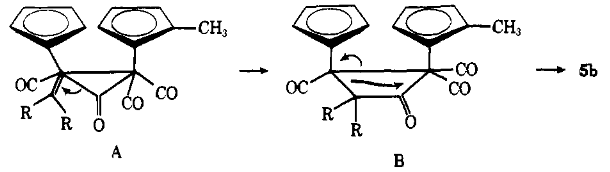
(8) Anal. Found for **5a:** C, 66.60; H, 3.48; Mn, 13.58; O, 16.37; mol wt, 379 (osmometrically in $CHCl_3$). Calcd for $C_{21}H_{13}MnO_4$ (396.3): C, 66.68; H, 3.31; Mn, 13.86; O, 16.15. Found for **5b:** C, 67.30; H, 3.87; Mn, 13.32; O, 15.46; mol wt, 402 (osmometrically in $CHCl_3$), 410 (field desorption mass spectroscopy). Calcd for $C_{23}H_{15}MnO_4$ (410.3): C, 67.33; H, 3.68; Mn, 13.40; O, 15.59. IR spectra (ν_{CO}, cm^{-1}; KBr): **5a**, 2000 (s–vs), 1939 (vs), 1758 (s, ketene), 1644 (s, ketone); **5b**, 2000 (s–vs), 1960 (vs), 1747 (s, ketene), 1648 (s, ketone). Physical properties: air-stable, red, refracting rhombs; dec pt 120 °C (**5a**), 129 °C (**5b**).

(9) In contrast, diphenylcarbene and (benzoyl)phenylcarbene complexes of this type can avoid steric interactions with the metal carbonyl fragment by noncoplanar arrangements of both carbene substituents. $(\eta^5\text{-}C_5H_5)Mn(CO)_2\{C[C(=O)C_6H_5]C_6H_5\}$: A. D. Redhouse, *J. Organomet. Chem.*, **99**, C29 (1975). $(\eta^5\text{-}C_5H_5)Mn(CO)_2[C(C_6H_5)_2]$: B. L. Haymore, personal communication. A similar structure has been reported for $(CO)_5W[C(C_6H_5)_2]$ in which the planes of the phenyl rings are twisted ~42° from the plane defined by the carbene carbon atom and the atoms directly bonded to it: C. P. Casey, T. J. Burkhardt, Ch. A. Bunnell, and J. C. Calabrese, *J. Am. Chem. Soc.*, **99**, 2127 (1977).

(10) Note that in $(\eta^5\text{-}C_5H_4R)Mn(CO)_2(CRR')$ complexes the plane defined by Mn, C(carbene), and the atoms directly attached to C(carbene) is a mirror plane of the $cpMn(CO)_2$ fragment: G. Huttner and D. Regler, *Chem. Ber.*, **105**, 1230 (1972); E. Hädicke and W. Hoppe, *Acta Crystallogr., Sect. B*, **27**, 760 (1971). This is in agreement with MO calculations on compounds of this type containing single-faced π-acceptor ligands (P. Hofmann, Universität Erlangen—Nürnberg, personal communication; B. E. R. Schilling, R. Hoffmann, and D. L. Lichtenberger, *J. Am. Chem. Soc.*, **101**, 585 (1979)).

(11) This route of diazoalkane decomposition is well established in metal-catalyzed reactions; see S. Patai, "The Chemistry of Diazonium and Diazo Groups", Parts 1 and 2, Wiley, New York, 1978.

(12) At present, it is hard to say how this carbene transfer proceeds. As one referee suggested, one could think of a mechanism initiated by CO dissociation from the intermediate carbene complex which, in turn, should be open to attack by the parent carbonyl $(\eta^5\text{-}RC_5H_4)Mn(CO)_3$ forming the binuclear intermediates A and B. However, *stable* carbene complexes of



type $(\eta^5\text{-}C_5H_5)Mn(CO)_2(CRR')$ (e.g., R, R′ = C_6H_5) do not show any sign of ^{13}CO exchange (THF or THF–benzene, 25 °C), nor do they react with $(\eta^5\text{-}C_5H_5)Mn(CO)_3$, even under prolonged heating in THF. Thus, the stability of carbene complexes seems to be one of the factors which govern carbene transfer capability.

(13) (a) K. Schorpp and W. Beck, *Z. Naturforsch. B*, **28**, 738 (1973); (b) W. A. Herrmann, *Angew. Chem., Int. Ed. Engl.*, **13**, 335 (1974); (c) A. D. Redhouse and W. A. Herrmann, *ibid.*, **15**, 615 (1976); (d) H. Hoberg and J. Korff, *J. Organomet. Chem.*, **152**, 255 (1978).

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Direct Observation of the Methyl Diazonium Ion in Fluorosulfuric Acid

Sir:

Alkyl diazonium ions have been observed in solution in strongly acidic media only when substituted with strongly electron-withdrawing groups.[1,2] Recent kinetic studies on the hydrolysis of diazomethane have shown that in acidic aqueous tetrahydrofuran the methyl diazonium ion **1** may have an appreciable lifetime, half-life of 0.3 s at 25 °C.[3] We now report that protonation of diazomethane by a fluorosulfuric acid-sulfuryl chlorofluoride solution at −120 °C yields two unstable species, considered to be the methyl diazonium ion and the isomeric methylene diazenium ion **2**[4] on the basis of their NMR spectra at −106 °C.

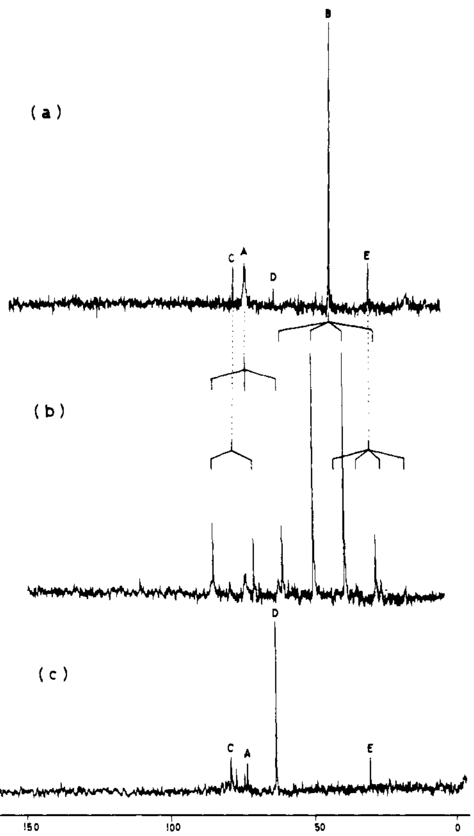

Figure 1. ^{13}C spectra of species formed by reaction of CH_2N_2 with $HFSO_3$: (a) at −106 °C, proton decoupled; (b) at −106 °C, proton coupled; (c) at −85 °C, proton coupled (peak A, $CH_2N_2H^+$; peak B, $CH_3N_2^+$; peak C, $CHCl_3$ (reference); peak D, CH_3OSO_2F; peak E, byproduct.

$$CH_2N_2 + HFSO_3 \rightarrow \underset{\mathbf{1}\ (80\%)}{CH_3{-}{}^+N{\equiv}N} + \underset{\mathbf{2}\ (20\%)}{CH_2{=}{}^+N{=}N{-}H} + FSO_3^- \quad (1)$$

Samples were prepared by passage of a nitrogen stream containing gaseous diazomethane into the acid solution at −120 °C. This method avoids high local concentrations of substrate, thus preventing the polymer formation which was consistently observed in attempts to extract the diazomethane into the acid solution from a matrix of dichloromethane at −120 °C.

The proton decoupled ^{13}C spectrum of the $HFSO_3$ sample at −106 °C (Figure 1a) showed two major peaks, one broad at 73.28 (peak A) and one fine at 43.78 ppm (peak B), in the ratio 1:4 (relative integral intensity), and two minor peaks (<5%), one of which corresponds to methyl fluorosulfate, δ 63.20 ppm (lit.[5] δ 62.5 ppm in CCl_4). As the sample was heated to −85 °C both the principal peaks diminished in intensity, while the methyl fluorosulfate peak increased to finally comprise 85% of the sample, accompanied by 15% of unidentified material. The disappearance of peak A was less rapid than that of peak B indicating that they belong to different species.

In the proton coupled ^{13}C spectrum (Figure 1b) peak A was split into a triplet while peak B became a quadruplet, corresponding to CH_2 and CH_3 groups. When the sample was prepared with $DFSO_3$ instead of $HFSO_3$, peak B appeared as a triplet in the proton decoupled spectrum instead of the singlet previously observed, implying monodeuteration on carbon; in contrast peak A remained a broad singlet (no protonation on carbon). A similar pattern was observed in the ^1H spectrum of the deuterated sample where the major resonance was a triplet (J = 2.2 Hz), indicating H-D coupling, and the remaining one was a broad singlet. The methyl fluorosulfate

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Table I. Chemical Shifts and Coupling Constants for the Methyl Diazonium and Methylene Diazenium Ions

	species[a]				
	$CH_2LN_2^+$	$CH_2N_2^+L$	CH_2LOSO_2F	$CH_3OH_2^+$	CH_2N_2
$\delta(^1H)$[b]	4.75	6.09	4.21	4.7, 9.4[c]	3.28[d]
$\delta(^{13}C)$	43.78	73.28	63.20	62.9[e]	23.1[f]
$^2J_{HD}$[g]	2.2		1.6		
$^1J_{HC}$	163.3	176.0	155.5	157.5[e]	
$^1J_{DC}$	24.7		23.5		

[a] L signifies H or D. [b] Chemical shifts were measured in parts per million relative to $Me_4Si = 0$. [c] Reference 6. [d] Reference 7. [e] Reference 8. [f] Reference 9. [g] Coupling constants were measured in hertz.

formed on heating this sample was monodeuterated, as witnessed by triplet resonances in its ^1H and ^{13}C spectra; therefore H-D exchange and, consequently, reversible protonation on carbon is insignificant in the intermediates.

The most reasonable structures compatible with these observations are **1** for the major intermediate and **2** for the minor one; their chemical shifts and coupling constants are collected in Table I along with reference data for diazomethane, methyl fluorosulfate, and the methyl oxonium ion.

It is possible that the methyl diazonium ion be not free in solution, but rather associated with, or bonded to, the fluorosulfate counterion.[10] This is considered unlikely, however, as incorporation of antimony pentafluoride (up to 50% the acid concentration) to the solution did not change the ^1H or ^{13}C shifts. Furthermore, the ^{19}F spectrum of the reaction mixture[11] at −100 °C showed only the peaks of SO_2ClF at −99.1 ppm and $HFSO_3$ at −41.7 ppm (relative to $CFCl_3$). After the mixture was heated to −80 °C, the resonance of methyl fluorosulfate appeared at −31.4 ppm (lit.[12] −31.2 ppm).

Protonated diazirene could be considered as an alternative structure to **2**.[10] It can be excluded, however, as introduction of diazirene[13,11] into the reaction medium at −120 °C did not produce any previously observed species, but only one with ^{13}C shift of 33.8 ppm ($\delta(^{13}C)$ of diazirene 10.9 ppm), which was unaffected by heating the mixture to −80 °C.

In accordance with the proposed structures **1** and **2**, both the ^1H and ^{13}C chemical shifts of **2** are considerably greater than those of **1**. Surprisingly, although the proton chemical shift of **1** is very similar to those of methyl fluorosulfate and the methyl oxonium ion, indicating similar electron distributions in the three methyl groups, the ^{13}C shift of **1** is almost 20 ppm upfield from the other two, though nonetheless 20 ppm downfield from the diazomethane value. As the one-bond coupling constants $^1J_{CH}$ and $^1J_{CD}$ in Table I indicate that the diazonium group is slightly more electron withdrawing than the fluorosulfate or oxonium groups, this must be taken as another example of the unreliability of the ^{13}C shift as a measure of electron density, at least for diazo and diazonium compounds.[14]

The broadening (15 Hz) of the ^{13}C resonance of **2** was observed not only for the singlet in the proton decoupled spectrum, but also for the triplet in the proton coupled spectrum, and so is unlikely to derive from poor resolution of fortuitously close peaks. An alternative explanation—rapid exchange of the N-H proton—is acceptable only if confined to an intimately bound complex, as otherwise the diazomethane formed would also be reprotonated on carbon, leading to the eventual demise of the N-protonated species. A probable source of broadening for the resonance of **2** but not of **1** is a greater degree of ^{13}C-^{14}N coupling in the former. It has previously been shown that, whereas in diazomethane this coupling can be observed at room temperature,[15] less symmetrically substituted diazoalkanes have merely broadened lines for the diazo carbons. The electrical field gradient around the central nitrogen in **1** is less symmetrical than that in **2**, entailing a more rapid ^{14}N quadrupolar relaxation. This in turn removes the ^{13}C-^{14}N coupling and gives a narrower line for the diazonium ion resonance.

The C-protonated species **1** has been calculated to have in the gas phase a lesser free enthalpy of formation than that of the N-protonated isomer by 125 kJ mol^{-1} (basis set 4-31G), or 209 kJ mol^{-1} (basis set STO-3G).[16] The solvational energy assigned to an ^+N-H bond in fluorosulfuric acid is 46 kJ mol^{-1};[17] so from these values **1** would be predicted to be the only observable isomer in $HFSO_3$-SO_2ClF. Hence, the isomer ratio of 4:1 observed in our study could indicate the relative rates of irreversible protonation on the two basic centers of diazomethane.

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3a-Hydroperoxypyrroloindole from Tryptophan. Isolation and Transformation to Formylkynurenine

Sir:

Since the early 1950s, when the first report on Methylene Blue sensitized photooxygenation of tryptophan appeared,[1] this field of study has been developed as a tool for the elucidation of the active site in enzymes, and as a model reaction for the dioxygenase-catalyzed reaction of tryptophan to formylkynurenine.[2] There is, however, considerable variation in the earlier results and very little attention has been given to the reaction mechanism.

Recently we reported that Rose Bengal sensitized photooxygenation of tryptophan[3] and tryptophan derivatives[4] followed by Me_2S reduction gave 3a-hydroxypyrroloindoles,

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