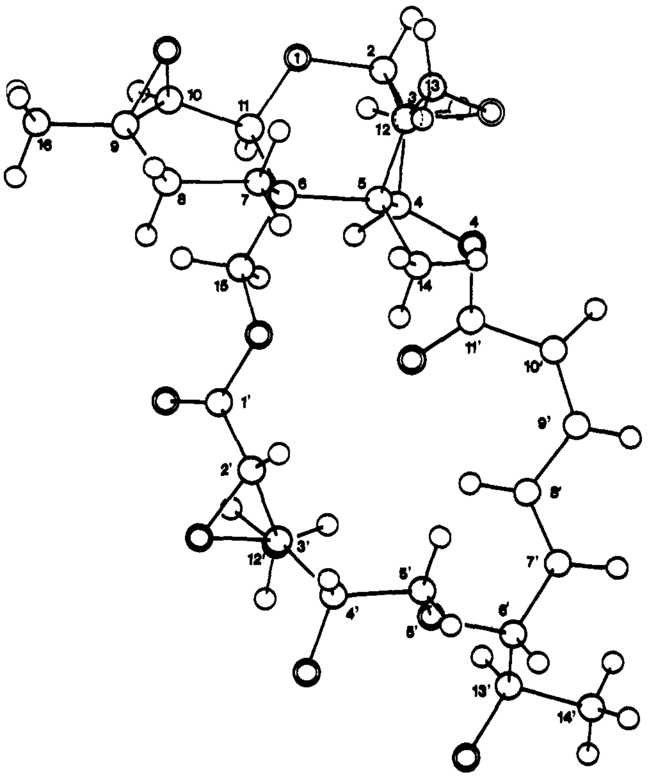

Figure 1. Diagrammatic representation of the structure of baccharin as found in the crystal. Carbon atoms are represented by the larger single circles, oxygen by double circles, and hydrogen by the smaller circles. Hydrogen atoms not located, at the O(4′) and O(13′) hydroxy groups, are omitted.

contamination; however, inspection of the plant material does not reveal any obvious contamination, and the baccharins have been isolated from two separate collections of plant material. Furthermore, the compounds are estimated to comprise ca. 0.02% of the dry plant material, a rather high percentage for such a putative contamination. What does seem a distinct possibility is that the baccharins may be plant-altered fungal metabolites.

References and Notes

(1) Tumor Inhibitors. 119. Part 118: S. M. Kupchan and D. R. Streelman, *J. Org. Chem.*, in press.

(2) This investigation was supported by research grants from the National Cancer Institute (N.C.I.) (CA-11718, CA-11760, and CA-12059) and the American Cancer Society (CI-102K), and contracts with the Division of Cancer Treatment, N.C.I., National Institutes of Health (NO1-CM-12099 and NO1-CM-67002).

(3) Leaves, twigs, and flowers were collected in Brazil in May, 1975. The authors acknowledge with thanks receipt of the dried plant material from Dr. R. E. Perdue, Jr., U.S. Department of Agriculture, Baltimore, Md., in accordance with the program developed by the National Cancer Institute.

(4) Antileukemic activity was assayed under the auspices of the National Cancer Institute by the procedures described by R. I. Geran, N. H. Greenberg, M. M. MacDonald, A. M. Schumacher, and B. J. Abbott, *Cancer Chemother. Rep., Part 3*, **3**, 1 (1972). Baccharin showed optimal T/C values of ca. 200 at dose levels of 1.25–5.0 mg/kg. The cytotoxicity (ED_{50}) against KB cell cultures of **1** and the other related baccharins is ca. 10^{-3}–10^{-4} μg/ml. The cytotoxicity of **1** is in a range typical for trichothecenes, but the antileukemic activity (PS) of **1** exceeds substantially those of reported trichothecenes.[6]

(5) Ch. Tamm, *Fortschr. Chem. Org. Naturst.*, **31**, 63 (1974).

(6) For an excellent review of the chemical and spectral properties of 12,13-epoxytrichothecenes, see J. R. Bamburg and F. M. Strong in "Microbial Toxins", Vol. 7, S. Kadis, A. Ciegler, and S. J. Ajl, Ed., Academic Press, New York, N.Y., 1971, pp 207–292.

(7) Baccharin (**1**) is the only active principle isolated from *B. megapotamica* in which the central 12,13-epoxytrichothecene 9,10 double bond is epoxidized. The remaining active principles (to date, six) all give the same central ring system upon base hydrolysis: 4β,8α,15-trihydroxy-12,13-epoxytrichothecene, a heretofore unknown trichothecene. There are no reports of naturally occurring trichothecenes with an epoxide at the 9,10 position, although peracid oxidation of the 9,10 double bond in roridin A[8] gives as the principal product a β-epoxide having the same configuration at C9,C10 as in **1**.

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(11) Visiting Scholar, 1975–1976; on sabbatical leave, University of Maryland, College Park, Md. Receipt of a National Research Service Award (1F32 CA05368-01) from the National Institutes of Health is gratefully acknowledged.

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$[Mo_3(OAc)_6(CH_3CH_2O)_2(H_2O)_3]^{2+}$ and Other New Products of the Reaction between Molybdenum Hexacarbonyl and Acetic Acid

Sir:

The preparation of dimolybdenum tetraacetate $Mo_2(OAc)_4$ by refluxing $Mo(CO)_6$ in an acetic acid-acetic anhydride mixture[1] was characterized by a noticeably low yield.[2] The dark brown solution from which the crystals of the tetraacetate had been removed contained the greater part of the molybdenum products of the reaction. These products were separated by ion exchange chromatography. The solution was absorbed on a cation exchange column (Dowex 50 X2) and eluted by 0.1 M CF_3SO_3H. This elution removed a green-brown molybdenum ion (I) with an absorption maximum at 595 nm. The elution behavior of this species indicated an ionic charge of 1+. Several green bands of species with higher ionic charges remained on the column. All these products were also obtained when acetic anhydride was omitted from the reaction mixture; i.e., they were produced by the reaction of $Mo(CO)_6$ and acetic acid.

The green-brown solution of I was oxidized by permanganate to a deep red solution which was absorbed on a cation exchange column. Elution with 0.1 M acid removed a brown band of the remaining unreacted ion I. Elution with 0.5 M acid removed a red molybdenum ion II. The spectrum of II is presented in Figure 1.

When trifluoromethylsulfonic acid was used for elution of II, spontaneous crystallization took place in the eluted solution. The red crystals were filtered, rinsed with acetone and ether, and dried under vacuum. Elemental analysis[3] suggested the formula $Mo_3(OAc)_6(CH_3CH_2O)_2(H_2O)_3(CF_3SO_3)_2$. Crystallization also occurred when the ion II was eluted with perchloric acid and *p*-toluenesulfonic acid.[4] The trifluoromethylsulfonate salt was subjected to x-ray diffraction structure determination.[5,6] The structure of the complex is shown in Figures 2 and 3.

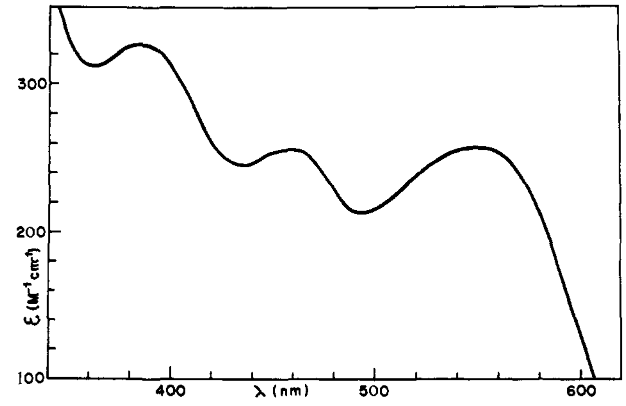

Figure 1. Absorption spectrum of $[Mo_3(OAc)_6(CH_3CH_2O)_2(H_2O)_3]^{2+}$.

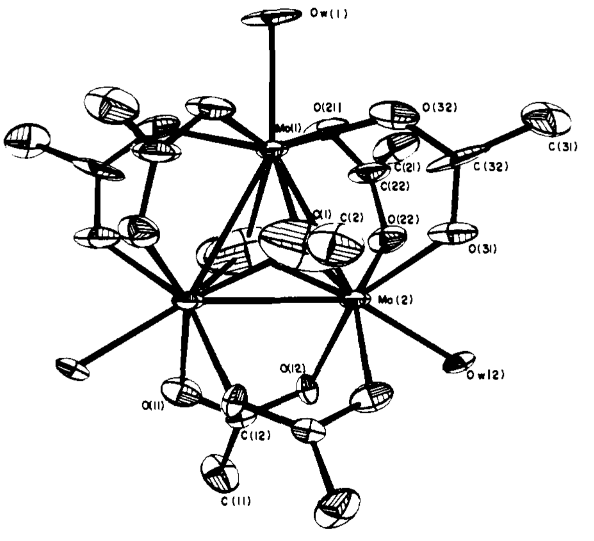

Figure 2. The structure of $[Mo_3(OAc)_6(CH_3CH_2O)_2(H_2O)_3]^{2+}$, showing vibrational elipsoids at the 50% probability level.

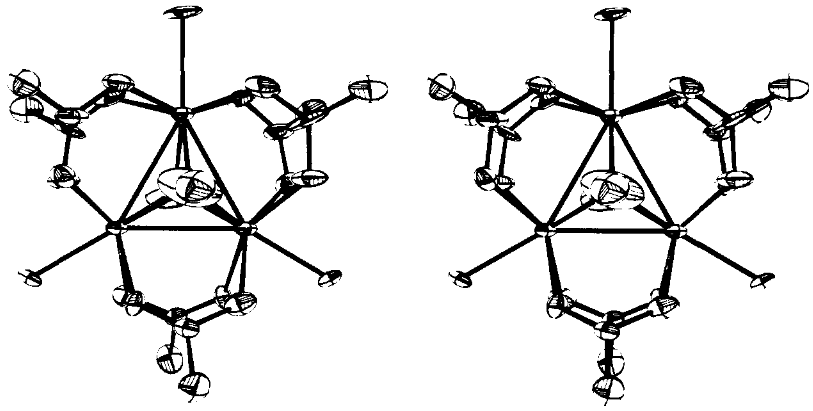

Figure 3. Stereoscopic view of the ion $[Mo_3(OAc)_6(CH_3CH_2O)_2(H_2O)_3]^{2+}$.

The molybdenum atoms which occupy the corners of an equilateral triangle (Mo-Mo distance 2.854 (2) Å) are bridged by acetato ligands and by the oxygen atoms of ethanolato groups which lie above and below the triangle plane. In addition, each molybdenum atom is coordinated to a water molecule. The complex is required to possess a crystallographic twofold axis (which coincides with the Mo_1-$O_1(H_2O)$ vector), but the overall symmetry of the complex is very nearly D_{3h}. The six independent Mo-O(OAc) distances are essentially the same and average 2.108 (5) Å, and the average Mo-O(H_2O) distance is 2.160 (5) Å.

The overall geometry of the complex is reminiscent of the structure of basic chromium acetate.[7] The major difference is the replacement of the oxo ligand in the center of the metal triangle by the two ethanolato groups with a Mo-O(Eto) distance of 2.067 (5) Å. The β-carbon atoms of the ethanolato ligand could not be observed because of disorder; however, the presence of this ligand was established unequivocally by high resolution mass spectrometry.

The structure described here revealed an interesting feature of the reaction between molybdenum hexacarbonyl and acetic acid. The ethanolato ligand could be formed only by the reduction of acetic acid. Thus the oxidation of $Mo(CO)_6$ was carried out at least in part by the acetic acid/ethanol couple and not exclusively by the H^+/H_2 couple as suggested by Holste and Schaefer.[2]

Of particular interest in this structure is the electronic structure of the molybdenum trimer. The 2+ charge of the complex necessitates a nonintegral oxidation number for the metal atoms. Formally, we can assume that two of the metal atoms are in the 3+ oxidation state and one in the 4+ oxidation state. However, the crystallographic data clearly suggest that the three metal atoms are equivalent and therefore, a better description would be an average oxidation state of 3.33 with eight electrons involved in the Mo-Mo bonding. On the basis of Cotton's MO results for metal clusters[8] it is reasonable to suggest that two electrons occupy antibonding orbitals resulting in a Mo-Mo bond order of $\frac{2}{3}$, in agreement with the observed Mo-Mo distance of 2.854 (2) Å. This is also in agreement with Cotton's suggestion[9] that the average Mo-Mo distance of 2.76 Å in Mo_3Se_4[10] is consistent with a bond order of $\frac{5}{6}$.

The aqueous solution of the red ion II is reduced by a Jones reductor to the original green-brown ion I. The fact that the oxidation of I to II is reversible in solutions which do not contain any free acetate or ethanol indicates that the two ions may have the same coordination sphere, which remains intact during the redox reactions. The two species may differ from each other by the oxidation state of the molybdenum triangle. The lowering of the ionic charge from 2+ to 1+ upon reduction of the red ion II to the green-brown ion supports the view that all three molybdenum atoms in the green-brown ion are in the 3+ oxidation state; i.e., that its structure is $Mo_3(OAc)_6(C_2H_5O)_2(H_2O)_3^+$.

Another interesting property of the red ion II is its slow decomposition in aqueous solution. After several hours at room temperature the red solution of II turned green-brown. Ion exchange chromatography of this green-brown solution revealed that it contained the ion I and a new red ion III with absorption maxima at 508 and 420 nm (sh) and an ionic charge greater than 2+, probably 3+. This result indicated that the red ion II underwent a disproportionation reaction in solution to a lower oxidation state (I) and a higher oxidation state (III). We are at present engaged in crystallization of salts of I and III for structural determination. The chemistry of these species in solution will also be investigated further.

Preliminary experiments indicate that tungsten hexacarbonyl reacts with acetic acid to form species which may be related to those obtained with $Mo(CO)_6$.

Acknowledgment. The authors thank Professor F. A. Cotton for very helpful discussions.

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(3) Calcd: Mo, 26.56; C, 19.92; S, 5.90; H, 3.13. Found: Mo, 26.76; C, 20.76, S, 5.88; H, 2.89.
(4) Calcd for $Mo_3(OAc)_6(CH_3CH_2O)_2(H_2O)_5(C_7H_7SO_3)_2$: Mo, 24.74; C, 30.92; S, 5.49; H, 4.46. Found: Mo, 24.80; C, 30.96; S, 5.41; H, 4.55. The per-

chlorate is explosive.

(5) The crystal is monoclinic, a = 15.210 (5) Å, b = 11.637 (5) Å, c = 19.069 (5) Å, β = 109.30 (5)°, space group $C_{2/c}$, Z = 4. Independent reflections (1500) with $F_o > 3\sigma(F_o)$ were used in the structure solution and refinement. The structure was solved by the heavy atom method. Least-squares refinement converged to a discrepancy of 0.09.

(6) Full details of the x-ray structure determination will be included in a subsequent publication.

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The [6 + 4] Cycloadditions of Diethylaminobutadiene to Fulvenes. A New Synthesis of Azulenes

Sir:

Fulvenes can undergo concerted cycloadditions to dienes as 6π or as 2π addends.[1-3] We have previously rationalized variations in periselectivity of cycloadditions to fulvenes by an application of frontier molecular orbital theory.[4] The argument follows from considerations of the coefficients of the HOMO and LUMO of fulvene, represented in Figure 1. The reactions of relatively electron-deficient 4π electron systems occur across the C-1,C-2 alkene moiety because of the high frontier density in these positions and the node through the exocyclic position. Only strongly electron-donating substituents at C-6 raise the second highest occupied MO sufficiently to afford reactions of fulvenes as trienes with electron-deficient 4π systems.[4,5] Thus, alkyl or aryl fulvenes react as 2π dienophiles or dipolarophiles with most dienes and 1,3-dipoles, respectively.[4] The LUMO of fulvene is more heavily centered at C-6 and C-1, so that sufficiently electron-rich 4π species were predicted to react across the 1 and 6 positions of fulvene, with the more nucleophilic atom of the diene or 1,3-dipole becoming attached to C-6 of fulvene.[4] Diazoalkanes[3] and azomethine ylides[6] are the only 1,3-dipoles which have been investigated that are sufficiently electron-rich to add in a [6 + 4] fashion to fulvenes. Tropone, the first molecule observed to cycloadd across the fulvene 6π system, apparently does so because of ideal secondary orbital interactions.[1,6] On the basis of these considerations, we predicted that electron-rich dienes would add in a [6 + 4] fashion to fulvenes.[4] We wish to report a confirmation of this prediction, and a new synthetic route to azulenes.

A 1:3 mixture of 1-diethylaminobutadiene and dimethylfulvene became dark red after 2 days at room temperature. Evaporation of excess dimethylfulvene, treatment with MeI to remove amines, and chromatography on silica gel (cyclohexane) gave a 65% yield of deep orange **1a** (Scheme I) resulting from loss of diethylamine from a 1:1 adduct. This adduct could be purified by short path distillation (36-37 °C/0.05 mm). The NMR spectrum of **1a** ($CDCl_3$) has a sharp singlet at δ 1.10 due to the protons of methyl groups attached to a saturated carbon, a doublet at δ 2.25 (J = 5.0 Hz) due to two allylic protons,[7] and a complex multiplet at δ 5.8 to 6.5 due to six olefinic protons. The ultraviolet spectrum of **1a** ($\lambda_{max}^{cyclohexane}$ 317 nm, log ε 4.10) is very similar to that of alkyl substituted vinylfulvenes (e.g., 6-propenylfulvene, $\lambda_{max}^{cyclohexane}$ 317 nm, log ε 4.31).[8]

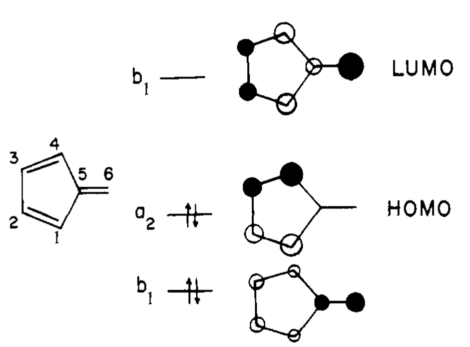

Figure 1. The frontier molecular orbitals of fulvene.

The reaction of **1a** with dimethyl acetylenedicarboxylate (DMAD) provided further evidence for the identity of the carbon skeleton in **1a**. Heating **1a** and DMAD in CCl_4 at 80 °C for 24 h gave, after chromatographic purification, a 79% yield of a white crystalline solid, mp 62-63 °C. The Diels-Alder adduct proved to be an inseparable mixture of conformational isomers, **2** and **2′**. The NMR spectra of this adduct (Figure 2) indicated the presence of two isomers in a ratio of about 2:1. Thus, in $CDCl_3$, methyl singlets at δ 1.00 and 1.17 were twice as intense as those at δ 1.09 and 1.35. A complex pattern at δ 1.6-2.05 and at 2.4-3.0 can be attributed to overlapping multiplets due to the methylene protons in each isomer. Two methoxyl singlets overlapped at δ 3.72, and methoxyl resonances at δ 3.81 and 3.82 were also observed. The bridgehead protons in both adducts accidentally have the same chemical shift and appear as a doublet of doublets at δ 4.11 (J = 3.2 and 1.1 Hz), coupled to the olefinic protons on the norbornadiene moiety. In the major isomer, these appeared as a pair of doublets of doublets at δ 6.82 (J = 5.5, 1.1 Hz) and 7.06 (J = 5.5, 3.2 Hz). These couplings were confirmed by double resonance experiments. The three cycloheptadiene vinyl protons appeared as partially resolved multiplets centered at δ 4.85 (one proton from each isomer) and 5.6 (two protons from each isomer). In C_6D_6, the four high-field methyl singlets changed position, those due to the major isomer now appearing at δ 0.98

Scheme I