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Oxidation of Diethyl ω-Phenylalkenylmalonates by High Valent Metal Salts.

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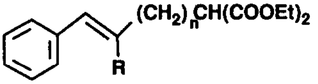
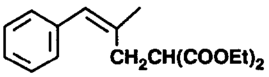
Abstract : The oxidation of diethyl ω-phenylalkenylmalonates by Mn(III) acetate in acetic acid and Fe(III) perchlorate nonahydrate in acetonitrile or acetonitrile/acetic anhydride is investigated. Diethyl cinnamylmalonates **1**, **2** and **3** afford intramolecular addition products to the double bond (cyclopropanes **10**) and to the aromatic ring (tetrahydronaphthalenes **8** or **9**). A mechanism based on a fast and reversible 3-*exo-trig*-addition of malonyl radicals leading to *cis-trans* equilibration of the double bond, followed by competition between oxidation of benzyl radicals and intramolecular aromatic substitution, is suggested. Trapping experiments with styrene and metal ions elucidate some of the kinetic parameters involved. Similarly, compounds **4** and **5** are oxidized by Mn(III)/AcOH and FEP/AN to 4- and 5-*exo-trig*- cyclization products. In contrast, an outer-sphere electron-transfer mechanism is suggested in the oxidation of **1**, **4** and **5** at the styrenic double bond by FEP/AN-Ac_2O and of benzalketones **6** and **7** by Mn(III)/AcOH to α-oxygenation products **21-22**.

In recent years the oxidative metal-induced addition of carbonyl compounds to olefins and aromatics has been the subject of extensive mechanistic and synthetic studies[1-4]. The homolytic nature of these processes has been unambiguously ascertained from the factors affecting the reactivity and selectivity of the addition step and by comparison with free-radical chain processes involving hydrogen or halogen atom abstractions[5,6]. Recent determinations[4-7] of addition rates of representative electrophilic radicals to olefins and aromatics have recognized the main parameters governing the process. In the intermolecular additions, polar and enthalpic factors play important roles determining typical U-shaped plots of addition rates vs. ionization potentials[3,4,7]. However, when strongly electron-rich olefins or aromatics were used in these reactions, competitive or exclusive oxidation of C=C double bonds was observed. By using unsaturated carbonyl derivatives, selective oxidations at the α position of the carbonyl group (with subsequent intramolecular additions that exhibited a strong dependence on the ring size and stereoelectronic factors) were observed[1,4] without examples of oxidations at the unsaturated carbon-carbon bonds.

Our interest in the reactivity of free-radicals, coupled to the remarkable synthetic potential of homolytic oxidative addition processes, has prompted us to investigate the oxidation of ω-phenylalkenylmalonates and benzalketones derivatives (**1** - **5**, and **6** - **7**, respectively), which contain electron-rich styrenic double bonds and carbonyl groups in positions appropriate for potentially competitive reactions.



1 ; R = H, n = 1
2 ; R = Me, n = 1
4 ; R = H, n = 2
5 ; R = H, n = 3



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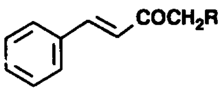
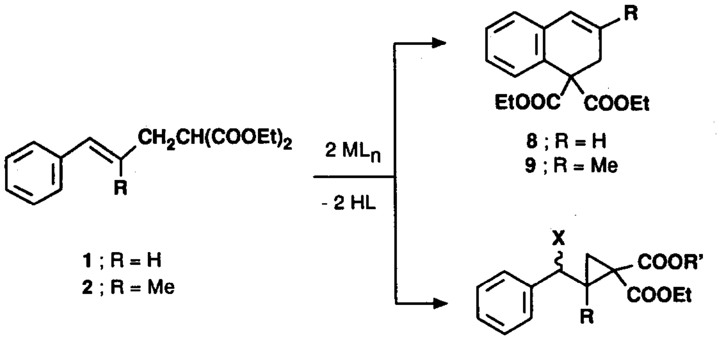


6 ; R = H
7 ; R = $(CH_2)_2CO_2H$

Results

The oxidation of **1** by $Mn(OAc)_3$ in acetic acid at 60 °C for 8 h affords three products in high yield (Tab. 1). The product of 6-*endo-trig* ring closure, **8**, prevails over the diastereoisomeric mixture of 3-*exo-trig* ring closure **10** (**10a** and **10b**) (eq.1).



eq. 1

The product distribution was nearly independent of temperature in the range 50-100 °C. However, compounds **8** and **10** are formed in competitive processes, as indicated from the dependence of their ratio on Manganese(III) and sodium acetate concentrations (Fig. 1). The slope observed in the former case (0.96) indicates that the oxidation rate to **10** slower than cyclization to **8**. This data allows us to identify conditions in which dihydronaphthalene **8** can be obtained in a synthetically useful yield, as for instance in electrochemical experiments (Table 1, entry 6), where a low stationary concentration of Mn(III) is involved.

By changing the metal from $Mn(OAc)_3$ in acetic acid to $Fe(ClO_4)_3 \cdot 9\ H_2O$ (FEP) in acetonitrile[8], the oxidation of **1** affords cyclopropyl lactones **10c** and **10d** (48%) along with a low yield of **8** (12%) and ketone **11** (6%) (Table 1). The formation of **11** suggests that the oxidation of the conjugated double bond can compete, under appropriate conditions, with the oxidation of the malonate group.

TABLE 1

Oxidation of diethyl cinnamylmalonate (1) by Mn(III) acetate and Fe(III) perchlorate.

Entry	Metal	Additive	1[a] (Conv %)	----- Products (yield %)[b] ---- 8	10	11	12
1	$Mn(OAc)_3$[c]	-	90	78	18[d]	-	-
2	$Mn(OAc)_3$[c,e]	-	94	74	26[d]	-	-
3	$Mn(OAc)_3$[c,e,f]	-	88	85	12[d]	-	-
4	$Mn(OAc)_3$[c]	$Cu(OAc)_2$	91	70	28[d]	-	-
5	$Mn(OAc)_3$[c]	AcONa	95	83	14[d]	-	-
6	$Mn(OAc)_3$[g]	AcONa	92	87	5[d]	-	-
7	FEP[h]	-	76	12	48[i]	6	-
8	FEP[l]	Ac_2O	86	-	-	5	63
9	FEP[l]	$Ac_2O/Cu(OAc)_2$	100	-	-	-	90

a) GC analysis. b) Isolated product, based on converted **1**. c) [Mn(III)] = 0.2 M, N_2, 60°C, AcOH, 12h; d) **10a**/**10b** = 1.5; e) anhydrous $Mn(OAc)_3$; f) [Mn(III)] = 0.01 M; g) Anodic oxidation (experimental part); h) N_2, 20°C, AN, 8h; i) **10c**/**10d** = 1.4; l) N_2, 20°C, AN, 2h.

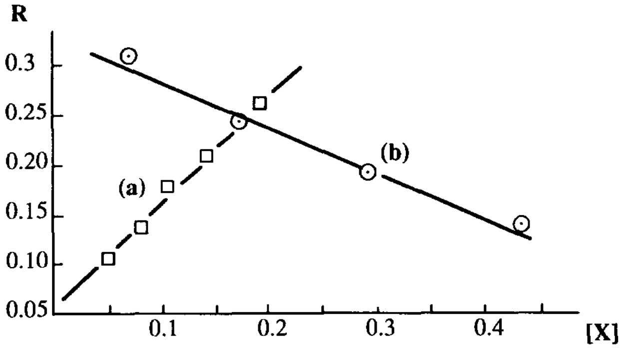
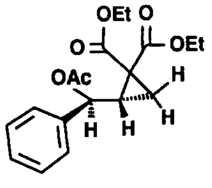
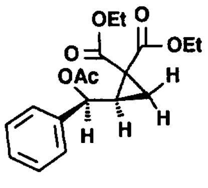
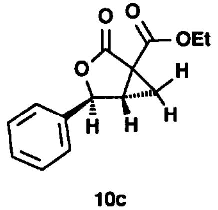
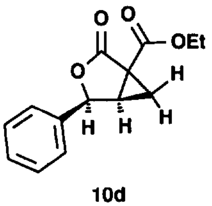


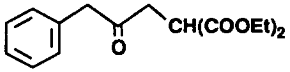
Fig. 1. Effect of (a) $X=Mn(OAc)_3$ or (b) X= NaOAc Concentration on the Ratio R=[**10**]/[**8**] in the oxidation of **1** by $Mn(OAc)_3$ (AcOH, 60 °C, N_2).


10a


10b


10c


10d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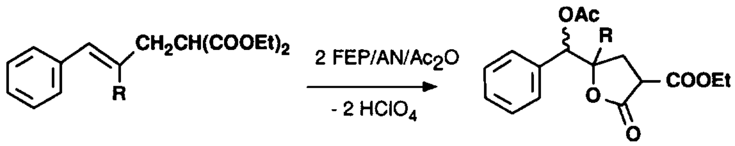
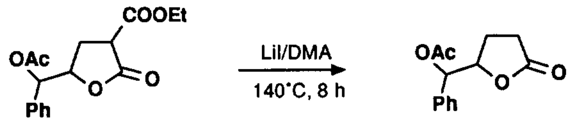
With the more strongly oxidizing system FEP in AN/$Ac_2O^{3,8}$, the oxidation of **1** affords mainly lactones **12** and **13** as a mixture of four diastereoisomers (eq. 2), and was particularly clean when carried out in the presence of cupric acetate (5-10% molar amount with respect to FEP).


eq. 2

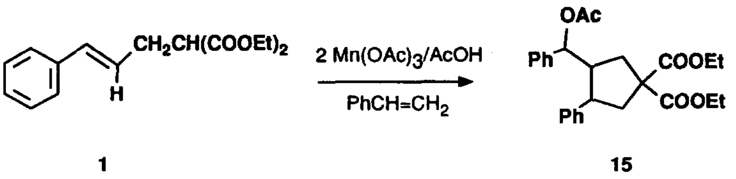
1 : R = H
2 : R = Me

12 : R = H
13 : R = Me

The separation of isomers **12** was unsuccessful and the mixture was characterized by IR, NMR and GC-MS analyses, and by thermal hydrolytic decarboxylation to isomeric lactones **14**.


12 **14**

To obtain some details on the rate constants of the reaction steps involved, competition experiments of the oxidation of **1** by $Mn(OAc)_3$ in the presence of styrene were made. Compound **15** (four diastereoisomers, eq. 3) was in fact found to compete with the products of the intramolecular oxidative additions (compounds **8**, **10a** and **10b**).



eq. 3

From the linear dependence of the ratio **15**/(**8** + **10a** + **10b**) against styrene concentration (fig. 2), a relative rate of 210 ± 11 between the intramolecular and intermolecular additions is estimated.

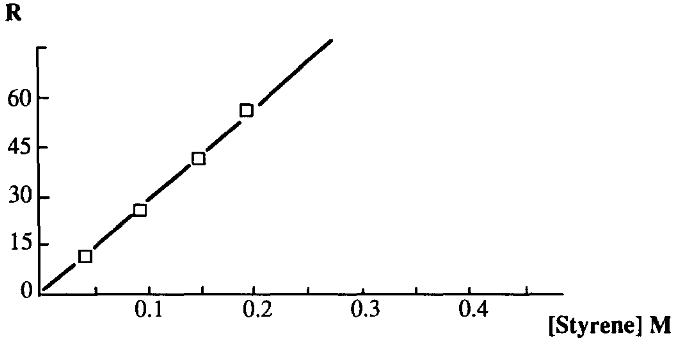


Fig. 2. Dependence of R = **15**/(**8** + **10a** + **10b**) Against the Styrene Concentration in the Oxidation of **1** by Mn(III) Acetate in the Presence of Styrene (AcOH, 60 °C).

Table 2 collects the results of oxidations of the other substrates investigated (**2**-**7**). Tetrahydronaphthalene derivative **9** is obtained from substrates **2** and **3** even more efficiently than is **8** from **1**. The oxidation is only slightly more selective with pure Z isomer **3** than with E isomer **2**, and consequently the synthetic mixture (2:8) cyclizes to **9** in good yield (Table 2, entry 10 - 12).

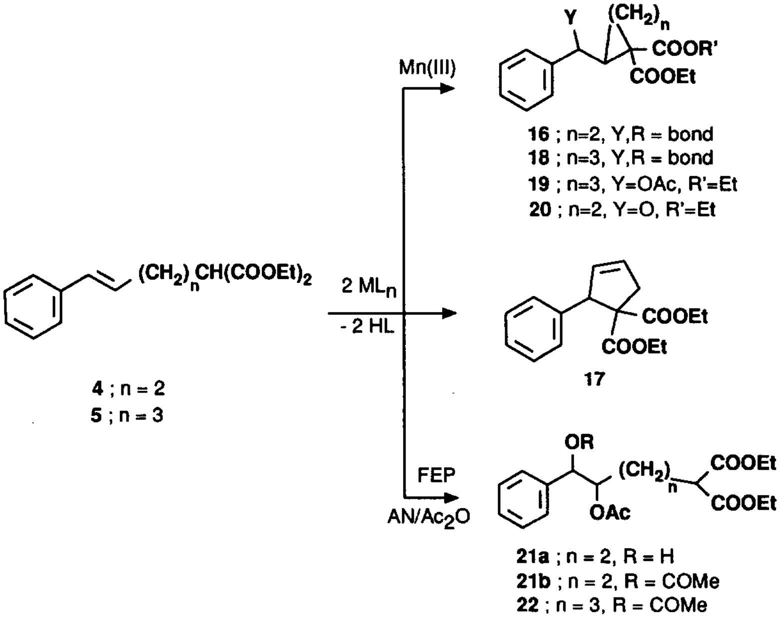
On the contrary, the intramolecular aromatic substitution does not occur in the oxidation of **4** and **5** with Mn(III) acetate or FEP. Substrate **5** affords exclusive oxidation of the malonate group followed by intramolecular addition to the double bond to give the 5-*exo-trig* cyclization derivatives **18-20**. Whereas substrate **4** yields in a slow reaction a complex mixture of products between which prevaled the oxidation products at the double bond (acetates and hydroxyacetates **21a** and **21b**) and the 4-*exo-trig* and 5-*endo-trig* cyclization products **16** and **17**. Other expected cyclization products (i.e. benzylic acetates in the 4-*exo-trig* addition and acetoxylated or styrenic products in the 5-*endo-trig* addition) were not found, indicating a quite specific behaviour of the corresponding carbon-centered radical adducts towards oxidation by Mn(III). The addition of acetic anhydride to the couple FEP/AN directd the oxidations of **4** and **5** to the styrenic double bond, affording mainly diacetoxy derivatives **21a** and **22**, respectively.

TABLE 2

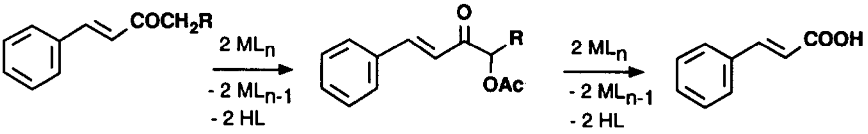
Product Distribution in the Oxidation of Compound 1-7 by $Mn(OAc)_3$ (60°C, N_2, AcOH)

Entry	Compound	Products (yield %)					
		8/9	**10**	**16-20**	**21-22**	**23-24**	**25**
10	**1**	88	12[a]	-	-	-	-
11	**2**	88	4	-	-	-	-
12	**3**[b]	96	tr	-	-	-	-
13	**4**	-	-	32[c] (tr)[e]	43[d] (69)[e]	-	-
14	**5**	-	-	89[f] (20)[g]	- (63)[g]	-	-
15	**6**	-	-	-	-	9 (4)[h]	37 (68)[h]
16	**7**	-	-	-	-	3 (tr)[i]	42 (83)[i]

a) **10a** : **10b** = 1.2. b) Mixture E/Z (8:2). c) **16** (80%), **17** (20%). d) **21a** (35%), **21b** (65%). e) Reaction with FEP/AN/Ac_2O. Compound **21b** (69%) was isolated. f) **18** (65%, **18a**:**18b** = 10), **19** (25%), **20** (10%). g) Reaction with FEP/AN/Ac_2O. Compounds **18** (20%) and **22** were isolated. h) [Mn(III)]/[**6**] = 4. i) [Mn(III)]/[**7**] = 4.



The oxidation of substrates **6** and **7** by $Mn(OAc)_3$ yields α-acetoxylation products **23** and **24**, along with cinnamic acid **25**, the product of oxidative fragmentation. **25** strongly prevails in the oxidation of **7**, even at relatively low conversion (20%). No polymer was observed in the oxidation of **6**.[9]



6 ; R = H
7 ; R = $(CH_2)_2COOH$

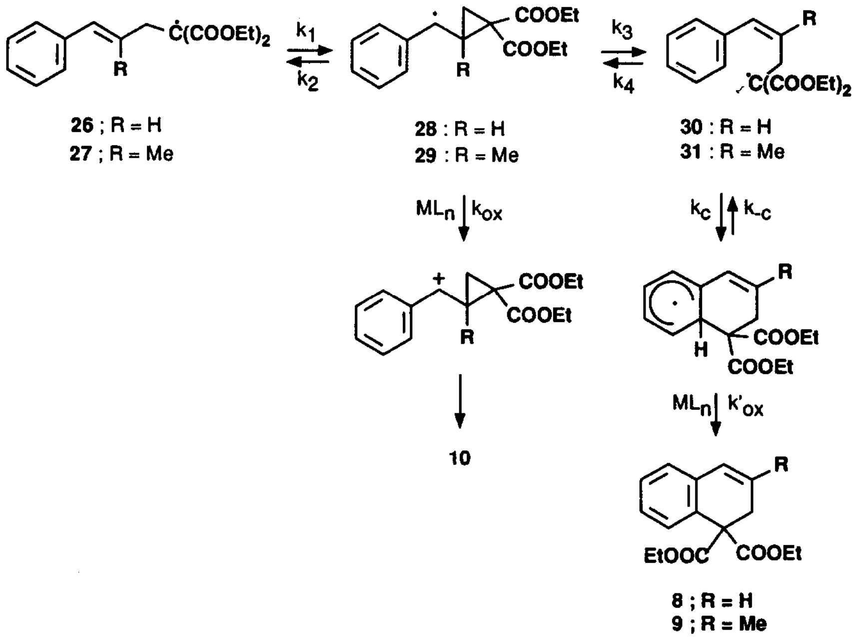
23 : R = H
24 : R = $(CH_2)_2COOH$

25

Discussion

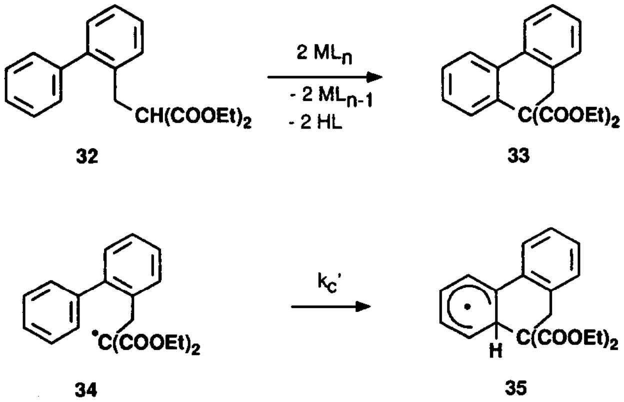
The results of this study indicate that, in the oxidations of substrates **1-5** by high valent metal salts, malonate C-H or C=C bonds are viable but infrequently competitive sites of attack. As a general rule, the oxidation of the alkene C=C bond is more efficient when the metal complexes possess high redox potentials (FEP/AN-Ac_2O) and the π systems are strongly electron-rich (as in compounds **6**, **7**), i.e. under conditions which favor oxidations via an outer-sphere electron-transfer mechanism. Under more basic and less oxidizing conditions, the oxidation of the C=C double bond becomes significant in the case of slow trapping of the initially formed α-carbonylalkyl radical intermediates (i.e. **4**). The sensitivity of the oxidation rate to the substrate structure and the dependence of the oxidation rate on the olefin concentration supports the hypothesis that the generation of α-carbonylalkyl radicals by high valent metal complexes involves a reversible complexation of the carbonyl compound to the metal followed by reversible bond homolysis or inner-sphere electron-transfer from the ligand to the metal[3].

The majority of reactions with the moderate oxidant $Mn(OAc)_3$ take place at the malonate C-H bond and the different products observed can be rationalized on the basis of the reactivity of malonyl radical intermediates. Thus, the formation of cyclization products **8** and **9**, despite the *trans* arrangement of the double bond in **1** and **2**, can be explained taking into account the rapid rate of homolytic aromatic substitution of malonyl radicals after isomerization of the double bond. A fast and reversible intramolecular addition of the 4-aryl-3-butenyl radicals **26** or **27** to the styrenic double bond allows the equilibration of the *trans* radicals **26** and **27** to the *cis* radical **30** and **31** via the cyclopropylmethyl radical **28** and **29** (scheme 1). Homoallylic radicals are known to rearrange through 1,3-vinyl migration with the intermediate formation of distinct cyclopropylmethyl radicals[10]. The extensive studies on this topic have provided kinetic information for this ring-forming ring-opening reaction with model radicals and have ascertained the kinetic preference for the ring-forming reaction in the case of 4-phenyl-3-butenyl radical ($k_c = 10^6\ s^{-1}$, $k_{-c} = 0.5\text{-}4 \times 10^5\ s^{-1}$ at 20 °C)[10].



Scheme 1

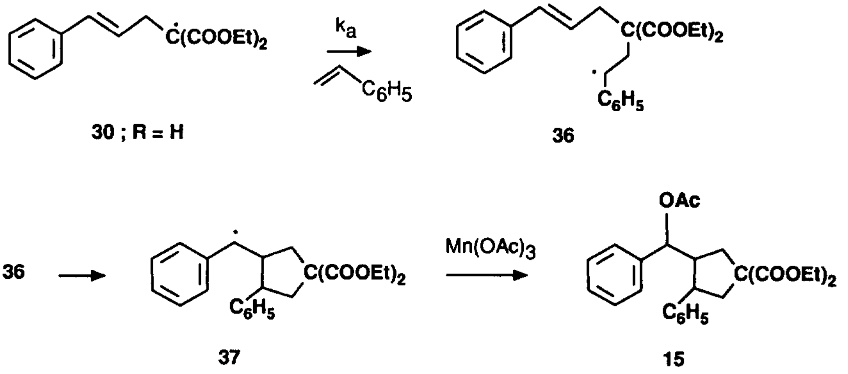
Previous studies on the oxidation of substituted benzylmalonates[4] by high valent metal salts have concluded that radical **34**, an intermediate in the oxidation of **32** to **33** (scheme 2) and is structurally similar to radicals **30** and **31**, cyclizes at a rate ($k'_c = 6.4 \times 10^5$ s^{-1} at 60 °C) slighly lower than its addition rate to styrene ($k_a = 8 \times 10^6$ $M^{-1}s^{-1}$) and 90 times faster than the intramolecular substitution of diethyl 4-phenylbutylmalonyl radicals.



Scheme 2

The results of competitive trapping of diethyl α-(3-phenylpropenyl)malonyl radicals **30** with styrene (Fig. 2) show an overall rate of cyclization of 3.9 x 10^4 s^{-1}, one order of magnitude lower than the one observed with radical **34**. This value is probably a lower limit for the addition rate, owing to the complex mechanism for the formation of radicals **30** and the unfavorable trans-cis equilibration. All the other rate constants involved in Scheme 1 appear to be higher than 10^6 s^{-1} at 60°C. Therefore, malonyl radicals add to the electron rich styrenic double bond at rates similar or higher than primary alkyl radicals, a result related to the electrophilic properties of the former radicals since it is contrary to the expectations of the influence of steric and enthalpic effects on the homolytic addition rate. Anyhow, the rotation around the benzylic σ bond in **28** and **29** must be faster than fragmentation. The process of *cis-trans* isomerization of double bonds by radical addition is well documented[12], and it is generally used to convert the less thermodynamically stable Z isomer to the more stable E isomer. The behaviour of substrates **1** - **3** suggests that also the contrary can be synthetically exploited when appropriate fast processes involving the *cis* radical intermediates are available to drift the equilibrium to the right. Also, the trend observed for the ratio between the yield of cyclopropane derivatives **10a** - **10b** to that of dihydronaphthalene **8** (R in Fig. 1) is in accord with scheme 1, and parallels the oxidizing property of the medium which increases with the Mn(III) concentration and decreases with the NaOAc concentration[3].

Similarly, a fast intramolecular 5-*exo-trig* addition of radical **36** (arising from the addition of radical **30** to styrene) to the conjugated double bond followed by the oxidation of the resulting benzyl radical **37**, can explain the formation of cyclopentane derivative **15** (scheme 3).

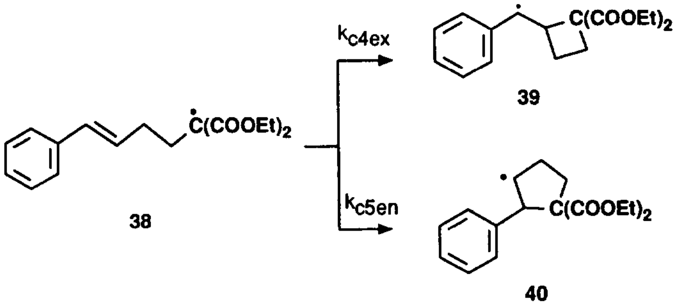


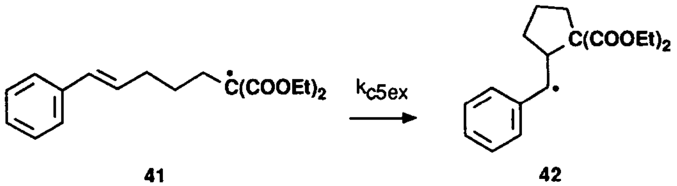
Scheme 3

From the trace amounts of oxidation products of benzyl radical **36**, we can estimate a lower limit of 10^7 s^{-1} for the cyclization rate of this radical[13]. The stabilization of radical adduct **37** and steric compression of *gem*-dicarbethoxy groups probably contribute to enhance the cyclization rate, despite the thermodynamic stabilization present in starting benzyl radicals. The effect parallels the one observed upon introduction of a *gem*-dimethyl substituent in the 5-hexenyl radical cyclization[14]. The more efficient cyclization of methyl substituted radical **31** compared with **30** can be similarly rationalized.

In line with this interpretation radical **41**, formed by oxidative α-deprotonation of **5**, undergo fast

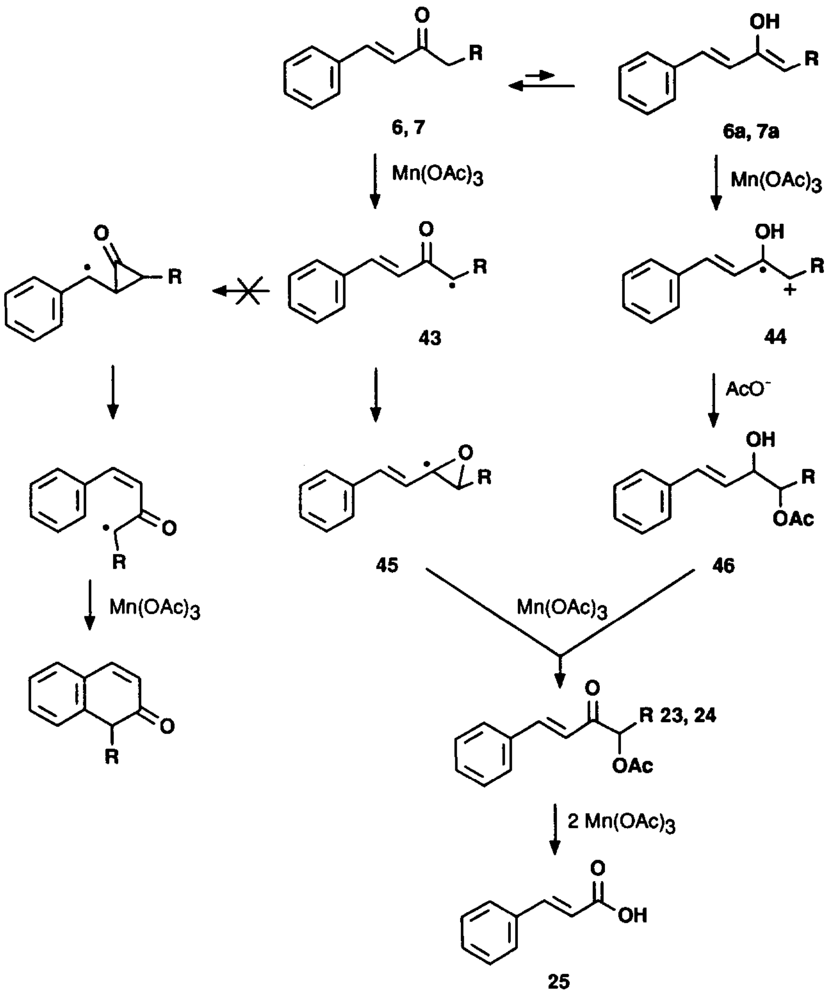
5-*exo-trig* cyclization to cyclopentane derivatives **18-20** without trace of aromatic substitution or olefin oxidation. On the contrary, substrate **4**, for which the process of 4-*exo-trig* cyclization of intermediate radicals **38** is expected to be slow[15], is oxidized less efficiently than **1** and **5** and affords oxidation products of the double bond and of malonic C-H bond. The slow rate k_{c4ex} for the 4-*exo-trig* cylization to give **39** (and, after oxidation, **16**) is further confirmed by the isolation of compound **17** arising from the 5-*endo-trig* cylization to **40**. From the ratio of products **16** and **17** a value of 4 can be deduced for the ratio k_{c4ex}/k_{c5en} for radical **38**.





The dominant effect of the stabilization of benzyl radicals to favor the cyclization of **38** and **41** has previously been observed[15,8]. However in the present case, also the 5-*endo-trig* addition rate appears to be increased, despite the presence of steric hindrance due to the phenyl group, further supporting the electrophlic properties of malonyl radicals in the addition to both α and β styrenic carbon atoms.

The fact that processes of intramolecular homolytic aromatic substitution were not observed in the oxidation of compounds **6** and **7** points to the absence of *trans-cis* isomerization of radicals **43** (Scheme 4). This outcome may be related to a lower rate of addition to the styrenic double bond due to the less favorable interaction in the transition state between the electrophilic malonyl radicals and the less electron rich double bond. However, the easy formation of α-acetoxylated products and the efficient further oxidation to cinnamic acid indicate a specific behaviour of radicals **43** compared with the unconjugated ones or the involvement of different intermediates. The behaviour observed in this work is fully consistent with previous results of $Mn(OAc)_3$ oxidation of α,β-unsaturated ketones, where α-acetoxylation products were efficiently obtained under specific conditions[16]. On the contrary, non conjugated ketones undergo the oxidative α-acetoxylation with remarkably lower efficiency.[17]



Scheme 4

Two alternatives are possible for these Mn(III) induced α-oxygenations : a) intramolecular 1,3-addition of the oxygen-centered enol radical to the double bond with formation of conjugated α-oxiranyl radical **45**, followed by easy oxidation of this strongly nucleophilic radical with subsequent nucleophilic attack by the acetate ion, or b) formation of the radical cation of the conjugated enol (**44**) followed by addition of acetate ion and further oxidation of α-hydroxyalkyl radicals **46** (Scheme 4). The reported irreversibility of the ring-opening of oxiranyl radical to α-carbonylalkyl radicals[18] seem to exclude the first hypothesis, despite the benzylic stabilization of the radical **45**. Moreover, the higher proclivity for oxidative α-cleavage of compound **7** relative to **6** suggests a key role of the enolization induced by the side-chain carboxylic acid and supports the involvement of conjugated radical cation intermediates.

Mn(III) is known to work as an efficient electron-transfer agent towards electron rich aromatics[19] or alkenes[20], and we can expect that the low ionization potentials of electron rich conjugated enol forms of α,β-unsaturated carbonyl compounds can promote efficient outer-sphere electron-transfer processes to produce highly stabilized radical cations even with the weak oxidant Mn(III) acetate. Addition of acetate ions to the conjugated radical cation and further oxidation of the resulting strongly reducing tertiary α-hydroxyalkyl radicals can account for the α-acetoxylation products. The electron-withdrawing properties of the acetate substituent is probably sufficient to prevent further oxidation in simple conjugated carbonyl derivatives, but can not inhibit the fragmentation observed in compounds **6** and **7**, owing to the extensive conjugation of the enol form of these derivatives.

Finally, the effect of additives ($Cu(OAc)_2$, NaOAc, etc.) on product distribution can be rationalized by the change of trapping efficiency of carbon free-radical intermediates by metal oxidants. So, the increase of the ratio R = [**10**]/[**8**] upon addition of $Cu(OAc)_2$ parallel the results at higher concentrations of Mn(III) acetate (Fig. 1, (a)) and at lower concentrations of sodium acetate (Fig. 1, (b)). The trend follows the increase of the redox potential of the Mn(III)/Mn(II) couple or the change to a more efficient oxidant of carbon radicals (Cu(II) vs. Mn(III)). On the contrary, the more selective oxidation of **1** to **12** by FEP/MeCN/Ac_2O in the presence of $Cu(OAc)_2$ than in its absence (Table 2, run 9 vs. 8) is marginally due to an higher efficiency of trapping of benzyl radicals. $Cu(OAc)_2$ in this medium has probably the effect to increase the selectivity of the initiation step (oxidation of double bond of **1** by FEP through an electron transfer mechanism), preventing **12** from further oxidation by buffering the strong acidity of the medium.

Experimental Section

General Methods

Melting points were obtained on a Hoover capillary melting point apparatus and are uncorrected. Boiling points were determined in a short path distillation apparatus (Büchi). ^1H and ^{13}C-NMR spectra were obtained in $CDCl_3$ on a Bruker AM 250 or AM 300 spectrometers; the data are in ppm relative to tetramethylsilane. Mass spectra (MS) were obtained at 70 eV on a Hitachi RMU-6 or VG ZAB. GC-MS analyses were obtained on a Finnigan TSQ 70 GC-MS spectrometer equipped with a SE 54 coated fused silica capillary column (30 m x 0.22 mm i.d.) with helium as a carrier gas. Quantitative gas chromatographic analyses for the determination of conversions and isomer distributions were performed by the internal standard method on a DANI 6500 HR capillary gas chromatograph, equipped with a PTV injector, a WSCOT capillary column (25 m x 0.22 mm i.d.) coated with polydimethylsiloxane (CP-Sil 5, film thickness 1 μm), FID detector, hydrogen as carrier gas, and temperature programmed from 50 °C to 190-250 °C at 10°/min. Integration of chromatographic traces was carried out using a Spectra Physics SP 4200 computing integrator or a PC computer using the Chromstar software from Bruker. HPLC analyses were performed on a Bruker LC 21-51 instrument equipped with an autosample injection device under isocratic conditions using a Si 60 column (5 μm, 20 x 0.25 cm i.d. or 5 μm, 20 x 1 cm i.d.) (Merck) and a mixture of hexane : ethyl acetate (95 : 5 to 70 : 30) as eluent at a flow rate of 1 mL/min and UV detection at 254 nm. Preparative separations were carried out on silica gel 60 (230-400 mesh, Merck) using the flash chromatography technique. In the case of high yield reactions, the residue was directly crystallized from pentane/diethyl ether or distilled.

Materials

Mn(III) acetate dihydrate (Fluka) was tested by iodometric titration for purity. Anhydrous Mn(III) acetate was obtained from Mn(II) nitrate and acetic anhydride[21]. Acetic acid and acetonitrile were freshly distilled from P_2O_5. Compound **7** (m.p. 145 °C) was prepared by basic condensation of benzaldehyde and levulinic acid. Benzalacetone (**6**) and cinnamic acid (**25**) were commercial products. Compounds **21a**, **21b** and **22** were synthesized from **4** and **5**, respectively, by Br_2 addition and acetate substitution. Compounds **23** and **24** were synthesized from **6** and **7** in 80% and 73% yield by bromination with NBS and nucleophilic substitution with potassium acetate. Starting materials **1**, **2** and **3** were synthesized from cinnamyl or 2-methylcinnamyl chloride (8 : 2 mixture of E and Z isomers) by reaction with the anion of diethyl malonate (prepared from NaH in THF), followed by stirring and refluxing the mixture under N_2 for 12 h. The resulting mixture was concentrated, dissolved in the minimum amount of diethyl ether, and, after addition of water, the organic layer separated and the water extracted with diethyl ether. The combined extracts were washed with water, dried, concentrated and distilled through a Vigreux column under vacuum. Compounds 2 and 3 were separated by preparative gas chromatography.

Diethyl cynnamylmalonate (1) : b.p. 120 °C/0.3 mmHg; UV $\lambda_{max}(\epsilon)$: 250 (18800), 205 (22500); ^{1}H-NMR ($CDCl_3$, δ) : 7.2-7.4 (m, 4H, Ar), 6.48 (dt, 1H, CH-Ar, J = 16 and 1.5 Hz), 6.15 (dt, 1H, =$C\underline{H}$-CH_2, J = 16 and 8 Hz), 4.2 (q, 4H), 3.49 (t, 1H, CH_2-$C\underline{H}$-, J = 8 Hz), 2.8 (ddt, =CH-$C\underline{H}_2$-, J = 8, 8 and 1.5 Hz), 1.26 (t, 6H, Me); MS m/z : 276 ($M^{\cdot+}$,40), 230 (9), 203 (8), 202 (48), 157 (20), 130 (14), 129 (100), 128 (33), 117 (46), 115 (28), 91 (14).

Diethyl (E) 3-Phenyl-2-methyl-2-propenylmalonate (2) : b.p. 125 °C/0.3 mmHg; ^{1}H-NMR ($CDCl_3$, δ) : 7.1-7.4 (m, 4H, Ar), 6.33 (s broad, 1H, CH=), 4.21 (q, 4H), 3.66 (t, 1H, CH-CO, J = 7.5 Hz), 2.78 (d, 2H, =C-CH_2, J = 7.5 Hz), 1.87 (d, 3H, CH_3-C=, J = 1 Hz), 28 (t, 6H); MS m/z : 290 ($M^{\cdot+}$,43), 244 (55), 198 (78), 171 (27), 170 (40), 143 (100), 142 (28), 131 (17), 129 (23), 128 (21), 115 (16), 91 (16).

Diethyl (Z) 3-Phenyl-2-methyl-2-propenylmalonate (3) : b.p. 125 °C/0.3 mmHg; ^{1}H-NMR ($CDCl_3$, δ) : 7.2-7.4 (m, 4H, Ar), 6.39 (s broad, 1H, Ar-CH=), 4.21 (q,4H), 3.57 (t, 1H, CH-CO, J = 7.5 Hz), 2.91 (d, 2H, =C-CH_2-, J = 7.5 Hz), 1.89 (d, 3H, C=CH_2, J = 1.5 Hz), 1.26 (t, 6H); MS m/z : 290 ($M^{\cdot+}$,41), 244 (56), 198 (78), 171 (27), 170 (38), 143 (100), 142 (26), 131 (17), 129 (23), 128 (20), 115 (14), 91 (10).

Diethyl 4-phenyl-3-butenylmalonate (4). Synthesized via benzylic bromination with NBS (0.1 M in CCl_4 in the presence of 7% AIBN, reflux for 5h) and careful distillation under vacuum and flash chromatography. B.p. 135 °C/0.5 mmHg; ^{1}H-NMR ($CDCl_3$, δ) : 7.1-7.4 (m, 4H, Ar), 6.40 (dt, 1H, Ar-CH=, J = 15.8 and 1 Hz), 6.16 (dt, 1H, Ar-C=CH-, J =15.8 and 6.8 Hz), 4.20 (q,4H), 3.40 (t, 1H, CH-CO, J = 7.5 Hz), 2.27 (tdd, 2H, =CH-CH_2-, J = 7.0, 6.8 and 1 Hz), 2.09 (dt, 2H, CH-CH_2-, J = 7.5 and 7.0 Hz), 1.26 (t, 6H); MS m/z : 290 (11), 245 (4), 199 (5), 131 (10), 130 (100), 129 (17), 115 (10).

Diethyl 5-phenyl-4-pentenylmalonate (5). Synthetized as **4**. B.p. 142 °C/0.3 mmHg; ^{1}H-NMR ($CDCl_3$, δ) : 7.1-7.4 (m, 4H, Ar), 6.39 (dt, 1H, =CH, J = 15.5 and 1,5 Hz), 6.18 (dt, 1H, =CH, J = 15.5 and 6.6 Hz), 4.2 (q, 4H), 3.35 (t, 1H, J = 7.8 Hz), 2.25 (ddt, 2H, =CH-$C\underline{H}_2$-, J = 7.7, 6.6 and 1.5 Hz), 1.96 (dt, 2H, J = 7.8 and 7.8 Hz), 1.52 (tt, 2H, J = 7.8 and 7.8 Hz), 1.27 (t, 3H); MS m/z : 304 ($M^{\cdot+}$,36), 258 (16), 212 (11), 185 (30), 184 (100), 173 (46), 160 (20), 130 (40), 129 (25), 128 (10), 115(21), 91 (14).

General procedure for reactions between 1 - 7 and Mn(III) acetate.

Acetic acid (15 mL) was added in a two-necked flask equipped with reflux condenser, a N_2 inlet device and magnetic stirring bar. N_2 was flushed for 5 min, then Mn(III) acetate was added once and the resulting slurry was stirred and heated at 60 °C. A solution of **1** (5.0 mmol) in acetic acid (2 mL) was added and the mixture maintained at 60 °C until the color faded or for 12 h, when the mixture remained dark. Biphenyl was added as internal standard, a sample (0.1 mL) was withdrawn from the solution and added to diethyl ether (1 mL) and the suspension filtrated through silica gel (0.3 g), eluting further with diethyl ether (1 mL). The resulting solution was analyzed by GC or HPLC for the determination of the conversion of **1** and the distribution of products. The remaining mixture was evaporated at 30 mmHg, the residue taken up with ethyl acetate and water (10 mL), the layers separated and the aqueous layer extracted twice with ethyl acetate (10 mL). The combined extracts were washed with 10% $NaHCO_3$ and water, dried, evaporated and flash chromatographed to isolate compounds **8-25**. When the first separation did not succeed, further purification by preparative HPLC was made to obtain analytically pure samples of products.

1,1-diethoxycarbonyl-3,4-dihydronaphthalene (8). b.p. 111 °C/0.5 mmHg. IR $\nu_{max}(cm^{-1})$: 1735 (C=O); ^{1}H-NMR ($CDCl_3$, δ): 1.25 (t, 3H, $OCH_2C\underline{H}_3$), 3.03 (dd, 2H, $=CH-C\underline{H}_2$, J = 4 and 1.5 Hz), 4.3 (q, 4H, $OC\underline{H}_2CH_3$), 6.00 (dt, 1H, $ArCH=C\underline{H}-$, J = 8.5 and 4 Hz), 6.46 (dt, 1H, $Ar-C\underline{H}=$, J = 8.5 and 1.5 Hz), 7.09 (m, 1H, Ar), 7.2-7.4 (m, 3H, Ar). MS m/z: 274 ($M^{\cdot+}$,24), 202 (14), 201 (100), 200 (53), 173 (25), 172 (18), 156 (14), 155 (98), 129 (91), 128 (46), 127 (35).

1,1-diethoxycarbonyl-3-methyl-3,4-dihydronaphthalene (9). b.p. 118 °C/0.5 mmHg; IR $\nu_{max}(cm^{-1})$: 1730-40 (C=O); ^{1}H-NMR ($CDCl_3$, δ): 1.24 (t, 3H, $OCH_2C\underline{H}_3$), 1.93 (q, 3H, Me, J = 1.4 Hz), 2.92 (q, 2H, $=C-CH_2$, J = 1.4 Hz), 4.1 - 4.3 (m, 4H, $OC\underline{H}_2CH_3$), 6.21 (sextet, 1H, =CH-, J = 1.4 Hz), 7.02 (dd, 1H, Ar, J = 7 and 1 Hz), 7.1-7.3 (m, 3H, Ar); MS m/z: 288 ($M^{\cdot+}$, 8), 215 (50), 214 (45), 169 (40), 143 (100), 142 (30), 141 (52), 128 (25), 115 (20).

Eritro 1,1-diethoxycarbonyl-2-acetoxybenzylcyclopropane (10a). Liquid; IR $\nu_{max}(cm^{-1})$: 1735; ^{1}H-NMR ($CDCl_3$, δ): 7.2-7.4 (m, 5H, Ar), 5.73 (d, 1H, $ArC\underline{H}-$, J = 7 Hz), 4.1 - 4.3 (m, 4H, $OC\underline{H}_2CH_3$), 2.40 (ddd, 1H, $C\underline{H}-CH_2-$, J = 7.0, 7.1 and 9.1 Hz), 2.02 (s, 3H, $OCOCH_3$), 1.92 (dd, 1H, $C\underline{H}_2CH-$, J = 4.9 and 7.1 Hz), 1.51 (dd, 1H, $C\underline{H}_2-CH$, J = 4.9 and 9.1 Hz), 1.24 and 1.17 (2t, 6H, $OCH_2C\underline{H}_3$); MS m/z : $M^{\cdot+}$ (absent), 292 (11), 274 (33), 247 (23), 245 (21), 228 (27), 218 (41), 200 (31), 199 (38), 173 (100), 127 (34), 120 (44), 115 (21), 105 (38), 91 (16); Anal. Calcd. for $C_{18}H_{22}O_6$: C 64.66, H 6.63; found : C 64.8, H = 6.7.

Threo 1,1-diethoxycarbonyl-2-acetoxybenzylcyclopropane (10b). Liquid; IR $\nu_{max}(cm^{-1})$: 1735; ^{1}H-NMR ($CDCl_3$, δ): 7.1-7.4 (m, 5H, Ar), 5.31 (d, 1H, $ArC\underline{H}-$, J = 10.2 Hz), 4.0 - 4.2 (m, 4H, $OC\underline{H}_2CH_3$), 2.48 (ddd, 1H, $C\underline{H}-CH_2-$, J = 7.5, 9.5 and 10.2 Hz), 1.98 (s, 3H, $OCOCH_3$), 1.56 (dd, 1H, $C\underline{H}_2CH-$, J = 5.0 and 7.5 Hz), 1.32 (dd, 1H, $C\underline{H}_2-CH$, J = 5.0 and 9.5 Hz), 1.21 and 1.18 (2t, 6H, $OCH_2C\underline{H}_3$); MS m/z : $M^{\cdot+}$ (absent), 292 (4), 274 (11), 247 (13), 228 (17), 218 (25), 200 (13), 199 (14), 173 (100), 127 (37), 120 (62), 115 (15), 105 (25), 99 (16), 91 (16); Anal. Calcd. for $C_{18}H_{22}O_6$: C 64.66, H 6.63; found : C 64.6, H = 6.8.

General procedure for the oxidation of 1 by FEP in AN.

In a two necked flask under N_2, FEP (10.3 g, 20 mmol) was weighed with moisture exclusion; a magnetic stirring bar was added and the flask cooled at 0°C and flushed with N_2. Acetonitrile (20 mL) was added at 0-5 °C under magnetic stirring. After 15 min, the additive and a solution of **1** (2.76 g, 10 mol) in AN (5 mL) was added once in sequence. The cooling bath was removed and the mixture was kept at room temperature (20 ± 2 °C) for 2h. The solution was poured into a mixture of water and diethyl ether (5 and 15 mL, respectively), the phases separated and the water extracted twice with diethyl ether (10 mL). The organic phase was dried on $CaCl_2$ and concentrated. The residue was separated by flash chromatography (hexane/ethyl acetate from 9 : 1 to 1 : 1). After small amounts of **1** (5%) and **8** (12%), the following compounds were isolated : **(10c)** - (28% yield); IR ν_{max}(cm^{-1}) : 1735, 1780; UV (EtOH), $\lambda_{max}(\epsilon)$: 209 (8000); ^{1}H-NMR : 1.34 (dd, 1H), 1.96 (dd, 1H, J = 6 and 7.5 Hz), 3.07 (dd, 1H, J = 6, 7.5 and 10 Hz), 4.3 (q, 2H), 5.77 (d, 1H, J = 6 Hz), 7.2 - 7.5 (m, 5H); ^{13}C-NMR : 11.09 (q, $OCH_2\underline{C}H_3$), 18.50 (t, CH-$\underline{C}H_2$, $J_{C\text{-}H}$ = 162 Hz), 29.68 (s, $\underline{C}$-(COOEt)CO-), 32.23 (d, PhCH-$\underline{C}$H-, $J_{C\text{-}H}$= 180 Hz), 62.10 (t, $O\underline{C}H_2$), 77.17 (d, Ar-$\underline{C}$H, $J_{C\text{-}H}$= 154 Hz), 125.36, 128.51 and 128.77 (d, arom.CH), 136.30 (s, arom. -C-), 166.10 (s, COO-), 170.14 (s, COOEt); MS m/z : 246 (M$^{\cdot+}$, 70), 218 (28), 217 (30), 200 (12), 173 (32), 172 (36), 145 (27), 129 (37), 127 (100), 105 (18), 99 (23), 85 (17), 77 (8). Elemental Anal. calcd. for $C_{14}H_{14}O_4$: C 68.28, H 5.73; found : C 68.1, H 5.9. **(10d)**; (20% yield); UV (EtOH) $\lambda_{max}(\epsilon)$: 209 (7800); IR ν_{max}(cm^{-1}) : 1735, 1780; ^{1}H-NMR : 1.56 (dd, 1H, J = 5 and 5.5 Hz), 2.16 (dd, 1H, J = 5 and 7.5 Hz), 2.72 (dd, 1H, J = 5.5 and 7.5 Hz), 4.3 (q, 2H), 5.29 (s, 1H), 7.2 - 7.5 (m, 5H,); ^{13}C-NMR : 11.09 (q, $OCH_2\underline{C}H_3$), 20.79 (t, CH-$\underline{C}H_2$, $J_{C\text{-}H}$= 160 Hz), 29.97 (s, $\underline{C}$-(COOEt)CO-), 34.52 (d, PhCH-$\underline{C}$H-, $J_{C\text{-}H}$= 178 Hz), 62.11 (t, $O\underline{C}H_2$), 79.15 (d, Ar-$\underline{C}$H, $J_{C\text{-}H}$= 152 Hz), 125.60, 129.09 and 129.17 (d, arom.CH), 138.68 (s, arom. -C-), 166.11 (s, COO-), 170.18 (s, COOEt). MS m/z : 246 (M$^{\cdot+}$, 65), 218 (18), 217 (19), 200 (11), 173 (21), 172 (20), 145 (19), 129 (100), 126 (32), 127 (45), 105 (10), 85 (12), 77 (8). Elemental Anal. calcd. for $C_{14}H_{14}O_4$: C 68.28, H 5.73; found : C 68.2, H 5.7.

α-(3-phenyl-2-oxopropyl)malonate (11) (6%). b.p. 112-3/0.05 mmHg; ^{1}H-NMR ($CDCl_3$, δ) : 7.2 -7.4 (m, 5H, Ar), 4.17 (q, 4H), 3.84 (t, 1H, CH(CO)), 3.26 (s, 2H, $ArCH_2$), 3.06 (d, 2H, CH-C$\underline{H_2}$-), 1.26 (t, 3H). MS m/z : 292 (M$^{\cdot+}$,8), 247 (20), 201 (57), 173 (83), 155 (22), 127 (83), 99 (33), 91 (100), 65 (22), 55 (43). Elemental Anal. calcd. for $C_{16}H_{20}O_5$: C 65.74, H 6.90; found : C 65.6, H 7.1.

Oxidation of 1 at variable Mn(III) or Sodium Acetate Concentration.

Following the above reported general procedure, **1** (2.0 mmol) in acetic acid (1 mL) was added to a solution of $Mn(OAc)_3$ (0.03-0.2 M in experiments at variable Mn(III) concentrations and 0.2 M in experiments at variable NaOAc concentrations) and sodium acetate (0.05-0.4 M) in acetic acid at 60 °C. The mixture was stirred for 30-10 min depending on the Mn(III) concentration, then treated as above with water and ethyl acetate. The organic phase was dried and directly analyzed by g.l.c. for the quantitative determination of the yield of **10a**, **10b** and **8** by using the internal standard method. The conversion of **1** was in all cases less then 15%. The results obtained are plotted in Figure 1 as (**10a** + **10b**)/**8** ratio against the Mn(III) concentration (curve a) and NaOAc concentration (curve b).

Anodic oxidation of 1 induced by Mn(III) Acetate.

A solution of $Mn(OAc)_3\cdot 4H_2O$ (0.5 mmol) and **1** (4.5 mmol) in AcOH (12 ml) containing KOAc (10 mmol) was introduced in a H-shaped divided cell under an N_2 with magnetic stirring, and the apparatus was heated at 70 ± 2 °C. A graphite rod (2.5 cm^2) and a platinum wire were used as anode and cathode, respectively. Electrolysis of the solution was carried out under constant current intensity (I = 25 mA) by using 2 F per mol of **1** (10 h). The anolyte was then subjected to the extractive work-up and purified as described before. The conversion of **1** and the yield of **8** and **10** are reported in Table 1 (run 6).

Oxidation of 1 by FEP in acetonitrile/acetic anhydride.

FEP (3.0 g, 5.8 mmol) was weighed under N_2 in a flask cooled at 0 °C and acetonitrile (25 mL) was added once under stirring. Ater stirring for 10 min. acetic anhydride (5.4 mL) was added in 15 min., then the malonate **1** (801 mg, 2.9 mmol) and $Cu(OAc)_2$ (58 mg, 0.29 mmol) were added and the mixture allowed to return to room temperature in 1 h. The solvent was removed by evaporation in vacuo at 20 °C to 5 ml. A mixture of diethyl ether and water (50 mL) was added, the phases separated and the water extracted with diethyl ether (2 x 10 mL). The combined organic extracts were washed with 10% $NaHCO_3$ solution and water, then dried on Na_2SO_4. After evaporation, the residue (810 mg) was chromatographed on SiO_2 with hexane/ethyl acetate (9 : 1) to give mixtures of isomers **12** (inseparable by HPLC and GC). Their structures were assigned on the basis of the following data of the mixture : IR $\nu_{max}(cm^{-1})$: 1735 and 1780; ^{1}H-NMR (four doublets at 5.81 (J = 6 Hz), 5.85 (J = 7.5 Hz), 5.98 (3.5 Hz) and 6.06 (J = 4 Hz) for benzylic hydrogens and four singlets at 1.86, 1.90, 1.95, 1.99 for methyl of acetate groups); The unresolved peaks in GC-MS show very similar MS spectra : m/z 306 ($M^{\cdot+}$, very small), 264 (5), 247 (15), 246 (25), 201 (18), 200 (11), 173 (24), 157 (29), 149 (35), 129 (18), 112 (14), 111 (29), 107 (100), 105 (16)).

The four isomers **12** were decarboxylated to two isomers **14** (75% yield) by heating at 140°C for 12 h in dimethylformamide containing an equimolecular amount of lithium iodide.

Treo 5-acetoxybenzylbutyrolactone (14a) : b.p. 132-4 °C/0.01 mmHg; IR $\nu_{max}(cm^{-1})$: 1735 and 1780; ^{1}H-NMR : 7.3 -7.4 (m, 5H, Ar), 5.83 (d, 1H, ArCH-, J = 6.5 Hz), 4.79 (ddd, 1H, J = 6.5, 6.5 and 6.7 Hz), 2.49 (dd, 1H, CHCO, J = 15.5 and 7.5 Hz), 2.39 (ddd, 1H, CHCO, J = 15.5, 9.5 and 6.0), 2.12 (s, 3H, OCOMe), 2.02 (m, 2H, $C\underline{H}_2CH$); MS m/z : 234 ($M^{\cdot+}$, 0.5), 192 (4), 174 (18), 149 (80), 108 (11), 107 (100), 91 (13), 85 (66), 79 (14), 77 (14), 43 (75).

Eritro 5-acetoxybenzylbutyrolactone (14b) : b.p. 131-2 °C/0.01 mmHg; IR $\nu_{max}(cm^{-1})$: 1735 and 1780; ^{1}H-NMR : 7.3 -7.4 (m, 5H, Ar), 5.98 (d, 1H, ArCH-, J = 3.5 Hz), 4.80 (q, 1H), 2.34 (m, 2H, CH_2CO), 2.42 (s, 3H, OCOMe), 1.9-2.1 (m, 2H, $C\underline{H}_2CH$); MS m/z : 234 ($M^{\cdot+}$, 0.5), 192 (4), 174 (18), 149 (80), 108 (11), 107 (100), 91 (13), 85 (66), 79 (14), 77 (14), 43 (75).

Oxidation of 1 by $Mn(OAc)_3$ in the presence of styrene

Two stock solutions (50 mL, 0.50 M) of **1** and styrene in acetic acid were prepared. Appropriate amounts of these solutions (2.0, and 2-6 mL, respectively) were mixed together under N_2 at 20 °C and the resulting solution was taken up in 20 mL of acetic acid and heated at 60 °C. Then $Mn(OAc)_3$ (0.3 mmol) was added once with stirring and the reaction was run for 6 h. GC analyses of the crude reaction mixture give the ratio R = [**15**]/([**8**] + [**10a**] + [**10b**]) which is plotted against the initial styrene concentration in Fig. 2. Least square analysis of these data provides a ratio $k_a/k_c = 210 \pm 11$.

In a parallel preparative experiment a mixture of $Mn(OAc)_3$ (20 mmol), styrene (10 mmol) and **1** (10 mmol) in acetic acid was heated at 60 °C for 13 h. Acetic acid was distilled at 60 °C and 100 mmHg and the residue dissolved in water (20 mL) and diethyl ether (10 mL) under stirring. The water layer was extracted with Et_2O (3 x 10 mL) and the combined extracts were washed with 10% Na_2CO_3 solution (2 x 20 mL) and water. The solvent was evaporated and the residue flash chromatographed on SiO_2 (100 g) (hexane/ethyl acetate 9:1) to obtain **15**. All attempt to separate the four isomers of compound **15** by HPLC were unsuccessful; therefore, their structures were assigned on the basis of elemental analysis of their mixture (calcd. for $C_{26}H_{30}O_6$: C 71.21, H 6.90, O 21.89; found : C 71.1, H 7.0); IR $\nu_{max}(cm^{-1})$: 1735; GC-MS spectra (four peaks showing very similar patterns and highest ion at m/z 378, corresponding to the loss of acetic acid from molecular ion of **15**); MS m/e (first isomer eluted) : 378 ($M^{\cdot+}$-AcOH, 56), 333 (2.5), 305 (34), 304 (100), 275 (15), 258 (10), 231 (75), 215 (22), 173 (23), 141 (20), 115 (19), 107 (30), 91 (49). (second eluted) : 378 ($M^{\cdot+}$-AcOH, 39), 304 (100), 231 (49), 215 (12), 207 (185), 169 (10), 107 (18), 91 (41);

(third eluted) : 378 ($M^{\cdot+}$-AcOH, 49), 333 (11), 305 (28), 304 (100), 275 (19), 258 (12), 231 (80), 215 (21), 173 (20), 141 (22), 129 (14), 121 (14), 115 (26), 107 (27), 105 (21), 91 (58), (fourth eluted) : 378 ($M^{\cdot+}$-AcOH, 52), 333 (5), 305 (24), 304 (95), 275 (18), 231 (100), 215 (27), 173 (21), 141 (18), 115 (33), 107 (37), 105 (23), 91 (71); NMR spectra (four doublets at 5.81, 5.85, 5.98 and 6.60 for benzylic hydrogens and four singlets at 1.86, 1.90, 1.95, 1.99 for methyl of acetate groups). The isomer distribution in the crude mixture was 24 : 5.4 : 67.5 : 3.1, statistically coincident with those obtained in experiments with variable concentration of styrene.

Oxidation of 4 by $Mn(OAc)_3$. Following the general procedure used for **1**, the Mn(III) oxidation of **4** afforded a residue which was chromatographed on SiO_2 using mixtures of hexane/ethyl acetate (9:1 - 7:3) giving samples of the following compounds, in order of elution :

2-Phenyl-3,3-diethossicarbonyl- cyclopentene (16) (6%) IR ν_{max}(cm^{-1}) : 1735. ^{1}H-NMR ($CDCl_3$, δ): 7.2-7.4 (m, 5H, Ar), 5.86 (ddd, 1H, C$\underline{H}$=, J = 6.5, 4.6 and 2.3 Hz), 5.70 (ddd, 1H, C$\underline{H}$=, J = 6.5, 4.6 and 2.3 Hz), 4.87 (ddd, 1H, J = 1, 2,3, 4.6 Hz), 4.1-4.3 (m, 2H), 3.69 and 3.39 (dq, 2H, OCH_2), 3.50 (ddd, 1H, J = 16.6, 4.7, 2.4 Hz), 2.78 (ddd, 1H, J = 16.6, 2.4, 1 Hz), 1.26 (t,3H), 0.82 (t,3H); MS m/z : 288 ($M^{\cdot+}$, 40%), 261 (6), 214 (100), 169 (8), 141 (12).

1-Ethossicarbonyl-4-phenyl-3-oxabiciclo[3,2,0]eptan-2-one (17a) (26%) IR ν_{max}(cm^{-1}) : 1735 and 1780; ^{1}H-NMR ($CDCl_3$, δ): 7.2-7.4 (m, 5H, Ar), 5.86 (ddd, 1H, C$\underline{H}$=, J = 6.5, 4.6 and 2.3 Hz), 5.70 (ddd, 1H, C$\underline{H}$=, J = 6.5, 4.6 and 2.3 Hz), 4.87 (ddd, 1H, J = 1, 2,3, 4.6 Hz), 4.1-4.3 (m, 2H), 3.69 and 3.39 (dq, 2H, OCH_2), 3.50 (ddd, 1H, J = 16.6, 4.7, 2.4 Hz), 2.78 (ddd, 1H, J = 16.6, 2.4, 1 Hz), 1.26 (t,3H), 0.82 (t,3H); MS m/z : 260 ($M^{\cdot+}$, 3), 215 (3), 173 (100), 127 (20). Lactone isomer **17b** was detected in traces (2% estimated by GC-MS); MS m/z : 260 ($M^{\cdot+}$, 1), 215 (8), 173 (100), 127 (33). Compound **21b** (27%) and **21a** (15%) were identified by comparison (IR, NMR, MS) with authentic samples.

Oxidation of 5 by $Mn(OAc)_3$. Following the general procedure used for **1**, the Mn(III) oxidation of **5** afforded a residue which was chromatographed on SiO_2 using mixtures of hexane/ethyl acetate (7 : 3) giving pure samples of the following compounds, in order of elution: **Lactone 18a**. liquid; IR ν_{max}(cm^{-1}) : 1735 and 1780; ^{1}H-NMR ($CDCl_3$, δ): 7.3-7.4 (m, 5H, Ar), 5.05 (d, 1H, ArC$\underline{H}$-, J = 4.2 Hz), 4.17 (q, 2H, OC$\underline{H}_2$CH$_3$), 3.13 (m, 1H, ArCH-C$\underline{H}$), 2.45 (ddd, 1H, C$\underline{H}$-COOEt, J = 13.6, 10.5, 6.5 Hz), 2.32 (dddd, 1H, C$\underline{H}$-COOEt, J = 13.6, 7.5, 2.5 and 1.0 Hz), 1.89 - 2.1 (m, 3H, aliph), 1.66 - 1.83 (m, 1H, aliph),0 1.20 (t, 3H, OCH$_2$C$\underline{H}_3$); MS m/z : 274 ($M^{\cdot+}$,46), 246 (22), 200 (18), 184 (24), 141 (45), 140 (100), 112 (26), 95 (24), 91 (13), 67 (25).

Lactone 18b. (detected only by GC-MS on crude reaction mixture); MS m/z : 274 ($M^{\cdot+}$,38), 246 (31), 200 (42), 141 (100), 140 (18), 112 (12), 105 (18), 95 (36), 67 (16).

1,1-dicarbethoxy-2-acetoxybenzylcyclopentane (19). IR ν_{max}(cm^{-1}) : 1735; ^{1}H-NMR ($CDCl_3$, δ): 7.2-7.4 (m, 5H, Ar), 6.12 (d, 1H, ArC$\underline{H}$-, J = 3.0 Hz), 4.16 (q, 2H), 3.09 (m, 1H, ArCH-C$\underline{H}$), 1.4 - 2.3 (m, 6H, aliph), 1.22 (t, 3H, OCH$_2$C$\underline{H}_3$); MS m/z : 362 ($M^{\cdot+}$,6), 319 (46), 273 (100), 199 (10), 155 (9), 141 (12), 105 (15), 67 (10).

1,1-dicarbethoxy-2-benzoylcyclopentane (20). IR ν_{max}(cm^{-1}) : 1690 and 1735; ^{1}H-NMR ($CDCl_3$, δ): 7.2-7.4 (m, 5H, Ar), 4.8 (dd, 1H), 4.2 (q, 4H), 1.6-2.4 (m, 6H, aliph), 1.20 (t, 6H, OCH$_2$C$\underline{H}_3$); MS m/z : 318 ($M^{\cdot+}$,8), 273 (10), 245 (6), 213 (11), 199 (8), 140 (6), 105 (100), 77 (19), 67 (10).

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