

- (2) For recent examples of hydride transfer, see M. K. Murphy and J. L. Beauchamp, *J. Am. Chem. Soc.*, **98**, 1433–1440 (1976); Z. Karpas and F. S. Klein, *Int. J. Mass Spectrom. Ion Phys.*, **18**, 65–68 (1975); and M. Meot-Ner and F. H. Field, *J. Am. Chem. Soc.*, **97**, 2014–2017 (1975).
- (3) E. E. Ferguson, F. C. Fehsenfeld, and A. L. Schmeltekopf, *Adv. At. Mol. Phys.*, **5**, 1–56 (1969).
- (4) V. M. Bierbaum, C. H. DePuy, R. H. Shapiro, and J. H. Stewart, *J. Am. Chem. Soc.*, **98**, 4229–4235 (1976).
- (5) Typical experimental conditions: helium density  $\approx 10^{16}$  cm $^{-3}$ , neutral reactant density  $\approx 10^{11}$ – $10^{13}$  cm $^{-3}$ , ion density  $\approx 10^6$  cm $^{-3}$ , average flow velocity  $\approx 80$  m s $^{-1}$ , ion–neutral reaction time  $\approx 5$  ms.
- (6) For a discussion of the base strength of HNO $^{-}$ , see S. A. Sullivan, Ph.D. Thesis, California Institute of Technology, 1978.

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

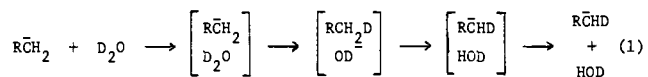
Department of Chemistry, University of Colorado  
Boulder, Colorado 80309

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

Sir:

We have recently reported<sup>1</sup> that in the presence of D<sub>2</sub>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<sub>2</sub>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



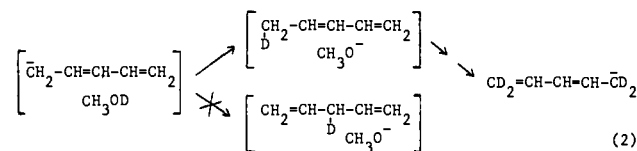
proton abstraction from benzene or 1,3-butadiene, react with D<sub>2</sub>O primarily by deuterium abstraction. Less basic anions, such as those formed by proton abstraction from aldehydes, ketones, and conjugated dienes, do not exchange under these conditions, presumably because deuterium transfer from D<sub>2</sub>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<sub>3</sub>OD and CF<sub>3</sub>CH<sub>2</sub>OD.<sup>2</sup> 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<sup>3,4</sup> we generate organic anions in a stream of helium buffer by proton abstraction from organic neutrals with NH<sub>2</sub> $^{-}$  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.<sup>5</sup>

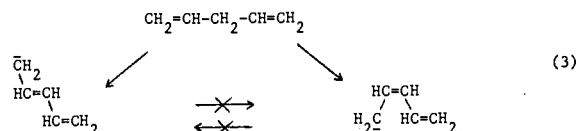
The anions produced by proton abstraction from acetone, acetaldehyde and 3-pentanone do not exchange with D<sub>2</sub>O. However, all three anions exchange with CH<sub>3</sub>OD, acetone anion giving up to five, acetaldehyde anion up to two, and 3-pentanone anion up to three exchanges. All three of these anions react with the still more acidic alcohol CF<sub>3</sub>CH<sub>2</sub>OD by deuterium transfer, to produce CF<sub>3</sub>CH<sub>2</sub>O $^{-}$  ion. By contrast the still less basic nitromethane anion exchanges with neither D<sub>2</sub>O nor CH<sub>3</sub>OD but does undergo up to two exchanges with CF<sub>3</sub>CH<sub>2</sub>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-

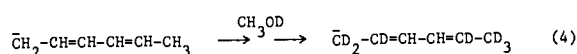
cially interesting information. The 1,3-pentadienyl anion exchanges a maximum of four hydrogens with CH<sub>3</sub>OD showing that reprotonation on the central carbon atom, which would lead to the intermediacy of a nonconjugated diene (and a maximum of five exchanges), does not occur<sup>6</sup> (eq 2). Under



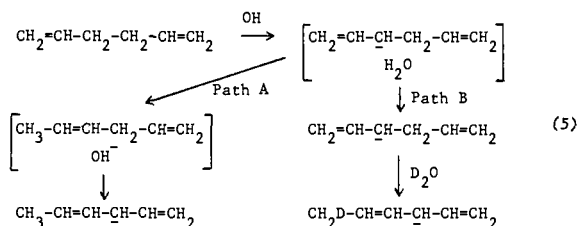
identical conditions of flow and reaction time the pentadienyl anion derived from *cis*-1,3-pentadiene exchanges less readily than that from *trans*-1,3-pentadiene, showing that these isomeric ions do not interconvert. Deprotonation of the unconjugated isomer, 1,4-pentadiene, leads to an approximately 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<sub>3</sub>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<sub>2</sub>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<sub>2</sub>O. We find, however, that over half of the anions do not exchange with D<sub>2</sub>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<sub>2</sub>O usually produces the conjugated anion after a single deuterium is incorporated. When a mixture of NH<sub>2</sub> $^{-}$  and OH $^{-}$  is used in the initial proton abstraction step, relatively more of the resulting anions exhibit a single exchange with D<sub>2</sub>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<sub>3</sub> molecule. When CH<sub>3</sub>OD reacts with the anion of 1,5-hexadiene, the expected exchange of up to seven hydrogens is observed.<sup>7</sup> Finally, the anion generated by proton abstraction from 1,4-cyclohexadiene exchanges all hydrogens upon reaction with CH<sub>3</sub>OD. This result is expected since all sites in the cyclic anion can become adjacent to a conjugated

system. Related studies designed to determine the maximum number of protonations and abstractions which can occur in a single carbanion-deuterated neutral encounter are planned.

In summary, hydrogen-deuterium exchange studies promise to be a continuing source of detailed information about the structure of gas phase ions and the nature of gas phase ion-molecule interactions.

**Acknowledgments.** We are grateful to Professor D. F. Hunt for disclosure of information in advance of publication, to the National Science Foundation for financial support under Grant CHE76-11248, and to the Guggenheim Foundation for a fellowship (1977-1978) to C.H.D.

## References and Notes

- (1) J. H. Stewart, R. H. Shapiro, C. H. DePuy, and V. M. Bierbaum, *J. Am. Chem. Soc.*, **99**, 7650-7653 (1977).
- (2) D. F. Hunt has also observed hydrogen-deuterium exchange in carbanions using deuterated alcohols (private communication).
- (3) E. E. Ferguson, F. C. Fehsenfeld, and A. L. Schmeltekopf, *Adv. At. Mol. Phys.*, **5**, 1-56 (1969).
- (4) V. M. Bierbaum, C. H. DePuy, R. H. Shapiro, and J. H. Stewart, *J. Am. Chem. Soc.*, **98**, 4229-4235 (1976).
- (5) Typical experimental conditions: helium density  $\approx 10^{16}$  cm $^{-3}$ , neutral reactant density  $\approx 10^{11}$ - $10^{14}$  cm $^{-3}$ , ion density  $\approx 10^9$  cm $^{-3}$ , velocity  $\approx 80$  m s $^{-1}$ .
- (6) See R. B. Bates, S. Brenner, C. M. Cole, E. W. Davidson, G. D. Forsythe, D. A. McCombs, and A. S. Roth, *J. Am. Chem. Soc.*, **95**, 926-927 (1973), and references therein for the protonation of the pentadienyl anion in solution.
- (7) In a similar revealing contrast, the anion from 3-hexyne exchanges all nine of its hydrogens with CH $_3$ OD, but exchange stops with D $_2$ O after primarily two deuterons have been incorporated. We interpret this to mean that multiple exchanges occur within the initially formed complex with the triple bond isomerizing until irreversible deprotonation of the terminal alkyne (CH $_3$ CH $_2$ CD $_2$ CH $_2$ C $\equiv$ CH) by OH $^-$  occurs. When CH $_3$ OD is the exchange acid, this last step is reversible and so all protons can be exchanged.

C. H. DePuy,\* Veronica M. Bierbaum\*  
Gary K. King, R. H. Shapiro

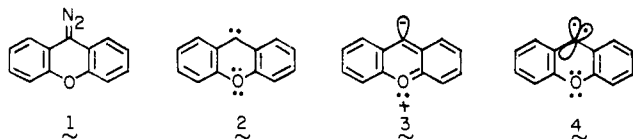
Department of Chemistry, University of Colorado  
Boulder, Colorado 80309

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## Reinvestigation and Reevaluation of Addition and Insertion Reactions of 9-Diazoxanthene and 9-Xanthylidene

Sir:

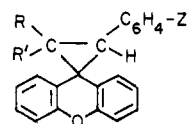
9-Diazoxanthene (**1**) is reported to be a limited nucleophile on the basis that it is inert to styrene.<sup>1a</sup> Of particular note are the conclusions that 9-xanthylidene (**2**), as generated photolytically from **1**, is theorized to be a weak electrophile<sup>1a-c</sup> or a stabilized nucleophile<sup>1d</sup> as a singlet (**3**) and/or a highly selective triplet (**4**)<sup>1a</sup> because it does not insert into the C—H



bonds of saturated hydrocarbons<sup>1b</sup> or the C=C or C—H bonds of olefins,<sup>1a,2</sup> but adds to styrene<sup>1a</sup> to form (2-phenylcyclopropane)-1,9'-xanthene (**5**, Z = H). We now report that much of the behavior ascribed above to **1** and **2** is in error. It has thus been found that (1) **1** reacts as a nucleophilic dipolarophile with styrenes to yield (2-arylcyclopropane)-1,9'-xanthenes (**5**, **6**, and **7**) stereospecifically, (2) **2** generated thermally or photolytically from **1** inserts into saturated C—H bonds and adds to olefins to give alkylcyclopropanes, and (3) **2** or its ex-

cited precursors do not add effectively to styrenes as nucleophilic reagents. Further, **2** inserts into allylic C—H bonds without double-bond rearrangement and adds to styrenes and their derivatives for which the stereochemistries and relative reactivities are consistent with triplet processes.

Thus, styrenes (H $_2$ C=CHC $_6$ H $_4$ Z) react with **1** (0.5–2.0 h, 25 °C) with nitrogen evolution to give cyclopropanes (**5**, ~70%) as readily isolable solids.<sup>3a</sup> The relative reactivities of **1** with the various styrenes at 25 °C follow: Z = 4-OCH $_3$ , 1.00; 4-CH $_3$ , 1.12; 4-H, 1.81; 4-Cl, 2.74; 4-Br, 2.86; and 3-Br, 4.62.<sup>3b</sup> The rate data give a linear free-energy correlation with  $\sigma$  substituent values and  $\rho + 0.97$  (standard deviation of 0.051) and reveal that **1** functions nucleophilically with possible formation and intimate collapse of the subsequent pyrazolines. Further, **1** reacts stereospecifically at 25 °C with *cis*- and *trans*-propenylbenzenes to give (2-methyl-*cis*-3-phenylcyclopropane)-1,9'-xanthene (**6**) and (2-methyl-*trans*-3-phenylcyclopropane)-1,9'-xanthene (**7**), respectively.<sup>4</sup>

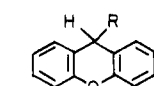


**5**; R and R' = H

**6**; R = CH $_3$ ; R' and Z = H

**7**; R and Z = H; R' = CH $_3$

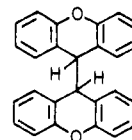
The behavior of **2** as derived thermally and photochemically has been investigated. Decomposition of **1** in cyclooctane at 145 °C results in C—H insertion to give 9-cyclooctylxanthene (**8**, >54%). Cumene reacts with **2** at 140 °C to yield 9-(1-methyl-1-phenylethyl)xanthene (**9**, 61%) and bixanthyl (**10**, 5%). Toluene is converted by **2** at 110 °C to 9-benzylxanthene (57%) and 9-benzyl-9-(9'-xanthyl)xanthene (25%). Thus **2**



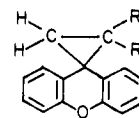
**8**; R = CH(CH $_2$ ) $_7$

**9**; R = C(CH $_3$ ) $_2$ C $_6$ H $_5$

**12**; R = CH(CH $_2$ ) $_3$ -CH=CH



**10**



**11**; R and R' = OCH $_3$

**14**; R = CH $_2$ C $_6$ H $_5$ , R' = H

**15**; R = CH(CH $_3$ ) $_2$ , R' = H

reacts as a discriminating electrophilic carbene with various C—H bonds. Whether **2** inserts into C—H as a singlet (**3**) and/or reacts as a triplet (**4**) by abstraction-recombination of intimate radical pairs is not yet clear. Formation of **10** from **2** and cumene is indicative of a triplet process, at least in part, in which **4** abstracts hydrogen to give 9-xanthyl and counter radicals; dimerization of 9-xanthyl radicals will give **10**.

Decomposition of **1** in olefins results in addition to C=C or/and insertion into allylic C—H bonds. Thus **2** reacts with methylenecyclohexane and 1,1-dimethoxyethylene at 78 °C to form dispiro[cyclohexane-1,1'-cyclopropane-2',9'-xanthene] (**71**%) and spiro[2,2-dimethoxycyclopropane-1,9'-xanthene] (**11**, 40%), respectively. Thermolysis (46%) of **1** at 78 °C or photolysis of **1** at 20–25 °C in cyclohexene results in selective C—H insertion to give 9-(3-cyclohexenyl)xanthene (**12**).

Certain carbenes, presumably as triplets, abstract hydrogen from allylic positions of olefins with partial double-bond migration before radical recombination.<sup>5</sup> Photolysis of sodium 9-xanthone tosylhydrazonate at 23 °C<sup>6</sup> in allylbenzene yields, however, 9-(1-phenyl-2-propenyl)xanthene (**13**, 85%) and spiro[2-benzylcyclopropane-1,9'-xanthene] (**14**, <15%). Irradiation of sodium 9-xanthone tosylhydrazonate in 3-