

## Facile Synthesis of Dihydrofurans by the Cerium(IV) Ammonium Nitrate Mediated Oxidative Addition of 1,3-Dicarbonyl Compounds to Cyclic and Acyclic Alkenes. Relative Superiority over the Manganese(III) Acetate Mediated Process

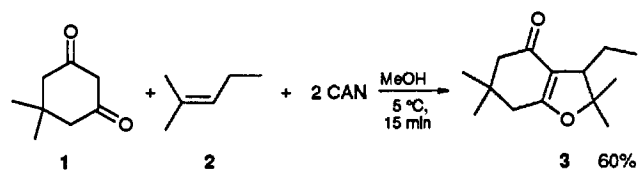
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Radicals generated from dimedone and acetylacetone by CAN undergo addition to cyclic and acyclic alkenes to give dihydrofurans in good yields. In view of the experimental simplicity and higher yields of products formed CAN appears to be superior to the more commonly used  $\text{Mn}(\text{OAc})_3$ .

The emergence of radical methodology as a powerful alternative to ionic reactions in the construction of complex carbocyclic compounds<sup>1</sup> has aroused great interest in developing novel reagents and procedures for the generation of radicals.<sup>2</sup> Among the oxidants used to generate radicals,  $\text{Mn}(\text{OAc})_3$  has received the most attention,<sup>3</sup> but in spite of its widespread use it is not always reliable<sup>3a</sup> and it is of interest to develop other one-electron oxidants. The pioneering work of Heiba and Dessau<sup>4</sup> and the subsequent investigations of Kurz<sup>5</sup> have demonstrated the usefulness of  $\text{Ce}^{\text{IV}}$  reagents for the generation of carbon radicals. Later, Baciocchi and Ruzziconi reported the oxidative addition of ketones and 1,3-diketones to enol acetates.<sup>6</sup> More recently, the same workers have extended the use of CAN [cerium(IV) ammonium nitrate]-mediated additions to enol silyl ethers<sup>7</sup> and styrenes.<sup>8</sup>

In spite of the above investigations, only scant information has been available on the CAN-mediated addition of active methylene compounds to cyclic and acyclic alkenes, especially unactivated ones. Moreover, there are no data available which allow direct comparison of CAN- and  $\text{Mn}(\text{OAc})_3$ -mediated reactions. We have initiated some work in this area and our preliminary results indicate that the CAN-mediated addition of dimedone and acetylacetone to cyclic and acyclic alkenes occurs rapidly to afford 4,5-dihydrofurans<sup>8,9</sup> in high yields. An illustrative example is shown in Scheme 1. In comparison, the

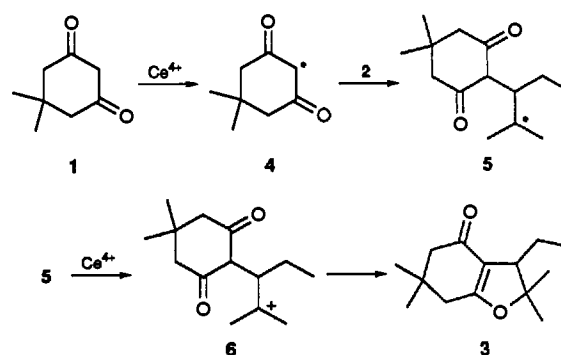


Scheme 1

corresponding reaction mediated by  $\text{Mn}(\text{OAc})_3$  takes place in refluxing glacial acetic acid† and the product 3 is obtained in only 41% yield. Similar results obtained with dimedone as well as acetylacetone and a number of alkenes are summarized in Table 1. It is noteworthy that the CAN-mediated reactions are generally higher yielding compared with the  $\text{Mn}(\text{OAc})_3$ -mediated ones.

In all the cases studied, 2 equiv. of CAN are required for the completion of the reaction. When less than 2 equiv. are used, a

† No reaction was observed in refluxing ethanol.



Scheme 2

proportional amount of the alkene is left unchanged. While the mechanistic details of the reaction remain unclear, a rationalization along the lines shown in Scheme 2 may be made. It should, however, be pointed out that an alternative mechanism that excludes cation formation cannot be ruled out.

In summary, the CAN-mediated addition of dimedone and acetylacetone to alkenes offers a facile and simple method for the synthesis of dihydrofurans. It may be emphasized that in terms of experimental simplicity and higher yields of products this reagent appears to be superior to the more commonly used  $\text{Mn}(\text{OAc})_3$ . The solubility of CAN in common organic solvents is an added advantage. In view of these facts it is anticipated that CAN will find wider use in C–C bond forming reactions.

### Experimental

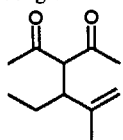
**Typical Procedure:** 3-Ethyl-2,2,6,6-tetramethyl-2,3,4,5,6,7-hexahydro-1-benzofuran-4-one 3.—A solution of CAN (3.15 g, 4.6 mmol) in methanol (20 cm<sup>3</sup>) was added dropwise to an ice-cooled mixture of 2-methylpent-2-ene (0.21 g, 2.5 mmol) and dimedone (5,5-dimethylcyclohexane-1,3-dione) (0.24 g, 3 mmol) in methanol (10 cm<sup>3</sup>) with stirring. After the disappearance of the colour of CAN (15 min), the reaction mixture was diluted with water (150 cm<sup>3</sup>) and extracted with  $\text{CH}_2\text{Cl}_2$  (3 × 50 cm<sup>3</sup>). The combined organic extracts were washed with water and saturated brine, dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated under reduced pressure. The residue obtained was subjected to column chromatography, eluting with 10% ethyl acetate–light petroleum (b.p. 60–80 °C) to afford the pure product 3 (0.334 g, 60%) as a colourless oil,  $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$  2964, 1644 and 1395;  $\delta_{\text{H}}(60 \text{ MHz}; \text{CCl}_4)$  2.8–2.4 (1 H, m,  $-\text{CHCH}_2-$ ), 2.25 (2 H, s), 2.1 (2 H,

**Table 1** Reactions of 1,3-dicarbonyl compounds with alkenes

Entry	Dicarbonyl compound	Alkene	Product <sup>a</sup>	Yield <sup>b,c,d</sup> (%)
1				98 (84)
2				58 (47)
3				48 (50)
4				55 -
5				96 (83)
6				85 <sup>e</sup> (54)
7				60 (39)

<sup>a</sup> *cis* Stereochemistry assigned for products in entries 1, 2, 4, 5 and 6 (*cf.* ref. 9b). <sup>b</sup> Isolated yield. <sup>c</sup> All products gave satisfactory <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR and microanalytical data. <sup>d</sup> Isolated yields obtained by us with Mn(OAc)<sub>3</sub> mediated reactions are given in parenthesis. <sup>e</sup> In

acetonitrile. <sup>f</sup> Along with this product



was isolated in 16% yield [8% with Mn(OAc)<sub>3</sub>].

s), 1.75–1.5 (2 H, m), 1.35 (6 H, s, CH<sub>3</sub>), 1.1 (6 H, s, CH<sub>3</sub>) and 0.89–0.69 (3 H, m, CH<sub>3</sub>);  $\delta_c$ (22.5 MHz) 194, 174, 114.5, 92, 51, 48.5, 37, 33.5, 29, 28, 27.5, 21.5, 21 and 11.5 (Found: M<sup>+</sup>, 222.1613. C<sub>14</sub>H<sub>22</sub>O<sub>2</sub> requires M, 222.1620).

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