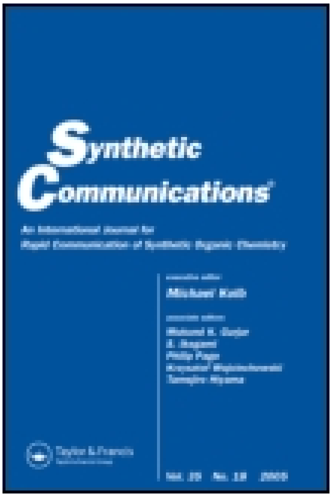

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Cerium(IV) Ammonium Nitrate Mediated Addition of 1,3-Dicarbonyl Compounds to Dienes

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CERIUM(IV) AMMONIUM NITRATE MEDIATED ADDITION OF 1,3-DICARBONYL COMPOUNDS TO DIENES

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Abstract: *Cerium(IV) ammonium nitrate mediated addition of dimedone and acetylacetone to cyclic dienes provided novel dihydrofuran derivatives in moderate to good yields.*

The generation of carbon centred radicals mediated by metal salts like those of Mn(III), Co(II), Cu(II), V(V) and Ce(IV) and their addition to alkenes has been extensively studied[1-5] and these investigations have provided novel synthetic routes to a variety of complex organic compounds. Our own investigations have demonstrated[6-9] that cerium(IV) ammonium nitrate(CAN) is superior to the commonly used manganese(III) acetate in the oxidative addition of 1,3-dicarbonyl compounds to unactivated alkenes. In view of these results it was of interest to investigate the CAN mediated addition of 1,3-dicarbonyl compounds to dienes. A survey of the literature revealed that except for the isolated reports

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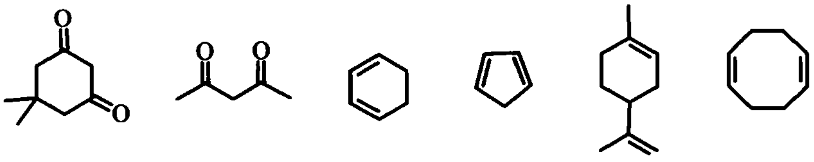
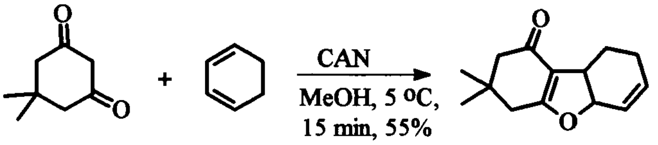
*To whom correspondence should be addressed on the reaction of ethyl acetoacetate[10] and dimethyl malonate[11] to 1,3-butadiene, there has been no work in this area. It is especially noteworthy that cyclic dienes were not used in any oxidative addition reactions mediated by CAN. Therefore we studied the Ce(IV) mediated reaction of the readily available dicarbonyl compounds dimedone(**1**) and acetylacetone(**2**) with 1,3-cyclohexadiene(**3**), cyclopentadiene(**4**), limonene(**5**) and 1,5-cyclooctadiene(**6**), and the results are presented here.



Scheme 1

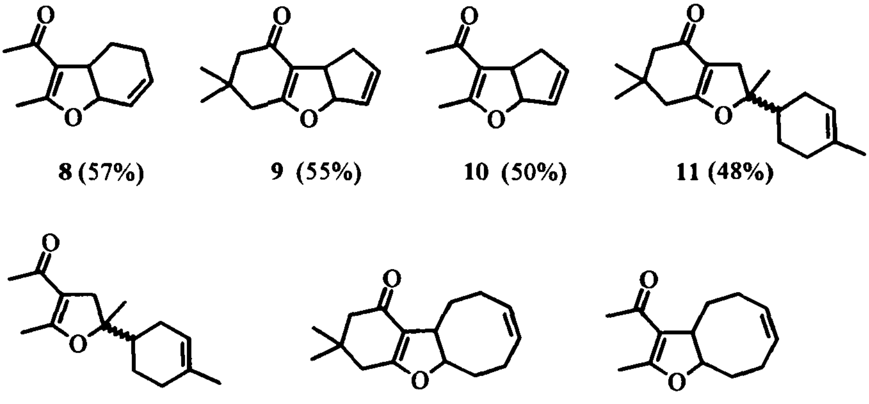
In all the cases studied dihydrofuran derivatives were isolated. The following example is illustrative.



7

Eqn 1

The reaction of acetylacetone with **3** furnished the analogous product **8**. In its reaction with dimedone and acetyl acetone, limonene was expected to undergo tandem radical additions to the two double bonds, but the only product isolated was the dihydrofuran derivatives **11** and **12**. Similarly in the addition of **1** and **2** to 1,5-cyclooctadiene the dihydrofurans **13** and **14** (scheme 2) was obtained in low yields; no transannular cyclization was observed. The reason for the failure of these systems to undergo tandem cyclization is unclear. It, however, may be speculated that the initial adduct radical is metal bound and that transannular addition of such a species is disfavoured due to steric factors.



8 (57%) **9** (55%) **10** (50%) **11** (48%)

12 (46%) **13** (20%) **14** (30%)

Scheme 2

In summary, the CAN mediated addition of dimedone and acetyl acetone to cyclic dienes provided novel dihyrofuran derivatives in moderate to good yields.

Experimental

Infrared spectra were recorded on a Perkin-Elmer model 882 spectrophotometer. Proton and carbon nuclear resonance spectra were recorded on Jeol-EX-90 or Hitachi R-24B-60 NMR spectrometers with tetramethyl silane as internal standard. Silicagel (100-200 mesh) was used for column chromatography. Petroleum ether refers to the fraction boiling between 60-80 °C. All solvent extracts were dried over anhydrous sodium sulphate.

3,3-Dimethyl-1,2,3,4,5a,8,9,9a-octahydrodibenzofuran-1-one (7)

A solution of CAN (3.15 g, 5.75 mmol) in methanol (30 mL) was added dropwise to an ice-cooled mixture of 1,3-cyclohexadiene (0.20 g, 2.5 mmol) and dimedone (0.420 g, 3.0 mmol) in methanol (15 mL). Worked up after decolourisation of the reaction mixture (20 min) and the residue was purified by column chromatography (petroleum ether : ethyl acetate, 9:1). Pure product **7** was obtained as a colourless oil (0.278 g, 55%). IR (neat, cm^{-1}) 2964, 1627, 1404; ^{1}H NMR (90 MHz) δ 6.22-5.68 (m, 2 H, olefinic), 4.91-4.70 (m, 1 H, CH), 3.22-2.88 (m, 1 H), 2.20 (s, 2 H, CH_2), 2.10 (s, 2 H, CH_2), 1.95-1.76 (m, 4 H, CH_2), 1.10 (s, 3 H, CH_3), 0.95 (s, 3 H, CH_3); ^{13}C NMR (22.4 MHz) δ 194.1, 175.8, 134.8, 123.1, 116.0, 80.2, 50.9, 38.1, 36.9, 33.5, 29.1, 27.9, 23.3, 22.2; GC-MS *m/z* 219 (M^+-1, 5), 217 (100), 199 (5),140 (30), 115 (15).

3-Acetyl-2-methyl-3a,4,5,7a-tetrahydrobenzofuran(8):

The reaction of a mixture of 1,3-cyclohexadiene (0.240 g, 3.0 mmol) and acetylacetone (0.360 g, 3.6 mmol) with CAN (3.78 g, 6.9 mmol) in methanol (50 mL), work-up and purification of the residue furnished **8** (0.303 g, 57%) as a colourless oil. IR (neat, cm^{-1}) ν_{max} 2939, 1663, 1618; ^{1}H NMR (90 MHz) δ 6.35-5.85 (m, 2 H, olefinic), 4.82-4.64 (m, 1 H), 3.16-2.87 (m, 1 H), 2.25 (s, 3 H, CH_3), 2.21 (s, 3 H, CH_3), 2.12-1.85 (m, 4 H, CH_2); ^{13}C NMR (22.4 MHz) δ 193.1, 167.1, 133.4, 121.8, 117.7, 77.0, 39.5, 27.9, 23.9, 22.1, 14.4; GC-MS *m/z* 178 (M^+, 70), 163 (22), 159 (30), 145 (18), 135 (20), 121 (7), 117 (85).

Dihydrofuran 9:

A solution of dimedone (0.504 g, 3.6 mmol) and cyclopentadiene (0.198 g, 3 mmol) in methanol (20 mL) on reaction with CAN (3.78 g, 6.9 mmol) in methanol (50 mL) for 20 min, work-up and column chromatography of the residue afforded **9** in 83% yield (0.513 g). IR (CH_2Cl_2, cm^{-1}) 2958, 1622, 1400; ^1H NMR (90 MHz): δ 6.2-5.7 (m, 3 H), 3.95-3.6 (m, 1 H), 2.9-2.5 (m, 2H), 2.3 (s, 2 H), 2.25 (s, 2 H), 1.1 (s, 6 H); ^{13}C NMR (22.4 MHz): δ 194.34, 174.59, 137.33, 127.69, 115.48, 95.49, 51.01, 40.30, 38.24, 37.76, 33.83, 28.61, 28.40; GC-MS *m/z* 204 (M^+, 100), 189 (9), 148 (40), 120 (95), 106 (25).

***Dihydrofuran 10*:**

A mixture of acetylacetone(0.36 g, 3.6 mmol) and cyclopentadiene(0.198 g, 3 mmol) in methanol (20 mL) was reacted with CAN (3.78 g, 6.9 mmol) and worked up. The crude reaction mixture on purification afforded **10** (0.258 g, 51 %) as a viscous liquid. IR (CH_2Cl_2, cm^{-1}) 2932, 1696,1669, 1602; ^1H NMR (90 MHz): δ 6.0-5.3 (m, 3H), 4.0-2.5 (m, 3H), 2.1 (s, 6 H); ^{13}C NMR (22.4 MHz): δ 193.14, 166.05, 136.01, 127.87, 116.53, 91.05, 43.61, 39.85, 28.39, 14.43; GC-MS *m/z* 164 (M^+, 100), 149 (48), 121 (42), 107 (52).

***2-(Cyclohex-3-enyl-4-methyl)-2,3,4,5,6,7-hexahydro-2,6,6-trimethyl-benzo-furan-4-one (11)*:**

The reaction of a mixture of limonene (0.272 g, 2.0 mmol) and dimedone (0.336 g, 2.4 mmol) in methanol (10 mL) with CAN (2.52 g, 4.6 mmol) dissolved in methanol (20 mL), work-up and column chromatography of the residue (petroleum ether: ethyl acetate, 9:1) furnished an isomeric mixture of **11** (0.262 g, 48%) as a colourless oil. This product is a mixture of isomers. IR (CH_2Cl_2, cm^{-1}) 2934, 1638, 1405; ^1H NMR (60 MHz): δ 5.25 (brs, 1 H, olefinic), 2.55-2.32 (m, 2 H, CH_2), 2.20 (s, 3 H), 2.11 (s, 2 H), 1.95-1.66 (brs, 6 H, CH_2), 1.55 (s, 3 H, CH_3), 1.31 (s, 3 H, CH_3), 1.05 (s, 6 H, CH_3); ^{13}C NMR (22.4 MHz): δ 194.2, 174.9, 135.5, 119.9, 110.9, 95.1, 94.9, 50.5, 42.7, 42.5, 37.5, 34.8, 34.0, 33.5, 29.9, 28.3, 28.1, 25.9, 25.5, 24.4, 24.2, 22.6; GC-MS *m/z* 274 (M^+-2, 30), 259(5), 245 (7), 181 (5),141 (8), 134(100), 121 (70).

3-Acetyl-2,5-dimethyl-5-(4-methyl-cyclohex-3-enyl)-4,5-dihydrofuran (12)

Limonene (0.272 g, 2.0 mmol) and acetylacetone (0.240 g, 2.4 mmol) dissolved in methanol (10 mL) were treated with a solution of CAN (2.52 g, 4.6 mmol) in methanol (20 mL). The reaction mixture was worked up and the residue purified by column chromatography to obtain **12** (elution with 10% ethyl acetate in petroleum ether, 0.215 g, 46%) as a colourless oil. This product is a mixture of isomers. IR (CH_2Cl_2, cm^{-1}) 2927, 1673, 1601, 1385; ^1H NMR (60 MHz) δ 5.25 (brs, 1 H, olefinic), 2.94-2.32 (m, 3 H), 2.15 (s, 6 H, CH_3), 1.92-1.70 (m, 6 H, CH_2), 1.55 (s, 3 H, CH_3), 1.20 (s, 3 H, CH_3); ^{13}C NMR (22.4 MHz) δ 194.4, 166.3, 133.5, 119.9, 111.7, 91.1, 90.9, 42.9, 42.6, 39.2, 38.8, 30.2, 30.0, 29.1, 26.2, 25.7, 24.1, 23.8, 23.1, 14.9; GC-MS *m/z* 234 (M^+-2), 191 (25), 173 (32), 134 (100), 119 (50).

3,3-Dimethyl-1,2,3,4,5a,6,7,10,11,11a-decahydro-octabenzofuran-1-one(13) :

To an ice-cooled mixture of 1,5-cyclooctadiene (0.270 g, 2.5 mmol) and dimedone (0.420 g, 3.0 mmol) in methanol (10 mL) was added a solution of CAN (3.15 g, 5.75 mmol) in methanol (25 mL) and stirred for 15 min. Worked up by the usual procedure and the residue was subjected to column chromatography. On elution with 5% ethyl acetate in petroleum ether, **13** (0.123 g, 20%) was obtained as a pale yellow oil. IR (CH_2Cl_2, cm^{-1}):2958, 1629, 1405; ^1H NMR (60 MHz): δ 5.35-5.27 (m, 2 H, olefinic), 4.65-4.21 (m, 1 H, CHO), 3.30-2.95 (m, 1 H), 2.31-1.95 (m, 12 H), 1.15 (s, 3 H, CH_3), 0.97 (s, 3 H, CH_3); ^{13}C NMR (22.4 MHz):

δ 194.5, 175.3, 130.1, 128.2, 114.0, 92.2, 51.2, 44.9, 37.8, 33.6, 31.5, 28.7, 28.5, 28.2, 24.3, 22.1.

3-Acetyl-2-methyl-3a,4,5,8,9,9a-hexahydrooctafuran (14):

A mixture of 1,5-cyclooctadiene (0.270 g, 2.5 mmol) and acetylacetone (0.30 g, 3.0 mmol) was reacted with CAN (3.15 g, 5.75 mmol) as described in the preparation of **13**. The product **14** (0.154 g, 30%) was obtained as a colourless oil. IR (CH_2Cl_2, cm^{-1}): 2928, 1641, 1601, 1420, 1260 cm^{-1}; ^1H NMR (60 MHz) : δ 5.58-5.28 (m, 2 H, olefinic), 4.48-4.01 (m, 1 H), 3.30-2.85 (m, 1 H), 2.35-1.85 (m, 14 H); EI-MS *m/z* : 206 (M^+, 10), 191 (5), 178 (16), 163 (8), 151 (17), 137 (22).

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