A Convenient and Efficient Synthesis of 1-Aryl-2,2-dichloroethanones

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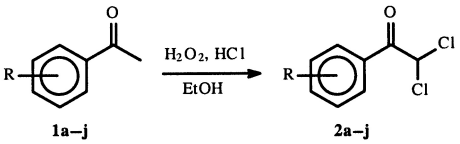
Abstract: 1-Arylethanones are readily chlorinated with an aqueous HCl–H_2O_2 system using ethanol as a cosolvent. The reaction proceeds rapidly and results in selective conversion of 1-arylethanones into 1-aryl-2,2-dichloroethanones in yields of 48–89%, depending on the nature of the substituent in the aryl group.

Key words: 1-arylethanones, 1-aryl-2,2-dichloroethanones, chlorination, hydrogen peroxide

1-Aryl-2,2-dichloroethanones are versatile synthetic intermediates for the preparation of arylhydroxyacetic acids,[1,2] arylglyoxals,[3,4] their acetals,[4,5] α-chloroepoxides,[6,7] α-chloroketones,[7] and 3-aryl-4-halogeno-1,2,5-thiadiazoles.[8] There are two main procedures for the preparation of 1-aryl-2,2-dichloroethanones: chlorination of 1-arylethanones with chlorine in acetic acid[1,2,5,6,8,9] and Lewis acid catalyzed acylation of arenes with dichloroacetyl chloride.[3,4,10] Both methods have drawbacks. The use of gaseous chlorine requires special equipment and calls for rigorous safety measures. The reaction of dichloroacetyl chloride with arenes is unsuitable for the preparation of 1-aryl-2,2-dichloroethanones containing electron-withdrawing substituents in the aryl group.

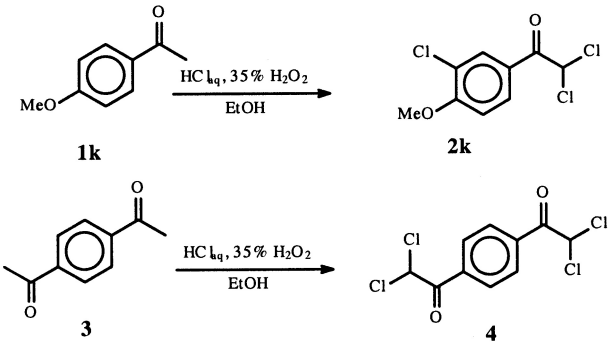
Other approaches to 1-aryl-2,2-dichloroethanones, e.g. based on reactions of 1-arylethanones with copper chloride[11] and benzyltrimethylammonium tetrachloroiodate,[12] phenylmagnesium bromide with 1,2,2-trichloro-*N*,*N*-diethyleneamine,[13] ozonolysis of 4,4-dichloro-3-phenylbut-2-enoic acid,[14] arylacetylenes with hypochlorites[15] or *N*-chlorosuccinimide,[16] and 1-arylethanones with ammonium chloride in the presence of $Mn(OAc)_3$,[9] are of little use as versatile methods for the preparative synthesis of 1-aryl-2,2-dichloroethanones. On this point, the methods for the halogenation of organic compounds with aqueous hydrohalogenic acid–H_2O_2 systems are much more promising. They have been intensively developed since the end of 1980s.[17–23]

In the present study, we report the use of an analogous method for chlorination of 1-arylethanones **1a–j** (Scheme 1) with concentrated hydrochloric acid–35% H_2O_2 system. The reaction was carried out by rapid addition (1 min) of H_2O_2 to a boiling mixture of substrate **1**, hydrochloric acid and ethanol (1:1) followed by refluxing the reaction mixture until the complete conversion of **1** and oxidants (negative KI test). Under these conditions it took 2.7 equivalents of H_2O_2 (the stoichiometric coefficient is 2) and only ten minutes to complete conversion of unsubstituted and alkyl substituted **1a–d** and their selective transformation into the corresponding 1-aryl-2,2-dichloroethanones **2a–d** and 3.3–4 equivalents of H_2O_2 and 15 minutes for the transformation of 1-arylethanones containing electron-withdrawing substituents **1e–j** into the corresponding 1-aryl-2,2-dichloroethanones **2e–j** (Table 1).



Scheme 1 R = H (**1a**), 4-Me (**1b**), 4-*t*-Bu (**1c**), 3,4-$(CH_2)_4$- (**1d**), 3-Br (**1e**), 4-Br (**1f**), 4-Cl (**1g**), 4-NO_2 (**1h**), 3-NO_2 (**1i**), 4-I (**1j**)

In the case of 1-(4-methoxyphenyl)ethanone (**1k**), the electron-rich ring undergoes substitution when the molar ratio H_2O_2/**1k** = 5.5 to give **2k** in 86% yield. In the case of 1,4-diacetylbenzene **3**, both acetyl groups are transformed to dichloroacetyl groups when the ratio of H_2O_2/**3** = 6.2 to give **4** in 77%yield (Scheme 2).



Scheme 2

To optimize the conditions for the synthesis of 1-aryl-2,2-dichloroethanones, we studied the influence of the temperature, the nature of alcohol used as a cosolvent, and the amount of hydrochloric acid on the ratio of 2-chloro-1-phenylethanone (**5**) and 2,2-dichloro-1-phenylethanone (**2a**) and their overall yield using acetophenone **1a** as an example. We found that chlorination of **1a** at 20 °C and under other standard conditions gives **2a** only in 4% yield

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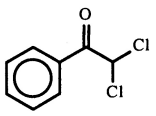
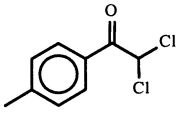
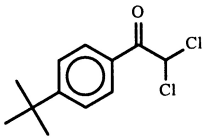
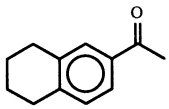
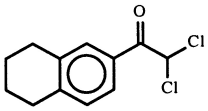
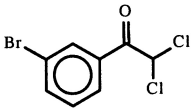
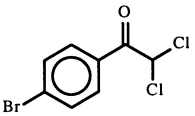
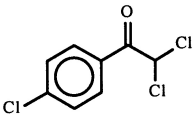
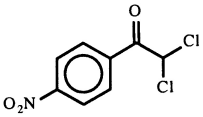
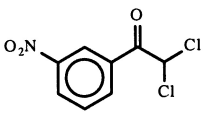
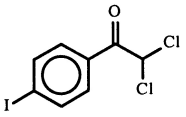
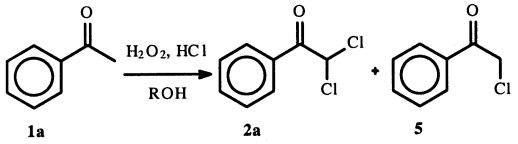
Table 1 Synthesis of 1-Aryl-2,2-dichloroethanones[a]

1-Arylethanone **1**	Molar Ratio H_2O_2/**1**	1-Aryl-2,2-dichloroethanone **2**	Yield (%)[b]
PhCOMe **1a**	2.7	 **2c**	85
4-MeC_6H_4COMe **1b**	2.7	 **2b**	87
4-*t*-BuC_6H_4COMe **1c**	2.7	 **2c**	80
 **1d**	2.7	 **2d**	72
3-BrC_6H_4COMe **1e**	4.0	 **2e**	83
4-BrC_6H_4COMe **1f**	3.3	 **2f**	87
4-ClC_6H_4COMe **1g**	3.3	 **2g**	89
4-$NO_2C_6H_4COMe$ **1h**	3.3	 **2h**	85
3-$NO_2C_6H_4COMe$ **1i**	4.0	 **2i**	85
4-IC_6H_4COMe **1j**	3.3	 **2j**	48

[a] Rapid addition of H_2O_2 (1 min) to a boiling mixture of **1** (1 g, 3.17–8.33 mmol), conc. HCl (20 mL), and EtOH (20 mL) followed by refluxing the reaction mixture for 10–15 min.
[b] Based on the isolated product.

and a mixture of **2a** and **5** in an overall yield of 90% in the ratio 1.9:1 when the reaction time was extended to 12 hours (Scheme 3, Table 2).



Scheme 3 R = Me, Et, *i*-Pr

Table 2 Optimization of the Conditions for the Chlorination of **1a**[a]

Cosolvent	Temp (°C)	Yield (%)[b]		Molar Ratio	Selectivity **2a/2a + 5 =** 100%
		2a	**5**	**2a/5**	
EtOH	20	4	26	0.15	13
EtOH[c]	20	59	31	1.9	65
EtOH	91–93	85	4.5	19	95
MeOH	85–86	89	3.5	25	96
i-PrOH	90–92	81	7	12	92
EtOH[d]	79–81	74	19	3.9	79

[a] Standard conditions: **1a** (8.33 mmol); conc. HCl (20 mL); alcohol (20 mL); molar ratio H_2O_2/**1a** = 2.7; reaction time: 15 min.
[b] Based on the isolated product.
[c] Reaction time: 12 h.
[d] Conc. HCl = 5 mL.

Boiling a mixture of equal volumes of concentrated hydrochloric acid and ethanol or isopropanol (90–93 °C) results in the suppression of the formation of **5** and the production of **2a** as a practically sole product. This product was also obtained in about 100% selectivity and quantitative yield by the chlorination of **1a** in a boiling mixture of equal volumes of hydrochloric acid and methanol (85–86 °C). The reaction is less selective in a boiling mixture of hydrochloric acid and ethanol with the volume ratio 1:4 (79–81 °C). Thus, on the basis of the reported findings on optimizing the conditions for the preparation of **2a** by chlorination of **1a** under the action of aqueous HCl–H_2O_2 system it can be concluded that the most selective and efficient transformation of **1a** to **2a** takes place in a boiling mixture of equal volumes of concentrated hydrochloric acid and ethanol or methanol.

In conclusion, we have developed a new, convenient and efficient method for the preparation of 1-aryl-2,2-dichloroethanones from 1-arylethanones using aqueous HCl–H_2O_2 as a chlorinating agent and ethanol as a co-solvent. The attractive features of the method are high selectivity and yields, easy and fast operation, using cheap and safe raw materials in comparison with traditional reagents used in the chlorination reactions.

Melting points were determined on a Kofler hot stage. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC-200, Bruker WM-250, and Bruker AM-300 instruments in $CDCl_3$ solutions. Analytical TLC: Silufol UV-254, Silpearl as the sorbent, starch as the binder. Column chromatography was performed on silica gel (63–200 mesh, Merck). 1-Arylethanones **1a–c**, **1e–k** and 1,4-diacetylbenzene (**3**) were purchased from Aldrich and Acros. Compound **1d** was synthesized according to a known procedure,[24] bp 150–152 °C/10 mm Hg.

The reactions were carried out using 31% HCl (reagent grade) and a 35% aq solution of H_2O_2. Petroleum ether (bp 40–60 °C), Et_2O, $CHCl_3$, EtOAc, MeOH, EtOH, *i*-PrOH, dioxane, AcOH, and benzene (all of reagent grade) were used as solvents without additional purification.

Chlorination of 1-Arylethanones 1a–k and 1,4-Diacetylbenzene (3); General Procedure

1-Arylethanone **1** (3.17–8.33 mmol) was dissolved in a mixture of 31% aq HCl (20 mL, 0.2 mol) and EtOH (20–25 mL) and the mixture was heated to reflux (91–93 °C). A solution of 35% aq H_2O_2 in EtOH (2 mL, 2.7–6.2 mol of H_2O_2 per mole of ketone **1**) was added with stirring over 1 min. The reaction mixture was refluxed with stirring for 10–15 min and cooled to r.t. H_2O (10 mL) was added and the mixture was extracted with $CHCl_3$ (4 × 25 mL). The combined organic extracts were washed with H_2O (4 × 10 mL), dried ($MgSO_4$), and concentrated. Products **2a–e**, **2h–k**, **4** and **5** were isolated by column chromatography of the crude product. Compounds **2f** and **2g** were isolated by recrystallization of the crude product from petroleum ether. Results are given in Table 1. Experiments on optimizing the conditions for the synthesis of 1-aryl-2,2-dichloroethanones (see Table 2) were carried out using the general procedure and changing reaction temperature, cosolvent, reaction time and the volume ratio of conc. HCl and cosolvent. The melting points of **2a–d**, **2f**, **2g,** and **5** were measured after recrystallization from petroleum ether, the melting points of **2h–k** were determined after recrystallization from a petroleum ether–$CHCl_3$, and the melting point of **4** was measured after recrystallization from EtOH.

2,2-Dichloro-1-phenylethanone (2a)[25]

White crystals; mp 19–20.5 °C (Lit.[25] mp 20–21.5 °C); R_f 0.27 (petroleum ether–EtOAc, 94:6).

^{1}H NMR (200.13 MHz, $CDCl_3$): δ = 6.76 (s, 1 H, CH), 7.42–7.72 (m, 3 H, ArH), 8.04–8.16 (m, 2 H, ArH).

^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 67.7 ($CHCl_2$), 128.8, 129.6 (CH_{arom}), 131.2 (C_{arom}), 134.5 (*C*HCHCHC), 185.8 (C=O).

2,2-Dichloro-1-(4-methylphenyl)ethanone (2b)[6]

White crystals; mp 54–55 °C (Lit.[6] mp 54.5–55.3 °C).

R_f = 0.35 (TLC, petroleum ether-EtOAc, 94:6).

^{1}H NMR (200.13 MHz, $CDCl_3$): δ = 2.43 (s, 3 H, CH_3), 6.72 (s, 1 H, CH), 7.30 (d, 2 H, *J* = 8 Hz, ArH), 7.97 (d, 2 H, *J* = 8 Hz, ArH).

^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 21.7 (CH_3), 67.7 ($CHCl_2$), 128.6 (*C*C=O), 129.5, 129.7 (CH_{arom}), 145.8 (*C*CH_3), 185.4 (C=O).

1-(4-*tert*-Butylphenyl)-2,2-dichloroethanone (2c)[26]

White crystals; mp 51.5–52.5 °C (Lit.[26] mp 47–49 °C); R_f 0.85 (petroleum ether–EtOAc, 91:9).

^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 1.38 (s, 9 H, *t*-C_4H_9), 6.72 (s, 1 H, CH), 7.54 (d, 2 H, *J* = 8.5 Hz, ArH), 8.03 (d, 2 H, *J* = 8.5 Hz, ArH).

^{13}C NMR (62.9 MHz $CDCl_3$): δ = 31.0 (CH_3), 35.4 [*C*$(CH_3)_3$] 67.9 ($CHCl_2$), 126.0 (CH_{arom}), 128.6 (*C*C=O), 129.8 (CH_{arom}), 158.8 [*C*C$(CH_3)_3$], 185.6 (C=O).

1-(5,6,7,8-Tetrahydronaphthalen-2-yl)ethanone (2d)[27]

White crystals; mp 41.5–42.5 °C (Lit.[27] mp 42–42.5 °C); R_f 0.6 (petroleum ether–EtOAc, 94:6).

^{1}H NMR (200.13 MHz, $CDCl_3$): δ = 1.70–1.90 (m, 4 H, $CH_2CH_2CH_2CH_2$), 2.70–2.85 (m, 4 H, ArCH_2), 6.75 (s, 1 H, CH), 7.17 (d, 1 H, *J* = 8.5 Hz, ArH), 7.76 (m, 2 H, ArH).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 22.4, 22.6 ($CH_2CH_2CH_2CH_2$), 29.1, 29.6 (ArCH_2), 67.7 ($CHCl_2$), 126.4, 128.6, 129.5, 130.4, 137.9, 145.1 (Ar).

1-(3-Bromophenyl)-2,2-dichloroethanone (2e)[12]

Pale yellow oil; R_f 0.2 (petroleum ether–EtOAc, 94:6).

^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 6.65 (s, 1 H, CH), 7.40 (m, 1 H, ArH), 7.76 (m, 1 H, ArH), 8.02 (m, 1 H, ArH), 8.19 (m, 1 H, ArH).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 67.5 ($CHCl_2$), 123.0 (C–Br), 128.1, 130.3, (CH_{arom}), 132.8 (*C*C=O), 132.5, 137.3 (CH_{arom}), 184.6 (C=O).

1-(4-Bromophenyl)-2,2-dichloroethanone (2f)[6]

White crystals; mp 61–62 °C (Lit.[6] mp 61.2–62 °C).

^{1}H NMR (200.13 MHz, $CDCl_3$): δ = 6.58 (s, 1 H, CH), 7.65 (d, 2 H, *J* = 8 Hz, ArH), 7.95 (d, 2 H, *J* = 8 Hz, ArH).

^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 67.7 ($CHCl_2$), 129.8, 130.0 (C–Br, *C*C=O), 131.2, 132.2 (CH_{arom}), 185.1 (C=O).

2,2-Dichloro-1-(4-chlorophenyl)ethanone (2g)[28]

White crystals; mp 58–59 °C (Lit.[28] mp 61–62 °C).

^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 6.63 (s, 1 H, CH), 7.48 (d, 2 H, *J* = 8.8 Hz, ArH), 8.03 (d, 2 H, *J* = 8.8 Hz, ArH).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 67.7 ($CHCl_2$), 129.9 (*C*C=O), 129.2, 131.1 (CH_{arom}), 141.1 (C–Cl), 184.6 (C=O).

2,2-Dichloro-1-(4-nitrophenyl)ethanone (2h)[8]

Pale yellow crystals; mp 26.8–27.8 °C (Lit.[8] mp 27–28 °C); R_f 0.58 (benzene).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 6.72 (s, 1 H, CH), 8.22–8.39 (m, 4 H, ArH).

^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 67.7 ($CHCl_2$), 123.9, 130.9 (CH_{arom}), 135.8 (*C*C=O), 150.6 (C–NO_2), 184.6 (C=O).

2,2-Dichloro-1-(3-nitrophenyl)ethanone (2i)[12]

Pale yellow crystals; mp 52.5–54.0 °C (Lit.[12] mp 51.5–53.5 °C; R_f 0.55 (benzene).

^{1}H NMR (200.13 MHz, $CDCl_3$): δ = 6.72 (s, 1 H, CH), 7.77 (m, 1 H, ArH), 8.48 (m, 2 H, ArH), 8.92 (s, 1 H, ArH).

^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 67.6 ($CHCl_2$), 124.5, 128.5, 130.2, (CH_{arom}), 132.3 (*C*C=O), 135.2 (CH_{arom}), 148.2 (C–NO_2), 184.1 (C=O).

2,2-Dichloro-1-(4-iodophenyl)ethanone (2j)[29]

Slightly yellow crystals; mp 59–60.5 °C (Lit.[29] mp 62–63 °C); R_f 0.33 (petroleum ether–EtOAc, 94:6).

^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 6.60 (s, 1 H, CH), 7.8 (d, 2 H, *J* = 8.6 Hz, ArH), 7.91 (d, 2 H, *J* = 8.6 Hz, ArH).

^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 67.7 ($CHCl_2$), 103.1 (C–I), 130.4 (*C*C=O), 131.0 (CH_{arom}), 138.3 (CH_{arom}), 185.5 (C=O).

2,2-Dichloro-1-(3-chloro-4-methoxyphenyl)ethanone (2k)[5]

Light yellow crystals; mp 101.5–102.5 °C (Lit.[5] mp 102 °C); R_f 0.32 (petroleum ether–EtOAc, 94:6).

^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 4.01 (s, 3 H, CH_3), 6.61 (s, 1 H, CH), 6.99 (d, 1 H, *J* = 9.2 Hz, ArH), 8.0 (m, 1 H, ArH), 8.08 (m, 1 H, ArH).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 56.6 (CH_3), 67.8 ($CHCl_2$), 111.5 (CH_{arom}), 124.4, 129,2 (C_{arom}), 130.6, 132.0 (CH_{arom}), 159.9 ($COCH_3$), 183.9 (C=O).

1,4-Bis(dichloroacetyl)benzene (4)[8]

White crystals; mp 153.5–155.5 °C (Lit.[8] mp 154–156 °C); R_f 0.28 (benzene).

^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 6.62 (s, 2 H, CH), 8.22 (s, 4 H, ArH).

^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 67.8 ($CHCl_2$), 130.1 (CH_{arom}), 135.4 (*C*C=O), 185.4 (C=O).

2-Chloro-1-phenylethanone (5)[30]

White crystals; mp 54–55 °C (Lit.[30] mp 54–55 °C); R_f 0.12 (petroleum ether–EtOAc, 94:6).

^{1}H NMR (200.13 MHz, $CDCl_3$): δ = 4.71 (s, 2 H, CH_2Cl), 7.41–7.65 (m, 3 H, ArH), 7.87–7.99 (m, 2 H, ArH).

Acknowledgment

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