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The Inhibitory Effect of Several Olefins on the Formation of the Zinc-carbenoid Reagent from Diethylzinc and Chloroiodomethane

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In a previous paper[1] we reported that styrene greatly inhibits the formation of the zinc-carbenoid reagent from diethylzinc and diiodomethane or chloroiodomethane. In this respect, it appeared of interest to examine the effects of several olefins on the zinc-carbenoid reaction of cyclohexene with diethylzinc and chloroiodomethane (Table 1). Norcarane was obtained in a good yield when diethylzinc was allowed to react with a mixture of cyclohexene and chloroiodomethane under a nitrogen atmosphere. On the other hand, in the presence of 5 mol % of 1-phenyl-1,3-budadiene only 18% of the initial chloroiodomethane was consumed within 5 hr. When dry air was introduced into the reaction mixture, chloroiodomethane completely reacted within 0.5 hr, giving norcarane in the yield of 98%.[2] This shows that 1-phenyl-1,3-butadiene retards the step of the formation of the zinc-carbenoid reagent from diethylzinc and chloroiodomethane. The order of the inhibiting effect of an added olefin on the zinc-carbenoid reaction seems to be in accordance with that of the reactivity of the olefin toward radicals. These results are consistent with the proposed radical-chain mechanism for the formation of the zinc-carbenoid reagent (Eqs. (1)—(3));[1] that is, the more reactive the olefin is toward radicals, the more the olefin seems to trap the ethyl or chloromethyl radiacl, and stop the chain:

$$\mathrm{EtZnR} \xrightarrow{\text{initiator}} \mathrm{Et}\cdot \qquad (1)$$

$$\mathrm{Et}\cdot + \mathrm{CH_2ClI} \longrightarrow \mathrm{EtI} + \cdot\mathrm{CH_2Cl} \qquad (2)$$

$$\cdot\mathrm{CH_2Cl} + \mathrm{EtZnR} \longrightarrow \mathrm{ClCH_2ZnR} + \mathrm{Et}\cdot \qquad (3)$$

(R=Cl or Et)

The reason why isoprene was not so effective as was expected from its reactivity toward the methyl radical[3] or from the Q-value is not yet obvious, but the absence of a conjugating phenyl group and/or its volatility (bp 34 °C, while the reaction temperature was 35 °C) may be partly responsible.

TABLE 1. EFFECT OF THE ADDITION OF AN OLEFIN ON THE ZINC-CARBENOID REACTION[a]

Added olefin	Norcarane yield[b], (%)	Reacted CH_2ClI (mmol)
None	67	9.8
2-Heptene	65	9.7
1-Heptene	64	10
Isoprene	45	8.3
trans-Stilbene	34	5.8
1,4-Diphenyl-1,3-butadiene	25	4.7
Styrene	22	4.6
α-Methylstyrene	16	3.1
1,1-Diphenylethylene	12	2.3
1-Phenyl-1,3-butadiene	8	1.8

a) Reaction conditions: diethylzinc; 10 mmol, chloroiodomethane; 15 mmol, cyclohexene; 10 mmol, added olefin; 5 mol % based on cyclohexene, 35°C, 5 hr, under a nitrogen atmosphere.
b) Based on cyclohexene.

Experimental

Materials. The 1-phenyl-1,3-butadiene[4] (bp 81.5 °C/9 mmHg), 1,4-diphenyl-1,3-butadiene[5] (mp 152—152.5 °C), and 1,1-diphenylethylene[6] (bp 111—113 °C/2 mmHg) were

1) S. Miyano and H. Hashimoto, This Bulletin, **46**, 892 (1973).

2) For the accelerating effect of oxygen on the zinc-carbenoid reaction, see Ref. 1).

3) a) F. Leavitt, M. Levy, M. Szwarc, and V. Stanett, *J. Amer. Chem. Soc.*, **77**, 5493 (1955). b) A. Rajkenbach and M. Szwarc, *Proc. Roy. Soc. Ser., A*, **251**, 394 (1959).

4) H. Hashimoto, M. Hida, and S. Miyano, *J. Organometal. Chem.*, **10**, 518 (1967).

5) B. B. Corson, "Organic Syntheses," Coll. Vol. II (1948), p. 229.

6) C. F. Allen and S. Converse, "Organic Syntheses," Coll. Vol. I (1956), p. 226.

prepared by conventional methods. The other materials were purified by methods which have been reported before.[1]

Reaction Procedure. The following procedure is representative. The reaction was carried out in a 100 ml, round-bottomed flask equipped with a magnetic stirrer, a reflux condenser, a pressure-equilibrating dropping funnel topped with a gas inlet cock, thermometer, and inlet carrying a rubber septum cap. The flask was flushed with nitrogen. In the flask was placed 30 ml of benzene containing 15.4 mmol of chloroiodomethane, 10.2 mmol of cyclohexene, and 0.865 g of ethylbenzene. To the solution we then added 67.2 mg 1-phenyl-1,3-butadiene (5.2 mmol). The temperature of the solution was kept at 35 °C, and 1 ml of diethylzinc (10 mmol) was injected into the solution with a hypodermic syringe through the septum cap. The reaction was then carried out under a nitrogen atmosphere for 5 hr at 35 °C. At the end of the reaction period, a sample (*ca.* 1 ml) was withdrawn through the septum cap with a hypodermic syringe and quenched with 3 ml of a dilute hydrogen chloride solution which had been saturated with nitrogen. After three extractions of the aqueous layer with benzene, the combined organic phase was analysed by glc. The amounts of the products were estimated from the peak areas, using ethylbenzene as the internal standard. Dry air was passed into the space above the remaining reaction mixture at a rate of 10 ml/min for 0.5 hr, after which the reaction products were analysed similarly.