriate solvents, liquid solutions of the olefins were obtained with negligible low-temperature vapor pressures, thus allowing the system to be evacuated without significant olefin vaporization. Chloroform was added at a rate of about 1 g/10 min; the olefin–chloroform ratio was usually >20; the substrate temperature was monitored by means of an iron–constantan thermocouple immersed in the reaction mixture.

Reactions were run in which olefin pairs were allowed to compete for the free dichlorocarbene. The resulting dichlorocyclopropane mixtures were separated by gas chromatography. The reaction products were identified by identity of vpc retention times and infrared, nmr,

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(2) P. S. Skell and R. M. Etter, *Proc. Chem. Soc.*, 443 (1961).

(3) W. von E. Doering and Knox, *J. Am. Chem. Soc.*, 78, 4947 (1956).

(4) P. Yates, *ibid.*, **74**, 4376 (1952).

(5) W. R. Moser, *ibid.*, **91**, 1135, 1141 (1969).

(6) P. S. Skell, 141st National Meeting of the American Chemical Society, Washington, D. C., March 1962, Carbene Symposium; for review of this subject, see W. Kirmse, *Angew. Chem. Intern. Ed. Engl.*, **4**, 1 (1965); G. Köbrich, *ibid.*, **6**, 41 (1967).

(7) H. S. Skovronek, Ph.D. Thesis, The Pennsylvania State University, 1961.

(8) It had been demonstrated by Simmons and Smith that cyclopropanation without insertion was the outstanding property of this reagent system; see ref 9.

(9) H. E. Simmons, E. P. Blanchard, and R. D. Smith, *J. Am. Chem. Soc.*, **86**, 1347 (1964); G. Wittig and F. Wingler, *Chem. Ber.*, **97**, 2139, 2146 (1964).

(10) G. L. Closs and J. J. Coyle, *J. Am. Chem. Soc.*, **87**, 4270 (1965).

(11) J. Hine and S. J. Ehrenson, *ibid.*, 80, 824 (1958).

(12) W. J. leNoble, *ibid.*, 87, 2434 (1965).

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

(14) D. F. Hoeg, D. I. Lusk, and A. L. Crumbliss, *ibid.*, **87**, 4147 (1965).

(15) G. Köbrich, K. Flory, and R. Fischer, *Chem. Ber.*, **99**, 1793 (1966).

(16) L. Andrews and T. G. Carver, *J. Phys. Chem.*, **72**, 1743 (1968).

(17) L. D. Wescott and P. S. Skell, *J. Am. Chem. Soc.*, **87**, 1721 (1965).

(18) P. S. Skell and M. S. Cholod, *ibid.*, in press.

Table I. Relative Reactivities of Olefins with Free CCl_2 (1400° $CHCl_3$ Pyrolysate)

Olefin pair	Reaction temp, °C	Olefin ratio	Dichlorocyclopropane ratio	k/k
1-Octene–cyclohexene	-78 ± 1	7.48	0.68 ± 0.07	$0.091 \pm 0,01$
1-Octene–cyclohexene	-127 ± 2	6.42[a]	0.37 ± 0.03	0.057 ± 0.006
Isobutylene–tetramethylethylene	-125 ± 3	1.94[a,b]	1.2 ± 0.1	2.3 ± 0.3
Isobutylene–tetramethylethylene	-125 ± 3	1.94[c]	1.3 ± 0.1	2.5 ± 0.2
Trimethylethylene–isobutylene	-125 ± 3	1.50[d]	1.4 ± 0.1	2.1 ± 0.2

[a] Pentane diluent. [b] After reaction, ratio 2.1, presumably the result of reaction with HCl, etc. [c] Twice as much pentane diluent. [d] Isopentane diluent.

and mass spectra with authentic samples. The major by-products were tetrachloroethylene and hexachloroethane, along with smaller amounts of trichloroethylene, products of olefin chlorination, and minor unidentified products.

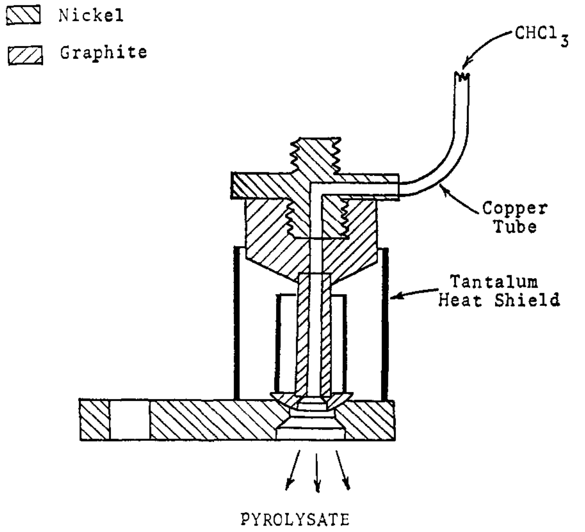


Figure 2. Pyrolysis zone.

The competition results are given in Table I.

Discussion

The relative reactivities for free dichlorocarbene fall on the extrapolated Arrhenius plots[18] of relative reactivities determined for the intermediate of {MCX_3 + olefin} reactions (Figure 3). The correspondence of relative reactivity values is shown in Table *II*. A common Arrhenius line is obtained independent of the mode of generation of the CCl_2, α elimination, or chloroform pyrolysis. Since both methods of generating CCl_2 give an intermediate showing the same selectivity it is probable that these intermediates are the same, free CCl_2.

Table II

Olefin pair	Competition temp ±3°	Log k/k ± 0.06	Log k/k calcd[a]
cis-2-Butene–isobutylene	−152	−0.86	−0.79
	−127	−0.75	−0.70
1-Octene–cyclohexene	−127	−1.25	−1.19
	−78	−1.04	1.02
Tetramethylethylene–isobutylene	−125	0.38	0.43
Trimethylethylene–isobutylene	−125	0.32	0.43

[a] Condensed phase α eliminations, extrapolated from data over the range 0 to −100°.[18]

Jones, *et al.*,[19] tentatively came to this same conclusion when they found that CCl_2 transferred to olefins during photolysis of 1,1-dichloro-2-phenylcyclopropane at −78° had the same selectivity toward olefins as the intermediate from *t*-BuOK and $CHCl_3$. The most probable explanation was that both reactions involved free CCl_2, but it was not possible to eliminate the direct transfer of dichlorocarbon from an electronically excited 1,1-dichloro-2-phenylcyclopropane molecule to the olefins, similar to the postulates of transfer of CCl_2 from $MCCl_3$ (*vide infra*).

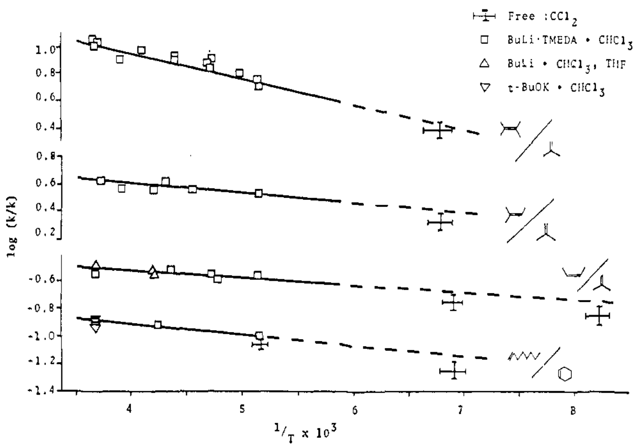


Figure 3. Arrhenius plots.

Seyferth and Burlitch[20] reached the same conclusion basing their argument on the similarity of relative rates (olefin additions) for the intermediate from thermolyses of Cl_3CCO_2Na and $PhHgCCl_2Br$; this is inconclusive evidence since in both cases the transfer of CCl_2 from MX is common to both reagents. Seyferth, Mui, and Burlitch[21] presented kinetic observations consistent with the reversible formation of free CCl_2: the rate of disappearance of $PhHgCCl_2Br$ is enhanced by olefins and *retarded by PhHgBr;* this requires an intermediate which can react with both of these substances.

Two groups[12,13] have independently investigated the properties of $LiCCl_3$ at low temperatures in THF. Produced by the action of BuLi on $CHCl_3$ or $CBrCl_3$ at $<-100°$, $LiCCl_3$ was found to be a partially soluble material, stable indefinitely even in the presence of olefins. At higher temperatures ($\sim -70°$), in the absence

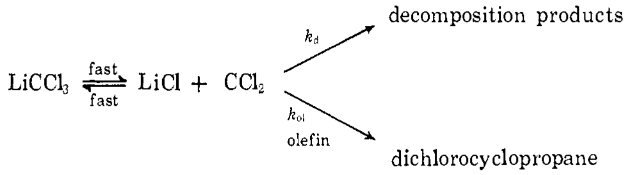
(19) M. Jones, Jr., W. H. Sachs, A. Kulczycki, Jr., and F. J. Walker, *J. Am. Chem. Soc.*, **88**, 3167 (1966).

(20) D. Seyferth and J. M. Burlitch, *ibid.*, **86**, 2730 (1964).

(21) D. Seyferth, J. Y.-P. Mui, and J. M. Burlitch, *ibid.*, **89**, 4953 (1967).

of olefins, the precipitate dissolved accompanied by a dramatic temperature increase and the formation of a dark polymer. In the presence of olefins the decomposition was accelerated and good yields of the corresponding dichlorocyclopropanes were obtained. They proposed that CCl_2 was not the cyclopropanating reagent, arguing that olefins should not accelerate its formation. Although these authors[14,15] favor the direct reaction of $LiCCl_3$ with olefin, this mechanism is not imperative. Three considerations weaken their conclusion.

(1) The observation that in the presence of olefin $LiCCl_3$ is consumed more rapidly than in the absence is also consistent with a fast reversible formation of CCl_2 from $LiCCl_3$ as follows.

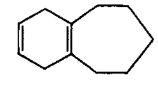


In the absence of olefin the rate of decomposition is determined by k_d; dichlorocyclopropane formation adds to this rate. This explanation is similar to that of Seyferth[21] for $PhHgCCl_2Br$ thermolyses. (2) The electrophilicity of the reagent is not consonant with the carbanion formulation, MCX_3. (3) The competition data in Table I show $LiCCl_3$–olefin reactivities plot on the same Arrhenius line as those for free CCl_2.

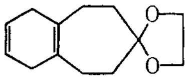
There remains no substantive evidence for an intermediate other than free CCl_2 in dichlorocyclopropanation of olefins, regardless of source. Dichlorocarbene complexed to solvent or other nucleophilic species is not sufficiently reactive in transfer of CCl_2 to olefins; $LiCHCl_2$ and MCH_2X do transfer directly to olefins the fragments CHCl and CH_2, respectively. Of course it does not follow that MCX_3 is incapable of participating in a direct transfer of CX_2 to some as yet unstudied substrate.[22]

Acknowledgment. We acknowledge the financial support of the Air Force Office of Scientific Research.

[22] Vogel[23] has observed that CCl_2 from $CHCl_3$ + base adds to each of the double bonds in



at about the same rate. In contrast, CCl_2 addition to the internal double bond in



occurs three times faster than to the peripheral double bond. This enhanced reactivity can be ascribed to initial formation of a carbene–oxygen complex followed by an intramolecular CCl_2 transfer to the nearer double bond.

[23] E. Vogel, private communication.

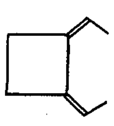
The Stereochemistry of Allene Dimerization[1]

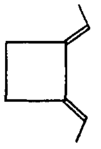
Thomas L. Jacobs, John R. McClenon, and Oliver J. Muscio, Jr.

Contribution No. 2390 from the Department of Chemistry, University of California, Los Angeles, California 90024. *Received May 20, 1969*

Abstract: The main dimer of chloroallene has been shown to have the structure and stereochemistry shown in IXa. The main dimer of 1-chloro-3-methyl-1,2-butadiene has structure IV, but the stereochemistry of the ring chlorines remains in doubt. Ozonization of IV gave *dl*-α,α'-dichlorosuccinic acid, but the dipole moment (2.63 D) does not agree with values calculated for *cis* (3.50 D) or *trans* (1.44 D) isomers. The mechanism of allene dimerizations is discussed.

Allene dimerization which results in the formation of substituted 1,2-dimethylenecyclobutanes has been known and studied for more than 50 years, but, until recently, little was known of the stereochemistry of this reaction. Vicinal substituents on the cyclobutane ring may lie either *cis* or *trans* to each other, and those on the exocyclic double bonds may face either inward toward each other (A), outward (B), or be unsymmetrically arranged (C).


A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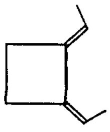
C

Some recent work has indicated that halogen cyclobutyl substituents may be *trans* to each other. Ozonolysis of I, the major dimer of 1-bromo-3-methyl-1,2-butadiene,[2] and of II, the dimer of tribromoallene,[3] yielded *dl*-α,α'-dibromosuccinic acid, which was taken as proof of *trans*-bromines in these dimers; the nmr spectrum of the dimer mixture from trichloroallene[4] was interpreted as suggesting that the chlorines were *trans* in the major isomer, assigned structure III.

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[1] This research was supported by Grants GP-5530 and GP-8489 from the National Science Foundation, and by earlier grants from the National Science Foundation and from the U. S. Army Research Office (Durham). Many of the results are taken from the Ph.D. Thesis of John R. McClenon, University of California, Los Angeles, 1964.

[2] T. L. Jacobs and W. L. Petty, *J. Org. Chem.*, 28, 1361 (1963).

[3] A. Roedig and N. Detzer, *Liebigs Ann. Chem.*, 710, 1 (1967).

[4] A. Roedig and N. Detzer, *Angew. Chem.*, 80, 482 (1968).