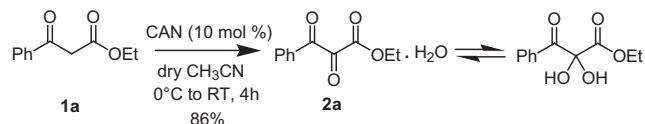


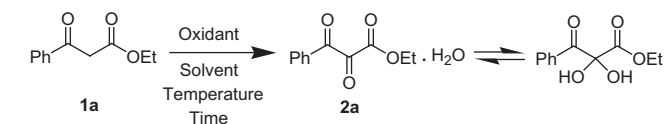
Scheme 2. Reaction of 1,3-diones with CAN.

As an exploratory experiment, ethyl benzoylacetate **1a** was treated with CAN (10 mol %) in dry acetonitrile. Work-up followed by column chromatography afforded the product **2a** in 86% yield. The structure of the product was established by spectroscopic analysis and the data were compared with those available in the literature.¹¹ In the IR spectrum of **2a**, the appearance of a broad absorption peak at 3443 cm^{-1} clearly indicated the presence of an OH group while the carbonyl groups showed stretching frequencies at 1744 , 1691 and 1639 cm^{-1} , respectively. In the ^1H NMR spectrum, the OH protons were seen as a broad singlet centred at δ 5.39. The quaternary carbon appeared at δ 91.7 in the ^{13}C NMR spectrum while the three carbonyl carbons were recorded at δ 193.3, 191.5 and 191.0. The mass spectrum data also agreed with the proposed structure.¹⁶ All the above spectral evidence in conjunction with literature reports^{11,17} confirmed that the VTCs were formed as a mixture of the dihydroxy and keto forms as expected (Scheme 3).

The reaction was then studied thoroughly and the exact amount of CAN required was investigated. It was observed that usage of 5 mol % CAN as catalyst resulted in longer reaction time and lower product yield indicating the insufficient amount of the catalyst (Table 1, entry 1). Increasing the amount of CAN to 10 mol % resulted in 86% product yield (entry 2), whereas when the catalyst loading was increased to 15 mol % (entry 3) the yield of the VTC was found to decrease proportionately. The use of stoichiometric amounts of CAN resulted in the formation of dimer (structure



Scheme 3. Synthesis of ethyl 2,3-dioxo-3-phenylpropanoate.

Table 1
Optimization of reaction conditions

Entry	Oxidant	mol %	Solvent	Temperature	Time (h)	Yield ^a (%)
1	CAN	5	CH ₃ CN	0 °C to rt	12	35
2	CAN	10	CH ₃ CN	0 °C to rt	4	86
3	CAN	15	CH ₃ CN	0 °C to rt	3.5	51
4	CAN	100	CH ₃ CN	0 °C to rt	4	37
5	CAN	10	CH ₃ CN	0 °C to rt	4	60 ^b
6	CAN	10	CH ₃ OH	0 °C to rt	12	54
7	CAS ^c	10	CH ₃ CN	RT-reflux	12	0
8	FeCl ₃	10	CH ₂ Cl ₂	RT-reflux	24	10
9	Mn(OAc) ₃	10	CH ₃ CO ₂ H	RT-reflux	12	51

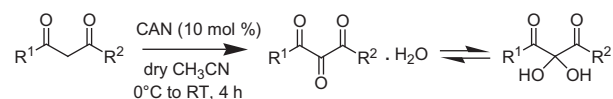
^a Reactions performed in an inert atmosphere (N₂ gas).

^b Reaction performed in the presence of oxygen.

^c CAS-cerium(IV) ammonium sulfate.

shown in Scheme 2)¹⁴ in 56% yield and the desired product **2a** in 37% yield (entry 4). Passing oxygen gas through the reaction mixture (entry 5) resulted in a decrease of the product yield to 60% along with formation of other oxidation products. The use of cerium(IV) ammonium sulfate (CAS) in place of CAN did not yield any product (entry 7) while use of other single electron oxidants such as FeCl₃ and Mn(OAc)₃ resulted in lower product yields (entries 8 and 9) compared to that shown in entry 2. From these results the optimized condition for the formation of VTC was found to be usage of 10 mol % CAN in dry CH₃CN under N₂ atmosphere (entry 2).

The generality of the reaction was studied and the results are presented in Table 2. Moderate to good yields of VTCs were obtained by using various β -ketoesters (entries 1–5), 1,3-diketones (entries 6–8) and β -diesters (entries 9 and 10). It was observed that the reaction of 1,3-dicarbonyls containing aromatic and electron-donating aromatic substituents resulted in higher product yields (entries 1, 4, 6, 7) while those with alkyl and electron-withdrawing substituents furnished the VTCs in lower yields (entries 2, 3, 5, 8).

Table 2
Reaction of various acyclic 1,3-diones with catalytic amounts of CAN

Entry	Substrate	Product	Yield ^a (%)
1	Ph-C(=O)-CH ₂ -C(=O)-OEt (1a)	Ph-C(=O)-CH(OH)-C(=O)-OEt (2a)	86
2	Me-C(=O)-CH ₂ -C(=O)-OEt (1b)	Me-C(=O)-CH(OH)-C(=O)-OEt (2b)	71
3	Cl-CH ₂ -C(=O)-CH ₂ -C(=O)-OEt (1c)	Cl-CH ₂ -C(=O)-CH(OH)-C(=O)-OEt (2c)	62
4	MeO-C ₆ H ₃ (MeO) ₂ -C(=O)-CH ₂ -C(=O)-OEt (1d)	MeO-C ₆ H ₃ (MeO) ₂ -C(=O)-CH(OH)-C(=O)-OEt (2d)	88
5	MeO-C ₆ H ₄ (N)-C(=O)-CH ₂ -C(=O)-OMe (1e)	MeO-C ₆ H ₄ (N)-C(=O)-CH(OH)-C(=O)-OMe (2e)	43
6	Ph-C(=O)-CH ₂ -C(=O)-Ph (3a)	Ph-C(=O)-CH(OH)-C(=O)-Ph (4a)	82
7	Ph-C(=O)-CH ₂ -C(=O)-Me (3b)	Ph-C(=O)-CH(OH)-C(=O)-Me (4b)	65
8	Me-C(=O)-CH ₂ -C(=O)-Me (3c)	Me-C(=O)-CH(OH)-C(=O)-Me (4c)	52
9	EtO-C(=O)-CH ₂ -C(=O)-OEt (5a)	EtO-C(=O)-CH(OH)-C(=O)-OEt (6a)	69
10	<i>i</i> -PrO-C(=O)-CH ₂ -C(=O)-O- <i>i</i> -Pr (5b)	<i>i</i> -PrO-C(=O)-CH(OH)-C(=O)-O- <i>i</i> -Pr (6b)	72

^a Isolated yield.

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