

TABLE VI  
SUMMARY OF REACTANT RATIOS AND YIELDS FOR THE METHYLATIONS OF DIMETHYLNORBORNENYL TIN HALIDES BY GRIGNARD REAGENT. THE PRODUCT IS TRIMETHYLNORBORNENYL TIN. WEIGHTS ARE IN GRAMS

X in C <sub>9</sub> H <sub>16</sub> SnX	Halide		Magnesium		Methyl iodide		Product	
	Wt (g)	mmoles	Wt (g)	mg-atoms	Wt (g)	mmoles	Wt (g)	% yield
Cl	9.8	36	1.00	41.1	6.0	42.3	7.7	86 <sup>a</sup>
Br	9.0	28	0.75	30.6	5.0	35.2	6.3	88
I	10.0	27	0.75	30.6	5.0	35.2	6.1	88 (A)
							6.3	91 (B)

<sup>a</sup> Some product lost due to sudden foaming during vacuum distillation; maximum pure yield must be a few per cent greater than this.

product showed that the ratio of (exo-5 + tricyclo):(endo-5 + syn-7) was constant. (b) The first and last cuts of a distillation of a dimethylnorbornenyln tin halide mixture showed a similarly constant ratio. (c) An excess of Grignard reagent was used for each methylation, and completeness of methylation was verified by glpc analysis. Furthermore, all methylation yields were excellent. (d) The first and last cuts of a distillation of a trimethylnorbornenyln tin mixture showed identical isomer ratios. (e) Treatment of a sample of a dimethylnorbornenyln tin bromide isomer mixture with a deficiency of a methyl Grignard reagent showed no preferential reaction of the isomers under the conditions used for the complete methylation.

**Methylation of Dimethylnorbornenyln Tin Halides.**—The procedure for each of the halides was identical. That for the bromide is described here; the other reactions are summarized in Table VI. Methyl iodide (5.0 g, 35.2 mmol) in ether (20 ml) was added to magnesium (0.75 g, 30.6 mg-atoms); the mixture was refluxed briefly to allow complete dissolution of the metal. A sample of the dimethylnorbornenyln tin bromide mixture (9.00 g, 28.0 mmol) in ether (20 ml) was added dropwise with stirring to the refluxing solution. A mildly exothermic reaction occurred. The solution was refluxed further for 40 min, cooled, and poured onto a mixture of sulfuric acid (1.5 ml) and crushed ice (50 g). The ethereal layer was separated, washed with 10% aqueous sulfuric acid (two 10-ml portions) and water (two 15-ml portions), dried over calcium chloride, and distilled, yielding ether and a methylation product, bp 42–48° (0.6 mm), as a clear colorless liquid (6.3 g, 88%).

**Reaction of Dimethylnorbornenyln Tin Bromide with Deficiency of Methyl Grignard.**—Magnesium (0.397 g, 16.5 mg-atoms) in ether (5 ml) was dissolved in methyl iodide (2.7 g, 19.0 mmol) in ether-

al solution (15 ml), using the normal Grignard technique, and then added dropwise with stirring to a gently refluxing solution of dimethylnorbornenyln tin bromide (10.1 g, 31.4 mmol). Refluxing was continued for 30 min; the mixture was cooled and shaken with 2% aqueous hydrobromic acid (100 ml). The aqueous layer was extracted with ether (two 25-ml portions). The combined ethereal extracts were washed with water (two 25-ml portions), dried over calcium chloride, and distilled, yielding ether, trimethylnorbornenyln tin, bp 38–40° (0.5 mm) (3.2 g, 40%), and dimethylnorbornenyln tin bromide, bp 77–79° (0.5 mm) (4.5 g, 44%). Nmr analysis of the original and final bromide mixtures and of the trimethyl tin mixture showed that in each case the ratio (exo-5 + tricyclo):(endo-5 + syn-7) fell within the limits 51 ± 2.0:49 ± 2.0.

**Registry No.**—Trimethyl tin hydride, 1631-73-8; norbornadiene, 121-46-0; dimethylchlorotin hydride, 16561-41-4; dimethylbromotin hydride, 16561-23-2; dimethyliodotin hydride, 16561-40-3.

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## Halogenation with Copper(II) Halides. The Synthesis of Chloroiodoalkanes

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

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

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Vicinal chloroiodoalkanes have been synthesized by a simple, single-step reaction of olefins with copper(II) chloride and iodine or an iodine donor. The reaction is capable of application to substituted and unsubstituted olefins. Conjugated diolefins yield dichlorides *via* halide exchange reactions with initially formed chloroiodides.

The addition of halogens and of halogen derivatives to olefinic unsaturation has been the topic of substantial synthetic and mechanistic investigation.<sup>1</sup> While the interhalogen compounds, iodine and bromine monochloride, have been included in these studies as diagnostic tools for reaction mechanism, these reagents have been largely unexploited for synthetic purposes. The lack of simple and efficient syntheses for chloroiodoalkanes is particularly curious in view of the desirable agricultural<sup>2</sup> and chemical properties<sup>3</sup> exhibited by these organic halides.

(1) H. P. Braendlin and E. T. McBee, "Friedel-Crafts and Related Reactions," Vol. III, G. A. Olah, Ed., Wiley, New York, N. Y., 1964, pp 1563-1579.

(2) (a) H. Johnston, U. S. Patent 2,808,444 (1957); (b) G. O. Turner, U. S. Patent 2,875,118 (1959).

(3) For example, the energy difference between the carbon-chlorine and the carbon-iodine bonds in 1-chloro-2-iodoethane permits its selective pyrolysis to vinyl chloride and iodine.<sup>4</sup>

Chloroiodoalkanes have not generally been prepared by the addition of preformed iodine monochloride to olefins. This is due to two factors: one is the necessity of preparing the reagent from the elemental halogens;<sup>5</sup> the other is the dissociable nature of the compound which frequently leads to high yields of unstable diiodides along with small amounts of desired product.<sup>6-8</sup> Attempts to generate chloroiodoalkanes through the addition of hydrogen iodide to olefinic chlorides have also been only partially successful owing

(4) (a) E. T. Butler, E. Mandel, and M. Polanyi, *Trans. Faraday Soc.*, **41**, 298 (1945); (b) D. M. Fenton, U. S. Patent 3,206,517 (1965).

(5) L. F. Fieser and M. F. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 502.

(6) M. Simpson, *Justus Liebig's Ann. Chem.*, **125**, 101 (1863); **127**, 372 (1863).

(7) V. Voorhees and G. S. Skinner, *J. Amer. Chem. Soc.*, **47**, 1124 (1925).

(8) A. W. Francis, *ibid.*, **47**, 2340 (1925).

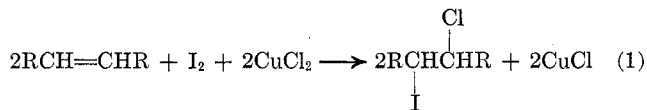
to the occurrence of rearrangement, halogen exchange, and reduction reactions.<sup>9</sup> Various  $\beta$ -chloroethyl phosphites have been treated with methyl iodide to give 70–85% yields of 1-chloro-2-iodoethane;<sup>10,11</sup> however, the reaction has limited synthetic scope since other requisite  $\beta$ -chloro alcohols are generally not available. A similar comment may be applied to the synthesis of chloriodides by sodium iodide displacement on  $\beta$ -chloroalkyl sulfates.<sup>12</sup>

The *in situ* generation of iodine monochloride by the reaction of iodine with mercury(II), gold(I), silver(I), and copper(I) chlorides has been described.<sup>13–15</sup> When these reagents were combined in an ethereal solution of cyclohexene, 80–85% yields of 1-chloro-2-iodocyclohexane were recovered after 7–14 days at room temperature. Under these circumstances half of the halogen was degraded to inactive metal iodide. A related system was more recently described in which olefins were reacted with iodine and various Lewis acid metal chlorides in aqueous solution.<sup>4b</sup> Conversions based on iodine ranged from 30 to 60% indicating that much of the halogen was lost from the reaction, most likely through hydrolysis of alkyl iodide or conversion to metal iodide.

The reactions of olefins with copper(II) halides in various media have been a topic of investigation in these laboratories.<sup>16,17</sup> During these studies it was found that olefins reacted readily with copper(II) chloride and iodine to give high yields of vicinal chloroiodoalkanes. The remainder of this paper presents the scope and the utility of this novel synthetic procedure.

### Results and Discussion



The general reaction of olefins with copper(II) chloride and iodine is illustrated by eq 1; typical yield data



are summarized in Table I. Gaseous olefins were reacted as solutions in various alkane, aromatic, or chloro-carbon solvents. Liquid olefins were allowed to react in the same diluents, or, alternatively, an excess of the olefinic substrate served as the reaction medium. Temperatures of 25–100° and reaction periods of a few minutes to 3–4 hr were required.

Although the reaction was generally insensitive to the choice of diluent, an exception was afforded by the reaction of ethylene in carbon tetrachloride. In this medium no chloroiodoethane was formed, and 1,2-diiodoethane was the sole product. Conversely, all olefins higher than ethylene reacted smoothly to give excellent yields of chloroiodides. While carbon tetrachloride would be anticipated to retard the reaction to some degree as a consequence of copper(II) complexation by the chloro-

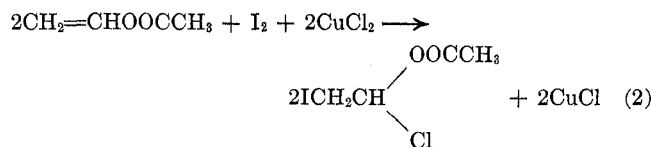
TABLE I  
REACTION OF OLEFINS WITH COPPER(II) CHLORIDE AND IODINE

Olefin	Product	Yield, %
$CH_2=CH_2$	$ICH_2CH_2Cl$	82
$CH_3CH=CH_2$	$CH_3CHCH_2I$ (73%)	75
	$CH_3CHCH_2Cl$ (27%)	
$CH_3(CH_2)_8CH=CH_2$	$CH_3(CH_2)_8CHCH_2I$ (80%)	91
	$CH_3(CH_2)_8CHCH_2Cl$ (20%)	
		95
$CH_2=CHOOCCH_3$	$ICH_2CHOOCCH_3$	88
$CH_2=CHCH=CH_2$	$ClCH_2CH=CHCH_2Cl$ (84%)	78
	$CH_2=CHCHCH_2Cl$ (16%)	
$C_6H_5CH=CH_2$	$C_6H_5CHCH_2Cl$	79

carbon,<sup>18</sup> this factor alone should not totally inhibit the ethylene reaction. The fact that the diiodides derived from other simple olefins are labile relative to diiodoethane under the reaction conditions,<sup>19,20</sup> indicates that facile dissociation of the diiodide contributes to driving the reaction to completion.

Propylene and hexene-1 gave rise to mixtures of isomeric chloroiodoalkanes (Table I). The isomer distributions were comparable to those that had been observed in the addition of iodine monochloride to propylene.<sup>21–23</sup> Since the previous results had been interpreted in terms of an iodonium ion intermediate, which yielded ultimately Markovnikov (SN1) and anti-Markovnikov (SN2) products, it is apparent that a comparable species is involved in the present case.

Vinyl acetate reacted smoothly with iodine and copper(II) chloride to give a single product, 1-chloro-2-iodoethylacetate (eq 2). The structure of this ma-



terial was established in part by a positive iodoform test and reaction with 2,4-dinitrophenylhydrazine reagent.<sup>24</sup> In contrast to the difficulties experienced in adding iodine monochloride to vinyl acetate,<sup>25</sup> this facile addition was reminiscent of the rapid reaction observed during the addition of iodine isocyanate to

(18) (a) D. C. Nonhebel, *J. Chem. Soc.*, 1216 (1963); (b) R. G. R. Bacon and H. A. O. Hill, *ibid.*, 1097 (1964).

(19) E. E. Royals, "Advanced Organic Chemistry," Prentice-Hall, New York, N. Y., 1954, p 343.

(20) G. Sumrell, B. M. Wyman, R. G. Howell, and M. C. Harvey, *Can. J. Chem.*, **42**, 2710 (1964).

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

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

(23) S. Winstein and E. Grunwald, *J. Amer. Chem. Soc.*, **70**, 828 (1948).

(24) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," Wiley, New York, N. Y., 1964, p 253.

(25) D. Swern and E. F. Jordan, Jr., *J. Amer. Chem. Soc.*, **70**, 2334 (1948).

(9) J. R. Shelton and L.-H. Lee, *J. Org. Chem.*, **23**, 1876 (1958).

(10) J. Lorenz and J. Auer, *Angew. Chem.*, **77**, 218 (1965).

(11) E. L. Gefter and M. I. Kabachnik, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 194 (1957); *Chem. Abstr.*, **56**, 11238d (1957).

(12) F. L. M. Pattison and J. E. Millington, *Can. J. Chem.*, **34**, 757 (1956).

(13) L. Brunel, *C. R. Acad. Sci.*, **135**, 1055 (1902).

(14) L. Birckenbach, J. Goubeau, and E. Berringer, *Ber.*, **65**, 1339 (1932).

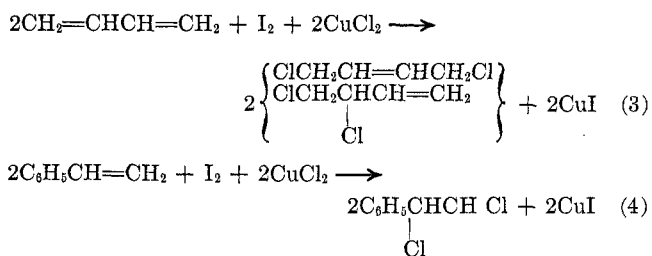
(15) L. Birckenbach and J. Goubeau, *ibid.*, **67**, 1420 (1934).

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

(17) W. C. Baird, Jr., and J. H. Surridge, *ibid.*, **35**, 3436 (1970).

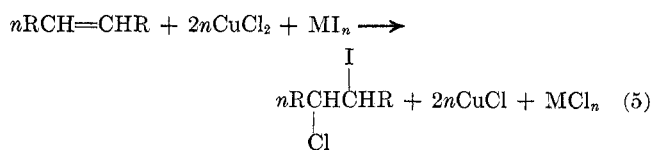
this olefinic ester.<sup>26</sup> The latter reaction has been shown to involve the electrophilic addition of iodonium ion,<sup>27</sup> and it is reasonable to consider a similar intermediate in this case.

The conjugated olefins, butadiene (eq 3) and styrene



(eq 4), did not yield chloriodides but did produce high yields of the corresponding dichlorides. These results are attributed to the halide exchange reactions that occurred between initially formed chloriodides and copper(I) chloride.<sup>15b</sup> The driving force for these exchange processes is provided by the reactivity of the carbon-iodine bonds in these dihalides and by the greater stability of copper(I) iodide relative to the chloride.<sup>28</sup> The dominance of the 1,4 isomer in the mixture of dichlorobutenes was a reflection of the equilibrium distribution over copper halides.<sup>29</sup>

While molecular iodine is a preferred iodine donor for the synthesis of chloriodoalkanes, iodine may also be supplied to the reaction as a covalent metal iodide. The stoichiometry of this reaction is illustrated by eq 5; the Experimental Section gives representative results.

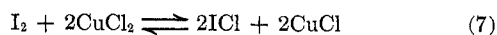


These reactions proceeded with the release of elemental iodine in accord with the equilibrium shown in eq 6.<sup>28b</sup>



While reactions involving metal iodides could be carried out in the hydrocarbon media previously cited, these systems were totally inhibited in carbon tetrachloride. This inhibition was attributed to the influence of chloro-carbon complexation on eq 6. Similarly, highly ionic iodides, e.g., potassium iodide, were not suitable iodine donors, a fact which was also ascribed to the failure of the requisite redox reaction (eq 6) to occur.

The consideration of the mechanism operating in these reactions has precluded the intermediate participation of iodine monochloride (eq 7). If the inter-

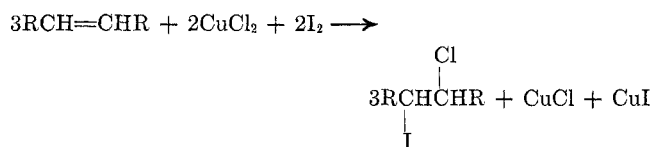


halogen compound were being generated by this equilibrium, all olefins would be expected to yield chloro-

iodides independent of olefinic structure or reaction medium. The failure of ethylene to react in carbon tetrachloride has refuted this scheme. Less convincing, but supporting, evidence was the recovery of unchanged inorganic reagents in control reactions free of olefin.

A consistent picture of the reaction is provided by eq 8a-d. Two initial reactions are possible. One involves the addition of iodine to olefin catalyzed by copper(II) chloride<sup>30</sup> to generate the iodonium salt 3. Alternatively, 3 arises from the interaction of iodonium complex 1 with copper(II) chloride. Loss of copper(II) chloride from 3 with concomitant addition of iodide yields the labile diiodide 2. Transfer of chloride, however, irreversibly produces chloriodoalkane 5 and the unstable copper(II) chloriodide; the latter decomposes to copper(I) chloride and iodine (eq 8a). The appearance of copper(I) chloride in the system initiates the reaction sequence represented by eq 8c. The introduction of copper(I) iodide (eq 8c) in the presence of unreacted copper(II) chloride establishes reaction 8d. The net result of these individual steps is the general reaction previously illustrated by eq 1.<sup>31</sup>

While definitive analysis of such a complex system is difficult, the credibility of reactions 8b-d is provided by their independent observation.<sup>18-15, 19, 28b</sup> Reaction 8a is feasible by analogy to 8c. A consequence of this scheme is that limiting the initial charge of copper(II) chloride prevents the occurrence of reaction 8d. In that case the reaction stoichiometry becomes that shown below. This reaction sequence also predicts



that swamping the system with olefin will depress the overall reaction rate owing to the increased concentration of olefin-iodine and olefin-copper(I)  $\pi$  complexes, which retard reactions 8a, 8c, and 8d. A reaction in neat cyclohexene (olefin:copper:iodine, 50:5:1 mol) required 4 hr to go to completion at room temperature; reaction of this olefin in *n*-pentane (olefin:copper:iodine, 2:2:1 mol) was >80% complete after 25 min.

The isomer distributions obtained with unsymmetrical olefins are ascribed to the reaction being governed by normal iodonium ion behavior in intermediates 3 and 4. The facile reaction with vinyl acetate may be attributed to greater polarization of the reagents than was possible with iodine monochloride.<sup>25</sup> The formation of a single product from vinyl acetate is believed to reflect a unique bonding situation in the iodonium

(30) Copper(I) and copper(II) chlorides are known Lewis acids: G. A. Olah, "Friedel-Crafts and Related Reactions," Vol. I, G. A. Olah, Ed., Wiley, New York, N. Y., 1963, pp 215-216.

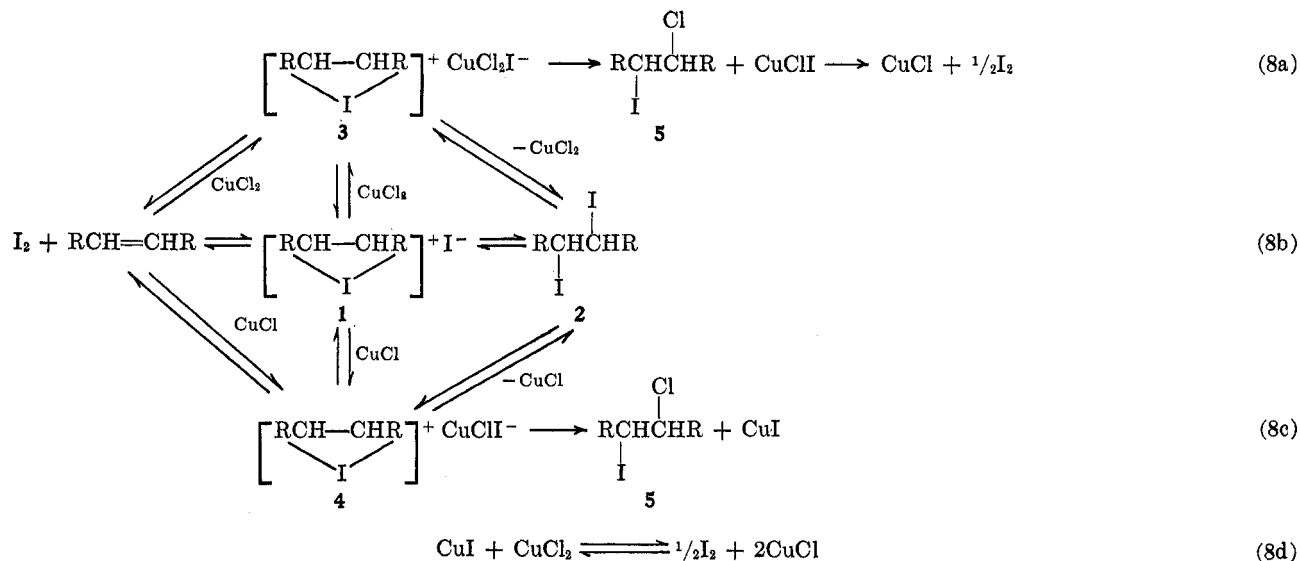
(31) A referee has suggested a free-radical mechanism for these reactions. A radical reaction had been considered and was rejected as being inconsistent with this and related studies. The  $\text{CuCl}_2$ - $\text{I}_2$  system has previously been shown to effect the iodination of aromatic rings via Lewis acid catalyzed iodonium ion attack,<sup>27</sup> a reaction analogous to eq 8a and 8c. A radical mechanism precludes the formation of copper(I) iodide, an observed reaction product, for a radical sequence yields ultimately only copper(I) chloride as the inorganic by-product. A radical reaction for eq 8c requires the formation of metallic copper, which has not been observed in copper(II) chloride deficient reactions where copper(0) would not be removed by disproportionation to copper(I) chloride ( $\text{Cu} + \text{CuCl}_2 \rightarrow 2\text{CuCl}$ ).

(26) C. G. Gebelein and D. Swern, *Chem. Ind. (London)*, 1462 (1965).

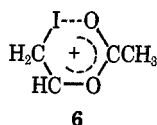
(27) A. Hassner and C. Heathcock, *J. Org. Chem.*, **29**, 3640 (1964); *Tetrahedron*, **20**, 1037 (1964); *Tetrahedron Lett.*, 393 (1963); 1125 (1964).

(28) (a) L. Pauling, "College Chemistry," W. H. Freeman and Co., San Francisco, Calif., 1951, pp 553-555; (b) "Gmelins Handbuch der Anorganischen Chemie," Vol. 60 (B1), Verlag Chemie, Weinheim, Ger., 1958, p 389.

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



ion which tends to localize and stabilize the positive charge on the methine carbon (6).



### Experimental Section

Infrared spectra were recorded on a Beckman IR-5A spectrophotometer. Vapor phase chromatography (vpc) was performed utilizing a Perkin-Elmer 154D fractometer, a Perkin-Elmer Model 226 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. All reagents were obtained from commercial sources and were used as received. All gaseous olefins were CP grade.

**Synthesis of Vicinal Chloroiodoalkanes. Ethylene.**—Into a Parr high pressure reactor<sup>22</sup> were placed 200 ml of cyclohexane, 26.6 g (0.2 mol) of copper(II) chloride, 25.4 g (0.1 mol) of iodine, and 0.2 mol of ethylene. The reaction was stirred at 75–85° for 2 hr. The reaction mixture was filtered to give 23.5 g of copper salts, which corresponded to 12.3 g (0.125 mol) of copper(I) chloride, 4.7 g (0.025 mol) of copper(I) iodide, and 6.7 g (0.05 mol) of unreacted copper(II) chloride. From the filtrate was recovered 31.2 g (0.17 mol) of 1-chloro-2-iodoethane (85%): bp 55–57° (37 mm);  $n_D^{25}$  1.5636;  $d_4^{25}$  2.12; nmr (neat)  $\delta$  3.2–3.6 (m, 2, HCCl), 3.7–4.1 (m, 2, HCl). Vpc analysis (2 m  $\times$  0.25 in. 20% diethylene glycol succinate column, 125°, 15-psig helium) gave a single peak,  $t_r$  5.1 min from air. *Anal.* Calcd for  $C_2H_4ClI$ : C, 12.61; H, 2.12; Cl, 18.62; I, 66.65. Found: C, 12.91; H, 2.34; Cl, 18.80; I, 67.70.

If the reaction was performed at room temperature, no chloroiodoethane was produced. From the reaction was recovered unreacted copper(II) chloride and a 98% yield of 1,2-diiodoethane; the latter was shown to be identical with an authentic sample.

The reaction was repeated using a stoichiometric deficiency of copper(II) chloride; the reactor was charged with 0.3 mol of ethylene, 0.2 mol of copper(II) chloride, and 0.2 mol of iodine. From the reaction was isolated 54.5 g (96%) of 1-chloro-2-iodoethane and 29.3 g of copper(I) salts. The latter was a mixture of 0.1 mol of copper(I) chloride and 0.1 mol of copper(I) iodide.

When the reaction of ethylene was performed in carbon tetrachloride, an 80% yield of diiodoethane was isolated. A 10-g sample of this diiodide was refluxed with 5 g of copper(II) chloride in 50 ml of carbon tetrachloride for 2 hr. The bulk of the diiodide (91%) was recovered unchanged.

**Propylene.**—The same procedure was followed as described for ethylene. The yield of chloroiodopropanes was 75–80%; bp

54–55° (24 mm);  $n_D^{25}$  1.5403; nmr (neat)  $\delta$  1.65 (d, 2.3,  $\text{CH}_3\text{-CHCl}$ ), 1.95 (d, 0.7,  $\text{CH}_3\text{CHI}$ ), 3.2–4.4 (m, 3,  $\text{CH}_2$ , CH). Analysis of the methyl group areas showed the composition of the product to be 76.5% 1-iodo-2-chloropropane and 23.5% 1-chloro-2-iodopropane.

**Cyclohexene.**—Into a round-bottom flask were placed 50 ml of cyclohexene, 13.3 g (0.1 mol) of copper(II) chloride, and 12.7 g (0.05 mol) of iodine. The reaction was stirred at room temperature for 4 hr. The reaction mixture was filtered, and the filter cake was washed with *n*-pentane to give 9.8 g (0.1 mol) of copper(I) chloride. From the filtrate was isolated 24.2 g (99%) of 1-chloro-2-iodocyclohexane: bp 37° (0.2 mm);  $n_D^{25}$  1.5700; nmr (neat)  $\delta$  4.4 (m, 2, HCCl, HCl), 1.2–2.8 (m, 8,  $\text{CH}_2$ ). Vpc analysis (2 m  $\times$  0.25 in. 20% diethylene glycol succinate column, 125°, 15 psig) gave a single compound,  $t_r$  31.4 min. *Anal.* Calcd for  $C_6H_{10}ClI$ : C, 29.47; H, 4.12; Cl, 14.50; I, 51.90. Found: C, 29.57; H, 4.13; Cl, 14.40; I, 51.40.

A duplicate experiment was permitted to stir at room temperature for 15 min. Filtration gave 12.3 g of copper(II) chloride (93% recovery); from the filtrate was obtained ~20 g of a mixture of cyclohexene and iodine.

In another experiment a solution of 8.2 g (0.1 mol) of cyclohexene in 50 ml of pentane was stirred with 13.3 g (0.1 mol) of copper(II) chloride and 12.7 g (0.05 mol) of iodine at room temperature for 25 min. The reaction produced 20.0 g (82%) of chloroiodocyclohexane and 12.7 g of a mixture of copper(I) chloride (6.3 g, 0.064 mol), copper(I) iodide (3.4 g, 0.018 mol), and copper(II) chloride (2.4 g, 0.018 mol).

A mixture of 15 ml (0.15 mol) of cyclohexene, 13.3 g (0.1 mol) of copper(II) chloride, 25.4 g (0.1 mol) of iodine, and 50 ml of cyclohexane was stirred at room temperature for ~20 hr. A 95% yield of chloroiodocyclohexane was isolated. The inorganic product (14.4 g) was a mixture of 4.9 g (0.05 mol) of copper(I) chloride and 9.5 g (0.05 mol) of copper(I) iodide.

**Hexene-1.**—A mixture of 100 ml of hexene-1, 27 g (0.2 mol) of copper(II) chloride, and 26 g (0.1 mol) of iodine was stirred at reflux for 15 min. From the reaction was isolated 44.7 g (91%) of isomeric chloroiodohexanes. The nmr spectrum indicated a mixture containing 80% 1-iodo-2-chlorohexane and 20% 1-chloro-2-iodohexane.

**Vinyl Acetate.**—To 100 ml of vinyl acetate was added 26 g (0.1 mol) of iodine and 27 g (0.2 mol) of copper(II) chloride. The reaction was stirred at 80° for 2 hr. The usual work-up gave 50.1 g (88%) of 1-chloro-2-iodoethylacetate: bp 38–40° (0.15 mm); nmr (neat)  $\delta$  6.50 (t, 1, HC $\leq$ ), 3.68 (d, 2,  $\text{CH}_2$ ), 2.15 (s, 3,  $\text{CH}_3\text{CO}$ ). *Anal.* Calcd for  $C_5H_8ClIO_2$ : C, 19.33; H, 2.44; Cl, 14.27; I, 51.07. Found: C, 20.07; H, 2.36; Cl, 14.40; I, 50.10. The ester gave a positive iodoform test; reaction with 2,4-dinitrophenylhydrazine reagent gave a dark red crystalline product, mp 80° dec. *Anal.* Calcd for  $C_5H_8N_2O_4$ : C, 43.25; H, 2.72; N, 25.26. Found: C, 43.31; H, 2.89; N, 24.56.

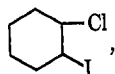
**Iodine Donors and Diluents for Synthesis of Chloroiodoalkanes.**—Cyclohexene was used as a model olefin. In a typical experiment a solution of 16.4 g (0.2 mol) of cyclohexene in 100 ml of inert diluent was heated and stirred with 26.6 g (0.2 mol) of

copper(II) chloride and the indicated quantity of iodine donor. The reaction mixture was worked up in the usual manner. The results are summarized in Table II.

TABLE II

Diluent	Iodine donor <sup>a</sup>	Temp, °C	Time, hr	yield, %
C <sub>6</sub> H <sub>12</sub>	I <sub>2</sub>	60	0.3	88
C <sub>6</sub> H <sub>6</sub>	I <sub>2</sub>	80	0.1	91
CCl <sub>4</sub>	I <sub>2</sub>	80	0.1	90
C <sub>6</sub> H <sub>10</sub> <sup>b</sup>	CuI	80	1	83
C <sub>6</sub> H <sub>10</sub>	KI	80	2	0
C <sub>6</sub> H <sub>10</sub>	LiI	80	4	92
C <sub>6</sub> H <sub>10</sub>	BiI <sub>3</sub> <sup>c</sup>	80	2	93
CCl <sub>4</sub>	CuI	80	2	0
C <sub>7</sub> H <sub>16</sub>	CuI	98	2	66

<sup>a</sup> 0.1 mol. <sup>b</sup> 100 ml of cyclohexene as diluent. <sup>c</sup> 0.02 mol.



**Reaction of Conjugated Olefins. Butadiene.**—A Parr reactor was charged with 100 ml of benzene, 26.6 g (0.2 mol) of copper(II) chloride, 25.4 g (0.1 mol) of iodine, and 0.2 mol of butadiene. The reaction was stirred at 70° for 2 hr. The reaction mixture was filtered to give 37 g of copper(I) iodide. The benzene was removed from the filtrate on a rotary evaporator, and the residue was distilled to give 19.4 g (78%) of isomeric dichlorobutenes, bp 48–53° (14 mm). Vpc analysis (5 ft × 0.25 in. 20% diethylene glycol succinate column, 125°, 48 ml/min) gave the following isomer distribution: 3,4-dichlorobutene-1, 16% (*r<sub>t</sub>* 3.7 min); *cis*-1,4-dichlorobutene-2, 3% (*r<sub>t</sub>* 10.0 min); *trans*-1,4-dichlorobutene-2, 81% (*r<sub>t</sub>* 12.0 min). The products were identified by comparison with authentic samples.

If 0.1 mol of copper(I) iodide was used as the iodine source, a 23% yield of dichlorobutenes was realized after 3 hr at 70°. When carbon tetrachloride was used as a reaction diluent, no reaction occurred with copper(I) iodide. This diluent in combination with molecular iodine gave a 90% yield of dichlorobutenes in 90 min.

In a control experiment 1 g (4.6 mmol) of 1-chloro-4-iodobutene-2<sup>3c</sup> and 1 g (10.2 mmol) of copper(I) chloride were stirred at 70° for 90 min in 10 ml of benzene. The benzene solution was analyzed by vpc and was shown to contain the three isomeric dichlorobutenes; the isomer distribution was comparable with that described above.

**Styrene.**—To a mixture of 13 g (0.05 mol) of iodine, 13.3 g (0.1 mol) of copper(II) chloride, and 60 ml of *n*-octane at reflux was added dropwise a solution of 10.4 g (0.1 mol) of styrene in 40 ml of *n*-octane. The addition required ~40 min.; the reaction was maintained at reflux for an additional 10 min. The reaction mixture was cooled and filtered to give 17.6 g of copper(I) iodide (theory, 19.0 g). The filtrate was washed with 20% sodium thiosulfate solution and was dried over magnesium sulfate. The *n*-octane was removed on a rotary evaporator [60° (15 min)] to give 17.4 g of crude product. Distillation gave 13.8 g (79%) of 1,2-dichloro-1-phenylethane: bp 67–73° (0.2 mm); nmr (neat) δ 7.2 (s, 5, C<sub>6</sub>H<sub>5</sub>), 4.85 (t, 1, >CHCl), 3.75 (d, 2, -CH<sub>2</sub>Cl). Vpc analysis [2 m × 0.25 in. 20% silicone (DC-200) column, 150°, 105 ml/min] showed a single peak, *r<sub>t</sub>* 16.0 min; a small amount of styrene, *r<sub>t</sub>* 2.6 min, was present as an impurity (~3–5%). *Anal.* Calcd for C<sub>8</sub>H<sub>8</sub>Cl<sub>2</sub>: C, 54.89; H, 4.60; Cl, 40.51. Found: C, 54.92; H, 4.47; Cl, 39.67.

A sample of the dichlorophenylethane was dehydrochlorinated with methanolic sodium hydroxide to give *α*-chlorostyrene: bp 74–77° (14 mm); *n<sub>D</sub><sup>20</sup>* 1.5561 (lit.<sup>21</sup> *n<sub>D</sub><sup>20</sup>* 1.5590); nmr (neat) δ 7.1–7.5 (m, 5, C<sub>6</sub>H<sub>5</sub>), 5.43 (q, 2, =CH<sub>2</sub>).

The reaction of styrene was repeated at room temperature for a period of 20 hr. The reaction produced 4.5 g (26%) of dichlorophenylethane and 8.6 g (0.083 mol) of polystyrene. The inorganic by-product was a mixture of unreacted copper(II) chloride (6.0 g) and copper(I) iodide (11.8 g); unreacted iodine (0.02 mol) was determined by titration with thiosulfate.

**Registry No.**—Copper(II) chloride, 7447-39-4; 1-chloro-2-iodoethane, 624-70-4; 1-iodo-2-chloropropane, 29568-69-2; 1-chloro-2-iodopropane, 29568-70-5; 1-chloro-2-iodocyclohexane, 29641-86-9; 1-chloro-2-iodoethylacetate, 29568-71-6; 1,2-dichloro-1-phenylethane, 1074-11-9.

## Paramagnetic Metallocenes. Oxidation of Ferrocenyl Ketones<sup>1</sup>

JOHN J. McDONNELL\* AND DONALD J. POCHOPIEN

Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois 60616

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Ferrocenyl ketones which have an *α*-methylene group were oxidized to the stable paramagnetic semidiones. An excess of oxygen resulted in ortho oxygenation of the metallocene ring. The esr spectra indicated a remarkably small amount of electron spin delocalization into the metallocene ring. The simplicity of the esr spectra permitted the elucidation of the relative rates of semidione formation as a function of substituent on metal ion. Interannular substituent effects on electron distribution were shown to be primarily inductive in nature. Hydrogen-deuterium exchange of alkyl hydrogens *α* to the semidione when the oxidation was conducted in DMSO-*d*<sub>6</sub> was very slow; this observation was interpreted in terms of a dianion in the exchange reaction.

Ketones with an *α*-methylene group can be oxidized with molecular oxygen to the corresponding semidiones in dimethyl sulfoxide (DMSO) solution containing an excess of potassium *tert*-butoxide. The reaction is quite general and many semidiones prepared by this technique have been observed by esr spectroscopy.<sup>2</sup> Since our initial report on the conveniently prepared and stable semidione derivatives of metallocenes,<sup>3</sup> other stable metallocene radicals have been observed

by esr.<sup>4–7</sup> These species are of interest from a viewpoint of electron spin delocalization, metal ligand interaction, and chemical reactivity. Despite the application of metallocenes as antioxidants, combustion control additives, photoprotecting uv absorbers, and medicinals (areas which clearly involve radical chemistry), the chemical and physical properties of stable metallocene radicals have been almost uninvestigated<sup>8</sup> until very recently. Most of the previous studies concerning radi-

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(2) G. A. Russell, *et al.*, *Rec. Chem. Progr.*, **27**, 3 (1969); and E. I. Kaiser and L. Kevan, Ed., "Radical Ions," Wiley, New York, N. Y., 1969, Chapter 8.

(3) J. J. McDonnell, *Tetrahedron Lett.*, 2039 (1969).

(4) J. J. McDonnell, G. Capen, and R. Michealson, *ibid.*, 4251 (1969).

(5) A. R. Forrester, S. P. Hepburn, R. S. Dunlop, and H. H. Mills, *Chem. Commun.*, 698 (1969).

(6) C. Elschenbroich and M. Cais, *J. Organometal. Chem.*, **18**, 135 (1969).

(7) W. C. Danen and C. T. West, *Tetrahedron Lett.*, 219 (1970).

(8) V. M. Kazakava and Y. K. Syrkin, *Zh. Strukt. Khim.*, **3**, 536 (1962).