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Relative Rates for the Addition Reactions of the Malonyl Radical to Substituted Styrenes Induced by Cerium(IV) Ammonium Nitrate and Tributyltin Hydride. A Comparison

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The relative rates for the addition reactions of the malonyl radical to substituted styrenes induced by cerium(IV) ammonium nitrate (CAN) and tributyltin hydride have been determined. The two processes exhibit practically identical ρ^+ values (–1.05 and –1.06), thus suggesting that the coordination between the metal and the radical does not play a significant role in the CAN-promoted oxidative additions.

In the last decade there has been a growing interest in the synthetic exploitation of the oxidative addition of carbonyl compounds to alkenes promoted by metal ions (eq 1, where X is a ligand of the metal M or some other nucleophile present in the medium).[2]

$$R-\overset{O}{\overset{\|}{C}}-R + \diagup\hspace{-0.3em}=\hspace{-0.3em}R' \xrightarrow{+2M^{n+} + X^-} R-\overset{O}{\overset{\|}{C}}-\diagdown\hspace{-0.3em}\underset{X}{\diagup}R' + 2M^{(n-1)+} + H^+ \quad (1)$$

The mechanism of this reaction has long been described as in eqs 2–4: an electrophilic α-oxoalkyl radical, the critical intermediate, is first formed (eq 2), which adds to the alkene to give another carbon-centered radical. The latter is, however, a nucleophilic species, undergoing easy oxidation by the metal ion to the final adduct.

$$R-\overset{O}{\overset{\|}{C}}-R + M^{n+} \longrightarrow R-\overset{O}{\overset{\|}{C}}\cdot + M^{(n-1)+} + H^+ \quad (2)$$

$$R-\overset{O}{\overset{\|}{C}}\cdot + \diagup\hspace{-0.3em}=\hspace{-0.3em}R' \longrightarrow R-\overset{O}{\overset{\|}{C}}-\diagdown\hspace{-0.3em}\underset{\cdot}{\diagup}R' \quad (3)$$

$$R-\overset{O}{\overset{\|}{C}}-\underset{\cdot}{\diagdown}R' + M^{n+} + X^- \xrightarrow{-M^{(n-1)+}} R-\overset{O}{\overset{\|}{C}}-\underset{X}{\diagdown}R' \quad (4)$$

In view of the electrophilic character of the α-oxoalkyl radical, the reaction is favored by electron-donating substituents in the alkene moiety, thus representing the counterpart of the Michael addition.

Recently, more detailed mechanistic studies have, however, indicated that the mechanism could be somewhat more complex than originally thought. Accordingly, it has been suggested that the alkene attacking species might be a metal complexed radical or, in some case, not even a radical.[3,5,6]

In particular, for the cerium(IV) ammonium nitrate (CAN) promoted oxidative addition of carbonyl compounds to dienes the possibility has been discussed that the reactive species is a cerium(III) complexed α-oxoalkyl radical (1) in equilibrium with a cerium(IV) enolate (2).[6]

$$\overset{\bullet}{\diagup}\hspace{-0.3em}=\hspace{-0.3em}O \longrightarrow Ce^{III} \rightleftharpoons \diagdown\hspace{-0.3em}=\hspace{-0.3em}O-Ce^{IV}$$
$$1 \qquad\qquad\qquad 2$$

Clearly these hypotheses are of interest since they envisage an additional and specific role of the oxidizing metal, thereby it might significantly influence important properties (i.e., selectivity, steric requirements) of the attacking radical.

Therefore we felt that some insight on this problem could be provided by comparing the behavior of metal ion promoted additions of carbonyl compounds to alkenes with those of the corresponding reactions where the α-oxoalkyl radical clearly is generated in an uncomplexed form. Among these, particularly effective is that where the radical is generated photochemically by the reaction of an α-oxoalkyl halide with a trialkyltin radical (eqs 5–7).[7]

$$R-\overset{O}{\overset{\|}{C}}-X + Bu_3Sn\cdot \longrightarrow R-\overset{O}{\overset{\|}{C}}\cdot + Bu_3SnX \quad (5)$$

$$R-\overset{O}{\overset{\|}{C}}\cdot + \diagup\hspace{-0.3em}=\hspace{-0.3em}R' \longrightarrow R-\overset{O}{\overset{\|}{C}}-\underset{\cdot}{\diagdown}R' \quad (6)$$

$$R-\overset{O}{\overset{\|}{C}}-\underset{\cdot}{\diagdown}R' + Bu_3SnH \longrightarrow R-\overset{O}{\overset{\|}{C}}-\underset{X}{\diagdown}R' + Bu_3Sn\cdot \quad (7)$$

In this paper we report on a study of the selectivity of the addition reactions of malonyl radicals to ring-substituted styrenes 3a–g (a, Z = *p*-OMe; b, Z = *p*-Me; c, Z =

3a–g

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Table I. Yields of Products 4–6 via CAN- or Bu₃SnH-Induced Addition Reactions of Malonyl Radicals to Substituted Styrenes 3

styrene	reaction induced by CAN [4 + 5], %[a] (4/5)[b]	reaction induced by Bu₃SnH 6, %
p-methoxystyrene (3a)		40
p-methylstyrene (3b)	90 (0.7)	40
styrene (3c)	93 (2.9)	50
p-chlorostyrene (3d)	86 (2.7)	50
m-chlorostyrene (3e)	94 (5.2)	
m-nitrostyrene (3f)	84 (5.6)	
p-nitrostyrene (3g)		35

[a] Isolated yields. [b] Determined by NMR.

H; **d**, Z = *p*-Cl; **e**, Z = *m*-Cl; **f**, Z = *m*-NO₂; **g**, Z = *p*-NO₂) in MeOH. The attacking species has been formed either by reaction of CAN with dimethyl malonate or by the photochemical reaction of diethyl chloromalonate with tributyltin hydride. By competitive experiments the effect of ring substituents on the rate of the two reactions has been determined.

Results and Discussion

When CAN is reacted in MeOH with dimethyl malonate and a styrene derivative (3) (molar ratio 2:1:0.5–1), the adducts 4 and 5 are formed in overall yields close to 90%
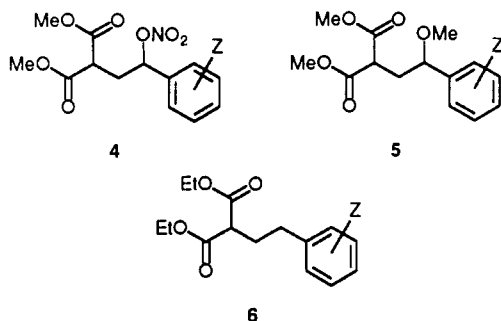
(Table I). Product 6 is formed when tributylstannane is added under irradiation to a solution of diethyl chloromalonate and the styrene derivatives. The adducts were obtained in 35–50% yield, depending on the nature of the substituent (Table I).

The competitive kinetic experiments using tributyltin hydride were carried out by reacting a suitable pair of substituted styrenes (at least 10 times with respect to the chloromalonate) and determining the relative amounts of the two adducts by GC. This procedure, however, was not suitable for the reactions promoted by CAN since two adducts are formed in each reaction, one of which (the nitrate 4) is thermally unstable. In this case the pair of styrenes 3 was reacted with 25–50% of the stoichiometric amounts of CAN and dimethyl malonate and the moles of the two styrenes left after the reaction was completed were determined by GC.

The relative rates for both reactions are reported in Table II. As expected, in both cases, electron-donating substituents increase and electron-withdrawing substituents retard the reaction rate, in line with the electrophilic character of the attacking radical.

The values in Table II seem to indicate some differences in the substituent effects for the two reactions. However, when these values are plotted against the σ^+ substituent constants (Figures 1 and 2) nearly identical ρ^+ values are calculated. These are –1.06 ($r = 0.998$) for the reaction induced by CAN[8] and –1.05 ($r = 0.983$) for the reaction

Table II. Relative Reactivities in the Addition Reactions of Malonyl Radicals to Z-Substituted Styrenes 3[a]

Z	reaction induced by CAN[b]	reaction induced by Bu₃SnH[b]
p-OCH₃ (3a)		4.6
p-CH₃ (3b)	2.1	1.1
H (3c)	1.0	1.0
p-Cl (3d)	0.70	0.40
m-Cl (3e)	0.35	0.25
m-NO₂ (3f)	0.18	
p-NO₂ (3g)		0.10

[a] For the reaction conditions, see text. [b] Average of at least two determinations. Error ±10%.
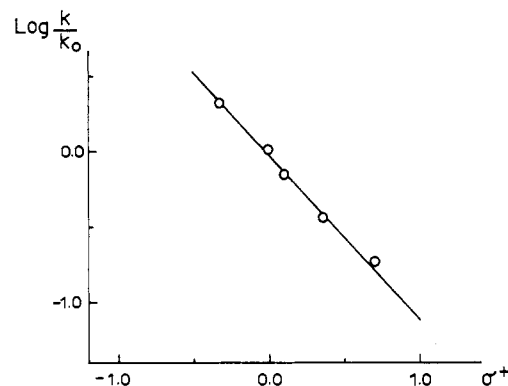
Figure 1. Hammett plot of the CAN-induced addition of malonyl radical to substituted styrenes: $\rho^+ = -1.06$; $r = 0.998$.
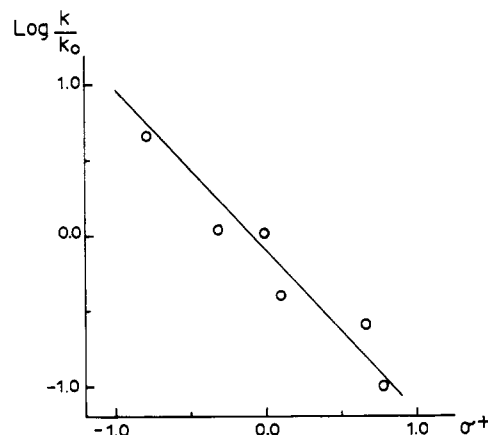
Figure 2. Hammett plot of the Bu₃SnH–*hν*-induced addition of malonyl radical to substituted styrenes: $\rho^+ = -1.05$; $r = 0.983$.

induced by tributylstannane. When the data for the two reactions are included in the same plot the ρ^+ value is –1.01 with $r = 0.97$.

Clearly, these values indicate an identical selectivity for the two reactions, and the differences noted in Table II are caused mainly by the experimental uncertainty.

Thus, the data presented in this paper give no support to the proposal that in the CAN-promoted addition of carbonyl compounds to alkenes a metal-coordinate α-oxoalkyl radical like 1 is involved. In the case of the malonyl radical either this metal-coordinated radical is not formed or the interaction between the radical and the metal is not strong enough to significantly modify the sensitivity to electronic effects of the addition reaction.

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(8) In ref 4 a more negative value is reported. That was a preliminary value obtained by using σ and not σ^+ constants and based on only four points (the result for *m*-nitrostyrene was not available).

This conclusion, of course, cannot be generalized. Coordination with the metal could be much stronger for radicals generated by, for example, 1,3-diketones and β-keto esters than for the malonyl radical. Also the nature of the metal can play a fundamental role in this respect. Further work in the area is certainly necessary to clarify these points.

A last notation is that the results presented here allow a quantitative assessment of the electrophilic character of the malonyl radical. The calculated ρ^+ value (ca. -1) indicates a substantial sensitivity to the electronic density at the double bond of styrenes. The effects are higher than those exhibited by other electrophilic radicals like $CCl_3{}^{\bullet}$ ($\rho^+ = -0.42$)[9] and $C_6H_5S^{\bullet}$ ($\rho^+ = -0.26$).[10]

Experimental Section

^{1}H NMR spectra were obtained on Bruker SY 80 and Bruker WM 300 instruments with $CDCl_3$ or tetramethylsilane as internal standard. IR spectra were obtained on a Perkin-Elmer 257 instrument, and gas chromatograms were run on Hewlett Packard 5880 A (30m, SP-B5, capillary column) and Carlo Erba 6000 Vega 2 (20m, SE-30, capillary column) instruments.

Kinetic Studies. (a) Reaction Induced by CAN. The relative rate constants of substituted styrenes 3 with respect to styrene in the CAN-promoted oxidative addition of dimethyl malonate were determined by the competitive method. To a solution of CAN (570 mg, 1.04 mmol) in 4 mL of methanol was added a solution of dimethyl malonate (ca. 65 mg, 0.5 mmol), substituted styrene 3 (0.6–1.0 mmol), styrene 3c (0.6–1.0 mmol), and m-chlorotoluene (ca. 0.75 mmol) as an internal standard in methanol (1.0 mL) at 20 °C. The mixture was allowed to react for 40 min (at this time more than 98% of CAN has reacted in all cases). The mixture was poured into water (50 mL) and extracted with n-hexane (3 × 25 mL). The collected organic phases were washed with water (75 mL), dried with anhydrous sodium sulfate, and analyzed by GC after suitable dilution. The relative rate constants (Table II) were determined by the equation $k_Y/k_H = \log (3x^0/3x)/\log (3c^0/3c)$ where 3^0 and 3 are the molar ratios of styrenes before and after reaction. In all cases the amount of reacted styrenes 3 corresponds ($\pm 5\%$) to the amount of malonate consumed in the reaction.

(b) Reaction Induced by Bu_3SnH. A solution of diethyl chloromalonate (0.2–0.3 mmol), one styrene (2.0 mmol), another styrene (2.0–10 mmol), and tributylstannyl chloride (0.2–0.3 mmol) in methanol (20 mL) was cooled to 20 °C. Under irradiation a solution of sodium borohydride (0.8–1.0 mmol) in methanol (2–3 mL) was added.[11] After 2–5 min of irradiation the mixture was concentrated and the adducts were analyzed by GC. Using pseudo-first-order kinetics,[12] from the concentrations of the educts 3 and products 6 the relative rate constants of Table II were calculated.

Structure Determination of the Reaction Products. (a) Reactions Induced by CAN. The structure of the addition products was determined in detail in the case of the reactions of styrene (3c) and m-nitrostyrene (3f). To a solution of CAN (5.0 g, 9.1 mmol) in methanol (90 mL) were added styrene (3c) or m-nitrostyrene (3f, 20 mmol) and dimethyl malonate (4.5 mmol) in 10 mL of methanol at 20 °C, and the mixture was allowed to react for 40 min (at this time the reacted CAN was 99% by iodometric titration). The methanolic solution was poured into water (250 mL) and extracted with diethyl ether (3 × 100 mL), the collected extracts were washed with water (300 mL) and dried with sodium sulfate, and the solvent was evaporated.

Products from Styrene. The ^{1}H NMR spectrum of the crude reaction mixture (1.51 g) in the presence of p-nitrotoluene as an internal standard shows the presence of 3,3-bis(methoxycarbonyl)-1-phenylpropan-1-ol nitrate (4c) in 69% yield by comparison with the ^{1}H NMR data reported in the literature[13] and a second product to which the structure of 1,1-bis(methoxycarbonyl)-3-methoxy-3-phenylpropane (5c) (24%) was provisionally assigned on the basis of the multiplet at δ 4.18 (four peaks, X portion of an ABX system) assigned to the benzylic proton and a singlet at δ 3.18 assigned to the ethereal methyl protons. Attempts to isolate the two adducts were unsuccessful. However, reflux of the crude product in methanol for 1 h transforms 4c into 1,1-bis(methoxycarbonyl)-2-phenylcyclopropane, which can be easily separated from the methoxy adduct by HPLC on silica gel (hexane/ethyl acetate = 99:1). The latter, a colorless oil, has the following spectroscopic characteristics which support the assigned structure 5c: ^{1}H NMR δ 7.3 (m, 5 H), 4.18 (four peaks, X portion of an ABX system, 1 H), 3.76 (s, 3 H), 3.72 (s, 3 H), 3.6–3.5 (m, 1 H), 3.18 (s, 3 H), 2.4–2.2 (m, 2 H); IR (film) λ_{max} 2950, 2820, 1740, 1105, 760 cm^{-1}; MS (eV) m/z 266 (M$^+$, 1), 251 (5), 235 (3), 134 (39), 121 (100), 91 (18), 77 (25).

Products from m-Nitrostyrene (3f). The ^{1}H NMR spectrum of the crude product shows the presence of 3,3-bis(methoxycarbonyl)-1-(3-nitrophenyl)propan-1-ol nitrate (4f) (71%) and 1,1-bis(methoxycarbonyl)-3-methoxy-3-(3-nitrophenyl)propane (5f) (13%) by analogy with the spectroscopic characteristics of the styrene adducts. The two products, isolated by HPLC on silica gel (hexane/ethyl acetate = 95:5), show the following spectral characteristics. 3,3-Bis(methoxycarbonyl)-1-(3-nitrophenyl)-propan-1-ol nitrate (4f): ^{1}H NMR δ 8.3–7.5 (m, 4 H), 6.12–5.93 (four peaks, X portion of an ABX system, 1 H), 3.78 (bs, 6 H), 3.9–3.5 (m, 1 H), 2.6–2.4 (m, 2 H); IR (film) λ_{max} 1735, 1642, 1530, 1353, 1275, 850, 735 cm^{-1}; MS (70 eV) m/z 310 (M$^+$ – CH_3OH, 17), 279 (34), 263 (57), 232 (100), 150 (61), 59 (64). 1,1-Bis(methoxycarbonyl)-3-methoxy-3-(3-nitrophenyl)propane (5f): ^{1}H NMR δ 8.3–7.5 (m, 4 H), 4.21–4.06 (four peaks, X portion of an ABX system, 1 H), 3.75 (s, 3 H), 3.71 (s, 3 H), 3.8–3.5 (m, 1 H), 3.20 (s, 3 H), 2.4–2.2 (m, 2 H); IR (film) λ_{max} 2955, 2820, 1740, 1530, 1150 cm^{-1}; MS (70 eV) m/z 296 (1), 234 (11), 166 (100), 132 (41), 100 (11), 59 (12). With all the other styrenes the NMR spectrum of the reaction products was essentially identical with that observed in the two reactions described above, indicating that these reactions also led to the same mixture of nitrate and methoxy adduct in a nearly quantitative yield.

(b) Reactions Induced by Bu_3SnH. General Procedure. At room temperature, under N_2 and irradiation (150 W Hg lamp), a solution of trybutylstannane (1.16 g, 4.00 mmol) and azobis(isobutyronitrile) (50 mg) in toluene (5 mL) was added within 15–20 min to a solution of diethyl chloromalonate (400 mg, 3.0 mmol) and the respective styrene 3 (15 mmol) in toluene (20 mL). After 30 min the solvent was distilled off, and the residue dissolved in diethyl ether (20 mL) and treated with a saturated aqueous solution of potassium fluoride (3 mL) for 30 min. Filtration over magnesium sulfate, concentration, distillation in a Kugelrohr apparatus, and chromatography on silica gel gave products 6 in yields that are shown in the Table I.

Ethyl 2-(ethoxycarbonyl)-4-(p-methoxyphenyl)butanoate (6a): ^{1}H NMR (300 MHz) δ 1.24 (t, $J = 7.5$ Hz, 6 H, 2 OCH_2CH_3), 2.15 (m, 2 H, H-3), 2.57 (t, $J = 7.5$ Hz, 2 H, 4-H), 3.30 (t, $J = 7.5$ Hz, 1 H, H-2), 3.77 (s, 3 H, methoxy), 4.10 (q, $J = 7.5$ Hz, 4 H, 2 OCH_2CH_3), 6.81, 7.00 (m, 4 H, Ar). Anal. Calcd for $C_{16}H_{22}O_5$: C, 65.30; H, 7.50. Found: C, 64.97; H, 7.60.

Ethyl 2-(ethoxycarbonyl)-4-(p-methylphenyl)butanoate (6b): ^{1}H NMR (300 MHz) δ 1.24 (t, $J = 7.5$ Hz, 6 H, 2 OCH_2CH_3), 2.15 (m, 2 H, H-3), 2.31 (s, 3 H, methyl), 2.59 (t, $J = 7.5$ Hz, 2 H, H-4), 3.30 (t, $J = 7.5$ Hz, 1 H, H-2), 4.15 (m, 4 H, 2 OCH_2CH_3), 7.00 (m, 4 H, Ar). Anal. Calcd for $C_{16}H_{22}O_4$: C, 69.06; H, 7.91. Found: C, 69.10; H, 8.01.

Ethyl 2-(ethoxycarbonyl)-4-phenylbutanoate (6c): ^{1}H NMR (300 MHz) δ 1.28 (t, $J = 7.5$ Hz, 6 H, 2 OCH_2CH_3), 2.24 (m, 2 H, H-3), 2.68 (t, $J = 7.5$ Hz, 2 H, H-4), 3.34 (t, $J = 7.5$ Hz, 1 H, H-2), 4.20 (m, 4 H, 2 OCH_2CH_3), 7.22 (m, 5 H, Ar). Anal. Calcd for $C_{15}H_{20}O_4$: C, 68.42; H, 7.27. Found: C, 68.25; H, 7.29.

Ethyl 2-(ethoxycarbonyl)-4-(p-chlorophenyl)butanoate (6d): ^{1}H NMR (300 MHz) δ 1.18 (t, $J = 7.5$ Hz, 6 H, 2 OCH_2CH_3), 2.15 (m, 2 H, H-3), 2.60 (t, $J = 7.5$ Hz, 2 H, H-4), 3.29 (t, $J = 7.5$ Hz, 1 H, H-2), 4.16 (m, 4 H, 2 OCH_2CH_3), 7.09, 7.22 (m, 4 H, Ar).

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Molecular Recognition Phenomena in the Excited State: The Meta Photocycloaddition of *cis*- and *trans*-2,5-Dihydro-2,5-dimethoxyfuran and *cis*-1,4-Dimethoxycyclopent-2-ene to Anisole[1]

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The meta photocycloaddition of *cis*-2,5-dihydro-2,5-dimethoxyfuran (**8**), *trans*-2,5-dihydro-2,5-dimethoxyfuran (**9**), and *cis*-1,4-dimethoxycyclopent-2-ene (**10**) to anisole (**7**) is described. The results are discussed in light of the most recent findings concerning the mechanism of this reaction.

Introduction

Much work has been done to elucidate the characteristics of the meta photocycloaddition of alkenes to arenes since its discovery in 1966.[2] Of the originally proposed reaction pathways, only those depicted in Scheme I are still under discussion:[3-9] (a) A concerted mechanism between the singlet excited arene (benzene or substituted benzene derivative, **1***) and the alkene in its ground state forming the biradical (**4**)[10] or "zwitterionic" intermediate (**4'**).[6] (b) A mechanism similar to a, however, via a polarized transition state (**2**).[6,7] (c) A mechanism involving an exciplex intermediate (**3**) with charge-transfer (CT) character depending on the electronic properties of the starting materials.[3-5] This exciplex is probably formed via a polarized transition state (encounter).[4,11] Within the bicyclic intermediate of the type **4** or **4'**, the third σ-bond is formed either between C1' and C3' or between C1' and C5', yielding the meta cycloadduct (in Scheme I only one alternative is shown).

Of these mechanisms, currently b and c are most probable and will be considered here. A common feature is that the electronic properties of the starting material (substitution pattern) strongly influence the mode of reaction (ortho or meta cycloaddition),[3,5] the regioselectivity,[4,5] and the stereoselectivity.[4,5] The observed selectivities can be attributed to a polarized transition state such as **2** or, alternatively, an exciplex intermediate **3**, the existence of which has been experimentally proven for certain arene-olefin systems.[12] Furthermore, the regio- and stereoselectivity may be influenced by intermediates of the type **4** or **4'** as well.[4,13-18] The recently reported correlation

(1) Part 27 of Radical Ions and Photochemical Charge Transfer Phenomena. For part 26, see: Vondenhof, M.; Mattay, J.: Sulfonic Acid Esters Derived from 1,1'-Binaphthalene As New Axially Chiral Photosensitizers. *Tetrahedron Lett.* **1990**, *31*, 985.

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