when synthesized by classical methods.)[15] Therefore, the synthesis of a water-soluble, high molecular weight polymer requires converting all reaction components, catalyst as well as monomers, into water-soluble species. To this end, a water-soluble zerovalent palladium catalyst (PdL_3, L = $P(C_6H_5)_2(m\text{-}C_6H_4SO_3Na)$ (II)) was prepared from $PdCl_2$ and monosulfonated triphenylphosphine[16] by an adaptation (see supplementary material) of Coulson's method for the synthesis of tetrakis(triphenylphosphine)palladium.[17] Complex II proved to be identical with the catalyst reported by Calabrese.[18] The ethylene glycol diester of 4,4′-biphenylylenebis(boronic acid) (III) served as one water-soluble monomer precursor (rapid hydrolysis of the water-insoluble III affords the sparingly soluble bis(boronic acid) hydroxyl adduct), while 4,4′-dibromodiphenic acid (IV) served as the second. Both monomers were prepared by modifications of known literature syntheses and were fully characterized.[19,20] The dibromide IV was chosen as a synthetic target after model studies revealed that Pd(0) cross couplings under homogeneous aqueous conditions exhibit a strong regiochemical limitation: Coupling of bromobenzoic acids and tolylboric acid proceeds readily and in essentially quantitative yield (as determined by ^1H NMR) for *m*-bromobenzoic acid, but gave no identifiable product for *o*-bromobenzoic acid.

Polymer I has been characterized by a number of techniques in order to confirm its composition, structure, and molecular weight.[21] NMR analysis of I is complicated by extreme peak broadening: The ^1H NMR spectrum (D_2O/NaOD) shows a broad resonance with secondary peaks from 6.0 to 8.2 ppm. The ^{13}C NMR spectrum consists of six broad resonances (width at half-height 2–3 ppm). The 11 individual resonances expected for I are apparently concealed by significant overlap. The IR (KBr pellet) spectrum displays expected bands at 3500–3100 cm^{-1} and 1709 cm^{-1} and a number of bands from 900 to 700 cm^{-1} associated with aromatic C–H out-of-plane bending modes of di- and trisubstituted benzenes.[22]

Polymer I exhibits the outstanding thermal stability typically found in rigid-chain polymers:[23] Thermogravimetric analysis (under N_2) shows the onset of thermal decomposition above 520 °C, while differential scanning calorimetry shows no apparent softening temperature. Both methods indicate that I undergoes dehydration at 300–330 °C to form a poly(anhydride) structure; this process has been confirmed by IR spectroscopy.[24]

Poly(acrylamide) gel electrophoresis[25] of I gives an approximate molecular weight (M_w) of 50 000 g/mol relative to single-stranded DNA. In the absence of an absolute reference, it is unreasonable to expect this method to give an accurate molecular weight, since I is much more rigid than single-stranded DNA. Thus, this result is best taken as an order-of-magnitude estimate. Viscometry experiments (standard Ubbelohde viscometers; identical results with different capillary diameters indicate that flow-induced shearing is not a significant complication[26]) yield an intrinsic viscosity of 0.49 dL/g for I in 0.100 M Na_2CO_3. A solution viscosity of 1.9 cP for a 1% solution of I in 0.1 M Na_2CO_3 compares favorably with a reported viscosity for a 10% aqueous solution of 45% sulfonated PPTA of 3 cP.[8a]

Current work is directed at determining the absolute molecular weight of I and at extending this aqueous coupling strategy to a number of monomer substrates to provide a host of architecturally diverse polymers ranging from rigid rods to flexible chains.

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Supplementary Material Available: Experimental procedures for the syntheses of water-soluble Pd complex II and polymer I, ^1H and ^{13}C NMR and IR spectra of I, IR spectrum of dehydrated polymer, and TGA trace of I (5 pages). Ordering information is given on any current masthead page.

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(21) ^1H NMR (500 MHz): $\delta = 6.38, 6.75, 7.01, 7.30, 7.68, 8.07$ (all br). ^{13}C NMR (125 MHz): $\delta = 128, 129, 130, 139.5, 141, 179$ (all br). Elemental anal. Expected for $(C_{13}H_8O_2)_n$: C, 79.58; H, 4.07. Found: C, 77.55; H, 4.31. (Poly(*p*-phenylenes) reported in the literature do not yield clean combustion analyses. (See refs 3 and 12b.) This has been attributed to difficulties in burning these materials quantitatively. Impurities and residual end-groups on oligomeric species have also been implicated. I leaves detectable residues in both combustion analysis and thermogravimetric analysis. Additionally, it has proven to be extremely difficult to remove trace amounts of water from I.

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The Intramolecular Salt Effect. An Acrylate Ester Bearing an Ion Pair Shows Enhanced Rates and Stereoselectivity in a Nitrone Cycloaddition[1]

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Understanding the effects that a nearby (4–25 Å) ion pair can exert on reaction processes will have practical applications in the area of chemical synthesis and will help to illuminate the necessary and sufficient components of biocatalysis. Here we show that in chloroform an acrylate ester tethered to an ion pair reacts faster than comparable neutral acrylates. Importantly, the three major diastereomeric pathways in this nitrone cycloaddition differ in sensitivity to this intramolecular salt effect.[3] The charged acrylate is both more reactive and more selective than its neutral congeners.

The effects of salts on ionization rates of organic substrates in nonpolar solvents have been studied for many years.[4] Simple salt effects are due to the Coulombic effects of ion pairs on the reactants and transition states of ionic processes, and a quantitative model of these effects has been proposed.[5,6] Effects of unreactive

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0002-7863/91/1513-7412$02.50/0

Chart I

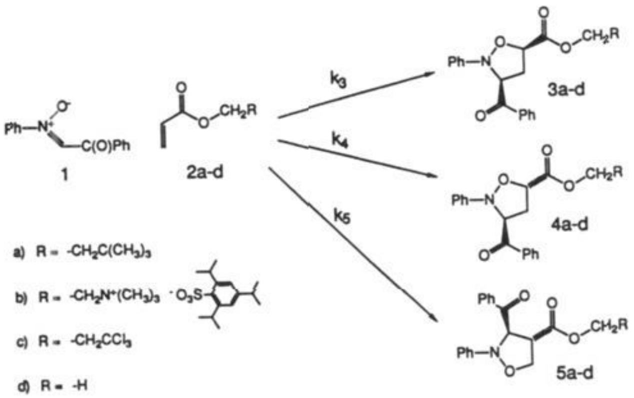

Table I. Second-Order Rate Constants ($M^{-1}\ s^{-1}$) for the Formation of Diastereomeric Isoxazolidines **3–5** and Resulting Product Ratios[a]

acrylate ester	k_{net}	k_3	k_4	k_5	ratio 3:4:5
2a	1.95×10^{-3}	7.12×10^{-4}	7.40×10^{-4}	4.62×10^{-4}	37:39:24
2b[b]	1.46×10^{-2}	1.05×10^{-2}	3.77×10^{-3}	6.31×10^{-4}	71:25:4
2c	5.04×10^{-3}	1.55×10^{-3}	1.72×10^{-3}	1.68×10^{-3}	31:35:34
2d	2.05×10^{-3}	7.98×10^{-4}	8.52×10^{-4}	4.22×10^{-4}	39:41:20
2a[c]	2.32×10^{-3}	8.87×10^{-4}	9.09×10^{-4}	5.42×10^{-4}	38:39:23

[a] Reactions were run at 40 mM each ester and nitrone unless otherwise noted. [b] Reaction run at 20 mM each ester and nitrone. [c] Reaction in the presence of 40 mM tetrabutylammonium tosylate.

ionic solutes on cycloaddition reactions in nonpolar solvents are known: Grieco has recently demonstrated the value of such effects.[7,8]

To initiate a study of *intramolecular* salt effects in cycloaddition reactions, we chose to examine the reaction of *N*-phenyl-*C*-benzoylnitrone (**1**) with acrylate esters **2a–d** (Chart I). This reaction is well behaved, follows an overall second-order rate law, and proceeds at a convenient rate under conditions suitable for NMR-based observations.[9] The reaction is fastest in nonpolar solvents, but like most 1,3-dipolar additions, the reaction is nearly insensitive to solvent polarity.[9a,10]

Kinetic measurements were made at 298 ± 1 K in $CDCl_3$. The nitrone was combined with the respective acrylate esters at equimolar concentrations, and the reaction was followed by NMR spectroscopy. The NMR method of observation allowed four rates to be determined simultaneously: the rate of acrylate disappearance (k_{net}); the rate of appearance of *cis*-5-isoxazolidine **3** (k_3); the rate of appearance of *trans*-5-isoxazolidine **4** (k_4); and the rate of appearance of *trans*-4-isoxazolidine **5** (k_5).

Four esters were evaluated. The object of central interest was the cationic choline acrylate with triisopropylbenzenesulfonate counterion (**2b**). This reactant had good solubility in chloroform.[11] For comparison purposes, 3,3-dimethylbutyl acrylate (**2a**) was chosen because it is sterically similar to choline acrylate **2b**. The inductive effects of ester substituents were of interest, so 2,2,2-trichloroethyl acrylate (**2c**) was also evaluated. Methyl acrylate was included so that we could compare our results with related previous work.[12] All reaction mixtures were homogeneous.

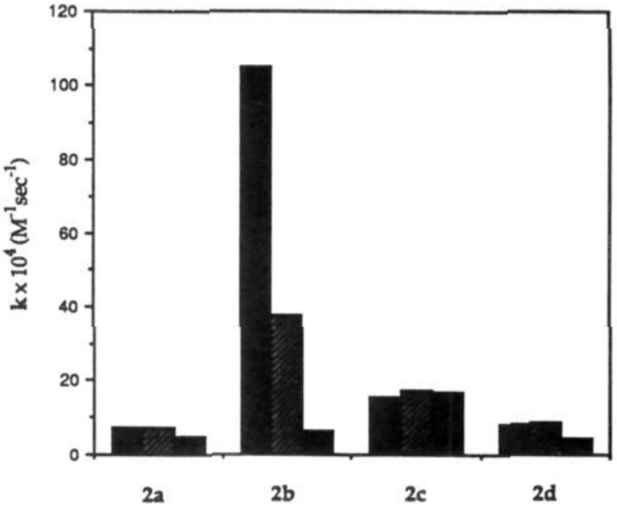

Figure 1. Comparison of the rate constants for reaction of esters **2a–d** leading to isoxazolidines **3** (solid bars), **4** (striped bars), and **5** (speckled bars). The ionic ester reacts fastest and gives the best control of product geometry.

It was found that 3,3-dimethylbutyl acrylate (**2a**) and methyl acrylate (**2d**) differ slightly in reactivity (Table I). Under the conditions employed, the reaction of methyl acrylate with **1** affords a mixture of three diastereomers (**3d**, **4d**, and **5d**) in a 1.9:2:1 ratio. The bulkier ester is less selective than the methyl ester and provides the three products in 1.5:1.6:1 ratio. The presence of 0.040 M tetrabutylammonium tosylate had little effect on reaction rate and selectivity in the reaction of ester **2a**. The trichloroethyl ester reacted 2.5 times faster than the 3,3-dimethylbutyl acrylate. This rate effect was greatest for the pathway leading to 4-isoxazolidine. In consequence, the trichloroethyl ester was the least selective of the four esters.

The charged acrylate is more reactive and more selective than the neutral acrylates. While 3,3-dimethylbutyl acrylate provides the three products in *1.5:1.6:1* ratio, the choline acrylate affords a *17:6:1* ratio of these same products. A comparison of the second-order rate constants for the three principle pathways (Figure 1) reveals that *the improved selectivity is due to selective rate enhancements*. The rate of *cis*-5-isoxazolidine formation is increased 15-fold and the rate of *trans*-5-isoxazolidine is increased 5-fold in comparison to 3,3-dimethylbutyl acrylate. The rate of formation of the 4-isoxazolidine is virtually unchanged.

These data demonstrate that the intramolecular salt effect can influence a reaction that is quite insensitive to solvent changes. Here, the salt effect accelerates a cycloaddition. The effect is not a simple medium polarity effect, because a more polar medium would lead to rate deceleration. Also, the effect is larger and more specific than the effect of an ionic solute. Importantly, the observed rate effects are different for each of three primary diastereomeric pathways. Reasonable interpretations of these results may be based on the polar interactions between the nearby ion pair, the initial reactant states, and transition states for the three pathways.[9a,13]

This is the first example of an intramolecular salt effect for a cycloaddition process. Although the magnitude of the effect is not large, a useful increase in diastereoselectivity is observed. Many cycloaddition processes are known to be more sensitive to polar solvents, and those reactions may well reveal larger intra-

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molecular salt effects. While it is steric effects that are most often turned to when better stereocontrol is desired in a chemical process, this paper shows that dipolar effects, especially the large dipoles associated with ion pairs in nonpolar solvents, can be an important aspect of stereocontrol. Further applications of these concepts are under study.

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The Absolute Heats of Formation of *o*-, *m*-, and *p*-Benzyne

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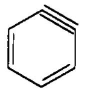
The dehydrobenzenes (benzynes), **1–3**, constitute a fascinating class of reactive organic intermediates that has inspired numerous experimental and theoretical investigations.[1] *o*-Benzyne (**1**) has been extensively studied over the last 40 years to establish its geometric and electronic structures, its chemical reactivity, and its thermodynamic properties.[2-12] Recently, derivatives of *p*-benzyne (**3**) have attracted considerable attention as intermediates in the DNA-cleaving action of calicheamicins and esperamicins.[13] However, little is known about the physical properties of *m*- and *p*-benzyne,[14-16] and the thermochemistry of *o*-benzyne has been controversial. We report here an experimental determination of the absolute heats of formation of **1–3** as derived from energy-resolved collision-induced dissociation (CID) measurements in a flowing afterglow–triple quadrupole apparatus.[17]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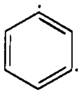
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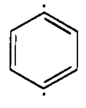
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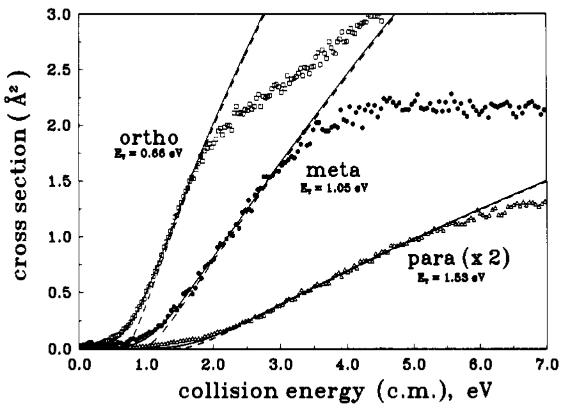
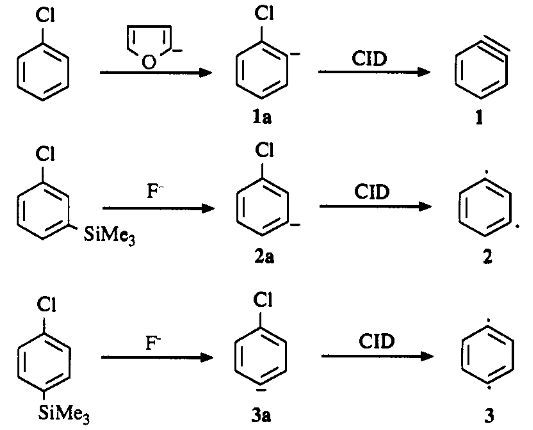


Figure 1. Cross sections for Cl$^-$ dissociation from *o*-, *m*-, and *p*-chlorophenyl anions resulting from collisional activation with argon target at 4.0 × 10^{-5} Torr. The solid line is the optimized, fully convoluted model appearance curve, and the dashed line represents the unconvoluted excitation function. The uncertainty in the absolute cross sections is estimated to be ±50%, while the relative cross sections are accurate to within ±20%.

Scheme I



We recently demonstrated the use of collision-induced α-elimination reactions of halocarbanions in the gas phase as a new method for obtaining carbene thermochemistry.[18,19] The basic

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