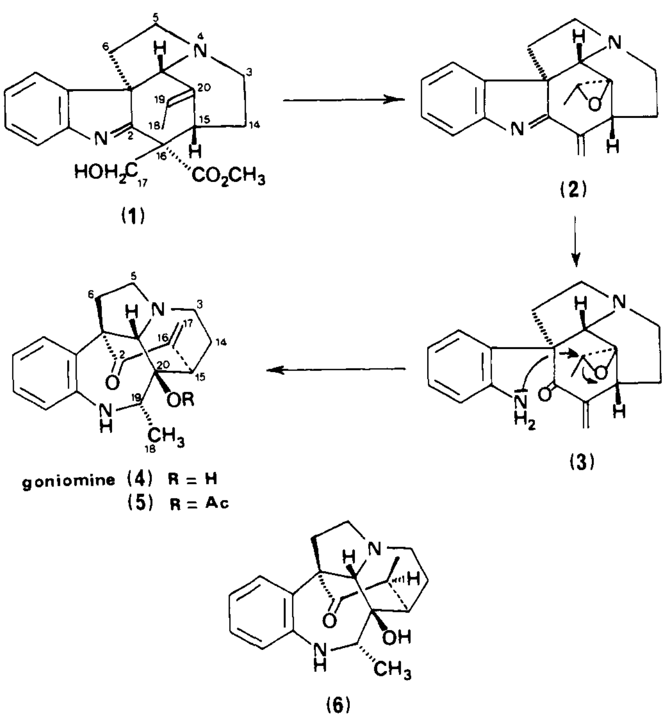
Scheme I



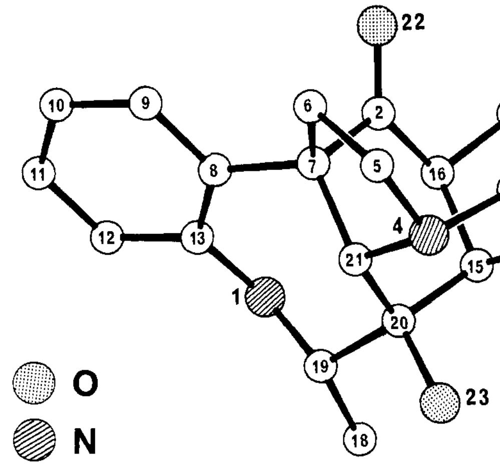
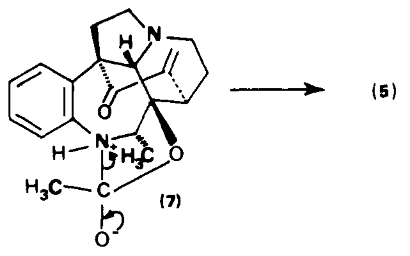


Figure 1. Perspective drawing of dihydrogoniomine (6).

(6) because crystals of goniomine itself were not suitable for such an analysis.

Crystals of 6 belonged to the monoclinic system, space group $P2_1$, with two molecules ($Z = 2$) in the unit cell of dimensions $a = 8.209$ (9), $b = 10.006$ (21), $c = 9.920$ (9) Å, $\beta = 102.0$ (1)°, $V = 797.02$ Å^3. A total of 1504 data were measured on a Philips PW 1100 diffractometer by using graphite-monochromated Mo Kα radiation ($\lambda = 0.7107$ Å) and the $\theta/2\theta$ scan technique. Of these reflections, 808 having $I > 3\sigma(I)$, σ deduced from counting statistics, were considered as observed. The coordinates of the nonhydrogen atoms were derived by using the direct-methods program MULTAN 77.[4] All the hydrogen atoms were located on successive difference electron-density maps. The structure was refined by the full-matrix least-squares methods with anisotropic thermal factors for the nonhydrogen atoms and the hydrogen atoms fitted geometrically. Those of the methyl and of the hydroxyl groups were located on a difference Fourier map. For the observed reflections, $\sum|F_o - |F_c||/\sum F_o$ was 0.044. Figure 1 shows a perspective view of the molecule with the labeling of the atoms. The seven- and the five-membered rings are in chair and half-chair conformations, respectively. An intramolecular hydrogen bond of 2.75 Å is observed between the nitrogen atom N(4) and the hydroxyl group O(23)-H (N···H = 2.0 Å, N···H-O = 128°). The nitrogen atom N(1) (sp^3) is hydrogen bonded to the keto group O(22) of another molecule (N···O = 3.07 Å, O···H = 2.22 Å, N-H···O = 142°). Further crystallographic details can be found in the supplementary data.

Scheme II



The formation of 5 from goniomine (4) in Ac$_2$O/pyridine is remarkable for two reasons: N(1) is not acetylated in conditions where this would be expected, and a tertiary O-acetyl derivative is formed. This result can be explained by the formation of an intermediate oxazolidine (7), the opening of which, during workup, leads to the *O*-acetyl derivative 5 (Scheme II).

A reasonable biogenetic hypothesis (Scheme I) starting from precondylocarpine (1) can be proposed for goniomine (4), involving the intramolecular opening of the 19,20-epoxide by attack of the primary amine formed by the cleavage of the N(1)-C(2) imine bond. With this hypothesis, The absolute configuration of goniomine should be that depicted in Scheme I, related to the condylocarpine series.[5]

Goniomine represents a new type of alkaloid derived from the tetrahydro-1*H*-1-benzazepine ring system and is almost certainly biogenetically related to monoterpenoid indole alkaloids. Until now, the only alkaloids following the same biosynthetic pathway and no longer having an indole nucleus were the quinoline alkaloids quinine and camptothecin.[6]

Acknowledgments. We thank Drs. A. Ahond and B. C. Das for fruitful discussions concerning the spectral data of goniomine and its derivatives.

Supplementary Material Available: Fractional coordinates (Table I), anisotropic thermal factors (Table II), bond distances and angles (Table III), principal torsional angles (Table IV), observed and calculated structure factors (4 pages) (Table V) (9 pages). Ordering information is given on any current masthead page.

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Persulfonium Salts: The Reaction of a Difluoropersulfurane with Lewis Acids

Sir:

We report evidence for stable, cationic, and pentacoordinate (10-S-5)[1] organosulfur species which we propose to call per-

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sulfonium ions (**1**). Just as sulfonium ions (8-S-3 species) can

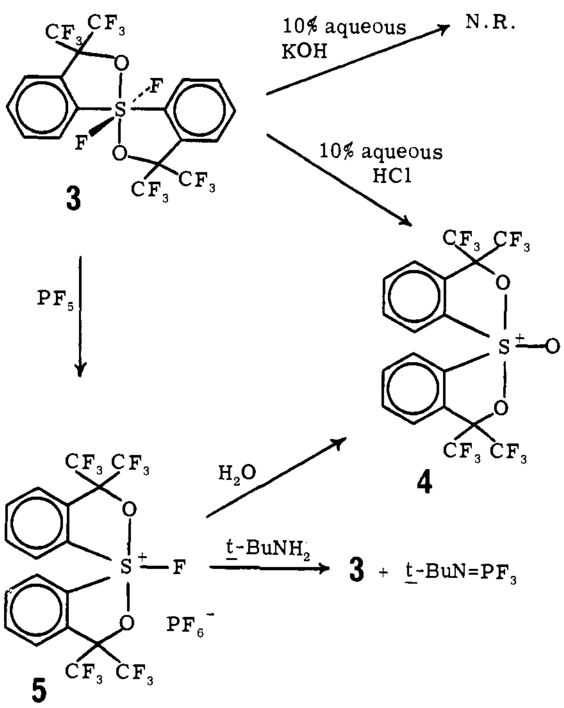
$$R_nSX_{6-n} \rightarrow R_nS^+X_{5-n} + X^-$$

be viewed as being derived from sulfuranes (10-S-4 species) by heterolysis of a bond joining one of the four ligands to sulfur,[2] a persulfonium ion (10-S-5) can be viewed as being derived in this same way from a persulfurane (12-S-6). Persulfonium ions are isoelectronic with similarly substituted, electrically neutral phosphoranes (10-P-5) in which the sulfur is replaced by a phosphorus atom. A compound which may be viewed as a persulfonium species is the recently reported adduct of methylenesulfur tetrafluoride and arsenic pentafluoride, postulated[3] to have structure **2** ($^-AsF_5—CH_2—^+SF_4$).

Although SF_5^- anions are known to be intermediates in substitution reactions of, e.g., $ClSF_5$,[4] no unequivocal evidence is known to us for heterolysis of a persulfurane in the opposite sense to form a persulfonium ion. A persulfonium ion was suggested as an intermediate in the reaction of CF_3SF_4Cl with dialkylaminosilanes;[5] however, certain mechanisms involving nucleophilic attack at chlorine cannot be ruled out in this reaction. Oxidation of Ph_2S by XeF_2 in the presence of a trace amount of HF was reported to yield diphenyl sulfone after hydrolysis.[6] No direct evidence was reported, however, for the postulated tetrafluoropersulfurane. Our work suggests that a persulfonium ion intermediate is very likely during the hydrolysis of appropriately substituted persulfuranes.

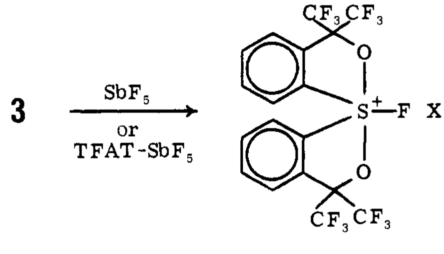
Although a tetrahydrofuran solution of difluoropersulfurane **3**[7] is indefinitely stable toward aqueous base, hydrolysis to sulfurane oxide **4**[9] is seen by ^{19}F NMR to be 90% complete after 2 days in the presence of excess 10% HCl (Scheme I). This suggests that the hydrolysis proceeds via relatively facile acid-catalyzed ionization to form a persulfonium intermediate. In keeping with this suggestion, condensation of excess PF_5 under vacuum at liquid nitrogen temperature into a Teflon bottle containing difluoropersulfurane **3** gives the moisture-sensitive persulfonium hexafluorophosphate **5** (mp 175–176 °C, 100%, anal. $C_{18}H_8SO_2F_{19}P$: C, H, P). The ^{19}F NMR spectrum of **4**, in SO_2ClF containing excess PF_5, shows two unresolved multiplets for the nonequivalent CF_3 groups at −70.9 and −72.0 ppm (using the convention in which ^{19}F shifts are expressed in ppm downfield from $CFCl_3$). The single fluorine attached to sulfur appears at 89.5 ppm. The ^{19}F resonance for octahedral S–F bonds in **3** (12-S-6) at 104 ppm is 14.5 ppm downfield of that for the presumably equatorial SF of **5** (10-S-5), despite the introduction of a positive charge on sulfur on going from **3** to **5**. The ^{19}F shifts for octahedral fluorophosphate anions (12-P-6) are also reported to be downfield of the equatorial P–F signal for the corresponding electrically neutral fluorophosphoranes (10-P-5), again showing an order of chemical shifts opposite to that predicted from charge alone.[10] The peak for fluorines on phosphorus is very broad because of PF_5–PF_6^- exchange and is centered at 68.2 ppm. The mass spectrum of **3** shows a large peak (25% of the base intensity) at m/e 535 for $M^+ - F$, presumably the persulfonium cation of **5**. Since **5** is in equilibrium with **3**, this peak must be in the mass spectrum of **5** also.

Scheme I



The formation of persulfonium salt **5** by the reaction of **3** with PF_5 appears to be reversible. Elemental analysis shows a loss of 30% of the phosphorus content in a sample of **5** after 24 h under vacuum at room temperature. The introduction of **5** into a CH_2Cl_2 solution containing excess *tert*-butylamine at −80 °C regenerates the difluoropersulfurane and gives $(CH_3)_3CN═PF_3$ or its hydrofluoride (identified by evidence for its hydrolysis products in the mass spectrum of the crude material).

Efforts are under way to prepare persulfonium ions with counterions which will not be in equilibrium with electrophilic species. Preliminary NMR results show that difluoropersulfurane **3** reacts with SbF_5 to form the persulfonium hexafluoroantimonate **6** and also reacts with trifluoroacetyl triflate (TFAT)[11] in the presence of a catalytic amount of SbF_5 to form the persulfonium triflate **7**. Chemical shifts (^{19}F) for these salts are identical with those for the cation of **5**, providing evidence against the formulation



6 ($X = SbF_6$)
7 ($X = OT_f$)

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(1) We have proposed (C. W. Perkins, J. C. Martin, A. J. Arduengo, W. Lau, A. Algria, and J. K. Kochi, *J. Am. Chem. Soc.*, submitted for publication) a method of characterizing species in terms of the number of formally valence-shell electrons (N) about an atom X and the number of ligands (L) bonded to X. We then describe the species as an N-X-L species. This makes **1** a 10-S-5 species.

(2) G. W. Astrologes and J. C. Martin, *J. Am. Chem. Soc.*, **99**, 4400 (1977).

(3) H. Bock, J. E. Boggs, G. Kleeman, D. Lentz, H. Oberhammer, E. Peters, K. Seppelt, A. Simon, and B. Solouki, *Angew. Chem., Int. Ed. Engl.*, **18**, 945 (1979).

(4) C. W. Tullock, P. D. Hoffman, and E. L. Muetterties, *J. Am. Chem. Soc.*, **86**, 357 (1964).

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(6) M. Zupan and B. Zajc, *J. Chem. Soc., Perkin Trans. 1*, 965 (1978).

(7) (a) The preparation of difluoropersulfurane **3** is accomplished by the reaction, in $CF_2ClCFCl_2$ solution in a Teflon Flask, of the previously reported[8] spirosulfurane with CF_3OF or BrF_3. Compound **3** precipitates from solution in analytical purity. The results of an X-ray crystallographic structure determination, which confirms the structure pictured for **3**, will be reported in another publication: R. S. Michalak and J. C. Martin, manuscript in preparation. For other examples of difluorosulfuranes and tetrafluoropersulfuranes, see: (b) L. D. Martin, E. F. Perozzi, and J. C. Martin, *J. Am. Chem. Soc.*, **101**, 3595 (1979); (c) D. B. Denney, D. Z. Denney, and Y. F. Hsu, *ibid.*, **95**, 4064 (1973); (d) D. B. Denney, D. Z. Denney, and H. F. Hsu, *ibid.*, **95**, 8191 (1973).

(8) E. F. Perozzi and J. C. Martin, *J. Am. Chem. Soc.*, **101**, 1591 (1979).

(9) Sulfurane oxide **4** was identified by elemental analysis, by a molecular ion in its mass spectrum, and by its ^{19}F NMR spectrum, which is analogous to the previously reported *tert*-butyl-substituted sulfurane oxide: E. F. Perozzi and J. C. Martin, *J. Am. Chem. Soc.*, **94**, 5519 (1972).

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(11) T. R. Forbus and J. C. Martin, *J. Org. Chem.*, **44**, 313 (1979).

of the product of reaction of **3** with PF_5 as a complex rather than salt **5**. Further work is under way to investigate the reactions of **7** with nucleophiles as a way to obtain new sulfur(VI) compounds.

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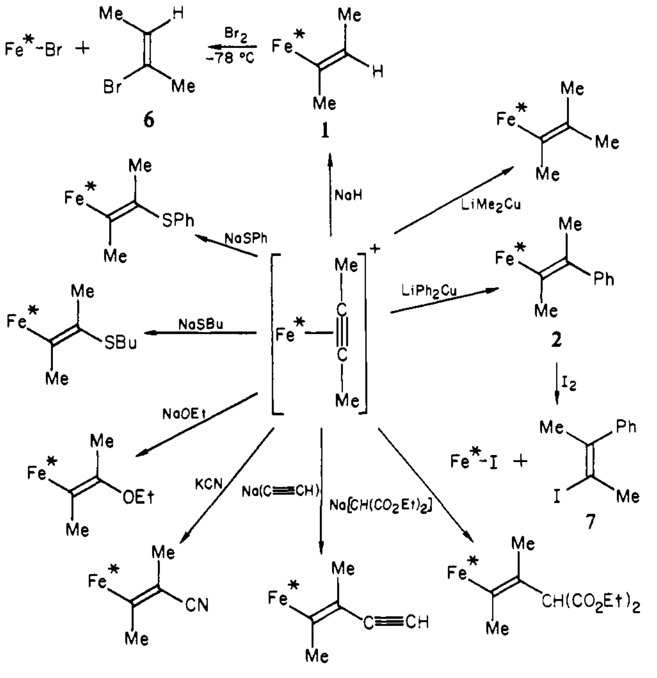
Versatile Preparation of Highly Functionalized σ-Alkenyl Complexes of Cyclopentadienyliron. A New Route to Substituted Alkenes

Sir:

We have recently reported a general synthetic route to $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(\eta^2\text{-alkyne})]BF_4$ complexes and briefly outlined their reduction with borohydride reagents to yield alkenyl complexes.[1] We now report that a wide variety of nucleophiles will react with these cationic π-alkyne[2] complexes to yield new substituted alkenyl complexes. This represents a different and more versatile route to alkenyl complexes than "insertion" of an alkyne into a metal-hydride bond.[3] The nucleophiles add trans to the metal, and alkenyl products in which the more bulky β substituent is cis to the iron undergo a cis-trans isomerization reaction above room temperature. Importantly, the alkenyl group can be cleaved from the metal with retention of stereochemistry. Thus, the sequence coordination of the alkyne to iron, addition of a nucleophile to the alkyne, and cleavage of the alkenyl group with halogen, represent a new route to specifically substituted alkenes that offers wide flexibility in control of the alkene substituents.

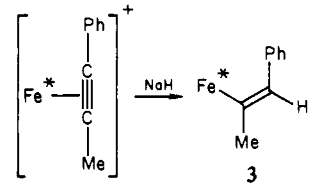
Shown in Scheme I are a number of these new addition reactions for the 2-butyne complex. Although these reactions can be carried out on the isolated pure π complex,[4] a more convenient and higher yield procedure is to use the crude product remaining after solvent evaporation of the filtered reaction mixture used to prepare the alkyne complex.[5] Yields are generally high, and the new alkenyl complexes[6] are thermally stable and only slowly decompose in solution when exposed to air. Because of the many types of reagents represented in Scheme I and the large variety of internal alkynes that will coordinate to the iron, this chemistry represents a very flexible route to many substituted iron-alkenyl complexes.

Scheme I



Fe* = CpFe(CO)(PPh₃)

As shown in Scheme I, the stereochemistry of the products is that which arises from trans addition of the nucleophile. Trans addition of nucleophiles to $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^2\text{-alkene})]^+$ complexes has been shown previously.[7] Proof of trans addition with these alkyne complexes was made with ^1H nuclear Overhauser effect (NOE) enhancement experiments[8] with **1** and **2** (see Scheme I) and the product shown in reaction **1**. Thus, irradiation



(1)

of the vinyl hydrogen atom resonance for **1** and the phenyl resonance for **2** leads to ca. a 20% enhancement of *both* methyl resonances, a result consistent only with the stereochemistries shown. For the product of reaction **1**, irradiation of the vinyl hydrogen atom resonance leads to a 20% enhancement of the methyl resonance whereas irradiation of the phenyl resonance produces no enhancement of the methyl resonance. It should be noted that reaction **1** is regioselective as only one product was obtained. We assigned structure **3** on the basis of the characteristic downfield shift of the vinyl hydrogen atom NMR resonance α to a phenyl substituent[9] (at δ 6.20 in $CDCl_3$; for comparison in compound **1**, the vinyl hydrogen atom resonates at δ 5.40) and on the small[10] (0.8 Hz) coupling constant between the methyl and

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(2) Complexes of terminal alkynes cannot be prepared in this system, presumably because of the formation of vinylidene complexes; see: Davison, A.; Selegue, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7763-7765. Boland, B. E.; Fam, S. A.; Hughes, R. P. *J. Organomet. Chem.* **1979**, *172*, C29-C32. Bruce, M. I.; Willis, R. C. *Aust. J. Chem.* **1979**, *32*, 1471-1485.

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(4) In a typical reaction, a THF (30 mL) solution of $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(\eta^2\text{-2-butyne})]BF_4$ (1.0 g, 2.0 mmol) was cooled to -78 °C and treated with $LiCu(CH_3)_2$ (2.0 mmol) in THF (10 mL). The reaction was allowed to warm to room temperature, the solvent evaporated, the residue extracted with CH_2Cl_2, and this solution placed on an alumina chromatography column. Elution with hexane-CH_2Cl_2 (3:2 v/v) developed a single red band which was collected and the solvent evaporated. The residue was dissolved in toluene (10 mL) and treated with hexane (10 mL). Cooling overnight at -10 °C yielded red crystals which were collected and dried (0.95 g, 97%). For the KCN, NaOEt, NaSPh, and NaSBu reactions, carefully dried methanol was used as the solvent. For the other reactions, THF was used as the solvent.

(5) The η^2-alkyne complexes are best prepared by adding cooled (below -20 °C) CH_2Cl_2 to an equimolar mixture of Fe*-I and $AgBF_4$ followed by addition of 1.1 equiv of the alkyne. After the mixture is warmed to room temperature, it is filtered (using filter-aid) and the solvent evaporated. The appropriate solvent is then added and the nucleophilic addition reaction carried out as above. The yield for this two-step sequence for the 2-butyne complex and $LiMe_2Cu$ is 96%.

(6) Complete characterization (IR, ^1H and ^{13}C NMR, and melting-point data) and analytical figures have been obtained on all of the alkenyl complexes reported in this paper.

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(9) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. "Spectrometric Identification of Organic Compounds", 3rd ed.; Wiley: New York, 1974; p 223.

(10) Geminal CH_3-H coupling for compound **1** is 6.0 Hz.