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REACTION OF BENZALDEHYDE WITH ZINC–POLYHALOMETHANE COMPLEXES OBTAINED FROM POLYHALOMETHANES AND ZINC–COPPER COUPLE

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SUMMARY

Styrene formation by the reactions between benzaldehyde and zinc–polyhalomethane complexes in the presence of an excess of zinc was studied. Styrene was obtained in fairly good yields from four methylene halides (CH_2I_2, CH_2Br_2, ICH_2Cl, $BrCH_2Cl$), of which chloroiodomethane gave the best result. Iodoform and bromoform also gave styrene in lower yields. On the other hand, polychloromethanes (CH_2Cl_2, $CHCl_3$, CCl_4) did not give styrene. Benzaldehyde was recovered almost unchanged in the reaction with zinc–methylene iodide complex in the absence of zinc. Possible reaction paths for styrene formation were proposed in considering about the effects of an excess of zinc.

INTRODUCTION

It is known that the zinc–methylene iodide complex obtained from zinc–copper couple and methylene iodide behaves as an electrophile towards olefinic double bonds and forms cyclopropanes[1]. In contrast, in the presence of an excess of zinc the complex (*vide infra*) reacts with aldehydes in a nucleophilic manner to form the corresponding α-olefins in good yields, and thus this reaction affords a convenient method for the preparation of α-olefins[2].

The present study was undertaken to examine whether other polyhalomethanes also could give the corresponding organozinc complexes which react with benzaldehyde to give styrene. After a polyhalomethane had been stirred with zinc–copper couple and benzaldehyde in THF for 6 h at 35°, the reaction mixture was hydrolyzed with saturated ammonium chloride solution. The reaction products, styrene and benzyl alcohol, and unchanged benzaldehyde were determined by VPC. Results are summarized in Table 1. Styrene was obtained in fairly good yields from all methylene halides used except methylene chloride, and chloroiodomethane gave the best yield of styrene with least side reactions. It may be concluded that methylene chloride does not give a zinc–methylene complex, since 97% of the methylene chloride was recovered unchanged after being treated with zinc–copper couple in ether for 6 h at 35°. Styrene was not obtained from methylene chloride even in the presence of sodium iodide or zinc iodide, but the yield of benzyl alcohol increased. Simmons and Smith reported[1b] that methylene bromide did not react with zinc–copper couple which

TABLE 1

REACTIONS OF ZINC–POLYHALOMETHANE COMPLEXES WITH BENZALDEHYDE IN THE PRESENCE OF EXCESS ZINC[a]

Polyhalomethane	PhCHO reacted (%)	$PhCH=CH_2$[b] yield (%)	$PhCH_2OH$[c] yield (%)
CH_2Cl_2	22	0	7.0
CH_2Cl_2[d]	48	0	18
CH_2Cl_2[e]	50	0	17
CH_2BrCl	50	56	< 0.2
CH_2Br_2	60	65	< 0.2
CH_2ClI	54	80	< 0.2
CH_2I_2	75	72	5.6
$CHCl_3$	33	0	12
CCl_4	25	0	3.2
$CHBr_3$	31	11	0.7
CHI_3	75	11	8.3
[f]	25	0[c]	8.7
[g]	23	0[c]	4.1

[a] Reactions were carried out in 100 ml of THF at 35° for 6 h using 0.100 mole of polyhalomethane, 0.51 mole of zinc–copper couple, and 0.200 mole of benzaldehyde. [b] Based on polyhalomethane. [c] Based on benzaldehyde used. [d] NaI (0.010 mole) was added. [e] ZnI_2 (0.010 mole) was added. [f] No polyhalomethane was used. [g] The mixture of zinc–copper couple, benzaldehyde, 100 ml of THF was stirred in 20 ml of saturated ammonium chloride solution for 20 min below 10°.

was prepared from zinc dust and cupric oxide in hydrogen. In our experiment, on the other hand, the zinc–copper couple prepared by LeGoff's method[3] reacted even with bromochloromethane*. It is known that the method used for the preparation of the zinc–copper couple is an important factor in determining its reactivity towards polyhalomethanes. Chloroform and tetrachloromethane did not give styrene, but bromoform and iodoform did. Hence, it seems likely that reduction of bromoform and iodoform, of their zinc complexes or of halogenated styrenes occurred in the course of the latter two reactions, although halogenated styrenes have not been isolated as yet from the reaction mixtures.

The structure of the complexes formed from zinc–copper couple and polyhalomethanes have been discussed by several authors, but the exact nature of the organometallic species involved remains uncertain. Blanchard and Simmons[1c] claimed that "$IZnCH_2I$" is first formed from methylene iodide and zinc–copper couple, and is in equilibrium with "$(ICH_2)_2Zn\cdot ZnI_2$", which is the active intermediate for the Simmons–Smith reaction. On the other hand, Gault *et al.*[4] reported recently that "$(IZn)_2CH_2$" is the active species which is in equilibrium with "$IZnCH_2I$". Wittig and his coworkers, however, suggested that in the presence of zinc iodide stable bis(benzoyloxymethyl)zinc, $(PhCO_2CH_2)_2Zn$, is also able to form norcarane from cyclohexene[5], and thus "Hal–CH_2–ZnR" type species[6], where R is I or CH_2I, also seem to be responsible for the Simmons–Smith reaction** in the case of zinc–methylene

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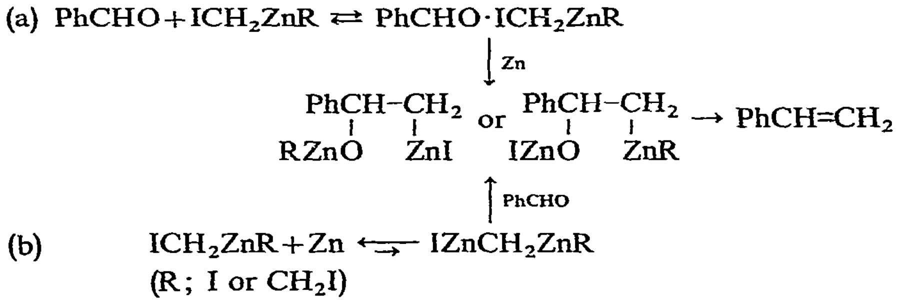
* In the case of chloroiodomethane or bromochloromethane, the organozinc complex first formed presumably contains the unit [I–Zn–CH_2–] or [Br–Zn–CH_2–] as was suggested by Blanchard and Simmons[1c].

** ICH_2HgI is also able to form norcarane[7]. For other organometallic CH_2 transfer reagents, see, for example, ref. 1d, 8, and literature cited therein.

iodide complex. In contrast, Fried *et al.* suggested[9] that in the presence of an excess of zinc, "$Zn(CH_2ZnI)_2$" is formed from methylene iodide, and that this is the active species for the replacement reaction of the 3-ketone function in 17β-acetoxy-11α-hydroxyester-5(10)-en-3-one by methylene.

We suggest two possible reaction paths for styrene formation from zinc–methylene iodide complex and benzaldehyde in the presence of an excess of zinc:



$$\text{(a)}\ PhCHO + ICH_2ZnR \rightleftarrows PhCHO{\cdot}ICH_2ZnR \xrightarrow{Zn} \underset{RZnO\quad ZnI}{PhCH{-}CH_2} \text{ or } \underset{IZnO\quad ZnR}{PhCH{-}CH_2} \rightarrow PhCH{=}CH_2$$

$$\text{(b)}\ ICH_2ZnR + Zn \rightleftarrows IZnCH_2ZnR \xrightarrow{PhCHO} \underset{RZnO\quad ZnI}{PhCH{-}CH_2} \text{ or } \underset{IZnO\quad ZnR}{PhCH{-}CH_2}$$

(R; I or CH_2I)

Benzaldehyde was recovered almost unchanged when allowed to react with the filtered solution of the organozinc complex formed from methylene iodide and zinc–copper couple*, *i.e.*, in the absence of an excess of zinc metal (see Table 2). Therefore, if the path (a) is operative, the benzaldehyde–zinc–methylene iodide adduct would regenerate benzaldehyde on the hydrolysis with saturated ammonium chloride solution, or, if the path (b) is operative "$IZnCH_2ZnR$" is the active intermediate for the styrene formation, and its concentration in the reaction mixture in the absence of zinc would be expected to be low. Table 2 shows that the yield of styrene depends greatly on the molar ratio of methylene iodide to zinc–copper couple, thus demon-

TABLE 2

INFLUENCE OF THE AMOUNT OF ZINC ON THE STYRENE YIELD[a]

CH_2I_2 (mole)	CH_2I_2/Zn molar ratio	$PhCH{=}CH_2$[b] yield (%)	PhCHO[c] reacted (%)
0.253	1.05	13	39
0.202	0.84	16	50
0.101	0.42	37	38
		36	37
0.0513	0.021	52	17
0	0	0[c]	7.2
		0[c]	10
0.101[d]	0.42	3.5	3.5
0.101[e]	0.42	48	29

[a] Reactions were carried out in 100 ml of ether at 40° for 6 h using 0.20 mole of benzaldehyde and 0.24 mole of zinc–copper couple. [b] Based on CH_2I_2. [c] Based on benzaldehyde used. [d] Reaction was continued for 4.25 h between benzaldehyde and the filtered solution of the organozinc complex formed from methylene iodide and zinc–copper couple. [e] After the zinc–methylene iodide complex had been prepared, benzaldehyde was allowed to react with the complex for 5 h in the presence of an excess of zinc.

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* The zinc–methylene iodide complex has been said to be unreactive towards carbonyl functions[1b,10].

strating the important role of zinc metal for the styrene formation. These observations are compatible with the above two reaction paths. We cannot decide from the present work if either of the two paths is correct. Studies of the precise features of these reactions are in progress.

EXPERIMENTAL

Polyhalomethanes

Methylene bromide[11] and methylene iodide[12] were synthesized by the conventional methods. Chloroiodomethane was conveniently obtained by a modification of Kosower and Schwager's method[13] as follows. Methylene chloride (90 ml), acetone (60 ml), and sodium iodide (72 g) were placed in an autoclave, and heated with stirring at 100° for 6 h. The reaction mixture was poured into water, organic layer was separated. After washing with dilute sodium hydrogen sulfite and portions of water, and drying with sodium sulfate, the oily product was distilled at atmospheric pressure through a Widmer column. The portion boiling at 108° was collected as pure material; yield, 50 g (59 %). Other halides were of commercial reagent grades and purified as usual before use.

Reaction between zinc–methylene iodide complex and benzaldehyde in the presence of an excess of zinc in ether

Zinc–copper couple[3] prepared from 0.24 g-atom of zinc dust and 1 g of $Cu(OAc)_2 \cdot H_2O$ was washed with portions of ether until the ethereal washings were almost insensitive to litmus. The zinc–copper couple and 40 ml of ether were placed in a 200 ml reaction flask, stirred with a magnetic stirrer, and heated in a water bath until gentle reflux began (34~35°). To the stirred zinc–copper couple was added methylene iodide (0.100 mole) and benzaldehyde (0.200 mole, dissolved in 60 ml of ether) over a 1 h period. A gentle, exothermic reaction continued during the addition and the reaction temperature was raised to 39~41° to maintain gentle reflux. After addition had been completed, the reaction was continued for additional 5 h at 40° with stirring. At the end of the reaction period, the flask was cooled with ice–water, and the reaction mixture was treated with saturated ammonium chloride solution* (50 ml) and filtered. The ethereal layer was separated from the filtrate and washed successively with 3 % hydrochloric acid (40 ml), saturated ammonium chloride solution (3 × 40 ml), sodium chloride solution (2 × 40 ml) and water (40 ml). The water layer of the filtrate and the aqueous washings were combined and extracted three times with ether. The ether extracts were washed similarly. The combined ether layer and ether extracts were diluted with additional ether to 250 ml, from which a 10 ml portion was used for the quantitative determination of unreacted benzaldehyde, benzyl alcohol, and styrene by VPC. The remaining ether solution was treated with 40 % sodium hydrogen sulfite solution (50 ml) to remove benzaldehyde, filtered,

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* After hydrolysis, methylene iodide was not detected. But in hydrolysis after removal of the remaining zinc, the unchanged methylene iodide remained in ether layer. The styrene yield was not effected by the method of hydrolysis. So hydrolysis of the reaction mixture in the presence of zinc may provide a useful method for the removal of unchanged methylene iodide in the olefin syntheses[2] or Simmons–Smith's cyclopropane syntheses.

washed with another portion of sodium hydrogen sulfite solution and water, and dried over sodium sulfate. After solvent was removed by distillation with a Widmer column, the residue was distilled under reduced pressure to give 1.25 g of styrene [b.p. 41–42° (17 mm)] (Found: C, 92.10; H, 7.80. C_8H_8 calcd.: C, 92.26; H, 7.74%.), and 70 mg of benzyl alcohol [b.p. 72° (7 mm)] (Found: C, 77.58; H, 7.72. C_7H_8O calcd.: C, 77.75; H, 7.46%.). After distillation, 4.7 g of tarry residue remained. The recovered styrene was converted to its dibromide, which showed no depression of melting point on mixing with authentic sample (m.p. 73.6–74.0°).

Reaction of benzaldehyde with the filtered organozinc complex formed from methylene iodide and zinc–copper couple

To the stirred suspension of zinc–copper couple [prepared from 0.24 g-atom of zinc dust and 1 g of $Cu(OAc)_2 \cdot H_2O$] in 40 ml of ether, methylene iodide (0.100 mole) in 10 ml of ether was added during 30 min under gentle reflux. After the addition, gentle reflux was continued for another 1 h. Then the reaction mixture was chilled in ice–water and filtered under nitrogen. To the filtrate was added 0.200 mole of benzaldehyde in 50 ml of ether for 15 min under gentle reflux. Then reaction was continued for another 4 h at 40°. After the reaction period, the reaction mixture was treated as mentioned above. On VPC analysis, 3.5% of styrene and 96.5% of unchanged benzaldehyde were determined. The solid part which was not filtered was also suspended in ether and allowed to react with benzaldehyde, but no styrene was formed.

Reaction between zinc–iodoform complex with benzaldehyde in THF

Zinc–copper couple was prepared from 0.505 g-atom of zinc powder and 2 g of $Cu(OAc)_2 \cdot H_2O$, washed with portions of THF until almost insensitive to litmus. The reaction procedure was almost the same as mentioned above except that the reaction temperature was kept at 35° throughout the reaction. Distillation of the reaction mixture gave 60 mg of crude styrene [b.p. 35° (35 mm)], 1.7 g of benzyl alcohol [b.p. 77° (6 mm)], and 0.54 g of high-boiling viscous liquid(s) [90–112° (4 mm)]. After distillation, 6.4 g of the residue remained.

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