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Facile synthesis of 1,2,3-tricarbonyls from 1,3-dicarbonyls mediated by cerium(IV) ammonium nitrate

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ABSTRACT

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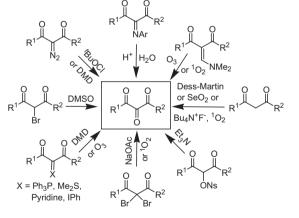
1,2,3-Tricarbonyls or vicinal tricarbonyl compounds (VTCs) have gained attention among the organic chemists ever since the first synthesis of diphenyl triketone in 1890 by von Pechmann and de Neufville.¹ Their importance stems from the challenges involved in the synthesis and their inherent reactivity. The chemistry of these compounds has been widely studied by Rubin. Wasserman and their co-workers.² Numerous biological targets such as FK-506,³ rapamycin and protease inhibitor molecules have been successfully synthesized from VTCs.² In addition, these compounds have also been used for the construction of heterocycles having unusual substitution patterns.⁴ Of the various methods currently available for the synthesis of VTCs, those from β-dicarbonyl compounds constitute an important route. This involves a two-step procedure consisting of functionalizing the central carbon followed by oxidation with suitable reagents such as Dess-Martin periodinane,^{5a} selenium dioxide,^{5b} singlet oxygen,^{5c,6,7} ozone^{7,8} and DMSO^{5b,9} (Scheme 1). Very recently, the synthesis of 2-oxo-1,3propanedial, the smallest VTC, by the oxidation of acetone¹⁰ and that of substituted VTCs by the oxidation of Morita-Baylis-Hillman (MBH) adducts¹¹ formed from substituted benzaldehydes and acrylate have been reported.

Apart from an isolated report,¹² there has not been any systematic investigation on the use of single electron oxidants for the synthesis of VTCs from β -dicarbonyl compounds. In light of our recent

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A mild and efficient protocol for the synthesis of vicinal tricarbonyl compounds from β -dicarbonyls in a single step using cerium(IV) ammonium nitrate as a catalytic oxidant is described. Ease of execution, wide substrate scope and the suitability for the synthesis of commercially important compounds like nin-hydrin, alloxan and oxoline make this reaction particularly noteworthy.

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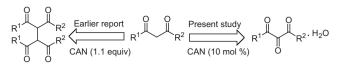
Scheme 1. Various routes for VTC synthesis from 1,3-diones.

investigation on the addition of radical cations, generated from β -dicarbonyls to terminal acetylenes¹³ and that of a recent report on the dimerization of β -dicarbonyls¹⁴ in the presence of stoichiometric amounts of cerium(IV) ammonium nitrate (CAN),¹⁵ we were quite curious to explore the fate of radical cations derived from β -dicarbonyls in the presence of catalytic amounts of CAN (Scheme 2). Our studies in this direction have now led to the facile synthesis of VTCs, in moderate to good yields, and the results are presented in this Letter.





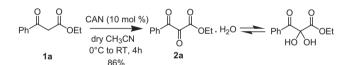
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Scheme 2. Reaction of 1,3-diones with CAN.

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 ¹³C 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).

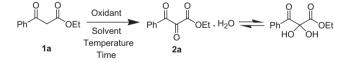
The reaction was then studied thoroughly and the exact amount of CAN required was investigated. It was observed that usage of 5 mol % CAN as catalyst resulted in longer reaction time and lower product yield indicating the insufficient amount of the catalyst (Table 1, entry 1). Increasing the amount of 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 1Optimization of reaction conditions

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Entry	Oxidant	mol %	Solvent	Temperature	Time (h)	Yield ^a (%)
1	CAN	5	CH₃CN	0 °C to rt	12	35
2	CAN	10	CH ₃ CN	0 °C to rt	4	86
3	CAN	15	CH₃CN	0 °C to rt	3.5	51
4	CAN	100	CH₃CN	0 °C to rt	4	37
5	CAN	10	CH₃CN	0 °C to rt	4	60 ^b
6	CAN	10	CH₃OH	0 °C to rt	12	54
7	CAS ^c	10	CH₃CN	RT-reflux	12	0
8	FeCl ₃	10	CH_2Cl_2	RT-reflux	24	10
9	$Mn(OAc)_3$	10	CH_3CO_2H	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.

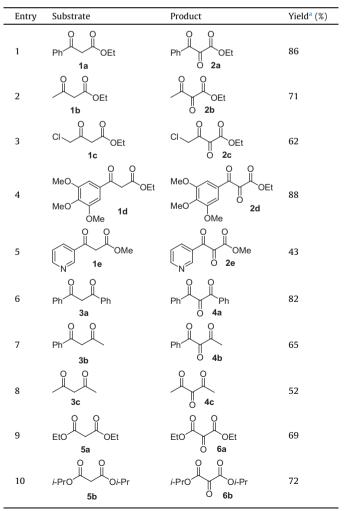
shown in Scheme 2)¹⁴ in 56% yield and the desired product **2a** in 37% yield (entry 4). Passing oxygen gas through the reaction mixture (entry 5) resulted in a decrease of the product yield to 60% along with formation of other oxidation products. The use of cerium(IV) ammonium sulfate (CAS) in place 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

$$R^{1} \xrightarrow{O} R^{2} \xrightarrow{CAN (10 \text{ mol } \%)}_{\text{dry CH}_{3}CN} R^{1} \xrightarrow{O} R^{2} \cdot H_{2}O \xrightarrow{O} R^{1} \xrightarrow{O} O \\ \xrightarrow{H_{0}} R^{2} \cdot H_{2}O \xrightarrow{O} R^{1} \xrightarrow{O} O \\ \xrightarrow{H_{0}} O$$



^a Isolated yield.

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