Illustrated by combining a "wolf and lamb" reaction, as described above, with a third polymeric reagent, situated in a different vessel. The reaction is described in Scheme VI.

The product of the "wolf and lamb" acylation of acetophenone, dibenzoylmethane anion, was passed without isolation into Amberlyst 15 resin (a macroporous sulfonic acid resin) loaded with hydrazine. A 91% yield of 3,5-diphenylpyrazole (based on acetophenone) was obtained upon filtration of the latter polymer.

Other examples of multipolymer reactions, using additional advantages of these reactions, are being studied at present.

Acknowledgment. The authors wish to thank the Camille and Henry Dreyfus Foundation for financial support.

References and Notes
(1) Dedicated to Professor R. B. Woodward on the occasion of his 60th birthday.
(9) Isaiah 11:6, "And the wolf shall dwell with the lamb. . . ."
(11) Macroreticular XE-305 "Rohm and Haas" polystyrene was used. The commercial polymer was ground to particles of 100-150 mesh size.

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Protonated Cycloocta[def]fluorenone Dication. A New 14π-Electron Aromatic System

Sir:

The validity of Huckel's (4n + 2) π electron rule for aromaticity has been extensively tested during the past 20 years. Early attempts to prepare the cyclooctatetraenylum dication (1) failed, and only very recently has Olah succeeded in oxidizing 1,3,5,7-tetramethylcyclooctatetraene, related protonated cycloocta[def]fluorenone dication 2 (vide supra), a benzannelated derivative of 1 which is stable at room temperature. The formation of 2 is not accompanied by the formation of any discernible amount of a homotropilium type cation.

Oxidation of cycloocta[def]fluorene with oxygen in the presence of "Triton B" or in air in the presence of KOH and 18-crown-6 afforded after chromatography 3 (90% yield, mp 126 °C), 4 the maximum eigenvalue (cm⁻¹) 1710 (C=O stretching); m/e 231 (M + 1, 19%), 230 (M, 74%), 202 (M - CO, 100%); λmax (ethyl alcohol) 194 (e 42 000), 295 (12 000), 350 (s) (1050), 430 nm (640); λmax [B] 34.6 267 (e 20 000), 300 (s) (7200), 415 (6200), 500 (s) (1000) with tailing to longer wavelengths. 1H NMR (CDCl₃): δ (ppm) 5.79 (s, 4 H, H₂-H₄), 6.90-7.44 (m, 6 H, H₃-H₆ and H₈-H₉). Treatment of 3 at -40 °C with "magic acid" (1:1 M FSO₃H-HBF₄) in SO₂ produced 5, 1H NMR, δ (ppm) 7.12 (m, 2 H, aromatic), 7.32 (t, 2 H, aromatic), 7.52 (t, 2 H, aromatic), 8.08 (s) (1 H, OH). Oxidation to the dication occurred upon elevating the temperature to +31 °C and the following 1H NMR was observed: δ (ppm) 7.59 (dd, 2 H, J₁ = 7.0, J₂ = 4.0 Hz, H₂, H₃), 8.1 (m, 4 H, aromatic), 8.58 (s,

\[ R = \text{H, CH}_3 \]

δ (ppm) 5.23 (d, 1 H, J = 8.0 Hz, H₄), 5.60 (d, 1 H, J = 6.0 Hz, H₅), 6.34 (dd, 1 H, J₁ = 11.0, J₂ = 8.0 Hz, H₆), 6.76 (dd, 1 H, J₁ = 11.0, J₂ = 6.0 Hz, H₇), 7.31-7.90 (m, 5 H, aromatic), 12.86 (s, 1 H, OH). The spectrum of this species has been assigned to 4, formed by the protonation of the carbonyl group of 3. It should be noted that the vinlylic protons H₄-H₅ exhibit an ABCD pattern. The validity of Huckel's (4n + 2) π electron rule for aromaticity has been extensively tested during the past 20 years. Early attempts to prepare the cyclooctatetraenylum dication (1) failed, and only very recently has Olah succeeded in oxidizing 1,3,5,7-tetramethylcyclooctatetraene, thus obtaining the diatropic aromatic dication (1 R = CH₃). One of the difficulties in obtaining 1 is the ready formation of the stable homotropilium ion. We wish to report the preparation and characterization of the protonated cycloocta[def]fluorenone dication 2 (vide supra), a benzannelated derivative of 1 which is stable at room temperature. The formation of 2 is not accompanied by the formation of any discernible amount of a homotropilium type cation.

Oxidation of cycloocta[def]fluorene with oxygen in the presence of "Triton B" or in air in the presence of KOH and 18-crown-6 afforded after chromatography 3 (90% yield, mp 126 °C), 4 the maximum eigenvalue (cm⁻¹) 1710 (C=O stretching); m/e 231 (M + 1, 19%), 230 (M, 74%), 202 (M - CO, 100%); λmax (ethyl alcohol) 194 (e 42 000), 295 (12 000), 350 (s) (1050), 430 nm (640); λmax [B] 34.6 267 (e 20 000), 300 (s) (7200), 415 (6200), 500 (s) (1000) with tailing to longer wavelengths. 1H NMR (CDCl₃): δ (ppm) 5.79 (s, 4 H, H₂-H₄), 6.90-7.44 (m, 6 H, H₃-H₆ and H₈-H₉). Treatment of 3 at -40 °C with "magic acid" (1:1 M FSO₃H-HBF₄) in SO₂ produced 5, 1H NMR, δ (ppm) 7.12 (m, 2 H, aromatic), 7.32 (t, 2 H, aromatic), 7.52 (t, 2 H, aromatic), 8.08 (s) (1 H, OH). Oxidation to the dication occurred upon elevating the temperature to +31 °C and the following 1H NMR was observed: δ (ppm) 7.59 (dd, 2 H, J₁ = 7.0, J₂ = 4.0 Hz, H₂, H₃), 8.1 (m, 4 H, aromatic), 8.58 (s,
Molybdenum Complexes of Aliphatic Thiois. Isolation and Characterization of Two Isomeric Forms of the Redox Active Binuclear Mo(V) Anion, [Mo$_2$S$_4$(S$_2$C$_2$H$_4$)$_2$]$^2^-$

Sir:

Research on the coordination chemistry of molybdenum–sulfur compounds has been stimulated by evidence that oxidation–reduction reactions which are catalyzed by molybdoenzymes occur at sites where the molybdenum is coordinated by one or more S atoms.\(^1\) A variety of reactions are now known to produce stable diamagnetic binuclear di-$\mu$-sulfido bridged Mo(V) species in which each Mo atom is also strongly bound to a terminal oxo or sulfido group.\(^2\) As emphasized previously,\(^3\) additional ligands lead to pseudotetragonal coordination geometry about each Mo atom. Two structures (A and B) are possible for two tetragonal pyramids sharing a basal edge.

Structure A has a bent Mo$_2$S$_2$ moiety with a dihedral angle between the two Mo$_2$ planes of $\sim$150$^\circ$; structure B has a planar Mo$_2$S$_2$ moiety.\(^4\) Several compounds of structure A with $Y = S$ or O are known,\(^2,3,5\) and three cyclopentadienyl derivatives related to B ($Y = O, S,^7$ and NC(CH$_3$)$_3)^8$ have been reported. However, there is no prior example of structures A and B both being observed with the same ligands. Herein we describe redox active binuclear Mo(V) complexes of both geometries with $Y = S$ and one 1,2-dimercaptoethanato (dme) ligand per Mo.

Reflexing mixtures of MoC$_3$, NaHS, NaOCH$_3$, and 1,2-dimercaptoethane in anhydrous oxygen-free methanol produces intractable black solids and dark red solutions. Two forms of diamagnetic crystals of what proved to be tetrathialammonium di-$\mu$-sulfido(bisulfido-1,2-dimercaptoethanato)molybdate(V)\(^-,\) [N(C$_2$H$_5$)$_4$][Mo$_2$S$_4$(S$_2$C$_2$H$_4$)$_2$], have been isolated from the intensely colored filtrates by adding a 1:2:2:2 molar ratio of the refluxed reagents, and form 3 as small red-violet rhombohedral plates from a 1:1:3:2:2:2.5 ratio of reagents. The yields of both reactions are low, 6 and 3%, respectively.\(^9\) Infrared spectra of the two samples (KBr) are identical, \(1470, 1433, 1360, 1260, 1100, 880, 760, 720, 640, 600, 460, 440, 340, 310, 260, 240, 220, 180, 160, 140, 120, 100, 80, 60, 40, 30, 20, \) cm$^{-1}$.

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References and Notes

(1) E. Huckel, Z. Phys., 70, 204 (1931).
(3) G. A. Olah, J. S. Staral, and L. A. Paquette, J. Am. Chem. Soc., 98, 1267 (1976). Upon warming of \(1 (R = CH_3)\) Isomerization to a bicyclic dication was observed. The formation of \(1 (R = CH_4)\) is accompanied by varying amounts of the corresponding homopropylion ion.
(5) All new compounds gave satisfactory C, H analyses.
(6) The $^1$H NMR spectra were recorded at 10 MHz in SO$_2$-d$_7$-magic acid. A Mo$_2$Si$_4$ capillary was used for looking the instrument. Depcoupling experiments assisted the assignments and were carried out on a Model 4204 A Hewlett Packard oscillator. The $^1$C NMR spectra were recorded at 20 MHz on a Varian CFT-20 spectrometer. Acetone-d$_6$ was used for locking and as a reference.
(8) Prepared from 4,5-methylphenylmethane.
(9) The $^1$C NMR spectrum of 5 showed 15 bands pointing to a nonsymmetrical configuration while 6 showed only 8 bands. A total downfield shift of 62 ppm was observed in agreement with a doubly charged species.

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