

nation from the cationic amine moiety of **3** to exert the push,<sup>21,23,33</sup> the slope of a Bronsted-type plot for  $k_{-1}/k_3$  must be  $\beta_{-1}$ . For the reaction of **2** the value found of the slope of this plot (not shown) is  $-0.54$ , lower than that determined for **1**. Nevertheless this value must be taken with care due to the errors involved in both the determination of  $k_1$  (and therefore  $k_{-1}/k_3$ ) and the estimation of  $\beta_N$  ( $=0 \pm 0.1$ ) for  $k_3$ .<sup>33</sup> Assuming  $\beta_{-1}$  is ca.  $-0.7$ , one concludes that the effective charge on the nitrogen atom of **3** is  $(\beta_1 - \beta_{-1}) = +0.9$ <sup>33</sup> and that on the nitrogen atom of the transition state for the first step is  $+0.2$ .

The rate equations, the reactivity difference found in the aminolysis of both substrates, and the structure-re-

activity relations are in accord with the proposed reaction scheme, but probably more data are needed to confirm this mechanism.

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**Registry No.** **1**, 3278-38-4; **2**, 99358-06-2; piperidine, 110-89-4; piperazine, 110-85-0; 1-( $\beta$ -hydroxyethyl)piperazine, 103-76-4; morpholine, 110-91-8; 1-formylpiperazine, 7755-92-2; piperazinium ion, 22044-09-3.

## Synthesis of Substituted Tetrahydronaphthalenes by Mn(III), Ce(IV), and Fe(III) Oxidation of Substituted Diethyl $\alpha$ -Benzylmalonates in the Presence of Olefins

Attilio Citterio,\* Roberto Sebastiano, and Antonio Marion

Dipartimento di Chimica del Politecnico, P.za L. da Vinci, 32, 20133 Milano, Italy

Roberto Santi

Istituto G. Donegani, Via Fauser 4, 28100 Novara, Italy

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The oxidation of substituted diethyl  $\alpha$ -benzylmalonates (**1a-m**) by manganese(III) acetate in acetic acid, cerium(IV) ammonium nitrate in methanol, or iron(III) perchlorate in acetonitrile in the presence of substituted olefins **2a-u** was investigated. The results are consistent with a common mechanism. It involves selective generation of malonyl radicals from high-valent metal malonyl complexes, their addition to the olefin, and competition of the adduct radical between intramolecular cyclization to produce highly functionalized tetrahydronaphthalenes (**3**) and oxidation by metal salt to give mainly  $\gamma$ -lactones (**5**). Several electron-withdrawing and releasing substituents on the aromatic ring and on the olefin can be successfully used in the synthesis of **3** without olefin telomerization. The influence of metal and olefin or aromatic substituents on the homolytic addition and intramolecular aromatic substitution is discussed.

The oxidation of carbonyl compounds by high-valent metal salts (Fe(III),<sup>1</sup> Ce(IV),<sup>2</sup> and mainly Mn(III))<sup>3,4</sup> has attracted the attention of synthetic organic chemists as a tool to obtain efficiently highly functionalized derivatives. In particular, we<sup>1,4</sup> and others<sup>5,6</sup> have recently reported examples for homolytic aromatic alkylation by these radical sources showing high yield and selectivity. In an attempt to extend further the potentiality of these oxidations, we were interested to know the limit of application of the previously reported intramolecular aromatic substitution by oxidative addition of carbonyl compounds to

Table I. Oxidative Addition of X-Substituted Benzylmalonates (**1a-m**) to 1-Octene Induced by Mn(III) Acetate (AcOH, 60 °C, 12 h)

	<b>1</b> (conv, %)	<b>3</b> (yield, %)
<b>1a</b>	95	90
<b>1b</b>	96	86
<b>1c</b>	90	85
<b>1d</b>	91	85
<b>1e</b>	93	89 <sup>a</sup>
<b>1f</b>	90	83 <sup>b</sup>
<b>1g</b>	88	80 <sup>c</sup>
<b>1h</b>	95	85 <sup>d</sup>
<b>1i</b>	88	79
<b>1j</b>	98	91
<b>1k</b>	93	trace
<b>1m</b>	55	48 <sup>e</sup>

<sup>a</sup> Ortho/para ratio of addition-cyclization isomers:  $3eb'/3eb = 1.64$ ;  $3fb'/3fb = 1.33$ ;  $3gb'/3gb = 0.62$ ;  $3hb'/3hb = 0.88$ .  
<sup>e</sup> After 48 h.

olefins.<sup>6,7</sup> In his pioneering work,<sup>7</sup> Heiba reported moderate yields of tetralones when acetophenones were oxidized by Mn(III) acetate in the presence of monosubstituted or 1,2-disubstituted alkenes in excess. More re-

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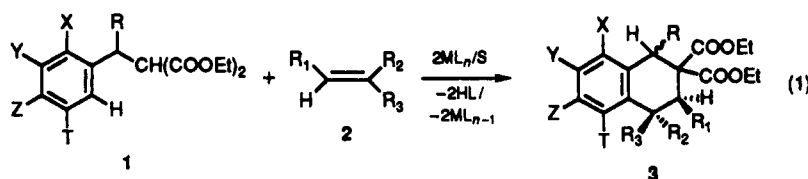
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Chart I



	R	X	Y	Z	T	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>
1a	H	H	H	H	H	H	H	H
1b	H	H	H	Cl	H	H	n-C <sub>6</sub> H <sub>13</sub>	H
1c	H	H	H	F	H	H	Me	CH <sub>2</sub> Bu- <i>t</i>
1d	H	H	H	COOMe	H	H	-(CH <sub>2</sub> ) <sub>4</sub> -	H
1e	H	H	F	H	H	H	CH <sub>2</sub> COOEt	H
1f	H	H	OMe	H	H	H	CH <sub>2</sub> OH	H
1g	H	H	NO <sub>2</sub>	H	H	H	-CH=CHCH <sub>2</sub> -	H
1h	H	H	Me	H	H	H	CH=CHMe	H
1i	H	Me	H	H	Me	H	C(Me)=CH <sub>2</sub>	Me
1j	H	-CH=CHCH=CH-	H	H	H	H	Ph	H
1k	H	Ph	H	H	H	H	OAc	H
1m	Me	H	H	H	H	H	CN	H

	X	Y	Z	T	R	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>
3ba	H	H	Cl	H	H	H	H	H
3bc	H	H	Cl	H	H	H	Me	CH <sub>2</sub> Bu
3bd	H	H	Cl	H	H	(CH <sub>2</sub> ) <sub>2</sub>	H	(CH <sub>2</sub> ) <sub>2</sub>
3bd'	H	H	Cl	H	H	H	-(CH <sub>2</sub> ) <sub>4</sub> -	H
3be	H	H	Cl	H	H	H	H	CH <sub>2</sub> COOEt
3bh	H	H	Cl	H	H	H	H	CH=CHMe
3bk	H	H	Cl	H	H	H	H	OAc
3bm	H	H	Cl	H	H	H	H	CN
3bn	H	H	Cl	H	H	H	H	COOMe
3bp	H	H	Cl	H	H	COOEt	H	COOEt
3br	H	H	Cl	H	H	H	COOEt	COOEt
3bs	H	H	Cl	H	H	Me	H	COOEt
3bt	H	H	Cl	H	H	Me	H	CH=CHCOOEt
3bt'	H	H	Cl	H	H	Me	CH=CHCOOEt	H
3au	H	H	H	H	H	H	H	SiMe <sub>3</sub>
3ab	H	H	H	H	H	H	H	n-C <sub>6</sub> H <sub>13</sub>
3bb	H	H	Cl	H	H	H	H	n-C <sub>6</sub> H <sub>13</sub>
3cb	H	H	F	H	H	H	H	n-C <sub>6</sub> H <sub>13</sub>
3db	H	H	COOMe	H	H	H	H	n-C <sub>6</sub> H <sub>13</sub>
3eb	H	F	H	H	H	H	H	n-C <sub>6</sub> H <sub>13</sub>
3eb'	H	H	H	F	H	H	H	n-C <sub>6</sub> H <sub>13</sub>
3fb	H	OMe	H	H	H	H	H	n-C <sub>6</sub> H <sub>13</sub>
3fb'	H	H	H	OMe	H	H	H	n-C <sub>6</sub> H <sub>13</sub>
3gb	H	NO <sub>2</sub>	H	H	H	H	H	n-C <sub>6</sub> H <sub>13</sub>
3gb'	H	H	H	NO <sub>2</sub>	H	H	H	n-C <sub>6</sub> H <sub>13</sub>
3hb	H	Me	H	H	H	H	H	n-C <sub>6</sub> H <sub>13</sub>
3hb'	H	H	H	Me	H	H	H	n-C <sub>6</sub> H <sub>13</sub>
3ib	Me	H	H	Me	H	H	H	n-C <sub>6</sub> H <sub>13</sub>
3jb	-CH=CHCH=CH-	H	H	H	H	H	H	n-C <sub>6</sub> H <sub>13</sub>
3mb	H	H	H	H	Me	H	H	n-C <sub>6</sub> H <sub>13</sub>
3mb'	H	H	H	H	Me	H	n-C <sub>6</sub> H <sub>13</sub>	H
3kj	Ph	H	H	H	H	H	H	Ph

cently,<sup>6</sup> Snider reported excellent yields of polycyclic compounds arising from an intramolecular version of the Heiba reaction on unsaturated  $\beta$ -keto esters and  $\beta$ -diketones. In these studies, remarkable differences between alkyl substituents present on the double bond and between phenyl and 4-methoxyphenyl derivatives were observed. These results prompted us to analyze in greater detail the influence of metal, olefin, and the aromatic ring substitution upon the selectivity of these addition-cyclization processes.

As the model reaction we analyzed the oxidation of substituted diethyl  $\alpha$ -benzylmalonates (1a-m) in the presence of substituted olefins 2a-u, to afford the tetra-

hydronaphthalene derivatives 3 (eq 1 in Chart I). Mn(III) acetate dihydrate in acetic acid, Fe(III) perchlorate decahydrate (FEP) in acetonitrile, and Ce(IV) ammonium nitrate (CAN) in methanol were used as oxidant reagents (ML<sub>n</sub>/S).

## Results

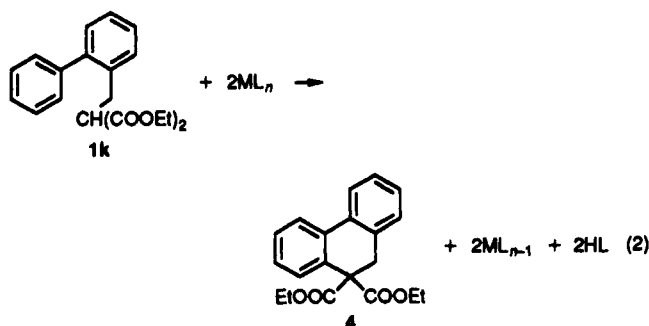
**Effect of Substituents on the Aromatic Ring.** The influence of substituents X, Y, Z, and T of benzylmalonates 1 on the yield of reaction 1 was investigated by using 1-octene (2b) as olefin and Mn(III) acetate as oxidant at 60 °C using a 1:1.5:2 molar ratio, respectively. The results are reported in Table I. The addition-cyclization process

**Table II. Mn(III) Acetate Oxidation of Diethyl  $\alpha$ -(4-Chlorobenzyl)malonate (1b) in the Presence of Substituted Olefins 2 (AcOH, 60 °C, 13 h)**

2	2 (conv, %)	product yield, %					others	rel rate
		3	5	6	9			
2a	87	76	-	-	-	-	nd	
2b	96	86	1	-	-	-	1	
2c	83	63	12 <sup>a</sup>	-	-	9 <sup>b</sup>	4.5	
2d	93	46 <sup>c</sup>	-	-	-	42 <sup>d</sup>	0.08	
2e	92	74	-	-	-	-	0.56	
2f	86	71 <sup>e</sup>	-	-	-	-	nd	
2g	57	52	2	-	-	-	nd	
2h	75	37	21	18	-	-	nd	
2i	92	0	30	55	-	-	70	
2j	91	0	56	36	-	-	81	
2k	90	80	-	-	-	-	0.6	
2m	86	75	-	-	-	-	0.7	
2n	88	82	-	-	-	-	0.64	
2p	84	28	-	-	48	-	0.011	
2q	85	64	-	-	15.6	-	0.002	
2r	71	38	-	-	-	29 <sup>f</sup>	nd	
2s	70	18 <sup>g</sup>	-	-	40	8 <sup>h</sup>	nd	
2t	90	40 <sup>i</sup>	42	-	-	-	nd	
2u	nd	78 <sup>m</sup>	-	-	-	-	nd	

<sup>a</sup> Mixture of 5bc and 5bc' (2.5:1). <sup>b</sup> 8bc. <sup>c</sup> 3bd:3bd' = 0.73. <sup>d</sup> 2-Cyclohexenyl acetate. <sup>e</sup> Lactone of compound 3bf. <sup>f</sup> Mixture of stereoisomers (6:74:4:16%, determined by GC assuming an identical response factor). <sup>g</sup> Diethyl  $\alpha$ -(acetoxymethyl)malonate. <sup>h</sup> Ethyl 4-acetoxy-2-butenate. <sup>i</sup> Mixture of six isomers (5:13:20:47:14:2%, determined by GC assuming an identical response factor). <sup>m</sup> Reaction performed on diethyl benzylmalonate.

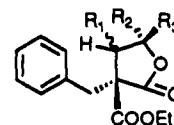
is efficient with a large variety of substituents in ortho, meta, and para positions. The only exceptions are the *o*-phenyl derivative 1k, which affords in high yield the dihydrophenanthrene derivative 4 (eq 2), and the diethyl  $\alpha$ -(1-phenylethyl)malonate (1m), which gives moderate yield of 3 in a slow reaction.



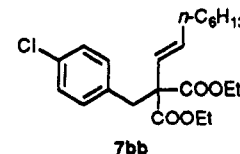
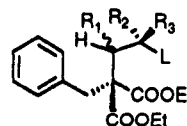
Substituents in meta position direct the cyclization at the ortho and para positions and steric hindrance inhibits the formation of the ortho product.<sup>8</sup> Only traces of products coming from the free-radical chain addition<sup>7</sup> of malonic ester 1 to olefins 2 (XPhCH<sub>2</sub>C-(COOEt)<sub>2</sub>CHR<sub>1</sub>CHR<sub>2</sub>R<sub>3</sub>) are observed. The reaction rates are only marginally affected by substituents, except with substrates 1k or 1m, for which the reaction is faster or slower than with other substrates, respectively.

**Effect of Substituents on the Olefin.** The influence of the olefin substitution was investigated by using 1b as substrate and Mn(III) acetate at 60 °C. The results obtained are summarized in Table II. The addition-cyclization products 3 are observed in good yield with terminal alkenes substituted either by electron-releasing or -withdrawing groups; but 2,4,4-trimethylpentene (2c) affords a significant amount of addition-oxidation products (lactones 5bc and 5bc' and olefin 8bc). The competition between addition-oxidation and addition-cyclization processes is observed also with conjugated dienes (i.e. 2i,

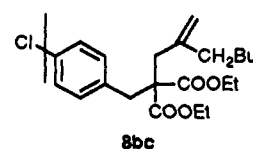
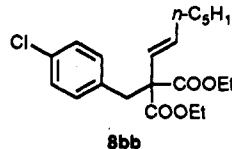
2j, 2t, 2g, and 2h). The first process was particularly efficient with 2i and 2j to give lactones 5bi, 5bi', 5bj, 5bj', and acetoxy derivatives 6bi and 6bj (L = OAc), respectively.



	X	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>
5bb	4-Cl	H	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	H
5bb'	4-Cl	H	H	<i>n</i> -C <sub>6</sub> H <sub>13</sub>
5bc	4-Cl	H	CH <sub>2</sub> Bu	Me
5bc'	4-Cl	H	Me	CH <sub>2</sub> Bu
5bh	4-Cl	H	CH=CHMe	H
5bh'	4-Cl	H	H	CH=CHMe
5bi	4-Cl	H	C(Me)=CH <sub>2</sub>	Me
5bi'	4-Cl	H	Me	C(Me)=CH <sub>2</sub>
5bj	4-Cl	H	H	Ph
5bj'	4-Cl	H	Ph	H
5kj	2-Ph	H	H	Ph
5kj'	2-Ph	H	Ph	H



	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>
6bb	H	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	H
6bh	H	CH=CHMe	H
6bi	H	C(Me)=CH <sub>2</sub>	Me
6bj	H	Ph	H



(4-ClPhCH<sub>2</sub>C(COOEt)<sub>2</sub>)<sub>2</sub>

(8) A detailed study on the ortho/para isomer distribution will be reported elsewhere.

**Table III. Product Distribution in the Oxidation of 1b by Mn(III) Acetate (AcOH, 60 °C, 13 h), FEP (MeCN, 20 °C, 13 h), and CAN (MeOH, 20 °C, 8 h) in the Presence of Some Representative Olefins**

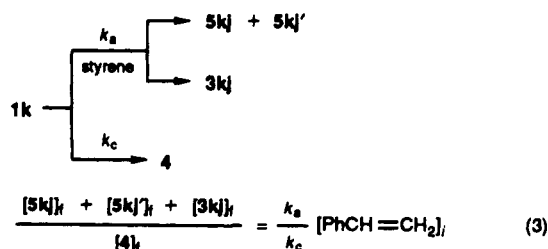
entry	olefin	metal	1b (conv. %)	product yield, %				
				3	5	6	7-8	9
1	2b	Mn(III)	96	86	2	-	-	-
2	2b	Fe(III)	87	36	19	8	16 <sup>a</sup>	-
3	2b	Fe(III) <sup>b</sup>	85	82	5	2	4	-
4	2b	Fe(III) <sup>c</sup>	100	90	-	-	-	-
5	2b	Fe(III) <sup>d</sup>	52	80	10	3	6	-
6	2b	Ce(IV)	86	21	10	36	5	-
7	2j	Mn(III)	91	2	56 <sup>e</sup>	36	-	-
8	2j	Fe(III)	100	-	93 <sup>f</sup>	-	2	-
9	2j	Ce(IV)	58	-	-	-	46 <sup>f</sup>	-
10	2m	Mn(III)	86	75	-	-	-	-
11	2m	Fe(III)	81	73	-	-	-	-
12	2m	Ce(IV)	88	70	-	-	-	-
13	2q	Mn(III)	85	71	-	-	-	10
14	2q	Fe(III)	78	68	-	-	-	7
15	2q	Ce(IV)	89	73	-	-	-	11

<sup>a</sup>7bb:8bb = 0.8. <sup>b</sup>In the presence of pyridine (20 mmol). <sup>c</sup>In the presence of bipyridine (20 mmol). <sup>d</sup>In the presence of water (100 mmol). <sup>e</sup>Mixture of diastereoisomers (1:1.53). <sup>f</sup>Mixture of diastereoisomers (1:1.43). <sup>g</sup>1,2-Dinitrostyrene.

Compounds **3** also formed in moderate yield in reactions with 1,2-disubstituted olefins and diethyl methylenemalonate. The lower efficiency of reaction 1 is due to competitive processes, i.e. allylic hydrogen abstraction (for substrates **2d** and **2s**), dimerization at the malonic position to give **9** (for substrates **2p**, **2q**, and **2s**), and telomerization and nucleophilic addition (for **2r**), respectively. The stereochemistry of addition-cyclization products **3** with 1,2-disubstituted olefins is mainly (or exclusively) trans with **2d** (or **2p** and **2q**), but with cyclopentadiene (**2g**) the ring junction is cis. The stereochemical assignment is made on the basis of the coupling constants between the two tertiary hydrogens and by comparison with the products obtained by Pd-catalyzed cyclization of the appropriate iodo derivative.<sup>9</sup>

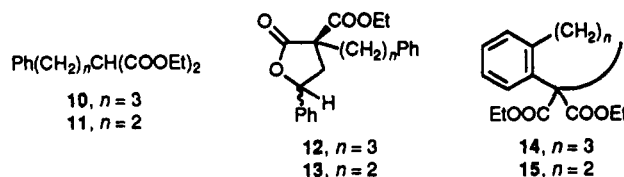
**Relative Reactivity of Olefins and Aromatics toward Malonyl Radicals.** Competitive experiments at low conversion between couples of olefins are used to determine the relative reactivity of malonyl radical intermediates toward double bonds. The results obtained are collected in the last column of Table II. Diethyl maleate is estimated to be 0.17 less reactive than diethyl fumarate from the ratio between dimer **9** and the product **3bq**.

Also the reactivity of aromatics toward malonyl radicals was investigated. The experiments involve the oxidation at low conversion of compound **1k** by Mn(III) and Fe(III) in the presence of variable amount of styrene. A competition between products of addition to styrene (lactones **5kj** and **5kj'** and tetrahydronaphthalene **3kj**) and the product of intramolecular aromatic alkylation (**4**) is observed. From the linear correlation of eq 3 (see Experi-



mental Section), a ratio  $k_a/k_c$  of 12.4 is deduced at low conversion of styrene. Similar competition studies, carried out on diethyl  $\alpha$ -(3-phenylpropyl)malonate (**10**) and diethyl  $\alpha$ -(2-phenylethyl)malonate (**11**), afford the products of

addition-oxidation (lactones **12** and **13**<sup>1b</sup>) with high preference over the addition-cyclization products **14** and **15**.<sup>4b</sup>



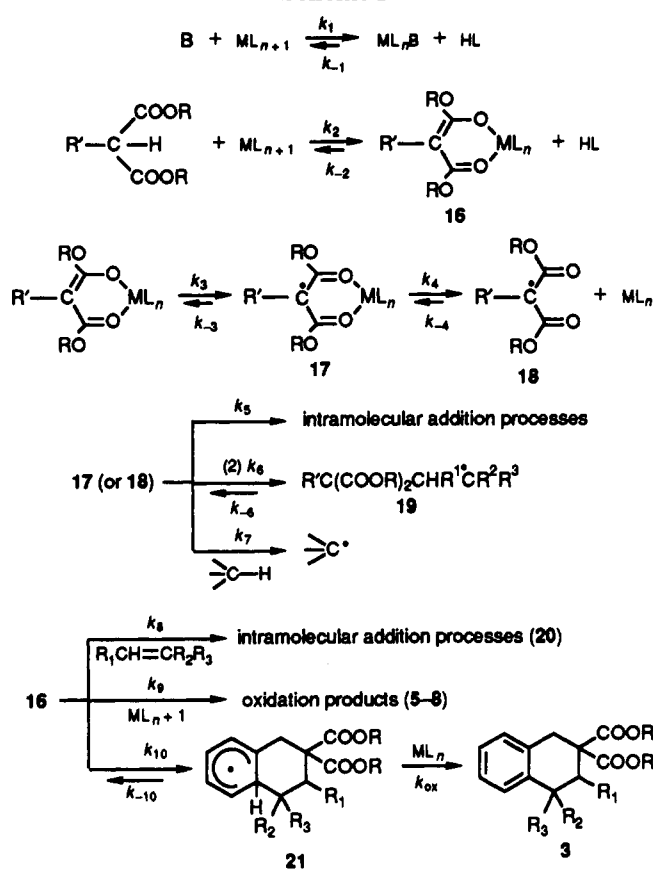
By using a relationship similar to eq 3, a ratio of  $1.1 \times 10^3$  between the addition rate to styrene and the intramolecular cyclization rate of radical **23** is deduced. A lower limit of  $5 \times 10^3$  was estimated for radical **24**.

**Effect of the Metal Oxidant.** The influence of the nature of the metal oxidant on the product distribution was also checked. Diethyl 4-chlorobenzylmalonate (**1b**) and some representative olefins (1-octene (**2b**), styrene (**2j**), acrylonitrile (**2m**), and diethyl fumarate (**2q**)) were used as substrates. Mn(III) acetate in acetic acid at 60 °C, Ce(IV) ammonium nitrate in methanol at 20 °C, and Fe(III) perchlorate in acetonitrile at 20 °C were used as oxidants. The results obtained are collected in Table III. The three oxidants afford a comparable yield of **3** with olefins substituted by electron-withdrawing groups (i.e. **2m** and **2q**). However, with styrene (**2j**) the oxidation proceeds differently, and lactones **5bj** and **5bj'** are obtained selectively only with FEP. With 1-octene as substrate (entries 1-3), the reaction gives cleanly the addition-cyclization product **3bb** with Mn(III) acetate. On the contrary, FEP and CAN afford a complex mixture of addition-cyclization (**3bb**), addition-elimination (**7bb**, **8bb**),  $\gamma$ -lactones (**5bb**, **5bb'**), and ligand-transfer oxidation products (**6bb** (L = ONO<sub>2</sub> and OH, respectively)). Under preparative conditions, the ratio between the cyclization to oxidation products,  $R = 3/(5 + 6 + 7 + 8)$  is 43, 0.84, and 0.41 for Mn(III) acetate, FEP, and CAN, respectively. Typically, in oxidation experiments of **1b** in the presence of **2b**,  $R$  decreases linearly with the metal salt concentration. From these data we can deduce a value of  $0.35 \pm 0.07$  for the ratio  $k_{10}/k_9$  (Scheme I). The presence of a base (i.e. pyridine, 2,2'-bipyridine, and water, entries 3, 4, and 5 of Table III) decreases both conversions and oxidation rates  $k_9$ , resulting in a more selective synthesis of **3bb**.

### Discussion

This study indicates that reaction 1 is a quite general and synthetically useful process. Aromatics and olefins substituted by a variety of electron-releasing and elec-

Scheme I



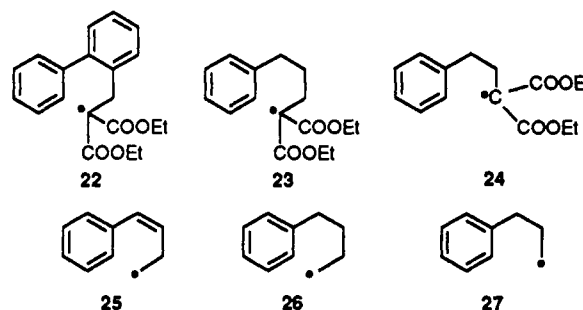
tron-withdrawing groups can be successfully used. However, some limits, not related to the initial oxidation of the malonate ester, are apparent. They are due to (1) fast intramolecular addition processes to  $\pi$ -systems without olefin addition, (2) allylic oxidation of olefins, and (3) formation of open-chain addition products to the olefin.

The dependence of the yield of reaction 1 and side reactions upon the structure of malonic ester, metal oxidants, and substituents on the olefin point to a common mechanism, despite the different metal, ligand, and solvent used (Scheme I).

Malonate complexes of high-valent metal (16) are in equilibrium with malonyl radicals (complexed to the metal (17) or free (18)). They partition between intramolecular processes, if unsaturation in appropriate positions are present, and intermolecular addition. In turn, the resulting substituted alkyl radicals 19 partition between intramolecular aromatic substitution to give 3, olefin addition, and oxidation by the metal salt to give products 5-8. The notable dependence of the oxidation rate of carbonyl compounds by metal salts on the base and olefin can be accounted for by the high reversible and base-inhibited formation of malonyl radicals and their trapping rate by the olefin, significantly dependent on substituents. The coupled high-valent metal salts/carbonyl compound can be considered as a buffered source of  $\alpha$ -carbonylalkyl radicals, sensitive to all factors affecting the stationary concentration attainable at the experiment temperature.<sup>10</sup>

The intramolecular processes of malonyl radicals are mainly related to the presence of C=C bonds in appropriate positions to give 5- or 6-membered rings. The relative rates of inter and intramolecular addition to the  $\pi$ -system ( $k_5$  and  $k_6$ ) determine the relevance of the process. So, intramolecular cyclization of compound 1k to give

4 is preferred unless an efficient scavenger of malonyl radical, i.e. styrene, is present, whereas compound 10 does not form cyclic compound 14, also in the presence of 1-octene. The hindered rotation around the  $\beta$ - $\gamma$  bond to the radical center of 22 clearly favors the intramolecular addition to the aromatic ring of radical 22 compared with the saturated analogues 23 and 24.



Assuming the addition rate of  $\alpha$ -( $\omega$ -arylalkyl)malonyl radicals to styrene independent of the substitution on the aryl residue and on the alkyl chain length and equal to that of diethyl benzylmalonate to the same substrate ( $k_{10} = (8 \pm 2) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ),<sup>11</sup> the cyclization rates  $k_5$  at 293 °C for radicals 22, 23, and 24 can be estimated to be  $6.4 \times 10^5$ ,  $7.1 \times 10^3$ , and  $<10^3 \text{ M}^{-1} \text{ s}^{-1}$ , respectively. These rates are slightly lower than the ones reported for the corresponding primary alkyl radicals 25-27, but strictly correlated ( $6 \times 10^5 \text{ s}^{-1}$  for radical 25,<sup>12</sup>  $(1-5) \times 10^4 \text{ s}^{-1}$  for radical 26,<sup>13</sup> and  $(2-8) \times 10^2$  for radical 27<sup>7</sup>). These values explain the quantitative formation, in the absence of any olefin, of cyclic compounds 4 and 14 by oxidation of 1k and 10, whereas compound 15 is always associated to the dimer of radical 24.<sup>4b</sup>

The results of competitive experiments reported in the last column of Table II indicate that malonyl radicals add efficiently to olefins substituted either by electron-withdrawing or -releasing groups. Assuming the rate constant for addition of malonyl radicals from 1b to styrene  $k_{10} = 8 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  at 20 °C, the monosubstituted olefins tested (2b, 2e, 2m, and 2n) present rate constants  $k_8$  in the narrow range  $(6-10) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ . The trend of rate constants is close to the one reported for analogous additions of (alkoxycarbonyl)alkyl<sup>14</sup> and dicyanomethyl radicals<sup>15</sup> to alkenes at 293-303 K. The possible interference arising from the frequently reported reversibility in the addition of malonyl radicals to olefins<sup>16</sup> is minimized in the model here reported because all subsequent reactions of the adduct radical 16 are fast  $k_9$  and  $k_{10} > 10^4 \text{ M}^{-1} \text{ s}^{-1}$ .

Previous results of malonyl radicals addition to olefins<sup>17</sup> and aromatics<sup>4</sup> have shown a clear electrophilic character

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of these intermediates. However, the results of Table II support some ambiphilic character<sup>14,18</sup> for these radicals, with large preference for the electrophilic (SOMO-HOMO) than nucleophilic (SOMO-LUMO) contribution of frontier orbitals interaction. No definite minimum can be detected in the plot of addition rate constants toward ionization potential or electron affinity of the olefins, as observed<sup>14</sup> with the (*tert*-butoxycarbonyl)methyl radical. However, competitive experiments indicate qualitatively that diethyl methylenemalonate presents a higher reactivity than ethyl acrylate. On the other hand, the 10-fold decrease in relative rates of addition to the couple 1-octene/acrylonitrile from diethylmalonyl to (*tert*-butoxycarbonyl)methyl radical supports the higher electrophilic character of the first radical. The lower ionization potential of latter radical (10.30 eV<sup>14</sup> vs 11.0 eV<sup>19</sup> for malonyl radical) can explain the prevalence of the SOMO-LUMO interaction.

As generally observed in the addition of free-radicals to olefins, steric inhibition by the presence of the  $\alpha$ -substituent reduces considerably the addition rate of malonyl radicals and increases the reactivity of the trans over the cis isomer.<sup>20</sup> This effect is well evident in the progressive lowering of the yield for reaction 1 and increase of dimer 9 in the addition reaction to cyclohexene, ethyl 2-butenate, diethyl fumarate, and diethyl maleate (Table II). However, the inefficiency of reaction 1 with cyclohexene and, to a minor extent, with ethyl 2-butenate is mainly related to a competitive reaction of allylic hydrogen atom abstraction, whereas dimerization to 9 is the main fate of radical adduct to diethyl fumarate and diethyl maleate. With these last substrates the addition rate constants can be estimated from the data of Table II to be  $1.1 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$  and  $21 \text{ M}^{-1} \text{ s}^{-1}$ , respectively. Interferences due to allylic or benzylic hydrogen abstraction in malonyl radicals addition to  $\pi$ -systems have been previously reported by using reducing<sup>21</sup> and oxidant radical sources.<sup>4</sup> Therefore, the rate constants for the abstraction of secondary allylic hydrogen by alkyl-substituted malonyl radicals are in the range  $(5\text{--}10) \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$  at 20 °C. The relatively high value of the ratio of hydrogen abstraction to double bond addition is a further evidence of the electrophilic behavior of these radicals.

As concerns the 1,6 intramolecular homolytic aromatic alkylation of  $\delta$ -phenylbutyl radical 21, the substitution on the radical center does not appear to modify considerably the addition rate  $k_{10}$  ( $10^4\text{--}10^5 \text{ M}^{-1} \text{ s}^{-1}$  at 293–303 °C)<sup>7</sup> but shows a remarkable influence on the oxidation rate by the metal salt. As the results of Table III indicate, open-chain addition derivatives are obtained more efficiently, more oxidant is the medium, and more reducing is the radical (i.e. allyl, secondary alkyl, benzyl, and tertiary alkyl). In fact, Fe(III) perchlorate in acetonitrile presents a higher oxidation potential than Ce(IV) ammonium nitrate in methanol, and in turn than Mn(III) acetate in acetic acid.<sup>22</sup> The oxidation rate of secondary alkyl radicals ( $k_2$ ) by FEP

in acetonitrile and Mn(III) acetate in acetic acid can be estimated from our data to be  $5.7 \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$  and  $8 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$  at 20 °C, respectively, taking  $k_{10}$  for secondary alkyl radicals  $1 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ .<sup>7</sup> On the contrary, no difference is observed for electrophilic  $\alpha$ -cyano and  $\alpha$ -carbonylalkyl radicals, owing to their higher redox and ionization potentials. With conjugated olefins (i.e. styrenes and butadienes<sup>1b</sup>), the oxidation proceeds mainly to give  $\gamma$ -lactones, and from this point of view FEP is the most selective oxidant.<sup>1b</sup> Mixtures of lactones and other oxidation products (by addition/ $\beta$ -elimination and ligand-transfer) were obtained with other metal and olefins. In particular, the oxidation of secondary and tertiary alkyl radicals by FEP in the reactions with 2b and 2c to olefins 7 and 8 is reminiscent of the behaviour of Cu(II) acetate.<sup>23</sup> Steric inhibition in the  $\beta$ -proton elimination is clearly seen when the results with olefin 2b and 2c are compared. However, subtle effects seem to operate in substituted allyl radicals. So, radical adducts to 2,3-dimethylbutadiene are preferentially oxidized, whereas radical adducts to butadiene or cyclopentadiene add preferentially or exclusively to the aromatic ring. The complete stereospecificity of cis junction in fused five- to six-membered rings observed with cyclopentadiene is typical of carbon radical cyclization<sup>24</sup> and excludes an electrophilic aromatic substitution process.

In conclusion, the oxidation of carbonyl compounds by high-valent metal salts represents an efficient and frequently selective method of functionalization of olefins and aromatics whose limit can be now set up with good approximation. The main drawback presented by these reactions is the use of stoichiometric amount of metal salts.<sup>25</sup> However, the possibility to choose different metal salts, in particular the relatively inexpensive iron(III) salts, and the easy and efficient electrochemical regeneration of the oxidant metal salts<sup>26</sup> can open interesting industrial applications to homolytic oxidations of carbonyl compounds by indirect electrochemistry.

### 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). <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained in CDCl<sub>3</sub> on 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 Varian Mat 112 F GC-MS spectrometer equipped with a SP 2100 coated fused silica capillary column (25 m  $\times$  0.22 mm i.d.) with helium as a carrier gas. Quantitative gas chromatographic analyses for the determination of conversions and isomers 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  $\times$  0.22 mm i.d.) coated with polydimethylsiloxane (CP-Sil 5, film thickness 1  $\mu\text{m}$ ), FID detector, hydrogen as carrier gas, and temperature programmed from 50 to 190–250 °C at 10 deg/min. Integration of chromatographic traces was carried out using a Spectra Physics SP 4200 computing integrator or a PC computer

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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  $\mu$ m, 20  $\times$  0.25 cm i.d. or 5  $\mu$ m, 20  $\times$  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 a 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) and anhydrous Mn(III) acetate<sup>20</sup> were tested for purity by iodimetric titration. Acetic acid and acetonitrile were freshly distilled from P<sub>2</sub>O<sub>5</sub>; methanol was distilled from Mg turning. All the olefins were commercial products having a purity higher than 98%; they were distilled before the use. Cyclopentadiene was obtained by slow distillation of dicyclopentadiene. 1,3-Pentadiene was used as a mixture of *Z* and *E* isomers (70:30). Diethyl methylenemalonate was obtained following the reported procedure.<sup>20</sup> Starting materials 1a–m were synthesized from the corresponding alkyl bromide or chloride with the anion of diethyl malonate (prepared from NaH in THF), followed by stirring or refluxing the mixture under N<sub>2</sub> for 4–12 h. The resulting mixture was concentrated and dissolved in the minimum amount of diethyl ether, and after addition of water, the organic layer was separated and the water layer extracted with diethyl ether. The combined extracts were washed with water, dried, concentrated, and distilled through a Vigreux column under vacuum or chromatographed on a silica gel column, and the fractions containing the product were distilled. The compounds 1a–m, 10, and 11 present the following melting or boiling points (°C/mmHg): 1a (161–3/10), 1b (130/0.5), 1c (93/1), 1d (138/0.01), 1e (90/0.05), 1f (108/0.1), 1g (140/0.01), 1h (108/0.5), 1i (118/0.5), 1j (29–30), 1k (160–2/0.01), 1m (110/0.5), 10 (120/0.3), 11 (105/0.3).

Compounds 4, 13, and 14<sup>4</sup> and diastereoisomeric lactones 12 and 13<sup>1b</sup> were obtained as reported. Dimer 9 (mp 82–4 °C, analytical data reported in Table VI of the supplementary material) was isolated in 58% yield by Mn(OAc)<sub>3</sub> oxidation of 1b in acetic acid at 70 °C for 13 h.

**General Procedure for Reactions between 1a–m, 2a–u, and Mn(III) Acetate.** Acetic acid (15 mL) was added in a two-necked flask equipped with a reflux condenser, a N<sub>2</sub> inlet device, and a magnetic stirring bar. The system was flushed with nitrogen for 5 min, Mn(III) acetate was then added all at once, and the resulting slurry was stirred and heated at 60 °C. A solution of 1 (5.0 mmol) and 2 (5.5 mmol) in acetic acid was added, and the mixture was maintained at 60 °C until the color faded or for 12 h, when the mixture remained dark. To the cooled solution was added biphenyl as internal standard; a sample (0.1 mL) was withdrawn from the solution and added to diethyl ether (1 mL), and the suspension was 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 isomer distribution of 3. The remaining mixture was evaporated at 30 mmHg, the residue was taken up with ethyl acetate and water (10 mL), the layers were separated, and the aqueous layer was extracted twice with ethyl acetate (10 mL). The combined extracts were washed with 10% NaHCO<sub>3</sub> and water, dried, evaporated, and flash chromatographed to isolate compound 3. When the first separation did not succeed, further purification by preparative HPLC was made to obtain analytical samples of products.

The analytical data of tetrahydronaphthalenes 3ab–3gb obtained in the reactions between 1a–1m and 1-octene are reported in Table IV (supplementary material); those obtained in the reaction between 1b and olefins 2a–k are in Table V (supplementary material), whereas lactones 5 are reported in Table VI (supplementary material). Compound 3ba was identified, after hydrolysis and thermal decarboxylation, by comparison with an authentic sample of 1,2,3,4-tetrahydro-2-naphthoic acid (mp 98–99 °C).

The reactions with olefins 2s and 2t afforded complicated mixtures; so, compounds 3 were identified by combination of GC–MS and 250-MHz NMR spectra of partially purified samples. It was possible to isolate by preparative HPLC the major components of these mixtures (compounds 3bs, 3bt, and 3bt' in 92,

95, and 80% purity by GC, respectively). The spectroscopic data for these samples are reported in Table V (supplementary material).

Modifications to the general procedure were introduced in the reactions with olefins 2a, 2g, and 2r. The reaction with ethylene (2a) was carried out on a 5-fold scale in a 200-mL Teflon-coated autoclave, introducing 2a at 1.5 atm. The reactions with 2g and 2r were carried out by adding the olefins to the mixture of the other reagents in 0.5 h.

**General Procedure for Reactions between 1a–m, 2a–u, and FEP or CAN.** In a two-necked flask under N<sub>2</sub>, FEP or CAN (20 mmol) was added to acetonitrile (20 mL) or methanol (20 mL) at 5–10 °C with magnetic stirring. After 15 min at 20 °C, the additive and a solution of 1 and 2 in acetonitrile or methanol (5 mL) was added once in sequence. The reaction was run for 4–13 h, following by GC the decay of 1. The analyses and the isolation procedure was carried out as above. In experiments with FEP and 1-octene (2b) or 2,4,4-trimethyl-1-pentene (2c), a complex mixture of products was obtained: tetrahydronaphthalenes 3bb, lactones 5bb, 5bb' or 5bc and 5bc', ligand transfer oxidation products 6bb or 6bc, and olefins 7bb, 8bb, or 8bc. The quantitative analyses of these reactions were carried out by GC on the crude reaction mixtures by the internal standard method (*n*-butyl 4-phenylbutanoate). GC–MS analyses of the mixtures and column chromatography on SiO<sub>2</sub> with hexane/ethyl acetate (95:5) of the residue obtained on 10-fold scale experiments allow analytical data to be obtained for all products. Olefins 7bb, 8bb, and 8bc were further purified by preparative GC of fractions obtained by SiO<sub>2</sub> chromatography. The spectroscopic properties of compounds 3bb and 3bc are reported in Table IV (supplementary material); those of lactones 5bb and 5bc are in Table V (supplementary material) and those of olefins 7bb, 8bb, and 8bc are in Table VI (supplementary material).

Via the above reported conditions, some experiments were carried out by oxidation of 1b and 2b using different initial concentrations of FEP (0.132, 0.265, 0.397, 0.53, 0.662, 0.794). The ratios between the oxidation to cyclization products were 5.82, 6.62, 7.14, 7.94, 8.70, and 9.71, respectively. Regression of these data allow us to estimate the ratio of addition to oxidation rate constants for secondary alkyl radicals by FEP in acetonitrile ( $k_9/k_{10} = 5.7 \pm 0.3$ ;  $r = 0.9972$ ).

**Competitive Experiments.** Two set of experiments were carried out: (i) via the general procedure for reactions with Mn(III), a solution of 1b (10 mmol) and a couple of olefins (5 mmol, each) in acetic acid was added. The reaction was stopped at different times by withdrawing a sample (1 mL), which was quenched in a mixture of 1 M TiCl<sub>3</sub> and diethyl ether (3 and 7 mL, respectively). The organic solution was washed with water (3 mL), dried, and directly analyzed by capillary GC, using 4-chlorobenzophenone as internal standard. Generally, the conversion of the olefins was less than 15% at 10 min of reaction time. (ii) The general procedure was followed by using 0.3 mmol of Mn(III). The results obtained with the two methods were very similar; the main differences were observed in experiments which afford mixtures of addition–oxidation and addition–cyclization products. In these cases, the results following method i were more reproducible. The relative rates so deduced are collected in the last column of Table III as a mean of three independent experiments.

**Oxidation of 1k by FEP in the Presence of Styrene.** Three stock solutions (50 mL, 0.30 M) of 1k, styrene, and FEP in dry acetonitrile were prepared. Appropriate amounts of these solutions (10, 4.4–17, and 4.5 mL, respectively) were mixed together in the order under N<sub>2</sub> at 20 °C, and the resulting solution was immediately taken up at 35 mL with acetonitrile. The reaction was run for 3 h. Workup and separation as before allowed isolation of compounds 3kj, 5kj, 5kj', and 4. Quantitative GC analyses of the crude reaction mixture by the internal standard method give the ratio  $R = ([5kj] + [5kj'] + [3kj])/[4]$ . *R* values were 0.38, 0.71, 1.02, and 1.31 in experiments at 0.037, 0.063, 0.090, and 0.111 M initial concentration of styrene, respectively. Least-squares analysis of these data allows to obtain by eq 3 a ratio  $k_a/k_c = 12.4 \pm 0.3$  ( $r = 0.9995$ ).

**Oxidation of 10 and 11 by Mn(III) Acetate in the Presence of Styrene.** Two stock solution (50 mL, 0.05 M) of 10 or 11 and styrene in acetic acid were made. Appropriate amounts of these



solutions (2.0 and 2-6 mL, respectively) were mixed together, and the resulting solution was taken up at 20 mL with acetic acid and heated at 60 °C. Then Mn(III) acetate (0.03 and 0.05 mmol, respectively) was added once with stirring, and the reaction was run for 6 h. The results of quantitative GC analyses of the cyclization product 14 and diastereoisomers 12 allows to deduce the [12]/[14] ratio (*R*). The mean values of *R* in two independent experiments with 10 were 10.2, 21.2, 32.5, 44.3, and 55.6 by using an initial styrene concentration of 0.011, 0.019, 0.030, 0.040, and 0.051 M, respectively. Least-squares analysis of these data, by using a relationship analogous to eq 3, allows to deduce a ratio  $k_a/k_c = 1126 \pm 28$  ( $r = 0.9991$ ) for 10.

With compound 11 only lactones 13 were formed in quantitative yield also at concentrations 1/10 lower than the one used for 10. Dihydroindene 15 was not detected even in trace amount. These results indicate a lower limit of  $k_a/k_c = 5000$  for 11.

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**Registry No.** 1a, 607-81-8; 1b, 37556-13-1; 1c, 59223-74-4; 1d, 134260-78-9; 1e, 59223-73-3; 1f, 61227-48-3; 1g, 59803-36-0; 1h, 6432-79-7; 1i, 37765-73-4; 1j, 2107-84-8; 1k, 78383-16-1; 1m, 14618-12-3; 2a, 74-85-1; 2b, 111-66-0; 2c, 107-39-1; 2d, 110-83-8; 2e, 1617-18-1; 2f, 107-18-6; 2g, 542-92-7; 2h, 504-60-9; 2i, 513-81-5; 2j, 100-42-5; 2k, 108-05-4; 2m, 107-13-1; 2n, 96-33-3; 2p, 141-05-9; 2q, 623-91-6; 2r, 3377-20-6; 2s, 623-70-1; 2t, 2396-84-1; 2u, 754-05-2;

3ab, 134260-79-0; 3au, 134260-80-3; 3ba, 134260-81-4; 3bb, 134260-82-5; 3bc, 134260-83-6; 3bd, 134260-84-7; 3bd', 134260-85-8; 3be, 134260-86-9; 3bf lactone derivative, 134260-87-0; 3bh, 134260-88-1; 3bk, 134286-48-9; 3bm, 134260-89-2; 3bn, 134260-90-5; 3bp, 134286-49-0; 3bq, 134260-91-6; 3br, 134260-92-7; 3bs, 134260-93-8; 3bt, 134260-94-9; 3bt', 134260-95-0; 3cb, 134260-96-1; 3db, 134260-97-2; 3eb, 134260-98-3; 3eb', 134260-99-4; 3fb, 134261-00-0; 3fb', 134261-01-1; 3gb, 134261-02-2; 3gb', 134261-03-3; 3hb, 134261-04-4; 3hb', 134261-05-5; 3ib, 134261-06-6; 3jb, 134261-07-7; 3kj, 134261-08-8; *cis*-3mb, 134261-09-9; *trans*-3mb, 134261-10-2; 4, 118598-49-5; 5bb, 134261-11-3; 5bb', 134261-12-4; 5bc, 134261-13-5; 5bc', 134261-14-6; 5bh, 134261-15-7; 5bh', 134261-16-8; 5bi, 128597-41-1; 5bi', 128597-40-0; 5bj, 128597-30-8; 5bj', 128597-31-9; 5kj, 134261-17-9; 5kj', 134261-18-0; 6bb, 134261-19-1; 6bh, 134261-20-4; 6bi, 134261-21-5; 6bj, 134261-22-6; 7bb, 134261-23-7; 8bb, 134261-24-8; 8bc, 134261-25-9; 9, 134261-26-0; 10, 26395-09-5; 11, 6628-68-8; 12 (isomer 1), 128597-34-2; 12 (isomer 2), 128597-35-3; 13 (isomer 1), 134261-27-1; 13 (isomer 2), 134261-28-2; 14, 115860-33-8; 15, 115860-31-6; FEP, 13537-24-1; CAN, 16774-21-3; Mn(III) acetate, 993-02-2; 1,2-dinitratostyrene, 134261-29-3; diethyl  $\alpha$ -(acetoxymethyl)malonate, 30379-13-6; ethyl 4-acetoxy-2-butenate, 65330-98-5; 2-cyclohexenyl acetate, 14447-34-8.

**Supplementary Material Available:** Elemental analyses and proton NMR and MS spectra of tetrahydronaphthalenes 3ba-3kj, lactones 5bb-5kj', dimer 9, and olefins 7bb, 8bb, 8bc (Tables IV-IX) (10 pages). Ordering information is given on any current masthead page.

## Oxidation of Diethyl (Pyridylmethyl)malonates with Mn(III) Acetate, Ce(IV) Ammonium Nitrate, and Iron(III) Perchlorate in the Presence of Alkenes and Alkynes

Attilio Citterio,\* Roberto Sebastiano, and Magaly Caceres Carvayal

Dipartimento di Chimica del Politecnico, P.zza L.da Vinci, 32, 20133 Milano, Italy

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The oxidation of substituted diethyl 2-, 3-, or 4-picolylmalonates (1a-g) by Mn(III) acetate in acetic acid, Ce(IV) ammonium nitrate in methanol or acetic acid, and Fe(III) perchlorate in acetonitrile in the presence of substituted alkenes (2) and alkynes (3) affords substituted tetra- or dihydroquinolines and/or isoquinolines (4-9) in good to excellent yield. The influence of reaction medium on yield and isomer distribution has been investigated. A mechanism involving oxidative deprotonation of malonic esters by high-valent metal salts to malonyl radicals, their addition to olefins, and intramolecular homolytic substitution to protonated or metal-complexed heteroaromatic bases by the resulting substituted carbon radicals is suggested.

In recent years attention has been placed on the synthetic opportunities offered by high-valent metal salt oxidations of carbonyl compounds in the presence of unsaturated substrates.<sup>1-3</sup> Our group was specifically involved in the research of synthetic applications of homolytic aromatic alkylation promoted by these radical sources<sup>4</sup> and in the extension of these reactions to different

metal salt and conditions.<sup>5</sup> In the preceding paper we have reported examples of oxidative addition-cyclization reaction of diethyl benzylmalonates and substituted olefins induced by high-valent metal salts. Now, we present the results of similar reactions between substituted diethyl picolylmalonates (1a-g) and alkenes (2) or alkynes (3) to

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