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Ghasem Aghapour <sup>a</sup> & Asieh Afzali <sup>a</sup> <sup>a</sup> School of Chemistry, Damghan University of Basic Sciences, Damghan, Iran Published online: 20 Oct 2008.

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# Facile Conversion of Aldehydes and Ketones to gem-Dichlorides Using Chlorodiphenylphosphine/ N-Chlorosuccinimide as a New and Neutral System

Ghasem Aghapour and Asieh Afzali

School of Chemistry, Damghan University of Basic Sciences, Damghan, Iran

**Abstract:** Aldehydes and ketones are easily converted to their corresponding *gem*-dichlorides using a mixture of chlorodiphenylphosphine and N-chlorosuccinimide (ClPPh<sub>2</sub>/NCS) in dichloromethane under neutral conditions and at room temperature.

Keywords: Aldehyde, chlorodiphenylphosphine, gem-dichloride, ketone, N-chlorosuccinimide

The conversion of aldehydes and ketones to the corresponding *gem*dichlorides is a very important transformation in organic synthesis because these compounds can serve as precursors to transition-metal alkylidenes for carbonyl olefination<sup>[1]</sup> and also the product dichloroarylmethanes are of value in the pharmaceutical and agricultural industries.<sup>[2]</sup> Generally, PCl<sub>5</sub> is used to generate geminal dichlorides.<sup>[3]</sup> Other methods include the use of SOCl<sub>2</sub>/*N*,*N*-dimethylformamide (DMF),<sup>[4]</sup> WCl<sub>6</sub>,<sup>[5,6]</sup> BCl<sub>3</sub>,<sup>[7]</sup> PPh<sub>3</sub>/CCl<sub>4</sub>,<sup>[8]</sup> alkylboron chloride derivatives,<sup>[9]</sup> acid halides in the presence of acid catalysts,<sup>[10]</sup> and (PhO)<sub>3</sub>P/Cl<sub>2</sub>,<sup>[11]</sup> as chlorination reagents. Also, synthesis of *gem*-dichlorides from the reaction of hydrazones prepared by the treatment of aldehydes and ketones with hydrazine

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Address correspondence to Ghasem Aghapour, School of Chemistry, Damghan University of Basic Sciences, Damghan 3671641167, Iran. E-mail: Gh\_Aghapour@dubs.ac.ir

hydrate in the presence of 4-Å molecular sieves with copper(II) chloride– lithium *tert*-butoxide as an oxidizing agent, has been reported,<sup>[12]</sup> and also in a minor modification of this procedure, this transformation has been carried out via treatment of aldehyde- and ketone-derived *N-tert*-butyldimethylsilylhydrazones with CuCl<sub>2</sub> and a catalytic amount of Sc(OTf)<sub>3</sub>.<sup>[13]</sup>

However, these methods contain some disadvantages such as use of toxic reagents, operation at high temperature or in acidic conditions, long reaction times, applicability for either aldehydes or ketones, unsuitability for carbonyl compounds containing enolizable hydrogens, formation of undesired products, and low yields. Consequently, there is a need for the development of new methods within neutral media that are more convenient for this important synthetic transformation.

In continuation of our work on the new applications of trivalent phosphorus in organic synthesis,<sup>[14]</sup> we now report a facile conversion of both aldehydes and ketones to their corresponding *gem*-dichlorides using a mixture of chlorodiphenylphosphine/N-chlorosuccinimide (ClPPh<sub>2</sub>/NCS) under neutral conditions (Scheme 1).

First, we selected *p*-chlorobenzaldehyde as an example and optimized the reaction conditions for its conversion to 1-chloro-4-dichloromethylbenzene **1** using  $ClPPh_2/N$ -chlorosuccinimide (NCS). In this connection, we found that the solvent-free use of  $ClPPh_2$  and NCS simultaneously is highly exothermic and vigorous for this purpose. Thus, for ease and mild performance of this transformation, we carried out it in  $CH_2Cl_2$  as solvent. The results of this study are shown in Table 1. Comparison of entries 2 and 3 show that heating the reaction mixture does not highly improve the yield or rate of this transformation. Also, this conversion was unsuccessful by  $ClPPh_2$  (4 eq.) in the absence of NCS even under heating (Table 1, entries 5 and 6). In these cases, the desired *gem*-dichloride **1** was obtained in only 20% yield at room temperature and 25% yield under reflux conditions after 23 h.



*Scheme 1.* Conversion of aldehydes and ketones to *gem*-dichlorides using chlorodiphenylphosphine/*N*-chlorosuccinimide.

**Table 1.** Conversion of *p*-chlorobenzaldehyde to its corresponding *gem*-dichlorides 1 in  $CH_2Cl_2$  in various conditions



Entry	Reagents	Molar ratio <sup>a</sup>	Time (h)	Temp. (°C)	Yield (%)
1	ClPPh <sub>2</sub> /NCS	1/1/1	24	rt	10
2	ClPPh <sub>2</sub> /NCS	1/1.5/1.5	17	rt	20
3	ClPPh <sub>2</sub> /NCS	1/1.5/1.5	9	reflux	30
4	$ClPPh_2/NCS$	1/2/2	2	rt	90
5	$ClPPh_2$	1/4	23	rt	20
6	ClPPh <sub>2</sub>	1/4	23	reflux	25
7	ClPPh <sub>2</sub> /NCS	1/2/2	4.5	rt	$20^{b}$
8	ClPPh <sub>2</sub> /NCS	1/2/2	4.5	reflux	$20^{b}$
9	PPh <sub>3</sub> /NCS	1/2/2	23	rt	40

<sup>a</sup>Molar ratio is related to aldehyde/tertiary phosphine/NCS.

<sup>b</sup>This reaction was carried out in acetonitrile as solvent.

In addition, increasing the molar ratio of the mixed reagent (ClPPh<sub>2</sub>/NCS) causes the increase of both yield and rate of this reaction (Table 1, entries 1, 2, and 4) so that the best result was obtained in the case of entry 4: 1 was obtained in 90% yield after 2 h at room temperature. Also, this conversion was unsuccessful in acetonitrile instead of dichloromethane as solvent (Table 1, entries 7 and 8). In this case, 1 was produced using ClPPh<sub>2</sub>/NCS (2:2) in only 20% yield after 4.5 h even under reflux conditions.

Also, we found that performing this transformation using PPh<sub>3</sub>/NCS instead of ClPPh<sub>2</sub>/NCS requires a longer reaction time and affords a lower yield of 1 (Table 1, entry 9). This result shows the better efficiency of ClPPh<sub>2</sub>/NCS for this transformation. Thus, we extended the optimized reaction conditions (Table 1, entry 4) with variable molar ratio of the present mixed reagent for conversion of other aldehydes and ketones to their corresponding *gem*-dichlorides. The results are shown in Table 2.

As shown in this table, aldehydes and ketones are conveniently converted to their corresponding *gem*-dichlorides using  $ClPPh_2/NCS$  in  $CH_2Cl_2$  at room temperature in good to excellent yields. In addition, the yield and rate of this transformation for aldehydes are more than

Table 2. Coi	nversion of aldehydes and keton	es to gem-dichlorides using ClP $h_2/$	NCS in CH <sub>2</sub> Cl <sub>2</sub> at r	oom temperature	
Entry	Aldehydes or ketones	gem-dichlorides	Molar ratio <sup>a</sup>	Time (h)	Yield $(\%)^b$
	CI-CHO	ci-CHCl <sub>2</sub>	1:2:2	2	06
0	O <sub>2</sub> N	O <sub>2</sub> N CHCl <sub>2</sub>	1:2:2	1.75	82
ς,	CHO NO2	CHCI <sub>2</sub> NO <sub>2</sub> 3	1:2.5:2.5	0	60
4	O <sub>2</sub> N-CHO	O <sub>2</sub> N-CHCl <sub>2</sub>	1:3:3	1.5	73

4026

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Table 2. Continued

Entry	Aldehydes or ketones	gem-dichlorides	Molar ratio <sup>a</sup>	Time (h)	Yield $(\%)^b$
10	O <sub>2</sub> N-COCH <sub>3</sub>	O <sub>2</sub> N-CCI <sub>2</sub> CH <sub>3</sub>	1:2.5:2.5	7	68°
Ξ	COCH <sub>3</sub>	CCI2CH <sub>3</sub>	1:3:3	9	60 <sup>d</sup>
12	CHO	CHBr <sub>2</sub>	1:2:2	Q	7S <sup>e,f</sup>
<sup>a</sup> Molar <sup>b</sup> Isolatec <sup>c</sup> In this e	ratio is related to aldehyde or keto 1 yields. case, equimolar amounts of the rel MR analysis	one/CIPPh <sub>2</sub> /NCS. ated <i>gem</i> -dichloride <b>10</b> and 1-(1-chlo	oroethenyl)-4-nitrobe	nzene 13 were ol	otained on the

SIS Of INMIK analysis.

<sup>d</sup>Bp 71–72°C (4 mm) (lit.<sup>[15]</sup> 71°C, 4 mm).

"NBS was used instead of NCS in this case. A mixture of dibromomethylbenzene **12** and bromochloromethylbenzene **14** was produced in a 4:1 ratio together with a trace amount of dichloromethylbenzene 7 in this case.

4028

ketones because of steric and electronic factors. Also, the conversion of 3phenylpropanal as an aldehyde containing enolizable hydrogen to 1,1dichloro-3-phenylpropane **9** was successfully carried out using the present method (Table 2, entry 9), contrary to the previously reported method.<sup>[7]</sup> The lower yields in the case of the ortho isomer of substituted aromatic aldehydes may be due to steric hindrance of the substituent (Table 2, entries 3 and 5).

However, we found that the conversion of *p*-methoxybenzaldehyde to its corresponding *gem*-dichloride was unsuccessful using the presented method. In this transformation using ClPPh<sub>2</sub>/NCS (2.5:2.5), 80% of the starting material remained after 10 h. This observation is probably related to the methoxy group in the para position, which decreases the stability of this product toward hydrolysis in accordance with the literature.<sup>[16]</sup>

In the case of 4'-nitroacetophenone, a mixture of two products containing the corresponding *gem*-dichloride **10** and 1-(1-chloroethenyl)-4nitrobenzene (*p*-O<sub>2</sub>NPhCCl = CH<sub>2</sub>) **13** were isolated from the reaction mixture. The NMR spectra of these mixed products (in CDCl<sub>3</sub>) were recorded and revealed that the characteristic <sup>13</sup>C resonance for carbonyl group was absent but that new <sup>13</sup>C NMR resonances were present at 86.37 ppm (CCl<sub>2</sub> group of **10**) and 116.83 ppm (=CH<sub>2</sub> group of **13**) and also new <sup>1</sup>H NMR resonances at 2.56 ppm (s) for methyl group of **10**, 5.73 ppm (d, J=2.1 Hz) and 5.94 ppm (d, J=2.2 Hz) both for (=CH<sub>2</sub>) group of **13**. Also, the molar ratio of 1:1 was obtained for these products (**10**, **13**) from this study (Table 2, entry 10).

In addition, the possibility of preparing of mixed *gem*-dihalides was investigated via exchanging NCS with N-bromosuccinimide (NBS). For this purpose, benzaldehyde was treated with a mixture of ClPPh<sub>2</sub>/NBS (2:2) in CH<sub>2</sub>Cl<sub>2</sub> at room temperature. After completion of the reaction (6 h), the solvent was evaporated. A mixture of products was obtained using column chromatography. NMR and gas chromatography (GC)–mass analysis of this mixture showed the formation of different *gem*-dihalides containing dibromomethylbenzene **12** and bromochloromethylbenzene **14** in a 4:1 ratio together with a trace amount of dichloromethylbenzene **7** in 75% yield (Table 2, entry 12).

On the basis of differences between reaction rates of aldehydes and ketones in the present method, we studied the possibility of the conversion of aldehydes in the presence of ketones in a binary mixture. In treatment of a binary mixture containing *p*-nitrobenzaldehyde and 4'-nitroacetophenone (1:1) with ClPPh<sub>2</sub>/NCS (3:3) in CH<sub>2</sub>Cl<sub>2</sub> at room temperature, *p*-nitrobenzaldehyde was completely converted to **4** but 4'-nitroacetophenone completely remained after 35 min, indicating that this new method selectively converts aldehydes to their corresponding *gem*-dichlorides in the presence of ketones (Scheme 2).



Scheme 2. Selective conversion of *p*-nitrobenzaldehyde to its corresponding *gem*-dichloride 4 in the presence of 4'-nitroacetophenone in a binary mixture (1:1) using  $ClPPh_2/NCS$ .

Although the exact mechanism of this reaction is not clear, on the basis of the reports<sup>[14a,b]</sup> on the reaction of  $Ph_3P$  and NCS, the formation of complex (A) can be assumed from the reaction of  $ClPPh_2$  and NCS with concomitant releasing of the chloride anion (Scheme 3).Treatment of aldehydes or ketones with (A) could produce (B), which later reacts with the chloride anion to give the intermediate (C). Finally, subsequent attack of the second chloride anion to this intermediate affords the desired *gem*-dichloride. The major deriving force for this reaction could well be the formation of a double bond between oxygen and oxophilic phosphorus (P = O).

In conclusion, the present investigation has demonstrated that the use of  $ClPPh_2/NCS$  offers a simple, novel, and convenient method, avoiding the use of molecular halogen with its harsh handling for the conversion of aldehydes and ketones to their corresponding *gem*-dichlorides. Availability, ease of handling, and low cost of the reagent; excellent selectivity; easy workup; operation at room temperature in neutral media; and applicability for aldehydes, ketones, and also carbonyl compounds containing enolizable hydrogens can be considered as other advantages of this method. Further studies toward the other applications of this reagent in organic synthesis are in progress in our laboratory.

#### EXPERIMENTAL

Solvents, reagents, and chemicals were obtained from Merck (Germany) and Fluka (Switzerland) chemical companies. Products are known compoundsand were characterized by comparison of their physical data, IR, NMR, and mass spectra with those prepared according to literature procedures. Fourier transform infrared (FT-IR) spectra were recorded on a Perkin-Elmer RXI spectrophotometer. NMR spectra were recorded on a Brucker Avance DRX-500 spectrometer. Mass spectra were determined on a HP 5973 msd at 70 ev. Thin-layer chromatography (TLC) was carried out on silica-gel 254 analytical sheets obtained from Fluka.

# Typical Procedure for the Conversion of 3-Nitrobenzaldehyde to 1-dichloromethyl-3-nitrobenzene (2)

To a flask containing a stirring mixture of ClPPh<sub>2</sub> (0.368 ml, 2 mmol) and NCS (0.268 g, 2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 ml), 3-nitrobenzaldehyde (0.151 g, 1 mmol) was added at room temperature. The stirring was continued until TLC showed the completion of the reaction (1.75 h). The solvent was evaporated. Compound **2** was obtained after short column



*Scheme 3.* Mechanism of the conversion of aldehydes and ketones to *gem*-dichlorides using CIPPh<sub>2</sub>/NCS.

chromatography of the crude mixture on silica gel 60 (0.063-0.200 mm) using petroleum ether-ethyl acetate (40:1) as eluent in 82% yield, 0.169 g; mp 64–65°C (lit.<sup>[17]</sup> 65°C).

## Data

1-Dichloromethyl-4-nitrobenzene (4)

Yield 73%; mp 45–46°C (lit.<sup>[17]</sup> 46°C);<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  6.77 (s, 1H), 7.74–7.77(m, 2H), 8.24–8.27 (m, 2H) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125.77 MHz):  $\delta$  70.26, 124.55, 127.81, 146.67, 148.97 ppm; FT-IR (neat): 3110 (w), 3081 (w), 2926 (m), 2857 (m), 1609 (m), 1531 (s), 1494 (m), 1348 (s), 1110 (m), 863 (m), 823 (s), 767 (s), 713 (s) cm<sup>-1</sup>; mass spectra m/e: 209 (M+4), 207 (M+2), 205 (M), 172 (M+4–<sup>37</sup>Cl and M+2–<sup>35</sup>Cl, 34.46%), 170 (M+2–<sup>37</sup>Cl and M–<sup>35</sup>Cl, 100%), 163 (M+4–NO<sub>2</sub>), 161 (M+2–NO<sub>2</sub>), 159 (M–NO<sub>2</sub>).

1-Dichloromethyl-2-nitrobenzene (3)

Yield 60%; mp 26–27°C (lit.<sup>[18]</sup> 26–27°C); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  7.55–7.58 (m, 1H), 7.56 (s, 1H), 7.74–7.78 (m, 1H), 7.97–7.99 (dd, 1H, J = 8.2, 0.91 Hz), 8.18–8.20 (dd, 1H, J = 7.97, 1 Hz) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125.77 MHz):  $\delta$  66.36, 125.04, 130.34, 131.16, 134.65, 135.25, 146.51 ppm.

1-Chloro-4-dichloromethylbenzene (1)

Yield 90%; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  6.67 (s, 1H), 7.37–7.39 (m, 2H), 7.50–7.52 (m, 2H) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125.77 MHz):  $\delta$  71.24, 127.96, 129.42, 136.29, 139.31 ppm; FT-IR (neat): 3100 (w), 2926 (m), 2854 (m), 1598 (m), 1492 (s), 1406 (m), 1090 (s), 1015 (m), 840 (s), 740 (s), 689 (s) cm<sup>-1</sup>. Anal. calcd. for C<sub>7</sub>H<sub>5</sub>Cl<sub>3</sub>: C, 43.01; H, 2.58. Found: C, 43.04; H, 2.56.

1-Chloro-2-dichloromethylbenzene (5)

Yield 68%; bp 228–229°C (lit.<sup>[17]</sup> 228.5 °C); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  7.17 (s, 1H), 7.30–7.40 (m, 3H), 7.93–7.95 (dd, 1H, *J*=7.8, 1.41 Hz) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125.77 MHz):  $\delta$  68.37, 128.19, 129.26, 129.93, 131.30, 131.42, 138.04 ppm.

#### gem-Dichlorides

1-Bromo-4-dichloromethylbenzene (6)

Yield 75%; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  6.66 (s, 1H), 7.43–7.46 (m, 2H), 7.53–7.55 (m, 2H) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125.77 MHz):  $\delta$  71.34, 124.51, 128.24, 132.43, 139.78 ppm. Anal. calcd. for C<sub>7</sub>H<sub>5</sub>BrCl<sub>2</sub>: C, 35.04; H, 2.10. Found: C, 35.06; H, 2.06.

Dichloromethylbenzene (7)

Yield 71%; bp 205–206 °C (lit.<sup>[17]</sup> 205.2 °C); mass spectra m/e: 164 (M+4, 0.9%), 162 (M+2, 5.7%), 160 (M, 8.8%), 127 (M+4–<sup>37</sup>Cl or M+2–<sup>35</sup>Cl, 33%), 125 (M+2–<sup>37</sup>Cl or M–<sup>35</sup>Cl, 100%), 90 (M+4–2Cl, M+2–2Cl or M–2Cl, 4.9%).

1-Dichloromethyl-4-methylbenzene (8)

Yield 65%; mp 47–48 °C (lit.<sup>[19]</sup> 48.5 °C); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  2.38 (s, 3H), 6.69 (s, 1H), 7.20–7.22 (d, 2H, J=7.99 Hz), 7.45–7.47 (d, 2H, J=8.14 Hz) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125.77 MHz):  $\delta$  21.67, 72.27, 126.43, 129.81, 138.09, 140.53 ppm.

1,1-Dichloro-3-phenylpropane (9)

Yield 72%; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  2.50–2.54 (m, 2H), 2.87–2.90 (t, 2H, J = 7.5 Hz), 5.66–5.68 (t, 1H, J = 6.2 Hz), 7.20–7.25 (m, 3H), 7.30–7.33 (m, 2H) ppm; <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125.77 MHz):  $\delta$  32.54, 45.42, 73.12, 126.92, 128.88, 129.10, 139.78 ppm; mass spectra m/e: 192 (M + 4, 4%), 190 (M + 2, 22%), 188 (M, 34.17%), 155(M + 2–<sup>35</sup> Cl and M + 4–<sup>37</sup>Cl), 153 (M–<sup>35</sup>Cl and M + 2–<sup>37</sup>Cl), 91 (M–CH<sub>2</sub>CHCl<sub>2</sub>, 100%). Anal. calcd. for C<sub>9</sub>H<sub>10</sub>Cl<sub>2</sub>: C, 57.17; H, 5.33. Found: C, 57.14; H, 5.35.

Dibromomethylbenzene (12)

Mass spectra m/e: 252 (M + 4, 1%), 250 (M + 2, 2%), 248 (M, 1%), 171 (M +  $4^{-81}$ Br or M +  $2^{-79}$ Br, 100%), 169 (M +  $2^{-81}$ Br or M $^{-79}$ Br, 100%), 90 (M +  $4^{-2}$ Br, M +  $2^{-2}$ Br or M $^{-2}$ Br, 33.1%).

Bromochloromethylbenzene (14)

Mass spectra m/e: 208 (M+4, 0.15%), 206 (M+2, 0.67%), 204 (M, 0.5%), 171 (M+4 $^{37}$ Cl or M+2 $^{35}$ Cl, 3.3%), 169 (M+2 $^{37}$ Cl or

 $M^{-35}$ Cl, 3.3%), 127 (M + 4<sup>-81</sup>Br or M + 2<sup>-79</sup>Br, 33.6%), 125 (M + 2<sup>-81</sup>Br or M<sup>-79</sup>Br, 100%), 90 (M + 4-Br-Cl, M + 2-Br-Cl or M-Br-Cl, 8.8%).

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