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Ultrasonic irradiation in a single-stage synthesis of chloroiodomethane from iodoalkanes and dichloromethane under aluminum mediation

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In the presence of iodine, a mixture of dichloromethane, iodoalkanes (alkyl = Me, Et, Pr, iso-Pr, Bu, iso-Bu, pentyl) and aluminum powder was irradiated at room temperature with ultrasound to give readily chloroiodomethane ICH_2Cl. The preferred reactant to give the best yield of ICH_2Cl was PrI. Alkylaluminum sesqui-iodides were postulated as intermediates.

Keywords: Ultrasonically improved synthesis, aluminum mediation, chloroiodomethane, organoaluminum compounds

INTRODUCTION

Chloroiodomethane (**III**) has been used as a methylene source for the synthesis of α-olefins from aldehydes[1] and oxygen-catalyzed cyclopropanation of olefins in zinc–carbenoid reactions.[2–4] Compound **III** (for compounds **I–III** see Scheme 1) is usually synthesized from dichloromethane and sodium iodide by refluxing in acetone for several days,[5] or stirring at 100 °C for 6 h in an autoclave,[1] or heating in dimethylformamide (DMF) for several hours.[6–7] In an early report,[8] Rolla improved the synthesis using a phase-transfer catalyst and under severe heating conditions at 100–110 °C for 18–20 h at 4–5 atm. The synthesis procedures mentioned above all required a lengthy reaction time. Recently, Tundo and Venturello[9] reported that the production of compound **III** can be achieved in the presence of a gas–liquid phase-transfer catalyst.

Ultrasonic irradiation has been known to facilitate certain organic reactions, especially those of a heterogeneous nature.[10–23] However, little work[24–26] on ultrasonic irradiation in the synthesis of organometallic compounds of Group IIIA metals has been reported thus far. Previously,[27–29] we found that ultrasonic irradiation could be used as a facile and effective method to induce reaction between haloalkanes and aluminum powder.

In this study, a new and convenient synthetic method to obtain compound **III** from iodoalkanes via alkylaluminum sesqui-iodides under ultrasonic irradiation is reported.

EXPERIMENTAL

Aluminum powder (150–250 mesh), dichloromethane (E. Merck) and alkyl iodides (E. Merck) were used without further purification.

All reactions were carried out under a nitrogen atmosphere. The calculated amounts of iodoalkanes, aluminum powder, dichloromethane and iodine were introduced into a round-bottomed flask (250 cm^3) connected to a reflux condenser. The flask was then immersed in the water bath of the ultrasonic cleaner. After an induction period, the reaction started due to reflux and finished when the reflux ended. At the end of the reaction, 50 cm^3 of H_2O was added to the flask to react with the intermediates resulting in a two-phase solution. The organic layer was separated and the aqueous layer was extracted several times with portions of dichloromethane. The combined organic layers were dried over calcium chloride and the mixture was analyzed by gas chromatography (GC) for the determination of the resulting chloroiodomethane using bromobenzene as an internal standard. Pure chloroiodomethane can be distilled through a 20 cm Vigreux column twice from the organic portion, b.p. 107–108 °C (lit. b.p. 108–109 °C).

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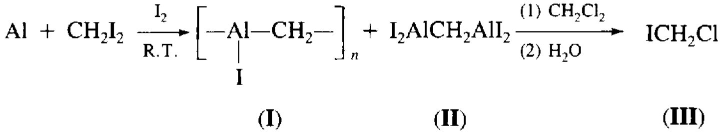
RESULTS AND DISCUSSION

Recently,[30] we found that compound **III** could be prepared from a stirred mixture of di-iodomethane, dichloromethane and aluminum powder at room temperature in the presence of iodine (Scheme 1).

A mixture of aluminum methylene compounds, **I** and **II**, was assumed[30] as intermediates which rapidly mediate transhalogenation with CH_2Cl_2 to give compound **III**. In an extension of the above preliminary study, a single-stage reaction between iodoalkanes and CH_2Cl_2 was readily irradiated with ultrasound in the presence of iodine and aluminum powder to generate compound **III**. The reaction pathway can be expressed as Scheme 2.

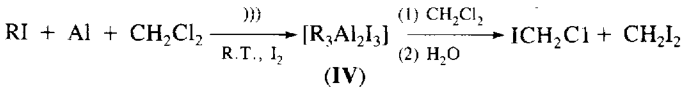
Without ultrasonic irradiation, this reaction does not occur at room temperature even in the presence of I_2. However, under magnetic stirring and reflux conditions the reaction could proceed mildly as shown in Table 1, yet a lengthy reaction time is required. Meanwhile no apparent induction period was observed. The best yield of compound **III** is obtained generally for iodoalkanes higher than propyl iodide. In the present case, ultrasonic irradiation could be used to promote a single-stage synthesis of compound **III** from some iodoalkanes, as shown in Table 2. Reaction yields follow the same tendency as those shown in Table 1, but ultrasound significantly shortens the reaction time. As can be seen in Table 2, the reaction times are similar when the carbon atoms in the iodoalkanes range from three to five.

More interestingly, a short reaction period under ultrasonic irradiation tends to produce by-products of 1,2-dichloroethane, especially for iodoalkanes containing fewer carbons, which tends not to occur under thermal conditions. This by-product formation could be explained as an induced coupling reaction of CH_2Cl_2 under ultrasonic irradiation, for which a similar phenomenon has been reported by Suslick and co-workers.[31,32] We found that the preferred reactant



$$Al + CH_2I_2 \xrightarrow[R.T.]{I_2} \left[-\underset{\displaystyle I}{\underset{|}{Al}}-CH_2- \right]_n + I_2AlCH_2AlI_2 \xrightarrow[(2)\ H_2O]{(1)\ CH_2Cl_2} ICH_2Cl$$

Scheme 1



$$RI + Al + CH_2Cl_2 \xrightarrow[R.T.,\ I_2]{)))} \underset{(IV)}{[R_3Al_2I_3]} \xrightarrow[(2)\ H_2O]{(1)\ CH_2Cl_2} ICH_2Cl + CH_2I_2$$

))) = ultrasonic irradiation

Scheme 2

Table 1 The yield of ICH_2Cl obtained from the reflux method alone (amounts of reactants used: Al, 0.1 mol; RI, 0.125 mol; I_2, 5 mmol; CH_2Cl_2, 2.5 mol)

	t = 1 h[b]	t = 2 h			t = 4 h		
	Products (%)[a]						
RI	ICH_2Cl	ICH_2Cl	$C_2H_4Cl_2$	CH_2I_2	ICH_2Cl	$C_2H_4Cl_2$	CH_2I_2
CH_3I	56.0	82.0	15.6	—	—	—	—
C_2H_5I	7.2	65.2	5.6	—	82.0	17.2	—
n-C_3H_7I	15.3	87.7	—	—	90.7	—	8.2
iso-C_3H_7I	21.5	85.7	—	—	—	—	—
n-C_4H_9I	7.1	84.7	5.8	6.5	—	—	—
iso-C_4H_9I	2.6	92.4	3.9	—	—	—	—
n-$C_5H_{11}I$	4.9	90.2	5.0	4.0	—	—	—

[a] ICH_2Cl was identified by comparing its NMR data with the standard (see Ref. 38). $C_2H_4Cl_2$, CH_2I_2 were identified by comparison with 1,2-dichloroethane and iodomethane by GC analysis. [b] t, reaction time.

Table 2 The yield of ICH_2Cl produced under ultrasonic irradiation (amounts of reactants used: RI, 0.125 mol; I_2, 5 mmol; CH_2Cl_2, 2.5 mol; Al, 0.1 mol)

Reactants, RI	Time for initiation, T_i (min)	Time for reflux end, T_r (min)	Reaction time, ΔT (min)	Products (%)		
				ICH_2Cl	CH_2I_2	$C_2H_4Cl_2$
CH_3I	†	†	60	25.0	—	8.0
	†	†	240	84.6	2.4	10.5
C_2H_5I	†	†	60	30.0	—	8.4
n-C_3H_7I	11	17	6	88.6	6.0	2.0
iso-C_3H_7I	11.5	17.5	6	89.0	4.5	1.6
n-C_4H_9I	11.5	18	6.5	88.2	5.9	1.9
iso-C_4H_9I	7.5	13	5.5	87.4	7.5	2.4
n-$C_5H_{11}I$	11.5	18.5	7.0	88.6	6.6	2.5

†No apparent induction period is observed.

for ICH_2Cl formation is $C_nH_{2n+1}I$ for $n > 2$. In this work, propyl iodide is selected as the reactant for preparing compound **III**.

Previously,[27–29] we reported that the quantity of iodine added to the reaction influences the induction time for formation of alkylaluminum sesquihalides. Figure 1 shows the effect of added iodine on the reaction under ultrasonic irradiation and indicates that a ratio of I_2/propyl iodide = 20×10^{-3} seems to be an optimum for the formation of propylaluminum sesqui-iodide. At the same time, the higher the ratio of I_2/propyl iodide, the shorter the induction time. But the reaction time remained unchanged, with the overall process far shorter than those reactions without ultrasound. The numerical data are tabulated in Table 3, which shows that use of an increasing amount of iodine moderately increases the yield of compound **III**. The iodine added plays a catalytic role.

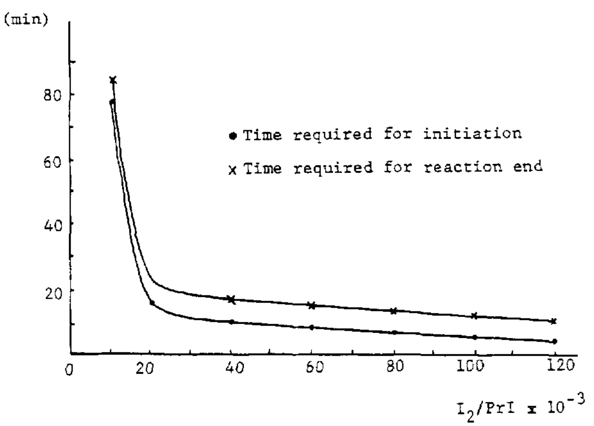


Figure 1 The effect of added I_2 on the reaction under ultrasonic irradiation.

Despite the fact that the lower alkyl aluminum sesqui-iodides could be isolated as noted in our earlier work,[28] intermediate **IV** has not been worked up prior to further conversion and must remain entrapped to react with CH_2Cl_2 to give compound **III**. Otherwise it readily decomposes. Apparently the amount of CH_2Cl_2 used is closely proportional to the yield of compound **III** in the overall reaction. As summarized in Table 4, the yield of **III** is influenced by altering the CH_2Cl_2/propyl iodide ratio. A large excess amount of CH_2Cl_2 is favorable to the formation of **III**, due to its function as both reactant and solvent. With a reduced amount of CH_2Cl_2 not only will an increase in the decomposition of intermediate **IV** occur to some extent, but also the formation of by-product CH_2I_2 will increase through a double transhalogenation on the original CH_2Cl_2 molecule with **IV**. The variation of CH_2Cl_2/propyl iodide ratio in this experiment does not influence the reaction time significantly.

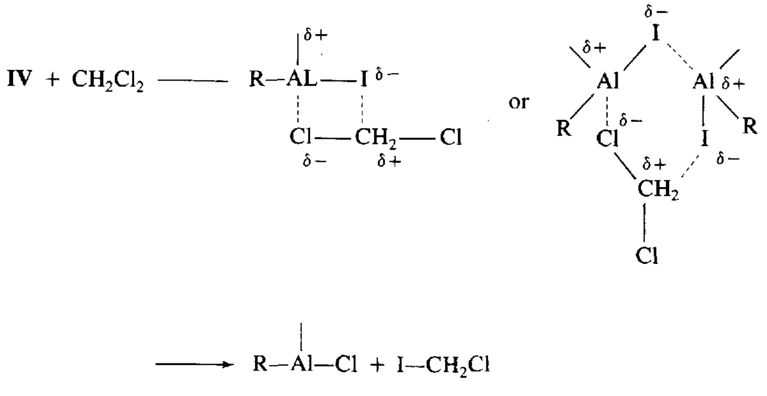
In order to confirm that the pathway of the reaction proceeds via alkylaluminum sesqui-iodide intermediates, the system involving alkyl iodides, $C_nH_{2n+1}I$ ($n = 1-3$), reacting with aluminum powder without CH_2Cl_2 was reacted to give the reactive intermediates $(C_nH_{2n+1})_3Al_2I_3$. The intermediates had been isolated and identified with the data reported.[33] When CH_2Cl_2 was reacted with the intermediate, the compound **III** instantly formed in a high yield. Hence, a transhalogenation between **IV** and CH_2Cl_2 could be depicted by a four- or six-center species (Scheme 3). The tendency for dative links of aluminum compounds with electron-rich donors such as CH_2Cl_2 could be considered as the motive force of this transhalogenation.[34–37]

Table 3 The yield of ICH_2Cl_2 produced (under ultrasonic irradiation) from different I_2/propyl iodide ratios used (amount of reactants used: Al, 0.1 mol; PrI, 0.125 mol; CH_2Cl_2, 2.5 mol)

I_2/PrI ($\times 10^{-3}$)	Time for initiation, T_i (min)	Time for reflux end, T_r (min)	Reaction time, ΔT (min)	Products (%)		
				ICH_2Cl	CH_2I_2	$C_2H_4Cl_2$
0	No reaction					
10	78	84	6	84.5	5.2	3.2
20	16	22	6	86.6	5.3	2.4
40	11	17	6	88.7	6.0	2.0
60	9.5	15.5	6	92.6	5.3	2.2
80	7.0	13.0	6	90.0	6.7	2.2
100	6.0	12	6	96.2	3.2	1.8

Table 4 The influence of the CH_2Cl_2/propyl iodide ratio on the yield of ICH_2Cl under ultrasonic irradiation (amount of reactants used: Al, 0.1 mol; PrI, 0.125 mol; I_2, 5 mmol)

CH_2Cl_2/PrI	Time for initiation, T_i (min)	Time for reflux end, T_r (min)	Reaction time, ΔT (min)	Products (%)			Overall yield (%)
				ICH_2Cl	CH_2I_2	$C_2H_4Cl_2$	
30	27.5	33	5.5	100	—	—	100
20	11	17	6	88.6	6.0	2.0	96.6
15	10	15.5	5.5	80	9.8	2.4	92.2
10	9.5	15.5	6	74	12.7	3.5	90.2
5	4.5	10	5.5	57.4	19.0	4.4	80.8
3	3.0	9	6	42.5	25.4	2.6	70.5
1	Complete decomposition						



Scheme 3

Other unsymmetric dihalomethanes XCH_2X' (X,X' = I, Cl, Br) could be obtained if appropriate haloalkanes were used. Table 5 shows the yield of $ClCH_2I$, $BrCH_2I$ and $ClCH_2Br$, indicating that the reactivity of dihalomethanes towards formation of organoaluminum compounds decreases as follows: PrI > PrBr > PrCl. The extent of transhalogenation is directly related to the ease of bond cleavage: Al—I > Al—Br > Al—Cl. These results are consistent with our proposed mechanism and it is feasible to extend this method to synthesize other mixed halocarbons.

In conclusion, an improvement for the synthesis of chloroiodomethane can be achieved via an organoaluminum intermediate under ultrasonic irradiation.

Table 5 The yield of unsymmetric dihalomethanes

Starting[a] materials		Final products			NMR of XCH_2X_2'	
					δ (ppm)	
PrX	CH_2X_2'	$Pr_3Al_2X_3$	XCH_2X'	Yield (%)	^1H	^{13}C
PrCl	CH_2Cl_2	No reaction				
PrI	CH_2Cl_2	$Pr_3Al_2I_3$	ICH_2Cl	88.6	4.97 (4.90)[b]	1.16
PrI	CH_2Br_2	$Pr_3Al_2I_3$	ICH_2Br	72	4.60	−19.72 (−25.2)[c]
PrBr	CH_2Cl_2	$Pr_3Al_2Br_3$	$BrCH_2Cl$	61	5.18 (5.12)[c]	37.20 (38.5)[c]

[a] Reactants used: PrX, 0.125 mol; Al, 0.1 mol; CH_2X_2', 2.5 mol. [b] Data in parentheses were taken from Ref. 38. [c] The calculated data were taken from Ref. 39.

Compared with other existing methods, the process described in this investigation shows distinct advantages. These include the simplicity of one-pot, single-stage reaction, a shorter reaction time, milder reaction conditions, and better yields.

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