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- (18) The structural assignment of this compound is in accord with (a) its spectral properties and (b) its combustion analyses with 0.4% of theory.
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- (20) A trace of the Δ^2 isomer is suggested in the NMR spectrum of **21**. For reasons which are not apparent to us, compound **21** is much more stable with respect to isomerization of the double bond than the 5-methoxy compound, **29**.
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- (24) Compound **30** is chromatographically somewhat unstable with respect to β -elimination of methanol and formation of phenol **31**. A trace of **31** is suggested in NMR spectrum of **30**.
- (25) Several previous strategies, using Diels-Alder reactions together with other manipulations to afford "meta" type cyclohexenes are seen in the studies of Büchi,²⁶ Trost,²⁷ Cohen,²⁸ and Valenta.¹¹ The research described herein provides a direct solution to "meta" type cyclohexadienes.
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Samuel Danishefsky,* Michael P. Prisbylla, Steven Hiner

Department of Chemistry, University of Pittsburgh
Pittsburgh, Pennsylvania 15260

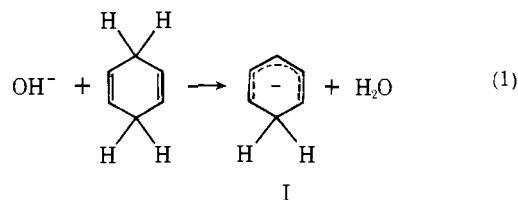
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Gas Phase Oxidation and Reduction Reactions with C₆H₇⁻, HNO⁻, and HO₂⁻

Sir:

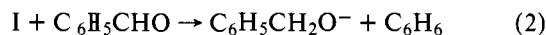
Although gas phase proton transfer reactions have been extensively studied,¹ there have been few investigations of hydride transfer between ions and neutral molecules in the gas phase, primarily because of a lack of methods for the synthesis of hydride donors.² We wish to report that the cyclohexadiene anion (I) readily transfers a hydride ion to a number of substrates, both organic and inorganic, and so provides a convenient entry into extensive new fields of gas phase ion-molecule chemistry.

We produce hydroxide or amide ions in the ionization region of a flowing afterglow system^{3,4} and add 1,4-cyclohexadiene 10 cm downstream. The anion I is formed by rapid proton transfer (eq 1). Other reactants may be added through fixed

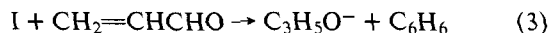


or movable inlets further downstream before the ions are sampled and analyzed by a quadrupole mass filter.⁵

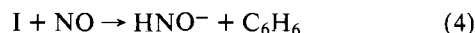
Reaction of benzaldehyde (mol wt 106) with I results in rapid formation of a new ion of m/e 107. We formulate this species as the anion of benzyl alcohol generated by nucleophilic hydride addition to the carbonyl group:



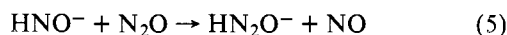
Acrolein (mol wt 56) is also reduced by I to an ion of m/e 57:



Cyclohexadiene anion also reacts rapidly with nitric oxide to give HNO⁻,

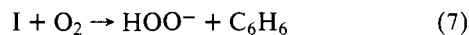


which in some ways is an even more useful hydride donor. For example, HNO⁻ reduces nitrous oxide to HN₂O⁻ and carbon dioxide to formate ion.

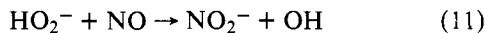
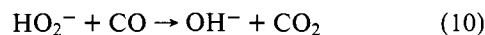
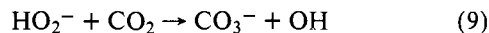


I, on the other hand, does not react with nitrous oxide and only the addition product C₆H₇CO₂⁻ is observed upon reaction with carbon dioxide. HNO⁻ also reduces benzaldehyde and acrolein, in the latter case more cleanly than does I, whose reaction is complicated by a competing addition reaction. HNO⁻ is also known² to hydride transfer to R₃B and can thus serve as a precursor of gas phase borohydride ions.

Hydride transfer from I to oxygen occurs rapidly to form the hydroperoxide ion,



a potent oxidizing agent in the gas phase just as in solution. Benzaldehyde is oxidized to the benzoate ion by HO₂⁻, and carbon dioxide, carbon monoxide, and nitric oxide are also readily oxidized.



All three anions, I, HNO⁻, and HO₂⁻, can serve as bases in the gas phase, so that proton abstraction from substrates with relatively acidic protons can be a complicating factor.⁶ Nevertheless, these anions, and many others which they can be used to create, promise to be of great value for the study of gas phase ion-molecule reactions.

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C. H. DePuy,* Veronica M. Bierbaum*
Robert J. Schmitt, R. H. Shapiro

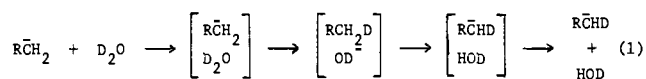
Department of Chemistry, University of Colorado
Boulder, Colorado 80309

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Hydrogen–Deuterium Exchange Reactions of Carbanions with Deuterated Alcohols in the Gas Phase

Sir:

We have recently reported¹ that in the presence of D $_2$ O in the gas phase highly basic anions, such as allyl, hexenyl, and benzyl, undergo hydrogen–deuterium exchange, and showed how this technique can be used to distinguish among structures for isomeric anions with different numbers of potentially exchangeable hydrogens. Such exchange was postulated to occur in a complex between the organic anion and D $_2$ O in which deuterium addition and proton abstraction occurs, with subsequent separation of the complex to produce the deuterated organic ion (eq 1). More basic anions, such as those formed by



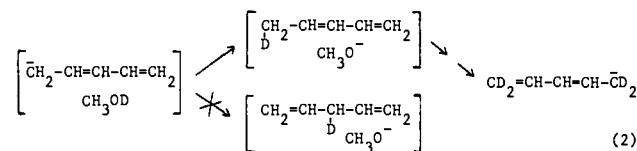
proton abstraction from benzene or 1,3-butadiene, react with D $_2$ O primarily by deuterium abstraction. Less basic anions, such as those formed by proton abstraction from aldehydes, ketones, and conjugated dienes, do not exchange under these conditions, presumably because deuterium transfer from D $_2$ O to the anion is too endothermic to occur. We now wish to report the extension of this technique to exchange in these less basic anions using the more acidic deuterium sources CH $_3$ OD and CF $_3$ CH $_2$ OD.² The extent of exchange with different deuterium sources can be used, not only to give structural information, but also to probe the details of the mechanisms of ion–molecule reactions.

Using the flowing afterglow technique^{3,4} we generate organic anions in a stream of helium buffer by proton abstraction from organic neutrals with NH $_2^-$ or OH $^-$. The deuterated reagent gas is added downstream, ensuring thermalization of the anions. About 5-ms reaction time is allowed before ion sampling and detection by a quadrupole mass filter.⁵

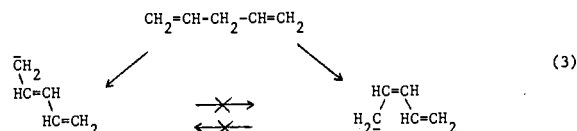
The anions produced by proton abstraction from acetone, acetaldehyde and 3-pentanone do not exchange with D $_2$ O. However, all three anions exchange with CH $_3$ OD, acetone anion giving up to five, acetaldehyde anion up to two, and 3-pentanone anion up to three exchanges. All three of these anions react with the still more acidic alcohol CF $_3$ CH $_2$ OD by deuterium transfer, to produce CF $_3$ CH $_2$ O $^-$ ion. By contrast the still less basic nitromethane anion exchanges with neither D $_2$ O nor CH $_3$ OD but does undergo up to two exchanges with CF $_3$ CH $_2$ OD. The cyclopentadiene anion is still less basic, and does not exchange with any of these deuterated reagents under our experimental conditions.

Exchanges with the anions derived from dienes give espe-

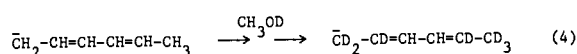
cially interesting information. The 1,3-pentadienyl anion exchanges a maximum of four hydrogens with CH $_3$ OD showing that reprotonation on the central carbon atom, which would lead to the intermediacy of a nonconjugated diene (and a maximum of five exchanges), does not occur⁶ (eq 2). Under



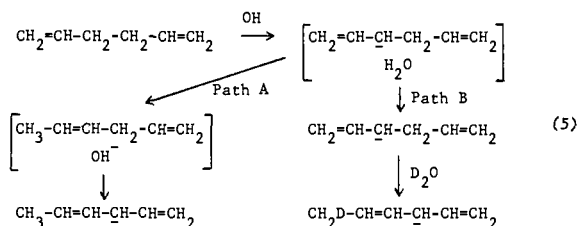
identical conditions of flow and reaction time the pentadienyl anion derived from *cis*-1,3-pentadiene exchanges less readily than that from *trans*-1,3-pentadiene, showing that these isomeric ions do not interconvert. Deprotonation of the unconjugated isomer, 1,4-pentadiene, leads to an approximately equal mixture of the *cis* and *trans* anions, since its extent of exchange under the same conditions is almost exactly the average of those above (eq 3).



Studies of exchanges in hexadiene anions give additional insight into the details of ion–neutral interactions. Starting from a conjugated isomer, up to seven hydrogens can be exchanged with CH $_3$ OD (eq 4). This result is expected by anal-



ogy to the pentadiene example, with addition occurring only at the ends of the conjugated system. No exchange occurs with D $_2$ O since the conjugated anion is not sufficiently basic to cause deuterium transfer. Next consider the anion formed by proton abstraction by OH $^-$ from 1,5-hexadiene. The initially formed ion should be unconjugated and so be sufficiently basic to undergo reaction with D $_2$ O. We find, however, that over half of the anions do not exchange with D $_2$ O, while, of the rest, most incorporate only a single deuterium. We interpret this to mean that, even in the initial proton abstraction step, a complex is formed in which some reprotonation and re-abstraction occurs, leading to the formation of a conjugated anion (eq 5, path A).



Less frequently, separation of the complex occurs before isomerization (path B). Reaction of this unconjugated anion with D $_2$ O usually produces the conjugated anion after a single deuterium is incorporated. When a mixture of NH $_2^-$ and OH $^-$ is used in the initial proton abstraction step, relatively more of the resulting anions exhibit a single exchange with D $_2$ O. This is consistent with the expectation that fewer anions have been brought into conjugation during proton abstraction; there should be little or no reprotonation of the initial anion by the weakly acidic NH $_3$ molecule. When CH $_3$ OD reacts with the anion of 1,5-hexadiene, the expected exchange of up to seven hydrogens is observed.⁷ Finally, the anion generated by proton abstraction from 1,4-cyclohexadiene exchanges all hydrogens upon reaction with CH $_3$ OD. This result is expected since all sites in the cyclic anion can become adjacent to a conjugated