RESEARCH PAPER | CHEMISTRY | Volume : 5 | Issue : 12 | December 2015 | ISSN - 2249-555X

Synthesis and Characterisation of Some Novel Substituted 1,2-Diones

KEYWORDS: Synthesis, 1,2-Diones, α-methylene carbonyl

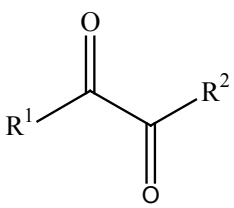
Dr. Indu Shastri
Department of Chemistry, R.D. National Arts & Commerce & W.A. Science College, Linking Road, Bandra (W), MUMBAI-400 050.

Rajesh Mishra
Department of Chemistry, R.D. National Arts & Commerce & W.A. Science College, Linking Road, Bandra (W), MUMBAI-400 050.

ABSTRACT An efficient benign oxidation of α-methylene carbonyl compounds and cyclic α-carbonyl compounds for a facile and one pot synthesis of 1,2- diones was carried out with non- toxic and metal free condition at ambient temperature. Short reaction time , easy work up and moderate to high yield are the special features of this method.

INTRODUCTION

The past decade has witnessed appreciable heightening of interest in 1,2-dicarbonyl compounds of general type



(Where R^1 and R^2 represent aliphatic or aromatic groups), which are finding ever wider application in organic synthesis in virtue of their high reactivity. Such compounds provide a basis for obtaining aliphatic, aromatic, and heterocyclic products, whether of low or high molecular weight, possessing several valuable properties. Previous reviews have paid insufficient attention to methods for the preparation of α-diketones, and have completely disregarded their chemical reactions and practical application.

The first observations indicating that benzoin could be oxidized by nitric acid to benzil, were made more than a century ago by Zinin.[1] Since then the reaction conditions and the oxidizing agents have been varied. The most widely used oxidants have been copper (II) salts, applied in the presence of regenerating agents (air, ammonium nitrate): e.g.[2]

In 1932, Riley et al.[3] first showed that selenium dioxide is a specific reagent for oxidizing a methylene-carbonyl group to dicarbonyl.

Since then the dioxide has been widely used for obtaining α-dicarbonyl compounds from aliphatic or aliphatic-aromatic aldehydes and ketones under mild conditions.

Conventionally, 1,2-dione derivatives are prepared by the oxidation of corresponding benzoins with oxidizing agents such as $CuSO_4$/Py, Bi_2O_3/H+, HNO3 in aq. solution,[4] RuO_4,[5] oxidation of acyloins,[5] oxidative hydrolysis of silver salts of α-keto dithianes,[6] coupling of acid chlorides using SmI_2,[7] and SeO_2 oxidation of mono ketones.[8] Oxidation of acetylenes with $NaIO_4/RuO_2$,[9] $Tl(NO_3)_3$[10] and $KMnO_4$[11] has been reported to afford 1,2-diones in low yields.

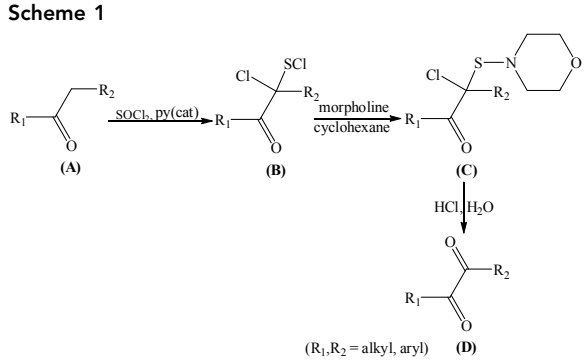
But all these procedures have its drawbacks in terms of expensive reagents, difficult reaction conditions and low yields. In some cases, even the starting materials require a series of steps for their preparation.

From the synthesis standpoint, the traditional processes have its drawbacks in terms of expensive reagents, difficult reaction conditions and low yields. In some cases, even the starting materials require a series of steps for their preparation.

RESULTS AND DISCUSSION

1,2-diones were successfully synthesized from some easily available α-methylene carbonyl compounds (Scheme 1).

Scheme 1



The literature[12a-d] shows clearly that the substitution reaction of excess thionyl chloride with active methylene compounds gives α-chlorosulfonyl chlorides.

α-methylene carbonyl compound **(A)** was taken as starting material which are easily available laboratory reagent. It was treated with excess thionyl chloride to afford α-chlorosulfenyl chloride **(B)**.

Simple hydrolysis under neutral, acidic, and basic conditions of chlorosulfenyl chloride **(B)** regenerated the original compound **(A)**. To overcome this difficulty, compound **(B)** was treated with slightly excess amount of morpholine in presence of cyclohexane as solvent to get the required morpholide compound **(C)** exclusively.

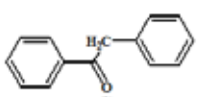
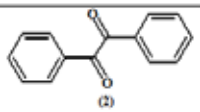
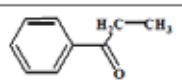
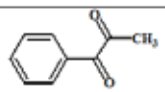
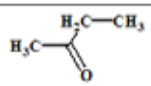
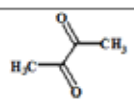
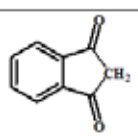
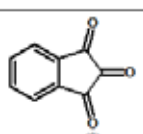
The hydrolysis of morpholide **(C)** proceeded smoothly in cy-

Volume : 5 | Issue : 12 | December 2015 | ISSN - 2249-555X

clohexane with 10% hydrochloric acid at ambient temperature to afford 1,2-dione **(D)** and was confirmed by spectral and physical constant data reported in the literature.

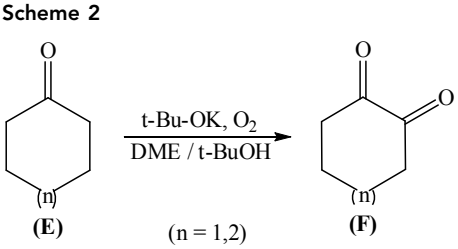
With different unsymmetrical α-methylene carbonyl compound corresponding 1,2-diones were synthesized which are listed in table-1 below:

Table-1

Sr. No.	α-methylene carbonyl compound (A)	1,2-dione (D)
I	 (1)	 (2)
II	 (3)	 (4)
III	 (5)	 (6)
IV	 (7)	 (8)

We synthesized some cyclic 1,2-diones with auto oxidation of cyclic α-carbonyl compounds in presence of a base (Scheme 2).

Scheme 2



(E) (n = 1,2) **(F)**

The reaction proceeded by auto oxidation of cyclic ketone **(E)** in presence of strong base, potassium t-butoxide in mixture of solvent (Dimethoxyethane / t-butanol) at temperature -15 to -7°C.

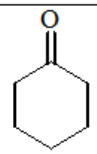
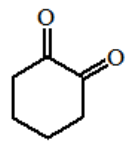
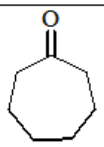
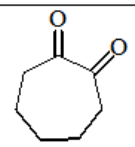
It was also noted that the cyclic ketone should not be maintained in contact with the base because of the tendency of the cyclic ketone to undergo self-condensation.

Different molar ratio of cyclic ketone to potassium t-butoxide was tried out and the optimized ratio was 1: 1.35. With decreased molar ratio, reaction was not gone to desired level of conversion and with increased molar ration, yield was drastically gone down.

The amount of solvent mixture employed in the reaction was 1500 ml/mole of cyclic ketone and ratio of dimethoxyethane to t-butanol was 2:1 (v/v). It was observed that lower amount of solvent leads to side product formation. This may be due to less amount of oxygen absorbed by the solvent available for the reaction to proceed.

Two different cyclic ketones were used to synthesized the corresponding cyclic 1,2-diones are listed in table-2 below:

Table-2

Sr. No.	CYCLIC KETONE (E)	CYCLIC 1,2-DIONE (F)
I	 (9)	 (10)
II	 (11)	 (12)

PROCEDURE

I] Synthesis of benzil (2)

Benzylphenylketone 9.80 g (0.05 mole) & pyridine 39.50 mg (1 mole %) were dissolved in thionyl chloride (40 ml) and the mixture was heated at 60-65°C till evolution of SO_2 and HCl ceased (60 min.).The excess thionyl chloride was evaporated under diminished pressure. The resulting residue was dissolved in cyclohexane (50 ml) and a solution of morpholine 9.58 g (0.11 mole) in cyclohexane (50 ml) was added dropwise at 0-5°C.

Resulting mixture was stirred for an additional 30 min at 0-5°C and added 10% aqueous HCl (60 ml). Cyclohexane layer was separated, filtered, washed with 2 x 25 ml water and dried over anhydrous sodium sulphate. Solvent was evaporated. Recrystallisation from methanol followed by charcoal treatment gave 7.8 g (Yield: 74%) of yellow crystalline powder of compound **(2)**. M.P.: 93°C ; IR (KBr, cm^{-1}) : 1594 (aromatic C=C stretching), 1660 (C=O stretching), 3064 (=C-H stretching); PMR ($CDCl_3$, δ): 7 . 5 - 8 . 0 (10H, m, aromatic)

II] Synthesis of 1-Phenyl-propane-1,2-dione (4)

Propiophenone 13.40 g (0.10 moles) & pyridine 79 mg (1 mole%) were dissolved in thionyl chloride (80 ml) and the mixture was heated at 60-65°C till evolution of SO_2 and HCl ceased (60 min.).The excess thionyl chloride was evaporated under diminished pressure. The resulting residue was dissolved in cyclohexane (75 ml) and a solution of morpholine 19.16 g (0.22 moles) in cyclohexane (75 ml) was added dropwise at 0-5°C.

Resulting mixture was stirred for an additional 30 min at 0-5°C and added 10% aqueous HCl (100 ml). Cyclohexane layer was separated, filtered, washed with 2 x 25 ml water and dried over anhydrous sodium sulphate.

Cyclohexane was distilled and the remaining residue was subjected to distillation under reduced pressure. The fraction boiling at 103-105°C at 15 mm. Hg amounted to 9.0 g. (Yield: 61%) of compound **(4)** as greenish yellow liquid.

Volume : 5 | Issue : 12 | December 2015 | ISSN - 2249-555X

IR (neat, cm^{-1}) : 1597 (aromatic C=C stretching)., 1693 (C=O stretching), 2984 (C-H stretching, methyl group), 3064 (=C-H stretching); PMR ($CDCl_3$, δ):2.5 (3H, 1s, $-CH_3$), 7.5-8.0 (5H, m, aromatic)

III] Synthesis of butane-2,3-dione (6)

Ethyl methyl ketone 7.20 g (0.10 moles) & pyridine 79 mg (1 mole%) were dissolved in thionyl chloride (80 ml) and the mixture was heated at 60-65°C till evolution of SO_2 and HCl ceased (60 min.).The excess thionyl chloride was evaporated under diminished pressure. The resulting residue was dissolved in cyclohexane (75 ml) and a solution of morpholine 19.16 g (0.22 moles) in cyclohexane (75 ml) was added dropwise at 0-5°C.

Resulting mixture was stirred for an additional 30 min at 0-5°C and added 10% aqueous H_2SO_4 (100 ml). Cyclohexane layer was separated, filtered, washed with 2 x 25 ml water and dried over anhydrous sodium sulphate.

Cyclohexane was distilled and the remaining residue was subjected to fractional distillation at atomospheric pressure. The fraction boiling at 88°C amounted to 2.15 g. (Yield: 25%) of compound **(6)** as greenish yellow liquid. IR (neat, cm^{-1}) :1693 (C=O stretching), 3421 (O-H stretching, enol form)

IV] Synthesis of Indane-1,2,3-trione (8)

Indane-1,3-dione 14.60 g (0.10 moles) & pyridine 79 mg (1 mole%) were dissolved in thionyl chloride (80 ml) and the mixture was heated at 60-65°C till evolution of SO_2 and HCl ceased (60 min.).The excess thionyl chloride was evaporated under diminished pressure. The resulting residue was dissolved in cyclohexane (75 ml) and a solution of morpholine 19.16 g (0.22 moles) in cyclohexane (75 ml) was added dropwise at 0-5°C.

Resulting mixture was stirred for an additional 30 min at 0-5°C and added 10% aqueous HCl (100 ml). Layers were separated. Aqueous layer was filtered and concentrated to $1/10^{th}$ volume at 50°C under reduced pressure. Remaining mass was chilled to 10-15°C for three hours to complete the crystallization. Product was filterd and purified in water followed by charcoal treatment. Hydrated product was dehydtraed with thionyl chloride in cyclohexane at 70-75°C and filtered. Washed with cyclohexane and solvent was evaporated under vacuum at 40-45°C to afford 3.52 g (Yield: 22%) of compound **(8)** as light beige coloured crystallined product. M.P.: 250°C; IR (KBr, cm^{-1}) : 1716 & 1748 (C=O stretching); PMR (D_2O, δ): 7.7-8.0 (5H, m, aromatic).

V] Synthesis of Cyclohexane-1,2-dione (10)

A suspension of 7.56 g (0.0675 mole) of potassium t-butoxide in a mixture of 50 ml of dimethoxyethane and 25 ml of t-butyl alcohol was stirred and cooled to -15°C. A steady stream of oxygen was bubbled through the reaction mixture. Cyclohexanone 9.8 g (0.1 mole) & a suspension of remaining 7.56 g (0.0675 mole) of potassium t-butoxide in a mixture of 50 ml of dimethoxyethane and 25 ml of t-butyl alcohol were added concurrently at constant rate maintaining temperature -15 to -7°C. Bubbling of oxygen was continued at that temperature for next one hour.

Reaction mass was quenched in 100 ml chilled water and unreacted cyclohexanone was extracted in 2 x 50 ml MDC(methylenedichloride) washes. MDC was distilled off yielding 1.6 g (0.016 mole) unreacted cyclohexanone. Aqueous layer was acidified with 10 % hydrochloric acid to pH 2.5, and product was extracted in 2 x 50 ml of MDC.

MDC layer was washed with 2 x 25 ml water, 1 x 25 ml 5% sodium bicarbonate solution & dried over anhydrous sodium sulphate and distillation of solvent under vacuo yield crude product.Crude product was distilled out under vacuum to give 5.3 g (Yield: 56%) of compound **(10)** as faint yellow product. M.P.: 38°C; IR (KBr, cm^{-1}) :1667 (C=O stretching), 2940 (C-H stretching), 3416 (O-H stretching, enol form).

VI] Synthesis of Cycloheptane-1,2-dione (12)

A suspension of 3.78 g (0.0338 mole) of potassium t-butoxide in a mixture of 25 ml of dimethoxyethane and 12 ml of t-butyl alcohol was stirred and cooled to -15°C. A steady stream of oxygen was bubbled through the reaction mixture. Cycloheptanone 5.6 g (0.05 mole) & a suspension of remaining 3.78 g (0.0338 mole) of potassium t-butoxide in a mixture of 25 ml of dimethoxyethane and 12 ml of t-butyl alcohol were added concurrently at constant rate maintaining temperature -15 to -7°C. Bubbling of oxygen was continued at that temperature for next one hour.

Reaction mass was quenched in 50 ml chilled water and unreacted cycloheptanone was extracted in 2 x 25 ml MDC washes. MDC was distilled off yielding 0.78 g (0.007 moles) unreacted cycloheptanone.Aqueous layer was acidified with 10% hydrochloric acid to pH 2.5, and product was extracted in 2 x 25 ml of MDC.

MDC layer was washed with 2 x 25 ml water, 1 x 25 ml 5% sodium bicarbonate solution & dried over anhydrous sodium sulphate and distillation of solvent under vacuo yield crude product. Crude product was distilled out under vacuum to give 2.2 g (Yield: 41%) of compound **(12)** as pale yellow product. IR (KBr, cm^{-1}) : 1673&1729 (C=O stretching),2866 & 2935(C-H stretching), 3435 (O-H stretching, enol form); PMR ($CDCl_3$, δ):2.0 (4H, m, $-CH_2$) & 2.4 (2H, 1t, $-CH_2$) 2.6 (2H, 1t, $-CH_2$) & 6.1 (1H, 1s, =C-H)

CONCLUSIONS:

In summary, The present work includes synthesis of 1,2-diones with different substituent without use of any toxic metal catalyst and then it may find different applications & uses to synthesize hetrocyclic derivatives. The methodology developed in this work for the synthesis of 1,2-diones with different substituent uses simple and easily available laboratory reagents.

Acknowledgement

We are thankful to the authorities of R.D. National & W.A. Science College and Jay Chemicals, Vapi for providing us with the necessary facilities to carry out the research work. Our thanks to the IIT-Bombay for providing us with the NMR and IR spectra.

REFERENCE

1] N. Zinin, Annalen, 34, 188 (1840). 2] M. Weiss and M. Appel, J. Amer. Chem. Soc, 70, 3666 (1948). 3] H. L. Riley, J. I.Morley, and N. A. Friend, J. Chem. Soc, 1875, 2342(1932). 4] (a) Clarke, H. T.; Dreger, E. E. Org. Synth. Coll. Vol. 1, 1941, 87–89; (b) Rigby, W. J. Chem. Soc. 1951, 793–795; (c) Fieser, L. F.; Fieser, M.; John Wiley and Sons: New York, 1967; Vol. 1, p. 734. 5] Baskaran, S.; Das, J.; Chandrasekaran, S. J. Org. Chem. 1989, 54, 5182–5184. 6] Girard, P.; Counffignal, R.; Kagan, H. B. Tetrahedron Lett. 1981, 22,3959– 3960. 7] Souppe, J.; Namy, J.-L.; Kagan, H. B. Tetrahedron Lett. 1984, 25, 2869–2872. 8] (a) McElvain, S. M. Org. React. 1948, 4, 256–268; (b) Rabjohn, N. Org. React. 1949, 5, 331–386. 9] Zibuck, R.; Seebach, D. Helv. Chim. Acta 1988, 71, 237–240. 10] McKillop, R.; Oldenziel, O. H.; Swann,B. P.; Taylor,E. C.; Robey, R. L. J. Am. Chem. Soc. 1973, 95, 1296–1301. 11] Lee, D. G.; Chang, V. S. Synthesis 1978, 462–463. 12] (a) K. Oka and S. Hara, Tetrahedron Letters, 2783 (1976); (b) M. Ohoka, T. Kojitani, S. Yanagida, M. Okahara, and S. Komori, J. Org. Chem., 40, 3540 (1975); (c) T. Higa and A.J. Krubsack. ibid., 40, 3037 (1975) (d) M.S. Simon, J.B. Rogers, W. Saenger, and J. Z. Gougoutas, J. Am. Chem. Sot., 89, 5838 (1967).