

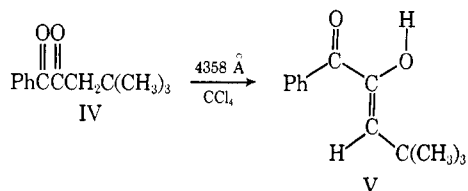
Table I. Photoreactivity of Some 1-Phenyl-1,2-alkanediones at 25° (PhCOCOCH₂R)^a

R	Solvent	Φ_{HCB}^b	$\Phi_{\text{-DK}}^c$	$k_q\tau^d$	$1/\tau,^e$ 10 ⁵ sec ⁻¹	$k_s,^f$ 10 ⁵ sec ⁻¹	$k_d,$ 10 ⁵ sec ⁻¹
I CH ₃	Benzene	0.04	0.23	30,000 ^g	1.7	0.10	1.6
	wet CH ₃ CN	0.06	0.33	53,000 ^g	1.9	0.11	1.8
II CH ₂ CH ₃	Benzene	0.58 ^h	0.63	10,700 ^{h-i}	5.7	3.3	1.4
	wet CH ₃ CN	0.71	0.80	16,800 ⁱ	6.0	4.2	1.8
III CH(CH ₃) ₂	Benzene	0.81 ^{h,k}	0.88	3,400 ^{h-i}	14.7	13.0	1.7
	wet CH ₃ CN	0.88	0.93	6,800 ⁱ	14.7	13.0	1.7
IV C(CH ₃) ₃	Benzene	<0.001	0.62	22,000 ^g	2.3		2.3

^a Irradiated at 3660 Å in sealed degassed tubes. ^b Quantum yield for hydroxycyclobutanone formation, determined relative to benzophenone-piperylene actinometer. All values extrapolated to zero diketone concentration to correct for concentration dependence. ^c Quantum yield for disappearance of 0.05 M diketone. ^d Stern-Volmer quenching slopes with pyrene as quencher. ^e Calculated assuming that $k_q = 5 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ in benzene and $1 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ in acetonitrile. ^f Calculated by multiplying Φ_{HCB} in acetonitrile by $1/\tau$. ^g From phosphorescence quenching, 0.005 M diketone. ^h Same values obtained with 4358-Å radiation. ⁱ From quenching of cyclobutanone formation, extrapolated to zero diketone. ^j Same values observed with anthracene as quencher. ^k 0.82 for benzophenone-sensitized reaction.

the major photoproduct from I is not the cyclobutanone. Although a peak corresponding to the major product does appear under low-temperature vpc conditions, at 200° injector temperature the new product peak is replaced by a peak corresponding to starting α -diketone. Likewise, after 100% disappearance of III, vpc analysis of photosylate regenerates 8% III.

Diketone IV has no hydrogens γ to the 1-carbonyl. Quenching of its phosphorescence indicates that its triplet decay rate is very similar to the k_d values of I-III. Vpc analysis reveals no photoproducts arising either from γ -hydrogen abstraction by the 2-carbonyl or from δ -hydrogen abstraction by the 1-carbonyl. A degassed CCl₄ solution 0.2 M in IV does photobleach very efficiently, however. After complete disappearance of the 405-nm band characteristic of the α -diketone, the solution had the following spectral properties: uv λ_{max} 282 nm ($\epsilon \sim 7000$); ir new absorbances at 3410 (concentration independent), 1670, 1630 cm⁻¹ (no absorbance in 1700-1800-cm⁻¹ region); nmr δ 1.18 (s, 9 H), 5.35 (s, 1 H), 6.55 (s, 1 H) washed out by shaking solution with D₂O, 7.4 (multiplet center, 5 H). In acetonitrile, the photolysate displays two λ_{max} 's, one at 252 nm (ϵ 7000) and one at 279 nm (ϵ 7500). Solutions of the photolysate are stable for days at room temperature, but aqueous acid or base or a 200° vpc injector rapidly regenerate diketone IV. All the observed properties fit the enol structure V as the photoproduct from IV.



Lemaire suggested such a photoenolization of biacetyl 3 years ago⁸ and Bishop and Hamer⁹ have just reported that an aliphatic diketone similar to IV yields a photoproduct with spectral characteristics very similar to those we find. What we consider remarkable is that the process is fast enough to compete with intramolecular hydrogen abstraction in compounds I-III. It is a reasonable assumption that the $k_d \sim 2 \times 10^5 \text{ sec}^{-1}$ represents the same process(es) in all four diketones studied, since they all have the same structure around the chromophore.

(8) J. Lemaire, *J. Phys. Chem.*, **71**, 2653 (1967).

(9) R. Bishop and N. K. Hamer, *J. Chem. Soc. C*, 1197 (1970).

V may well undergo more chemistry than just reversion to IV. When the solvent is removed from the photolysate of IV, the ir absorbances ascribed to V slowly disappear (half-life 15 hr) and are replaced both by those characteristic of IV and by new absorbances, in particular a strong one at 1700 cm⁻¹ and a weaker one at 1740 cm⁻¹. We are studying this problem further.

Finally, we note that the thermal stability of dilute V is not too surprising in light of the known preference for cyclic α -diketones to exist in their enolic form.¹⁰ Probably more important, the uncatalyzed thermal reketonization would require a symmetry-forbidden suprafacial [1,3] sigmatropic shift. Whether the photoenolization can be viewed simply as an allowed [1,3] sigmatropic shift is another question.

Acknowledgment. This work is being supported by grants from the National Science Foundation. It is a pleasure to thank Professor Nicholas Turro for sharing information and ideas about his similar, independent studies.

(10) R. Bakule and F. A. Long, *J. Amer. Chem. Soc.*, **85**, 2309 (1963).

(11) Alfred P. Sloan Fellow, 1968-1970.

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Photochemistry of Some α -Ketopropiophenones. Evidence for an Unusual Cyclic Transition State for Hydrogen Abstraction¹

Sir:

Photoinduced intramolecular hydrogen abstraction reactions of ketones possessing an alkyl side chain are believed to generally proceed *via* six-membered cyclic transition states which lead to biradical intermediates.² Evidence has been produced which leads

(1) Molecular Photochemistry. XXXVI. Paper XXXV: N. J. Turro, J. C. Dalton, G. Farrington, M. Niemczyk, and D. M. Pond, *J. Amer. Chem. Soc.*, **92**, 6978 (1970). The authors wish to thank the Air Force Office of Scientific Research (Grants AFOSR-68-1381 and AFOSR-70-1848) for its generous support of this work.

(2) (a) Exceptions to this rule generally involve seven-membered (or larger) cyclic transition states: see, for example, P. Yates and J. M. Pal, *Chem. Commun.*, 553 (1970); R. Breslow and S. Baldwin, *J. Amer. Chem. Soc.*, **92**, 732 (1970); J. Meinwald and J. W. Kobzina, *ibid.*, **91**, 5177 (1969); N. C. Yang, *React. Photoexcited Org. Mol., Proc. Conf.*

Table I. Photochemical Kinetic Data for Some α -Ketopropiophenones

α -Diketone ^a	Φ_{-K} ^b	Φ_{oy} ^c	$k_q\tau$ ^d	k_r^{\max} ^e	k_r^{\min} ^f
PhCOCOCH ₃ (1H)			1.0×10^8	5.0×10^3	
PhCOCOCD ₃ (1D)			1.1×10^8	4.5×10^3	
PhCOCOCH ₂ CH ₃ (2H)	0.23	0.043	1.9×10^4	2.6×10^6	6.0×10^4
PhCOCOCD ₂ CH ₃ (2D)	0.12	0.052	3.8×10^4	1.3×10^6	1.6×10^4
PhCOCOCH ₂ CH ₂ CH ₃ (3H)	0.45	0.40	7.6×10^3	6.6×10^6	3.0×10^5
PhCOCOCD ₂ CH ₂ CH ₃ (3D)	0.38	0.37	9.0×10^3	5.6×10^6	2.1×10^5
PhCOCOCH ₂ CH(CH ₃) ₂ (4)	0.65	0.60	1.7×10^3	2.9×10^6	1.9×10^6
(+)-(S)-PhCOCOCH ₂ CHCH ₃ (C ₂ H ₅) (5)	0.63		1.7×10^3	2.9×10^6	1.8×10^6

^a α -Diketones **1–5** were prepared by Kornblum's method: N. Kornblum, *J. Amer. Chem. Soc.*, **88**, 865 (1966). The deuterated compounds were prepared by exchange with D₂O–DCl. Nmr analyses indicated the following: **1D**, 60% d₃, 40% d₂; **2D**, 75% d₂, 25% d₁; **3D**, 70% d₂, 30% d₁. Optically active **5** was prepared by Stork's method (G. Stork, *et al.*, *J. Amer. Chem. Soc.*, **85**, 2178 (1963)) employing the optically active tosylate of amyl alcohol. ^b Measured by disappearance of uv of α -diketone at 395 nm. Ferrioxalate employed as comparison actinometer. Solutions 0.06 M benzene for **2** and 0.20 M for others; 10–15% conversion; excitation at 435 nm. ^c Measured by appearance of cyclobutanone by vpc on a 10 ft \times 1/4 in. column packed with 4% QF-1 and 1% Carbowax 20M on Chromosorb G, programmed from 100 to 150° at 6°/min. Other conditions the same as in footnote b. ^d For **1** the $k_q\tau$ values are derived from pyrene quenching of phosphorescence (0.01 M in benzene, excitation at 410 nm). For compounds **2–5**, benzene solutions which were either 0.2 M (excitation at 435 nm) or 0.1 M (excitation at 366 nm) in α -diketone yield the same value of $k_q\tau$ ($\pm 20\%$) as determined by pyrene quenching of either the disappearance of α -diketone (measured by uv) or appearance of cyclobutanone (measured by vpc). The uv analyses were taken to a maximum conversion of 15–20%, and the vpc analyses were taken to a maximum conversion of 5–10%. ^e This value (sec⁻¹) is equal to $1/\tau$, as calculated by assuming k_q for pyrene quenching of **1–5** is 5×10^9 M⁻¹ sec⁻¹ in benzene. ^f This value (sec⁻¹) is equal to $1/\tau$ times Φ_{-K} .

to the conclusion that carbonyl singlet states may undergo stereospecific hydrogen reversal,³ cyclization,⁴ and cleavage.⁵ These results demand that any biradical intermediates produced from ketone singlets cannot possess lifetimes long enough to allow bond rotations to compete with chemical destruction of the singlet biradical. On the other hand, triplet ketones apparently lead to triplet biradicals³ whose lifetimes are sufficiently long to allow for bond rotations to occur and compete effectively with chemical destruction of the biradical intermediate. In an earlier study,⁶ we reported a quantitative investigation of the intramolecular photoreduction of dialkyl α -diketones, in which an α -hydroxycyclobutanone is produced (presumably *via* a cyclic six-membered transition-state hydrogen abstraction followed by cyclization).⁷ Although the rate constants for intramolecular (triplet) photoreduction were found to be considerably smaller than those for the analogous type II photoreactions of dialkyl⁸ or aryl alkyl monoketones,⁹ the relatively long triplet lifetimes¹⁰ of dialkyl α -diketones allow for a relatively efficient reaction when the abstracted hydrogen is secondary or tertiary. It was noted⁶ that formation of the cyclobutanone product *via* abstraction of a primary hydrogen did not proceed with high quantum efficiency.

Table I summarizes the results of a quantitative

Chem., **13th**, 1965, 145 (1967), and references therein. (b) For a recent example of a possible case of a five-membered cyclic transition state see H. J. Roth and M. H. El Raie, *Tetrahedron Lett.*, 2445 (1970). (c) Aqueous solutions of pyruvic acid may also photolyze *via* a cyclic five-membered transition state: P. A. Leermakers and G. F. Vesley, *J. Amer. Chem. Soc.*, **85**, 3776 (1963).

(3) N. C. Yang and S. P. Elliott, *ibid.*, **91**, 7550 (1969).

(4) J. Orban, K. Schaffner, and O. Jeger, *ibid.*, **85**, 3033 (1963); K. H. Schulte-Elte and G. Ohloff, *Tetrahedron Lett.*, 1143 (1964).

(5) This result is strongly implied to occur for ketones by the work of ref 3 and 4, but has only been demonstrated for esters to date: J. E. Gano, *Tetrahedron Lett.*, 2549 (1969).

(6) N. J. Turro and T.-J. Lee, *J. Amer. Chem. Soc.*, **91**, 5651 (1969).

(7) (a) W. H. Urry and D. J. Trecker, *ibid.*, **84**, 118 (1962); W. H. Urry, D. J. Trecker, and D. A. Winey, *Tetrahedron Lett.*, 609 (1962); (b) review of α -diketone photochemistry: M. B. Rubin, *Fortschr. Chem. Forsch.*, **13**, 251 (1969).

(8) F. S. Wettack, G. D. Renkes, M. G. Renkly, N. J. Turro, and J. C. Dalton, *J. Amer. Chem. Soc.*, **92**, 1793 (1970), and references therein.

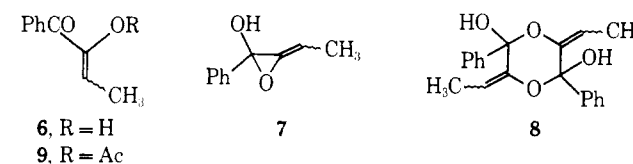
(9) P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **5**, 21 (1968).

(10) H. H. Richtol and A. Beroit, *J. Chem. Phys.*, **45**, 35 (1966).

study of the photoreactions of some α -ketopropiophenones in benzene. Since (1) pyrene ($E_3 = 48$ kcal/mol; known to be a diffusion-control quencher of biacetyl triplets)¹⁰ was shown not to affect the fluorescence of biacetyl or **1** at the concentrations employed, and (2) linear Stern–Volmer pyrene quenching plots were observed for all of the compounds studied, we conclude that only α -diketone triplets are involved in the photoreactions studied.⁶

Comparison of the $k_q\tau$ values for (1) pyrene quenching of the phosphorescence of **1H** and **1D** with (2) pyrene quenching of the disappearance of **2H**, **2D**, **3H**, and **3D** provides support for the proposition that the hydrogens attached to the carbon 3 atom of **2** are involved in the major process for deactivating **2**. Of the various possibilities to explain these data we propose that only two merit serious consideration: (a) intramolecular hydrogen abstraction from carbon 3 by the 1-keto or 2-keto groups *via* novel cyclic five- and four-membered transition states (see Scheme I for

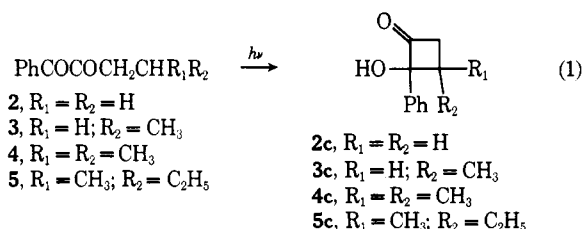
Scheme I



possible products) and (b) intermolecular photoenolization or hydrogen abstraction. Since the $k_q\tau$ values in Table I were found to be unaffected by a fourfold concentration change in α -diketone, we conclude that under our conditions for study, bimolecular events involving α -diketone molecules **1–5** are kinetically and mechanistically unimportant.¹¹

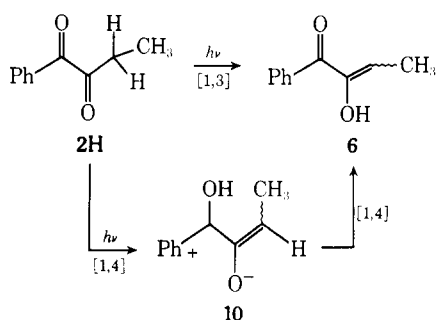
As will be seen by the discussion below, the photo-products derived from **2** are more in harmony with possibility a. Although irradiation of α -diketones (eq 1) **3H**, **3D**, and **4** yields the cyclobutanones **3cH**,

(11) We have shown earlier⁶ that the self-quenching rate constant for 2,3-pentanedione is about 2×10^6 sec⁻¹. Other workers have also shown that high intensities favor bimolecular triplet annihilation: (a) J. Lemaire, *et al.*, *C. R. Acad. Sci., Paris, Ser. C*, **267**, 33 (1968); (b) S. Murov, D. S. McClure, and N. C. Yang, *J. Chem. Phys.*, **45**, 2204 (1966).



3cD, and **4c**, respectively, in high yield, the cyclobutanone **2cH** is only a minor product from irradiation of **2H**. Analysis of the photolysate of **2** reveals that the major product is a material whose nmr shows a doublet at δ 1.83 ($J = 7$ Hz) and a quartet at 5.55 ($J = 7$ Hz). Three possibilities for this photoproduct are **6**, **7**, and **8**. Dimeric structures, such as **8**, are ruled out by the fact that as the initial concentration of **2** decreases, the yield of the new product increases, and **7** is ruled out by the presence of a strong C=O stretch, in the infrared of the photolysate, at 6.12μ . Further evidence in favor of the enol structure **6** is its rapid rearrangement to **2** when it is (a) heated (vpc), (b) treated with acid (aqueous HCl), or (c) treated with base (aqueous NaOH). Compound **6** is oxidized by air or periodate to benzoic acid. Perhaps the best evidence for **6** is its conversion to the enol acetate **9**. The latter was prepared independently from **2H**.¹² In addition, we have found that 1,3-diphenyl-1,2-propanedione undergoes a photoreaction analogous to the conversion of **2H** to **6**.^{13a} The formation of **6** may result (Scheme II) from a $\sigma^2 + \pi^2$ [1,3] hydrogen

Scheme II



transfer from C_3H to the C_2 carbonyl or a [1,4] hydrogen transfer from C_3H to the C_1 carbonyl.¹⁴ The

(12) Compound **9** was prepared by treatment of **2H** with Ac_2O in TsOH . This material shows: nmr δ 1.75 (d, $J = 7$ Hz), 6.05 (q, $J = 7$ Hz) in addition to the aromatic and acetyl proton absorption; ir 6.0μ . Compound **9** was also obtained by treating the photolysate of **2H** (complete conversion, no **2H** by ir or nmr analyses) with methyl lithium followed by addition of acetyl chloride and aqueous work-up. It was shown that **2H** does not produce **9** under the latter conditions.

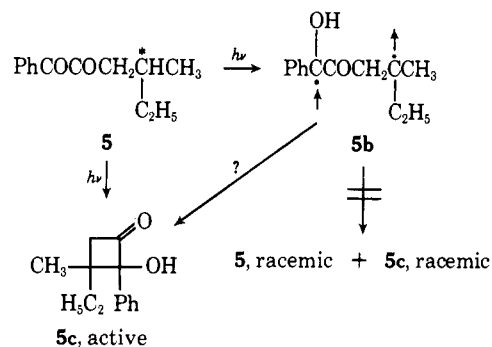
(13) (a) The enols of 1-phenyl-2,3-butanedione and 1,3-diphenyl-1,2-propanedione are relatively stable materials, although their tautomerization to diketones can be catalyzed by acids, bases, and glass surfaces: H. Moureu, *Justus Liebigs Ann. Chim.*, **14**, 283 (1930); G. Wheland, "Advanced Organic Chemistry," 3rd ed, Wiley, New York, N. Y., 1960, p 693. (b) A transient, tentatively identified as the enol of biacetyl, on the basis of its uv absorption spectrum, is formed when biacetyl is irradiated in hexane or aqueous solutions with light of wavelength shorter than 310 nm (excitation of the second singlet state of biacetyl); J. Lemaire, *J. Phys. Chem.*, **71**, 2653 (1967). (c) Yang first recognized the photoenolization of 2-alkylbenzophenones: N. C. Yang and C. Rivas, *J. Amer. Chem. Soc.*, **83**, 2213 (1961); see also N. D. Heindel, E. W. Sarver, and M. A. Pfau, *Tetrahedron Lett.*, 3579 (1968), and references therein. (d) Bishop and Hamer have suggested that a biradical intermediate does not lead to a photoenol in the photocyclization of α,β -unsaturated 1,2-diketones: R. Bishop and M. K. Hamer, *J. Chem. Soc. C*, 1193 (1970).

(14) [1,3] sigmatropic shifts are allowed to 4-electron systems in their excited states: R. B. Woodward and R. Hoffmann, "The Conservation

latter mechanism would then require a [1,4] hydrogen shift from the C_1 carbonyl to the C_2 carbonyl. Such a shift has analogy and occurs rapidly in the protonated biacetyl semidione radical.¹⁵ One would certainly expect, therefore, the process to occur very readily for the conversion of **10** to **6**.

The inefficiency of the photoreactions of diketones **2-4** could reasonably result from either (1) a low rate constant for intramolecular reaction relative to the rate constant, k_d , for inherent triplet decay or (2) reversal of some intermediate, formed from the α -diketone triplet, back to starting material. We attempted to resolve this question by studying the optically active ketone **5**.

In analogy to the work of Yang,³ we expected that if the cyclobutanones formed went through triplet biradical intermediates (e.g., **5b**), we would observe loss of optical activity of **5** and racemic **5c** when a partially photolyzed solution was worked up. Instead, however, we found that recovered **5**, after 35 and 55% conversion, showed no loss of optical activity and the cyclobutanone **5c** was found to be optically active.¹⁶ This result appears to rule out the intermediacy of any biradical intermediates whose lifetimes are long relative to the time scale of bond rotations, unless our measured quantum efficiency for **5** is much too low and is actually close to unity.



In summary, diketone **2** undergoes an unusual primary photorearrangement to **6**, presumably *via* a novel cyclic transition state. The more usual six-membered transition state for formation of **2c** is somewhat competitive with the predominant cyclic transition state for **2H**, and is more favored for **2D**.¹⁷ When the carbon 4 atom becomes secondary as in **3** or tertiary as in **4**, the six-membered transition state becomes highly favored, and cyclobutanone formation predominates, although our data are consistent with some enolization occurring for **3** and **4** also. It is unlikely that the inefficiency in the conversion of **5**

of Orbital Symmetry," Academic Press, New York, N. Y., 1970, p 114. However, it is not clear whether the rearrangement involves the n orbital of C_2 carbonyl or the (delocalized) π^* system. It is interesting to note, however, that the thermal reverse [1,3] shift is required to be $[\sigma_s^2 + \pi_a^2]$ or $[\sigma_a^2 + \pi_s^2]$ which may account for the stability of **6** and related enols relative to their corresponding diketones (in the absence of tautomeric catalysts).

(15) R. J. Pritchett, *Mol. Phys.*, **12**, 481 (1967).

(16) The amount of retention (or inversion) of optical activity of **5c** is unfortunately not yet known.

(17) In contrast to dialkyl α -diketones, which have a most probable planar ground-state geometry,¹⁸ 1-phenyl 1,2-alkyldiones are believed to be twisted about the OC-CO bond due to steric hindrance.¹⁹

(18) K. Noack and R. N. Jones, *Elektrochem.*, **64**, 707 (1960).

(19) I. Bernal, *Nature (London)*, **200**, 1318 (1963); P. H. Cureton, C. G. Le Fevre, and R. R. J. W. Le Fevre, *J. Chem. Soc.*, 4447 (1961); A. Kuboyama, R. Yamazaki, S. Yabe, and Y. Uehare, *Bull. Chem. Soc. Jap.*, **42**, 10 (1969).

to **5c** is due to hydrogen reversion from a triplet bi-radical such as **5b**, since if this were the case, we would expect racemization of recovered optically active **5** from partially photolyzed solutions.

Acknowledgment. The authors thank Professor P. J. Wagner for graciously communicating his results on the photochemistry of α -ketopropiophenones.

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**Organometallic Chalcogen Complexes. XIX.
Stereochemical Analyses of a
Tetramercapto-Bridged Molybdenum(III) Dimer,
[Mo(h^5 -C₅H₅)(SCH₃)₂]₂, Containing a Strong
Molybdenum–Molybdenum Interaction, and of Its
Corresponding Paramagnetic Cation**

Sir:

Our interest in the systematic preparation and characterization of a large assortment of organo-(transition metal) cluster systems has been focused on the stereochemical consequences caused by the addition or removal of valence electrons. A major objective of these studies is to obtain a better understanding of the detailed nature of metal–metal interactions in transition metal cluster systems in that from the observed changes in molecular parameters due to the change in the number of valence electrons it has proven possible to deduce qualitatively the topological nature of the MO containing the least stable valence electrons.^{1–9} The drastic influence of valence electrons on molecular geometry has been previously demonstrated from X-ray crystallographic measurements for metal cluster complexes in which the number of valence electrons has been varied by replacement with either different metal atoms and/or different ligands.^{1–9} In the first of a series of papers dealing with structural studies of metal cluster systems in which the number of valence electrons has been altered by oxidation (or reduction), we wish to report the chemical synthesis and characterization of the cationic complex [Mo(h^5 -C₅H₅)(SCH₃)₂]₂⁺, together with a characterization of its neutral parent [Mo(h^5 -C₅H₅)(SCH₃)₂]₂. The stereochemical relationship of this neutral and oxidized

molybdenum(III)–mercapto complex is of special interest not only in connection with the different modes of coordination and stereochemical behavior of reduced Mo(V)–oxidized Mo(VI) species in a number of sulfhydryl enzymes,¹⁰ but also with respect to providing a better understanding of the function of molybdenum in the catalysis of several oxidation–reduction reactions in biochemical systems. This investigation has established the detailed geometry of this type complex and together with a comparison of the structural features of the neutral and oxidized iron–sulfur dimer, [Fe(h^5 -C₅H₅)(CO)(SCH₃)₂]₂ⁿ ($n = 0, +1$),¹¹ has revealed that the particular molecular architecture (and especially the nature of the bridging ligands) has a dominant influence with respect to possible alteration of geometry due to a gain or loss of electrons.

The neutral [Mo(h^5 -C₅H₅)(SCH₃)₂]₂ complex was obtained from the reaction of [Mo(h^5 -C₅H₅)(CO)₃]₂ with dimethyl disulfide by the method of King,¹² who, from the compound's diamagnetic character (indicated from the proton nmr spectrum and confirmed by him from magnetic balance measurements), proposed a dimeric tetramercapto-bridged structure containing an electron-pair Mo–Mo bond. Crystals of this neutral complex form from CHCl₃ solution as orange-brown needle-like plates in the orthorhombic space group $P2_12_12_1$ (D_2^4 , No. 19). The unit cell containing four dimeric molecules has dimensions $a = 15.608$ (2) Å, $b = 14.767$ (2) Å, $c = 7.878$ (1) Å. The structure was determined from conventional methods based on data collection with a General Electric four-circle diffractometer by the θ – 2θ scan technique with Mo K α radiation. Least-squares refinement, in which each cyclopentadienyl ring was rigidly constrained as a regular pentagon (with C–C and C–H bond lengths of 1.405 and 1.08 Å, respectively), yielded an unweighted R_1 value of 4.2% for 1220 observed reflections. The four bridging sulfur atoms in the crystallographically independent dimeric molecule were found to be disordered such that there are two sets of four sulfur atoms experimentally weighted 4:1. However, each methyl carbon atom was treated as nondisordered in that the positions of the two methyl carbon atoms of each disordered pair of sulfur atoms were assumed to be coincident; no attempt was made to locate the presumably disordered methyl hydrogen atoms.

The monocation was chemically synthesized as the hexafluorophosphate salt by the oxidation of [Mo(h^5 -C₅H₅)(SCH₃)₂]₂ in methylene chloride with AgPF₆ in ethanol. This reaction leads to the formation of a deep purple solution from which, on addition of ether, a purple solid is deposited. Crystals of [Mo(h^5 -C₅H₅)(SCH₃)₂]₂PF₆ suitable for X-ray investigation were obtained by recrystallization from hot acetonitrile solution. Acetone or acetonitrile solutions of this compound are moderately stable to air, but reduction of the cation to the neutral species slowly occurs in solution. More rapid reduction may be effected by the addition of NaBH₄. The formulation of this new compound was substantiated by elemental analysis and conductivity measurements in acetone. [Mo(h^5 -C₅H₅)-

(1) Previous paper in this series: C. E. Strouse and L. F. Dahl, *Discuss. Faraday Soc.*, **93** (1969).

(2) Single-crystal X-ray and esr studies of the paramagnetic complexes Co₃(CO)₉X (X = S, Se) and their diamagnetic analogs Co₂Fe(CO)₉X (X = S, Se, Te)^{1,3} and X-ray measurements of the paramagnetic complex Ni₃(h^5 -C₅H₅)₃(CO)₂ and its diamagnetic analog NiCo(h^5 -C₅H₅)₃(CO)₂⁴ have shown that electrons in excess of the closed-shell electronic configuration of each metal atom in these triangular metal cluster systems occupy primarily the *antibonding* metal σ orbitals.⁵

(3) C. E. Strouse and L. F. Dahl, submitted for publication.

(4) V. A. Uchtman and L. F. Dahl, submitted for publication.

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