

A Free Radical Mechanism for the Formation of Zinc-Carbenoid Reagent from Diethylzinc and Chloriodomethane

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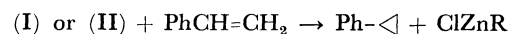
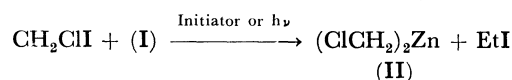
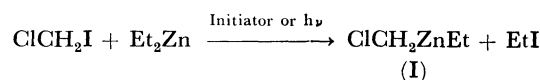
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Chloriodomethane is useful as a methylene source for the cyclopropanation of olefins by the oxygen catalyzed zinc-carbenoid reaction.¹⁾ Cyclohexene (99%), cyclooctene (99%), 1-heptene (79%), 2-heptene (94%), and 1-octene (88%) gave the corresponding cyclopropane in the yields given in parentheses.

We wish to present the possibility of a radical mechanism for the formation of the zinc-carbenoid reagent from diethylzinc and chloriodomethane. Chloriodomethane (38 mmol) was allowed to react with diethylzinc (25 mmol) in the presence of styrene (25 mmol) in benzene (20 ml) at 50°C under nitrogen atmosphere. The starting materials were recovered unchanged after 3 hr indicating that no reaction took place. By passing oxygen into the space above the reaction mixture at a rate of 10 ml/min, chloriodomethane completely reacted within 1.5 hr giving phenylcyclopropane in 66% yield. When oxygen was introduced just after the addition of chloriodomethane, the reaction was also completed within 1.5 hr giving phenylcyclopropane in 70% yield. AIBN and UV light also catalyzed the cyclopropanation of styrene (Table 1). Without diethylzinc, chloro-

iodomethane did not cyclopropanate styrene in the presence of AIBN or UV light, though peroxides²⁾ or UV light³⁾ catalyzed the cyclopropanation of olefins with diiodomethane.

When a mixture of styrene, chloriodomethane and diethylzinc in *n*-hexane was irradiated with a UV light at -70°C, chloriodomethane reacted with diethylzinc with the formation of ethyl iodide in equivalent amount to the reacted chloriodomethane, while styrene remained unchanged. When the light was turned off and the reaction mixture was allowed to stand at room temperature, an exothermic reaction took place, and phenylcyclopropane was obtained in 50% yield within 1 hr. This indicates the following reaction sequences (R=Et or CH₂Cl);⁴⁾



There are evidences that ethyl radical is formed by the reaction of diethylzinc with oxygen⁶⁾ or by the decomposition of AIBN in the presence of diethylzinc.⁷⁾

This suggests that the zinc-carbenoid reagent is formed via free radical processes from diethylzinc and chloriodomethane. The methylene transfer step from the zinc-carbenoid reagent to olefins seems to be a conventional, one-step and three-centered carbenoid reaction if we consider the stereospecific methylene addition to 2-heptenes, the absence of C-H insertion products, and the fact that the formed zinc-carbenoid reagent can cyclopropanate styrene without any free radical catalyst.

TABLE 1. CYCLOPROPANATION OF STYRENE^{a)}

Catalyst	Reaction		Phenylcyclopropane Yield (%)
	Time (h)	Temp (°C)	
— ^{b)}	3	50	0
—	4	70	0
—	7	70	3.7
Oxygen ^{b)}	1.5	50	70
AIBN ^{c, d)}	2	70	46
AIBN ^{e)}	4.5	70	22
UV light ^{e)}	1.5	23	73

a) Reactions were carried out under nitrogen atmosphere. Styrene 50 mmol; CH₂ClI 60 mmol; Et₂Zn 50 mmol; benzene 50 ml.

b) Styrene 25 mmol; CH₂ClI 38 mmol; Et₂Zn 25 mmol; benzene 20 ml.

c) AIBN 2.5 mmol.

d) CH₂ClI 94 mmol.

e) In 150 ml of benzene. High pressure mercury lamp (100 W) was used.

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3) D. C. Blomstrom, K. Hering, and H. E. Simmons, *J. Org. Chem.*, **30**, 959 (1965).

4) ICH₂ZnEt and (ICH₂)₂Zn are said methylene transferring reagent for the zinc-carbenoid reaction with diethylzinc and diiodomethane.⁵⁾

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