

Table VIII. Competitive Chlorinations^a

Compd. A	Compd. B	Relative reaction, A/B ^b
CH ₃ C≡CCH ₃	Toluene	2.60 ± 0.16 (3)
C ₆ H ₅ C≡CCH ₃	Toluene	2.86 ± 0.04 (2)
C ₆ H ₅ C≡CC ₂ H ₅	Toluene	6.75 ± 0.46 (2)
C ₆ H ₅ C≡CCH(CH ₃) ₂	Toluene	11.4 ± 1.2 (2)
Mesitylene	Toluene	4.32 ± 0.7 (3)
C ₆ H ₅ C≡CCH ₂ C ₆ H ₅	Mesitylene	7.06 ± 0.4 (3)
C ₆ H ₅ CH=CHCH ₂ C ₆ H ₅	Mesitylene	4.56 ± 0.95 (3)
C ₆ H ₅ CH ₂ CH=CH ₂	Mesitylene	1.07 ± 0.01 (2)
C ₆ H ₅ CH=CHCH ₃	Mesitylene	1.81 ± 0.10 (2)
C ₆ H ₅ CH=CHCH ₂ CH ₃	C ₆ H ₅ CH=CHCH ₃	1.60 ± 0.01 (2)
C ₆ H ₅ CH=CHCH(CH ₃) ₂	C ₆ H ₅ CH=CHCH ₂ CH ₃	1.03 ± 0.01 (2)

^a HO°. ^b Per molecule, number in parentheses is number of experiments and experimental error spread of duplicate or triplicate runs.

identified as 3-chloro-1-phenylpropyne by elemental analysis, and by infrared and n.m.r. spectra. *cis*- and *trans*-1,2-dichloro-1-phenylpropene were identified by g.l.c. retention time and n.m.r. spectra. Several other additional products were detected in minor amounts. Although the chief one appeared to be a dimer which lost HCl on heating, it was not further identified.

The authentic dichloro-1-phenylalkenes used in the above comparisons were prepared by chlorine addition to the corresponding acetylenes and separated by g.l.c. In each case the *trans* isomer was the major product, and stereochemistry was assigned on the basis of n.m.r. and infrared spectra. In n.m.r. spectra, *trans* isomers showed phenyl multiplets and *cis* isomers sharp singlets,³⁰ while in infrared spectra, *cis* isomers

showed strong absorption at 6.16 μ, virtually lacking in the *trans* compounds.³¹

Competitive experiments were run in sealed degassed tubes in CCl₄ solution (0.9–1.8 M in each hydrocarbon) containing suitable internal standards (chlorobenzene or *o*-dichlorobenzene) and irradiated in a 40° water bath, essentially as in previous work.² Under these conditions of dilution there was no fast dark reaction, and relative reactivities were calculated in the usual way² from g.l.c. analysis for unreacted hydrocarbons. Actual pairs investigated are listed in Table VIII.

(30) For comparison, aromatic protons of *cis*-stilbene yield a sharp singlet, while the *trans* isomer gives a doublet: D. Y. Curtin, H. Gruen, and B. A. Shoulders, *Chem. Ind. (London)*, 1205 (1958).

(31) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 38, 39.

Reactions of Free, Ground-State Dichlorocarbene

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Dichlorocarbene was generated under vacuum by the pyrolysis of chloroform or carbon tetrachloride, at temperatures in the neighborhood of 1500°, and allowed to react with olefinic substrates on a liquid nitrogen cooled surface. The products are the expected 1,1-dichlorocyclopropanes. The additions to cis- and to trans-2-butenes were stereospecific. Free CCl₂, the precursor of these products, had been generated under spin relaxing conditions, thus indicating a singlet ground state.

Since all studies of the chemical properties of CCl₂ have been carried out in condensed phase, where association of the carbene with solvent or other Lewis bases may occur, one must conclude that the properties which have been reported may not be those of the free carbene. The recent report of Miller and Whalen that LiCCl₃ in ether is thermally¹ stable at -100° and yet reacts readily with cyclohexene to produce 7,7-dichloronorcaradiene raises with force the alternative

that a free carbene was not an intermediate in earlier studies. A parallel study, equally forceful toward this conclusion with reference to CHCl, has been reported by Closs and Coyle.² We have also noted a number of instances in which solvents affect the selectivities of carbenes.

The singlet designations for CX₂ were made to accord with the observations that additions to olefins were stereospecific and electrophilic in selectivity. Are these the properties of CX₂ or a complex?

Thus it became a matter of some urgency to examine the properties of CX₂ unambiguously free. This was accomplished by pyrolyzing CHCl₃ and CCl₄ (1500°) under high vacuum, where free flight from the generating source to the cold walls (-196°) was required to encounter an olefinic reactant. Under these circumstances the primary reactions must be attributed to the free carbene.

Three pyrolysis techniques were applied to chloroform and carbon tetrachloride thus providing a wide range of residence times in the pyrolysis zones: (a) allowing the vapors to enter a heated porous graphite

(1) W. T. Miller, Jr., and D. M. Whalen, *J. Am. Chem. Soc.*, **86**, 2089 (1964).

(2) G. L. Closs and J. J. Coyle, *ibid.*, **84**, 4350 (1962).

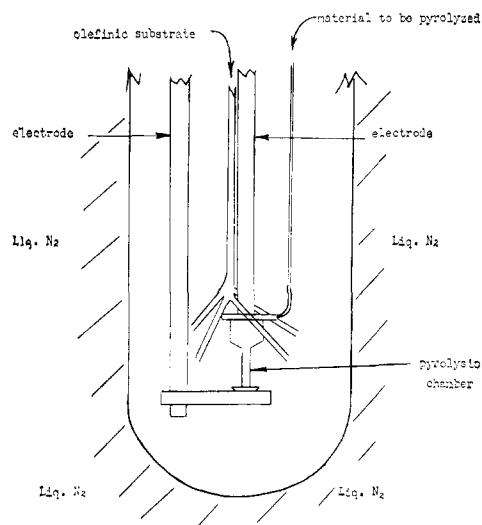
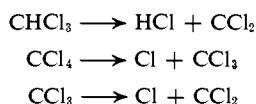


Figure 1. Reaction system.

chamber, (b) allowing the vapors to enter a heated graphite chamber perforated by a number of effusion holes, and (c) passing a molecular beam through a heated tungsten grid.

The surrounding apparatus is shown in Figure 1 and a detail of the perforated pyrolysis chamber in Figure 2. The system was evacuated to 10^{-4} mm. or less to ensure a mean free path in excess of the dimensions of the reaction vessel. Gaseous olefin was admitted (Figure 1) at a rate which did not affect the total pressure significantly. The vessel was cooled with liquid nitrogen to ensure complete condensation of reactants on collision with the wall (pyrolysis products from the olefin were not observed). The products were recovered by conventional procedures.

Previous pyrolysis studies of chloroform and carbon tetrachloride had demonstrated that CCl_2 could be detected by mass spectrometry.³ Although there is some lack of accord, kinetic studies⁴ support the following decomposition mechanisms.



Directing a molecular beam of chloroform at a heated tungsten grid (1450°) resulted in decomposition of 1% of the chloroform. The pyrolysis products were trapped in a large excess of isobutylene ($\text{C}_4\text{H}_8-\text{CHCl}_3 \sim 10^3$). The expected 1,1-dichloro-2,2-dimethylcyclopropane was isolated in 25% yield, the other products (75%) falling in the expected regions for mono- and dichloro C_4 compounds. No further identification was attempted other than to verify the absence of C_2Cl_4 among the products, a major product with longer residence times in the heated zones (*vide infra*).

At the other extreme, when the pyrolyses were carried out using the nonperforated porous graphite tube the only product observed was hexachlorobenzene,

(3) L. P. Blanchard and P. LeGoff, *Can. J. Chem.*, **35**, 89 (1957).

(4) A. E. Shilov and R. D. Sabirova, *Zh. Fiz. Khim.*, **33**, 1365 (1959) (*Russ. J. Phys. Chem. English Transl.*, **33**, 29 (1959)); A. E. Shilov and R. D. Sabirova, *Russ. J. Phys. Chem. English Transl.*, **34**, 408 (1960); G. P. Semeluk and R. B. Bernstein, *J. Am. Chem. Soc.*, **79**, 46 (1957).

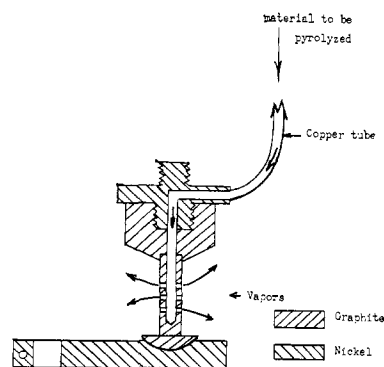


Figure 2. Pyrolysis chamber.

one of the products reported by Schmeisser and Schröter⁵ in the pyrolysis of carbon tetrachloride.

Most of the experiments reported in the present work were carried out with residence times between the extremes using the perforated graphite tube (Figure 2) in which conversions of the chloro compound were approximately 10%.

Examination of the products other than those resulting from CCl_2 showed the presence of some 2–5% of the HCl adducts of the olefin and dihalides, 40–60% in the case of carbon tetrachloride pyrolyses, and 10–15% in the case of chloroform pyrolyses. The relative percentages of products from CCl_2 are tabulated in Tables I and II.

Table I. Trapping of CCl_2 by *i*- C_4H_8

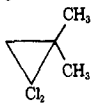
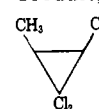
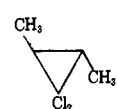
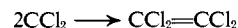
Pyrolysis of	Product, %	
	C_2Cl_4	
CHCl_3	65	35
CCl_4	85	15

Table II. Trapping of CCl_2 by *cis*- and *trans*-2-Butene

Trapping olefin	Product, %		
	C_2Cl_4		
A. CHCl_3 Pyrolyses			
<i>cis</i> -2- C_4H_8	83	17	0
<i>trans</i> -2- C_4H_8	86	0	14
B. CCl_4 Pyrolyses			
<i>cis</i> -2- C_4H_8	86	14	0
<i>trans</i> -2- C_4H_8	84	0	16

Discussion

The preferred formation of C_2Cl_4 at longer residence times in the heated zones indicates that it is formed in the pyrolysis chambers, probably by dimerization of



CCl_2 , although a pathway *via* dechlorination of C_2Cl_6

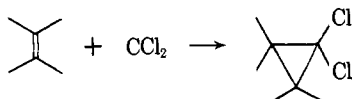


(5) M. Schmeisser and H. Schröter, *Angew. Chem.*, **72**, 349 (1960); M. Schmeisser, H. Schröter, H. Schilder, J. Massone, and F. Roskopf, *Ber.*, **95**, 1648 (1962).

cannot be eliminated from consideration. Hexachlorobenzene, obtained at much longer residence times, may result from trimerization of dichloroacetylene.

The neutral, one-carbon radicals which might survive the pyrolysis zone are CCl_3 , CHCl_2 , CCl_2 , CH , and CCl . Reactions of the first two are well known in solution radical chemistry; there has been no report of cyclopropanes from systems comprising olefins CCl_3 and CHCl_2 . Although the monovalent carbon radicals have not been studied in olefin-containing systems it is difficult to imagine cyclopropane formation from these substances in a dilute olefin matrix. Monochlorocarbene reacts with olefins to produce monochlorocyclopropanes, thus leaving CCl_2 as the only reasonable precursor of the dichlorocyclopropanes.

The reactions of isobutylene and the 2-butenes lead to dichlorocyclopropanes only, there being no indication of products which might be attributable to an insertion reaction.



The additions of dichlorocarbene to the isomeric 2-butenes are cleanly stereospecific, just as observed when it is generated in condensed phase from base and haloform.⁶ *The uncomplexed dichlorocarbene intermediate must be in a singlet state,⁷ and the conditions employed in its generation make it very probable this is also the ground state.* The ground-state designation for the CCl_2 trapped in these experiments is justified on several grounds.

1. There is no spin requirement for the decomposition of CCl_3 to CCl_2 and Cl , so that presumably the more stable form would be produced. Even if singlet and triplet CCl_2 had the same energies the expected triplet to singlet ratio would be 3.

2. The interior of the graphite chamber is an ideal zone for spin relaxation to the most stable spin state, by any of three routes: (a) collision with a doublet atom or molecule (Cl , CCl_3 , etc.), (b) collision with free electrons (thermionic emission), and (c) collision with the graphite walls which, by virtue of conducting electron bands, should behave as a paramagnetic catalyst.

Experimental

The pyrolyses were carried out by allowing the halogen compounds to pass from a 5-l. storage bulb through the hot zone, maintained at temperatures of the order of $1450 \pm 50^\circ$ by applying an a.c. potential, and then into the evacuated reaction chamber. The temperature was measured with an optical pyrometer. The rate of flow of the halogen compound was maintained constant and measured by observing the fall of pressure in the storage bulb. The pressure in the large chamber was of the order of 10^{-4} mm. (measured by a hot filament ionization gauge) during the reaction and the walls of the chamber were cooled by liquid nitrogen. During the pyrolysis, the olefin was ad-

(6) W. von E. Doering and W. A. Henderson, *J. Am. Chem. Soc.*, **80**, 5274 (1958).

(7) P. S. Skell and R. C. Woodworth, *ibid.*, **78**, 4496 (1956); P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956); R. C. Woodworth and P. S. Skell, *ibid.*, **81**, 3383 (1959).

mitted through the independent inlet system at a constant rate, monitored by a mercury differential manometer. The runs generally were of 5- to 60-min. duration, with rates of addition of 1 g. of halogen compound and 20 g. of olefin per 10 min. On completion the entire reaction mixture was pumped at high vacuum through a trap at -95 and -196° , the products and the unreacted halogen compound remaining in the former and the olefin in the latter.

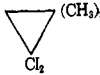
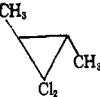
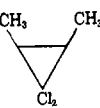
The perforated graphite tube (see Figure 2) was constructed from 0.125-in. diameter ultrapure (National Carbon Co.) graphite rod 1.125 in. long and drilled $1/16$ in. in diameter by 1 in. deep. The perforations (four holes) were drilled with a 0.021-in. drill. This was inserted into the larger graphite block attached to one electrode. In the case of the nonperforated graphite tube the entire graphite assembly was turned out of a 1-in. diameter ultrapure graphite rod to the same dimensions as the perforated assembly; the large upper portion was coated with an impervious cement to assure diffusion through the heated portion only. For pyrolyses on the open tungsten grid a G. E. DRS PH/IM/T20 MP projector lamp, from which the envelope had been removed, was mounted between the electrodes.

Gas chromatographic analyses were carried out on the products and in most cases individual components of the mixture were collected and identity was confirmed by infrared analysis.

Authentic samples of the 1,1-dichlorocyclopropanes were prepared by the procedure of Doering and Hofmann⁸ for comparison of gas chromatographic retention times and infrared spectra.

In cases where *cis*- or *trans*-2-butene were used as the trapping olefin the purity was checked on a 50-ft. hexanedione column (0°) before and after the reaction. In no case was any isomerization noted (see Table III).

Table III. Relative Retention Times of Compounds of Interest

Compd.	Column A (75°) ^a	Column B (60°) ^b
<i>t</i> -Butyl chloride	0.36	
<i>sec</i> -Butyl chloride		0.20
Chloroform	0.39	0.42
Carbon tetrachloride	0.42	0.30
C_2Cl_4	1.00	1.00
<i>meso</i> -2,3-Dichlorobutane	1.31	1.09
<i>dl</i> -2,3-Dichlorobutane	1.49	1.31
	1.39	
	1.48	1.10
	1.74	1.44

^a Column A, 22-ft. 0.25-in. o.d. copper column packed with 20% fluorosilicone on Gas Chrom Z. ^b Column B, 20-ft. 0.25-in. o.d. copper column packed with 20% tricresyl phosphate on Gas Chrom P.

Both *meso*- and *dl*-2,3-dichlorobutanes were obtained from either *cis*- or *trans*-2-butene, thus neces-

sitating an additional procedure for detection of the *trans*-dichlorodimethylcyclopropane. This was accomplished by trapping the appropriate fraction from a gas chromatographic separation and examining the infrared spectrum of the sample, strong absorption

bands at 8.73 and 9.20 μ being used for identification and determination of yield.

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Electron-Transfer Reactions of Aromatic Radical Ions

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Contribution from the Department of Chemistry, University of Kansas, Lawrence, Kansas. Received January 20, 1965

Studies have been made of one-electron oxidation-reduction reactions between normally stable molecules and resonance-stabilized radical ions. The combined techniques of electron paramagnetic resonance spectroscopy and electrochemistry rendered such reactions easy to follow. In all of the cases studied the reaction was predictable from a knowledge of the relative affinity for the extra electron by the two reactants involved. The reaction rates, although not specifically determined, were all quite rapid since all reactions were essentially complete within 1 min. from initial mixing. Steric and solvent effects were investigated and were found not to change the above results.

Considerable interest has developed concerning electron-transfer reactions of aromatic systems following the extensive studies of Russell and co-workers on spontaneous formation of radical anions in basic media and electron transfer between various anions and unsaturated electron-acceptor systems.¹⁻⁴ Throughout these studies one-electron-transfer reactions predominated, but the products and rates of some of the reactions reflected a variety of effects due to the mode of formation of the anions, influence of the solvent, etc. We have examined the simplest of electron interchange reactions between radical ions and various unsaturated aromatic molecules using electron paramagnetic resonance (e.p.r.) methods. The radical ions were generated electrochemically so that at least one variable, the mode of formation of the ion radical, is essentially invariant. It might be claimed that such studies are trivial and that the order and extent of such interactions could be predicted *a priori* via the formal reduction potentials ($E^{0'}$ values) of the compounds. This principle has never been satisfactory in inorganic oxidation-reduction reactions and there is no reason to presuppose it holds universally for organic processes. As examples of inorganic oxidation-reduction processes, which, in spite of having very favorable thermodynamic driving forces, do not proceed to any appreciable extent at room temperature without catalysts, are the oxida-

tion of Tl(I) by Ce(IV) and the oxidation of Sn(II) by Fe(III) in high acidities (without chloride present).^{5,6} The present studies were carried out to investigate any such anomalies in one-electron interactions between aromatic species. Only a few studies with a limited variety of compounds have appeared in this area previously.⁷⁻¹⁰

Experimental

The radical ions (R^- or R^+) were generated *via* standard external electrochemical techniques.¹¹ The radical ions were then transferred to a mixing chamber where they were allowed to interact with the nonradical aromatic system. A portion of this reaction mixture was transferred to the e.p.r. cell. All transfers and mixing were done in a closed system with a stream of nitrogen excluding air contact. The nitrogen also provided for stirring in the mixing chamber. The

Table I. Reaction Potentials of Aromatic Systems in DMF

No.	Parent compd.		$E^{0'}$ ^a
	Name		
1	<i>trans</i> -Stilbene		-2.22
2	1,5-Naphthalene-disulfonate		-2.15
3	Pyrazine		-2.09
4	Anthracene		-1.95
5	<i>p</i> -Nitroaniline		-1.41
6	9-Fluorenone		-1.29
7	<i>p</i> -Nitrotoluene		-1.18
8	Nitrobenzene		-1.13
9	<i>p</i> -Chloronitrobenzene		-1.04
10	9,10-Anthraquinone		-0.87
11	<i>p</i> -Nitrobenzotrile		-0.83
12	<i>p</i> -Nitropyridine N-oxide		-0.78
13	<i>p</i> -Benzoquinone		-0.48

^a $E^{0'}$ in v. vs. s.c.e. according to reaction 3. The uncertainties in $E^{0'}$ are ± 0.05 v. for pyrazine and ± 0.02 v. for all other systems.

(5) F. R. Duke, "Treatise on Analytical Chemistry," Vol. 1, I. M. Kolthoff and P. J. Elving, Ed., Interscience Publishers, Inc., New York, N. Y., 1959, Chapter 15.

(6) J. J. Lingane, "Electroanalytical Chemistry," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1958, p. 133.

(7) G. J. Hoijsink, E. deBoer, P. H. van der Meij, and W. P. Weijland, *Rec. trav. chim.*, **75**, 487 (1956).

(8) D. E. Paul, D. Lipkin, and S. I. Weissman, *J. Am. Chem. Soc.*, **78**, 116 (1956).

(9) D. L. Maricle, *Anal. Chem.*, **35**, 683 (1963).

(10) J. P. Paris, J. D. Gorsuch, and D. M. Hercules, *ibid.*, **36**, 1332 (1964).

(11) R. N. Adams, *J. Electroanal. Chem.*, **8**, 151 (1964).

(1) G. A. Russell and E. G. Janzen, *J. Am. Chem. Soc.*, **84**, 4153 (1962).

(2) G. A. Russell, A. J. Moye, and K. Nagpal, *ibid.*, **84**, 4154 (1962).

(3) G. A. Russell, E. G. Janzen, and E. T. Strom, *ibid.*, **84**, 4155 (1962).

(4) G. A. Russell, E. G. Janzen, and E. T. Strom, *ibid.*, **86**, 1807 (1964).