Catalytic Effect of Oxygen in the Carbenoid Reaction with Diethylzinc and Methylene Iodide

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Summary Cyclopropanation of olefins by the diethylzinc–methylene iodide system is greatly accelerated by oxygen.

FURUKAWA's cyclopropanation of olefins[1] using diethylzinc–methylene iodide has been carried out under a nitrogen atmosphere because of the well known high sensitivity of diethylzinc to oxygen.

We report that the carbenoid reaction is accelerated by oxygen (see Figure). To a mixture of diethylzinc and cyclohexene in benzene, methylene iodide was added dropwise at 40 °C during 30 min under nitrogen. When addition of methylene iodide was complete a 43% yield of norcarane had been produced; the rate of formation of norcarane then became very slow. After 3 h dry air was passed into the space above the reaction mixture at a rate of 10 ml/min; reaction was complete within 30 min to yield 87% of norcarane. Similarly, when air was introduced just after the addition of methylene iodide had been completed, the reaction was also completed within 30 min to yield 90% of norcarane.

This oxygen effect was used in the cyclopropanation of

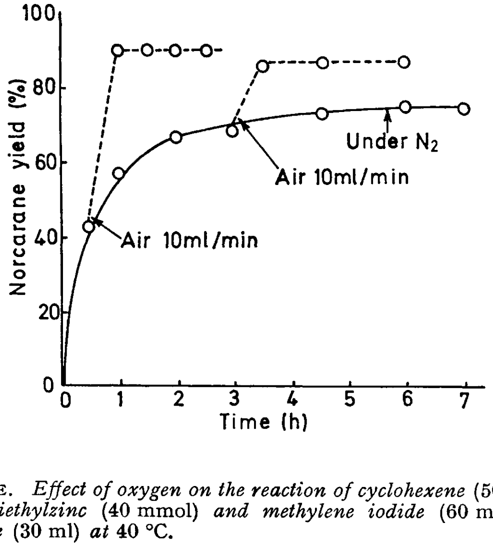

FIGURE. *Effect of oxygen on the reaction of cyclohexene* (50 mmol) *with diethylzinc* (40 mmol) *and methylene iodide* (60 mmol) *in benzene* (30 ml) *at* 40 °C.

TABLE

Cyclopropanation of some olefins[a]

Olefin	10^2 [Olefin]/M	10^2[CH_2I_2]/M	10^2[Et_2Zn]/M	Reaction time (h)[b]	Cyclopropane yield (%)[c]
Cyclohexene	5·1	7·5	6·5	1	91
Cyclo-octene	10[d]	15	13	1	98
Styrene	5·0	10	9·0	6	79
Hept-1-ene	10[d]	15	10	1	66
Oct-1-ene	2·7	3·9	2·5	1	66
Hept-2-ene[e]	3·6	5·2	3·5	1	90[e]

[a] At 50 °C in benzene (20 ml). [b] From the start of addition of methylene iodide. [c] Based on the olefin. [d] In benzene (50 ml). [e] Mixture of *cis*-, and *trans*-isomer.

some olefins with diethylzinc and methylene iodide (see Table). The reaction times are much shorter and the yields are improved compared with those of Furukawa *et. al.*[1]

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[1] J. Furukawa, N. Kawabata, and J. Nishimura, *Tetrahedron*, **1968**, **24**, **53**.