Reaction of 1,1-Diiodoethane with Copper Powder in the Presence of Olefins and/or Alkylbenzenes

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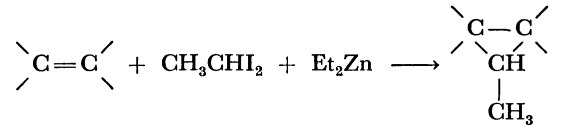
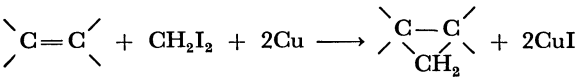
The treatment of 1,1-diiodoethane with copper powder in the presence of 1-heptene gave a 1.3 : 1 mixture of *cis*- and *trans*-1-methyl-2-pentylcyclopropane in 11% yield. The treatment in the presence of cyclohexene gave a 1 : 1.7 mixture of *endo*- and *exo*-7-methylbicyclo[4.1.0]heptane in 32% yield, together with 1-ethylcyclohexene in 8% yield, which was shown to be derived mainly from isomerization of the *endo*-isomer. These reactions were concluded to proceed *via* organocopper intermediate rather than free methylcarbene. The treatment of 1,1-diiodoethane with copper powder in the presence of alkylbenzene gave a mixture of *o*- and *p*-ethyl(alkyl)benzene contrary to the corresponding reaction of methylcarbenoid of zinc which gave cycloheptatriene derivatives.

This paper describes an α-elimination of iodine from 1,1-diiodoethane by the reaction with copper powder. Although α-elimination reactions provide the best route to most classes of carbenes and carbenoids,[1] only a few publications are available on the α-elimination of halogen from 1,1-dihaloalkane. Alkyl- and dialkylcarbenes are distinguished from other classes of carbenes by the predominance of intramolecular reactions leading to olefins and cyclopropane derivatives. Kirmse and Wächtershäuser[2] reported that the treatment of 1,1-diiodoalkane with sodium, lithium, and magnesium afforded predominantly cyclopropane derivatives, whereas the treatment with zinc and copper produced olefins *via* rearrangements of the Wagner-Meerwein type, but these workers did not refer to the α-elimination of 1,1-diiodoethane. The α-elimination of iodine from 1,1-diiodoalkane by zinc-copper couple was reported to give predominantly olefins.[3] The reaction of 1,1-diiodoethane with zinc-copper couple was reported to give ethylene.[4]

The α-elimination reactions of 1,1-dihaloalkanes in the presence of olefins give the corresponding cyclopropane derivatives by intermolecular cycloaddition of alkylcarbene or carbenoid to olefins.[4–6] Previously we have proposed an improved method for preparing methylsubstituted cyclopropane derivatives by the reaction of olefins with 1,1-diiodoethane and diethylzinc.[7]


(1)

Recently we found that the reaction of diiodomethane with copper powder in the presence of olefins gave the corresponding cyclopropane derivatives in good yields.[8]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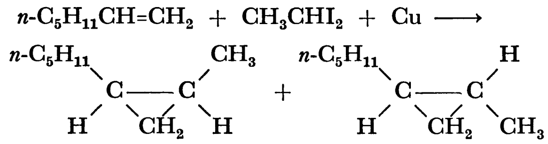
As an extension of this work, we have investigated the reaction of 1,1-diiodoethane with copper powder in the presence of olefins and/or alkylbenzenes.

Results and Discussion

The reaction of 1,1-diiodoethane with copper powder was carried out in toluene at 75 °C for 24 h. Gas chromatographic analysis of the liquid layer showed that 74% of 1,1-diiodoethane remained unchanged in the reaction mixture under the conditions. In the gaseous products was shown the formation of ethylene in 2% yield, but ethane was not detected. The experimental results indicate that 1,1-diiodoethane reacted with copper powder under the conditions. Methylcarbene or methylcarbenoid of copper would be reactive intermediates. The absence of ethane in the gaseous products indicates that the methylcarbene or carbenoid did not undergo the hydrogen abstraction under the conditions.

The treatment of 1,1-diiodoethane with copper powder in the presence of 1-heptene gave a 1.3 : 1 mixture of *cis*- and *trans*-1-methyl-2-pentylcyclopropane in 11% yield based on the olefin.

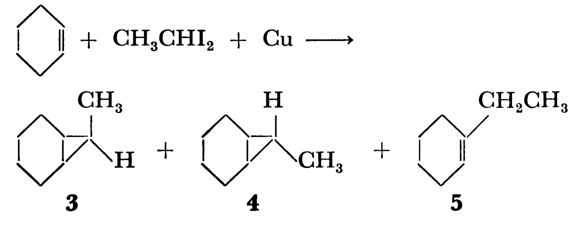

n-$C_5H_{11}CH{=}CH_2 + CH_3CHI_2 + Cu \longrightarrow$ (3)

1 **2**

Isomeric olefins were not detected in the reaction mixture which would be expected from the insertion of free methylcarbene into C–H bonds. Therefore, the α-elimination of iodine from 1,1-diiodoethane by copper powder may proceed *via* an organocopper intermediate (methylcarbenoid of copper) rather than free methylcarbene.

Since the *cis*-isomer **1** was obtained predominantly over the *trans*-isomer **2**, the methylcarbenoid of copper was concluded to show essentially the *syn*-selectivity[9] in the cycloaddition with olefins as the methylcarbenoid of zinc.[7]

1,1-Diiodoethane was allowed to react with copper powder in the presence of cyclohexene to give a 1 : 1.7 mixture of *endo*- and *exo*-7-methylbicyclo[4.1.0]heptane in 32% yield, together with 1-ethylcyclohexene (**5**) in 8% yield based on the olefin.


(4)

3 **4** **5**

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Table 1. Formatiom of ethyl(alkyl)benzene by reaction (5)

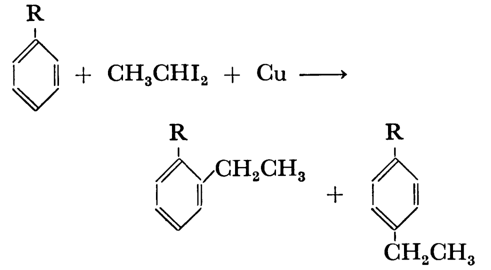
R	Copper (mmol)	Alkylbenzene (ml)	1,1-Diiodoethane (mmol)	Temp (°C)	Time	Yield (%)[a]	Isomer ratio (*p*/*o*)
H	72.0	15.0	32.0	75	17 day	1	—
CH_3	18.0	4.0	8.1	100	95 h	3	2.1
CH_3CH_2	72.0	15.0	31.3	125	40 h	27	2.4

a) Based on 1,1-diiodoethane.

Heating of an isolated mixture (77 : 23) of **3** and **5** in the presence of copper (I) iodide gave a 4 : 96 mixture of **3** and **5**. On the other hand, the *exo*-isomer **4** did not isomerize to **5** under the conditions. Therefore, **5** was concluded to be derived mainly from the isomerization of **3** during the reaction (Eq. 4) rather than the insertion of free methylcarbene into C–H bonds. When **5** was supposed to be completely derived from the isomerization of **3**, the reaction (Eq. 4) was led to give a nearly equimolar amount of **3** and **4**. In any case, the *endo*-isomer **3** did not predominate over the *exo*-isomer **4** in the reaction (Eq. 4), contrary to the corresponding reaction of methylcarbenoid of zinc. The reaction (Eq. 1) with cyclohexene gave a 1.5 : 1 mixture of **3** and **4**.[7)]

In order to compare the behavior of the organocopper intermediate (methylcarbenoid of copper) with that of the methylcarbenoid of zinc generated from 1,1-diiodoethane and diethylzinc in the reaction with alkylbenzene, we also studied on the reaction of 1,1-diiodoethane and copper powder in the presence of alkylbenzene.

1,1-Diiodoethane was found to react with copper powder in alkylbenzene to give mixtures of *o*- (**6**) and *p*-ethyl(alkyl)benzene (**7**) as are given in Table 1. *m*-Ethyl(alkyl)benzene was not significantly detected in the reaction mixture (see experimental for details). Cycloheptatriene derivatives were not detected in the above reaction mixtures.

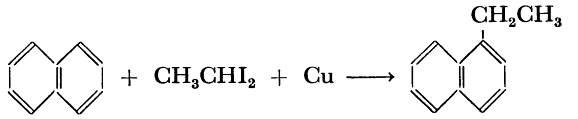


(5)

6 **7**

These experimental results form a sharp contrast with those observed in the reaction of methylcarbenoid of zinc with alkylbenzene. In the latter reaction, the ring expansion reaction was predominant to afford cycloheptatriene derivatives.[10)]

The reaction of the methylcarbenoid of zinc with naphthalene gave 7-methyl-2,3-benzobicyclo[4.1.0]hepta-2,4-diene (**8**).[10)] On the other hand, the treatment of 1,1-diiodoethane and copper powder in the presence of naphthalene in ethylbenzene gave α-ethylnaphthalene in 12% yield at 125 °C based on naphthalene together with *o*- and *p*-diethylbenzene. β-Ethylnaphthalene and **8** were not detected in the reaction mixture.



(6)

Since cycloheptatriene derivatives and **8** were not formed by the reactions (Eqs. 5 and 6), the following route should be excluded: the cycloaddition of the methylcarbenoid of copper to the aromatic carbon-carbon unsaturated bond to afford bicyclo[4.1.0]hepta-2,4-diene derivatives followed by isomerization to ethylbenzene derivatives. The *ortho-para* orientation in the reaction (Eq. 5) and the predominant formation of α-ethylnaphthalene in the reaction (Eq. 6) show the electrophillic nature of the reaction of 1,1-diiodoethane and copper powder with alkylbenzene to afford ethylbenzene derivatives, but further experiments are required to discuss the mechanism of the substitution.

Experimental

Gas chromatographic analyses were carried out on a Shimadzu GC-4A or GC-4B gas chromatograph. NMR spectra were obtained with a Varian Model T-60-A spectrometer using carbon tetrachloride as the solvent and tetramethylsilane as the internal standard. IR spectra were recorded on a Hitachi Model 215 or Japan Spectroscopic Model 402 G spectrophotometer.

Materials. 1,1-Diiodoethane was prepared according to the procedure of Letsinger and Kammeyer.[11)] Diethylzinc was prepared according to the procedure of Holler.[12)] Active zinc-copper couple was prepared according to the procedure of Shank and Shechter.[13)] The ordinary commercial grade of copper powder (particle size was 5—15 μ) provided by Nakarai Chemicals Ltd., Kyoto was used without further purification. Olefins, alkylbenzenes, and solvents were purified by distillation. Nitrogen was purified by being passed through a tube containing copper turnings in a furnace at 170 °C. Authentic samples of ethylene and ethane were prepared by hydrolyses of vinylmagnesium bromide and ethylmagnesium bromide, respectively. Authentic samples of **1**,[14)] **2**,[14)] **3**,[7)] and **4**[7)] were prepared by conventional methods, respectively. Commercial authentic samples and other chemicals were used without further purification.

Reaction of 1,1-Diiodoethane with Copper Powder. Copper powder (2.28 g, 36.0 mmol) was allowed to react with a small amount (0.10 g, 0.4 mmol) of iodine in 4.0 ml of toluene at room temperature in a flask equipped with a gas burrette and a magnetic stirrer. After the brown color of iodine disappeared, 1,1-diiodoethane (4.51 g, 16.0 mmol) was added, and the mixture was heated at 75 °C for 24 h with stirring. The total amount of the evolved gas was determined by the gas burrette, and the gaseous products were analyzed by gas chromatography. The liquid layer was also analyzed by gas chromatography after elimination of the inorganic materials from the reaction mixture by filtration. Results are given in the text.

Reaction of 1,1-Diiodoethane with Copper Powder in the Presence of 1-Heptene. Copper powder (2.28 g, 36.0 mmol) was allowed to react with a small amount (0.10 g, 0.4 mmol) of iodine in 6.0 ml of toluene at room temperature in a flask equipped with a reflux condenser and a magnetic stirrer. After the brown color of iodine disappeared, 1,1-diiodoethane (4.31 g, 15.3 mmol) and 1-heptene (0.88 g, 9.0 mmol) were added, and the mixture was heated at 85 °C for 91 h with stirring. After the reaction, inorganic materials were removed by filtration, and the organic layer was analyzed by gas chromatography. Yields were determined by the gas chromatographic analyses of the reaction mixture. The structures of the products **1** and **2** were determined by comparison of their retention times with those of authentic samples in gas chromatography using two types of different liquid phase, *i.e.*, Silicone DC 550 and Apiezon Grease L. Results are given in the text.

Reaction of 1,1-Diiodoethane with Copper Powder in the Presence of Cyclohexene. Copper powder (3.42 g, 54.0 mmol), iodine (0.15 g, 0.6 mmol), 1,1-diiodoethane (7.03 g, 24.9 mmol), and cyclohexene (1.04 g, 12.7 mmol) were reacted in 9.0 ml of benzene at 75 °C for 304 h in a similar way. Yields were determined by gas chromatographic analyses of the reaction mixture. Products **3**, **4**, and **5** were isolated by collection from the organic layer by gas chromatography. Structures of **3** and **4** were determined by comparison of their IR spectra with those of authentic samples. The structure of **5** was determined by its NMR spectrum. NMR (CCl_4) τ: 4.68 (1 H, m), 7.7—8.8 (8 H, m), 8.09 (2 H, q, $J=7$ Hz), and 9.01 (3 H, t, $J=7$ Hz).

A 77 : 23 mixture of **3** and **5** (0.14 g, 1.2 mmol) collected by gas chromatography was heated at 75 °C for 40 h in the presence of copper(I) iodide (0.95 g, 2.5 mmol) in 2.5 ml of benzene. Gas chromatographic analysis of this reaction mixture showed the presence of a 4 : 96 mixture of **3** and **5**, and **4** was not detected in this reaction mixture.

An isolated sample of **4** (0.09 g, 0.8 mmol) collected by gas chromatography was heated at 75 °C for 40 h in the presence of copper(I) iodide (0.65 g, 1.7 mmol) in 1.7 ml of benzene. Gas chromatographic analysis of this reaction mixture showed the presence of **4** without **3** and **5**.

Reaction of 1,1-Diiodoethane with Copper Powder in the Presence of Alkylbenzene. The reaction of 1,1-diiodoethane with copper powder in the presence of alkylbenzene was carried out in a similar way. Products were isolated by collection from the organic layer by gas chromatography. Structures were determined by comparison of their IR spectra with those of authentic samples. Yields were determined by gas chromatographic analyses of the reaction mixture. Results are given in the text.

Reaction of 1,1-Diiodoethane with Copper Powder in the Presence of Naphthalene. The reaction of copper powder (3.82 g, 60.0 mmol), 1,1-diiodoethane (8.12 g, 28.8 mmol), iodine (0.20 g, 0.8 mmol), and naphthalene (2.56 g, 20.0 mmol) was carried out in 10.0 ml of ethylbenzene at 125 °C for 22 h. Gas chromatographic analysis of the reaction mixture showed the formation of α-ethylnaphthalene in 12% yield based on naphthalene, together with *o*- and *p*-diethylbenzene. The sturcture of α-ethylnaphthalene was determined by comparison of the IR spectrum of an isolated sample collected by gas chromatography with that of an authentic sample.

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