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Convenient Synthesis of Chloroiodomethane from Dichloromethane and Sodium Iodide in DMF

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Organozinc reagent obtained from chloroiodomethane and zinc-copper couple is useful for the synthesis of α-olefins from aldehydes.1) Chloroiodomethane is usually synthesized from dichloromethane and sodium iodide by refluxing in acetone for several days.2) The reaction period can be shortened to several hours by the use of an autoclave.1) However, the procedure is not suitable for a large scale synthesis. It is well known that dipolar-aprotic solvents accelerate S_N2 type reaction remarkably.3) Suitable solvents and reaction conditions for the synthesis of chloroiodomethane were investigated.

Results and Discussion

Table 1 shows the effect of solvent on the reaction of dichloromethane and sodium iodide. Chloroiodomethane was obtained in only poor yield with acetone, while DMSO, DMF, and HMPA gave much better results. From its availability and the yield of chloroiodomethane, DMF seems to be the most suitable solvent. When the reaction was carried out in DMF for 10 hr, the yield of chloroiodomethane amounted to 83% based on the used sodium iodide, accompanying the formation of 10% of diiodomethane. In the synthetic procedure, pure chloroiodomethane was isolated by distillation in 63% yield, providing a convenient method for the synthesis. In a similar way, bromoiodomethane was also obtained from dibromomethane and sodium iodide.

Table 1. Effect of the solvent on the reaction of CH_2Cl_2 and NaI a)

Solvent	(m*l*)	Reaction temp. (°C)	Product Yield b)	
			CH_2ClI (%)	CH_2I_2 (%)
Actone	30	51	2.6	0
Acetonitrile	30	55—56	1.6	0
Methanol	30	41	0.5	0
DMSO	30	56—59	24.1	0
DMF	30	55—66	48.0	3.8
		55—75 c)	82.8	10.2
HMPA	30	51—61	54.6	2.9
{Acetone d)	30	54—56	18.7	<1.0
{DMF	10			
{THF d)	30	58—59	22.3	1.0
{DMF	10			
DMF e)	30	70 f)	CH_2BrI 84.5	14.8
DMF g)	30	63—68	CH_2ClBr 4.3	—

a) NaI 0.100 mol, CH_2Cl_2 0.47 mol. Reactions were carried out under gentle reflux for 5 hr.
b) Based on NaI.
c) Reaction was continued for 10 hr.
d) Mixed solvents were used.
e) CH_2Br_2 (0.47 mol) was used in place of CH_2Cl_2.
f) Reaction was carried out at constant temperature.
g) NaBr (0.100 mol) was used in place of NaI.

Table 2 shows that water retards the reaction, presumably because of the solvation of iodide ion. Preliminary experiments have shown that commercially available dichloromethane, DMF, and sodium iodide can be used without significant decrease in the yield of chloroiodomethane.

Table 3 shows the effects of the cation on the yield of chloroiodomethane. The degree of the solvation of cation by DMF seems to decrease in the order Li>Na

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1) S. Miyano, M. Hida, and H. Hashimoto, *J. Organometal. Chem.*, **12**, 263 (1968).

2) For example, E. M. Kosower, and I. Schwager, *J. Amer. Chem. Soc.*, **86**, 5528 (1964).

3) For example, A. J. Parker, *Chem. Rev.*, **69**, 1 (1969).

TABLE 2. EFFECT OF WATER ON THE REACTION OF CH_2Cl_2 AND NaI[a]

Added water (m*l*)	Reaction temp. (°C)	Product yield[b] CH_2ClI (%)	Product yield[b] CH_2I_2 (%)
0	55—66	48.0	3.8
0.3	55—64	46.6	3.1
0.6	54—63	38.4	1.9
1.0	54—61	38.9	1.8

a) NaI 0.100 mol, CH_2Cl_2 0.47 mol, DMF 30 m*l*. Reactions were carried out under gentle reflux for 5 hr.
b) Based on NaI.

$>$K.[4] This seems to account for the fact that sodium iodide gives a better yield of chloroiodomethane than potassium iodide. On the other hand, the lower yield of chloroiodomethane in case of lithium iodide can be ascribed to an occurrence of the reverse reaction. This is supported by the fact that the reaction of chloroiodomethane with lithium chloride is so fast that only 27% of initial chloroiodomethane is detected after 5 hr.

TABLE 3. EFFECT OF THE CATION ON THE REACTION OF CH_2Cl_2 AND NaI[a]

Alkali Metal Halide	CH_2Cl_2 (mol)	Reaction temp. (°C)	Product yield[b] CH_2ClI (%)	Product yield[b] CH_2I_2 (%)
NaI	0.47	55—66	48.0	3.8
KI	0.47	60—65	32.4	1.5
LiI[c]	0.47	53—58	24.6	1.8
LiCl	0.37 CH_2ClI 0.100	62—59	27.0[d]	1.4[d]

a) Alkali metal halide, 0.100 mol, DMF 30 m*l*. Reactions were carried out under gentle reflux for 5 hr.
b) Based on alkali metal halide.
c) Contained 0.12 g of water.
d) Based on CH_2ClI initially used.

Experimental

Materials. All solvents were purified by the usual methods before use. Alkali metal halides except for lithium iodide were dried at 150°C for 10 hr under reduced pressure (2mm Hg). Commercial lithium iodide trihydrate was dehydrated at temperatures up to 150°C for 20 hr under reduced pressure. The Vorhard titration showed that the resulting cake contained 91.8% of lithium iodide, the rest appearing to be water. Commercial dihalomethanes were dried with calcium chloride and fractionated before use.

Typical Experimental Procedure. As a typical reaction procedure, the reaction of dichloromethane and sodium iodide in DMF is described. The reaction was carried out in a 100 m*l* round-bottomed flask equipped with a magnetic stirrer, reflux condenser topped with drying tube, thermometer and dropping funnel. Sodium iodide (15.0g, 0.100 mol) and dichloromethane (40g, 0.47 mol) were placed in the flask and stirred at room temperature. DMF (30m*l*) was added in about 3 min, whereupon the temperature of the reaction mixture rose from 20°C to 50°C. The reaction mixture became almost homogeneous, but precipitation of sodium chloride was soon observed. After the addition of DMF, the flask was heated to maintain gentle reflux for 5 hr under stirring. At the end of the reaction period, 30 m*l* of water was added to the chilled reaction mixture. The organic layer was separated, and the aqueous layer was extracted several times with portions of dichloromethane. The combined organic layer was analysed by glc for the determination of resulting chloroiodomethane and diiodomethane using bromobenzene as an internal standard.

Synthesis of Chloroiodomethane. The reaction was carried out according to the same procedure as avobe, except that the reaction scale was 8 times larger, and was continued for 10 hr, during which period, the reflux temperature rose from 51°C to 71°C. The reaction mixture was allowed to stand overnight at room temperature. The content was then steam distilled. The organic layer was separated from the distillate, and washed with several portions of water. The aqueous layer was extracted with CH_2Cl_2, and the extract was washed with water. The combined organic layer was dried with calcium chloride. Distillation through a 20 cm Vigreux column yielded 93.5 g (63% based on NaI) of pure chloroiodomethane boiling at 108—109°C (lit,[2] bp, 108°C). The residue contained chloroiodomethane, DMF, and diiodomethane.

Dibromomethane (82.0 g, 0.472 mol) and sodium iodide (15.0 g, 0.100 mol) was allowed to react in DMF (30 m*l*) for 5 hr.

A similar work up gave 7.5 g of bromoiodomethane boiling at 138—139°C (lit,[5] bp 137.8—141.2°C), which was contaminated with 3% of diiodomethane (34% yield based on NaI).

Identity of each product was confirmed by comparison of the chemical shift of NMR with that of authentic sample: CH_2ClI, τ, 5.00; CH_2BrI, τ, 5.41 (TMS, 5 mol% solution in CCl_4).

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[4] Y. Yamashita and K. Ito, *Yuki Gosei Kagaku Kyokai Shi*, **25**, 1098 (1967).

[5] W. Bacherand and J. Wagner, *Z. Phys. Chem.* (Leipzig), **43**, 193 (1939).