Reactivity of Malonyl Radicals. Synthesis of Substituted Dihydronaphthalenes by Mn(III) Oxidation of Diethyl α-Benzylmalonate in the Presence of Alkynes

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Oxidation of diethyl α-benzylmalonate (1) by Mn(III) acetate in acetic acid at 70 °C in the presence of alkynes **2a–j** leads to dihydronaphthalene derivatives **3a–j** in moderate to good yields. A homolytic mechanism, involving oxidation of 1 to the corresponding malonyl radical, its addition to a triple bond, and intramolecular homolytic aromatic substitution of the vinyl radical adducts, is suggested. Propargylic hydrogen abstraction and dimerization at the malonic position for less reactive alkynes are the main side reactions observed. Relative and absolute rates of addition of α-benzylmalonyl radicals to representative alkynes and alkenes, deduced from competitive experiments, indicate a lower reactivity toward alkynes than toward the corresponding substituted alkenes. Both SOMO–LUMO and SOMO–HOMO interactions in the transition state lower the activation energy of these homolytic additions with alkenes, but only the SOMO–HOMO interaction dominates with the examined alkynes. 2-Naphthoic acid derivatives can be efficiently obtained by oxidative decarboxylation of **3** with NaI and air.

Introduction

Although extensive literature exists on the oxidation of carbonyl compounds by high valent metal salts in the presence of alkenes to obtain interesting functionalized products,[1,2] similar oxidations in the presence of alkynes have been investigated to a much smaller extent.[3] C–C triple bonds are generally less reactive toward carbon-centered radicals than similarly substituted C–C double bonds,[4] but the resultant vinyl radicals show higher reactivity in the addition to π-systems than alkyl radicals.[5] These opposed trends and the limited information on the behavior of α-carbonylalkyl radicals toward alkynes has not made straightforward the use in synthesis of the methodology which involves the oxidative addition of carbonyl compounds to C–C triple bonds induced by high-valent metal salts.

Following our report[6] on the efficient synthesis of substituted tetrahydronaphthalenes by oxidative addition–cyclization of diethyl α-benzylmalonates in the presence of alkenes, we now report on the extension of this model reaction to alkynes as radical traps. The demonstrated efficiency and selectivity of the initiation step involving these esters affords new insight on the reactivity of malonyl radicals and exploits the synthetic access to substituted naphthalenes in a more straightforward way.

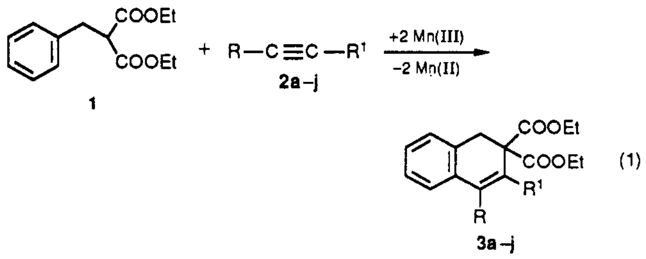
Results

Table I. Product Distribution in the Oxidation of Diethyl α-Benzylmalonate (1) by Mn(III) Acetate in the Presence of Alkynes 2a–j[a]

run	2	2/1 (molar ratio)	1 (convn, %)	products (yield, %) 3	4	5
1	**2a**	1.2	96	92	1	6
2[b]	**2b**	1.3	36	32	2	
2[c]	**2b**	1.3	66	50 + 18[d]	nd	
3	**2c**	3	95	91	<1	
4	**2d**	1.3	97	95	<1	
5	**2e**	1.3	79	70[e]	2	nd
6	**2f**	1.3	88	67	13	
7	**2g**	1.6	44	13	31	8[f]
8	**2g**	3	45	19	20	11[f]
9	**2h**	3	59	20 + 16[d]	21	
10	**2i**	3	50	12 + 10[d]	26	11[g]
11	**2j**	3	48	23	22	15[h]

[a] Mn(III) acetate, 4.2 mmol; **1** 2.1 mmol; AcOH, 25 mL; 70 ± 1 °C, 6–24 h, Ar. [b] Telomers were formed. [c] Solution 2.4 times more diluted. [d] Compounds **7b**, **7h**, and **7′h**, respectively. Treatment with SiO_2 in refluxing benzene converts **7** to **3b** and **3h** in nearly quantitative yield. [e] 34% and 36% mixture of the alcohol **3e** and of the corresponding acetate. 10% of the corresponding aldehyde was isolated also. [f] **5g**. [g] **5i**. [h] **5j**.

According to the results of Table I, the oxidation of diethyl α-benzylmalonate (1) by $Mn(OAc)_3$ in the presence of alkynes **2a–j** affords moderate to good yields of dihydronaphthalenes **3a–j** (eq 1).



(1)

a: R = n-C_6H_{13}, R^1 = H
b: R = COOEt, R^1 = H
c: R = Me_3Si, R^1 = H
d: R = Ph, R^1 = H
e: R = CH_2OH, R^1 = H
f: R = Ph, R^1 = Ph
g: R = C_2H_5, R^1 = C_2H_5
h: R = COOEt, R^1 = COOEt
i: R = COOMe, R^1 = CH_3
j: R = n-C_3H_7, R^1 = n-C_3H_7

The main side reactions observed are as follows: (a) dimerization at the malonic position to give **4**, (b) pro-

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[3] (a) Vinogradov, M. G.; Verenchicov, S. P.; Fedorova, T. M.; Nikishin, G. I. *Zh. Org. Khim.* **1975**, *11*, 947. (b) Vinogradov, M. G.; Direi, N. A.; Nikishin, G. I. *Zh. Org. Khim.* **1977**, *13*, 2498. (c) Vinogradov, M. G.; Dolinko, V. N.; Nikishin, G. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1984**, 2065. (d) Vinogradov, M. G.; Dolinko, V. N.; Nikishin, G. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1981**, 700.

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Table II. Reactivity of Some Alkynes and Alkenes toward Diethyl α-Benzylmalonyl Radical Relative to 1-Octene (AcOH, 60 ± 0.5 °C)

alkenes	k_{rel}	$k_o \times 10^{-4}$ (M^{-1} s^{-1})	alkynes	k_{rel} (M^{-1} s^{-1})	$k_a \times 10^{-4}$ (M^{-1} s^{-1})	k_o/k_a
$PhCH{=}CH_2$	82	800	$PhC{\equiv}CH$	10	98	8.2
n-$C_6H_{13}CH{=}CH_2$	1	9.8	n-$C_6H_{13}C{\equiv}CH$	0.33	3.3	3.0
$Me_3SiCH{=}CH_2$	0.41	3.9	$Me_3SiC{\equiv}CH$	0.22	2.1	1.9
$CH_2{=}CHCH_2OH$	0.20	1.9	$HC{\equiv}CCH_2OH$	0.12	1.2	1.6
$CH_2{=}CHCOOMe$	0.59	5.8	$HC{\equiv}CCOOEt$	0.063	0.6	9.7
(E)-$PhCH{=}CHPh$	0.4	3.8	$PhC{\equiv}CPh$	0.035	0.34	1.1
(E)-n-$PrCH{=}CH$-n-Pr	0.007	0.075	n-$PrC{\equiv}Cn$-Pr	0.003	0.03	2.5
$CH_2{=}C(Me)C(Me){=}CH_2$	70	686				
$CH_2{=}CHCN$	0.70	6.9				
$CH_2{=}CHOAc$	0.60	5.9				
$CH_2{=}CHCH_2COOEt$	0.56	5.5				
$CH_2{=}C(Me)$-i-Pr	4.5	44				
$CH_2{=}CHSiEt_3$	0.25	2.4				
c-C_6H_{10}	0.08	0.8				
(Z)-$EtOOCCH{=}CHCOOEt$	0.002	0.019				
(E)-$EtOOCCH{=}CHCOOEt$	0.011	0.11				

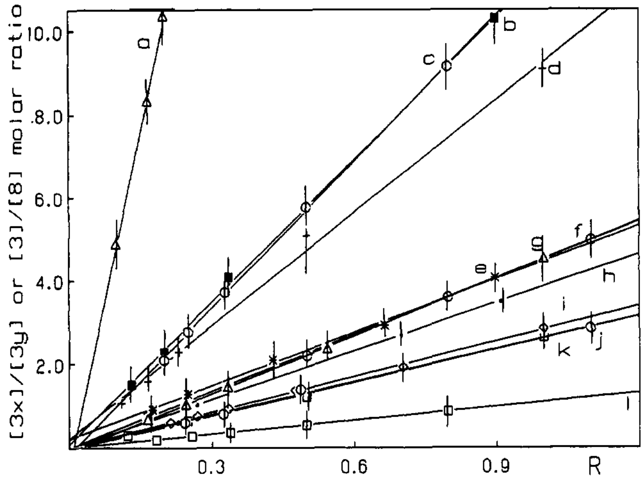


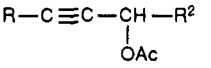
Figure 1. Dependence of the ratio [**3x**]/[**3y**] or [**3**]/[**8**] on initial molar ratio, R, of competing alkynes and/or alkenes.

pargylic hydrogen abstraction to give acetates **5**, and (c) nucleophilic addition of acetic acid to the activated double bond of **3**.

Process a is observed in reactions with internal alkynes (Table I, runs 6–11), and it is more important for alkyl-substituted internal alkynes (i.e., 3-hexyne (**2g**), ethyl 2-butenoate (**2i**), and 4-octyne (**2j**) (runs 8, 10, and 11)) than for alkynes substituted by conjugating groups (phenyl and ethoxycarbonyl, runs 6 and 9).

$[PhCH_2\text{-}C(COOEt)_2]_2$

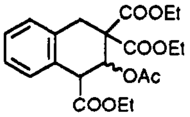
4



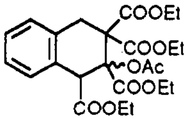
$$R{-}C{\equiv}C{-}\underset{\displaystyle OAc}{\underset{|}{CH}}{-}R^2$$

5

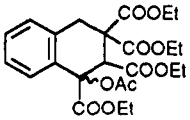
5g: $R = C_2H_5$, $R^2 = CH_3$
5i: $R = COOMe$, $R^2 = H$
5j: $R = n\text{-}C_3H_7$, $R^2 = C_2H_5$



7b



7h



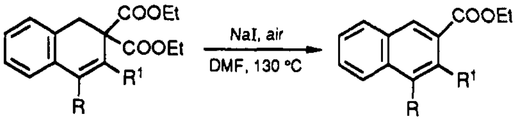
7'h

Process b occurs with all substrates having propargylic hydrogens (i.e., **2g**, **2i**, and **2j**). However, this acetoxylation process is not a direct oxidation of the alkyne but is induced by the presence of malonic esters. In fact, alkynes do not react appreciably at 70 °C with Mn(III) acetate in the absence of α-benzylmalonates.

The ionic process c occurs with substrates bearing ethoxycarbonyl groups (**2b** and **2h** in Table I, runs 3 and 9) and gives diastereomeric mixtures of acetates **7b**, **7h**, and **7'h**, respectively.

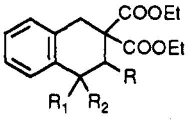
The importance of processes a and b can be in part limited using an excess of Mn(III) or malonic ester and the highest concentration possible of the alkyne. Products arising from process c can be converted back to dihydronaphthalenes **3b** and **3h** in almost quantitative yield by treatment of the crude reaction mixture with SiO_2 in refluxing benzene. In general, the oxidative addition of benzylmalonic esters to alkynes appears to be more complex than the analogous addition to alkenes, perhaps with the exception of the aryl derivatives.

In accord with the higher reactivity and lower oxidizability of intermediate vinyl radicals, open-chain products of addition of benzylmalonic ester to the alkyne were never observed. Furthermore, dihydronaphthalenes **3** can be rearomatized in good yield to 1,2-disubstituted 3-naphthoic acids derivatives **6** by thermal oxidative decarboxylation in DMF or N-methylpyrrolidone with NaI and air (eq 2).



3 **6** (2)

In order to investigate the effect of substituents on the reactivity of malonyl radicals toward alkynes, a series of competitive experiments at low conversion between couples of alkynes or between alkynes **2a–j** and some representative alkenes **9** were made (see Experimental Section).



8

$RCH{=}CR_1R_2$

9

Good linear correlations were generally observed between the ratio of addition–cyclization products [**3x**]/[**3y**] or [**3**]/[**8**] and the corresponding ratio of the alkynes or alkyne/alkene initial concentrations (R) according to eqs 3 and 4.

$$\frac{[\mathbf{3x}]}{[\mathbf{3y}]} = \frac{k_{ax}}{k_{ay}}R \tag{3}$$

$$\frac{[\mathbf{3}]}{[\mathbf{8}]} = \frac{k_a}{k_o}R \tag{4}$$

Typical results are collected in Figure 1. Owing to the low conversions and low concentration of Mn(III) acetate used in these experiments, very clean reactions were ob-

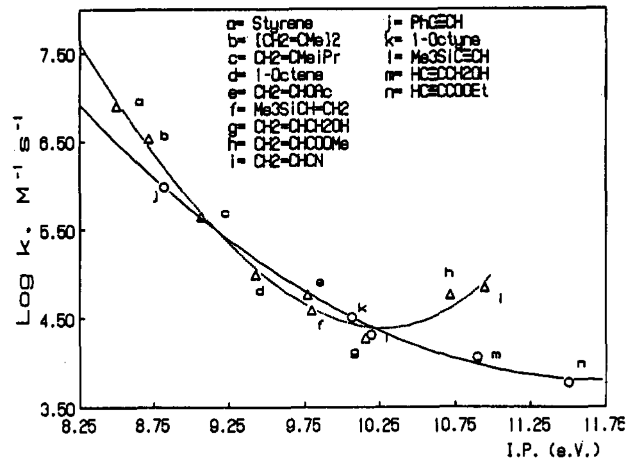


Figure 2. Dependence of absolute rate constants (log k) of addition of malonyl radical **10** on IP of alkynes (○) and alkenes (△): (a) ref 7a IP of a, e, i, f; ref 7b IP of b; ref 7c IP of c, k; ref 7d IP of d; ref 7e IP of h; ref 7f IP of j; ref 7g IP of l; ref 7h IP of m; ref 7i IP of n.

served also with substrates which afforded relatively complex reaction mixtures in preparative experiments (i.e., CH_2=$CHCH_2OH$, CH_2=CHOAc,[6] **2b**, and **2h**). Relative and absolute rate data for the addition of diethyl α-benzylmalonyl radical to alkenes and alkynes, deduced from the results of Figure 1 and from the ones reported in a previous paper for the absolute rate constants of addition to some alkenes,[6] are collected in Table II and plotted in Figure 2 against the ionization potential of the unsaturated substrates.[7a–i]

The independence of relative rates to the structure of starting benzylmalonates was tested with p-methyl and p-carbomethoxybenzyl derivatives, which yielded the same relative rates, in the limits of experimental error, for the couples 1-octene/trimethylvinylsilane (2.5 ± 0.3 and 2.7 ± 0.2, respectively, vs 2.4 ± 0.1 (Experimental Section).

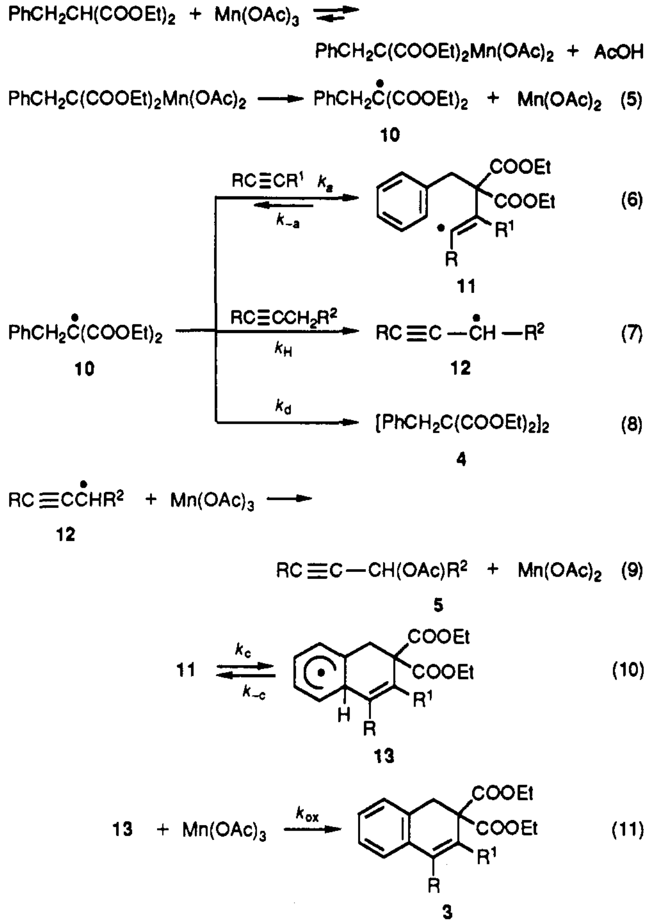
All the competitive experiments were carried out at 60 ± 0.5 °C owing to the small effect of the temperature on the relative rates of these highly exothermic processes characterized by a low difference in activation energies.[8]

Discussion

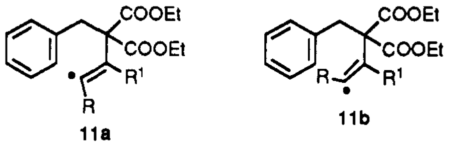
The results of this study are in accord with the homolytic stoichiometric oxidation mechanism reported in Scheme I.

Inner-sphere electron transfer or homolysis of the metal complexed anion of **1** generates α-benzylmalonyl radicals **10** (eq 5). Depending on the conditions of experiments and the nature of the alkyne, these intermediates partition between addition to triple bond (eq 6), hydrogen abstraction from propargylic positions (eq 7), and dimerization (eq 8). Propargylic radicals **12** are efficiently oxidized to acetates **5** (eq 9), whereas vinyl radicals **11** add to the aromatic ring (eq 10), affording dihydronaphthalenes **3** after oxidation of the cyclohexadienyl radical **13** by $Mn(OAc)_3$ (eq 11).

Scheme I



The stereochemical problem of vinyl radicals adducts[9] (eq 12), which depends on substituents R and could in principle prevent the aromatic substitution of the cis configuration **11b** owing to the σ nature of vinyl radicals, apparently does not limit the addition–cyclization reaction with any substituent in this series. This probably occurs because the isomerization rates of eq 12 are faster than the irreversible cyclization rate of eq 10 (>10^6–10^7 s^{-1} from the results of this work) while no significant competitive process for radicals **11b** is available.



(12)

The effect of substituents on the unsaturated carbon atom attacked is relevant, as generally observed in the addition of carbon radicals.[10] The steric nature of **10** determines in particular the regioselective addition to the unsubstituted end of terminal alkenes and alkynes. The sensitivity to steric effects exhibited in the addition to alkynes is 1 order of magnitude lower than the addition to alkenes, in accord with the lower steric demand of triple than double bonds (cf. $PhCH$=CH_2/(E)-$PhCH$=$CHPh$

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(8) Typical competitive experiments at different temperatures on the couple 1-octyne/1-nonene gave a differential activation energy of 1.54 ± 0.14 kcal/mol and a differential activation entropy of 2.8 ± 0.4 eu in the temperature range 50–100 °C. The relative reactivity ratio was 0.39 ± 0.05 at 60 °C and 0.50 ± 0.05 at 100 °C.

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Table III. Relative Rates k_o/k_a for Addition of Various Carbon-Centered Radicals to Alkene/Alkyne Couples

	$^\bullet CH_2CO$-O-*t*-Bu[a]	$CF_3^\bullet$ [b]	$PhCH_2C^\bullet$-$(COOEt)_2$[c]	*t*-Bu$^\bullet$ [d]	Cy$^\bullet$ [d]
$MeCH{=}CH_2$/$MeC{\equiv}CH$		24		0.92	
$PhCH{=}CH_2$/$PhC{\equiv}CH$	95.5	36	9.0	6.63	3.5
(*Z*)-$MeCH{=}CHMe$/$MeC{\equiv}CMe$		94	2.6		
$CH_2{=}CHCOOMe$/$HC{\equiv}CCOOMe$	2.22		9.7		3.0
(*Z*)-$MeOOCCH{=}CHCOOMe$/$MeOOCC{\equiv}CCOOMe$				2.5	
t-$BuCH{=}CH_2$/*t*-$BuC{\equiv}CH$	1.25			0.91	
$C_6H_{13}CH{=}CH_2$/$C_6H_{13}C{\equiv}CH$			3.0		
$PhCH{=}CH_2$/$HC{\equiv}CCOOMe$	9.65		1.3×10^3		

[a] Reference 7a, 296 K. [b] Reference 11b–c, 437 K. [c] This work, 333 K. [d] Reference 11d, 293 K.

and $C_6H_{13}CH{=}CH_2$/(*E*)-$C_3H_7CH{=}CHC_3H_7$ vs $PhC{\equiv}CH$/$PhC{\equiv}CPh$ and $C_6H_{13}C{\equiv}CH$/$C_3H_7C{\equiv}CC_3H_7$, Table II).

The main conclusion of this study concerns the addition step of eq 6. Owing to the irreversibility of subsequent reactions, the relative rate data of Table II do in fact give quantitative information on the effects of substituents in α and β positions to the attacked carbon of the unsaturated substrate. In general, alkynes are less reactive toward diethyl α-benzylmalonyl radicals than to the corresponding substituted alkenes ($k_o/k_a > 1$), as reported in Table II and in Table III (where literature data for similar addition of some other carbon-centered radicals are also reported). The ratio spans 1 order of magnitude, from the ethoxycarbonyl (9.7) to the hydroxymethyl substituent (1.6). The effect of 1,2-disubstitution on the ratio k_o/k_a is in the same direction but somewhat lower.

The relative reactivity of alkyne vs alkene derivatives is apparent in the plot of the absolute rate constants for the addition of **10** in both series versus the ionization potential of the unsaturated substrates (Figure 2). The curves are very close in a restricted range of ionization potentials, but diverge in favor of alkenes at higher ionization potentials. In the addition to olefins, a well-defined minimum is evident, whereas in the addition to alkynes the rates decrease with the decrease of the electron-donating properties of substituents. Because the ionization potential of alkynes are higher than the corresponding substituted alkenes (0.2–0.8 eV), the trend of curves in Figure 2 determines a lower difference in reactivity for those derivatives, which present an IP in the range of superimposition of the two curves. In any case, no linear correlation between the logaritm of the rates and ionization potentials (IP) or electron affinity (EA) of the unsaturated substrate is observed, as reported previously for the nucleophilic *tert*-butyl radical[11a] (χ_R = (IP + EA)/2 of 4.5 eV[12]). On the other hand, the correlation, in the case of alkenes, compares well with the one reported by Fisher for (*tert*-butoxycarbonyl)methyl radical.[7a] Such a comparison, reported in Figure 3, is in accord with the phylic properties of the radicals involved. From Figure 3, α-benzylmalonyl radicals appear to be more electrophilic species than the (alkoxycarbonyl)methyl radicals (χ_R = (IP + EA)/2 = 6.2 eV[7a]).

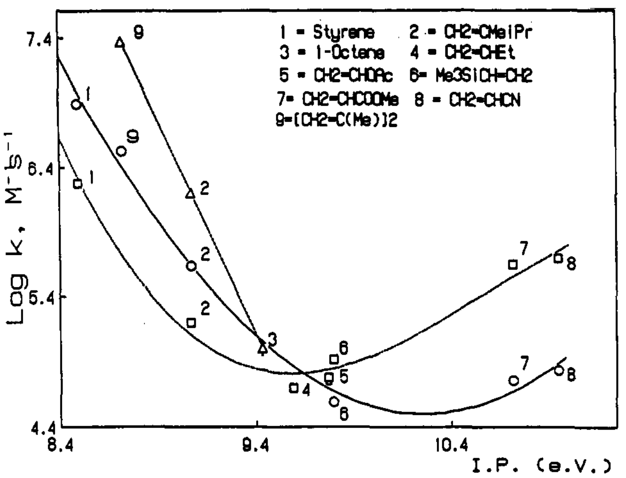
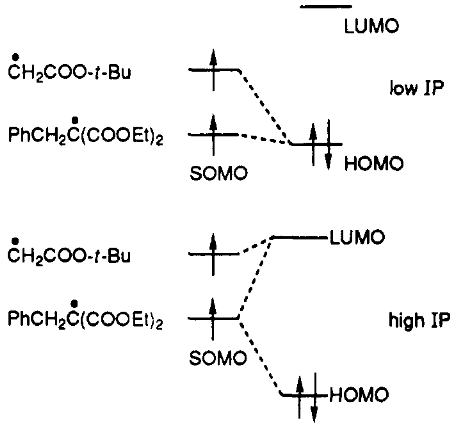


Figure 3. Log of absolute rate constant (k) for the addition to some alkenes of radical **10** (○), $^\bullet CH_2COO$-*t*-Bu (□) (ref 7a), and $^\bullet CH(CN)_2$ (△) (ref 15) vs IP of alkenes.

Scheme II



Malonyl radicals are therefore more reactive than alkoxycarbonyl methyl radicals toward electron-rich alkenes, the situation reverting with increasing the IP of the substrates. This is conceivable in term of frontier molecular orbital stabilization that moves from a SOMO–LUMO to a SOMO–HOMO control with increasing IP of the alkenes, as pictorially represented in Scheme II, provided that the HOMO–LUMO difference in energy is almost constant along the series.[7a,11a]

The σ nature of vinyl radical **11** prevents any significant stabilization by substituents. So, the trend of Figure 2 for monosubstituted alkynes depends only on the nature of the transition state of the addition which must be characterized by a significant charge transfer from the substrate to the radical (eq 13), in accord with the electrophilic character of malonyl radicals, due to a SOMO–HOMO frontier molecular orbital interaction.[14]

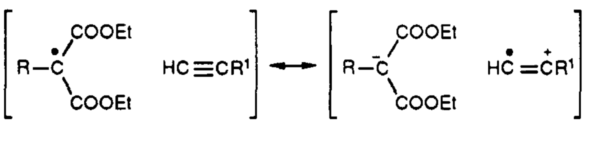


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Table IV. Absolute Rate Constants for the Addition of Various Radicals to Unsaturated Substrates

	$Bz\dot{C}$-$(COOEt)_2$[a]	$\dot{C}H_2COO$-tBu[b]	*t*-Bu•[c]	$\dot{C}H(CN)_2$[d]
$PhCH{=}CH_2$	8×10^6	1.9×10^6	1.0×10^5	
$CH_2{=}CHCN$	7×10^4	5×10^5	2.0×10^6	
$CH_2{=}CHCOOMe$	5.7×10^4	4.5×10^5		
$CH_2{=}CHOAc$	5.9×10^4	6×10^4	4.2×10^3	
$CH_2{=}CHSiMe_3$	3.9×10^4	8.4×10^4	9.6×10^3	
$CH_2{=}CHEt$		5×10^4	1.1×10^3	
$C_6H_{13}CH{=}CH_2$	9.8×10^4			1.0×10^5
$CH_2{=}C(Me)C(Me){=}CH_2$	6.86×10^6			2.37×10^7
$CH_2{=}C(Me)$-*i*-Pr	4.4×10^5	1.6×10^5		1.6×10^6
$EtOOCC{\equiv}CCOOEt$		5.57×10^5		

[a] This work, 333 K. [b] Reference 7a, 296 K. [c] Reference 11a, 293 K. [d] Reference 15, 301 K.

In the case of alkynes the LUMO orbitals lie too high in energy[15] because some SOMO–LUMO interaction takes place. Therefore, as a consequence, only a decrease in rate is observed due to a decreased SOMO–HOMO interaction. In Table IV are collected our and literature data for the absolute rates of addition of various radicals to olefins. Such a comparison yields the following scale of electrophilicity for the examined radicals: $^{\bullet}CH(CN)_2$ > $BzC^{\bullet}(COOEt)_2$ > $^{\bullet}CH_2COO$-*t*-Bu.

Notwithstanding the slower rate of addition of **10** to alkynes, derivatives **3** can be obtained in high yields, and Scheme I can accommodate the observed results.

Substantial amounts of dimers **4** can be observed when step 6 is sufficiently slow and radical **10** attains high stationary concentration so that path 8 becomes competitive. We can extimate that the lower limit of detection of the dimer in the case of stoichiometric ratio of reagents occurs at a k_a value lower than 6×10^3 M^{-1} s^{-1}.

For the case of diphenylacetylene it is possible to deduce how a stationary concentration of **10** of about 3.5×10^{-8} M is sufficient to make the formation of **4** competitive in respect to the formation of **3f** when k_d is assumed to be as high as 10^9 M^{-1} s^{-1}.

The relatively high ratio of propargylic hydrogen abstraction vs triple-bond addition for radicals **10** parallels the results of allylic hydrogen abstraction vs olefins addition previously reported for the same radical,[6] and it is a further indication of the electrophilic properties of malonyl radicals. Moreover, our data reasonably agree with the reported value of 1.8 kcal/mol for the difference in activation energy for the hydrogen abstraction by chlorine atoms,[16,17] suggesting a considerable reduction of the difference in enthalpy for the process as deduced from the reported difference of 5 kcal/mol between allylic vs propargylic C–H bond energies.[18] The allylic and propargylic acetoxylation by $Mn(OAc)_3$, mediated by malonic esters, is a clear limit for the reaction of eq 1 but can open new perspectives on selective C–H oxidation in complex molecules, and further work in this direction is in progress.

Experimental Section

General Methods. ^1H NMR spectra were obtained in $CDCl_3$ on a Bruker AM 200, and the data are reported in δ (ppm) relative to tetramethylsilane. Mass spectra were recorded on a Varian Mat 112F spectrometer and are reported as *m/e* (relative intensity). IR spectra were recorded on a Perkin-Elmer 1420 spectrophotometer. The GLC analyses were carried out on a Carlo Erba HRG 5300 chromatograph equipped with a Nordibond OV-1 column (25-m length, i.d. 0.32 mm) and a flame ionization detector. High-performance liquid chromatography (HPLC) analyses were performed with a SHIMADZU LC-8 apparatus on a LiChrosorb RP-18 (7-μm) column using $CH_3CN/CH_3OH/H_2O$ (52/15/33) as eluent. Thin-layer chromatography (TLC) was performed on Merck precoated silica gel 60 F-254 plates (0.25 mm). Flash chromatography was carried out on Merck silica gel 60 (230–400 mesh).

Materials. Manganese(III) acetate dihydrate was obtained from Fluka; anhydrous manganese(III) acetate was prepared as described.[19] Both salts were tested by iodometric titration for purity, and only samples having more than 98% manganese(III) were used. All the alkynes and alkenes were commercial products having a purity higher than 98%; they were distilled before use. Starting material **1** (161–2 °C (10 mmHg)) and tetrahydronaphthalenes **8** were synthesized as reported.[6] Propargylic acetoxylation products **5g**, **5i**, and **5j** were isolated by chromatography and compared with authentic samples. The addition product of **1** to allylic alcohol under competitive conditions was solely the 4-(hydroxymethyl)-2,2-bis(ethoxycarbonyl)tetrahydronaphthalene (**3e**) without trace of the corresponding acetate or internal lactone.[6]

General Procedure for Mn(III) Acetate Reactions. A 50-mL round-bottom flask equipped with a reflux condenser, magnetic stirrer, and an argon inlet was charged with **1** (2.15 mmol), manganese(III) acetate (4.3 mmol), the unsatured substrate **2** (in molar ratio ranging from 1.2:1 to 5:1 based on **1**), and acetic acid (25 mL). The mixture was heated at 70 ± 1 °C under argon until the color faded or for 24 h. The reaction mixture was then cooled, diluted with water (60 mL), and extracted with diethyl ether (4 × 15 mL). The combined extracts were washed with water and saturated sodium bicarbonate, dried ($MgSO_4$), and analyzed by gas chromatography with decane (or dodecane) as internal standard for the determination of the yield of products and the conversion of **1**. The results are reported in Table I. In parallel experiments, the dried final extracts were concentrated in vacuo and the crude reaction mixture was purified by column chromatography over silica gel eluting with ethyl acetate/hexane (9:1–6:4). Analytical data and gas chromatographic response factors were obtained on dried pure fractions (by TLC and GC).

2,2-Bis(ethoxycarbonyl)-4-*n*-hexyl-1,2-dihydronaphthalene (3a). ^1H-NMR: 0.96 (t, 3 H), 1.28 (t, 6 H), 1.45 (m, 8 H), 2.58 (t, 2 H), 3.42 (s, 2 H), 4.23 (q, 4 H), 6.04 (s, 1 H), 7.26 (m, 1 H), 7.28 (m, 1 H), 7.30–7.40 (m, 2 H). MS: 358 ($M^{\bullet+}$, 21), 285 (94), 213 (27), 157 (52), 141 (77), 129 (59), 85 (36), 43 (100). Anal. Calcd for $C_{22}H_{30}O_4$: C, 73.71; H, 8.44. Found: C, 73.9; H, 8.3.

2,2,4-Tris(ethoxycarbonyl)-1,2-dihydronaphthalene (3b). ^1H-NMR: 1.23 (t, 6 H), 1.40 (t, 3 H), 3.38 (s, 2 H), 4.22 (q, 4 H), 4.42 (q, 2 H), 7.15 (s, 1 H), 7.17–7.32 (m, 3 H), 7.76–7.9 (m, 1 H). MS: 346 ($M^{\bullet+}$, 7), 273 (80), 245 (17), 227 (25), 199 (26), 183 (35), 173 (25), 155 (93), 129 (100), 115 (22). Anal. Calcd for $C_{19}H_{22}O_6$: C, 65.88; H, 6.40. Found: C, 65.7; H, 6.3.

2,2-Bis(ethoxycarbonyl)-4-(trimethylsilyl)-1,2-dihydronaphthalene (3c). ^1H-NMR: 0.3 (s, 9 H), 1.19 (t, 6 H), 3.31 (s, 2 H), 4.16 (q, 4 H), 6.47 (s, 1 H), 7.13–7.31 (m, 4 H). MS: 346 ($M^{\bullet+}$, 6), 273 (37), 185 (25), 155 (100), 73 (85). Anal. Calcd for $C_{19}H_{26}O_4Si$: C, 65.86; H, 7.56. Found: C, 65.9; H, 7.7.

2,2-Bis(ethoxycarbonyl)-4-phenyl-1,2-dihydronaphthalene (3d). ^1H-NMR: 1.21 (t, 6 H), 3.47 (s, 2 H), 4.19 (q, 4 H), 6.17 (s, 1 H), 7.13 (m, 4 H), 7.35 (s, 5 H). MS: 350 ($M^{\bullet+}$, 21), 277 (72), 233 (27), 205 (100). Anal. Calcd for $C_{22}H_{22}O_4$: C, 75.41; H, 6.33. Found: C, 75.2; H, 6.2.

2,2-Bis(ethoxycarbonyl)-4-(hydroxymethyl)-1,2-dihydronaphthalene (3e). ^1H-NMR: 1.26 (t, 6 H), 3.40 (s, 2 H), 4.21 (q, 6 H), 4.62 (s, 2 H), 6.27 (s, 1 H), 7.15–7.35 (m, 2 H), 7.35–7.45 (m, 2 H). MS: 304 ($M^{\bullet+}$, 5), 231 (22), 213 (11), 201 (15), 185 (10), 169 (28), 157 (18), 141 (88), 129 (100), 115 (13). Anal. Calcd for

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$C_{19}H_{26}O_5$: C, 68.24; H, 7.84. Found: C, 68.5; H, 7.6.

2,2-Bis(ethoxycarbonyl)-4-(acetoxymethyl)-1,2-dihydronaphthalene (3e′). ^{1}H-NMR: 1.26 (t, 6 H), 2.13 (s, 3 H), 3.43 (s, 2 H), 4.20 (q, 6 H), 5.05 (s, 2 H), 6.33 (s, 1 H), 7.25 (s, 4 H). MS: 346 (2), 213 (45), 185 (15), 169 (30), 141 (100), 129 (12), 115 (12), 43 (44). Anal. Calcd for $C_{21}H_{28}O_6$: C, 67.00; H, 7.50. Found: C, 66.9; H, 7.7.

2,2-Bis(ethoxycarbonyl)-3,4-diphenyl-1,2-dihydronaphthalene (3f). ^{1}H-NMR: 1.1 (t, 6 H), 3.79 (s, 2 H), 4.06 (q, 4 H), 6.82 (d, 1 H), 7.0–7.42 (m, 13 H). MS: 426 ($M^{\bullet+}$, 63), 380 (3), 353 (34), 307 (100), 281 (65), 203 (23). Anal. Calcd for $C_{30}H_{32}O_4$: C, 78.92; H, 7.06. Found: C, 78.8; H, 6.9.

2,2-Bis(ethoxycarbonyl)-3,4-diethyl-1,2-dihydronaphthalene (3g). ^{1}H-NMR: 1.28 (t, 6 H), 1.32 (t, 6 H), 2.50 (q, 2 H), 2.73 (q, 2 H), 3.50 (s, 2 H), 4.24 (q, 4 H), 7.22–7.50 (m, 4 H). MS: 330 ($M^{\bullet+}$, 10), 257 (31), 213 (25), 185 (100), 169 (42), 157 (51), 141 (37), 129 (76), 115 (19). Anal. Calcd for $C_{22}H_{32}O_4$: C, 73.30; H, 8.95. Found: C, 73.4; H, 9.1.

2,2,3,4-Tetrakis(ethoxycarbonyl)-1,2-dihydronaphthalene (3h). ^{1}H-NMR: 1.14–1.41 (m, 12 H), 3.52 (s, 2 H), 4.22 (m, 6 H), 4.42 (q, 2 H), 7.10–7.50 (m, 4 H). MS: 418 ($M^{\bullet+}$, 1), 373 (6), 299 (67), 225 (63), 199 (100), 154 (17), 127 (13), 115 (17). Anal. Calcd for $C_{24}H_{32}O_8$: C, 64.27; H, 7.19. Found: C, 64.3; H, 7.0.

2,2,4-Tris(ethoxycarbonyl)-3-methyl-1,2-dihydronaphthalene (3i). ^{1}H-NMR: 1.14 (t, 6 H), 2.44 (s, 3 H), 3.42 (s, 2 H), 3.77 (s, 3 H), 4.14 (m, 4 H), 7.10–7.35 (m, 3 H), 7.4–7.5 (m, 1 H). MS: 346 ($M^{\bullet+}$, 3), 241 (96), 227 (22), 213 (57), 201 (50), 169 (87), 157 (88), 142 (100), 128 (30), 115 (47), 59 (46). Anal. Calcd for $C_{22}H_{30}O_6$: C, 67.67; H, 7.74. Found: C, 67.5; H, 7.4.

2,2-Bis(ethoxycarbonyl)-3,4-di-*n*-propyl-1,2-dihydronaphthalene (3j). ^{1}H-NMR: 0.98 (m, 6 H), 1.17 (t, 6 H), 1.47 (m, 4 H), 2.26 (m, 2 H), 2.52 (m, 2 H), 3.33 (s, 2 H), 4.62 (q, 4 H), 7.03–7.27 (m, 4 H). MS: 358 ($M^{\bullet+}$, 15), 285 (46), 239 (29), 213 (39), 199 (53), 183 (48), 169 (33), 157 (60), 141 (75), 129 (100), 43 (84). Anal. Calcd for $C_{24}H_{36}O_4$: C, 74.19; H, 9.34. Found: C, 74.3; H, 9.1.

General Procedure for Competitive Experiments. Following the general procedure for reaction with Mn(III), a solution of 1 (2.15 mmol) and a few unsaturated substrates (for a total of 22 mmol) in AcOH (25 mL) were reacted in a thermostatic bath at 60 ± 5 °C for 12 h. The relative molar ratio of the competing unsatured substrates was varied for each couple in the range 1:1–1:10 as reported in Figure 1.

Generally, the conversion of the more reactive substrate was less than 15% in these conditions. The following couples were examined: (a) $PhC{\equiv}CH/Me_3SiC{\equiv}CH$; (b) $PhC{\equiv}CPh/n\text{-}C_3H_7C{\equiv}C(n\text{-}C_3H_7)$; (c) $PhC{\equiv}CH/n\text{-}C_6H_{13}CH{=}CH_2$; (d) $CH_2{=}CHCOOEt/HC{\equiv}CCOOEt$; (e) $n\text{-}C_6H_{13}C{\equiv}CH/HC{\equiv}CCOOEt$; (f) $n\text{-}C_6H_{13}CH{=}CH_2/Me_3SiC{\equiv}CH$; (g) $n\text{-}C_6H_{13}CH{=}CH_2/Et_3SiCH{=}CH_2$; (h) $HC{\equiv}CCH_2OH/PhC{\equiv}CPh$; (i) $n\text{-}C_6H_{13}CH{=}CH_2/n\text{-}C_6H_{13}C{\equiv}CH$; (j) $n\text{-}C_6H_{13}CH{=}CH_2/Me_3SiCH{=}CH_2$; (k) $n\text{-}C_6H_{13}C{\equiv}CH/HC{\equiv}CCH_2OH$; (l) $Me_3SiC{\equiv}CH/CH_2{=}CHCH_2OH$; (m) $n\text{-}C_6H_{13}CH{=}CH_2/t\text{-}PhCH{=}CHPh$.

The results obtained as a mean of four independent experiments are plotted in Figure 1 with the limits of replication. Least-squares analysis of the experimental data gives the following relative rates: (a) 47 ± 3 (r = 0.9978); (b) 11.6 ± 0.4 (r = 0.991); (c) 10 ± 0.8 (r = 0.9985); (d) 9.7 ± 0.3 (r = 0.9995); (e) 5.3 ± 0.2 (r = 0.9998); (f) 4.6 ± 0.1 (r = 0.9991); (g) 4.1 ± 0.1 (r = 0.9955); (h) 3.4 ± 0.2 (r = 0.9992); (i) 3.0 ± 0.1 (r = 0.9995); (j) 2.4 ± 0.1 (r = 0.9990); (k) 2.8 ± 0.1 (r = 0.9996), (l) 1.1 ± 0.1 (r = 0.9987); (m) 2.5 ± 0.1 (r = 0.9990). These results allow us to obtain the absolute rate constants for the addition of malonyl radicals to unsaturated substrates reported in Table II.

Registry No. 1, 607-81-8; **2a**, 629-05-0; **2b**, 623-47-2; **2c**, 1066-54-2; **2d**, 536-74-3; **2e**, 107-19-7; **2f**, 501-65-5; **2g**, 928-49-4; **2h**, 762-21-0; **2i**, 23326-27-4; **2j**, 1942-45-6; **3a**, 141344-90-3; **3b**, 141344-91-4; **3c**, 141344-92-5; **3d**, 141344-93-6; **3e**, 141344-94-7; **3e′**, 141344-95-8; **3f**, 141344-96-9; **3g**, 141344-97-0; **3h**, 141344-98-1; **3i**, 141344-99-2; **3j**, 141345-00-8; *cis*-**7b**, 141345-01-9; *trans*-**7b**, 141345-02-0; *cis*-**7h**, 141345-03-1; *trans*-**7h**, 141345-04-2; *cis*-**7′h**, 141345-05-3; *trans*-**7′h**, 141345-06-4; Mn(III), 14546-48-6; $PhCH{=}CH_2$, 100-42-5; $n\text{-}C_6H_{13}CH{=}CH_2$, 111-66-0; $Me_3SiCH{=}CH_2$, 754-05-2; $CH_2{=}CHCH_2OH$, 107-18-6; $CH_2{=}CHCOOMe$, 96-33-3; (E)-$PhCH{=}CHPh$, 103-30-0; (E)-$n\text{-}PrCH{=}CH\text{-}n\text{-}Pr$, 14850-23-8; $CH_2{=}C(Me)C(Me){=}CH_2$, 513-81-5; $CH_2{=}CHCN$, 107-13-1; $CH_2{=}CHOAc$, 108-05-4; $CH_2{=}CHCH_2C(O)OEt$, 1617-18-1; $CH_2{=}C(Me)\text{-}i\text{-}Pr$, 563-78-0; $CH_2{=}CHSiEt_3$, 1112-54-5; $c\text{-}C_6H_{10}$, 110-83-8; (Z)-$EtOOCCH{=}CHCOOEt$, 141-05-9; (E)-$EtOOCCH{=}CHCOOEt$, 623-91-6; (Z)-$MeCH{=}CHMe$, 590-18-1; $MeC{\equiv}CMe$, 503-17-3; $HC{\equiv}CCOOMe$, 922-67-8; $CH_2CHCOOEt$, 140-88-5.

Regioselectivity and Stereoselectivity in the Photodimerization of Rigid and Semirigid Stilbenes

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The ($2\pi + 2\pi$)-photodimerizations of 2-phenylindene (1), 2-(4-methoxyphenyl)indene (9), and 5,10-dihydroindeno[2,1-*a*]indene (2) were investigated in a variety of homogeneous and micellar solvents. Four isomeric photodimers were formed from 1 and 9: syn-head-to-tail, syn-head-to-head, anti-head-to-tail, and anti-head-to-head. Relative yields of these as well as syn/anti- and head-to-tail (ht)/head-to-head (hh) ratios were determined in various solvents and as a function of temperature. In 1 syn/anti ratios ranged from 1.07 to 1.62 and ht/hh ratios from 0.88 to 1.28. In 9 syn/anti ratios between 0.83 and 2.55 and ht/hh ratios between 0.4 and 1.2 were found; preferred formation of anti and hh products was observed in micellar solvents as expected from preorientation of reactants. Two photodimers (ht and hh) were found upon irradiation of 2. ht/hh ratios ranged from 0.89 to 1.56. The variations of these ratios can be understood on the basis of a kinetic scheme, in which individual excimer states as precursors of the respective dimers are involved.

Introduction

Upon irradiation stilbene and its derivatives are known to undergo three different types of photoreactions: cis-trans isomerization,[1] and dihydrophenanthrene formation,[2] and dimerization.[3] Only the latter is possible when the central stilbene double bond is incorporated in a ring system, i.e., in rigid and semirigid stilbene compounds. Examples are 2-phenylindene (1) (semirigid) and 5,10-

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