Gas-Phase Hydrolysis of Phenyl Acetate and Phenyl Benzoate by Superoxide Ion

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Superoxide ion ($O_2^-\cdot$) is a powerful nucleophile in aprotic solvents[1] and a moderate base in the gas phase.[2] Development of Fourier transform mass spectrometers (FT MS),[3] with trapped ion cells,[4] has made possible the study of gas-phase ion/molecule reactions at low pressures (10^{-8}–10^{-7} torr) for reaction times that range from milliseconds to several seconds.[5] Under these conditions clustering and solvation effects are absent.

We report here an FT MS[6] study of the novel gas-phase ion chemistry of superoxide with phenyl acetate and phenyl benzoate. In contrast with the results of other recent studies of gas-phase reactions of phenyl acetate with a variety of nucleophiles,[7] acetate is a major ionic product. Furthermore, although the superoxide nucleophilicity observed in solution studies[8-10] continues to dominate the reactions, new products that do not correspond to the net result of ester hydrolysis also result. In solution, nucleophilic addition of $O_2^-\cdot$ to the carbonyl carbon is followed by subsequent steps to yield phenoxide and both carboxylate and percarboxylate anions.[8,9]

Gas-phase reaction of superoxide ion[11] in the presence of oxygen (3×10^{-7} torr) with phenyl acetate (5×10^{-8} torr) yields five ionic products. Time-resolved measurements have been accomplished by variation of delay times between superoxide ion formation and negative ion mass spectral observations.[13] The five ionic products[14] increase concurrent with decrease of $O_2^-\cdot$ and as a function of reaction time (Figure 1). Three of the products have m/z values that correspond to solution-phase products: m/z 59 (acetate, $C_2H_3O_2^-$), m/z 75 (peroxyacetate, $C_2H_3O_3^-$), and m/z 93 (phenoxide, $C_6H_5O^-$). In addition, two ionic products unique to the gas-phase reaction are observed.

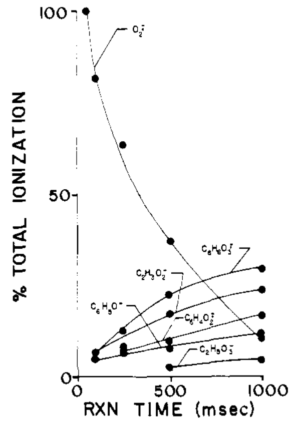
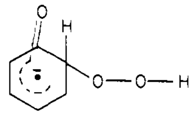
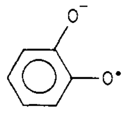
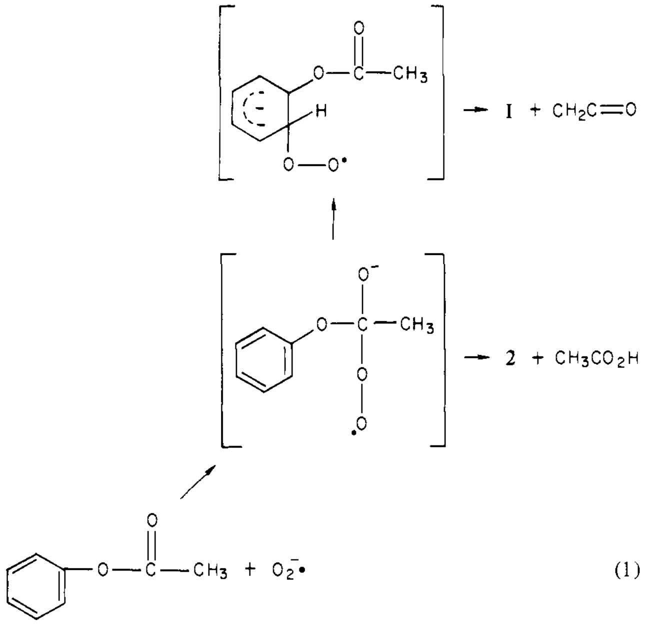


Figure 1. Time-resolved mass spectral intensities for the anions that result from the reaction of superoxide ion with phenyl acetate.


1 ($C_6H_6O_3^-\cdot$)


2 ($C_6H_4O_2^-\cdot$)



(1)

These ions, **1** (m/z 126) and **2** (m/z 108), are believed to result from an initial nucleophilic addition of superoxide to the ester, followed by decomposition with either elimination of ketene to produce **1** or loss of acetic acid to produce **2** (eq 1). Species **2** has also been observed to result from reaction of superoxide with diphenols and catechols.[15,16] Evidence in support of this hypothesis is shown by the following: (1) when CD_3 phenyl acetate is used, the m/z 126 ion is quantitatively replaced by m/z 127, but m/z 108 does not shift; (2) when $^{18}O_2$, is used, the m/z 126 peak is quantitatively replaced by m/z 130, the m/z 108 species now incorporates a single ^{18}O and moves to m/z 110, the m/z 75 species (peroxyacetate) shifts to m/z 79, and the acetate m/z 59 ion shifts to m/z 61; (3) collision-induced dissociation (CID)[17] of m/z 126 yields a single m/z 93 fragment ion (phenoxide), as does CID of

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[11] Superoxide was produced in two different ways: (a) the direct method involved ionization of oxygen with 7-eV electrons at 3.0×10^{-7} torr. A limitation of this method is that the major ionic product is $O^-\cdot$ (ca. 90%) and $O_2^-\cdot$ is a minor product (ca. 10%). Ejection of $O^-\cdot$ at its resonance frequency was easily accomplished, however, to allow studies of $O_2^-\cdot$ reactions uncomplicated by the presence of $O^-\cdot$; (b) indirectly, $O_2^-\cdot$ was produced by ionizing a mixture of water (1.0×10^{-7} torr) and a 1:1 mixture of oxygen and propylene (1.1×10^{-7} torr).[12]

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[14] These products, with the exception of phenoxide (m/z 93), result exclusively from the reaction of $O_2^-\cdot$ with the neutral ester because they are not observed when all of the $O_2^-\cdot$ is ejected prior to the reaction delay time. The m/z 93 peak is noticeably smaller under these conditions and probably arises from direct reaction of electrons with the ester.

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the m/z 130 ion when $^{18}O_2^{-}\cdot$ is used; (4) when phenyl benzoate is used as substrate, no m/z 126 ion is formed because ketene elimination has been blocked by substitution of phenyl for methyl and the requisite acidic hydrogen is no longer present. Thus, superoxide reacts with phenyl benzoate to give four anionic products: m/z 121 (benzoate), m/z 93 (phenoxide), m/z 108 (**2**), and m/z 137 (peroxybenzoate). As before, use of $^{18}O_2^{-}\cdot$ shifts the m/z 108 ion quantitatively to m/z 110, m/z 121 to m/z 123, and m/z 137 to m/z 141, which indicates that the products are formed by a mechanism similar to that for the phenyl acetate reaction.

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Registry No. 1, 85029-12-5; **2**, 20526-43-6; phenyl acetate, 122-79-2; phenyl benzoate, 93-99-2; superoxide, 11062-77-4; acetate, 71-50-1; peroxyacetate, 35683-46-6; phenoxide, 3229-70-7; peroxybenzoate, 35683-46-6; oxygen, 7782-44-7; propylene, 115-07-1; water, 7732-18-5; phenyl acetate-CD_3, 22705-27-7; $^{18}O_2^{-}$, 52227-59-5.

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[17] Collision induced dissociation (CID) in FT MS involves the selection of the desired parent ion by ejection of all other ions prior to its translational excitation by "tickling" at its resonance frequency in the presence of a collision gas at a suitable pressure (ca. 10^{-6} torr).[18–20]

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Asymmetric Carbon–Carbon Bond Formation via *B*-Allyldiisopinocampheylborane. Simple Synthesis of Secondary Homoallylic Alcohols with Excellent Enantiomeric Purities

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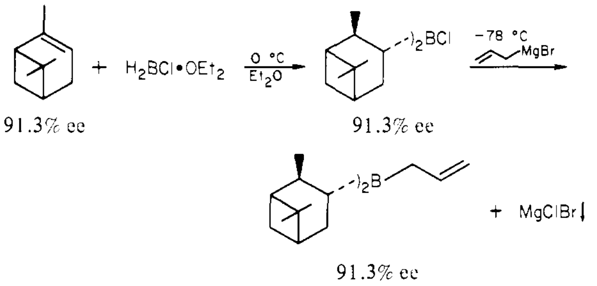
A new chiral allylborane, *B*-allyldiisopinocampheylborane ($Ipc_2BCH_2CH{=}CH_2$), has been conveniently prepared and successfully utilized for asymmetric carbon–carbon bond formation. Thus, *B*-chlorodiisopinocampheylborane (Ipc_2BCl), readily prepared by the hydroboration of α-pinene with chloroborane etherate ($H_2BCl{\cdot}OEt_2$), on treatment with allylmagnesium bromide, provides $Ipc_2BCH_2CH{=}CH_2$. Alternatively, it is prepared by the hydroboration–methanolysis of α-pinene, followed by the reaction of the borinate with allylmagnesium bromide. The new chiral allylborane undergoes condensation with a variety of aldehydes to furnish secondary homoallylic alcohols with enantiomeric purities in the range 83–96%.

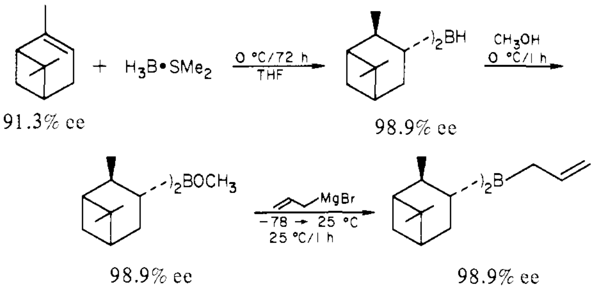
Allylboranes are extremely valuable intermediates in organic synthesis, particularly for carbon–carbon bond formation.[2] Use of chiral allylboranes for asymmetric carbon–carbon bond formation was not known until recently. Chiral allylboronates derived from camphor glycols have been successfully used for condensation with aldehydes.[3] In this reaction, the chirality of the boron ligand induces chirality at the new asymmetric center. In another report, chirality located in the allyl side chain of a borinic acid is efficiently transferred to form a new asymmetric center.[4] We now report a new chiral reagent, *B*-allyldiisopinocampheylborane, for the enantioselective, one-pot synthesis of a wide range of secondary homoallylic alcohols with excellent enantiometric purities.

Preparation of the chiral allylborane is extremely simple. Thus hydroboration of (+)-α-pinene with monochloroborane etherate[5] ($H_2BCl{\cdot}OEt_2$) in ethyl ether at 0 °C proceeds cleanly to Ipc_2BCl. This intermediate, on treatment with allylmagnesium bromide, at −78 °C, provides $Ipc_2BCH_2CH{=}CH_2$ (^{11}B NMR δ +78; eq 1).



(1)

An alternative procedure involves hydroboration of (+)-α-pinene with $BH_3{\cdot}SMe_2$,[6] equilibration at 0 °C for 3 days to give a reagent approaching 100% ee,[7] followed by methanolysis of the Ipc_2BH to Ipc_2BOCH_3. the reaction of allylmagnesium bromide with Ipc_2BOCH_3 is slow at −78 °C but rapid at room temperature (eq 2). The reagent can be readily isolated as the neat liquid, free of magnesium salts and solvent, by passing the reaction mixture through a filtration chamber,[8] followed by pumping off the solvents. However, it is generally more convenient to react the reagent with the aldehyde without prior isolation.



(2)

Thus, *B*-allyldiisopinocampheylborane, on treatment with acetaldehyde at −78 °C, undergoes condensation to provide, after the usual alkaline hydrogen peroxide workup, 4-penten-2-ol in 93% ee (eq 3, R = CH_3).

Similarly, propionaldehyde, *n*-butyraldehyde, 2-methylpropionaldehyde, and 2,2-dimethylpropionaldehyde readily react at −78 °C with $Ipc_2BCH_2CH{=}CH_2$ to furnish, after oxidation, the corresponding homoallylic alcohols with remarkable enantiomeric purities (Table I). The percent ee of the alcohols are comparable in all cases and apparently do not depend on the steric requirements of the aldehydes.

The asymmetric induction in the case of benzaldehyde, 96% ee, is highly gratifying in comparison to the earlier report of ~30% ee.[3]

The following experimental procedure is representative.[8] Diisopinocampheylborane of 98.9% ee was prepared from $BH_3{\cdot}SMe_2$ and (+)-α-pinene [$[\alpha]^{23}{}_D$ +47.1° (neat), 91.3% ee] by following

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[1] Research associate on Grant 2R01 GM 10937-20 from the National Institutes of Health.

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