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

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Chloroiodomethane 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 chloroiodomethane. Chloroiodomethane (38 mmol) was allowed to react with diethylzinc (25 mmol) in the presence of styrene (25 mmol) in benzene (20 m*l*) 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 m*l*/min, chloroiodomethane completely reacted within 1.5 hr giving phenylcyclopropane in 66% yield. When oxygen was introduced just after the addition of chloroiodomethane, 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, chloroiodomethane did not cyclopropanate styrene in the presence of AIBN or UV light, though peroxides[2] or UV light[3] catalyzed the cyclopropanation of olefins with diiodomethane.

TABLE 1. CYCLOPROPANATION OF STYRENE[a]

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

a) Reactions were carried out under nitrogen atmosphere. Styrene 50 mmol; CH_2ClI 60 mmol; Et_2Zn 50 mmol; benzene 50 m*l*.
b) Styrene 25 mmol; CH_2ClI 38 mmol; Et_2Zn 25 mmol; benzene 20 m*l*.
c) AIBN 2.5 mmol.
d) CH_2ClI 94 mmol.
e) In 150 m*l* of benzene. High pressure mercury lamp (100 W) was used.

When a mixture of styrene, chloroiodomethane and diethylzinc in *n*-hexane was irradiated with a UV light at −70°C, chloroiodomethane reacted with diethylzinc with the formation of ethyl iodide in equivalent amount to the reacted chloroiodomethane, 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 CH_2Cl);[4]

$$ClCH_2I + Et_2Zn \xrightarrow{\text{Initiator or } h\nu} \underset{\text{(I)}}{ClCH_2ZnEt} + EtI$$

$$CH_2ClI + \text{(I)} \xrightarrow{\text{Initiator or } h\nu} \underset{\text{(II)}}{(ClCH_2)_2Zn} + EtI$$

$$\text{(I) or (II)} + PhCH{=}CH_2 \rightarrow Ph\text{-}\lhd + ClZnR$$

There are evidences that ethyl radical is formed by the reaction of diethylzinc with oxygen[6] 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 chloroiodomethane. 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.

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4) ICH_2ZnEt and $(ICH_2)_2Zn$ are said methylene transferring reagent for the zinc-carbenoid reaction with diethylzinc and diiodomethane.[5]

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