JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 9, 529–538 (1996)

MECHANISTIC ASPECTS OF AMINIUM SALT-CATALYZED DIELS–ALDER REACTIONS: THE SUBSTRATE IONIZATION STEP

WANG YUEH AND NATHAN L. BAULD*
Department of Chemistry and Biochemistry, University of Texas, Austin, Texas 78712, USA

Substituent effects in the aminium salt catalyzed Diels–Alder reactions of 2,3-dimethyl-1,3-butadiene with a series of *meta* and *para* substituted *β*-methylstyrenes are used to probe detailed mechanistic aspects of these reactions. Kinetic studies were carried out using two different aminium salt catalysts and also electrochemically, using anodic potentials corresponding to the oxidation potentials of the aminium salts. Substituent effects in the equilibrium oxidations of the styrene substrates to the corresponding cation radicals were also studied, *via* oxidation potential measurements. The results indicate rate determining one electron oxidation of the sytrenes to their cation radicals *via* an outer sphere electron transfer.

INTRODUCTION

Powerful catalysis of Diels–Alder cycloadditions by triarylaminium salts, especially tris(4-bromophenyl)aminium hexachloroantimonate ($\mathbf{1}^{+\cdot}$) was discovered in this laboratory in 1981, and a cation radical mechanism was proposed.[1] Since that time, a variety of further evidence has been presented in support of the involvement of cation radicals in these novel cycloadditions, and the cation radical mechanistic framework is now widely accepted.[2,3] Several mechanistic and theoretical studies by this research group have focused special attention on the cycloaddition step,[4,5] but much less attention has been directed to the ionization step, i.e. the step in which substrate molecules are converted into the corresponding cation radicals by $\mathbf{1}^{+\cdot}$. The present study was intended to elucidate some of the salient mechanistic aspects of this electron transfer reaction in the specific context of the Diels–Alder cycloadditions of 2,3-dimethyl-1,3-butadiene to a series of *trans-β*-methylstyrenes.

RESULTS AND DISCUSSION

The present study addressed four essential mechanistic issues relating to the ionization step. Perhaps the most subtle issue is the outer or inner sphere nature of the electron (or hole) transfer (Scheme 1). In the *outer sphere* mechanism, an electron is transferred between chemical species which have no significant covalent interaction between them. In an *inner sphere* mechanism, covalent interaction between the two species is an essential aspect of the electron transfer (ET) mechanism. As an extreme example, a full covalent bond might be formed between the species by a polar mechanism, followed by homolytic dissociation of this covalent bond, the net result being ET. A second important issue is the question of whether ionization is *rate limiting* or *reversible* (Scheme 2). Although the generation of a highly energetic and reactive species such as a cation radical via an endergonic process might be expected to be rate determining, it is noteworthy that the reverse electron transfer is substantially exergonic and undoubtedly very fast when significant amounts of **1** are present. Reversible ionization has, in fact, been observed in the reactions of *trans*-stilbenes with 2,3-dimethyl-1,3-butadiene, catalyzed by $\mathbf{1}^{+\cdot}$.[6] A third issue, which is especially significant from the viewpoint of synthetic applications, is the question of whether the substrate molecules are exclusively ionized by the aminium salt catalyst (the *catalytic* format) or primarily by product cation radicals (the cation radical *chain* format; Scheme 2). In the former case, the ionization is typically endergonic and relatively highly selective, whereas in the latter case, the ionization is typically exergonic and much less selective. Finally, in a Diels–Alder cycloaddition between two non-equivalent addends, there is the question of *role selectivity*, i.e. which component is

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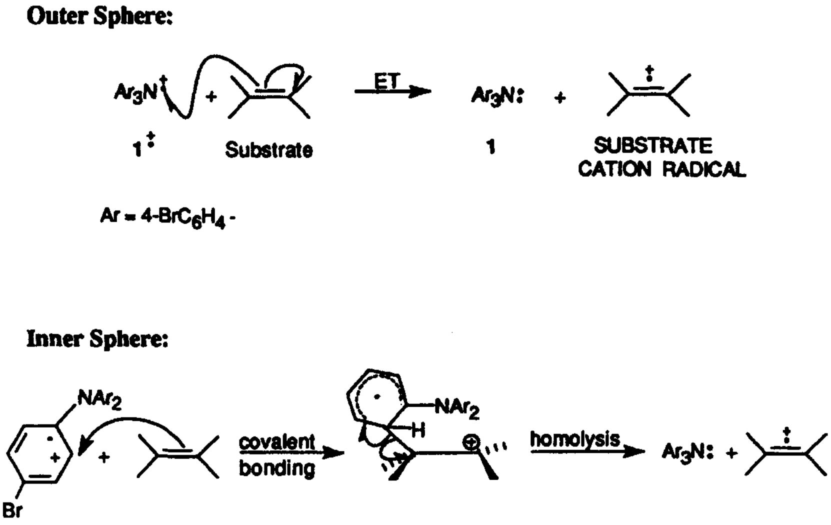
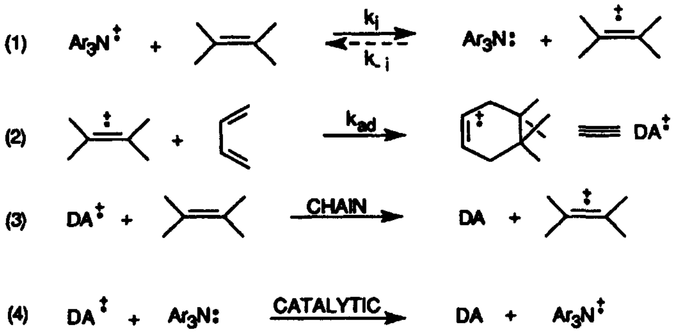
[*] Author to whom correspondence should be addressed.

CCC 0894–3230/96/080529–10

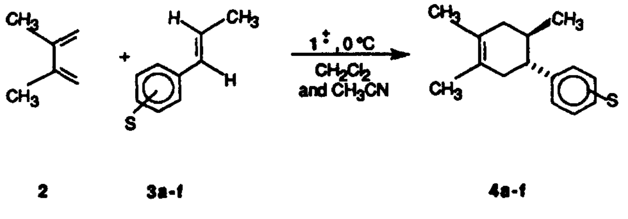
Received 1 November 1995
Revised 1 March 1996



Scheme 1. Outer sphere vs inner sphere electron transfer



Scheme 2. If $k_{ad}[\text{diene}] \gg k_{-i}[Ar_3N:]$, ionization is kinetically controlled; if $k_{-i}[Ar_3N:] \gg k_{ad}[\text{diene}]$, ionization is equilibrium controlled. Steps 1, 2 and 3 constitute a cation radical chain mechanism, with step 1 as the initiation and steps 2 and 3 as propagation. A mechanism involving steps 1, 2 and 4 is a classical catalytic mechanism. In the chain mechanism, the substrate is ionized by product cation radicals (DA$^{+\cdot}$). In the catalytic mechanism, the aminium salt ionizes the substrate



	S		S
3a	4-MeO	3d	3-Me
b	4-PhO	e	H
c	4-Me	f	4-Cl

Scheme 3. The Diels–Alder reactions of *trans*-β-methylstyrenes with 2,3-dimethyl-1,3-butadiene, catalyzed by $1^{+\cdot}$

Table 1. Relative rate constants for the Diels–Alder cycloadditions of substituted *trans*-β-methylstyrenes to 2,3-dimethyl-1,3-butadiene, catalyzed by $\mathbf{1}^{+\cdot}$

Substrate	$k_{\text{rel}}(\text{CH}_2\text{Cl}_2)$	$k_{\text{rel}}(\text{MeCN})$
4-Methoxy-β-methylstyrene (**3a**)	9716·7	3137·3
4-Phenoxy-β-methylstyrene (**3b**)	411·7	214·9
4-Methyl-β-methylstyrene (**3c**)	19·2	15·8
3-Methyl-β-methylstyrene (**3d**)	1·0	1·0

ionized to the cation radical and which reacts as a neutral molecule.[7] Since ionization of a substrate molecule involves the development of positive charge, substituent electronic effects were targeted for investigation and have been found to be a versatile tool for probing the mechanistic details of the ionization step.[8]

The competition kinetics of the Diels–Alder cycloadditions of a series of six *trans*-β-methylstyrenes (**3**) with a tenfold excess of 2,3-dimethyl-1,3-butadiene (**2**) were first studied at 0 °C in dichloromethane using $\mathbf{1}^{+\cdot}$ as the catalyst (Scheme 3) The kinetic runs were carried out to less than 10% conversion and the material balances were at least 98%. No products (including possible cyclobutane adducts) other than the Diels–Alder adducts were detected. The relative rate data are given in Table 1. The plot of log k_{rel} vs σ^+ is nicely linear (Figure 1; $r^2 = 0{\cdot}996$, $\rho = -5{\cdot}70$). An analogous series of kinetic runs was then carried out in acetonitrile, and these data (Table 1) also correlate very well with σ^+ (Figure 2; $r^2 = 0{\cdot}995$, $\rho = -4{\cdot}99$). The observation of large, negative ρ values for these reactions is obviously consistent with the ionization of the styrene component (the dienophile). However, more quantitative insight into the extent of positive charge development on the styrene moiety was considered desirable and was sought by measuring the oxidation potentials of the styrenes (Table 2). The data for seven β-methylstyrenes again correlate extremely well with the σ^+ parameter ($r^2 = 0{\cdot}992$) and the slope of this plot (0·628) corresponds to a ρ value of $-10{\cdot}6$ in acetonitrile at room temperature (298 K)[8] [obtained, as noted in Ref. 8, from the equation $\rho = \text{slope}(23{\cdot}06)(1{\cdot}000)/-2{\cdot}303(1{\cdot}987)(298)$]. Since the kinetic data were measured at a different temperature (0 °C) and because solvent dielectric constants typically increase as the temperature is decreased, it was considered desirable to measure the oxidation potentials at 0 °C. The correlation of these new oxidation potentials (Table 2) with σ^+ is again very good (Figure 3; $r^2 = 0{\cdot}989$) and the slope of the plot (0·565) yields the new value $\rho = -10{\cdot}4$. The effect, incidentally, is qualitatively in the expected direction for an increase in solvent dielectric constant at the lower temperature, but represents only about a 2% decrease in ρ.

A comparison of the kinetic ρ value in acetonitrile at 0 °C ($-4{\cdot}99$) with the equilibrium ρ value under the same conditions ($-10{\cdot}4$) indicates that substituent electronic effects under kinetic conditions are almost

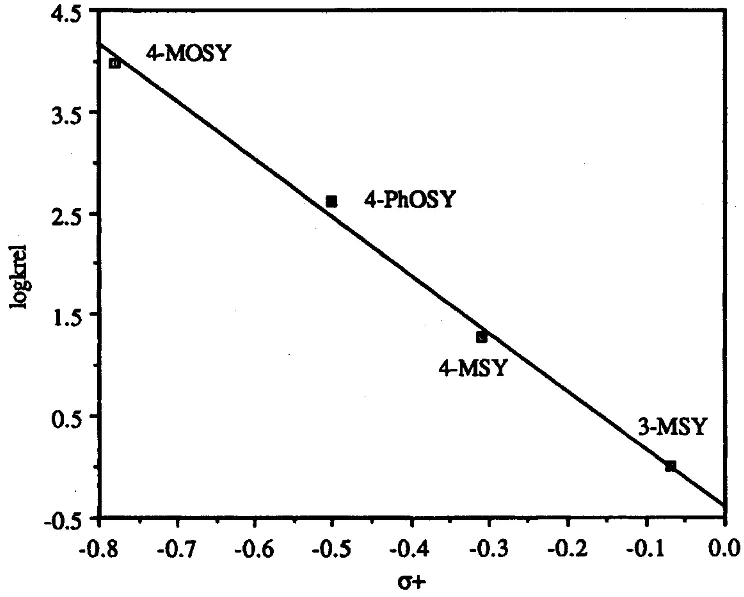


Figure 1. Hammett–Brown plot for the Diels–Alder cycloadditions of substituted *trans*-β-methylstyrenes to 2,3-dimethyl-1,3-butadiene, catalyzed by $\mathbf{1}^{+\cdot}$ in dichloromethane at 0 °C. SY = *trans*-β-methylstyrene; MO = methoxy; PhO = phenoxy; M = methyl; $\rho = -5{\cdot}70$; $r^2 = 0{\cdot}996$

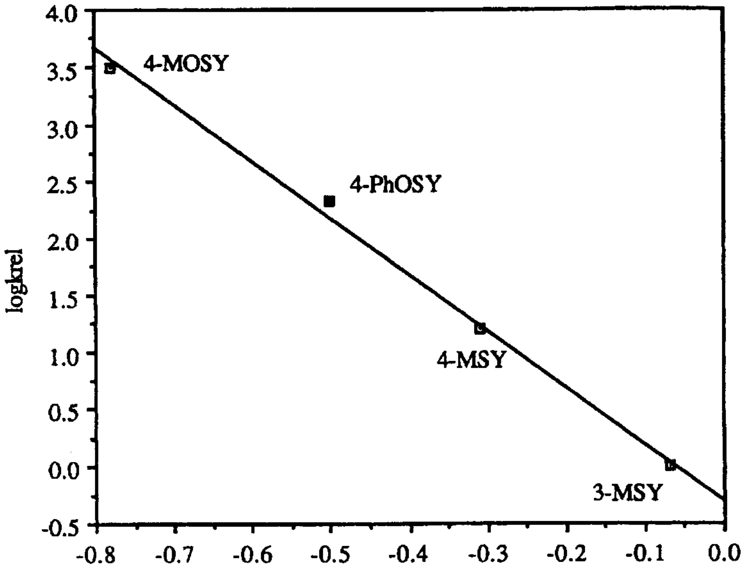


Figure 2. Hammett–Brown plot for the Diels–Alder cycloadditions of substituted *trans*-β-methylstyrenes to 2,3-dimethyl-1,3-butadiene, catalyzed by $1^{+\cdot}$ in acetonitrile at 0 °C. $\rho = -4{\cdot}99$; $r^2 = 0{\cdot}995$

exactly half (more precisely, 48%) of the corresponding effects under equilibrium (or near equilibrium) conditions. This would be generally consistent with a kinetically controlled (i.e. rate-determining) ionization of the β-methylstyrene derivatives in which positive charge development in the transition state is fractional and sufficient to deliver substituent electronic free energy effects approximately half of those in the full-fledged cation radical. These conclusions are further supported by the observation (Table 3) that the absolute rate of reaction of **3c** with **2** is independent of the concentration of **2**. If the ionization step were significantly reversible, the rate should increase with increasing concentration of **2**. Further, if **2** were the species being ionized by $\mathbf{1}^{+\cdot}$, the rate of product formation should also increase as [**2**] is increased. The preferential ionization of **3**, rather than **2**, is plausible and expected on the basis of the relative ionization potentials of these species (1·68 for **3a**, *ca* 1·95 for **2**).

Table 2. Peak oxidation potentials (E_{ox}, V vs SCE) for substituted *trans*-β-methylstyrenes in acetonitrile, by differential pulse voltammetry

Substrate	E_{ox}(25 °C)	E_{ox}(0 °C)
4-Methoxy-β-methylstyrene (**3a**)	1·173	1·180
4-Phenoxy-β-methylstyrene (**3b**)	1·316	1·290
4-Methyl-β-methylstyrene (**3c**)	1·468	1·458
3-Methyl-β-methylstyrene (**3d**)	1·576	1·540
β-Methylstyrene (**3e**)	1·676	1·620
4-Chloro-β-methylstyrene (**3f**)	1·700	1·680
3-Chloro-β-methylstyrene (**3g**)	1·896	1·812

Finally, based upon the stilbene precedent,[6] the ρ value for a mechanism involving equilibrium controlled ionization (rate determining cycloaddition) would be expected to approach closely the value $\rho = -10{\cdot}4$ observed for the electrochemical oxidations. The observation of a much smaller kinetic ρ value than that expected for equilibrium-controlled ionization also rules out a mechanism in which the cation radicals of two competing substrate molecules (styrenes) equilibrate by means of hole transfer between the cation radical of one substrate molecule and the neutral form of the other substrate molecule. The ρ value for such an equilibrium should closely approximate that for the electrochemical oxidations ($-10{\cdot}4$). Furthermore, the ρ value in such a case should be unaffected by the nature of the catalyst. As noted below, the use of a more potent aminium salt catalyst results in a significantly diminished ρ value.

Kinetic results using a more potent aminium salt catalyst

An analogous kinetic study was then carried out using the considerably more powerful catalyst tris(2,4-dibromophenyl)aminium hexachloroantimonate ($\mathbf{5}^{+\cdot}$).[9] The oxidation potential of the corresponding triarylamine **5** (1·50 V) is 0·44 V greater than that of **1** (1·06 V).

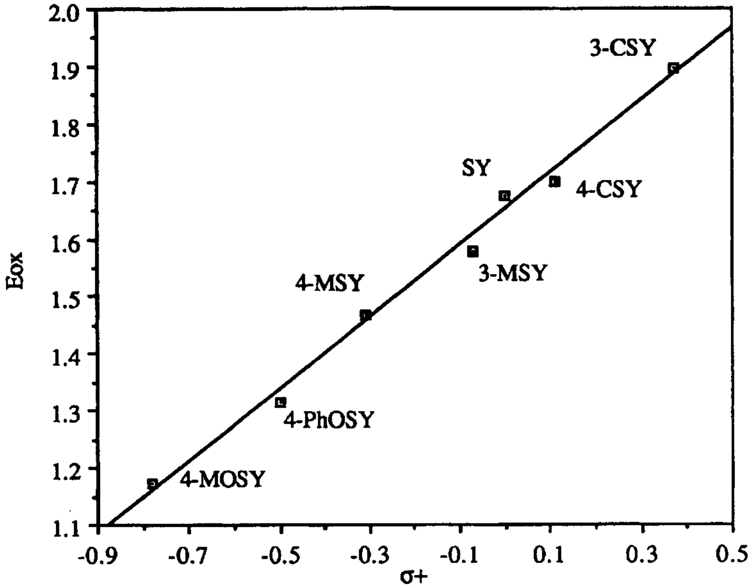


Figure 3. Plot of the oxidation potentials (E_{OX}) of substituted *trans*-β-methylstyrenes vs σ^+. Slope = 0·628; $r^2 = 0{\cdot}992$

These studies could only be carried out in dichloromethane, since $\mathbf{5}^{+\cdot}$ decomposes rapidly in acetonitrile. The relative rate constants (Table 4) correlate acceptably well with σ^+ (Figure 4), and in this case $\rho = -3{\cdot}82$, a value substantially lower than that observed (−5·70) for $\mathbf{1}^{+\cdot}$ in the same solvent. Clearly, these reaction systems cannot both proceed via chain mechanisms. This conclusion follows from the circumstance that the ionizing species in this mechanism is the product cation radical ($\mathbf{4}^{+\cdot}$), which is identical for both reaction systems ($\mathbf{1}^{+\cdot}$ and $\mathbf{5}^{+\cdot}$).

To proceed further, it must be noted that, at least for $\mathbf{1}^{+\cdot}$, ionization by the catalyst is much more endergonic than ionization by the product cation radical. (The oxidation potentials of **4b** and **4c** are 1·452 and 1·456, respectively; these were measured as described in the Experimental section.) Consequently, the transition state for ionization of **3** by $\mathbf{1}^{+\cdot}$ should have more product ($\mathbf{3}^{+\cdot}$) character than does the ionization of **3** by $\mathbf{4}^{+\cdot}$. The ρ value for the catalytic process should therefore be greater than for the chain mechanism. As a result, the formal possibility that the $\mathbf{1}^{+\cdot}$ reactions are of the chain type, whereas the $\mathbf{5}^{+\cdot}$ reactions are catalytic can be confidently ruled out on the basis of the relative ρ values observed for $\mathbf{1}^{+\cdot}$ and $\mathbf{5}^{+\cdot}$. The converse possibility, that the $\mathbf{5}^{+\cdot}$ reactions are of the chain type and those of $\mathbf{1}^{+\cdot}$ are catalytic is plausible, however, as is the possibility that both reaction systems have a catalytic mechanism. In either case, the $\mathbf{1}^{+\cdot}$ reactions are established as being of the catalytic type. Distinction between the chain and catalytic mechanisms for the reactions induced by $\mathbf{5}^{+\cdot}$ does not appear feasible on the base of these data alone (however, see below).

Table 3. Effect of the concentration of 2,3-dimethyl-1,3-butadiene (**2**) on the absolute reaction rate of Diels–Alder cycloadditions to 4-methyl-β-methylstyrene

[2] (M)	Time (s)	Conversion (%)
0·084	20	25·3
0·169	20	25·9
0·084	40	35·4
0·169	40	36·7
0·084	60	45·5
0·169	60	45·7
0·084	80	53·8
0·169	80	54·6

Table 4. Relative rate constants for the Diels–Alder cycloadditions of substituted *trans*-β-methylstyrenes to 2,3-dimethyl-1,3-butadiene, catalyzed by $\mathbf{5}^{+\cdot}$

Substrates	$k_{rel}(CH_2Cl_2)$
4-Methyl-β-methylstyrene (**3c**)	15·8
3-Methyl-β-methylstyrene (**3d**)	3·8
β-Methylstyrene (**3e**)	1·0
4-Chloro-β-methylstyrene (**3f**)	0·4

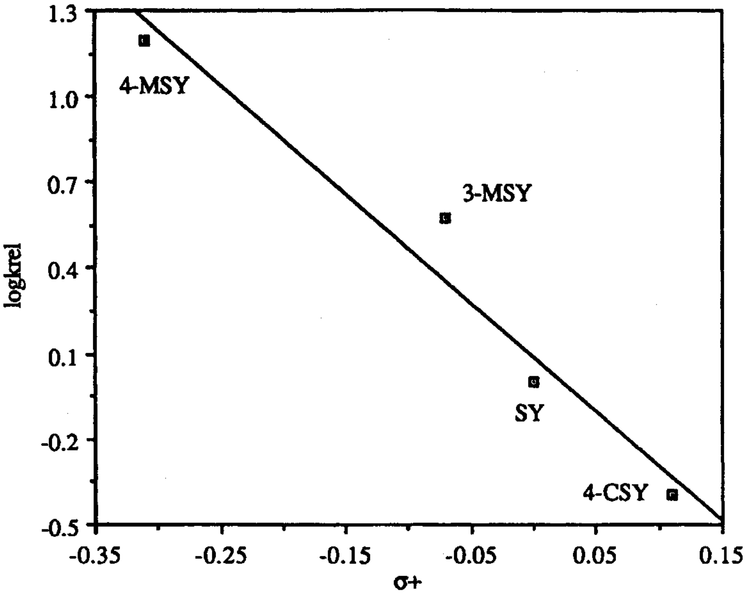


Figure 4. Hammett–Brown for the Diels–Alder cycloaddtions of substituted *trans*-β-methylstyrenes to 2,3-dimethyl-1,3-butadiene, catalyzed by $5^{+\cdot}$ in dichloromethane at 0°C. $\rho = 3{\cdot}82$; $r^2 = 0{\cdot}953$

Electrochemical criteria

If cation radicals are the actual intermediates in these aminium salt-catalyzed Diels–Alder additions, it is eminently reasonable to expect the formation of the same adducts under analogous electrochemical (EC) oxidation conditions. This has been expressly verified in the present work using a reticulated carbon anode in acetonitrile solution. The EC reactions between **3a–f** and excess **2**, at least at the relatively low conversions studied (*ca* 10%), yield essentially only the same Diels–Alder adducts as produced in the corresponding aminium salt reactions. Further, when an anodic potential (1·1 V vs SCE) is used which is approximately equal to the oxidation potential of **1** [$E_{\mathrm{OX}}(\mathbf{1}) = 1{\cdot}06$ V], the relative Diels–Alder reaction rates of the series of *trans*-β-methylstyrene derivatives with excess *2* (Table 5) under EC conditions correlate well (Figure 5, $r^2 = 0{\cdot}987$) with σ^+, with a ρ value ($-4{\cdot}85$) which is impressively close to that observed when $\mathbf{1}^{+\cdot}$ is the catalyst ($-4{\cdot}99$). Such a close correspondence of intramolecular selectivities (ρ values) for reactions catalyzed by $\mathbf{1}^{+\cdot}$ and an anode of the same potential is not demanded theoretically, but has been previously observed for the reaction of *trans*-stilbenes with **2**.[10] Furthermore, the ρ value under EC (1·5 V) conditions ($-3{\cdot}94$, Figure 6) is very close to that observed for $\mathbf{5}^{+\cdot}$ ($-3{\cdot}82$) and different from the ρ value under EC (1·1 V) conditions.

Table 5. Relative rate constants for the Diels–Alder cycloadditions of substituted *trans*-β-methylstyrenes to 2,3-dimethyl-1,3-butadiene, under electrochemical oxidation conditions (EC) at 1·1 V and 1·5 V vs SCE

Substrate	k_{rel}(1·1 V)	k_{rel}(1·5 V)
4-Methoxy-β-methylstyrene (**3a**)	12095·2	1295·9
4-Phenoxy-β-methylstyrene (**3b**)	1221·7	325·6
4-Methyl-β-methylstyrene (**3c**)	96·2	57·0
3-Methyl-β-methylstyrene (**3d**)	4·7	4·4
β-Methylstyrene (**3e**)	1·0	1·0

At a minimum, the observation of identical products and virtually identical selectivities under corresponding aminium salt and anodic oxidation conditions is construed as strong, qualitative support for the intermediacy of cation radicals of **3** in the aminium salt-catalyzed reactions. The observation of nearly equal ρ values for ionizations by aminium salts and anodes of equal potential would also appear to provide support for the catalytic as opposed to a chain mechanism, since the much higher potential of product cation radicals ($\mathbf{4}^{+\cdot}$) would be expected to result in a lower ρ value in this latter instance. Beyond this, the close correspondence of the intermolecular selectivities (ρ values) in the aminium salt and anodic reactions suggests identical ionization mechanisms for these two disparate reactions. On the natural assumption that the anodic oxidations are of the outer-sphere type, it appears likely that substrate ionization via the aminium salt is also likely to be an outer-sphere process.

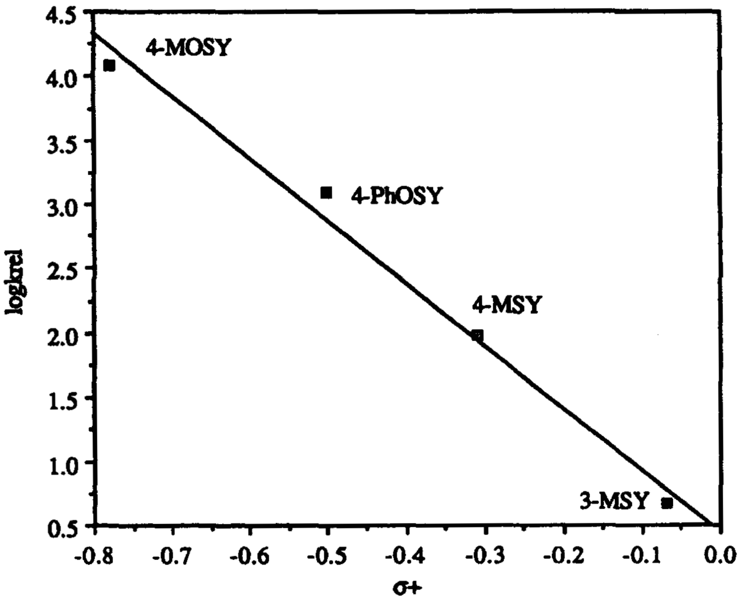


Figure 5. Hammett-Brown plot for the electrochemically induced cycloadditions of substituted *trans*-β-methylstyrenes to 2,3-dimethyl-1,3-butadiene in acetonitrile at +1·1 V vs SCE. $\rho = -4{\cdot}85$; $r^2 = 0{\cdot}987$

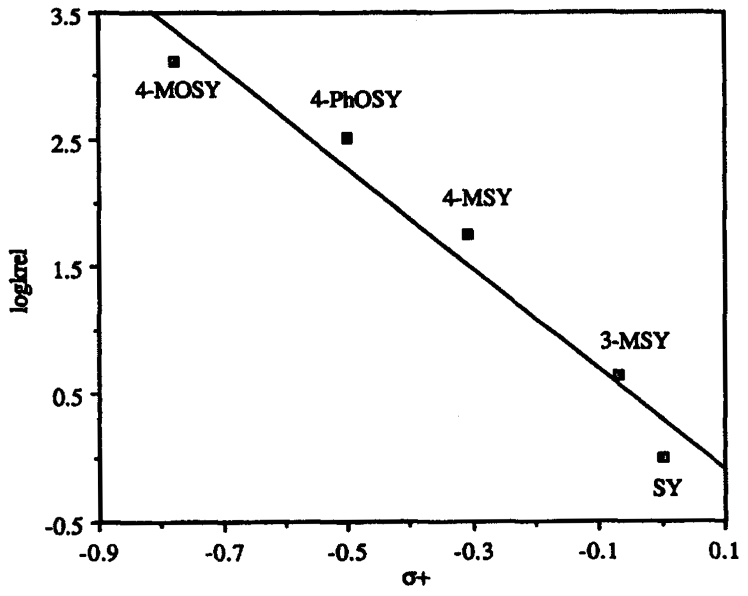


Figure 6. Hammett-Brown plot for the electrochemically induced cycloadditions of substituted *trans*-β-methylstyrenes to 2,3-dimethyl-1,3-butadiene in acetonitrile at +1·5 V vs SCE. $\rho = -3{\cdot}94$; $r^2 = 0{\cdot}958$

CONCLUSION

Competition kinetic studies of substituent effects have been carried out for aminium salt-catalyzed Diels–Alder reactions between 2,3-dimethyl-1,3-butadiene (**2**) and a series of *trans*-β-methylstyrenes (**3**). When the catalyst is tris(4-bromophenyl)aminium hexachloroantimonate ($\mathbf{1}^{+\cdot}$), the Hammett–Brown ρ value (−4·99, CH_3CN, 0 °C) is essentially half of the ρ value (−10·4, CH_3CN, 0 °C) for the equilibrium oxidation of these substrates (**3**) to the corresponding cation radicals, and the absolute reaction rates are independent of the concentration of **2** over the range studied. Both of these observations are consistent with rate determining oxidation of **3** to the corresponding cation radical ($\mathbf{3}^{+\cdot}$). The involvement of $\mathbf{3}^{+\cdot}$ in the Diels–Alder reaction mechanism is further supported by the observation of the efficient formation of the same cycloadducts under anodic oxidation conditions. When the anodic potential is the same as that of $\mathbf{1}^{+\cdot}$, the observed ρ value (−4·85) is found to be impressively close to that found in the reactions catalyzed by $\mathbf{1}^{+\cdot}$ (−4·99). When the more potent aminium salt catalyst tris(2,4-dibromophenyl)aminium hexachloroantimonate ($\mathbf{5}^{+\cdot}$) is used, the ρ value (−3·82) is smaller than that for $\mathbf{1}^{+\cdot}$, as expected for a less highly endergonic ionization step. The circumstance that the ρ values for the $\mathbf{5}^{+\cdot}$ reactions are not equal to those in the $\mathbf{1}^{+\cdot}$ reactions immediately rules out the possibility that both reactions occur by chain mechanisms and permits the conclusion that the $\mathbf{1}^{+\cdot}$ reactions, at least, occur via a catalytic mechanism. When an anode of potential equal to that of $\mathbf{5}^{+\cdot}$ is used, the ρ value (−3·94) is very similar to that found for $\mathbf{5}^{+\cdot}$ (−3·82), suggesting that the $\mathbf{5}^{+\cdot}$ reactions may also occur via a catalytic mechanism. The close correspondence between the ρ values for the kinetically controlled reactions of two different aminium salt catalysts with those for electrochemical oxidations at anodes of the same potential is construed as an indication that ionization of the substrates (**3**) by the aminium salt is, as the anodic oxidations are assumed to be, of the outer-sphere variety.

EXPERIMENTAL

Analysis. ^1H spectra were recorded on a Bruker AC 250 spectrometer as solutions in $CDCl_3$. Chemical shifts are reported in parts per million (ppm) downfield from the reference, tetramethylsilane (TMS). Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; p, pentet; dd, doublet of doublets; m, multiplet. Analytical gas chromatographic (GC) analyses were performed on a Perkin-Elmer Model 8500 instrument using a PE Nelson Model 1020 reporting integrator for data collection. The instrument was equipped with flame ionization detectors and a DB-1 (J & W Scientific) capillary column (30 m × 0·25 mm i.d., 1 μm film thickness) using helium as the carrier gas. Naphthalene was used as internal standard for all the quantitative analyses, and detector response factors were calculated for all the products. Low-resolution mass spectrometry (LRMS) was performed on a Hewlett-Packard Model 5971A GC-MS spectrometer equipped with a DB-1 capillary column (15 m × 0·25 mm i.d., 1 μm film thickness). Electrochemical measurements were performed using a Bioanalytical Systems Model 100 electrochemical analyser in the differential-pulse voltammetry (DPV) mode scanning in the range 500–1900 mV at a scan rate of 4 mV s^{-1} with a pulse amplitude of 50 mV, a pulse width of 50 ms, a pulse period of 1000 ms and a sensitivity of 1×10^{-6}. The DPV measurements were carried out using a divided cell equipped with a platinum disk working electrode (anode), a reticulated vitreous carbon counter electrode and an Ag/Ag^+ reference electrode (calibrated against ferrocene/ferrocene$^+$) in 0·1 M $LiClO_4$ in acetonitrile. The analyte concentration was 1–10 mg ml^{-1}.

Solvents and reagents. Methylene chloride (CH_2Cl_2) and acetonitrile (AN) were dried over phosphorus pentoxide (P_2O_5), hexane was dried ova CaH_2 and tetrahydrofuran (THF) was dried over Na–benzophenone. All other reagents were commercially available and used as received, unless specified otherwise. The stilbenes and styrenes in this study were synthesized via a Grignard procedure (see below). All of the stilbenes[10] and styrenes[11] had been synthesized and characterized previously.

General procedure for the Grignard method for preparation of trans-β-methylstyrenes. To a dry 250-ml round-bottomed flask equipped with a reflux condenser, stirrer, nitrogen inlet and addition funnel were added 30 ml of 3·0 M ethylmagnesium bromide (in diethyl ether, Aldrich) with an ice–water bath. Then, a solution of 60 mmol of an appropriate benzaldehyde in 10 ml of THF was added dropwise (via the addition funnel) to the Grignard reagent. After all of the aldehyde had been added, the reaction mixture was brought to gentle reflux for a period of 2 h and then allowed to cool to room temperature. The alkoxymagnesium bromide salt was hydrolyzed by dropwise addition of 6 M HCl until the aqueous solution was acidic to litmus paper. The layers were separated and the aqueous layer was washed with 100 ml of diethyl ether several times. The combined ether layers were dried over anhydrous $MgSO_4$. After removal of the $MgSO_4$ and evaporation of the volatile materials under reduced pressure, the crude desired alcohol product was obtained. The crude alcohol was placed in a 250 ml round-bottomed flask which was equipped with a stirrer, a nitrogen inlet, a reflux condenser and 100 ml of pyridine. With stirring, 18·0 ml (193 mmol) of phosphorus oxychloride was slowly added via a syringe through a rubber septum to the reaction mixture. After the addition was completed, the mixture was refluxed for 2 h and allowed to cool to room temperature. To this solution 20 ml of water were slowly added, and the desired product was separated from the aqueous layer by extraction with diethyl ether and the aid of brine solution. The ethereal solution was then dried over anhydrous $MgSO_4$. After removal of the $MgSO_4$ and evaporation of the volatile materials under reduced pressure, the product was purified by distillation.

General procedure for the preparation of the Diels–Alder products of trans-β-methylstyrenes, catalyzed by $Ar_3N^{+\cdot}$ ($1^{+\cdot}$). Approximately 5 mol% of $\mathbf{1}^{+\cdot}$ relative to the styrene substrate was weighed into a 25 ml volumetric flask containing a magnetic stirrer. The flask was then capped with a septum, immersed in an ice–water bath and purged with nitrogen. Methylene chloride (15 ml) was added and the solution stirred for 5 min. To this was then added (syringe) a solution containing 0·5 mmol of appropriate styrenes and an excess (tenfold) of 2,3-dimethyl-1,3-butadiene in methylene chloride (10 ml). After an appropriate interval (30 min, or when the color of the aminium salts had disappeared), the reaction mixtures was quenched with 3 ml of saturated methanolic potassium carbonate. Water (20 ml) and methylene chloride (10 ml) were added and the organic layer was separated and dried ($MgSO_4$). After removal of the $MgSO_4$ and evaporation of the volatile materials under reduced pressure, the Diels–Alder adducts were purified by TLC [hexane–ethyl acetate (9:1, v/v)] and characterized (NMR, LRMS).

(±)-4*S*-(4′-Methoxyphenyl)-1,2,5*S*-trimethylcyclohexene (**4a**): isolated yield 80%; ^{1}H NMR ($CDCl_3$), δ 6·82–7·12 (m, 4 H), 3·75 (s, 3 H), 2·35 (m, 1 H), 2·16 (m, 2 H), 2·03 (m, 1 H), 1·88 (m, 2 H), 1·68 (s, 3 H), 1·63 (s, 3 H), 0·72 (d, 3 H); LRMS, *m/z* 230 (M^+), 148 (base), 117, 77.

(±)-4*S*-(4′-Phenoxyphenyl)-1,2,5*S*-trimethylcyclohexene (**4b**): isolated yield 88%; ^{1}H NMR ($CDCl_3$,) δ 6·95–7.38 (m, 9 H), 2·39 (m, 1 H), 2·15 (m, 2 H), 2·05 (m, 1 H), 1·85 (m, 2 H), 1·65 (s, 3 H), 1·61 (s, 3 H), 0·73 (d, 3 H); LRMS, *m/z* 292 (M^+), 210 (base), 117, 77.

(±)-4-(4′-Methylphenyl)-1,2,5*S*-trimethylcyclohexene (**4c**): isolated yield 65%; ^{1}H NMR ($CDCl_3$), δ 6·80–7·08 (m, 4 H), 2·38 (m, 1 H), 2·28 (s, 3 H), 2·14 (m, 2 H), 2·08 (m, 1 H), 1·90 (m, 2 H), 1·64 (s, 3 H), 1·60 (s, 3 H), 0·75 (d, 3 H); LRMS, *m/z* 214 (M^+), 132 (base), 117, 77.

General procedure for the preparation of the Cycloaddition products of trans-β-methylstyrenes catalyzed by $Ar'_3N^{+\cdot}$ ($5^{+\cdot}$). Approximately 10–15 mol% of $\mathbf{5}^{+\cdot}$ were weighed into a 25 ml volumetric flask containing a magnetic stirrer. The flask was then capped with a septum, immersed in an ice–water bath, and purged with nitrogen. Methylene chloride (15 ml) was added and the solution stirred for 5 min. To this was then added (syringe) a solution containing 0·5 mmol of appropriate stilbenes (styrenes) and an excess (fivefold) of 2,3-dimethyl-1,3-butadiene in methylene chloride (10 ml). After an appropriate interval (3 min, or when the color of the aminium salts had disappeared), the reaction mixtures was quenched with 3 ml of saturated methanolic potassium carbonate. Water (20 ml) and methylene chloride (10 ml) were added and the organic layer was separated and dried ($MgSO_4$). After removal of the $MgSO_4$ and evaporation of the volatile materials under reduced pressure, the Diels–Alder adducts were purified by TLC [hexane–ethyl acetate (9:1, v/v)] and characterized (NMR, LRMS).

(±)-4*S*-(3′-Methylphenyl)-1,2,5*S*-trimethylcyclohexene (**4d**): isolated yield 40%; ^{1}H NMR ($CDCl_3$), δ 6·78–7·10 (m, 4 H), 2·35 (m, 1 H), 2·25 (s, 3 H), 2·10 (m, 2 H), 2·04 (m, 1 H), 1·88 (m, 2 H), 1·66 (s, 3 H), 1·61 (s, 3 H), 0·77 (d, 3 H); LRMS, *m/z* 214 (M^+), 132 (base), 117, 77.

(±)-4*S*-Phenyl-1,2,5*S*-trimethylcyclohexene (**4e**): isolated yield 35%; ^{1}H NMR ($CDCl_3$), δ 6·90–7·02 (m, 4 H), 2·35 (m, 1H), 2·10 (m, 2 H), 2·04 (m, 1 H), 1·91 (m, 2 H), 1·68 (s, 3 H), 1·62 (s, 3 H), 0·73 (d, 3 H); LRMS, *m/z* 200 (M^+), 118 (base), 117, 77.

(±)-4*S*-(4′-Chlorophenyl)-1,2,5*S*-trimethylcyclohexene (**4f**): isolated yield 32%; ^{1}H NMR ($CDCl_3$), δ 6·80–7·08 (m, 4 H), 2·38 (m, 1 H), 2·28 (s, 3 H), 2·14 (m, 2 H), 2·08 (m, 1 H), 1·90 (m, 2 H), 1·64 (s, 3 H), 1·60 (s, 3 H), 0·75 (d, 3 H); LRMS, */z* 216, 214 (M^+), 132 (base), 117, 77.

General procedure for the competitive cycloadditions of trans-β-methylstyrenes with 2,3-dimethyl-1,3-butadiene catalyzed by aminium salts. Approximately 5–10 mol% of $\mathbf{1}^{+\cdot}$ or 0·1–0·5 mol% of $\mathbf{5}^{+\cdot}$ were weighed into a 10 ml volumetric flask containing a magnetic stirrer. The flask was then capped with a septum, immersed in an ice–water bath and purged with nitrogen. Methylene chloride (5 ml) was added and the solution stirred for 5 min. To this was then added (syringe) a solution containing equimolar amounts (*ca* 0·12 mmol) of styrenes and an excess (tenfold) of 2,3-dimethyl-1,3-butadiene in methylene chloride (5 ml). After an appropriate interval (timed so that the conversion was less than 10%), a 0·5 ml aliquot of the reaction mixture was quenched with 1 ml of saturated methanolic potassium carbonate. Water (5 ml) and methylene chloride (2 ml) were added and the organic layer was separated and dried ($MgSO_4$). After removal of $MgSO_4$, the competition ratios were determined by GC and corrected for varying response factors. In all cases, the results of at least three runs were averaged. The resulting relative rate ratios were cross-checked by pairing each substrate with at least two other reaction partners. At the 10% conversion to product level, the mass balances were 97–99%. Competitive experiments in acetonitrile were performed in exactly the same manner as indicated above but using acetonitrile as the solvent.

Effect of the concentration of 2,3-dimethyl-1,3-butadiene on the absolute reaction rates of cycloaddition. The conversions to Diels–Alder products were measured for samples which were of identical composition except for the concentration of 2,3-dimethyl-1,3-butadiene run in parallel and for identical reaction times.

ACKNOWLEDGEMENTS

The authors thank the Robert A. Welch Foundation (F-149) for support of this research.

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