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OXIDATIVE ADDITION OF DIMETHYL MALONATE TO STYRENES MEDIATED BY CERIUM(IV) AMMONIUM NITRATE: SOME NOVEL OBSERVATIONS

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Abstract: The oxidative addition of dimethyl malonate to ring substituted styrenes leads to the formation of substituted dimethyl (2-oxo-2-phenylethyl) malonate and methyl 2-oxo-5-phenyltetrahydrofuran-3-carboxylate along with small amounts of substituted dimethyl [2-(nitrooxy)-2-phenylethyl] malonate and dimethyl 2-methoxy-2-phenylethyl) malonate. A tentative mechanism which supports the formation of these products is also presented.

In recent years there has been considerable interest in the generation of carbon centred radicals, mediated by one electron oxidants, and their synthetically useful addition reactions to a variety of substrates[1]. Heiba and Dessau's pioneering work[2] and the subsequent investigations of Kurz[3] have demonstrated the usefulness of Ce(IV) reagents for the generation of electrophilic radicals. Later cerium(IV) ammonium nitrate (CAN) mediated addition of dicarbonyl compounds to butadiene[4] and enol acetates[5] were reported. Some other CAN mediatied reactions that have appeared include malonylation of aromatic[6] and

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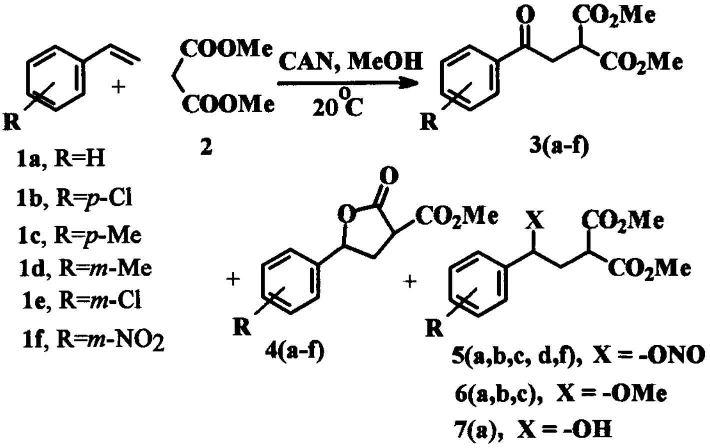
heteroaromatic[7] compounds,coupling of enamines[8] and allyl phenyl sulfides with enol silyl ethers[9], cross coupling[10] of enol silyl ethers and a few intramolecular reactions[11] .It has been reported that the oxidation of substituted benzylmalonate in presence of olefins afforded highly functionalized tetrahydronaphthalenes[12]. Similar oxidation of diethyl(pyridylmethyl) malonates to alkenes and alkynes furnished substituted tetra- or dihydroquinolines and isoquinolines[13]. Our own investigations[14] have evinced that CAN offers certain advantages over the more commonly used $Mn(OAc)_3$ in mediating the oxidative addition of 1,3-dicarbonyl compounds to unactivated alkenes.

The CAN mediated addition of dimethyl malonate to styrene has been reported[15] to give exclusively the nitrate **5a** and methyl ether **6a** . Very recently our reinvestigation[16] has shown that **3a** (42%) and **4a** (29%) are the major products of this reaction and that **5a** and **6a** are formed only in very small amounts; 6% and 5% respectively (scheme 1). Herein we report the details of an expanded study using a number of ring substituted styrenes undertaken to explore the generality of this reaction.

The addition of dimethyl malonate to 4-chloro-, 4-methyl- and 3-methyl substituted styrenes gave products analogous to those obtained in the reaction with unsubstituted styrene[16] (scheme 1). Thus the ketones **3b, 3c** and **3d** were formed in 30%, 14% and 43% yields respectively whereas the lactones **4b, 4c** and **4d** were obtained in 25%, 16% and 25% yields. In the case of 3-chlorostyrene, the corresponding reaction afforded only the ketone **3e** and the lactone **4e** in 42% and 14% yields respectively. 3-Nitrostyrene on the other hand furnished the ketone **3f** and the nitrate **5f** in 32% and 24% yields respectively. The structures were assigned with the aid of IR, ^{1}H NMR, and ^{13}C NMR spectral data. (see table).

Earlier we suggested[16] that formation of the ketone **3a** may be



Scheme 1

rationalized as involving the oxidative fragmentation of the radical anion **10**, formed by ligand transfer[17] or trapping of the benzylic radical **9** by NO_3^{-}. However, when the experiment was done under argon atmosphere, only the products **4a**, **5a** and **6a** were isolated. The absence of **3a** under inert atmosphere suggests that its formation under aerobic conditions may involve the trapping of the benzylic radical **9** by molecular oxygen[18]; the quenching of carbon radicals, generated by CAN or $Mn(OAc)_3$ by oxygen is well precedented[19,20]. The peroxy radical **11** thus formed conceivably abstracts a hydrogen from malonate to give the hydroperoxide **12**. The oxidative cleavage of **12** would lead to the ketone **3a**. The fragmentation of radical anion **10** would give the carbinol **7a**, the precursor for the lactone **4a**. A mechanism for the formation of **5a** can involve either the oxidation of **10** or the trapping of the benzylic cation **13** derived from **9**, by NO_3^{-}. Similarly **13** can be trapped by methanol to afford **6a**. Our efforts to convert **6a** and **7a** to **3a** by oxidation with CAN failed and the attempted methanolysis of **5a** provided only the lactone **4a**. Thus the formation of **3a** by the oxidation of **6a** and **7a** or the formation of **6a** by the solvolysis of the

Table 1. Spectral Data

Compd	IR cm^{-1}	^{1}H NMR ($CDCl_3$)	^{13}C NMR	GC /MS ,m/z
3b	2961, 1755, 1743, 1691, 1594, 1439.	7.9(2H,d,J=6.8Hz,ArH),7.43(2H, d,J=7.7HzArH),4.06(1H,t,J=7.1Hz ,CH),3.77(3H,s,$COOCH_3$),3.76(3H, s,$COOCH_3$)3.592H,d,J=7.1 Hz,CH_2)[a]	195.22,169.23,140.04, 134.39,129.53 129,152.82,46.78,37.8[c]	284(M+,5),266(6), 253(4),221(10),195 (6),139(100),111(25)
4b	2963,1788, 17451356, 1161	7.45-7.2(4H,m,ArH),5.68(t,J=7.2 Hz),5.42 (dd,J=10.0,6.4 Hz),3.85(s,$COOCH_3$),3.8 (s$COOCH_3$),3.75-3.60(1H,m,CH),3.5-2.20(2H,m,CH_2)[a]	169.6,166.3,135.5,135, 133.2,127.5,127.4,125.6, 125.1,77.6,74.1,51.7,51.5, 45.9,45.2,33.2, 33.1[d]	254(M+,10),226(8) 194(9),154(15),139 (35),115(30),87(100)
3c	2960, 1758, 1741, 1693, 1439.	7.86(2H,d,J8.2Hz,ArH),7.25(2H,d,J=7.9Hz, ArH),4.07(1H,t,J=7.1Hz,CH),3.77(3H,s, $COOCH_3$),3.76(3H,s,$COOCH_3$),3.61(2H, d,J=7.1 Hz,CH_2)[a]	195.96,169.44,144.39, 133.62,129.33,128.24, 52.74,46.8837.77,21.61[c]	264(M+,5),246(4), 233(5)201(7),173 (4),119(100).
4c	2962,1783, 1734,1459, 1165.	7.29-7.18(4H,m,ArH),5.67(t,J=7.2 Hz),5.40 (dd,J=10.2,6.1Hz),3.83(s,$COOCH_3$),3.81 (s,$COOCH_3$),3.75-3.68(1H,m,CHCOO-CH_3)2.84-2.40(2H,m,CH_2),2.36(3H,s,CH_3)	171.45,168.08,138.89, 138.65,135.5134.93, 129.49,125.92,125.34, 80.6180.13,53.15,53, 47.75,46.88,34.87, 34.75 ,21.14.	234(M+,15),219(5), 206(10),191(6),174 (10),159(10),147(9), 131(20),119(70).
5b	2961,1754, 1741,1642, 1441,1279.	7.3(4H,s,ArH),5.87(1H,dd,J=8,6.2Hz, $CHONO_2$),3.75(s,6H,$COOCH_3$),3.62-3.35(1H,m,CH),2.65-2.35(2H,m,CH_2)[b]	168.5,135.3,134.9, 129.0,127.6,81.8,52.6, 47.7,33.[d]	268(M+NO2-1,10), 236(25),204(60),155 (100),149(80)
6b	2957, 1755, 1743, 1483.	7.31(4H,s,ArH),4.23-4.06(1H,m, $CHOCH_3$), ,3.75(s,3H,$COOCH_3$),3.71(3H,s,$COOCH_3$), 3.65-3.30(1H, m, CH), 3.15(3H, s, OCH_3) 2.32-2.15(2H,m,CH_2)[b]	169.6,169.5, 139.6, 128.6, 127.8, 80.6,56.7, 52.4, 48.5,37.0[d].	300(M+,4)285(5), 269(7),237(4), 209(10),168(45), 155(100).

Table 1. Spectral data contd....

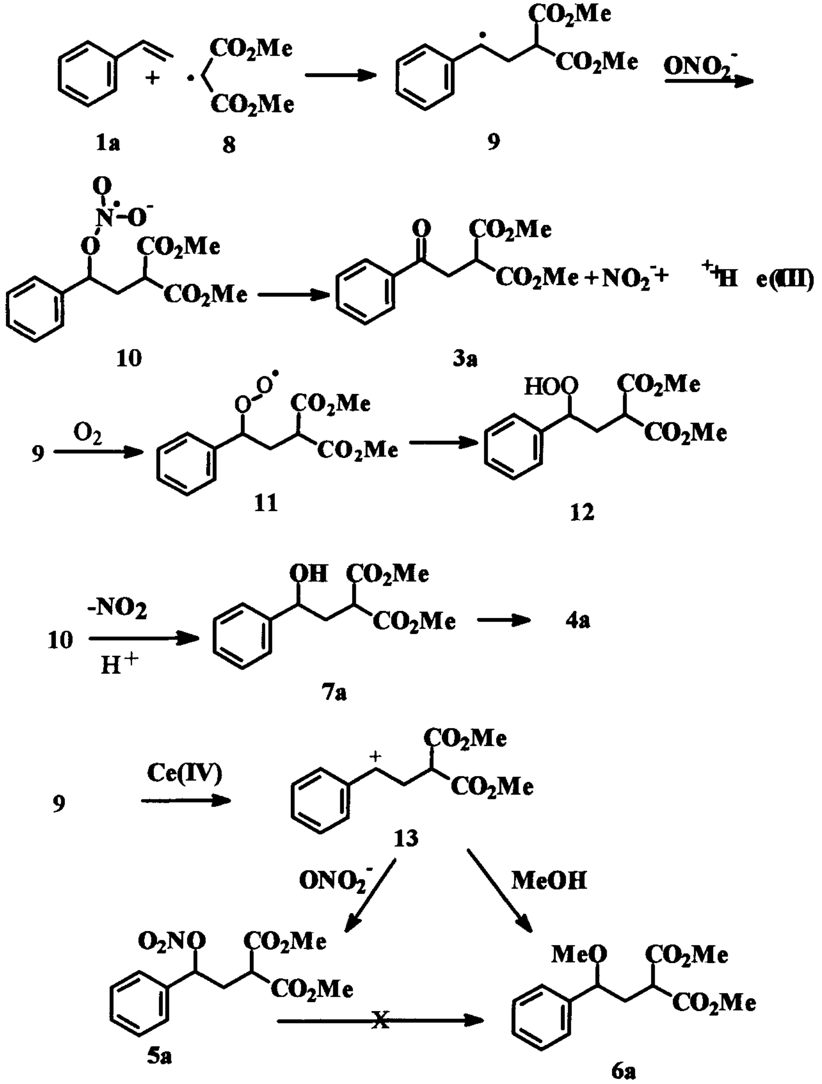
Compd	IR cm^{-1}	^{1}H NMR ($CDCl_3$)	^{13}C NMR	GC MS ,m/z
3d	2961, 1742, 1691,1440, 1161.	7.85-7.71(4H,m,,ArH),4.17-4.02(1H,m,CH), 3.75(6H,s,COOCH$_3$),3.70-3.55(2H,m,CH$_2$) 2.41(3H,s,CH$_3$)	196.2,169.0,138.1,128.2, 125.0,52.4,46.5,37.6,21 ^{d}	264(M+,4),246(5),233(3) 201(10),173(5),119(100).
3e	2960,1757, 1693,1435	7.9-7.77(2H,m,ArH),7.62-7.23(2H,mArH), 4.03(1H,t,J=7.5Hz,CH),3.74(6H,s, COOCH3) ,3.55(2H,d,7.5Hz,CH$_2$)b	194.8,168.8,137.2,134.6, 133,129.7,127.8,125.8, 52.4,46.3,37.6d	284(M+,5),266(7), 253(6),221(12),195(8), 139(100)
3f	2962,1702, 1537,1354.	8.94(1H,t,J=1.9Hz,ArH),8.59(1H,d,J=2.2Hz, ArH),8.57(1H,d,J=2.2Hz,ArH),8.46(1H,d,J= 1.2Hz,ArH),4.26(1H,t,J=7Hz,CH),3.94(6H,s, COOCH3),3.81(2H,d,J=7.0Hz,CH2)b	194.5,168.9,148.2,136.8, 133.5,130.2,127.5,122.5, 52.5,46.7,38.1^{d}	
5c	2960, 1754, 1743, 1638, 1442, 127	7.25(4H,s,ArH),5.89(1H,dd,J=8,6.3Hz, CHONO2),3.8(s,6H,COOCH$_3$), 3.62-3.44(1H,m,CH),2.61-2.45(2H,m,CH$_2$), 2.38(3H, s, CH$_3$)b	168.7, 139.2, 133.7, 129.5, 126.4, 82.7, 52.7, 48.0, 33.3, 21.1^{d}	248(M+-NO2-1),20), 216(5),189(8),139(100).
6c	2956, 1755, 1741, 1440	7.15(4H,s,ArH),4.22-3.95(1H,m, CHOCH$_3$), ,3.71(s,6H,COOCH$_3$),3.55-3.25 (1H, m, CH), 3.14(3H, s, OCH3) 2.31-(3H,S,CH3), 2.3-2.15(2H, M, CH$_2$)b	169.5, 169.3, 137.6, 137.1, 128.8,126.1, 80.8, 56.2, 51.9,48.3, 36.8, 20.6d	280(M+,4),265(5), 249(7),233(3),217(4), 201(4),185(10) 148(50),135(100).

(continued)

Table 1 Spectral Data Contd...

Compd	IR(cm^{-1})	^{1}H NMR(CDCl$_3$)	^{13}C NMR	GC MS, m/z
4d	2961,1784, 1742,1158.	7.41-7.15 (4H,m,ArH),5.66(t,J=7.3Hz),5.39 (dd,J=10.0,6.3Hz),3.80(s, COOCH$_3$), 3.79(s, COOCH$_3$),3.77-3.61(1H,m, CHCOOCH$_3$), 3.15-2.40(2H,m,CH$_2$),2.35(3H,s, CH$_3$)^b	171.4,171.3,167.8,138.3,138.2, 137.7,129.3,129.1,128.4,128.3, 126.1,125.6,122.6,122.0,80.3, 79.8,52.847.4,34.7,34.4,21.0^d	234(M+,26),206 (12),174(15),159 (10),146(8),131 (20),119(70), 87(100).
4e	2963,1788 1745,1356, 1161.	7.42-7.18(4H,m,ArH),5.66(1t,J=7.3Hz),5.48 (dd,J=9.9,6.4Hz),3.82(s,COOCH$_3$),3.80(s, COOCH$_3$),3.74-3.63(1H,m, CHCOOCH$_3$) 3.19-2.21(2H,m,CH$_2$)b	170.1,167.7,140.5,140.0,134.7, 134.6,130.5,128.8,128.7,125.7, 125.3,123.7,123.2,79.4,78.8, 53.1,52.9,47.2,46.5,34.6,34.4^d.	254(M+,12),226 (8),194(10),154(12) 139(45),115(32).
5d	2961,1754, 1743,1640, 1440,1278.	7.3-7.15(4H,m,ArH),5.87(1H,dd,J=7.9,6.2Hz, CHONO$_2$) ,3.79(s,6H,COOCH$_3$),3.65-3.45 (1H,m,CH),2.66-2.45(2H,m,CH$_2$), 2.38(3H, s, CH$_3$)b	168.5,138.5,136.5,129.7,128.5, 126.6,123.1,82.6,52.5,47.8,33.2 21.1 ^{d}	
5f	2960,1740, 1646,1532, 1273.	8.34-8.30 (2H,m,,ArH),7.81-7.72(2H,m,ArH), 6.08(1H,dd,J=9.1.5.1Hz,CHONO$_2$)3.92(3H,s, COOCH$_3$)3.81(3H,s,COOCH$_3$),3.65(1H,t, J=7.1Hz,CH),2.68-2.58(2H,m,CH$_2$)a	168.4,148.8,139.2,132.1, 130.0,124.0,121.5,81.6, 52.9,47.48,32.9.^{c}	
6d	2957,1752, 1741,1440.	7.36-7.05(4H,m,ArH),4.14(1H,dd,J=7.6,5.8 Hz CHOCH$_3$),3.79(3H,s,COOCH$_3$),3.75(s,3H, COOCH$_3$),3.67-3.51(1H, m,CH), 3.21(3H, s, OCH$_3$),2.38(3H,s,CH$_3$),2.35-2.21(2H,m,CH$_2$)^b	169.4, 169.2 140.5,137.6,128.1, 127.9126.6,123.1,80.9,56.2, 51.9,48.3,36.7,20.9^d	280(M$^+$, 3), 265(4), 249(6),233(2), 217 (4), 201(3),185(10), 148(50),135(100)

Satisfactory elemental analyses were obtained for all stable compounds. a:-200MHz.,b:-90MHz, c:-50MHz., d:-22.4MHz


CO2Me
CO2Me
1a
8
CO2Me
CO2Me
9
ONO2-
O
N-O-
O
CO2Me
CO2Me
10
O
CO2Me
CO2Me + NO2- + +H e(III)
3a
9
O2
O
O
CO2Me
CO2Me
11
HOO
CO2Me
CO2Me
12
-NO2
10
H+
OH
CO2Me
CO2Me
7a
4a
9
Ce(IV)
+
CO2Me
CO2Me
13
ONO2-
MeOH
O2NO
CO2Me
CO2Me
5a
X
MeO
CO2Me
CO2Me
6a

Scheme 2

nitrate **5a** may be ruled out. The mechanistic rationale described above is illustrated in scheme 2. Thus the CAN mediated addition of dimethyl malonate to styrene is an interesting reaction both from the points of view of its mechanistic implications and its potential use in organic synthesis.

Experimental

IR spectra were recorded on a Perkin-Elmer Model 882 infrared spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on Nicolet GE-300, Varian XL-200 and Jeol EX-90 spectrometer using chloroform-*d* as solvent. Mass spectra were recorded on Hewlett Packard 5971 series mass selective detector. The relative intensities of the *m/z* values are given in paranthesis. Dry THF was obtained by distillation over sodium-benzophenone ketyl. NaH used was a 50% suspension in mineral oil. Styrene and 3-methylstyrene purchased from Aldrich were used directly. 4-Chloro-, 3-chloro-, 4-methyl- and 3-nitrostyrenes were prepared from the corresponding aldehydes by Wittig reaction.

Preparation of Substituted Styrenes: General Procedure

NaH (3.0 g, *ca.* 66 mmol) was suspended in dry THF (50 cm^3). Triphenylmethylphosphonium iodide (20.2 g, 50 mmol) was added to it and refluxed for 1.5 h. Substituted benzaldehyde (33 mmol) dissolved in THF (25 cm^3) was added and stirred at 40-45°C for 1-2 h. The reaction mixture was cooled, diluted with water (200 cm^3) and extracted with CH_2Cl_2 (3 x 100 cm^3). The combined organic extracts were washed with water, dried and evaporated. The residue was purified by column chromatography. Elution with petroleum ether afforded substituted styrene.

Oxidative Addition of Dimethyl Malonate to 4-Chlorostyrene

Dimethyl malonate (0.661 g, 5.0mmol) and 4-chlorostyrene (0.866 g, 6.25 mmol) were dissolved in methanol (30 cm^3) and treated with CAN (6.31 g, 11.5

g, 11.5 mmol) in methanol (80 cm^3) as described previously. Work-up and column chromatography furnished **3b** (colourless viscous liquid, 0.435 g, 30%), **3c** (colourless viscous liquid, 0.291 g, 23%), **5b** yellow oil, 0.220 g, 13%) and **6b** (pale yellowoil, 0.06 g,4%)

Oxidative Addition of Dimethyl Malonate to 4-Methylstyrene To a mixture of dimethyl malonate (0.528 g, 4.0 mmol) and 4-methylstyrene (0.615 g, 5.2 mmol) dissolved in THF (50 cm^3), a solution of CAN (5.04 g, 9.2 mmol) in methanol (30 cm^3) was added dropwise and stirred till the reddish brown colour of CAN disappeared (5°C RT, 3 h). Worked up as described earlier. The residue on column chromatography afforded **3c** (colourless viscous liquid, 0.151 g, 14%), **4c** (colourless viscous liquid, 0.150g, 16%),**5c** (yellow oil, 0.051 g, 4%) and **6c** (pale yellow oil, 0.064 g, 6%).

Oxidative Addition of Dimethyl Malonate to 3-Methylstyrene Dimethyl malonate (0.462 g, 3.5 mmol) and 3-methylstyrene (0.475 g, 4.02 mmol) dissolved in methanol (25 cm^3) was treated with CAN (4.41 g, 8.05 mmol) in methanol (55 cm^3) as described before. It was worked up and the residue was subjected to column chromatography. Pure products **3d** (colourless viscous liquid, 0.40 g, 43%), **4d**(colourless viscous liquid, 0.205 g, 25%), **5d** (yellow oil, 0.074 g, 7%) and **6d** (pale yellow oil, 0.079 g, 8%) were obtained.

Oxidative Addition of Dimethyl Malonate to 3-Chlorostyrene Dimethyl malonate (0.396 g, 3.0 mmol) and 3-chlorostyrene (0.498 g, 3.6 mmol) were dissolved in methanol (20 cm^3). This was subjected to the reaction with CAN (3.78 g, 6.9 mmol) in 50 cm^3 methanol as described previously. Work-up by the usual procedure and column chromatography afforded **3e** (0.361 g, 42%) and **4e** (0.106 g, 14%) as colourless viscous liquids.

Oxidative Addition of Dimethyl Malonate to 3-Nitrostyrene

Dimethyl malonate (0.330 g, 2.5 mmol) and 3-nitrostyrene (0.447 g, 3 mmol) were dissolved in methanol (15 cm^3) and treated with CAN (3.15 g, 5.75 mmol) in methanol (20 cm^3). Work-up and column chromatography furnished **3f** (yellow viscous liquid, 0.234 g, 32%) and **5f** (yellow oil, 0.195 g, 24%).

Oxidative Addition of Dimethyl Malonate to Styrene under Argon Atmosphere

Dimethyl malonate (0.369 g, 3.0 mmol) and styrene (0.374 g, 3.6 mmol) were dissolved in methanol (20 cm^3) and purged with argon for 15 minutes. A solution of CAN (3.78 g, 6.9 mmol) dissolved in methanol (50 cm^3) was also purged with argon and added dropwise to the above mixture which was stirred in an ice-bath under argon atmosphere for 1.5 h and then at room temperature for 2 h. The reaction mixture was processed as described above to afford **4** (0.218 g, 33%), **5** (0.162 g, 18%) and **6** (0.153 g, 19%).

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