

Halogenation with Copper(II) Halides. Halogenation of Olefins with Complexed Copper(II) Halides

WILLIAM C. BAIRD, JR.,* JOHN H. SURRIDGE, AND MARIS BUZA

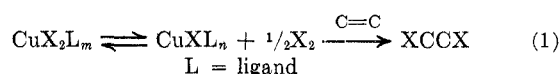
Corporate Research Laboratories, Esso Research and Engineering Company, Linden, New Jersey 07036

Received April 30, 1971

A new method for the halogenation of olefinic bonds without the utilization of molecular halogens is described. This synthetic technique is based on the reaction of olefins with copper(II) halides in the presence of strong coordinating agents. Simple olefins are converted to vicinal dihaloalkanes in good to excellent yields. Conjugated diolefins experienced predominately 1,4 addition. Complexed copper(II) halides in combination with different halide donors afforded an *in situ* synthesis of pseudohalogen compounds, which yielded ultimately chloriodo- and chlorobromoalkanes. The general scope of these reactions has been demonstrated for a variety of olefinic substrates and for a number of ligands. The synthetic utility and the mechanistic implications of these reactions are discussed.

While substitutive halogenation of reactive organic compounds by copper(II) halides has been known for several decades,¹ halogen addition in copper(II) halide-olefin reactions has been observed relatively recently. These addition reactions have involved either vapor phase halogenation over supported copper(II) halides² or liquid phase reactions at temperatures exceeding 100°. Under these circumstances thermal dissociation of the copper salt was considered to be an important factor.

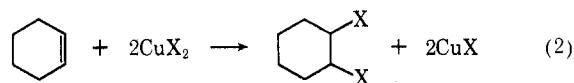
A previous paper from this laboratory has described copper(II) bromide-olefin systems where bromination occurred spontaneously at room temperature and was not dependent on thermal treatment.⁴ These results were rationalized on the basis of the influence of copper ion complexation on the reaction. This view was predicated on the known sensitivity of the relative stabilities of metal ion oxidation states to coordination with strong π -bonding ligands.^{5,6} In this case ligand induced dissociation of copper(II) halide in the presence of olefin yielded the corresponding halogen addition product (eq 1).^{4,7-9}



On the basis of these preliminary results a general investigation of the ability of complexed copper(II) halides to function as selective olefinic halogenation reagents was initiated. This paper presents the synthetic chemistry that has evolved from this program.

Results

Ligands for Copper(II) Halide Halogenation.—Potential ligands for copper(II) halide halogenation were screened utilizing the reaction of cyclohexene with copper(II) chloride and bromide as a model system (eq 2). Effective ligands are listed in Table I. Liquid



ligands were employed in stoichiometric excess; if a solid ligand, or a catalytic quantity of a ligand, were involved, the reaction was performed in excess olefin or a suitable inert diluent.

The most beneficial ligands were those nitrogen, phosphorus, and sulfur compounds that stabilize copper(I) through strong back donation.⁵ Acetonitrile emerged as a particularly useful reagent due to its effectiveness as a stabilizing ligand^{8,9,10} and the simplicity of the synthetic procedure. Powerful complexing agents like hexamethylphosphoramide, tetramethylguanidine, *N,N,N',N'*-tetramethylethylene- and -propanediamine were totally ineffective, a reflection of the preferential stabilization of copper(II) by these *n* donors.⁵ That the olefinic bond itself can promote halogenation^{4,11} is evidenced by reaction in solvents whose coordination with metal ions has no π component and a weak to moderate σ bond. Representative of these diluents are oxygenated compounds and dimethylformamide, which are included in Table I for convenience although they are not ligands in the strictest sense. Their function is to solubilize the reactants.

All of the ligands in Table I were capable of achieving bromination; only nitriles were effective for chlorination. This distinction is attributed to two factors. One was the relative lability of the copper(II) salts toward ligand-induced dissociation.^{9a} The other was

(1) Acetone: (a) V. Kohlschütter, *Chem. Ber.*, **27**, 1110 (1904). Ketones olefins: (b) J. K. Kochi, *J. Amer. Chem. Soc.*, **77**, 5274 (1955); (c) J. K. Kochi and D. M. Mog, *ibid.*, **87**, 522 (1965), and references cited therein; (d) E. R. Glazier, *J. Org. Chem.*, **27**, 2937, 4397 (1962); (e) P. B. Sollman and R. M. Dodson, *ibid.*, **26**, 4180 (1961); (f) K. B. Doifode and M. G. Marathe, *ibid.*, **29**, 2025 (1964); (g) L. C. King and G. K. Ostrum, *ibid.*, **29**, 3459 (1964); (h) A. W. Fort, *ibid.*, **26**, 765 (1961); (i) E. W. Kosover, W. J. Cole, G. S. Lou, D. E. Cardy, and G. Meisters, *ibid.*, **28**, 630 (1963); (j) E. W. Kosover and G. S. Lou, *ibid.*, **28**, 633 (1963). Aromatics: (k) D. C. Nonhebel, *J. Chem. Soc.*, 1216 (1963); (l) D. C. Nonhebel, *Proc. Chem. Soc.*, 307 (1961); (m) J. C. Ware and E. F. Borchert, *J. Org. Chem.*, **26**, 2263, 2267 (1961); (n) P. Kovacic and K. E. Davis, *J. Amer. Chem. Soc.*, **86**, 427 (1964). Carboxylic acids: (o) R. Louw, *Chem. Commun.*, 544 (1966). Chelates: (p) R. H. Barker, M. Kato, G. W. McLaughlin, and H. B. Jonassen, *Bull. Chem. Soc. Jap.*, **39**, 1327 (1966).

(2) (a) R. P. Arganbright and W. F. Yates, *J. Org. Chem.*, **27**, 1205 (1962); (b) P. P. Nicholas and R. T. Carroll, *ibid.*, **33**, 2345 (1968); (c) British Patent 907,435 (1962).

(3) (a) H. E. Holmquist, Canadian Patent 771,217 (1967), 771,218 (1967); (b) C. E. Castro, *J. Org. Chem.*, **26**, 4183 (1961); (c) C. E. Castro, E. J. Gaughan, and D. C. Owsley, *ibid.*, **30**, 587 (1965), and references cited therein; (d) T. Kayono, *Bull. Chem. Soc. Jap.*, **43**, 1439, 3501 (1970); (e) K. Ichikawa, S. Uemura, Y. Takagaki, and T. Hiramoto, *Bull. Jap. Petrol. Inst.*, **12**, 77 (1970); (f) M. L. Spector, H. Heinemann, and K. D. Miller, *Ind. Eng. Chem.*, **6**, 327 (1967).

(4) W. C. Baird, Jr., and J. H. Surridge, *J. Org. Chem.*, **35**, 2090 (1970).

(5) H. J. Emeleus and J. S. Anderson, "Modern Aspects of Inorganic Chemistry," Routledge and Kegan Paul Ltd., London, 1960, Chapter 6.

(6) J. C. Barnes and D. C. Hume, *Inorg. Chem.*, **2**, 444 (1963).

(7) W. Schneider and A. V. Zelevsky, *Helv. Chim. Acta*, **46**, 1848 (1963).

(8) (a) J. Gazo, *Chem. Zvesti.*, **19**, 826 (1965); *Chem. Abst.*, **64**, 4575c (1966); (b) H. C. Mruthyunjaya and A. R. Vasudeva Murthy, *Indian J. Chem.*, **7**, 403 (1969).

(9) (a) J. N. Cislava, G. Ondrejovic, and J. Gazo, *Z. Chem.*, **6**, 429 (1966);

(b) M. Asscher and D. Vofsi, *J. Chem. Soc.*, 1887 (1963).

(10) R. A. Walton, *Quart. Rev., Chem. Soc.*, **19**, 126 (1965).

(11) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience, New York, N. Y., 1966, pp 680, 772.

TABLE I

LIGANDS FOR COPPER(II) HALIDE HALOGENATIONS ^a			
Nitrogen compd	Phosphorus compd ^b	Sulfur compd	Oxygen compd
Acetonitrile ^{b,c}	Triphenylphosphine	Thiophene	Tetrahydrofuran
Benzonitrile ^{b,c}	Triphenylphosphine oxide	Tetrahydrothiophene	Methanol
Glutaronitrile ^b	Triphenyl phosphite	Sulfolane	Acetic acid
Succinonitrile ^b	Methyl phosphate	Dimethyl sulfoxide	Acetone
Tetracyanoethylene ^b	Methyl phosphite	Sulfur dioxide	
Dimethylformamide	Butyl phosphite		
	<i>tert</i> -Butyl phosphite		
	1,2-Bis(diphenylphosphinoethane)		
	4-Methyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane		

^a Yields ranged from 20 to 95%. ^b May be used catalytically for copper(II) bromide bromination. ^c Most effective ligands for copper(II) chloride chlorination.

halogenation of the ligand, particularly those bearing active ring systems (triphenyl phosphite, thiophene) or active hydrogens (alkyl phosphites, dimethyl sulfoxide). This halogenation is believed to occur within the copper(II) complex itself^{3c,12} and was particularly prevalent with copper(II) chloride. These difficulties did not manifest themselves in the more labile copper(II) bromide reactions.

The copper(II) halide reactions occurred with a minimum of solvent (ligand) participation to give β -haloalkyl products. The comparative data of Table II

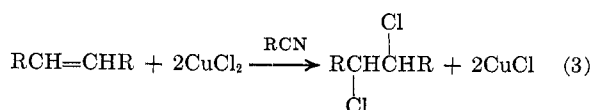
TABLE II
BROMINATION OF CYCLOHEXENE IN VARIOUS MEDIA

Bromine source	Solvent-ligand	Product distribution, ^a %		Ref
		1,2-Br ₂ -c-C ₆ H ₁₀	1-Br-2-Y-c-C ₆ H ₁₀	
CuBr ₂	CH ₃ CN	98-100	0-2	
Br ₂	CH ₃ CN	67	33	<i>b, d</i>
CuBr ₂	CH ₃ OH	79	21	<i>4</i>
Br ₂	CH ₃ OH	35	65	<i>c</i>
CuBr ₂	CH ₃ COOH	90	10	
Br ₂	CH ₃ COOH	74	26	<i>c</i>
CuBr ₂	(CH ₃) ₂ CO	59	41	
Br ₂	(CH ₃) ₂ CO	25	75	<i>c</i>

^a Cyclohexene conversion, 80-95% in all cases. ^b T. L. Cairns, P. J. Grayham, P. L. Barrick, and R. S. Schreiber, *J. Org. Chem.*, **17**, 751 (1952). ^c F. Boerwinkle and A. Hassner, *Tetrahedron Lett.*, 3921 (1968), and references cited therein. ^d Y = CH₂-CONH, CH₃O, CH₃COO, HO radicals.

highlight the differences between these reactions and those of molecular halogen in identical reaction media. Although capture of the reaction intermediate (bromonium ion) by such nucleophilic solvents is anticipated, the predominance of dibromide product in the copper(II) bromide reactions is believed to reflect the participation of a more active bromide ion source than bromide or tribromide ions.

Chlorination with Copper(II) Chloride.—Olefins reacted with copper(II) chloride in acetonitrile or benzonitrile solution to produce vicinal dichloroalkanes in yields of 30-80% (eq 3). The reactions were performed at 60-80° for 2-4 hr, and representative data are presented in Table III. The selectivity to the vicinal dichlorides was essentially quantitative, and



(12) J. G. Verkade and T. S. Piper, *Inorg. Chem.*, **1**, 453 (1962).

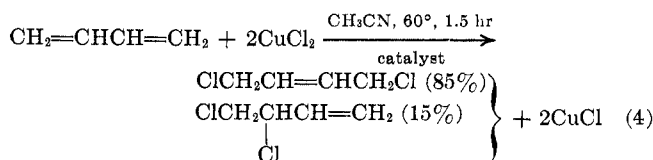
TABLE III
HALOGENATION OF OLEFINS WITH COPPER(II)
HALIDES IN ACETONITRILE

Olefin	—Yield of vicinal dihaloalkane, % ^a —			
	CuCl ₂ ^b ClCCl	CuBr ₂ ^c BrCCBr	I ₂ / CuCl ₂ ^d ICCl	Br ₂ / CuCl ₂ ^e BrCCl
CH ₂ =CH ₂	32	57	70	
CH ₃ CH=CH ₂			85 ^f	
CH ₃ CH=CHCH ₃		91 ⁱ		
(CH ₃) ₂ CCH=CH ₂	17	91	73	
(CH ₃) ₂ C=C(CH ₃) ₂	53	91		
Cyclohexene	73 ^j	80 ^j	95 ^j	55 ^j
PhCH=CH ₂		87	75 ^m	
Norbornene	68 ⁿ			
CH ₂ =CHCH=CH ₂	43 ^k	92 ^k	90 ^k	
Cyclopentadiene			70 ⁿ	
CH ₃ CH=CHCOOCH ₃		49 ^b		
CH ₂ =CHCl			81 ^o	
CH ₂ =CHCN		32 ^b		
CH ₂ =CHOOCCH ₃			83 ^p	

^a Based on olefin or copper(II) halide charged. ^b 60-80°, 2-4 hr. ^c 25°, 5-15 min. ^d 25-60°, 30-60 min. ^e 80°, 1 hr. ^f 93-97% trans. ^g Mixture of isomers. ^h 80% trans 1,4; 5% cis-1,4; 15% 3,4. ⁱ Cis → *dl*; trans → meso. ^j 100% trans. ^k 100% 1,4. ^l 76% 1-chloro-2-iodo, 24% 1-iodo-2-chloro. ^m 1-Chloro-2-iodo-1-phenylethane. ⁿ 85% 3,5; 15% 3,4 dichlorides. ^o 73% 1-iodo-2,2-dichloro; 27% 1-iodo-1,2-dichloro. ^p 1-Chloro-1-acetoxy-2-iodoethane.

the formation of allylic chlorides was not detected. The anhydrous and hydrated forms of copper(II) chloride were used without any effect on yield or stereochemistry. The addition of an equal molar amount of potassium chloride depressed the yield by a factor of 5 under identical reaction conditions. The deleterious influence of excess chloride ion is ascribed to the competitive formation of polychloro copper(II) complexes.¹³ This displacement of the activating nitrile ligand is reflected in a reversal of copper(II) chloride dissociation.

The reactions of the conjugated diolefins, butadiene and cyclopentadiene, merit some discussion. Although both substrates experienced chlorination in acetonitrile, the reactions were markedly sensitive to catalysis by iodine or iodine donors (eq 4; Table IV). The source



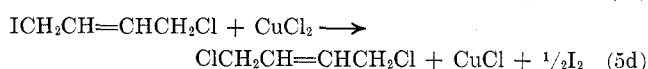
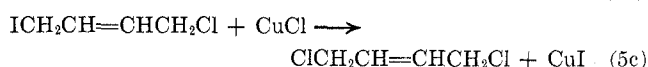
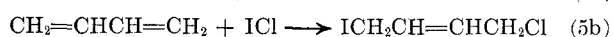
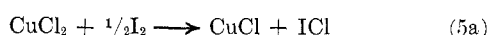
(13) S. E. Manahan and R. T. Iwamoto, *ibid.*, **4**, 1409 (1965).

TABLE IV
 CATALYSIS OF BUTADIENE CHLORINATION IN ACETONITRILE^a

Catalyst	Mol of CuCl ₂ : mol of catalyst	Yield, % ^b
CuCl	20:1	43
I ₂	50:1	80
CuI	40:1	76

^a 60°, 1.5 hr. ^b Based on copper(II) chloride charged.

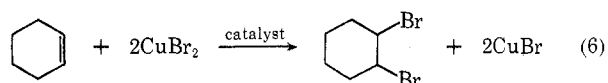
of this catalysis was the *in situ* generation, reaction, and regeneration of the interhalogen compound, iodine monochloride. While the synthesis of interhalogen compounds will be developed thoroughly in a subsequent section of this report, some remarks are relevant at this point. The reaction sequence is initiated by the formation of iodine monochloride from copper(II) chloride and iodine (eq 5a). Subsequent addition to



butadiene (5b) followed by halogen exchange with either copper(I) chloride (5c) or copper(II) chloride (5d) produced the isomeric dichlorobutenes and released iodine or copper(I) iodide for recycle (5d, 5e). The overall stoichiometry is represented by eq 4, and the catalytic role played by iodine is evident from the sequence 5a-c. The validity of the halogen exchange reactions (5c,5d) has been verified experimentally in control reactions. The observed isomeric distribution between 1,4- and 3,4-dichlorobutenes may reflect either S_N2 and S_N2' exchange reactions between the labile allylic iodide and the copper chlorides or the equilibrium distribution of these dihalides over copper(I) salts in nonaqueous media.¹⁴ The reaction of cyclopentadiene is considered to occur in a similar manner.

Bromination with Copper(II) Bromide.—Olefins reacted readily with copper(II) bromide in the presence of a variety of ligands (Table I) to produce exclusively vicinal dibromoalkanes in high yields (Table III). The reaction conditions were extremely mild, many olefins experiencing bromination at room temperature with reaction periods of 5–15 min. Certain deactivated olefins (Table III) required more forcing conditions. The formation of allylic bromides was not observed under any circumstances.

A unique feature of the copper(II) bromide system was the use of the activating ligands in catalytic quantities. Representative data are presented in Table V using cyclohexene as a model olefin (eq 6). The reac-



tion was carried out using excess olefin, or an inert alkane or aromatic hydrocarbon, as a diluent. This catalytic activity was not anticipated, for it seemed reasonable that the ligands would be removed from the

(14) F. J. Bellringer and H. P. Crocker, British Patent 800,787 (1958).

 TABLE V
 CATALYSIS OF CYCLOHEXENE BROMINATION^a

Catalyst	Mol of CuBr ₂ : mol of catalyst	Yield, % ^b
Acetonitrile	6:1	53
Triphenylphosphine	5:1	87
1,2-Bis(diphenylphosphino)ethane	18:1	97
<i>tert</i> -Butylphosphite	15:1	98

^a 25°, 1 hr. ^b Based on copper(II) bromide charged.

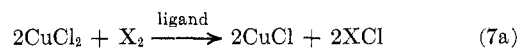
reaction by coordination with copper(I) bromide. In retrospect, it is suggested that the ligands are released from the copper(I) ion by the formation of the stable copper(I) bromide lattice.¹⁵

A control experiment with neat cyclohexene (eq 6) has shown that under these heterogeneous conditions the pure olefin was less effective in promoting reaction. Solubilization of the copper(II) salt would seem to be a prerequisite for participation by olefin by ligand exchange in the homogeneous phase. Potent olefinic ligands such as butadiene and norbornadiene¹⁶ react sluggishly in pure hydrocarbon media, but facile reaction occurs in methanolic solution⁴ or, alternatively, in the presence of a catalytic quantity of ligand.^{17,18}

Comparable catalysis has not been observed for copper(II) chloride reactions. This failure is ascribed to a requirement for high ligand concentration in order to encourage dissociation of this less reactive copper salt.

Fluorination with Copper(II) Fluorides.—No successful fluorinations have been realized utilizing a number of copper(II) fluoride–ligand combinations. The major obstacles were the extremely unfavorable fluoride–fluorine oxidation potential and the unstable nature of copper(I) fluoride.^{15b}

Synthesis of Interhalogen Compounds. Chloroiodoalkanes.—The ligand-induced dissociation of copper(II) chloride afforded an opportunity for the *in situ* formation and reaction of such interhalogens as iodine and bromine monochloride. This option was predicated on the rationale that the addition of a halogen or halide anion to the copper(II) chloride system would yield a redox reaction that produced the corresponding interhalogens (eq 7). If this redox reaction occurred



in the presence of an olefin, the subsequent addition reaction would produce vicinal chloro halides. In this way these organic dihalides could be synthesized without the necessity of independently preparing the requisite pseudohalogens from elemental halogens.

Iodine monochloride has been generated and reacted *in situ* by the reaction of molecular iodine or iodide

(15) (a) L. Pauling, "College Chemistry," W. H. Freeman and Co., San Francisco, Calif., 1951, pp 552–555; (b) T. Moeller, "Inorganic Chemistry," Wiley, New York, N. Y., 1952, pp 831–834.

(16) J. M. Harvelchuck, D. A. Aikens, and R. C. Murray, Jr., *Inorg. Chem.*, **8**, 539 (1969).

(17) For example, butadiene is brominated by copper(II) bromide in *n*-heptane containing acetonitrile as a catalyst at room temperature. In the absence of the nitrile the reaction temperature is increased to 75–100° at which point thermal dissociation of the copper salt becomes effective.

(18) The quantities of ligands being used are insufficient to drive the reaction through solubilization of copper(II) bromide *per se*.

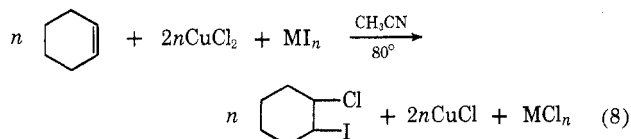
salts with copper(II) chloride. Acetonitrile was utilized as the ligand due to the ease of the procedure and the high reaction rates provided by this medium. Reactions involving molecular iodine occurred at room temperature and were complete within a few minutes. The reaction of gaseous olefins was sufficiently rapid that the reaction was accomplished by simply passing the olefin into the reaction mixture. Some representative examples are found in Table III. Reactions utilizing iodide salts as the iodine source (eq 8) were carried out at 70–80° for 30–60 min. Table VI illustrates the

TABLE VI
IODINE DONORS FOR SYNTHESIS OF
CHLOROIDOALKANES^a

Iodine source (MI _n)	Yield, % ^b	Iodine source (MI _n)	Yield, %
I ₂	90	CdI ₂	95
HI	94	TiI ₄	92
KI	78	SnI ₂	82
NH ₄ I	92	CuI	84
[Ph ₃ PCH ₃ ⁺]I ⁻	95	BaI ₂	67
AlI ₃	94	MnI ₂ ·4H ₂ O	96
FeI ₂	86		

^a 80°, 15–120 min. ^b Based on cyclohexene charged.

types of iodine donors that may be supplied to the reaction; cyclohexene was used as a model olefin, and the stoichiometry was as shown.



A control reaction in which *trans*-1,2-dichlorocyclohexane was treated with potassium iodide in acetonitrile at 80° for 3 hr yielded the dichloride unreacted. The result demonstrated that the chloriodide was the true product and did not arise from iodide displacement on initially formed dichloride. In another control experiment 1-chloro-2-iodocyclohexane was refluxed in acetonitrile with copper(II) chloride for 3 hr; no reaction took place indicating that no copper-catalyzed isomerization, elimination, or halide exchange reactions were occurring. Other potential side reactions were effectively suppressed by the solvent, acetonitrile. The reaction with hydrogen iodide (eq 8) was free of any cyclohexyl iodide due to the neutralization of this acid by the basic nitrile. In a similar manner the Lewis acid properties of several of the inorganic by-products, *e.g.*, AlCl₃, SnCl₂, etc., were neutralized by coordination with acetonitrile. Destruction of the olefin or chloriodide product through Lewis acid catalyzed alkylation reactions was successfully avoided.

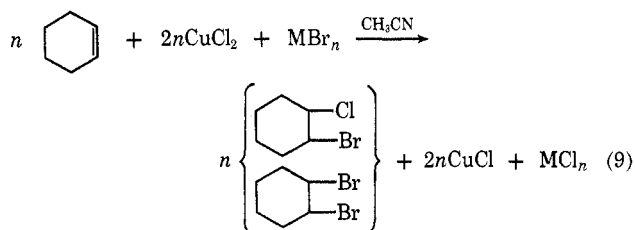
Unsymmetrical olefins yielded chloriodoalkanes structurally identical with those produced by the addition of preformed iodine monochloride (Table III). Propylene¹⁹ and vinyl chloride²⁰ gave mixtures of Markovnikov and non-Markovnikov oriented chloriodoalkanes. Styrene,²¹ vinyl acetate,²² and *tert*-

butylethylene²³ gave exclusively the Markovnikov products as anticipated on the basis of electronic and steric effects. The product orientation in all of these cases was consistent with classical iodonium ion S_N1 and S_N2 mechanisms.^{19,21,23}

The reaction of conjugated diolefins has been previously described, and that chemistry is in accord with the *in situ* production and reaction of iodine monochloride. The role played by copper(I) iodide (eq 5c, 5e) is supported by the demonstrated ability of this copper salt to supply iodine to the reaction (eq 8).

Although iodine monochloride has not been isolated from these reactions, the observed chemistry was consistent with the known behavior of this reagent and with the ability of chlorine to oxidize iodide ion. A comparison of these results with those obtained with identical systems in hydrocarbon or chlorocarbon media²² has shown that different reaction paths and halogen species are involved. While the latter reactions have been found to be sensitive to olefin structure and reaction medium,²² no such sensitivity has been noted in the present case. The hydrocarbon-based reactions proceeded through molecular iodine addition with Lewis acid catalysis by copper ion; a comparable mechanism in acetonitrile has been precluded by the observed suppression by this solvent of potential Lewis acid catalyzed reactions. Consequently, while no direct evidence for iodine monochloride formation is presented, the participation of this reagent in these systems is deemed reasonable.

Chlorobromoalkanes.—Bromine monochloride was synthesized from combinations of copper(II) chloride and bromine donors in acetonitrile. Cyclohexene, the only olefin studied, was converted to the extent of 50–60% by reaction at 80° for 1 hr (Table III, eq 9).



The product was consistently a mixture of *trans*-1-chloro-2-bromocyclohexane and *trans*-1,2-dibromocyclohexane, a normal by-product of bromine monochloride addition to olefins.^{24,25} The use of molecular bromine or copper(II) bromide as a bromine source increased the formation of the dibromide since the higher concentration of bromine facilitated competitive bromination (Table VII). In those cases where bromine was generated by oxidation of bromide ion, traditional bromine monochloride chemistry was observed.

Discussion

It is apparent that coordinated copper(II) halide systems are effective for the facile, selective halogenation of olefins, particularly for the synthesis of vicinal dibromo-, chloriodo-, and chlorobromoalkanes. Some

(19) C. K. Ingold and H. G. Smith, *J. Chem. Soc.*, 2742 (1931).

(20) M. L. Henry, *C. R. Acad. Sci., Ser. C*, **97**, 1491, (1883); **98**, 370, 518, 680, 741 (1884).

(21) R. E. Buckles and D. F. Knaack, *J. Chem. Educ.*, **37**, 298 (1960), and references cited therein.

(22) W. C. Baird, Jr., J. H. Surrledge, and M. Buza, *J. Org. Chem.*, **36**, 2088 (1971).

(23) W. H. Puterbaugh and M. S. Newman, *J. Amer. Chem. Soc.*, **79**, 3469 (1957).

(24) Reference 15b, pp 448, 449.

(25) A. P. Braendlin and E. T. McBee, "Friedel-Crafts and Related Reactions," G. A. Olah, Ed., Wiley, New York, N. Y., 1964, pp 1566, 1567.

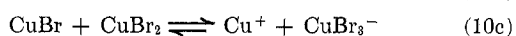
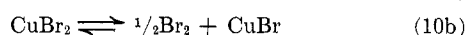
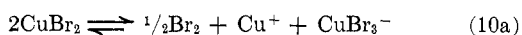
TABLE VII
BROMINE DONORS FOR SYNTHESIS OF
CHLOROBROMOCYCLOHEXANE^a

Bromine source (MBr _n)	1-Cl-2-Br- c-C ₆ H ₁₀	Selectiv- ity, % ^b	1,2-Br ₂ - c-C ₆ H ₁₀
NH ₄ Br CuBr KBr	~93		~7
Br ₂ CuBr ₂	~65-70		~30-35

^a 80°, 1 hr. ^b Based on cyclohexene charged; cyclohexene conversion ~77%.

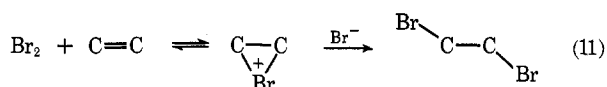
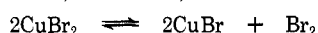
remarks concerning the mechanism of these reactions are appropriate at this point. A precise picture of the reaction path has not been developed, but some reasonably consistent statements along these lines can be made. The copper(II) bromide-acetonitrile combination has been utilized exclusively as a model due to the ease of handling this complex system.

Any mechanism proposed for copper(II) bromide bromination must be consistent with the following observations. (1) The reaction occurred with stereospecific trans addition as evidenced by the reactions of cyclohexene and *cis*- and *trans*-butene-2. (2) Norbornadiene reacted with copper(II) bromide in acetonitrile to produce the same mixture of nortricyclic and norbornenyl dibromides as did molecular bromide.²⁶ (3) *tert*-Butylethylene did not experience any methyl group migration during bromination. (4) A lower level of solvent participation was observed for copper(II) bromide reactions than for bromine (Table I). (5) The relative order of olefin reactivity toward copper(II) bromide parallels that observed for the electrophilic addition of bromine (R₂C=CR₂ > R₂C=CHR >> RCH=CHR > RCH=CH₂). (6) The bromination reaction is extremely rapid and commences immediately upon the addition of olefin. (7) Spectrophotometric studies of copper(II) bromide-acetonitrile solutions have shown that the copper(II) salt dissociates according to eq 10a,⁷ which is a composite of reactions 10b and 10c. (8) The addition of copper(I) bromide to aceto-



nitrile solutions of copper(II) bromide increases the concentration of CuBr₃⁻. (9) A spectrophotometric analysis of the reaction of *tert*-butylethylene with copper(II) bromide-acetonitrile shows that the CuBr₃⁻ concentration increases rapidly to a maximum during the first 10-20% of reaction and then declines gradually. (10) The rate of the reaction does not obey simple first-, second-, or third-order kinetics.²⁷

It was initially tempting to interpret this halogenation in terms of ligand induced copper(II) bromide dissociation followed by traditional bromine addition (eq 11). This picture, however, was not consistent with



(26) S. Winstein and M. Shatavsky, *Chem. Ind. (London)*, 56 (1956).

(27) The second-order kinetics observed in the thermal bromination of unsaturated alcohols with copper(II) bromide²⁶ were not noted in this case.

experimental findings. A more reasonable sequence was one initiated by attack on olefin by bromonium ion, or its kinetic equivalent, to generate a normal bromonium ion intermediate. In the early stages of the reaction this removal of "free" bromine would be accompanied by a buildup of copper tribromide ion (eq 10a). Bromide ion transfer from copper tribromide to dibromoalkane and concomitant release of copper(II) bromide yields more bromine *via* reactions 10b and 10c. Repetition of this path leads ultimately to a decline in the CuBr₃⁻ concentration as the reaction goes to completion.

This reaction scheme is simplistic and has ignored completely the solvating effects of the reaction medium (ion pair interactions, etc.). This study has not attempted to understand these mechanisms in detail, and this aspect of these reactions might justify further probing.

Experimental Section

Infrared spectra were recorded on a Beckman IR-5A spectrophotometer. Vapor phase chromatography (vpc) was performed using a Perkin-Elmer 154-D fractometer, a Perkin-Elmer Model 226 capillary gas chromatograph, and a Varian Aerograph Model 202 gas chromatograph. Nmr spectra were recorded on a Varian Associates A-60 spectrometer using tetramethylsilane as an internal standard. Melting points and boiling points are not corrected. Unless otherwise noted, all reagents were obtained from commercial sources and used as received.

Chlorination with Copper(II) Chloride.—In a typical experiment into a round-bottom flask equipped with a reflux condenser were placed acetonitrile (50-100 ml), the olefin (0.05-0.10 mol), and copper(II) chloride (0.10-0.20 mol). The reaction was stirred at 70-80° for 2-20 hr. The inorganic salts were separated by vacuum filtration, and the filter cake was rinsed with pentane. The filtrate was added to 200-500 ml of water, and the product was extracted with pentane (three times, 50-100 ml portions). The combined pentane washings and extracts were washed with water and dried over magnesium sulfate. The pentane was removed on a rotary evaporator, and the yield of dichloroalkane was determined by vpc on a 2 m × 0.25 in. 20% diethylene glycol succinate column at 80° and 15 psig of helium using tetradecane as an internal standard. The dichlorides were purified by distillation and identified by comparison of their physical and spectroscopic properties with those of authentic samples.

Reactions utilizing gaseous olefins were performed in a Parr low pressure reactor²⁸ at initial olefin pressures of 20-40 psig. The reactor was vented into a trap at -78° to recover any volatile chlorides; no such compounds were recovered. The reaction was worked up as described above.

Bromination with Copper(II) Bromide. Acetonitrile.—The general procedure was identical with that described for copper(II) chloride. The reaction was carried out at room temperature for 5 min to several hours or at 60-80° for 0.5-4 hr. The conclusion of the reaction was indicated by the precipitation of copper(I) bromide. The reaction work-up was performed as above; the pentane and excess olefin were removed on a rotary evaporator at 60° (14 mm). Vpc analysis utilized the same diethylene glycol succinate column at 125-175° and 15-30 psig of helium. The dibromides were identified by comparative techniques. Gaseous olefins were reacted utilizing either a Dry Ice condenser or a Parr low pressure reactor.

Ligands for Copper(II) Bromide Bromination.—Table VIII lists various ligands that were effective for bromination of olefins with copper(II) bromide. Cyclohexene was used as a model olefin, and the general procedure was identical with that described for acetonitrile.

Halogenation of Butadiene. Chlorination.—Into a Parr low pressure reactor were placed 100 ml of acetonitrile and 27 g (0.2 mol) of copper(II) chloride. The reactor was pressurized with butadiene to 20 psig at room temperature, and the reaction mixture was rocked at 60° for 1-2 hr. The reaction mixture was poured into 300 ml of water and was extracted with pentane

(28) Parr Instrument Co., Moline, Ill.

TABLE VIII
 LIGANDS FOR COPPER(II) BROMIDE BROMINATION

Ligand	Mol of CuBr ₂	Temp, °C	Time, hr	Yield, %
Dimethylformamide ^a (50 ml)	0.065	70	1	55
Dimethyl sulfoxide ^a (100 ml)	0.135	70	1	51
Sulfur dioxide ^a (50–75 ml)	0.086	25	10	100
Thiophene ^a (50 ml)	0.045	25	1	87
Tetrahydrothiophene ^a (50 ml)	0.09	25	2	57
Sulfolane ^a (50 ml)	0.09	25	2	66
Tetrahydrofuran ^a (50 ml)	0.09	25	2	100
Acetonitrile ^b (1.1 g, 0.027 mol)	0.18	25	0.3	87
Succinonitrile ^b (1.0 g, 0.013 mol)	0.09	25	1	92
Triphenyl phosphine ^b (5.0 g, 0.02 mol)	0.09	25	1	74
Trimethyl phosphate ^b (5.0 g, 0.035 mol)	0.09	25	1	79
1,2-Bis(diphenylphosphinoethane) ^b (2.0 g, 0.005 mol)	0.09	25	1	97
<i>tert</i> -Butyl phosphite ^b (1.5 g, 0.006 mol)	0.09	25	1	98
CH ₃ C(CH ₂ O) ₃ P ^{b,c} (1.0 g, 0.006 mol)	0.09	25	24	86
CH ₃ C(CH ₂ O) ₃ PS ^{b,d} (1.0 g, 0.005 mol)	0.09	80	1	74

^a 0.10 mol of cyclohexene; vpc analysis, 6 ft × 0.25 in. 20% FFAP column, 130°, 120 ml/min of helium, *r*_t 13.8 min. ^b 50 ml of cyclohexene, ligand catalysis. ^c C. W. Heitsch and J. G. Verkade, *Inorg. Chem.*, **1**, 392 (1962). ^d From thiophosphoryl chloride and 2-methyl-2-hydroxymethylpropane-1,3-diol: R. Ratz and O. J. Sweeting, *J. Org. Chem.*, **30**, 438 (1965).

(three times, 50-ml portions). The extracts were washed with water and dried over magnesium sulfate. The pentane was removed on a rotary evaporator, and the crude product was distilled to give a 43% yield of isomeric dichlorobutenes, bp 150–155°. The products were identified by comparative vpc and nmr analysis with authentic samples. Vpc analysis (2 m × 0.25 in. 20% diethylene glycol succinate column, 125°, 15 psig of helium) gave the following isomeric distribution: 3,4-dichlorobutene-1, *r*_t 2.9 min, 15–19%; *cis*-1,4-dichlorobutene-2, *r*_t 8.0 min, 3–7%; *trans*-1,4-dichlorobutene-2, *r*_t 9.6 min, 75–81%.

Bromination.—Butadiene was passed into a stirred solution of 15 g (0.067 mol) of copper(II) bromide in 100 ml of acetonitrile at room temperature for ~10 min. The reaction mixture was filtered; the filtrate was poured into 300 ml of water and was extracted with pentane. The extract was washed with water and dried over magnesium sulfate; the pentane was removed on a rotary evaporator at 60° (14 mm) to give 6.5 g (92%) of *trans*-1,4-dibromobutene-2, mp 52–53° (lit. mp 53–54°).²⁹ Vpc and nmr analysis showed the dibromide to be a single compound.

Synthesis of Chloroiodoalkanes. Ethylene.—Into a 1-l. flask were placed 500 ml of acetonitrile, 135 g (1.0 mol) of copper(II) chloride, and 130 g (0.51 mol) of iodine. Ethylene was passed into the reaction mixture for 35 min at room temperature; the reaction was stirred vigorously during the introduction of the olefin. The conclusion of the reaction was indicated by the discharge of the iodine color and the precipitation of copper(I) chloride. The reaction mixture was filtered, and the filter cake was washed with 100–200 ml of pentane. The filtrate was poured into 1500–2000 ml of water, and the product was extracted three times with 100-ml portions of pentane. The combined pentane solutions were washed with water, dried over magnesium sulfate, and concentrated on a rotary evaporator at 60° (20 mm). The

yield of 1-chloro-2-iodoethane was 130–140 g (69–74%). The dihalide was shown to be identical with an authentic sample.²²

Propylene.—A Parr low pressure reactor was charged with 100 ml of acetonitrile, 27 g (0.20 mol) of copper(II) chloride, 27 g (0.11 mol) of iodine, and propylene (20 psig). The reaction was rocked at 50° for 2 hr. The work-up (as above) gave 34.8 g (85%) of chloroiodopropanes.²² Nmr analysis of the methyl group areas showed the product composition to be 76.5% 1-iodo-2-chloropropane and 23.5% 1-chloro-2-iodopropane.

Styrene.—To 100 ml of acetonitrile were added 13.3 g (0.1 mol) of copper(II) chloride, 8.7 g (0.05 mol) of potassium iodide, and 5.2 g (0.05 mol) of styrene. The reaction was stirred at 80° for 1 hr; the product was isolated in the normal manner to give 10.1 g (75%) of 1-chloro-2-iodo-1-phenylethane, mp 36–37° (lit. mp 37–39°).^{21,22}

Vinyl Chloride.—The procedure was the same as that described for propylene except the reaction period was 15 hr. The yield of dichloroiodoethane was 36.4 g (81%): bp 31–32° (2.5 mm); *n*_D²⁰ 1.5672 (lit. *n*_D²⁰ 1.5774);²³ nmr (neat) δ 3.90 (d, 1.4 H, ICH₂), 4.15 (m, 0.6 H, ClCH₂), 5.65–6.00 (m, 1 H, X₂CH). Analysis of the spectrum gave a composition of 70% 1-iodo-2,2-dichloroethane and 30% 1,2-dichloro-2-iodoethane.²³

Anal. Calcd for C₂H₃Cl₂I: C, 10.68; H, 1.34; Cl, 31.54; I, 56.44. Found: C, 11.03; H, 1.47; Cl, 31.72; I, 55.57.

In a similar manner vinyl acetate was reacted at room temperature for 2 hr to give an 83% yield of 1-chloro-1-acetoxy-2-iodoethane.²²

Butadiene.—Into a Parr low pressure reactor were placed 100 ml of acetonitrile, 27 g (0.2 mol) of copper(II) chloride, 1 g (0.004 mol) of iodine or 1 g (0.005 mol) of copper(I) iodide, and butadiene (20 psig). The reaction was agitated at 60° for 90 min. After the standard work-up a 76–80% yield of isomeric dichlorobutenes was recovered. The isomer distribution was identical with that obtained in the absence of iodine catalysis (see above).

An authentic sample of 1-chloro-4-iodobutene-2³⁰ (1 g, 0.0046 mol) was stirred for 90 min at 50° in 10 ml of acetonitrile with 1 g (0.0075 mol) of copper(II) chloride, or with 1 g (0.010 mol) of copper(I) chloride. The inorganic salt was separated by filtration, and the acetonitrile filtrate was added to 25 ml of water. The product was extracted with pentane, and the extract was analyzed by vpc. In both cases a mixture of isomeric dichlorobutenes comparable to that described previously was present. No chloroiodide remained unreacted.

Cyclopentadiene.—To 500 ml of acetonitrile were added 270 g (2 mol) of copper(II) chloride, 6 g (0.024 mol) of iodine, and 80 g (1.2 mol) of freshly distilled cyclopentadiene. Benzene or cyclohexane (500 ml) was added as an inert diluent, and the reaction was stirred vigorously at room temperature for 15 hr. The reaction mixture was vacuum filtered, and the filtrate was poured into 500–700 ml of water. The hydrocarbon layer was separated, and the aqueous layer was extracted three times with 100-ml portions of pentane. The combined organic layers were washed with 15% sodium thiosulfate solution and then with water. The hydrocarbon solution was dried over magnesium sulfate, and the solvent was removed with a rotary evaporator [60° (80 mm)] to give 115–126 g of crude product. Distillation yielded 90–97 g (65–72%) of dichlorocyclopentenes, bp 64–67° (27 mm), *n*_D²⁰ 1.5055. Vpc analysis (5 ft × 0.25 in. 20% diethylene glycol succinate column, 109°, 57 ml/min) of the product mixture gave the following composition: *trans*-3,4-dichlorocyclopentene, 16% (*r*_t 6.4 min); *trans*-3,5-dichlorocyclopentene, 22–29% (*r*_t 22.6 min); *cis*-3,5-dichlorocyclopentene, 54–61% (*r*_t 19.6 min). Capillary vpc (300-ft Dow-Corning silicone 550, 40 psig of helium, 12 min at 42°, program at 10°/min to 125°) revealed the presence of three product peaks in essentially the same relative amounts. The nmr spectrum of the product mixture indicated a 3,5-dichlorocyclopentene content of ~88% and a 3,4-dichloro content of ~12%.

Anal. Calcd for C₅H₆Cl₂: C, 43.83; H, 4.42; Cl, 51.75. Found: C, 43.58; H, 4.66; Cl, 51.64.

Iodine Donors.—The general procedure was identical with that described above for styrene. The quantity of iodine donor charged was determined according to the stoichiometry of eq 8. Reaction periods ranged from 15–120 min; the reaction was terminated when the precipitation of copper(I) chloride appeared complete.

(29) "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, Ohio, 1969.

(30) H. Johnston, U. S. Patent 2,808,444 (1957).

Synthesis of 1-Chloro-2-bromocyclohexane.—To 100 ml of acetonitrile were added 27 g (0.2 mol) of copper(II) chloride, 10 g (0.1 mol) of ammonium bromide, and 8.2 g (0.1 mol) of cyclohexene. The reaction was stirred at 80° for 1 hr, and the work-up was carried out in the usual manner. Distillation of the crude product gave 10.1 g of *trans*-1-chloro-2-bromocyclohexane, bp 74–77° (6 mm), n_D^{20} 1.5247.³¹ Vpc analysis (5 ft × 0.25 in. 20% FFAP column, 150°, 70 ml/min of helium) showed the product to consist of 93% 1-chloro-2-bromocyclohexane (r_t 12.0 min) and 7% *trans*-1,2-dibromocyclohexane (r_t 18.8 min).

Solvent Participation in Copper(II) Bromide Bromination. Methanol.—The bromination of cyclohexene with methanolic copper(II) bromide has been described.⁴

Acetic Acid.—A mixture of 23 g (0.1 mol) of copper(II) bromide, 8.2 g (0.1 mol) of cyclohexene, 80 ml of acetic acid, and 1 ml of acetonitrile was stirred at room temperature for 3 hr. Copper(I) bromide began to precipitate after 15 min. The standard work-up gave 8.8 g of product. Vpc analysis (2 m × 0.25 in. 20% diethylene glycol succinate column, 140°, 220 ml/min of helium) gave the following result: 90% 1,2-dibromocyclohexane (r_t 5.0 min); 10% 1-bromo-2-acetoxycyclohexane (r_t 9.0 min). Saponification of the ester gave the bromohydrin, r_t 6.6 min.³²

Acetone.—To a solution of 8.2 g (0.1 mol) of cyclohexene in 40 ml of acetone was added 2.2 g (0.01 mol) of copper(II) bromide. The reaction was stirred at room temperature for 2 hr. A 3-ml aliquot was withdrawn and added to 1 ml of pentane and 8 ml of water saturated with sodium chloride. Analysis of the pentane layer by vpc (see above) showed 59% dibromide and 41% bromohydrin.

Acetonitrile.—To a stirred solution of 8.2 g (0.1 mol) of cyclohexene in 60 ml of acetonitrile at 0° was added dropwise over 45 min 16 g (0.1 mol) of bromine.³³ The reaction was stirred at 0° for another 45 min and then was poured into 250 ml of water. A white crystalline precipitate separated immediately; the precipitate was removed by filtration and air-dried to give 6 g (27%) of *N*-(2-bromocyclohexyl)acetamide, mp 121–123°. Recrystallization from 50:50 ethyl acetate–methanol gave white needles, mp 124–125° (lit. mp 109–110°).³³

Anal. Calcd for C₈H₁₄BrNO: C, 43.65; H, 6.41; N, 6.36. Found: C, 43.30; H, 6.45; N, 6.25.

The filtrate was extracted with pentane to recover 15.3 g (63%) of *trans*-1,2-dibromocyclohexane.

If the bromination was carried out in the presence of 0.05 mol of copper(I) or copper(II) bromide, no change in the yields of dibromide and bromoamide occurred. These results demonstrated that the copper salts did not induce the decomposition of the bromoamide.

To a stirred solution of 4.1 g (0.05 mol) of cyclohexene in 60 ml of acetonitrile at 0° was added 22.3 g (0.1 mol, bromine equivalent, 0.05 mol) of copper(II) bromide. The copper salt was added in four equal portions at 12-min intervals; the reaction was stirred for an additional 45 min at 0°. The mixture was poured into 250 ml of water, and the solids were separated by filtration. The filter cake was washed thoroughly with pentane (500 ml), and the filtrate was extracted with the pentane washings. The pentane solution yielded 11.3 g (93%) of *trans*-1,2-dibromocyclohexane. The filter cake and the aqueous filtrate were extracted with methylene chloride (five times, 50-ml portions). From this extract was recovered 0.1 g (0.9%) of crude *N*-(2-bromocyclohexyl)acetamide, mp 115–119°.

Mechanism Studies. Relative Rates of Olefins.—Solutions of olefin pairs in acetonitrile were prepared; *n*-hexane was added as

an internal standard for vpc analysis. Aliquots of these solutions were added to solutions of copper(II) bromide in acetonitrile; a stoichiometric deficiency of the copper salt was utilized so that total reaction of neither olefin was possible. The reactions were stirred at room temperature for 5 min. Samples (3 ml) were removed and added to 8 ml of water and 1 ml of an alkane solvent that would not interfere with the vpc analysis (*n*-pentane, *n*-heptane, *n*-octane, cyclohexane). Vpc analysis was carried out on a 2 m × 0.25 in. 20% polypropylene glycol (UCON-550B) column, 65°, 150 ml/min of helium. The relative rates were calculated from the equation

$$\frac{k_{\text{olefin A}}}{k_{\text{olefin B}}} = \frac{\log(\text{olefin A}_0/\text{olefin A})}{\log(\text{olefin B}_0/\text{olefin B})}$$

Some rates relative to octene-1 follow: 2-methylbutene-2 (120); *cis*-pentene-2 (80); 2,3,3-trimethylbutene-1 (40); cyclohexene (20); octene-1 (1); 3,3-dimethylbutene-1 (0.25).

Spectrophotometric Studies.—Spectrophotometric studies on the copper(II) bromide–acetonitrile–*tert*-butylethylene systems were performed on a Beckman DK-2 recording spectrophotometer using matched silica cells of 1.00 ± 0.01 cm path length.

Stock solutions of copper(I) and copper(II) bromide in acetonitrile were prepared. A solution of copper(II) bromide (0.0013 *M*) exhibited a copper tribromide ion absorbance at 620 nm, $A = 0.320$ (log ϵ 3.3).⁷ The addition of copper(I) bromide over the concentration range 0.001–0.008 *M* increased the absorbance to 1.153 corresponding to a three- to fourfold increase in the copper tribromide concentration.

Solutions of copper(II) bromide (0.002–0.003 *M*) and *tert*-butylethylene (0.004–0.008 *M*) in acetonitrile were prepared. Aliquots of the two solutions were mixed at 25.9°, and the course of the reaction was followed by vpc analysis for dibromide product and by spectrophotometric analysis of the copper tribromide ion concentration. The latter increased rapidly over the first 20% of reaction, stabilized briefly (~20–30% of reaction), and then declined. Plots of the reactants *vs.* time did not establish a simple order for either. Attempts to calculate rate constants for overall second- and third-order kinetics gave steadily decreasing values of k as a function of time over the reaction range, 0–35%.³⁴

Registry No.—Copper(II) bromide, 7789-45-9; copper(II) chloride, 7447-39-4; acetonitrile, 75-05-8; benzonitrile, 100-47-0; glutaronitrile, 544-13-8; succinonitrile, 110-61-2; tetracyanoethylene, 670-54-2; dimethylformamide, 68-12-2; dimethyl sulfoxide, 67-68-5; sulfur dioxide, 7446-09-5; thiophene, 110-02-1; tetrahydrothiophene, 110-01-0; sulfolane, 126-33-0; tetrahydrofuran, 109-99-9; triphenylphosphine, 603-35-0; trimethyl phosphate, 512-56-1; 1,2-bis(diphenylphosphino)ethane, 31572-37-9; *tert*-butyl phosphite, 31572-38-0; CH₃C(CH₂O)₃P, 1449-91-8; CH₃C(CH₂O)₃PS, 3196-56-3; methanol, 67-56-1; acetic acid, 64-19-7; acetone, 67-64-1; cyclohexene, 110-83-8; butadiene, 106-99-0; ethylene, 74-85-1; propylene, 115-07-1; styrene, 100-42-5; vinyl chloride, 75-01-4; 1-iodo-2,2-dichloroethane, 598-37-8; 1,2-dichloro-2-iodoethane, 31572-42-6; cyclopentadiene, 542-92-7; *trans*-3,4-dichlorocyclopentene, 31572-43-7; *trans*-3,5-dichlorocyclopentene, 31572-44-8; *cis*-3,5-dichlorocyclopentane, 31572-45-9.

(31) H. J. Hageman and E. Havinga, *Recl. Trav. Chim. Pays-Bas*, **85**, 1141 (1966).

(32) Table II, ref *c*.

(33) Table II, ref *b*.

(34) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," Wiley, New York, N. Y., 1961.