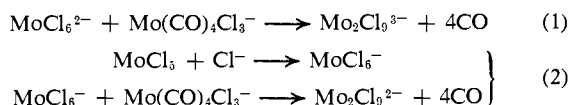Since the average oxidation state of the product is dependent solely upon the oxidation state of the metal in MCl_6^{n-}, this scheme indicates that it should be possible to prepare not only $Mo_2Cl_9^{3-}$ from MCl_6^{2-} but also $Mo_2Cl_9^{2-}$ from MCl_6^{-}. (The $W_2Cl_9^{2-}$ anion was previously obtained from the oxidation of $W_2Cl_9^{3-}$ with molecular halogens.[2c]) Indeed, we are now able to report the successful syntheses of $Mo_2Cl_9^{3-}$ and the new anion, $Mo_2Cl_9^{2-}$, according to this strategy and the following reactions

$$MoCl_6^{2-} + Mo(CO)_4Cl_3^- \longrightarrow Mo_2Cl_9^{3-} + 4CO \quad (1)$$

$$\left.\begin{array}{c} MoCl_5 + Cl^- \longrightarrow MoCl_6^- \\ MoCl_6^- + Mo(CO)_4Cl_3^- \longrightarrow Mo_2Cl_9^{2-} + 4CO \end{array}\right\} \quad (2)$$

Both reactions were conducted at the millimolar level in CH_2Cl_2 contained in glass vessels connected to a vacuum line. Procedures have been previously described.[4] Reaction 1 proceeded with the liberation of 87% of the available CO after 30 hr and the formation of orange $[(n\text{-}C_3H_7)_4N]_3Mo_2Cl_9$ (50% yield) in addition to some $Mo(CO)_6$ and an unknown carbonyl species. Complete evolution of CO occurred in reaction 2 after 24 hr and the yield of dark greenish brown $[(n\text{-}C_4H_9)_4N]_2\text{-}Mo_2Cl_9$ was virtually quantitative. Satisfactory elemental analyses were obtained in both cases. The two compounds are also easily distinguished by their electronic absorption spectra and their magnetic properties (Table I). The temperature dependence

Table I. The Electronic Spectra and Magnetic Properties of the $Mo_2Cl_9^{3-}$ and $Mo_2Cl_9^{2-}$ Anions

Compound	$\nu,^a$ cm^{-1}	$\mu_{eff},^b$ BM
$[(n\text{-}C_3H_7)_4N]_3Mo_2Cl_9$	~13,200 (23)^c	1.29 (302°)
	14,920 (33)	0.84 (204°)
	18,950 (638)	Diamagnetic (86°)
	23,300 (608)	
$[(n\text{-}C_4H_9)_4N]_2Mo_2Cl_9$	10,250 (163)	2.06 (300°)
	12,800 (171)	1.87 (236°)
	15,280 (265)	1.65 (140°)
		1.61 (95°)

^{a} Molar extinction coefficients appear in parentheses. ^{b} Absolute temperatures appear in parentheses. ^{c} Some fine structure was noted.

of the magnetic moment of $Mo_2Cl_9^{3-}$ is in general accord with a thermal equilibrium between the manifold of antiferromagnetic spin states, $S = 3, 2, 1,$ and 0, with $S = 1$ and 0 having only appreciable populations at room temperature. The magnetic moment at that temperature is considerably larger than the value of 0.6 BM found[3b] for $Cs_3Mo_2Cl_9$, but a dependence on the nature of the cation has been previously noted.[3d] The magnetic moment of $Mo_2Cl_9^{2-}$ is constant at about 1.6 BM at temperatures below 100°K, indicating a ground state having one unpaired electron with $g < 2$. As the temperature is increased, the increased magnetic moment is attributed to the thermal population of a manifold of the antiferromagnetic spin states, $S = \frac{5}{2}, \frac{3}{2},$ and $\frac{1}{2}$, with only the last two having appreciable populations at room temperature. The infrared spectrum of $Mo_2Cl_9^{2-}$ between 200 and 400 cm^{-1} resembles that of $W_2Cl_9^{2-}$. Both of these spectra

(4) W. H. Delphin and R. A. D. Wentworth, *Inorg. Chem.*, 12, 1914 (1973).

resemble those of the reduced anions, $Mo_2Cl_9^{3-}$ and $W_2Cl_9^{3-}$, and we assume that the oxidized anions retain the bioctahedral structure. A complete description of the magnetic and spectroscopic properties is planned for a subsequent publication.

The $Mo_2Cl_9^{2-}$ anion seems to react with most donor solvents, precluding conductivity measurements. As an example, the anion is instantly reduced by CH_3CN to $Mo_2Cl_9^{3-}$. Rapid, quantitative reduction to $Mo_2Cl_9^{3-}$ also occurs with tin metal and excess alkylammonium halide in CH_2Cl_2.

We believe that this work represents the only synthesis of polynuclear halometalates which purports to have a rational basis. However, the success of the method does not prove the proposed mechanism although it would seem to be the simplest explanation of the results. Moreover, we do not claim that the reaction scheme is universally useful at present since a similar (but not identical) reaction which was designed to yield $W_2Cl_9^{3-}$, *viz.*, $WCl_6 + W(CO)_5Cl^- + 2Cl^- \rightarrow W_2Cl_9^{3-}$, gave instead WCl_6^{2-} and $W(CO)_4Cl_2$ and/or $W(CO)_4Cl_3^-$.[4] It would appear that these products resulted either from an outer sphere mechanism or an inner sphere mechanism followed by decomposition of a bridged intermediate.

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Preferential Mode for Nucleophilic Attack by Methoxide Ion on O,S-Dimethyl Phenylphosphonothiolate. A Contrasting Behavior to Reactions on Analogous Phosphonium Salts

Sir:

Recently, the mode for nucleophilic attack by hydroxide ion on menthoxy(methylthio)methylphenylphosphonium hexachloroantimonate (1) has been shown[1,2] to be exclusively axial on phosphorus in the face opposite the alkoxy ligand to form intermediate A (eq 1). Eventual loss of the methylthio group only

$$(1)$$
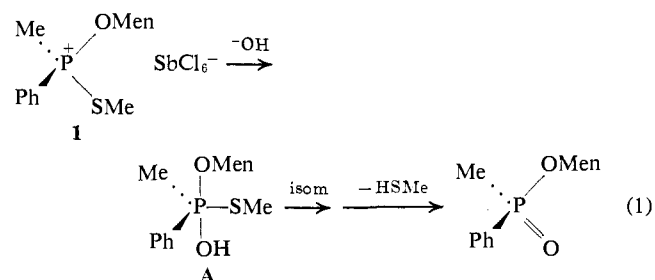
after an isomerization results in formation of the product with retention of configuration at phosphorus. In apparent contrast, the neutral ester analog of 1, O-menthyl S-methyl phenylphosphonothiolate (2), suf-

(1) N. J. De'ath, K. Ellis, D. J. H. Smith, and S. Trippett, *Chem. Commun.*, 714 (1971).
(2) K. E. DeBruin and D. M. Johnson, *J. Amer. Chem. Soc.*, 95, 4675 (1973).

fers displacement of the methylthio group by methoxide ion with inversion of configuration at phosphorus.[3,4] A possible rationale for the differing stereochemical outcomes in these two systems can be made from a consideration of the energetics of the proposed intermediates. Although intermediate B (Scheme I) result-

Scheme I
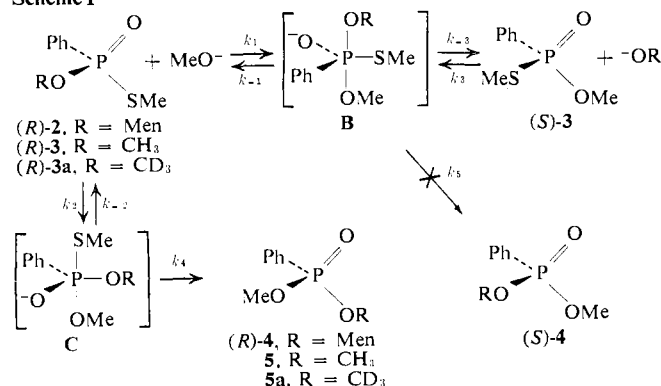
ing from attack of methoxide ion opposite the menthoxy ligand in **2** (the mode implicated in the hydrolysis of **1**) may be kinetically preferred, this intermediate would need to undergo a high energy isomerization[2] to place the methylthio ligand in the axial position required for displacement. Thus, ultimate cleavage of the methylthio group with inversion of configuration at phosphorus may occur by re-formation of **2** ($k_{-1} > k_{-3}$) followed by formation and decomposition of intermediate C. This rationale allows a single unifying mechanism to operate; that is, preferred attack of the nucleophile opposite the alkoxy ligand to form intermediate A or B from **1** or **2**, respectively, followed by their respective decomposition pathways. This communication provides a test for this rationale.

To probe whether a kinetic preference for attack of methoxide ion opposite the alkoxy ligand in **2** to form B does exist, we decided to make B operationally detectable by investigating the stereochemistry of the reaction of methoxide ion with optically active O,S-dimethyl phenylphosphonothiolate (**3**). Formation of B (R = Me) which is achiral would result in racemization of **3** prior to or competitive with displacement of the alkylthio ligand.

The kinetics of the reaction of (R)-(+)-**3**[5] with methoxide ion was investigated under pseudo-first-order conditions in methanol at 10.0°. Aliquots were taken at various time intervals, quenched by immediate extraction with dichloromethane, and analyzed by ^{1}H nmr spectroscopy for the amount of displacement of the methylthio ligand (k_{disp}) and by chiroptical methods for the amount of disappearance of optically active **3** (k_{rac}). A parallel study was carried out on racemic **3** containing deuterium in the methoxy group (**3a**) and analyzed by ^{1}H nmr spectroscopy for the amount of displacement of the methylthio ligand (k_{disp}) and the amount of disappearance of deuterated

(3) W. B. Farnham, K. Mislow, N. Mandel, and J. Donohue, *J. Chem. Soc., Chem. Commun.*, 120 (1972).

(4) Alkaline hydrolysis of the dithioate analog of **2**, O-menthyl S-methyl phenylphosphonodithioate, has also been shown to proceed with inversion of configuration at phosphorus. K. E. DeBruin and D. M. Johnson, *Phosphorus*, in press.

(5) The absolute configuration of **3** was obtained by chemical correlations: K. E. DeBruin and D. M. Johnson, unpublished results.

3a (k_{exch}). All reactions gave excellent pseudo-first-order kinetics over greater than 80% of the reaction with least-squares correlation coefficients of greater than 0.9994. Table I lists the results obtained. That

Table I. Pseudo-First-Order Rate Constants for the Reaction of Methoxide Ion with **3** in Methanol at 10.0°

| Concn, M | | | Rate constants[a] (sec⁻¹) × 10³ | | |
3	NaOMe	H_M	k_{disp}	k_{rac}	k_{exch}
0.0495	0.660	16.97	2.73[b]	3.35[b]	
0.0510	0.335	16.55	0.98 (0.01)	1.18 (0.02)	
0.0485	0.335	16.55	0.97[c] (0.03)		1.08[c] (0.02)
0.0254	0.177	16.20	0.43[b]		

[a] Average deviation of two determinations is shown in parentheses. [b] Single determination. [c] Reaction on **3a**.

the reaction is overall second order was shown by a plot of log (k_{disp}) against the methoxide in methanol acidity function H_M[6] yielding a slope of near unity (1.05, $r = 0.9999$).

The kinetic results are readily interpreted in terms of Scheme I where a competition exists between formation of two intermediates B or C from attack of methoxide ion opposite the methoxy ligand or the methylthio ligand, respectively. If the assumptions are made that C forms products much faster[7] than return to **3** ($k_4 \gg k_{-2}$) and that B cannot form product **5** by loss of the methylthio ligand,[8] the scheme can be represented by eq 2. Thus, in terms of the rate constants in eq 2,

$$ B \underset{k_1}{\overset{k_{-1}}{\rightleftarrows}} 3 \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} C \overset{k_4}{\longrightarrow} 5 \tag{2} $$
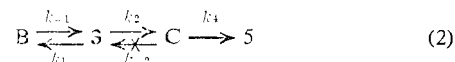
k_{disp} is equivalent to k_2, k_{rac} is the sum of the two rate constants for forming achiral B which gives racemic **3** (k_1) and achiral **5** (k_2), and k_{exch} is the sum of the rate constant for forming **5** (k_2) and half the rate constant for forming B ($^1/_2 k_1$). It follows from the results in Table I that in 0.335 M sodium methoxide in methanol solution at 10°, $k_1 = 2.0 \times 10^{-4}$ sec⁻¹ and $k_2 = 9.8 \times 10^{-4}$ sec⁻¹.

The surprising result from the above kinetic analysis is that although attack of methoxide ion on **3** occurs opposite both the methoxy ligand and the methylthio ligand, the *preferred attack is opposite the methylthio ligand* by a factor of ca. 5. The difference in the stereochemical outcomes of the reaction of hydroxide ion with **1** and the reaction of methoxide ion with **2** is now clearly linked to the difference in the preferred mode of nucleophilic attack in these two systems. We are currently taking advantage of the fact that a competition exists in the reaction of methoxide ion with **3** to probe the origin of this difference.

It should be pointed out that in the above discussion the controversial assumption that B and C are intermediates and not transition states was made. If they are in fact transition states, the kinetic analysis in terms of eq 2 becomes

$$ k_{rac} = k_2 + 2k_1 $$

$$ k_{exch} = k_2 + k_1 $$

(6) F. Terrier, *Bull. Soc. Chim. Fr.*, 1894 (1969).

(7) This assumption is based on the relative acidities of the two leaving groups.

(8) Such a process would have yielded (S)-**4** from (R)-**2**, which was not observed.

and subsequently, attack of methoxide ion opposite the methylthio ligand is preferred by a factor of 10. It is possible that the neutral esters are undergoing a direct displacement not involving a pentacoordinate species of ground-state geometry and thus the mode of attack may also be governed by the relative abilities of the various ligands to be displaced. This provides a working hypothesis to explain the differing modes for attack by nucleophiles on the two systems 1 and 2.

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An Efficient Total Synthesis of dl-Avenaciolide

Sir:

Herein we describe a stereospecific total synthesis of dl-avenaciolide (**1**), a novel fungicidal bislactone isolated from *Aspergillus avenaceus* G. Smith.[1] Salient features of this construction include: (a) substitution of both the β and α positions of a Michael receptor using a conjugate addition–halogenation sequence,[2] (b) transformation of an α-methyl-α-thiomethyl-butyrolactone into its corresponding α-methylene analog,[3] and (c) realization of the synthetic objective **1** in 70% overall yield starting from lactone **2**.[4]

R = n-octyl
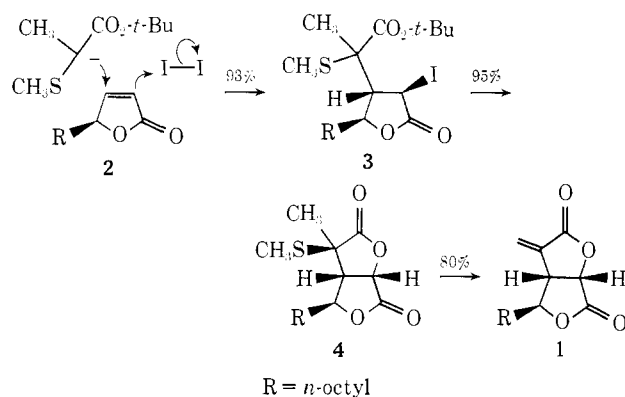
To a solution of *tert*-butyl α-lithio-α-thiomethylpropionate[5] (1 equiv, 1 *M* in THF) was added (20 min) at −78° lactone **2** (1 equiv, 1 *M* in THF). After stirring

(1) The isolation of avenaciolide was first reported by D. Brookes, B. K. Tidd, and W. B. Turner, *J. Chem. Soc., Chem. Commun.*, 5385 (1973). A total synthesis of avenaciolide, conceptually quite different from that described here, has been reported by W. L. Parker and F. Johnson, *J. Org. Chem.*, **38**, 2489 (1973).

(2) We have found this reaction quite general with respect to addend and receptor combinations.

(3) This reaction sequence is also quite general and constitutes a useful means of preparing structurally complex unsaturated acids and esters as well as lactones.

(4) A preparation of **2** (oil) has been described by A. Nobuhara, *Agr. Biol. Chem.*, **34**, 1745 (1970). We have prepared **2** (mp 36–38.5°) in 75% overall yield starting from nonylaldehyde by the scheme shown below (R = n-octyl).

RCHO + LiC≡CO₂Et ⟶ RCHOHC≡CCO₂Et ⟶

RCHOHC≡CCO₂H ⟶ **2**

(5) For a description of the preparation and handling of lithium enolates of simple ester systems, see R. J. Cregge, J. L. Herrmann, C. S. Lee, J. E. Richman, and R. H. Schlessinger, *Tetrahedron Lett.*, 2425 (1973).

for 2 hr at −78°, iodine (1.2 equiv, 1 *M* in THF) was added to the reaction mixture (30 min additional stirring at −78°). Standard acid–base work-up (0–5°) afforded the iodo lactone **3** (oil)[6] as the sole reaction product (93%).[7] Conversion of **3** into the bislactone **4** was carried out in two stages: first, reaction of **3** (1 equiv, 1 *M* in benzene) with *p*-toluenesulfonic acid monohydrate (10% by weight) at reflux for 3 hr, and second, stirring this mixture with solid sodium bicarbonate at room temperature for 30 min. Filtration and evaporation of this benzene solution gave **4** (oil)[6] in 95% yield.[7] Introduction of the α-methylene moiety was accomplished by oxidation of **4** (1 equiv, 0.5 *M* in CH₂Cl₂) with *m*-chloroperbenzoic acid (1 equiv) to its corresponding sulfoxide (CH₃S to CH₃SO) followed by treatment of the sulfoxide (1 equiv) with succinic anhydride (3 equiv) for 30 min at 140°.[8] Treatment of this mixture with 10% hydrochloric acid followed by extraction with sodium bicarbonate and one crystallization from ether–petroleum ether gave pure dl-avenaciolide (**1**, mp 55–56°) in 80% yield.[9]

It is worthy of note that pure avenaciolide can be obtained from the lactone **2** without purification of any synthetic intermediates. The methods described in the foregoing are being used in the construction of other naturally occurring lactone systems.

(6) All compounds exhibited satisfactory spectral and physical properties. The stereochemistry of intermediates 3 and 4 follows from their 100-MHz nmr spectra.

(7) The yields reported are for isolated products.

(8) Similar sulfoxide to olefin transformations have been recently reported by B. M. Trost and T. N. Salzmann, *J. Amer. Chem. Soc.*, in press. We thank Professor Trost for communicating an account of this work to us prior to its publication.

(9) The authors would like to thank Drs. J. J. Ellis, F. H. Stodola, and F. Johnson for samples of l-avenaciolide.

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Dimers of α,β,β-Trifluorostyrene

Sir:

Fluorinated olefins often cycloadd to other olefins in biradical fashion.[1] Some are known to cyclodimerize in a head-to-head manner, presumably *via* the most stable biradical.[2] The correspondingly facile dimerization of α,β,β-trifluorostyrene (TFS) has been reported,[3] but the product has been thought to be a 50:50 mixture of **3** and **4** on ¹⁹F nmr evidence.[4]

(1) References include: (a) D. D. Coffman, P. L. Barrick, R. D. Cramer, and M. S. Raasch, *J. Amer. Chem. Soc.*, **71**, 490 (1949), and references cited therein; (b) P. D. Bartlett, L. K. Montgomery, and B. Seidel, *ibid.*, **86**, 616 (1964); (c) P. D. Bartlett, *Science*, **159**, 833 (1968), and references cited therein; (d) J. D. Roberts and C. M. Sharts, *Org. React.*, **12**, 1 (1962).

(2) A. L. Henne and R. P. Ruh, *J. Amer. Chem. Soc.*, **69**, 279 (1947).

(3) M. Prober, *ibid.*, **75**, 968 (1953).

(4) M. P. Votinov, V. A. Kosobutskii, and A. F. Dokukina, *Vysokomol. Soedin., Ser. A*, **10**, 1137 (1968); *Polym. Sci. USSR*, **10**, 1318 (1968).