to Cp_2Mo, accentuated by the availability of an alternative mechanism, zirconium-assisted C–O heterolysis. This mechanism (see Scheme I) has the virtue that a 16-electron tungsten complex is never invoked. In any event, the ability to drastically influence product selectivity (alkane vs. alkene) in heterobimolecular CO hydrogenation with elements as similar as Mo and W is revealed in these studies. In addition, this work furnishes an example of one way of accomplishing the poorly understood carbon–oxygen bond scission step in Fischer–Tropsch hydrocarbon synthesis. It also reveals an alternative mechanism (to β-H elimination from a surface-bound alkyl moiety) for the production of olefinic Fischer–Tropsch products,[15] and it thus elaborates the results and proposals of Brady and Pettit concerning the intermediacy of surface-bound alkylidenes.[16]

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE 80-06331) and the M. H. Wrubel Computer Center. J. A. Marsella acknowledges a fellowship from the Lubrizol Foundation.

Supplementary Material Available: A table of atomic positional and thermal parameters for $Cp_2WC(H)Ph$ (1 page). Ordering information is given on any current masthead page.

(15) For a recent review of Fischer-Tropsch mechanisms, see: Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61.
(16) Brady, R. C.; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 6181.

Perfluoroallyl Fluorosulfate, a Reactive New Perfluoroallylating Agent[1]

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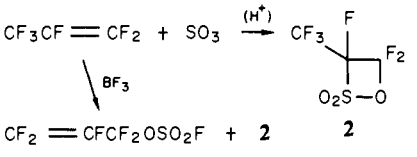
Received May 22, 1981

Previous studies[2-4] have shown that the principal reaction path for terminal fluoro olefins with sulfur trioxide is a [2 + 2] cycloaddition to produce β-sultones, although other products may also be isolated depending on reaction conditions and the fluoro olefin structure. We have now found that trivalent boron compounds are capable of catalyzing an unusual net insertion of SO_3 into an allylic C–F bond to give reactive fluorosulfates.[5] The formation of perfluoroallyl fluorosulfate (**1**) from hexafluoropropene and sulfur trioxide is of particular interest.

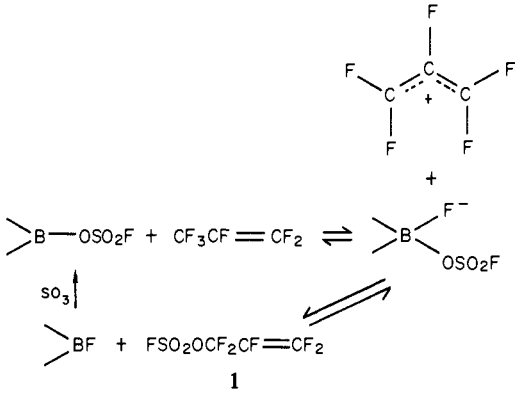


1 **2**

Pure distilled sulfur trioxide and hexafluoropropene at temperatures up to 100 °C under pressure lead to β-sultone **2** in high yield as the sole product. The presence of 0.5–2 wt % of BF_3 (or related materials, e.g., $B(OCH_3)_3$ or B_2O_3) in sulfur trioxide at temperatures of 20–60 °C diverts the reaction to one in which moderate yields of fluorosulfate **1** are formed along with **2**. Such reactions carried out at 25 °C or slightly higher over 10–60 h with a 1.5- to 2-fold excess of hexafluoropropene give **1** as the major product (50–60% yield), so that **1** is a reagent readily prepared in quantity.

The catalytic nature of the reaction is implied in the demonstration that fluorosulfate **1** is formed reversibly. A sample of **1** contacted with preformed 3:1 $SO_3/B(OCH_3)_3$ catalyst for 1 week at 25 °C gave ca. 30% of hexafluoropropene along with a small amount of BF_3. Sultone **2** was unaffected by the same catalyst composition.

Although a variety of catalyst compositions derived from BF_3 or $B(OCH_3)_3$ and SO_3 proved to be active, attempts to isolate a simple boron fluorosulfate derivative were unsuccessful. That the compounds present in the catalyst mixture are mainly derivatives of boroxin is indicated by elemental analyses and the formation of pyrosulfuryl fluoride as a byproduct. We believe that such fluorosulfated boroxins are capable of abstracting an allylic fluorine atom from hexafluoropropene to form the perfluoroallyl cation.[6] Transfer of fluorine back to the cation regenerates hexafluoropropene, while transfer of a fluorosulfate group gives **1**. The trivalent B–F species resulting from the latter transfer is rapidly converted to fluorosulfate by the excess sulfur trioxide present, thus driving the reaction in the forward direction.



1

Fluorosulfate **1**[7,8] is best isolated by preliminary rapid distillation to remove catalyst followed by careful fractionation; bp 63–64 °C; IR (CCl_4) 1785 (C=C), 1485 cm^{-1} (SO_2); NMR[9] (CCl_4) 46.1 (t of d, J_{FF} = 8.5, 1.8 Hz, 1 F, OSO_2F), −74.0 (d of d of d of d, J_{FF} = 28.2, 13.9, 8.5, 7.8 Hz, 2 F, CF_2), −91.2 (d of d of t, J_{FF} = 50.0, 40.5, 7.8 Hz, 1 F, *cis*-$CF_2CF{=}CFF$), −104.7 (d of d of t, J_{FF} = 119.4, 50.0, 28.2 Hz, 1 F, *trans*-$CF_2CF{=}CFF$), and −192.4 ppm (d of d of t of d, J_{FF} = 119.4, 40.5, 13.9, 1.8 Hz, 1 F, CF_2CF—). Anal. Calcd for $C_3F_6O_3S$: C, 15.66; F, 49.54. Found: C, 15.31; F, 49.59.

Nucleophilic displacement of fluorosulfate anion from **1** occurs with ease. For example,

$$\mathbf{1} + NaI \xrightarrow[30\ ^\circ C]{\text{acetone}} CF_2{=}CFCF_2I\ (68\%) + NaOSO_2F$$

Since attack by nucleophiles such as I^- on sp^3 carbon in highly fluorinated molecules does not occur, the reaction no doubt proceeds by attack at the terminal vinylic carbon in an S_N2' reaction or in a stepwise version of it involving an intermediate carbanion. The fluorosulfate anion produced is unreactive in this system, thereby allowing the use of **1** to introduce a double bond which remains in the terminal position. Perfluoroallyl chloride has previously been shown to undergo similar reactions, but it is difficult to make and purify.[10,11]

(1) Contribution No. 2924.
(2) England, D. C.; Dietrich, M. A.; Lindsey, R. V. *J. Am. Chem. Soc.* **1960**, *82*, 6181.
(3) Krespan, C. G.; Smart, B. E.; Howard, E. G. *J. Am. Chem. Soc.* **1977**, *99*, 1214.
(4) Knunyants, I. L.; Sokolski, G. A. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 583.
(5) Smart (Smart, B. E. *J. Org. Chem.* **1976**, *41*, 2353) reports the only related formation of an allylic fluorosulate of which we are aware. In this case, competitive cycloaddition with the substrate, hexafluorocyclobutene, was not a factor; so the possible involvement of a catalyst was not determined.
(6) Chambers et al. (Chambers, R. D.; Parkin, A.; Matthews, R. S. *J. Chem. Soc., Perkin Trans. 1* **1976**, 2107) report evidence for the generation of perfluoroallyl cation from hexafluoropropene and SbF_5. We observed no reaction between hexafluoropropene and BF_3 at moderate temperatures.
(7) U.S. Patent 4 235 804, 1980.
(8) Dr. G. Hofmann of the Polymer Products Department, Du Pont, first prepared perfluoroallyl fluorosulfate and characterized it as the dibromide.
(9) Downfield from $CFCl_3$ as internal reference.

0002-7863/81/1503-5598$01.25/0

A very general new α-olefin synthesis can be illustrated by reactions involving fluoride ion adducts with a fluoro ketone and an acid fluoride. The soluble perfluoroalkoxides so prepared displace fluorosulfate from **1** at 0 °C to form the corresponding perfluoroallyloxy derivatives in good yield.

$$(CF_3)_2C{=}O + KF \rightarrow (CF_3)_2CFOK \xrightarrow{1} (CF_3)_2CFOCF_2CF{=}CF_2$$

$$FSO_2CF_2COF + KF \rightarrow FSO_2CF_2CF_2OK \xrightarrow{1} FSO_2CF_2CF_2OCF_2CF{=}CF_2$$

Details of our studies on the synthesis of **1** and other allylic fluorosulfates as well as the use of these versatile reagents to perfluoroallylate various substrates will be subjects of future publications.

(10) Miller, W. T. U.S. Patent 2671799, 1950.
(11) Miller, W. T.; Fainberg, A. H. *J. Am. Chem. Soc.* **1957**, *79*, 4164.

Total Synthesis of the Quinonoid Alcohol Dehydrogenase Coenzyme (1) of Methylotrophic Bacteria

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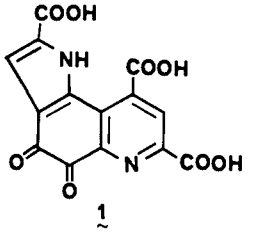
Methylotrophic bacteria which can survive by using one-carbon compounds such as methane or methanol as the sole carbon source contain a novel alcohol dehydrogenase which is neither NAD nor flavin dependent. The coenzyme for this dehydrogenase has recently been assigned structure **1** on the basis of an X-ray diffraction study of a derivative[1] and other evidence.[2-4] Only a few milligrams of this unique cofactor have been obtained thus far, and in consequence, its chemistry and its mode of action in cocatalysis have not been defined.[5] We describe herein a total synthesis of **1**, previously[1] termed methoxatin, which makes this substance readily available by a short and direct method that is well suited to multigram scale. There are several other interesting facets of this synthetic problem and its solution: (1) the general strategy of forming a fused tricyclic system by joining two precursors, each containing a terminal ring (A + C → ABC), which is frequently very powerful, does not appear to be appropriate; (2) two annulation steps involved in the synthesis (B → ABC) are smooth and highly regioselective; (3) the final steps of the synthesis were accomplished expeditiously despite the dearth of knowledge regarding the chemistry and stability of **1**.



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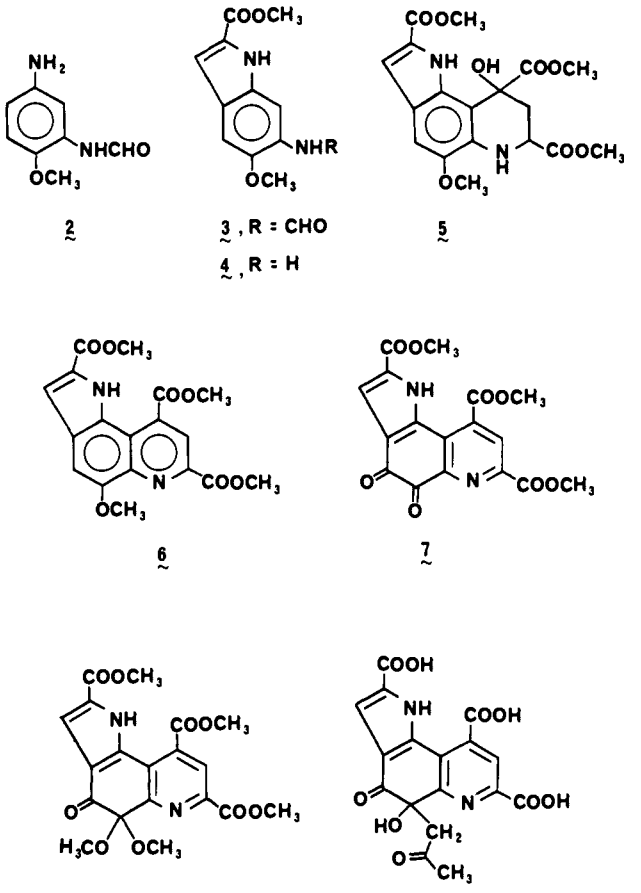
(1) Salisbury, S. A.; Forrest, H. S.; Cruse, W. B. T.; Kennard, O. *Nature (London)* **1979**, *280*, 843. The derivative used was an aldol addition product with acetone formed during extraction with the latter as solvent.
(2) Forrest, H. S.; Salisbury, S. A.; Kilty, C. G. *Biochem. Biophys. Res. Commun.* **1980**, *97*, 248.
(3) Duine, J. A.; Frank, J., Jr.; Verwiel, P. E. J. *Eur. J. Biochem.* **1980**, *108*, 187.
(4) Duine, J. A.; Frank, J., Jr. *Biochem. J.* **1980**, *187*, 213; **1980**, *187*, 221.
(5) This cofactor seems to be involved in the action of a number of nonmethylotrophic bacterial alcohol dehydrogenases including at least two which utilize glucose as substrate. See: (a) Houge, J. G. *J. Biol. Chem.* **1964**, *239*, 3630. (b) Duine, J. A.; Frank, J., Jr.; Van Zeeland, J. K. *FEBS Lett.* **1979**, *108*, 443.

Chart I



Commercially available 2-methoxy-5-nitroaniline was converted (in formic acid using excess formic–acetic anhydride at 25 °C for 10 min and 50 °C for 20 min) to the *N*-formyl derivative (95% yield, mp 197.0–198.5 °C, yellow needles), which was hydrogenated at 3 atm in ethanol at 65 °C over Adams platinum catalyst to give 2-methoxy-5-aminoformanilide (**2**) (93% yield, mp 146.0–147.5 °C) (Chart I).[6] Treatment of **2** in 2 equiv of aqueous 0.3 N hydrochloric acid at 0–5 °C with 1 equiv of sodium nitrite for 10 min produced the diazonium salt which was added to a solution of 1.2 equiv of methyl α-methylacetoacetate and 1.2 equiv of potassium hydroxide in 1:1 methanol–water at 0 °C. After 8 h the resulting arylhydrazone was isolated (80%) and heated at 80 °C in anhydrous formic acid for 9–10 h to produce the indole **3** as a granular solid, mp 215.5–217 °C (72%).[7] Deformylation of **3** with 3 equiv of hydrochloric acid in acetone–water (96:4) at reflux for 1 h produced the aminoindole **4** (79%).

Addition of a third ring was accomplished by a remarkably facile Doebner–vonMiller type of annulation in a single step.[8] A solution of **4** and 1.5 equiv of the dimethyl 2-oxaglutaconate[9] in

(6) Satisfactory proton magnetic resonance (^{1}H NMR), infrared (IR), ultraviolet (UV), and mass spectral data were obtained for each purified intermediate.
(7) This combination of the Japp–Klingemann reaction (Philpott, P. G. *J. Chem. Soc.* **1965**, 7185) and Fischer indolization afforded <3% of position isomeric indole.
(8) In contrast, the related Combes annulation (Jones, G. *Heterocycl. Comp.* **1977**, *32*, 119) could not be effected from **4** and dimethyl 2,4-dioxoglutarate, despite extensive experimentation.
(9) Although diethyl 2-oxoglutaconate has been described previously (Cornforth, J. W.; Cornforth, R. H. *J. Chem. Soc.* **1946**, 755), the yield reported was only 2%. However, crystalline dimethyl 2-oxoglutaconate (pure by NMR analysis) could be synthesized in 97% yield from dimethyl 2-ketoglutarate by the following sequence: (1) dropwise addition of 1.01 equiv of bromine in dry methylene chloride at reflux to the keto ester, (2) removal of solvent and hydrogen bromide in vacuo, and (3) treatment of the resulting α-bromo ketone with 1 equiv of triethylamine in ether at 25 °C for 20 min, filtration, passage of the filtrate through a pad of silica gel, and concentration in vacuo.

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