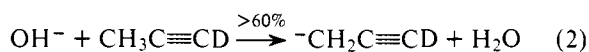
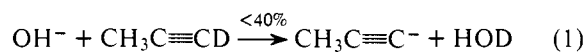


Generation of Specific Isomeric Carbanions in the Gas Phase

Sir:

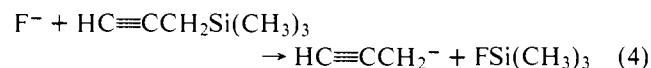
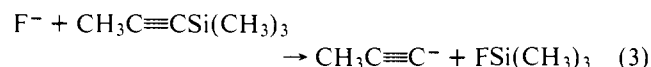
The study of the reactions of organic anions in the gas phase is a subject of increasing interest, since it provides information about the intrinsic reactivity¹ and basicity of ions,² the electron affinity of radicals,³ and other fundamental properties of ions unencumbered by solvation.⁴ Moreover, negative ion chemical ionization mass spectrometry is becoming a tool of increasing importance for chemical analysis and structural elucidation.⁵ A common method for the production of such anions is proton abstraction from neutral molecules using the strong gas phase bases, hydroxide or alkoxide ions.

However, carbanion production by proton abstraction is often ambiguous and unsatisfactory. There may be several abstractable protons in the hydrocarbon molecule, so that mixtures of anions may be formed. In some cases, as in proton abstraction from 2-pentene, the relative acidity of the two types of allylic protons is similar, and formation of both anions is expected. However, even in molecules where the proton acidities are expected to differ substantially, as in propyne, we have found in our flowing afterglow system⁶ that a majority of the less stable anion is formed:



A more subtle and hence more dangerous complication is the observed base promoted rearrangement of certain molecules in the very ion-molecule complex in which proton abstraction occurs.⁷ Thus double-bond migration and cis-trans isomerization may occur, leading to anions of unknown or unexpected structure.

We report herein that many organic anions can be generated efficiently and unambiguously by reaction of their trimethylsilyl derivatives with fluoride ion (easily formed by electron impact on NF_3 or CF_4). For example, each of the two isomeric C_3H_3^- ions can be separately generated in this manner:



The success of this method must depend upon the great strength of the silicon-fluorine bond which compensates for the greater electron affinity of fluorine atoms relative to organic radicals. The two ionic products of eq 3 and 4 differ substantially in their reactivity, confirming their isomeric structures. For example, the propargyl anion reacts with molecular oxygen seven times more rapidly than does the methyl acetylide anion⁸ and large differences in rates or products are observed with D_2O and other reagents.

In addition to anions stabilized by triple bonds, the fluoride-silane displacement reactions are useful for producing a variety of allyl and benzyl anions. Trimethylsilyl derivatives are generally easily prepared⁹ and can be handled without difficulty. We have applied this method to generate anions from the trimethylsilyl derivatives of propylene, *cis*- and *trans*-2-butene and toluene. We have not yet been successful in creating less stable anions; tetramethylsilane and vinyl and cyclopropyl trimethylsilane form adducts with F^- and only traces of C_6H_5^- are produced from phenyl trimethylsilane.

An equally important advantage of this method is production of anions in the absence of their hydrocarbon precursors. These acidic precursors frequently react with product ions to

regenerate the initial carbanion and thus greatly complicate the determination of rate constants and product distributions.

In conclusion, the displacement reaction of fluoride ion with trimethylsilyl derivatives allows the specific production of a single isomeric species in the absence of other anions or acidic neutrals; this method, therefore, will greatly facilitate the detailed correlation of structure and reactivity of gas phase organic anions.

Acknowledgments. We gratefully acknowledge support of the National Science Foundation under Grant CHE76-11248 and of the Guggenheim Foundation for a fellowship (1977-1978) to C.H.D.

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- (9) Our rate constant measurement for the reaction of the propargyl anion, generated from the trimethylsilane, with molecular oxygen ($1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) agrees with that of Bohme and Young who generated the propargyl anion by proton abstraction from allene. See Bohme, D. K.; Young, L. B. *J. Am. Chem. Soc.* **1970**, *92*, 3301-3309.
- (10) The silanes were prepared by reaction of the appropriate lithium or Grignard reagent with trimethylsilyl chloride. 1-Trimethylsilylpropyne was prepared by the method of Corey, E. J.; Kirst, H. A. *Tetrahedron Lett.* **1968**, *48*, 5041-5043. 3-Trimethylsilylpropyne was prepared by the method of Slutsky, J.; Kwart, H. *J. Am. Chem. Soc.* **1973**, *95*, 8678-8685. (There is an omission in the published procedure: anhydrous mercuric chloride must be used.) The product was purified by distillation or gas chromatography.

C. H. DePuy,* Veronica M. Bierbaum,* L. A. Flippin
Joseph J. Grabowski, Gary K. King, Robert J. Schmitt

Department of Chemistry, University of Colorado
Boulder, Colorado 80309

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Gas-Phase Reactions of Carbanions with Triplet and Singlet Molecular Oxygen

Sir:

We report herein the ion-molecule reactions of molecular oxygen, in both its ground state ($X^3\Sigma_g^-$) and first electronically excited state ($a^1\Delta_g$),¹ with organic anions in the gas phase. Molecular oxygen promises to be a powerful reagent for gas-phase chemical degradation and structural elucidation of ions since it appears to induce specific cleavage reactions which reflect the various sites of negative charge in the anion.

We generate organic anions in our flowing afterglow system² by proton abstraction with amide from neutral organic precursors or by the reaction of F^- with silanes.³ The ions are collisionally relaxed before they are mixed with the reactant molecular oxygen. The reactant and product ionic species are monitored by mass spectrometric detection.

As a typical example of a delocalized species, the 2,4-hexadienyl anion reacts readily with ground-state oxygen by addition and cleavage at each nonterminal carbon atom which

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- (1) In this paper, the ground state ($X^3\Sigma_g^-$) of oxygen will be designated as 3O_2 and the excited state ($a^1\Delta_g$) as 1O_2 .
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- (4) To preserve the isomeric integrity of this ion, amide rather than hydroxide ion must be used in the proton abstraction process. See DePuy, C. H.; Bierbaum, V. M.; King, G. K.; Shapiro, R. H. *J. Am. Chem. Soc.* **1978**, *100*, 2921–2922.
- (5) Hydride transfer also dominates in the reaction of oxygen with the cyclohexadienyl anion: DePuy, C. H.; Bierbaum, V. M.; Schmitt, R. J.; Shapiro, R. H. *J. Am. Chem. Soc.* **1978**, *100*, 2920–2921.
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- (7) Hunt, D. F.; Sethi, S. K.; Shabanowitz, J. Presented at the Twenty-Sixth Annual Conference on Mass Spectrometry and Allied Topics, St. Louis, Mo., May 28–June 2, 1978.
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- (11) O_2^- is observed as a product whenever electron transfer is exothermic.

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

Department of Chemistry, University of Colorado
Boulder, Colorado 80309

Received May 23, 1979

Photoreaction of Valence-Bond Isomers of Hexakis(trifluoromethyl)oxepin. Synthesis of a Stable Oxetene Derivative

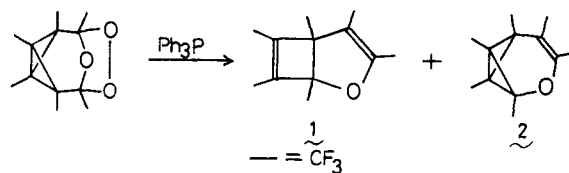
Sir:

The photoreaction of perfluoroalkylated compounds is especially interesting because of the possible isolation of strained compounds by the "perfluoroalkyl effect".¹ Previously we reported the reduction of hexakis(trifluoromethyl)benzvalene with triphenylphosphine, affording two valence-bond isomers of hexakis(trifluoromethyl)oxepin,² hexakis(trifluoromethyl)-2-oxabicyclo[3.2.0]hepta-3,6-diene (**1**) and hexakis(trifluoromethyl)-3-oxatricyclo[4.1.0.0²]heptene (**2**) (Scheme I).

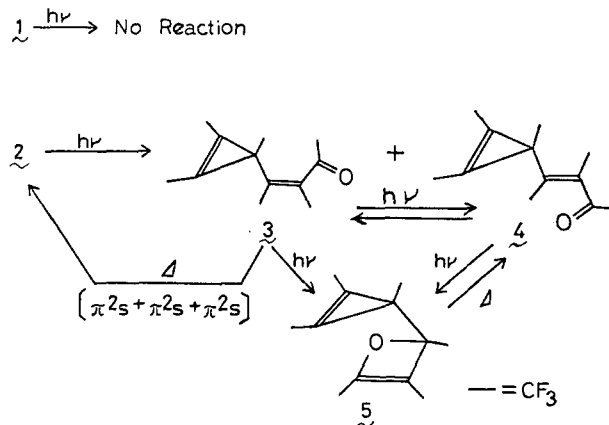
We now report the photoreaction of **1** and **2** including formation of a new stable oxetene derivative. Irradiation³ of a perfluoropentane solution of **1** in a silica tube at room temperature gave no isomeric product. Irradiation of **2** under the same condition gave a mixture of *Z* and *E* forms (**3** and **4**) of 1,2,3-tris(trifluoromethyl)-3-[1,2,3-tris(trifluoromethyl)cyclopropenyl]propenone in a quantitative yield (Scheme II). These isomers (**3** and **4**) could not be separated even by VPC. The molar ratio of **3** and **4** was 1:1. The structural assignment of **3** and **4** was based on the results of the following reactions and on their spectral data. When a mixture of **3** and **4** in pentane was heated at 140 °C and the reaction was followed by ¹⁹F NMR spectra, only the *Z* isomer **3** regenerated **2** and the *E* isomer **4** remained unchanged. On the other hand, irradiation of a mixture of **3** and **4** in perfluoropentane filtered with Pyrex gave only one product (**5**) in a quantitative yield. The ¹⁹F NMR spectrum⁴ of **5** in a pentane solution showed five multiplets centered at -3.5, -2.9, 1.4, 7.4, and 11.8 ppm (the intensity ratio of signals was 2:1:1:1:1⁵).

The IR spectrum of **5** in pentane revealed absorption bands at 1900 and 1735 cm⁻¹, ascribable to the cyclopropene double bond⁶ and the oxetene ring double bond,⁷ respectively, and the mass spectrum of **5** showed *m/e* 502 (M⁺) (calcd for C₁₂F₁₈O, mol wt 502). The UV spectrum of **5** showed only one absorption maximum at 207 nm (ϵ 2.80 × 10³, in *n*-hexane), while that of the mixture of **3** and **4** showed three absorptions at 198

Scheme I

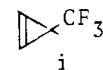


Scheme II



(ϵ 3.72 × 10³), 250 (sh, 146), and 305 nm (31). These data show that **5** has no carbonyl group, while **3** and **4** have.

From these data we concluded that **5** is a perfluoromethylated cyclopropenyloxetene,⁸ which is a colorless and stable liquid at room temperature and is exclusively converted into the *E* isomer **4** of the enone on being heated at 80 °C (*T* = 5.7 h in pentane). This result of thermal reaction of **5** is consistent with the results of the thermal reaction of transiently formed oxetene derivatives, which has been reported previously.⁹ From the thermal reaction of **5**, pure *E* isomer **4** was isolated in a quantitative yield: colorless liquid; ¹⁹F NMR (pentane) -3.6, -2.1, 3.2 (group i), 12.4 ppm (COCF₃) (each signal is broad,



intensity ratio 3:1:1:1); IR spectrum (pentane) ν (C=O) 1890 (cyclopropene double bond), 1770 cm⁻¹; mass spectrum *m/e* 502 (M⁺) (calcd for C₁₂F₁₈O, mol wt 502). The ¹⁹F NMR of *Z* isomer **3** is deduced from those of the mixture of **3** and **4**: -7.4, -4.2, 3.2 (group i), 13.3 ppm (COCF₃) (relative ratio 1:3:1:1).

A very rapid equilibrium between **3** and **4** was observed on the irradiation of the isolated isomer (**4**). This result shows that **3** and **4** are *Z/E* isomers. Moreover, regeneration of **2** from **3** (*Z* form) and not from **4** (*E* form) by thermal reaction supports each of the assigned structures, since regeneration of **2** from **3** is considered to be a thermally allowed ($\pi_2s + \pi_2s + \pi_2s$) concerted process and, in the case of **4** (*E* form), the thermally allowed concerted process cannot regenerate **2** because of the trans double bond.

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- (5) The ¹⁹F FT NMR of **5** splits to six peaks. 59.08, 59.50, 59.86, 64.37, 69.86, 74.71 (CFCl₃ as reference).
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