Characterization of π-$C_5H_5Fe(CO)_2C_4H_5SO_2$. A Novel Compound from the Reaction of Sulfur Dioxide with a 2-Alkynyl Complex of Iron[1]

Sir:

The reaction of sulfur dioxide with $Mn(CO)_5CH_2C{\equiv}CR^{2-4}$ or π-$C_5H_5Mo(CO)_3CH_2C{\equiv}CR^{3,4}$ (R = H, CH_3) affords stable 1:1 adducts of the parent compound and SO_2. From infrared and proton magnetic resonance spectra, $Mn(CO)_5(SO_2C_3H_3)$ was postulated[2] to contain an allenyl(oxy)sulfinyl array, Mn—S(O)—O—CH=C=CH_2, similar structures later being tentatively adopted for the products of analogous reactions.[4] More recently, additional reports of synthesis of 2-alkynyl transition metal complexes[5,6] and of their reactions with SO_2[6] have been published. The authors proposed an allenyl-O-sulfinate bonding sequence, M—O—S(O)—C(R)=C=CH_2, for each of the SO_2-containing products.

An X-ray diffraction study has now been carried out in order to provide an unambiguous structural assignment for the product of the reaction between π-$C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_3$ (I) and SO_2; the structure found is different from those previously proposed and possesses some interesting new characteristics.

I was prepared from $Na[C_5H_5Fe(CO)_2]$ and 1-chloro-2-butyne in a manner analogous to that for $Mn(CO)_5CH_2C{\equiv}CH$.[2] Purification by chromatography afforded yellow crystals in 50% yield, mp 46–48° (lit.[5] 50°). *Anal.* Calcd for $C_{11}H_{10}O_2Fe$: C, 57.39, H, 4.35. Found: C, 56.63, H, 4.29. The proton magnetic resonance spectrum shows a singlet at τ 5.24 (C_5H_5) and a complex pattern of the same intensity at τ 8.0–8.4 (C_4H_5), thus militating against the alternate, allenyl ($C_5H_5Fe(CO)_2C(CH_3)$=C=CH_2), formulation.[5,7]

A solution of I (0.5 g, 2.2 mmol) in 15 ml of liquid SO_2 was refluxed for 6 hr before allowing the solvent to boil away. The resultant orange-red solid was dried *in vacuo* at 25° and then dissolved in 25 ml of dichloromethane. The solution was filtered and the filtrate treated with 25 ml of hexane. Concentration in a stream of nitrogen yielded 0.6 g (91%) of yellow-brown crystalline $C_5H_5Fe(CO)_2(SO_2C_4H_5)$ (II), mp 136° dec. *Anal.* Calcd for $C_{11}H_{10}O_4SFe$: C, 44.89; H, 3.40; mol wt, 294. Found: C, 44.74; H, 3.53; mol wt (osmometry, $CHCl_3$ solution), 285.

Yellow needle-like parallelepipeds of II, obtained by the slow cooling of a solution of the complex in *sym*-dichloroethane–methylcyclohexane, crystallize in the centrosymmetric monoclinic space group $P2_1/c$ (C_{2h}^5; no. 14) with a = 10.029, b = 7.353, c = 16.072 Å, β = 94.33°, $\rho_{obsd} = 1.58 \pm 0.03$, ρ_{calcd} = 1.651 g cm^{-3} for M = 294.11 and Z = 4.

Complete X-ray diffraction data to sin θ = 0.40 (Mo Kα radiation, λ = 0.7107 Å) were collected on a 0.01°-incrementing Supper-Pace Buerger automated diffractometer using a stationary-background, ω-scan, stationary-background counting sequence. The structure was solved by a combination of Patterson, Fourier, and least-squares refinement techniques. All atoms other than the methyl hydrogens have been located. With the use of anisotropic thermal parameters for nonhydrogen atoms, the discrepancy index has been reduced to R_f = 5.80% for the 1178 independent nonzero reflections.

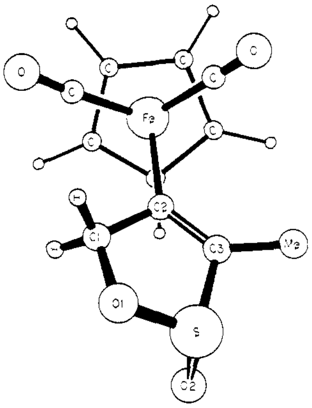

Figure 1. The π-$C_5H_5Fe(CO)_2$[—C=C(CH_3)—S(O)—OCH_2] molecule, projected onto the plane of the π-cyclopentadienyl ring.

The molecule is illustrated in Figure 1. The central iron atom is linked to two carbonyl ligands (Fe–CO distances being 1.774 (11) and 1.778 (11) Å), a π-cyclopentadienyl ring system (Fe–C distances ranging from 2.086 (11) to 2.097 (12) Å), and the 2-carbon of the former but-2-ynyl ligand (Fe–C(2) = 1.996 (8) Å). This last distance may be compared with Fe–C(sp^2) distances of 1.987 (5) Å in $[\pi$-$C_5H_5Fe(CO)_2]_2C_4H_4$[8] and 1.99 (2) Å in $(C_6H_5C_2CO_2CH_3)_3Fe(CO)_3$,[9] each of which is indicative of partial multiple bond character in the iron–(σ-vinyl) linkage.[10]

The incoming sulfur dioxide molecule participates in a

$$-[\overline{C{=}C(CH_3)-S(O)-O-CH_2}]$$

ring in which bond distances (Å) are C(1)–C(2) = 1.484 (12), C(2)–C(3) = 1.312 (12), C(3)–S = 1.781 (9), S–O(1) = 1.620 (7), and O(1)–C(1) = 1.462 (12). Peripheral bond distances are C(3)–Me = 1.508 (13) Å and S–O(2) = 1.480 (8) Å. These distances are all consistent with the structure as drawn in Figure 1 (*cf.* ref 11).

Bond angles about the sulfur atom are: O(1)–S–O(2) = 109.9 (0.4)°, O(1)–S–C(3) = 106.3 (0.4)°, and O(2)–S–C(3) = 92.1 (0.4)°. The sulfur atom thus has a pseudotetrahedral stereochemistry, with a sterically active lone pair of electrons occupying the fourth coordination position.

The proton nmr spectrum of II exhibits features which are remarkably similar to those observed pre-

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[1] Sulfur Dioxide Insertion. XI. For part X of this series see M. Graziani, J. P. Bibler, R. M. Montesano, and A. Wojcicki, *J. Organometal. Chem.*, **16**, 507 (1969).

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viously for $Mn(CO)_5(SO_2C_4H_5)$ and $C_5H_5Mo(CO)_3$-$(SO_2C_4H_5)$.[4] An analysis of the entire multiplet pattern in terms of an ABX_3 spin system gives for II the chemical shifts τ 7.60 (CH_3), 4.81, and 4.45 (CH_2), and the coupling constants $|J_{AB}| = 14$ Hz and $|J_{AX}| = |J_{BX}| \sim 2$ Hz. These are to be compared with τ 7.80–7.95 (CH_3), 4.87–4.94, and 4.48–4.57 (CH_2), and $|J_{AB}| =$ 14.5–15 Hz and $|J_{AX}| = |J_{BX}| \sim 2$ Hz for the other two compounds. In the infrared spectra of II and other SO_2-containing derivatives of 2-alkynyl transition metal complexes reported, the S–O stretching bands are observed in the ranges 1115–1100 and 910–890 cm^{-1}.[2,4,6,12] These spectral resemblances undoubtedly reflect the same type of structure for the $SO_2C_3H_2R$ (R = H and CH_3) moieties as is found in II (Figure 1).

Work in progress is concerned with reactions between 2-alkynyl metal carbonyls and other electrophilic substrates and with attempts at desulfonylation of the complexes reported herein. Particular interest attaches to an observation that II in CH_2Cl_2 solution undergoes partial (~45%) reconversion to I upon chromatography on alumina.

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(12) The product of the reaction between $(C_6H_5)_3SnCH_2C{\equiv}CH$ and SO_2 shows S—O stretching bands in the region 990–950 cm^{-1} and is best formulated as $(C_6H_5)_3SnOS(O)CH{=}C{=}CH_2$, as suggested by the authors: W. Kitching, C. W. Fong, and A. J. Smith, *J. Amer. Chem. Soc.*, **91**, 767 (1969).

(13) Research Fellow of the Alfred P. Sloan Foundation, 1968–1970.

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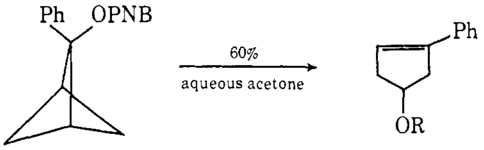
Solvolytic Reactivity of 2-Phenylbicyclo[1.1.1]pentan-2-ol *p*-Nitrobenzoate

Sir:

The generation of carbonium ions in strained ring systems has produced a host of highly interesting and important results of practical and theoretical interest.[1,2] While the solvolytic behavior of some bicyclo[*n*.1.1] systems has received considerable attention,[3] others have remained virtually unexplored. A study of the reaction rate and products of the solvolysis of the *p*-nitrobenzoate ester of bicyclo[1.1.1]pentan-2-ol would be of considerable interest since it should provide additional information on what effects ring size and strain have on the course of cyclobutyl carbonium ion type rearrangements.[4] Our recent photochemical entry into the bicyclo[1.1.1]pentanol system[5] makes these molecules available for a variety of physical organic studies. We now wish to report on the anchimeric assistance present in the solvolysis of 2-phenylbicyclo-[1.1.1]pentan-2-ol *p*-nitrobenzoate (**1**).

The preparation of the desired *p*-nitrobenzoate **1**, mp 78–80°, was carried out in the usual way by treating 2-phenylbicyclo[1.1.1]pentanol with *p*-nitrobenzoyl chloride in dry pyridine.[6] The ester was allowed to solvolyze in 60% aqueous acetone, and the course of the reaction was followed titrimetrically using standard techniques. For comparison purposes the related 1-phenylcyclobutanol (**2**) and dimethylphenylcarbinol (**3**) *p*-nitrobenzoates were prepared and their solvolytic behavior was also investigated. Table I lists the rates of solvolysis, and the associated thermodynamic parameters of **1**, **2**, and **3**, together with the rate of solvolysis of 7-phenyl-7-norbornyl *p*-nitrobenzoate (**4**)[7,8] for comparison purposes.

The solvolysis of **1** proceeded *via* rearrangement to the 3-cyclopenten-1-ol system giving 6% internal return to **5** and 92% 3-phenyl-3-cyclopenten-1-ol (**6**). The structure of alcohol **6**, mp 79–81°, is inferred from its composition, spectral data, and chemical behavior. The infrared spectrum of **6** was characterized by bands at 2.82, 3.50, 8.70, and 9.60 μ. The ultraviolet spectrum in 95% ethanol has a maximum at 255 mμ (ϵ 11,700). The nmr spectrum in deuteriochloroform showed a multiplet at τ 2.75 (5 H), a triplet at τ 3.98 (J = 2.3 Hz, 1 H), multiplets at τ 5.45 (1 H) and 7.39 (4 H), and a singlet at τ 7.40 (1 exchangeable proton). The mass spectrum exhibited peaks at *m/e* 160, 142 (base), 131, 115, and 91. Chemical confirmation was obtained by catalytic reduction of **6** to 3-phenylcyclopentanol (**7**) followed by oxidation of **7** to 3-phenylcyclopentanone (**8**).[9] Structure **8** was compared to an authentic sample prepared from the catalytic reduction of 3-phenyl-2-cyclopent-1-one (**9**).[11]



1

R = PNB (5)
R = H (6)

The above results point to the exceptional reactivity of the bicyclo[1.1.1]-2-pentyl cation and the high propensity for it to undergo bond reorganization. The products formed can best be rationalized in terms of a bicyclo[2.1.0]-2-pentyl cation intermediate (**11**) which

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(8) The solvolysis of 7-phenyl-7-norbornyl *p*-nitrobenzoate (**4**) was studied in 70% aqueous dioxane.[7] The *Y* values of 60% acetone and 70% dioxane are similar and consequently there should be small differences (±10%) in rate between the two solvents.

(9) Although the above spectral and chemical data are consistent with that of the proposed structure (**6**), it does not necessarily preclude 3-phenyl-2-cyclopenten-1-ol (**10**) as an alternate possibility. Alcohol **10** was therefore synthesized[10] and shown to be substantially different from the solvolysis product.

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