

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).
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- (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 ≈ 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.

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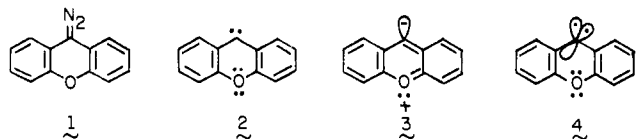
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Reinvestigation and Reevaluation of Addition and Insertion Reactions of 9-Diazoxanthene and 9-Xanthylidene

Sir:

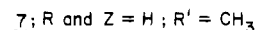
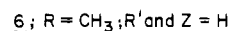
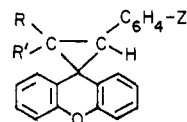
9-Diazoxanthene (**1**) is reported to be a limited nucleophile on the basis that it is inert to styrene.^{1a} Of particular note are the conclusions that 9-xanthylidene (**2**), as generated photolytically from **1**, is theorized to be a weak electrophile^{1a-c} or a stabilized nucleophile^{1d} as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



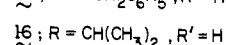
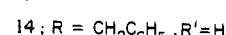
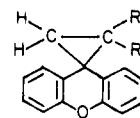
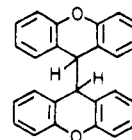
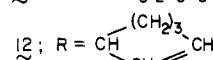
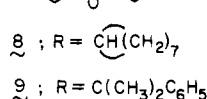
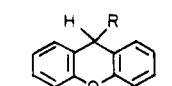
bonds of saturated hydrocarbons^{1b} or the C=C or C—H bonds of olefins,^{1a,2} but adds to styrene^{1a} to form (2-phenylcyclopropane)-1,9'-xanthene (**5**, Z = H). We now report that much of the behavior ascribed above to **1** and **2** is in error. It has thus been found that (1) **1** reacts as 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.^{3a} 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.^{3b} The rate data give a linear free-energy correlation with σ 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.⁴



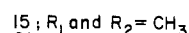
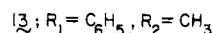
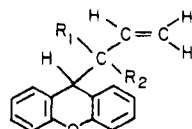
The behavior of **2** as derived thermally and photochemically has been investigated. Decomposition of **1** in cyclooctane at 145 °C results in C—H insertion to give 9-cyclooctylxanthene (**8**, >54%). Cumene reacts with **2** at 140 °C to yield 9-(1-methyl-1-phenylethyl)xanthene (**9**, 61%) and bixanthyl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



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**.

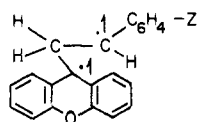
Decomposition of **1** in olefins results in addition to C=C or/and insertion into allylic C—H bonds. Thus **2** reacts with methylenecyclohexane and 1,1-dimethoxyethylene at 78 °C to form dispiro[cyclohexane-1,1'-cyclopropane-2',9'-xanthene] (71%) and spiro[2,2-dimethoxycyclopropane-1,9'-xanthene] (**11**, 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.⁵ Photolysis of sodium 9-xanthone tosylhydrazonate at 23 °C⁶ 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-

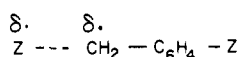


methyl-1-butene at -5°C gives 9-(1,1-dimethyl-2-propenyl)xanthene (**15**, 40%) and spiro[2-(2-propyl)cyclopropane-1,9'-xanthene] (**16**, 19%) along with **10** (4%). Thus reactions of photolytically generated **2** with the above olefins reveal that (1) insertion occurs on allylic C—H to give products without double-bond rearrangement and (2) C=C bonds undergo competitive addition to yield cyclopropanes. Insertion of **2** into allylic C—H bonds is thus highly specific and suggestive of a traditional singlet (**3**) process. If indeed allylic C—H insertion occurs via **3**, H abstraction, spin inversion, and recombination must be intimate (highly caged), possibly because of polar effects in dissimilar radical pairs, to occur without migration of C=C bonds. Formation of **10** from **2** and 3-methyl-1-butene indicates that 9-xanthyl radicals are formed at least in part in this system.

The stereochemistry and the relative reactivities of **2** with styrene derivatives have been studied under photochemical conditions in which thermal reactions of **1** and alteration of the initial olefins and the cyclopropanes formed are insignificant. Photolysis of sodium 9-xanthone tosylhydrazonate⁶ at $\sim -25^\circ\text{C}$ converts *cis*-propenylbenzene stereoselectively (0.5–2 h) to **6** (75–80%) and **7** (20–25%), whereas *trans*-propenylbenzene yields **7** (100%) stereospecifically. The competitive reactivities of styrenes ($\text{H}_2\text{C}=\text{CHC}_6\text{H}_4\text{Z}$) with **2** as derived from irradiation of sodium 9-xanthone tosylhydrazonate at $\sim -25^\circ\text{C}$ follow: Z = 4-H, 0.64; 4- CH_3 , 0.85; 4-Cl, 0.97; 4-O CH_3 , 1.00; 4-Br, 1.68; and 3-Br, 2.23.^{3,7} The relative reactivities do not give a linear free-energy correlation with σ or σ^+ values and reveal that **2** (and/or its excited precursors) does not behave as a dominant nucleophile or electrophile. The stereochemical results and the substituent kinetic effects are consistent, however, with addition of **4** to styrenes as in **17**. This



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interpretation is also compatible with observations that both electronegative and electropositive substituents stabilize free-radical transition states of the benzyl type (**18**) in which polar effects are unimportant.⁸ The stereochemical and reactivity data do not rule out, however, the possibility that additions to styrenes upon photolysis of **1** occur in part with **2** and/or excited **1**.

It is now clear that **1** and **2** do not exhibit the limited reactivities recently attributed there.¹ The present results thus allow **1** and **2** to take more usual positions among the legions of diazo compounds and carbenes that have been reported. We wish also to note that 14*H*-dibenzo[*a,j*]xanthylidene is an energetic carbene which behaves as a triplet in various environments and reacts with cumene to give 14-(1-methyl-1-phenylethyl)-14*H*-xanthene.⁹ Xanthylidenes will have to be further modified to be isolable as stable carbenes.

Acknowledgment. We acknowledge support of this research by the National Cancer Institute (5-R01-CA11185) and the National Science Foundation (GP-22545).

References and Notes

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- (2) 2-Methylpentane,^{1b} hexane,^{1b} cyclohexane,^{1b} ethylene,^{1a} 2-methyl-2-butene,^{1d} 2,3-dimethyl-2-butene,^{1d} 3,3-dimethyl-1-butene,^{1a} and 2,3,3-trimethyl-1-butene^{1a} are reported to be inert to **1** upon photolysis. The principal product reported from these experiments is conversion of **1** to 9-xanthone azine.
- (3) (a) All new compounds presently reported are of proper analysis and mass, IR, and ¹H NMR spectra, respectively. (b) The relative reactivities were determined by reaction with various styrene pairs in which each styrene was in 10-equiv excess; the cyclopropanes formed were isolated quantitatively by column chromatography.
- (4) (a) 3,5-*trans*-Diphenyl-1-pyrazoline decomposes stereospecifically to *trans*-1,2-diphenylcyclopropane: C. G. Overberger and J.-P. Anselme, *J. Am. Chem. Soc.*, **86**, 658 (1964). (b) For the complications in formation and decomposition of 1-pyrazolines and the varied behavior of 1,3 diradicals, see K. Mackenzie in "The Chemistry of Hydrazo, Azo, and Azoxy Groups", S. Patai, Ed., Wiley, New York, N.Y., 1975, p 329, and T. C. Clarke, L. A. Wendling, and R. G. Bergman, *J. Am. Chem. Soc.*, **99**, 2740 (1977).
- (5) R. A. Moss and U.-H. Dolling, *J. Am. Chem. Soc.*, **93**, 954 (1971), and references therein; R. A. Moss, private communication.
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Spin Trapping with α -Pyridyl 1-Oxide *N*-*tert*-Butyl Nitrones in Aqueous Solutions. A Unique Electron Spin Resonance Spectrum for the Hydroxyl Radical Adduct

Sir:

Much interest surrounds the possible intermediacy of hydroxyl radicals in reactions of chemical^{1,2} and biological^{3,4} interest. However direct methods for detecting hydroxyl radicals in solution are not satisfactory.⁵ The method of spin trapping⁶ using nitron spin traps would seem to be a suitable indirect method for detecting hydroxyl radicals. However, early attempts in our laboratory to verify the assignments of the ESR spectra thought to be due to the hydroxy spin adducts of PBN (α -phenyl *N*-*tert*-butyl nitron) and DMPO (5,5-dimethylpyrrolidine *N*-oxide) were unsuccessful.⁷ These spectra were later published by Harbour, Chow, and Bolton.⁸ In connection with a study of the spin trapping chemistry of water-soluble spin traps the pyridine *N*-oxide analogues of PBN have been synthesized.⁹ We wish to report that these nitrones readily trap hydroxyl radicals and that the ESR spectrum obtained from the **4** isomer can be unequivocally assigned to the hydroxyl adduct. Available results indicate that this spin trap is unique in its suitability for the detection of hydroxyl radicals in solution at pH 6 and 7.

