$$
\begin{array}{ll}
& \Delta H, \\
& \text{kcal mol}^{-1}
\end{array}
$$

$$
\begin{array}{lll}
C_3H_5^- + F_3CCO_2C_2H_5 \rightarrow & & \\
\quad F_3CCO_2^- + C_2H_4 + C_3H_6 & -52.2 & (10) \\
C_3H_5^- + F_3CCO_2C(CH_3)_3 \rightarrow F_3CCO_2^- + & & \\
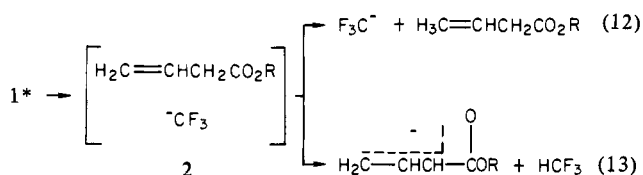\quad H_2C{=}C(CH_3)_2 + C_3H_6 & -50.0 & (11)
\end{array}
$$

To determine if the exoergicity of reaction 10 would be sufficient to effect the secondary decomposition of $F_3CCO_2^- \rightarrow F_3C^- + CO_2$ observed in the reaction of the ethyl ester, we examined the reaction of $C_3H_5^-$ with the *tert*-butyl ester, $F_3CCO_2C(CH_3)_3$. Here, again, a fast pseudo-first-order decay of $C_3H_5^-$ was observed ($k = (1.3 \pm 0.1) \times 10^{-9}$ cm$^3$ molecule$^{-1}$ s$^{-1}$)[9a] along with the formation of two product ions, $F_3CCO_2^-$ (*m/z* 113; 18%) and $H_2C{=}CHCH{=}C({-}O^-)CF_3$ (*m/z* 137; 82%). Significantly, *no* ion signals due to $F_3C^-$ or its addition adduct with the ester, $(F_3C)_2C({-}O^-)OC(CH_3)_3$,[11] were observed. These data and the striking similarities between the reactions in (10) and (11) lead to the conclusion that the E2 elimination reaction of $C_3H_5^-$ with $F_3CCO_2C_2H_5$ would *not* yield $F_3CCO_2^-$ with sufficient internal energy to allow it to decompose to produce $F_3C^-$. Therefore, *the major reaction channel in the reaction of $C_3H_5^-$ with $F_3CCO_2R$ (R = CH$_3$ and C$_2$H$_5$) involves nucleophilic displacement of $C_\alpha$ of R, but carbonyl addition by the nucleophile is a competing process.*

The above discussion has assumed that $F_3C^-$ will not be formed by decomposition of the carbonyl addition adducts **1**. Adduct **1** will be produced energetically "hot" and fragment before they are "cooled off" by collisions with the helium buffer gas. Considering the fragmentation channel where the $F_3C{-}C$ bond undergoes heterolysis, a long-lived, ion–neutral collision complex **2** would result.[12] While both exit channels (12) and (13) are overall exoergic (see reactions 5 and 6), proton transfer via exit channel



$$
1^* \rightarrow
\begin{bmatrix}
H_2C{=}CHCH_2CO_2R \\[4pt]
{}^-CF_3
\end{bmatrix}
\begin{cases}
\longrightarrow F_3C^- + H_3C{=}CHCH_2CO_2R \quad (12) \\[10pt]
\longrightarrow H_2C{-}CHCH{-}COR + HCF_3 \quad (13)
\end{cases}
$$

**2**

(13) is favored by $\geq 15$ kcal mol$^{-1}$.[7] This thermochemical argument for fragmentation of **1** by reaction 13 is supported by the observation that $F_3C^-$ was *not* formed in the reaction of $C_3H_5^-$ with $F_3CCO_2C(CH_3)_3$, where carbonyl addition followed by fragmentation of the adduct **1** was the principal reaction channel.

Therefore, we consider the source of the ion $F_3C^-$ in these reactions to be excited $F_3CCO_2^-$.[13] Since the decomposition of $F_3CCO_2^- \rightarrow F_3C^- + CO_2$ (reaction 7) is strongly endoergic (38.8 kcal mol$^{-1}$), we can expect it to occur only from the more exoergic reactions leading to excited $F_3CCO_2^-$ (reaction 4).[4] Such unimolecular decomposition will compete with stabilization by collisions with the buffer gas ($k_s[\text{He}]$).

The relatively low exoergicity ($-57$ kcal mol$^{-1}$) of the $S_N2$ channel in the reaction of $H_3CO^-$ with $F_3CCO_2CH_3$ (reaction 1) also suggests that $F_3C^-$ will not be formed by this channel. Thus, the observation of $F_3C^-$ as a product of this reaction is believed to arise by the carbonyl addition–anionic fragmentation shown in reaction 2.

Sweden, for synthesis of $F_3CCO_2C(CH_3)_3$.

## A Periodonium Trifluoromethanesulfonate. An Isolable 10-I-4 Organoiodine Species

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We report the isolation and characterization of a stable pseudotrigonal-bipyramidal (TBP) 10-I-4[1] species with organic ligands,[2a,b] periodonium trifluoromethanesulfonate (triflate) salt **1**.[3] Just as the familiar iodonium ion (an 8-I-2 species) can be viewed as having been derived from an iodinane (a 10-I-3 species) by heterolysis of a bond joining one of the three ligands to iodine, a periodonium ion (a 10-I-4 species) can be viewed as having been derived in this same way from a periodinane[4] (a 12-I-5 species).

$$R_nIX_{5-n} \rightarrow R_nI^+X_{4-n} + X^-$$

The periodonium ion of **1** is isovalent and isostructural with sulfurane **2a**[5] and the phosphoranide anion of **3a**.[6] Earlier studies



**1**          **2a**  R = H          **3a**  R = H
          **b**  R = C(CH$_3$)$_3$          **b**  R = CH$_3$
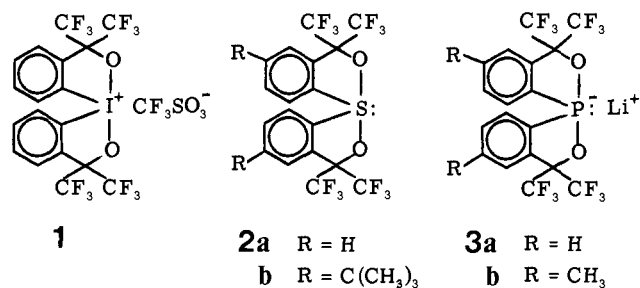
of **2a,b**[5,7] and **3a,b**[6,8] provided evidence for the efficacy of the bidentate ligand[5] common to all five structures in stabilizing pseudo-TBP 10-X-4 species which contain hypervalent[9] nonmetals. Sulfuranes **2a,b**, in particular, are very stable compounds. In sharp contrast to their acyclic analogues,[10] they are inert toward aqueous acid.[7,11]

The pictured structure for the periodonium cation **1** is consistent

(1) Perkins, C. W.; Martin, J. C.; Arduengo, A. J.; Lau, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753.

(2) (a) The salt $IF_4^+SbF_6^-$ has been made. It is extremely reactive, even toward compounds such as carbon tetrachloride. Its X-ray crystallographic structure shows a distorted TBP geometry for the $IF_4^+$ cation, with some evidence of bridging to two of the fluorine atoms of the hexafluoroantimonate counteranion. See: Woolf, A. A. *J. Am. Chem. Soc.* **1950**, *72*, 3678. Giber, D. D. *Nucl. Sci. Abstr.* **1973**, *28*, 26892. (b) The periodonium salt $C_6F_5IF_3^+SbF_6^-$ has been observed by $^{19}$F NMR spectroscopy in solution in SbF$_5$ and SO$_2$Cl$_2$ at temperatures below $-10$ °C. The salt decomposes after a few minutes at 40 °C. See: Bardin, V. V.; Furin, G. G.; Yakobson, G. G. *Zh. Org. Khim.* **1980**, *16*, 1256.

(3) Mp 288–291 °C; $^1$H NMR (CD$_3$CN) δ 8.031–8.253 (8 H, complex multiplet); $^{19}$F NMR (CD$_3$CN) δ $-72.10$ (6 F, q, $J_{FF} = 9$ Hz), $-75.05$ (6 F, q, $J_{FF} = 9$ Hz), $-75.04$ (3 F, s, CF$_3$ on CF$_3$SO$_3^-$); mass spectrum (field desorption) *m/e* 760 (M$^+$), 611 (M$^+$. $- $CF$_3$SO$_3$). Anal. (C$_{19}$H$_8$F$_{15}$IO$_5$S) C, H, F, I, S; osmometric *M*, (CH$_3$CN) 420.

(4) Amey, R. L.; Martin, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 5294.

(5) Perozzi, E. F.; Michalak, R. S.; Figuly, G. D.; Stevenson, W. H., III; Dess, D. B.; Ross, M. R.; Martin, J. C. *J. Org. Chem.* **1981**, *46*, 1049.

(6) Ross, M. R. Ph.D. Thesis, University of Illinois, 1981.

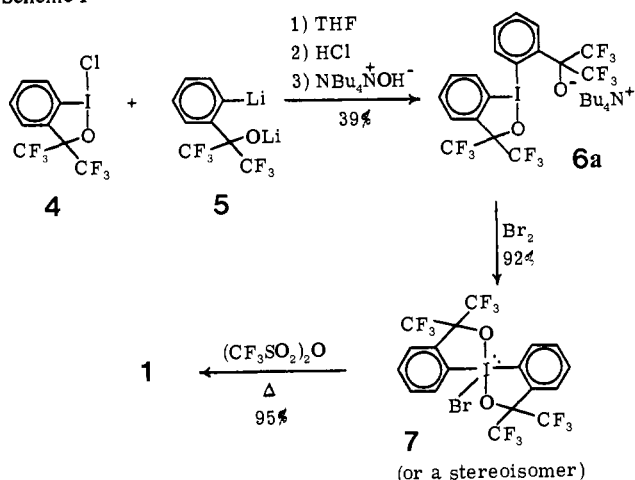(7) Martin, J. C.; Perozzi, E. F. *J. Am. Chem. Soc.* **1974**, *96*, 3155.

(8) (a) Granoth, I.; Martin, J. C. *J. Am. Chem. Soc.* **1979**, *96*, 4618. (b) Granoth, I.; Martin, J. C. *Ibid.* **1979**, *101*, 4623.

(9) Musher, J. I. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 54.

(10) Arhart, R. J.; Martin, J. C. *J. Am. Chem. Soc.* **1972**, *94*, 4997.

(11) Michalak, R. S.; Martin, J. C., to be published.

(11) Formation of the adduct $(F_3C)_2C({-}O^-)OC(CH_3)_3$ is the major reaction channel in the reaction $F_3C^- + F_3CCO_2C(CH_3)_3$. $F_3C^-$ has a considerably lower proton affinity (PA = 375.6 ± 2 kcal mole$^{-1}$)[8] compared to that of $C_3H_5^-$ (PA = 390.8 ± 2 kcal mole$^{-1}$).[8]

(12) Farneth, W. E.; Brauman, J. I., *J. Am. Chem. Soc.*, **1976**, *98*, 7891.

(13) The decomposition of $F_3CCO_2^-$ has direct solution analogies in the thermal decompositions of $X_3CCO_2^-M^+$ salts and the base cleavages of esters $X_3CCO_2R$ (where R has $C_\beta$-H bonds for elimination), producing $X_3C^-$ as sources for $X_2C^- + X^-$. See: Kirmse, W., "Carbene Chemistry," 2nd. Ed., Academic Press, New York, 1971; pp 137–140.

Scheme I



with the ${}^{19}$F NMR spectrum. Even at temperatures as low as –60 °C, the spectrum shows evidence for only two types of CF$_3$ peaks as expected for **1**. An X-ray crystallographic structure determination, to be published later,[12] confirms the proposed distorted TBP structure to be correct. The O–I–O angle is 162.8°.[12]

The synthesis of **1** is outlined in Scheme I. Preparations of **4**[5,13] and **5**[6] have been described in earlier papers. Alkoxydiaryliodinane **6a**[14] was at first believed to exist as bicyclic 12-I-4 species **6** (or its trans isomer), species analogous to XeF$_4$, a 12-Xe-4 species. The ${}^{19}$F NMR spectrum at room temperature shows only a single sharp singlet.[14] Low-temperature ${}^{19}$F NMR spectroscopy, however, shows the ground states to be unsymmetrical (**6a** and **6b**) with a $\Delta G^*$ of ca. 12 kcal/mol[15] at the coalescence temperature, –80 °C, for the two CF$_3$ singlets at 60 MHz.
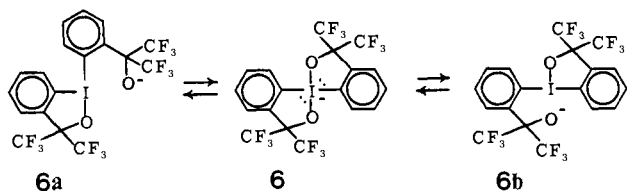


Bromoperiodinane **7**[16] provides the first example of a bond joining bromine to iodine(V). It is stable for an indefinite period at room temperature and does not react with atmospheric moisture. It reacts with tetrahydrofuran or acetonitrile to give reduced product **6a** with bromination of solvent. The periodonium triflate is, under the same conditions, inert toward these solvents. A molecular weight determination by osmometry showed the triflate to be almost completely dissociated in acetonitrile.[3] These observations indicate that the I–Br bond in **7** is covalent. Its reactivity toward certain solvents and its insolubility in other solvents have prevented us from obtaining NMR data to support the proposed structure of **7**.

The low electrophilicity observed for sulfuranes **2a,b** finds a parallel in the relatively low electrophilicity of the periodonium ion of **1**, despite the positive charge on iodine. The periodonium ion does not react with water in aqueous tetrahydrofuran, acetonitrile, or acetone nor with methanol or pyridine in acetonitrile. It does react with stronger nucleophiles such as *tert*-butylamine and hydroxide ion.

The reaction of *tert*-butylamine with **1** in acetonitrile provides a compound whose ${}^{19}$F NMR spectrum is consistent with a structure such as **8**.[17] Reaction of **1** with tetraethylammonium
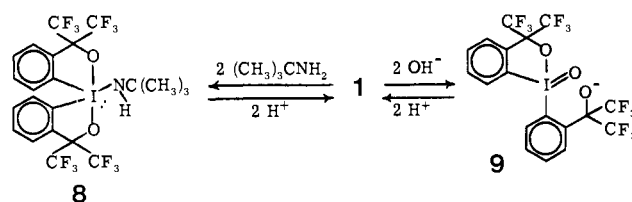


hydroxide in acetonitrile forms a compound whose ${}^{19}$F NMR spectrum is consistent with a structure such as **9**.[18] Both **8** and **9** react with acid to regenerate **1**. It has not yet been possible to isolate **8** or **9** as pure crystalline solids. Further work on these and related reactions with nucleophiles is in progress.

(12) Dess, D. B.; Martin, J. C., to be published.
(13) Amey, R. L.; Martin, J. C. *J. Org. Chem.* **1979**, *44*, 1779.
(14) Mp 200–202 °C; ${}^1$H NMR (CD$_3$CN) δ 7.58 (1 H, t), 7.76 (1 H, t), 7.94 (1 H, d, H ortho hexafluorocumyl group), 8.01 (1 H, d, H ortho I); ${}^{19}$F NMR (25 °C) (THF) δ –76.23 (12 F, s); ${}^{19}$F NMR (–80 °C) –72.93 (12 F, br s); ${}^{19}$F NMR (–100 °C) δ –71.33 (6 F, s), –73.89 (6 F, s); mass spectrum (field desorption) *m/e* 853 (M⁺·). Anal. (C$_{13}$H$_{42}$F$_{12}$I$_2$O$_2$N) C, H, F, I, N.
(15) Gutowsky, H. S.; Holm, C. H. *J. Chem. Phys.* **1956**, *25*, 1228.
(16) Mp 190–196 °C; mass spectrum (10 eV), *m/e* (rel intensity) 690, 692 (7, M⁺·), 621, 623 (30, M⁺· – CF$_3$), 611 (49, M⁺· – Br). Anal. (C$_{18}$H$_8$-F$_{12}$BrIO$_2$) C, H, F.

(17) ${}^{19}$F NMR (CH$_3$CN) δ –72.97 (2.9 F, q), –73.48 (3.5 F, q), –74.35 (2.9 F, q), –75.42 (2.8 F, q).
(18) ${}^{19}$F NMR (CH$_3$CN) δ –74.12 (5.9 F, m), –74.88 (2.3 F, q), –76.93 (2.8, q).

## Involvement of the Azide Radical in the Quenching of Singlet Oxygen by Azide Anion in Water

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Reactive oxygen intermediates generated in aqueous environment are responsible for many of the reactions observed in biological and chemical systems. It is a difficult task to determine which intermediate(s) is involved in a particular system. The utilization of nitrone spin traps[1] has proved useful for the identification of the hydroxyl (·OH) and superoxide (O$_2^-$) radical intermediates.[2] In 1975, Ching and Foote[3] demonstrated that cyclic nitrones quench ${}^1$O$_2$ in CDCl$_3$. We extended these results to aqueous medium and demonstrated that nitrone spin traps react with singlet oxygen (${}^1$O$_2$) in water[4] with rate constants of ~10$^8$ M$^{-1}$ s$^{-1}$. This reaction is readily followed by oxygen uptake measurements and demonstrates that nitrones can effectively be utilized in the detection of these three major oxygen intermediates.

A major diagnostic for ${}^1$O$_2$ in aqueous medium has been the quenching of ${}^1$O$_2$ by the azide anion, N$_3^-$.[5] A kinetic study[4] using oxygen uptake revealed that N$_3^-$ quenches the reaction between nitrones and ${}^1$O$_2$ with a rate constant $k = 1.5 \times 10^9$ M$^{-1}$ s$^{-1}$ (compared to literature value of $2 \times 10^9$ M$^{-1}$ s$^{-1}$).[6] The mechanism of this quenching is considered to proceed through a charge-transfer complex[5] (O$_2^- \cdots$N$_3$). This communication gives

(1) Janzen, E. G.; Liu, J. I. *J. Magn. Reson.* **1973**, *9*, 510–512.
(2) Harbour, J. R.; Chow, V.; Bolton, J. R. *Can. J. Chem.* **1974**, *52*, 3549–3552.
(3) Ching, T. -Y.; Foote, C. S. *Tetrahedron Lett.* **1975**, *44*, 3771–3774.
(4) Harbour, J. R.; Issler, S. L.; Hair, M. L. *J. Am. Chem. Soc.* **1980**, *102*, 7778–7779.
(5) Foote, C. S. *Org. Chem.* (*N.Y.*) **1979**, *40*, 139–171.
(6) Gupta, A. K.; Rohatgi-Mukherjee, K. K. *Photochem. Photobiol.* **1978**, *27*, 539–543.