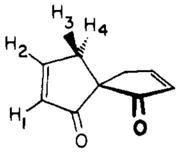
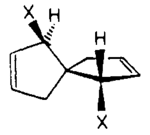
chloride during 1 hr at 25° to give, after hydrolysis with aqueous ammonium chloride, spiro[4.4]nona-2,6-diene-1,5-dione (**12**) in 51% yield:[7,8] mp 110.5–112° (crystals from benzene and sublimed); ^{1}H nmr ($CDCl_3$) each proton appeared as a doublet of triplets, δ 6.13 (H_1, J_{12} = 6.0 Hz, J_{13} = 2.5 Hz, J_{14} = 2.5 Hz), 7.85 (H_2, J_{23} = 2.6 Hz, J_{24} = 2.6 Hz), 3.09 (H_3, J_{34} = 18 Hz), and 2.58 (H_4); ir ($CHCl_3$) 1724 (s), 1696 (s), 1601 (m) cm^{-1}; uv max (ethanol) 220 nm (ϵ 20,100), 313 (103); mass spectral molecular weight, 148. Reduction of **12** with aluminum hydride[9] afforded the diol **13** (30%, mp 127–129°)[10] which was treated with thionyl chloride and pyridine in tetrahydrofuran at 0° for 15 min to produce (short-path distillation) a mixture of dichlorides (*e.g.*, **14**) which was used directly. To a solution of the dichloride mixture in tetraethylene glycol dimethyl ether at 25° was added potassium *tert*-butoxide (solid, 100% excess). The system was immediately evacuated (0.1 Torr) with a trap cooled to −196° between the reaction mixture and the pump. Over a period of 2.0 hr, a mixture of spiro[4.4]nonatetraene (**1**) and *tert*-butyl alcohol collected in the trap. The hydrocarbon was isolated by glpc (3 ft × 0.375 in. column, 10% DC 200 on Chromosorb Z at 75°) in an overall yield from **13** of *ca.* 15%. The ^{1}H nmr spectrum ($CDCl_3$) showed a pair of symmetrical, mirror-image related multiplets of equal area (δ 5.75 and 6.56): mass spectral molecular weight 116 (the fragmentation pattern is superimposable with that of indene); ir (neat) 3.24 (w), 5.43 (w), 6.01 (m), 6.55 (s), 7.82 (m), 9.38 (s), 9.60 (s), 10.30 (s), 12.21 (s) cm^{-1}.



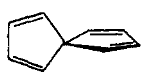
12



13, X = OH

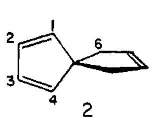
14, X = Cl

The most interesting spectral data for **1** are the uv maxima and extinction coefficients compared with those of **2** and spiro[4.4]nona-1,3-diene (**15**).[11] Both of the latter compounds show uv max 254 nm (ϵ 2750 for **2**, 2250 for **15**),[3b,11] whereas tetraene **1** has uv max 276 nm (ϵ 1120) and 218 (5350). The red shift and low extinction coefficient for the lowest energy transition of **1** compared to **2** and **15** is in accord with predictions of spiroconjugative effects in **1**.[1] The difference in energy for the transitions giving rise to the 276- and 218-nm bands may indicate the energy separation (*ca.* 27 kcal/mol) of the highest bonding levels in **1** due to interaction across the spiro carbon atom;[1] photoelectron spectroscopy should provide a definitive measure.



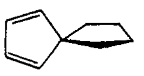
1

276 nm (1120),
218 nm (5350)



2

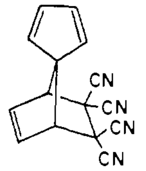
254 nm
(2750)



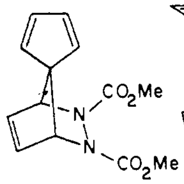
15

254 nm
(2250)

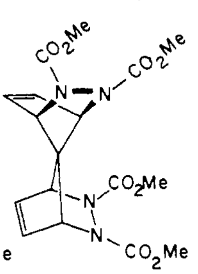
With excess tetracyanoethylene at 25° in chloroform, tetraene **1** reacts rapidly to form a monoadduct **16**; under similar conditions, dimethyl azodicarboxylate leads to a monoadduct **17**, and, at higher temperature, the diadduct **18**. Monoadduct **17** has been prepared independently by reaction of dimethyl azodicarboxylate and **2** followed by allylic bromination (*N*-bromosuccinimide) and base-promoted dehydrohalogenation.



16



17



18

Preliminary studies of the thermal stability of **1** indicate that rearrangement occurs (half-life: 66 min at 65°, in carbon tetrachloride) to give indene (67%) and a mixture of high molecular weight products. In contrast, the triene **2** shows no change after 8 hr at 67° in solution and rearranges only at elevated temperatures (>280°) in the gas phase.[12,13]

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[7] Most new compounds reported here (**1**, **6**, **8**, **11**, **12**, **13**, **16**, **17**, and **18**) show analytical and spectral data completely in accord with the proposed structures; intermediates **7**, **9**, **10**, and **14** have been obtained in *ca.* 95% purity and are identified from spectral data.

[8] We wish to acknowledge the valuable suggestions of Professor C. A. Brown (Cornell University) concerning this reaction.

[9] H. C. Brown and H. M. Hess, *J. Org. Chem.*, **34**, 2206 (1969).

[10] The single isomer which was obtained is assigned structure **13** based on the ^{1}H nmr spectrum. The assignment is tentative and will be discussed more fully in the article describing this work.

[11] C. F. Wilcox, Jr., and R. R. Craig, *J. Amer. Chem. Soc.*, **83**, 3866 (1961).

[12] M. Jones, Jr., R. N. Hochman, and J. D. Walton, *Tetrahedron Lett.*, 2617 (1970).

[13] Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Sun Oil Company for financial support of this work. We also thank Mr. J. Nunberg for technical assistance.

[14] National Science Foundation Undergraduate Research Participant, 1971.

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Received August 21, 1972

Photosolvation of Benzene. Mechanism of Formation of Bicyclo[3.1.0]hex-3-en-2-yl and of Bicyclo[3.1.0]hex-2-en-6-yl Derivatives[1]

Sir:

Photolysis of benzene in acidic hydroxylic solvents is known to yield *exo-* and *endo*-bicyclo[3.1.0]hex-3-en-2-yl derivatives **1** and **2** and -bicyclo[3.1.0]hex-2-en-6-yl derivatives **3** and **4**, respectively. Trifluoroethyl ethers[2] **1a** and **4a**, methyl ethers[2,3] **1b**, **3b**, and **4b**, acetates[4,5] **1c**–**4c**, and alcohols[4,5] **1d** and **2d** have been reported. Permissive evidence for formation of **1d**,[5,6]

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

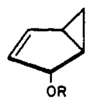
[2] L. Kaplan, J. S. Ritscher, and K. E. Wilzbach, *J. Amer. Chem. Soc.*, **88**, 2881 (1966).

[3] K. E. Wilzbach, J. S. Ritscher, and L. Kaplan, *ibid.*, **89**, 1031 (1967); **90**, 2732 (1968).

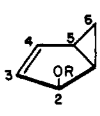
[4] E. Farenhorst and A. F. Bickel, *Tetrahedron Lett.*, 5911 (1966).

[5] (a) J. A. Berson and N. M. Hasty, Jr., *J. Amer. Chem. Soc.*, **93**, 1549 (1971); (b) N. M. Hasty, Jr., Ph.D. Thesis, University of Wisconsin, 1970.

[6] T. J. Katz, E. J. Wang, and N. Acton, *J. Amer. Chem. Soc.*, **93**, 3782 (1971).



1



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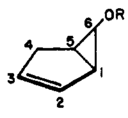
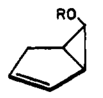


3

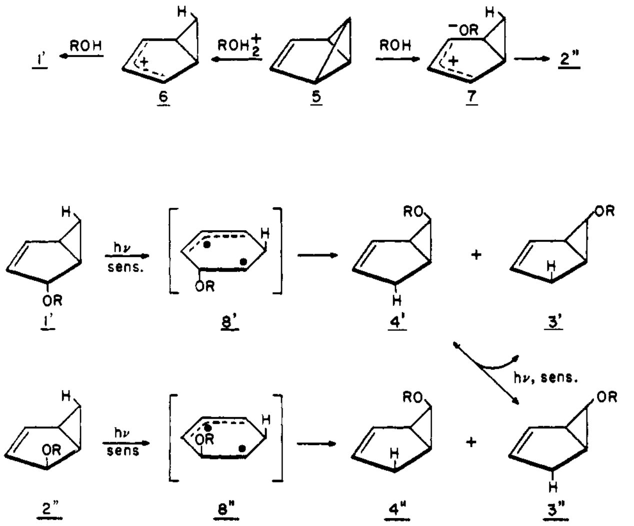


4

	R
a	CH_2CF_3
b	Me
c	Ac
d	H

1b^3, and, deceptively, **4b**^{3,7} by solvation of benzvalene **5** has appeared, but the course of solvation is obscured by epimerization^5 and an alternative pathway^8 has not been excluded. We now wish to report that photoadducts **1** and **2** are formed exclusively by solvation of **5**, in proportions which depend on the acidity and polarity of the solvent, and that adducts **3** and **4** are formed by sensitized vinylcyclopropane rearrangements of **1** and **2** (Scheme I).

Scheme I



Adducts **1–4** have now been isolated (gc^9) and identified (nmr^{10}) from photoadditions^{12} in CF_3CH_2OH and MeOH (with 0.1% HCl) as well as in HOAc.^{5b}. Making use of the highly stereoselective incorporation of solvent H at C-6^{5,6} in 2-yl adducts (established^{10} by photoadditions in benzene-d_5 to be ≥95% endo in the ethers), we have irradiated^{12} benzene-*1,3,5*-d_3 in both alcohols to determine the extent and manner of formation of **1** and **2** from **5**. If they were formed without intervention of **5**,^{8} the benzene-derived exo H at C-6 would appear only as a doublet (J_{gem} = 4 Hz). If formed from **5**, *one-half* of the molecules with exo H at C-6 would also have H at C-5 (or C-1) and show an additional coupling (J_{vic} = 8 Hz); the combination of doublet and doublet of doublets would appear as a pseudo-quartet, with close to 0.25 of total area in the outer wings. Observation of such quartets in the D-decoupled 100-MHz spectra of **1a**, **1b**, and **2a** (fractional area in outer wings determined^{13} to be 0.26, 0.24, and 0.27, respectively) indicates that each is derived entirely from **5**.^{14} If **1** or **2** were formed by addition of ROH across a cyclopropyl bond of **5**, one-half of the molecules with H at C-2 would have H at C-1; if C-2 and C-4 became indistinguishable prior to addition of OR, as in bicyclohexenyl cations **6** or **7**, only one-fourth would have H at C-1. The observation that 0.23 and 0.21 of the C-2 resonance areas in **1b** and **2a** appeared^{13} as the appropriate doublets (J = 2.6 and 6.5 Hz, respectively) indicates that equilibration of C-2 and C-4 occurred in both.

Benzene solutions of **5** were added to (20-fold volumes) of CF_3CH_2OH, MeOH with 0.1% HCl, HOAc, and (with shaking) 0.01 N H_2SO_4, and the products^{15} were analyzed by gc–mass spectrometry on several columns. In each case a major and a minor adduct having retentions^9 identical with those of **1** and **2**, respectively, were observed; neither **3** nor **4** was detected.^{9} Values of **2**:**1** were 0.35, 0.06, 0.5, and 0.02 for **a–d**, respectively (*cf.* photoadditions^{12}). The low ratio for **b** and the appreciably higher ratio for **a**, together with isotopic results indicating equilibration of C-2 and C-4 in both **1b** and **2a**, suggest that in the presence of strong acid **5** forms the "free" bicyclohexenyl cation **6** (for which **2b**:**1b** < 0.1^5), and that in less acidic media it can also form a captive ion **7** in which OR adds endo to C-2 and C-4. With decrease in concentration or acidity of ROH, predominant endo addition has been observed: 75% in a 1.5% solution of CF_3CH_2OH in isohexane; 60 and 75% in 10% solutions of HOAc in isohexane and ether, respectively.

Formation of **3** and **4** in benzene-sensitized photolyses of isolated 2-yl ethers and acetates was established by gc and nmr. Periodic gc^9 analysis of 254-nm irradiations in isohexane containing 5% benzene indicated that in each case **4** and **3** were formed in the same proportions from **1** or **2** (without interconversion of the latter), and that initially high ratios of **4** to **3** decreased to limiting values as **1** or **2** approached zero. Initial and final **4**:**3** ratios were (**a**) 7, 4; (**b**) 3.8, 1.1; (**c**) 5.5, 3.1. These results imply that a common precursor is (irreversibly) formed in the vinylcyclopropane rearrangement of **1** and **2**, and that **3** and **4** undergo sensitized epimerization.

The mechanisms of these transformations were investigated with stereoselectively labeled ethers isolated from photoadditions^{12} to benzene-d_6, determining the stereochemistry of H in reactants and products by nmr^{10} (and yields by gc). Vinylcyclopropane rearrangements of **1a**-d_6 and **2a**-d_6 are summarized by the following equations, in which H and OR are trans on

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(7) We now know that retentions of the minor methanolysis product of **5** correspond to **2b**, a then unknown photoadduct present in **4b**, but undetected by gc.

(8) D. Bryce-Smith, A. Gilbert, and H. C. Longuet-Higgins, *Chem. Commun.*, 240 (1967).

(9) Relative to anisole on Carbowax 20M at 100°, retentions of **1–4** are (**a**) 0.52, 0.45, 0.39, 0.39; (**b**) 0.41, 0.33, 0.28, 0.32; (**c**) 1.99, 1.64, 1.78, 1.89; (**d**) 1.71, 2.06, . . . , ... Relative to **1a** on DDP-Bentone 34 at 100° retentions of **2–4a** are 0.67, 0.56, 0.73. Relative to **1b**, retentions of **2–4b** are 0.75, 0.60, 0.60 on QF-1 at 25°; 0.53, 0.35, 1.0 on $AgNO_3$-glycerol at 40°.

(10) Resonances for C-1 to C-6 in corresponding ethers are very similar. Those in **1a** and **4a** have been reported.^{2} Those (δ, CCl_4) in **2b** and **3b** are 1.78, 4.69, 5.19, 5.92, 1.57, 0.6 (exo), 0.5 (endo), and 1.95, 5.37, 5.69, 2.51 (exo), 2.28 (endo), 1.62, 2.33, respectively. In **2a** protons at C-6 are better resolved in benzene (exo δ 0.45, endo δ 0.65). In **3–4b**, and in **3–4a**, lower field protons at C-4 exhibited $J_{4,5}$ = 6–7 Hz and were assigned^{11} exo. We thank Mrs. Gail Ryan and Mrs. Geraldine McDonald for nmr analyses.

(11) H. Prinzbach and E. Druckrey, *Tetrahedron Lett.*, 2959 (1965).

(12) Yields of **2–4** relative to **1** vary with time and benzene concentration; those in 1% benzene solutions (2 cm × 10 cm × 1 cm quartz cell, G8T5 mercury lamp, 12 hr) were (**a**) 0.34, 0.05, 0.30; (**b**) 0.03, 0.26, 0.63; (**c**) 0.5, 0.21, 0.86.

(13) Using a Du Pont 310 curve resolver.

(14) In neutral CF_3CH_2OH, **1a** $\not\rightleftharpoons$ **1b**; in acidic MeOH, **1b** slowly epimerizes to 5% **2b**.

(15) Extracted into ether or isohexane from aqueous acid after 5 min and from organic solvents after 15 min. None of the adducts epimerizes significantly under these conditions.

the six-membered rings in **1′–4′** and cis in **1″–4″** (*cf.* Scheme I).

$$\mathbf{1}\,(\mathbf{1}:\mathbf{1}'' = 19) \xrightarrow[\text{sens}]{h\nu} 7\%\ \mathbf{4}\,(\mathbf{4}':\mathbf{4}'' = 9) + 1\%\ \mathbf{3}\,(\mathbf{3}':\mathbf{3}'' \simeq 3) + \mathbf{1}\,(\mathbf{1}:\mathbf{1}'' = 19)$$

$$\mathbf{2}\,(\mathbf{2}'':\mathbf{2}' = 24) \xrightarrow[\text{sens}]{h\nu} 12\%\ \mathbf{4}\,(\mathbf{4}'':\mathbf{4}' = 10) + 2\%\ \mathbf{3}\,(\mathbf{3}'' > \mathbf{3}') + \mathbf{2}\,(\mathbf{2}'':\mathbf{2}' = 24)$$

The high retention of stereochemical relationships between H and OR in **1** (or **2**) → **4** and the unchanged stereopurity of **1** and **2** at C-6 indicate that rupture of the 1,5 bond in **1** or **2**, yielding planar **8**, occurs exclusively, or almost so; occurrence of some **4** → **3** probably accounts for the lower retention in **3**. Epimerization of **4b**-d_6 is similarly summarized

$$\mathbf{4}\,(83\%\ \mathbf{4}') \xrightarrow[\text{sens}]{h\nu} 25\%\ \mathbf{3}\,(67\%\ \mathbf{3}'') + \mathbf{4}\,(75\%\ \mathbf{4}')$$

The predominance of exo H in **3** indicates that **4b** → **3b**, like related epimerizations,[16,17] occurs largely by 1,6 bond rupture; increased endo H implies that **4b** ⇌ **3b** also occurs by 1,5 bond rupture.

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[16] D. L. Garin and D. J. Cooke, *J. Chem. Soc., Chem. Commun.*, 33 (1972).

[17] H. E. Zimmerman and G. A. Epling, *J. Amer. Chem. Soc.*, **94**, 3647 (1972).

[18] Argonne Faculty Research Participant.

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Received June 29, 1972

Reactions of Oxobis(*N*,*N*-dialkyldithiocarbamato)molybdenum(IV) with Unsaturated Organic Molecules and Their Biochemical Implications

Sir:

The similarity in patterns of reactivity of certain transition metals in particular oxidation states and very reactive organic species has recently been recognized.[1,2] This analogy, together with the suggestion that d^2 metal systems may act like carbenes[3–5] and the possible role of molybdenum in redox-active enzymes, has led us to examine the reactivity of pentacoordinate oxobis(*N*,*N*-dialkyldithiocarbamato)molybdenum(IV), MoO(S$_2$CNR$_2$)$_2$.

On mixing equimolar *dry* benzene solutions of oxobis(*N*,*N*-diethyldithiocarbamato)molybdenum(IV),[6,7] **1**, and diethyl azodicarboxylate, **2**, under argon, an intense purple color[8–10] developed immediately which changed to yellow (first-order reaction, half-life at 25° *ca.* 50 sec). A yellow compound, **3**, was precipitated with ether from concentrated mixtures and recrystallized from dichloromethane–hexane (mp 105–108° dec). Identical electronic spectra were obtained for pure **3** ($\lambda_{\max}$ 390 nm, ϵ 4 × 10^3 cm^2/mol; $\lambda_{\min}$ 348 nm, ϵ 3.25 × 10^3 cm^2/mol) and the reaction mixture after the color change was complete, signifying a quantitative reaction.

Analysis of **3** indicates a 1:1 adduct of **1** and **2**. It is diamagnetic (nmr). The ir spectrum of **3** shows both an oxomolybdenum(VI) moiety[11] and a coordinated azo group (ν(C=O) at 1705 cm^{-1}).[12] Similar 1:1 adducts have been prepared previously[13] with chlorocarbonylbis(triphenylphosphine)iridium(I) and tetrakis(triphenylphosphine)platinum(0). These latter reactions were postulated as oxidative additions to the metal complexes yielding adducts containing symmetrically bound substrates. Our similar spectral data suggest **3** is formally seven-coordinate molybdenum(VI) produced by oxidative addition of the azo linkage to molybdenum(IV).

Similar reactions of oxobis(*N*,*N*-dimethyldithiocarbamato)molybdenum(IV), **4**, gave crystalline products with: diethyl azodicarboxylate, **5**; dimethyl acetylenedicarboxylate, **6**; and tetracyanoethylene, **7**. The tetracyanoethylene adduct, **8**, of **1** was also prepared. Analysis and ir spectra (Table I) are consistent with **5**, **6**, **7**, and **8** being 1:1 adducts containing the substrate bound to molybdenum(VI).

Table I. Infrared Spectral Data (KBr disks, cm^{-1})

Compound no.	ν(Mo=O)	ν(C=O)	ν(C≡C)	ν(C≡N)
3	935 (s)[a]	1705 (s)[a]		
4	975 (s)[b]			
5	933 (s)	1710, 1725 (vs)[c]		
6	938 (s)	1710, 1720 (vs)[d]	1875 (s)	
7	935 (s)			2240 (m)
8	940 (s)			2240 (m)

[a] Chloroform solution. [b] Dichloromethane solution. [c] Broad single band at 1715 cm^{-1} (vs) in chloroform. [d] Broad single band at 1720 cm^{-1} (vs) in chloroform.

Solutions of **3** and **5** are stable when water is excluded. In *moist* chloroform, however, 10^{-2} *M* solutions are completely hydrolyzed in 1–3 hr to form 1,2-bis(ethoxycarbonyl)hydrazine, **9**, and the appropriate[9,10] *cis*-dioxobis(*N*,*N*-dialkyldithiocarbamato)molybdenum(VI), **10** and **11**. The reactions were monitored by ir, nmr, and visible spectroscopy. The stoichiometries were established by quantitative chromatography on alumina (chloroform elution) for **9** and by comparing electronic spectra with authentic samples[9,10] for **10** and **11**. The isolation of **9**, the two-electron reduction product of **2**, from the hydrolysis further supports the oxidative addition of **2** across **1** and **4**.

The low hydrolytic stability of the molybdenum ad-

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[1] J. Halpern, *Chem. Eng. News*, **44**, 68 (Oct 31, 1966).

[2] J. P. Collman, *Accounts Chem. Res.*, **1**, 136 (1968).

[3] M. E. Vol'pin, V. A. Dubovitskii, O. V. Nogina, and D. M. Kursanov, *Dokl. Akad. Nauk SSSR*, **151**, 1100 (1963).

[4] H. H. Brintzinger and L. S. Bartell, *J. Amer. Chem. Soc.*, **92**, 1105 (1970).

[5] J. E. Bercaw, R. H. Marvich, L. G. Bell, and H. H. Brintzinger, *ibid.*, **94**, 1219 (1972), and references therein.

[6] R. N. Jowitt and P. C. H. Mitchell, *J. Chem. Soc. A*, 2632 (1969).

[7] Contrary to ref 6, **1** was readily recrystallized from benzene and found to be diamagnetic (nmr).

[8] The purple color is not due to Mo$_2$O$_3$(S$_2$CNEt$_2$)$_4$[9,10] (by comparing visible spectra).

[9] R. N. Jowitt and P. C. H. Mitchell, *J. Chem. Soc. A*, 1702 (1970).

[10] F. W. Moore and M. L. Larson, *Inorg. Chem.*, **6**, 998 (1967).

[11] The decrease in ν(Mo=O) from 962 cm^{-1} in **1** to 935 cm^{-1} in **3** agrees with the previously observed sequence[9] Mo(IV) > Mo(VI), and supports the proposed increase in formal oxidation state of molybdenum.

[12] **9** has ν(C=O) at 1740 cm^{-1} and **2** ν(C=O) at 1780 cm^{-1} (benzene solution).

[13] M. Green, R. B. L. Osborn, and F G. A. Stone, *J. Chem. Soc. A*, 3083 (1968).