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SHORT COMMUNICATION

Formation of olefins from the zinc–methylene iodide complex and aldehydes

It is known that the zinc–methylene iodide complex, *i.e.*, the "Simmons–Smith reagent" obtained from zinc–copper couple and methylene iodide adds to olefinic double bonds to form cyclopropanes[1]. The behavior of such complexes toward carbon–heteroatom double bonds is of interest, but only few reports have appeared concerning this question. Wittig and Wingler reported that bis(chloromethyl)zinc, obtained from zinc chloride and diazomethane, reacts with benzophenone to give 2,2,4,4-tetraphenyl-1,3-dioxolane[2]. Recently, Fried and his coworkers reported that 17 β-acetoxy-11 β-hydroxyestr-5(10)-en-3-one reacts with the zinc–methylene iodide complex in the presence of an excess of zinc to give the product of replacement of the 3-oxo function by methylene[3]. We have found that reactions of the zinc–methylene iodide complex with benzaldehyde in ethers in the presence of zinc afford styrene[4]. This report describes further experiments with some other aldehydes and carbonyl compounds in which tetrahydrofuran (THF) was employed as solvent. The results of reactions with aldehydes are summarized in Table 1. All aldehydes used gave the corresponding olefins in fairly good yields. The olefins thus obtained generally were isolated in the pure state from the reaction mixtures by conventional methods such as vacuum distillation, showing that the reaction is applicable to synthesis of olefins in the laboratory. From the reaction mixture of cinnamaldehyde, 1,2-distyrylethylene glycol* was isolated in addition to *trans*-1-phenylbutadiene, but the cyclopropane

TABLE 1

REACTIONS OF ZINC–METHYLENE IODIDE COMPLEX WITH ALDEHYDES IN THF IN THE PRESENCE OF AN EXCESS OF ZINC[a]

R–CHO		*Zn–Cu*	*R–CH=CH$_2$*	
	(mole)	*(g-atom)*	*Yield*[b] *(%)*	*Isolated (%)*
p-Chlorobenzaldehyde	0.202	0.24	74	61
p-Methylbenzaldehyde	0.202	0.24	52	48
p-Methoxybenzaldehyde	0.202	0.24		48
1-Naphthaldehyde	0.100	0.505	73	42
2-Naphthaldehyde	0.100	0.505		55
9-Anthraldehyde	0.030	0.150	*ca.* 40[c]	
Cinnamaldehyde	0.101	0.505	29	18
n-Heptaldehyde[d]	0.100	0.252	73	47

[a] Reactions were carried out in 100 ml of THF at 40° for 6 h using 0.100 mole of methylene iodide. [b] Based on CH_2I_2, determined by VPC. [c] Determined by IR analysis. [d] CH_2I_2 (0.050 mole) was used.

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* The same type of compound, 1,2-diphenylethylene glycol also was isolated from the reaction mixture in the case of benzaldehyde and was identified.

derivative was not detected. This shows that addition of the complex to the carbonyl group and reductive dimerization of the carbonyl group are favored over addition of the complex to the C=C bond in cinnamaldehyde.

On the other hand, under the similar conditions acetophenone, benzophenone, diethyl ketone and methyl benzoate were almost unreactive and did not give the corresponding olefins.

Experimental

2-Naphthaldehyde[5] and 9-anthraldehyde[6] were synthesized by the usual methods, and other carbonyl compounds were of commercial reagent grade. They were distilled *in vacuo* under nitrogen before use.

Reaction between zinc–methylene iodide and cinnamaldehyde. Zinc–copper couple (0.505 mole) was freshly prepared[7] and was washed several times with THF. The zinc–copper couple, methylene iodide (0.100 mole) and cinnamaldehyde (0.101 mole) were allowed to react in THF (100 ml) at 40° for 6 h as described in the previous report[4]. The reaction mixture was treated with saturated ammonium chloride (50 ml) and filtered. The THF 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 extracted three times with ether. The combined THF layer and ether extracts were diluted with additional THF to 250 ml volume, from which 10 ml portion was used for the quantitative determination of unreacted cinnamaldehyde and *trans*-phenylbutadiene by VPC. The remaining ether solution was treated with 40 % sodium hydrogen sulfite solution to remove cinnamaldehyde, filtered, washed with water and dried over sodium sulfate. After ether was removed by distillation with a Widmer column, the residue was distilled under 10 mm Hg to give 2.4 g of *trans*-phenylbutadiene boiling at 75°. (Found: C, 92.24; H, 7.76. $C_{10}H_{10}$ calcd.: C, 92.24; H, 7.76 %.) The distillation residue was recrystallized from benzene to give 1.1 g of 1,2-distyrylethylene glycol, m.p. 156–156.8°, IR spectrum; 3400 (broad, doublet, OH stretching), 1020 (OH stretching), 965 cm^{-1} (olefinic double bond). (Found: C, 81.38; H, 6.84. $C_{18}H_{18}O_2$ calcd.: C, 81.20; H, 6.78 %.)

TABLE 2

ANALYTICAL AND INFRARED SPECTRAL DATA OF ISOLATED OLEFINS

Olefin	*B.p.(°C/mm)*	*Calcd.(%)*		*Found(%)*		*Infrared vinyl group*
		C	*H*	*C*	*H*	*(cm^{-1})*
p-Chlorostyrene	75–80/20	69.33	5.09	68.53	5.20	911, 987, 1627
p-Methylstyrene	52–54/11	91.53	8.54	88.98	8.19	906, 991, 1630
p-Methoxystyrene	88–90/13	80.06	7.51	79.91	7.53	900, 990, 1625
1-Vinylnaphthalene	133–133.5/18	93.45	6.54	92.83	6.49	915, 985, 1620[a]
2-Vinylnaphthalene	129–131/13[b]	93.45	6.54	93.31	6.48	896, 993, 1625
Phenylbutadiene	75/10	92.24	7.76	92.24	7.76	897, 1002, 1626
1-Octene	46/105	85.63	14.38	84.92	14.68	909, 990, 1636
9-Vinylanthracene[c]						925[a], 990[a]

[a] Doublet. [b] M.p. 64.8–65.5°. [c] Not separated from unchanged 9-anthraldehyde. It was identified by infrared spectrum of authentic sample[8].

The results obtained with other aldehydes and the analytical data for the olefins obtained are given in Tables 1 and 2.

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