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A Salt Effect on the Reaction of Zinc Carbenoid

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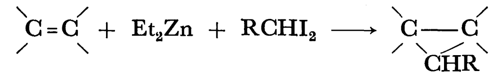
Bicyclo[4.1.0]heptane (norcarane) was obtained as the major product of the reaction of cyclohexene with diethylzinc and methylene iodide. In the presence of lithium halide or magnesium halide, however, the yield of norcarane considerably decreased. Large amounts of *n*-propyl and *n*-butyl iodides were formed which was interpreted in terms of an insertion mechanism, *viz.*, insertion of zinc carbenoid into the carbon-iodine bond of ethyl and *n*-propyl iodides.

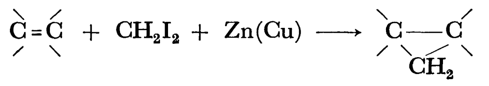
Reports were given on the synthesis of cyclopropane derivatives by the reaction of olefins with diethylzinc and *gem*-diiodoalkanes such as methylene, ethylidene and benzal iodides.[1]



(1)

($R=H, CH_3, C_6H_5$)

The reaction presumably proceeds *via* an intermediate zinc carbenoid species,[1e] and is closely related to the Simmons-Smith reaction:[2]



(2)

However, reaction (1) proceeds much more rapidly and *gem*-diiodoalkane should be added slowly to moderate the reaction. Reaction (1) was modified by the use of ethylidene and benzal iodides instead of methylene iodide. Diethylzinc is inflammable in air, making the reaction impracticable. In order to get rid of this inconvenience, we tried to use diethylzinc prepare *in situ* from zinc halide and ethyllithium or ethylmagnesium halide *i.e.*, to carry out the reaction in the presence of lithium or magnesium halide, and found a remarkable effect of these metal halides on the mode of reaction (1).

The reaction of cyclohexene with diethylzinc and methylene iodide in benzene or ether gave bicyclo-[4.1.0]heptane (norcarane) in good yield.[1a,1b]

TABLE 1. REACTION OF CYCLOHEXENE WITH DIETHYLZINC AND METHYLENE IODIDE IN THE PRESENCE OF METAL HALIDE[a]

Cyclohexene (mmol)	CH_2I_2 (mmol)	Et_2Zn[b] (mmol)	Metal	Halide (mmol)	Solvent	Products (%)[c]			
						Norcarane	n-C_3H_7I	n-C_4H_9I	n-$C_5H_{11}I$
20.0	20.0	13.3	—	—	Benzene	64.5	8.0	3.0	—
15.0	15.0	10.0	—	—	Ether	41.3	12.0	6.7	trace
15.0	15.0	10.0	LiCl	0.07	Ether	41.3	20.1	8.0	trace
14.9	15.0	10.0	LiBr	1.26	Ether	28.4	24.4	12.0	trace
15.0	15.0	10.0	LiBr	2.22	Ether	10.0	24.7	14.7	trace
15.0	15.0	10.0	LiBr	3.83	Ether	4.0	21.3	18.7	trace
7.5	7.5	5.0	LiI	0.52	Ether	12.7	27.3	20.3	trace
15.0	15.0	10.0	LiI	2.04	Ether	2.7	17.3	6.7	trace
7.5	7.5	5.0	LiI	4.78	Ether	trace	23.6	14.1	trace
15.0	15.0	10.0[d,e]	$MgCl_2$	20.0	Ether	trace	22.7	21.3	trace
15.1	15.0	10.0[d]	$MgBr_2$	20.0	Ether	2.7	22.7	10.7	2.0
15.0	15.0	10.0	MgI_2	2.77	Ether	28.0	17.5	6.0	trace
15.0	15.0	10.0	MgI_2	4.21	Ether	26.9	17.9	8.0	trace
15.0	15.0	10.0	MgI_2	8.42	Ether	13.5	19.5	9.1	trace
15.1	15.0	10.0[d]	MgI_2	20.0	Ether	7.5	20.4	13.9	trace
15.0	15.0	10.0	ZnI_2	2.19	Ether	40.0	18.7	10.7	trace

a) Reactions were carried out at 35°C for 14 hr under a nitrogen atmosphere.
b) Used as a 1.00 mol/*l* solution.
c) Based on methylene iodide.
d) Diethylzinc was prepared *in situ* from ethylmagnesium halide and zinc halide.
e) Diethylzinc was used as a 0.50 mol/*l* solution.

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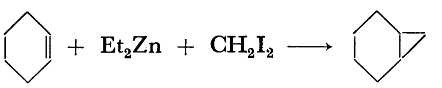
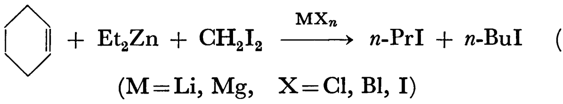
* To whom inquiries should be directed.

1) a) J. Furukawa, N. Kawabata, and J. Nishimura, *Tetrahedron Lett.*, **1966**, 3353; b) J. Furukawa, N. Kawabata, and J. Nishimura, *Tetrahedron*, **24**, 53 (1968); c) J. Furukawa, N. Kawabata, and J. Nishimura, *Tetrahedron Lett.*, **1968**, 3495; d) J. Furukawa, N. Kawabata, Y. Ueda, and J. Nishimura, *Kogyo Kagaku Zasshi*, **71**, 164 (1968); e) J. Furukawa, N. Kawabata, S. Taniguchi, and J. Nishimura, *ibid.*, **72**, 1963 (1969); f) J. Nishimura, N. Kawabata, and J. Furukawa, *Tetrahedron*, **25**, 2647 (1969); g) J. Nishimura, J. Furukawa, N. Kawabata, and T. Fujita, *ibid.*, **26**, 2229 (1970); h) J. Nishimura, J. Furukawa, and N. Kawabata, This Bulletin, **43**, 2195 (1970); i) J. Nishimura, J. Furukawa, N. Kawabata, and H. Koyama, *ibid.*, **44**, 1127 (1971); j) J. Nishimura, J. Furukawa, N. Kawabata, and M. Kitayama, *Tetrahedron*, **27**, 1799 (1971).

2) a) H. E. Simmons and R. D. Smith, *J. Amer. Chem. Soc.*, **80**, 5323 (1958); b) H. E. Simmons and R. D. Smith, *ibid.*, **81**, 4256 (1959); c) E. P. Blanchard and H. E. Simmons, *ibid.*, **86**, 1337 (1964); d) H. E. Simmons, E. P. Blanchard, and R. D. Smith, *ibid.*, **86**, 1347 (1964).


(3)

However, in the presence of lithium halide or magnesium halide, the yield of norcarane decreased considerably and large amounts of *n*-propyl and *n*-butyl iodides were formed.

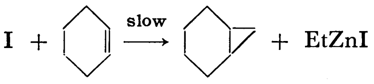

(4)

(M=Li, Mg, X=Cl, Bl, I)

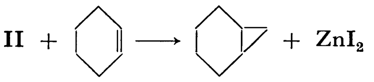
Results are given in Table 1.

Hydrolysis of the reaction mixture at an early stage of reaction (3) produced large amounts of methyl and ethyl iodides,[1e] while the amount of norcarane was small at this stage. The formation of methyl iodide after hydrolysis indicates the presence of iodomethylzinc compounds[3] in the reaction mixture. Thus, the first step was concluded to be the formation of ethyl iodide and iodomethylzinc compounds, *e.g.*, $EtZnCH_2I$ (I). The reaction of iodomethylzinc compounds with cyclohexene to form norcarane is slower than the first step.

$$\mathrm{Et_2Zn + CH_2I_2 \xrightarrow{fast} EtI + \underset{I}{EtZnCH_2I}} \qquad (5)$$


(6)

$$\mathrm{EtZnI + CH_2I_2 \longrightarrow EtI + \underset{II}{IZnCH_2I}} \qquad (7)$$


(8)

The formation of *n*-propyl and *n*-butyl iodides can be ascribed to the reaction of iodomethylzinc compounds with ethyl and *n*-propyl iodides, respectively.

$$\mathrm{I + EtI \longrightarrow \mathit{n}\text{-}PrI + EtZnI} \qquad (9)$$

$$\mathrm{I + \mathit{n}\text{-}PrI \longrightarrow \mathit{n}\text{-}BuI + EtZnI} \qquad (10)$$

$$\mathrm{II + EtI \longrightarrow \mathit{n}\text{-}PrI + ZnI_2} \qquad (11)$$

$$\mathrm{II + \mathit{n}\text{-}PrI \longrightarrow \mathit{n}\text{-}BuI + ZnI_2} \qquad (12)$$

In the presence of lithium halide or magnesium halide, reactions (9), (10), (11), and (12) predominated over (6) and (8). Zinc iodide also showed the same sort of effect as that given in Table 1. The yield of norcarane was lower and that of *n*-propyl and *n*-butyl iodides higher in ether than in benzene. The difference can be attributed partly to the difference of solubility of zinc iodide formed by (11) and (12).

Two mechanisms are possible for reactions (9) to (12), one is a coupling reaction between iodomethylzinc compounds and ethyl iodide or *n*-propyl iodide. This mechanism is conceivable since the presence of magnesium halide enhances the coupling reaction of dialkylcadmium with acyl halide.[4] Dialkylcadmium prepared *in situ* from alkylmagnesium halide and cadmium halide in ether reacts with acyl halide to form ketone. However, isolated (salt-free) dialkylcadmium does not react with acyl halide.

$$\mathrm{R_2Cd + R'COX \xrightarrow{MgX'_2} RCOR'} \qquad (13)$$

The other mechanism is an insertion reaction of iodomethylzinc compounds into the carbon-iodine bond of ethyl iodide or *n*-propyl iodide.

In order to distinguish the two mechanisms, we carried out the reaction of cyclohexene with diethylzinc and bromoiodomethane, giving a small amount of norcarane, and large amounts of *n*-propyl, *n*-butyl, and ethyl iodides. However, ethyl, *n*-propyl, and *n*-butyl bromides were not detected. The results are given in Table 2.

The presence of a large amount of ethyl iodide and the absence of ethyl bromide indicate that the first step is (14) rather than (15).

$$\mathrm{Et_2Zn + ICH_2Br \longrightarrow EtI + BrCH_2ZnEt} \qquad (14)$$

$$\mathrm{Et_2Zn + ICH_2Br \longrightarrow EtBr + ICH_2ZnEt} \qquad (15)$$

The formation of *n*-propyl and *n*-butyl iodides instead of *n*-propyl and *n*-butyl bromides makes the insertion mechanism preferable to the coupling mechanism.

Coordination of lithium or magnesium halide to organozinc compounds during the reaction is conceivable. However, extensive physicochemical studies may be necessary before proposing a definite mechanism of this salt effect.

Experimental

Materials. Diethylzinc was prepared by the conventional method.[5] Ethylmagnesium halides were prepared from ethyl halide and magnesium turnings in ether. Concentration of ethylmagnesium halide was determined by an acid-base titration. Commercial products of anhydrous zinc

TABLE 2. REACTION OF CYCLOHEXENE WITH DIETHYLZINC AND BROMOIODOMETHANE IN THE PRESENCE OF METAL HALIDE[a)]

Et_2Zn[b)] (mmol)	Metal	Halide (mmol)	Products (%)[c)] Norcarane	n-C_3H_7I	n-C_4H_9I	n-$C_5H_{11}I$
5.0	—	—	2.7	31.1	7.4	trace
5.0[d)]	$MgBr_2$	10.0	trace	12.3	2.0	trace

a) Reactions were carried out at 35°C for 14 hr in ether under a nitrogen atmosphere with 7.5 mmol of cyclohexene, 7.0 mmol of bromoiodomethane, and 5.0 mmol of diethylzinc.
b) Diethylzinc was used as a 1.00 mol/*l* solution.
c) Based on bromoiodomethane.
d) Diethylzinc was prepared *in situ* from ethylmagnesium bromide and zinc bromide.

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[3] Iodomethylzinc compounds would be $EtZnCH_2I$, $Zn(CH_2I)_2$, $IZnCH_2I$ and/or their associated molecules.

[4] a) J. Kollonitsch, *Nature*, **188**, 140 (1960); b) J. Kollonitsch, *J. Chem. Soc., A*, **1966**, 453, 456.

[5] C. R. Noller, "Organic Syntheses," Coll. Vol. II, (1943), p. 184.

chloride and bromide were dried by rapidly heating *in vacuo*. Commercial anhydrous zinc iodide was dissolved in ether, dried by calcium hydride; the clear supernatant layer was transferred to a flask and ether was removed *in vacuo* at room temperature. All the zinc halides purified in this manner were completely soluble in ether. Commercial anhydrous lithium chloride was dried by heating *in vacuo*. Anhydrous lithium bromide was prepared by heating its monohydrate *in vacuo*. Anhydrous lithium iodide was prepared by dehydration of its trihydrate, *i.e.*, lithium iodide trihydrate was dissolved in ether, dried with calcium hydride; the clear supernatant layer was transferred to a flask, and ether was removed *in vacuo* at room temperature. Anhydrous magnesium iodide was prepared from magnesium trunings and iodine in ether. Bromoiodomethane was prepared by the conventional method.[6] Commercial cyclohexene, methylene iodide, ethyl bromide, ethyl iodide, *n*-propyl bromide, *n*-propyl iodide, *n*-butyl bromide, and *n*-butyl iodide were purified by distillation. Authentic sample of norcarane was prepared from cyclohexene, methylene iodide and diethylzinc.[1a] Purity was confirmed by vapor phase chromatography. Solvents were purified by the usual method.[7] Nitrogen was purified as described previously.[1b]

Procedure. A three-necked flask equipped with a thermometer, dropping funnel, three-way cock and magnetic stirring bar was evacuated and filled with dry nitrogen. Metal halide was dissolved in ether and added to the flask *via* a hypodermic syringe. Diethylzinc was then added similarly. The concentration of diethylzinc was made to be 1.00 or 0.50 mol/*l* at this stage by controlling the amount of solvent. Cyclohexene was added *via* a hypodermic syringe to this solution. Methylene iodide was then added through a dropping funnel over a period of half an hour while stirring at room temperature. After the addition the reaction mixture was allowed to stand at 35°C for 14 hr. The reaction mixture was successively poured into a saturated aqueous solution of ammonium chloride. The organic layer was analyzed by vapor phase chromatography. Yields of products were determined by vapor phase chromatography with calibration curves.

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[6] S. Miyano and H. Hashimoto, This Bulletin, **44**, 2864 (1971).

[7] J. A. Riddick and W. B. Bunger, "Organic Solvents," Wiley-Interscience, New York (1970).