

New and Facile Synthesis of 2-Chloro-1,3-diketones

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DOI: 10.56201/ijccp.v8.no1.2022.pg28.33

Abstract

Background: Development of new methods for preparation of organic compounds is one of our major interests.

Aims: we aim to develop a new synthetic procedure to prepare previously reported compounds and novel compounds.

Methods: The methods that we used in this manuscript are novel.

Results: 1,1-Dichloro-acetone reacts with different aliphatic and aromatic aldehydes namely acetaldehyde, decanal, benzaldehyde, p-chlorobenzaldehyde, p-fluorobenzaldehyde, naphthaldehyde, 5-methylfuran-2-carbaldehyde, thiophene-2-carbaldehyde, and nicotinaldehyde. The reaction is in alkaline media using potassium hydroxide.

Conclusion: The synthesized compounds were structurally elucidated using mass spectroscopy, infrared spectroscopy, ¹H & ¹³C NMR.

Keywords: 2-chloro-1,3-diketone; facile synthesis; reactions.

Introduction

2-Chloro-1,3diketone compounds are very useful starting material for industrial scale production of various agrochemicals, pharmaceuticals, dyes and polymer because of their highly reactive multifunctional character through synergism of carbonyl group and chlorine atom. The reaction of 1,1dichloro-acetone with benzaldehyde was previously reported but with different reaction conditions.[1,2] The reaction of 1,1dichloro-acetone with benzaldehyde was done in chromium dichloride in tetrahydrofuran and in indium bromide in tetrahydrofuran (Figure 1).[1,2]

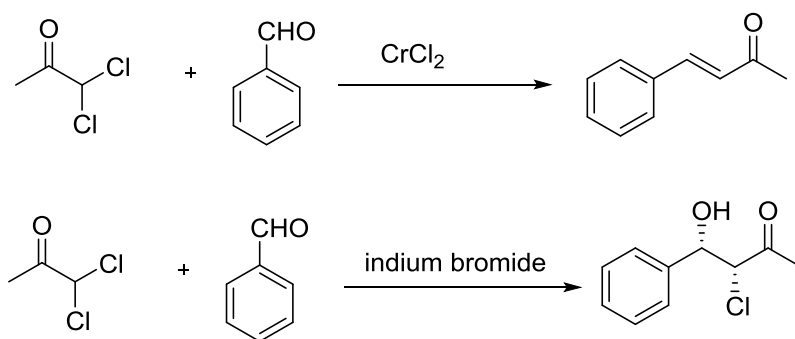


Figure 1

The reaction of p-chlorobenzaldehyde with 1,1-dichloro-acetone was also done in different reaction condition in a previously reported paper.[2,3,4] The reaction of p-chloro-benzaldehyde with 1,1-dichloro-acetone was done in indium bromide, and proline in ammonium acetate to give two different products (Figure 2).[2-4]

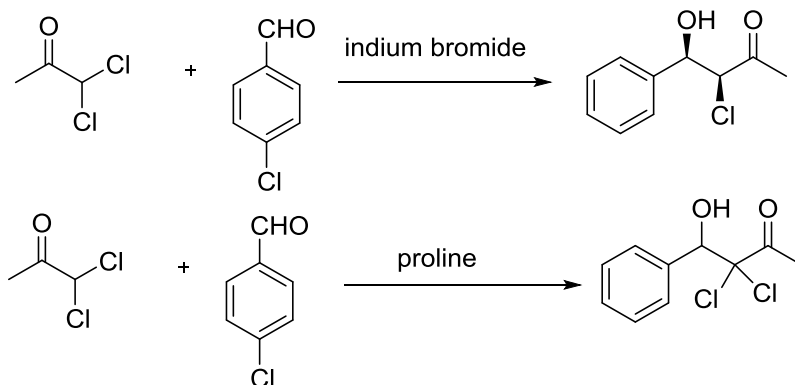
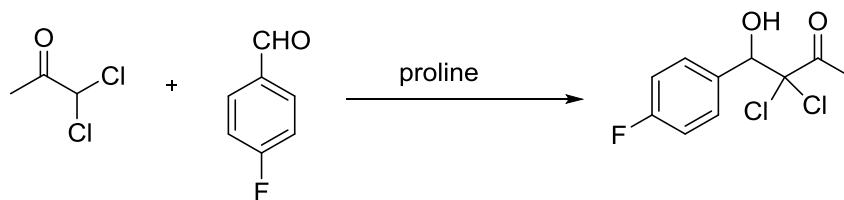


Figure 2

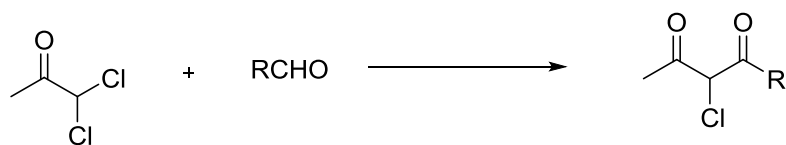
The reaction of 1,1-dichloro-acetone with p-fluorobenzaldehyde was done in proline in a previously reported paper.[4]



As a continuation of our previously reported work, we are going to publish a new, facile and cheap synthesis of 2-chloro-1,3-diketones starting from 1,1-dichloro-acetone in nearly quantitative yield.

Results and discussion

1,1-Dichloroacetone reacts with different aliphatic and aromatic aldehydes to produce 2-chloro-1,3-diketones **1a-i** in nearly quantitative yield under mild condition.



1a-i

- a, R=CH₃
- b, R=(CH₂)₉CH₃
- c, R=C₆H₅
- d, R=4-Cl-C₆H₄
- e, R=4-F-C₆H₄
- f, R=1-naphthyl
- g, R=2-methyl-furan
- h, R=2-thiophene
- i, R=3-pyridine

The mechanism of the reaction is done through elimination reaction and removal of water molecule followed by nucleophilic attack on carbonyl of aldehyde to give intermediate. The previous intermediate is eliminated to afford the final product 1a-I (Fig.1).

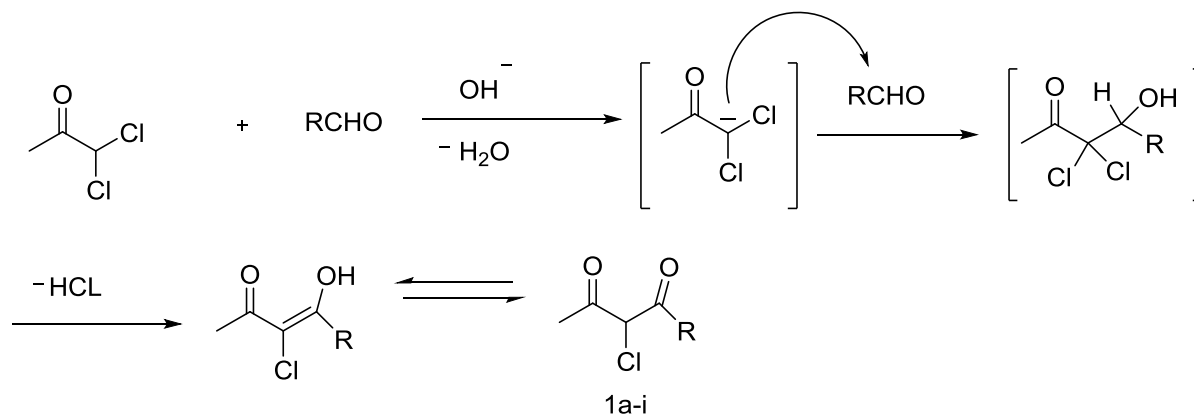


Fig.1

Conclusion

New and facile synthesis of 2-Chloro-1,3-diketones have been accomplished. The spectral analyses (MS, IR, ¹H & ¹³C NMR) are in agreement with the proposed structure.

Experimental

The instruments used in this paper were as previous reported paper.[7] Compounds **1a**, **1c**, **1d**, **1e**, **1g**, **1h** were previously reported.

General procedure for synthesis of 2-chloro1,3-diketones

A mixture of 1,1-dichloro acetone (0.01 mole) with 0.01 mol. of different aldehyde in 70 mL methanol are heated at 50 °C for 5 minutes. At room temperature add 10 ml potassium hydroxide solution containing 1 gm KOH with stirring for 2 hours. then, add 3 mL concentrated hydrochloric acid with cooling. Then, extract the mixture with ether to give the product in nearly quantitative yield.

3-chloropentane-2,4-dione **1a**[5]

Yield: 92%; m.p. 41-43 °C;[5] IR (KBr) cm^{-1} , ν : 1715, 1723 (2 C=O); ^1H NMR (CDCl_3) δ /ppm: 2.50 (s, 6H, 2 CH_3), 4.6 (s, 1 H, CHCl).[5] ^{13}C NMR (CDCl_3) δ /ppm: 27.10 (2 CH_3), 92.50 (CH), 192.10 (2 C=O). Anal. Calcd. for $\text{C}_5\text{H}_7\text{ClO}_2$: C, 44.63; H, 5.24; Cl, 26.35; Found: C, 44.70; H, 5.29; Cl, 26.43.

3-Chlorotetradecane-2,4-dione **1b**

Yield: 95%; oil; IR (KBr) cm^{-1} , ν : 1710, 1721 (2 C=O); ^1H NMR (DMSO) δ /ppm: 0.08 (t, 3H, J = 8 Hz, CH_3), 1.27 (m, 18 H, 9 CH_2), 2.24 (s, 3H, CH_3), 5.90 (s, 1H, CHCl). ^{13}C NMR (DMSO) δ /ppm: 14.12, 20.20, 21.24, 21.67, 21.90, 22.30, 24.54, 22.18, 26.17, 27.02, 29.30 (11C, CH_2 , CH_3), 85.18 (CHCl), 189.20, 190.41 (2 C=O). MS (m/z): 260.8 (M^+ , 41%). Anal. Calcd. for $\text{C}_{14}\text{H}_{25}\text{ClO}_2$: C, 64.48; H, 9.66; Cl, 13.59; Found: C, 64.52; H, 9.71; Cl, 13.63.

2-chloro-1-phenylbutane-1,3-dione **1c** [5]

Yield: 94%; m.p. 40 °C;[5] IR (KBr) cm^{-1} , ν : 1718, 1725 (2 C=O); ^1H NMR (CDCl_3) δ /ppm: 2.26 (s, 3H, CH_3), 5.64 (s, 1 H, CH), 7.20-7.80 (m, 5H, Ar).[5] ^{13}C NMR (CDCl_3) δ /ppm: 25.5, 64.1, 194.8, 198.2.[5] MS (m/z): 196.63 (M^+ , 41%). Anal. Calcd. for $\text{C}_{10}\text{H}_9\text{ClO}_2$: C, 61.08; H, 4.61; Cl, 18.03; Found: C, 61.23; H, 4.69; Cl, 18.10.

2-Chloro-1-(4-chlorophenyl)butane-1,3-dione **1d** [6]

Yield: 95%; IR (KBr) cm^{-1} , ν : 1719, 1723 (2 C=O); ^1H NMR (CDCl_3) δ /ppm: 2.31 (s, 3H, CH_3), 5.43 (s, 1 H, CH), 7.42 (m, 2H, Ar), 7.84-7.87 (m, 2H, Ar).[6] ^{13}C NMR (CDCl_3) δ /ppm: 27.0 (CH_3), 64.5 (CH), 128.7, 129.7, 131.1, 141.6 (Ar), 189.1, 198.9 (2 C=O).[6] MS (m/z): 231.07 (M^+ , 58%). Anal. Calcd. for $\text{C}_{10}\text{H}_8\text{Cl}_2\text{O}_2$: C, 51.98; H, 3.49; Cl, 30.68; Found: C, 52.07; H, 4.58; Cl, 30.76.

2-Chloro-1-(4-fluorophenyl)butane-1,3-dione **1e** [6]

Yield: 96%; IR (KBr) cm^{-1} , ν : 1716, 1722 (2 C=O); ^1H NMR (CDCl_3) δ /ppm: 2.29 (s, 3H, CH_3), 5.46 (s, 1 H, CH), 7.06-7.09 (m, 2H, Ar), 7.92-7.97 (m, 2H, Ar).[6] ^{13}C NMR (CDCl_3) δ /ppm: 25.6 (CH_3), 63.2 (CH), 115.1, 115.3, 131.2, 131.3 (Ar), 163.7, 167.7, 187.3, 197.6 (2 C=O).[6] MS (m/z): 214.6 (M^+ , 63%). Anal. Calcd. for $\text{C}_{10}\text{H}_8\text{ClFO}_2$: C, 55.96; H, 3.76; Cl, 16.52; Found: C, 56.05; H, 3.83; Cl, 16.61.

2-chloro-1-(naphthalen-1-yl)butane-1,3-dione **1f**

Yield: 97%; oil; IR (KBr) cm^{-1} , ν : 1718, 1725 (2 C=O); ^1H NMR (DMSO) δ/ppm : 2.21 (s, 3H, CH_3), 6.00 (s, 1H, CHCl), 7.41-7.6 (m, 7H, Ar). ^{13}C NMR (DMSO) δ/ppm : 25.14 (CH_3), 80.12 (CHCl), 120.12, 120.80, 120.90, 125.3, 127.30, 128.34, 129.32, 130.71, 132.80, 133.32 (10 C=), 188.21, 189.16 (2 C=O). MS (m/z): 246.6 (M^+ , 39%). Anal. Calcd. for $\text{C}_{14}\text{H}_{11}\text{ClO}_2$: C, 68.16; H, 4.49; Cl, 14.37; Found: C, 68.20; H, 4.54; Cl, 14.41.

2-Chloro-1-(5-methylfuran-2-yl)butane-1,3-dione **1g**

Yield: 97%; IR (KBr) cm^{-1} , ν : 1711, 1719 (2 C=O); ^1H NMR (CDCl_3) δ/ppm : 1.80 (s, 3H, CH_3), 2.14 (s, 3 H, CH_3), 4.83 (s, 1H, CH), 7.23 (d, 2H, $J=7.5$ Hz, Ar), 7.45 (d, 2H, Ar). ^{13}C NMR (CDCl_3) δ/ppm : 20.1, 23.4, 61.2, 120.3, 125.6, 141.2, 147.3 170.2, 175.7 (2 C=O). MS (m/z): 200.6 (M^+ , 43%). Anal. Calcd. for $\text{C}_9\text{H}_9\text{ClO}_3$: C, 53.88; H, 4.52; Cl, 17.67; Found: C, 53.95; H, 4.59; Cl, 17.74.

2-Chloro-1-(thiophen-2-yl)butane-1,3-dione **1h**

Yield: 98%; IR (KBr) cm^{-1} , ν : 1710, 1720 (2 C=O); ^1H NMR (CDCl_3) δ/ppm : 2.10 (s, 3H, CH_3), 3.56 (s, 1 H, CH), 7.21-7.30 (m, 3H, Ar). ^{13}C NMR (CDCl_3) δ/ppm : 22.1 (CH_3), 60.9 (CH), 127.2, 130.3, 135.4, 139.1 (Ar), 179.1, 183.7 (2 C=O). MS (m/z): 202.6 (M^+ , 35%). Anal. Calcd. for $\text{C}_8\text{H}_7\text{ClO}_2\text{S}$: C, 47.42; H, 3.48; Cl, 17.49; Found: C, 47.51; H, 3.53; Cl, 17.56.

2-Chloro-1-(pyridin-3-yl)butane-1,3-dione **1i**

Yield: 98%; oil; IR (KBr) cm^{-1} , ν : 1705, 1718 (2 C=O); ^1H NMR (DMSO) δ/ppm : 2.24 (s, 3H, CH_3), 5.80 (s, 1H, CHCl), 7.11-7.31 (m, 4H, Ar). ^{13}C NMR (DMSO) δ/ppm : 25.14 (CH_3), 82.17 (CHCl), 128.34, 129.32, 130.7, 141.74, 148.41 (5 C, Ar), 187.21, 189.37 (2 C=O). MS (m/z): 197.6 (M^+ , 42%). Anal. Calcd. for $\text{C}_9\text{H}_8\text{ClNO}_2$: C, 54.70; H, 4.08; N, 7.09; Found: C, 54.79; H, 4.15; N, 7.15.

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