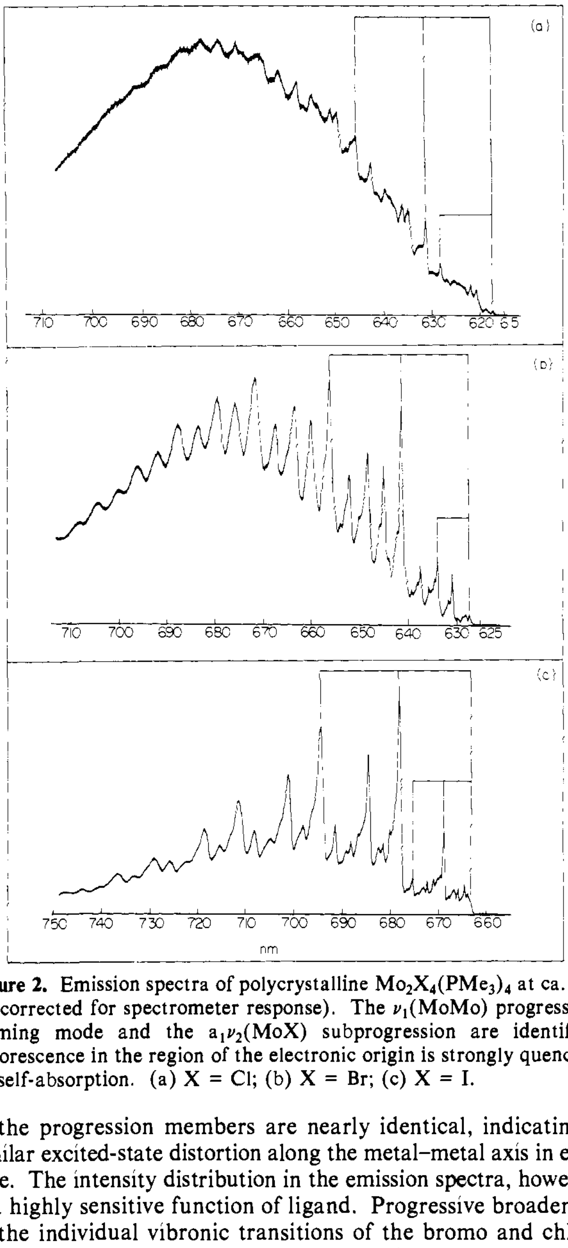

Figure 2. Emission spectra of polycrystalline $Mo_2X_4(PMe_3)_4$ at ca. 5 K (uncorrected for spectrometer response). The ν_1(MoMo) progression-forming mode and the $a_1\nu_2$(MoX) subprogression are identified. Fluorescence in the region of the electronic origin is strongly quenched by self-absorption. (a) X = Cl; (b) X = Br; (c) X = I.

of the progression members are nearly identical, indicating a similar excited-state distortion along the metal-metal axis in each case. The intensity distribution in the emission spectra, however, is a highly sensitive function of ligand. Progressive broadening of the individual vibronic transitions of the bromo and chloro complexes results in the striking deviation of their absorption and emission spectra from the mirror-image relationship displayed by the spectra of the iodo complex. Examination of the high-resolution emission spectrum of $Mo_2X_4(PMe_3)_4$ at 5 K (Figure 2) reveals that a remarkable number of other vibrational modes are Franck-Condon active and that the broadening observed for the bromo and chloro complexes arises from an increasing redistribution of intensity from the ν_1(MoMo) progression-forming mode into these vibronic sidebands. Although assignment of these additional vibrational modes is incomplete at present, each spectrum displays a major subprogression corresponding to the symmetric Mo-X stretching coordinate.[15]

Significant deviations of electronic spectra from mirror symmetry have been observed previously in the octahalodimolybdate and -dirhenate family of ions.[1,3,4,6] This behavior was attributed to a Duschinsky effect[16] originating from an excited-state distortion that was large relative to that of a species exhibiting symmetric spectra. In light of the above absorption spectroscopic and photophysical evidence that all three $Mo_2X_4(PMe_3)_4$ derivatives possess similar, relatively slightly distorted excited-state geometries, the unprecedented "variable mirror symmetry" exhibited by their spectra is thus quite surprising. We suggest that a large part of the observed deviation in the spectral intensity profiles of these species arises from the varying degrees of coupling present between the ν_1(MoMo) and $a_1\nu_2$(MoX) vibrational modes in the ground and excited states of each complex.[17] Specifically, larger *apparent* Huang-Rhys factors for the ν_2(MoX) subprogression would be anticipated as the difference in frequency between the two modes decreases. Accordingly, the asymmetric spectra of the chloro complex indicate that these modes are strongly coupled to different extents in the ground and excited states. In contrast, the symmetric spectra of the iodo complex show that the two modes are largely decoupled.

We note in closing that Fraser and Peacock have found[6] that the progression-forming mode is ν_2(MoCl) rather than ν_1(MoMo) in the emission spectrum of $Mo_2Cl_8^{4-}$. As an alternative to the proposed reassignment[6] of the $\delta\delta^*$ emission, we suggest that the variation in the coupling of these two modes in the ground and $\delta\delta^*$ excited states of $Mo_2Cl_8^{4-}$ is even greater than that observed here for $Mo_2Cl_4(PMe_3)_4$.

Acknowledgment. We gratefully acknowledge the contributions Vince Miskowski and Tom Zietlow have made to this work, mainly through helpful discussions, and we thank R. D. Peacock for providing us with a preprint of ref 6. This research was supported by National Science Foundation Grant CHE81-20419. M.D.H. thanks the Sun Co. for providing a graduate fellowship.

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(15) $a_1\nu_2$(MoX): X = Cl, 284 (5); X = Br, 165 (5); X = I, 143 (5) cm^{-1}.

(16) Ballhausen, C. J. "Molecular Electronic Structures of Transition Metal Complexes"; McGraw-Hill: New York, 1979; Chapter 1.

(17) Such coupling has been invoked to explain the electronic absorption and resonance Raman spectra of diruthenium(II,III) tetracarboxylate (Clark, R. J. H.; Ferris, L. T. H. *Inorg. Chem.* **1981**, *20*, 2759-2771. Miskowski, V. M.; Loehr, T. M.; Gray, H. B., unpublished results).

2-Alkoxybenzo-1,3-dithiole 1,1,3,3-Tetraoxide, a Carbonyl 1,1-Dipole Synthon

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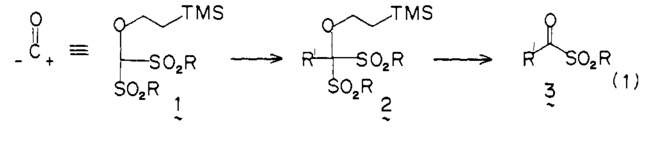
Acyl sulfones **3** are an almost unknown class of compounds.[1] Their potential as acylating agents led us to explore methods to generate them that did not depend upon oxidation.[1,2] The possibility that unmasking an alkoxybis(sulfonyl)methane such as **2** could generate **3** in situ and that alkylation of **1** should provide an entry to **2** led us to propose that **1** could be a useful carbonyl 1,1-dipole synthon[3,4] as summarized in eq 1. Of great importance



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(1) Schank, K.; Frisch, A.; Zwanenburg, B. *J. Org. Chem.* **1983**, *48*, 4580. Schank, K.; Werner, F. *Justus Liebigs Ann. Chem.* **1980**, 1477; **1979**, 1927 and references therein. For sulfonyl formates and related compounds, see: Ferdinand, G.; Schank, K. *Synthesis* **1976**, 408. Barton, D. H. R.; Manly, D. P.; Widdowson, D. A. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1568. Ferdinand, G.; Schank, K.; Weber, A. *Justus Liebigs Ann. Chem.* **1975**, 1484. Olijnsma, T.; Engberto, J. B. F. N.; Strating, J. *Recl. Trav. Chim. Pays-Bas* **1970**, *89*, 897. Senning, A.; Sorenson, O. N.; Jacobsen, C. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 734. Gaul, R. J.; Fremuth, W. J. *J. Org. Chem.* **1961**, *26*, 5103.

(2) Cf.: Kumamoto, T.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 2111. Minato, H.; Kodama, H.; Miura, T.; Kobayashi, M. *Chem. Lett.* **1977**, 413. However, acyl sulfoxides are believed to be the intermediates in these reactions.

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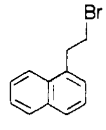
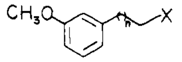
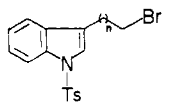
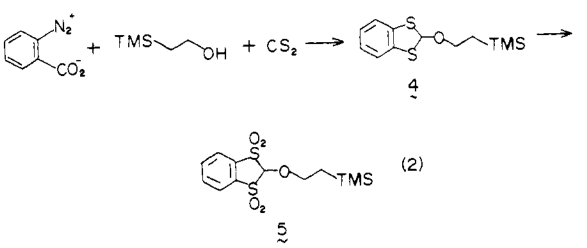
Table I. Alkylation of **5** with Alkyl Halides

entry	alkylating agent	time, h	yield[a]
			
1	$n = 7$	20	73
2		30	73
			
3	$n = 1$, X = Br	20	81
4	$n = 2$, X = I	12	87
5		20	55
			
6	$n = 1$, X = I	30	30
7	$n = 3$, X = Br	30	64
			
8	$n = 1$	12	48
9	$n = 2$	24	65

[a] All yields are for isolated pure products. All products have been fully characterized by spectral means and elemental composition established by combustion analysis and/or high-resolution mass spectroscopy.

is the possibility that the alkoxybis(sulfone) group may serve as a protected form of a highly reactive acylating agent. Transformations at other reactive functional groups such as a reduction of or organometallic addition to a carbonyl group could be performed prior to the unmasking.

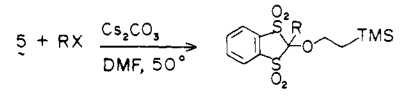
The ready availability of 2-alkoxybenzo-1,3-dithiole by the gentle thermolysis of benzenediazonium carboxylate generated in situ from anthranilic acid in the presence of carbon disulfide and an alcohol[5] led to the formation of **4**, bp 140–142 °C (0.2 mm), in 50% yield. Oxidation was best accomplished with $MoO_5 \cdot HMPA \cdot H_2O$[6] in methylene chloride at 0 °C to room temperature in 63% yield to give beautiful needles of **5** (eq 2): mp



(2)

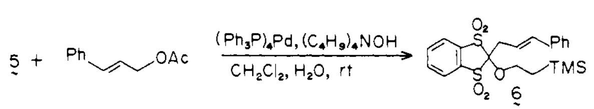
174–174.5 °C [IR ($CHCl_3$) 1445, 1350, 1170, 1130, 1100 cm^{-1}; NMR ($CDCl_3$) δ 8.00–7.81 (4 H, m), 5.29 (1 H, s), 4.22 (2 H, m), 1.16 (2 H, m), 0.00 (9 H, s)].

Three types of alkylations of **5** were explored—alkylation with halides, palladium-catalyzed allylation, and Michael reactions. Alkylation with halides was best performed by using Cs_2CO_3 (1.1 equiv) in DMF at 50 °C (eq 3). Some of the results are summarized in Table I.



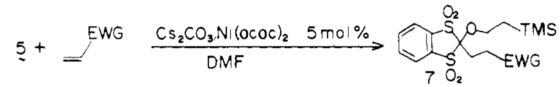
(3)

A palladium-catalyzed allylic alkylation[7] failed under our standard conditions. However, a good yield was obtained under phase-transfer conditions as shown in eq 4 to give **6**[8]—a type of reaction condition that has not been previously used in palladium-catalyzed alkylations.[9]



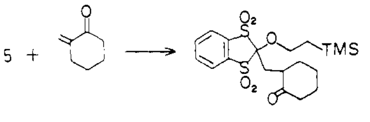
(4)

Michael reactions also failed under standard conditions even after extensive effort. On the other hand, a newly devised, nearly neutral set of conditions using nickel catalysts (2–5 mol %)[10] succeeded nicely to give the Michael adducts as summarized in eq 5 and 6. While $Ni(acac)_2$ alone succeeded in the case of MVK (neat), in most cases use of cesium carbonate in conjunction with the nickel salt proved advantageous.



(5)

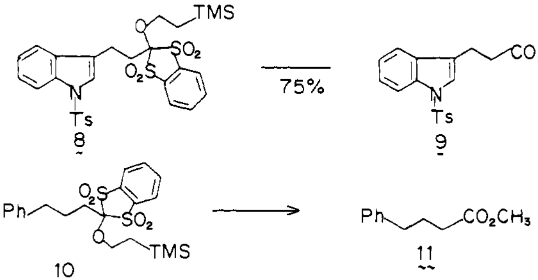
EWG	
$COCH_3$	64%[8]
CN	46%[8]
SO_2Ph	74%[8]



69%[8] (6)

With the establishment of the nucleophilic properties of the anion of **5**, we turned our attention to the manipulation of the adducts. Our initial work focused on fluoride-initiated unmasking, but all nucleophilic fluoride sources either failed to unmask the alkylated substrates or did so poorly.

Our success in initiating an ionization of a sulfone with Lewis acids[11] led us to subject **6** to boron trichloride (−78 °C, CH_2Cl_2) followed by addition of methanol and warming to 0 °C, which produced **8** in 57% yield. Under these conditions, the initial unmasking to a reactive acylating agent must be very rapid since exposing **8** and **10** to boron trichloride (2–5 equiv) at −78 °C for only 5–10 min before adding methanol led to the methyl esters **9** and **11** as the only products. Other alcohols like allyl alcohol



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(3) For carbomethoxy anion synthons, see: Ogura, K.; Watanabe, J.; Iida, H. *Tetrahedron Lett.* **19818** *22*, 4499. Wade, P. A.; Hinney, H. R.; Amin, N. V.; Vail, P. D.; Morrow, S. D.; Hardinger, S. A.; Saft, M. S. *J. Org. Chem.* **1981**, *46*, 765. Woessner, W. D. *Chem. Lett.* **1976**, *43*. Manas, A. R. B.; Smith, R. A. J. *Chem. Commun.* **1975**, 216. Seebach, D. *Chem. Ber.* **1972**, *105*, 487. Seebach, D.; Geiss, K.-H.; Beck, A. K.; Graf, B.; Daum, H. *Ibid.* **1972**, *105*, 3280. Also see: Seebach, D.; Lubosch, W.; Enders, D. *Ibid.* **1976**, *109*, 1309. Damon, R. E.; Schlessinger, R. H. *Tetrahedron Lett.* **1976**, 1561. Fletcher, A. S.; Smith, K.; Swaminathan, R. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1881.

(4) Use of acyl anions followed by oxidation represents an alternative carboxy anion synthon. For reviews, see: Grobel, B. T.; Seebach, D. *Synthesis* **1977**, 357. Lever, O. W., Jr. *Tetrahedron* **1976**, *32*, 1943. Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 329; *Synthesis* **1969**, 17.

(5) Nakayama, J. *Synthesis* **1975**, *38*; *J. Chem. Soc., Perkin Trans. 1* **1975**, 525. For some uses in synthesis, see: Nakayama, J. *Ibid.* **1976**, 540.

(6) Benneche, T.; Undheim, K. *Chem. Scripta* **1982**, *20*, 11.

(7) For reviews, see: Trost, B. M.; Verhoeven, T. R. *Compr. Organomet. Chem.* **1982**, *8*, 779. Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385; *Pure Appl. Chem.* **1981**, *53*, 2357.

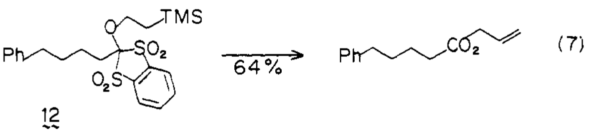
(8) All new compounds have been fully characterized spectroscopically and elemental composition determined by combustion analysis or high-resolution mass spectroscopy.

(9) For uses of phase-transfer conditions in transition-metal-catalyzed reactions, see: Alper, H. *Adv. Organomet. Chem.* **1981**, *19*, 183.

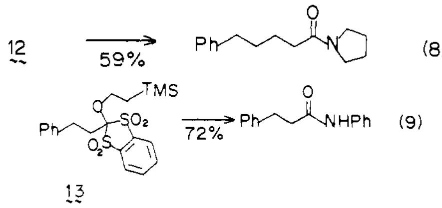
(10) Nelson, J. H.; Howells, P. N.; DeLullo, G. C.; Landen, G. L.; Henry, R. A. *J. Org. Chem.* **1980**, *45*, 1246.

(11) Trost, B. M.; Adams, B. *J. Am. Chem. Soc.* **1983**, *105*, 4849.

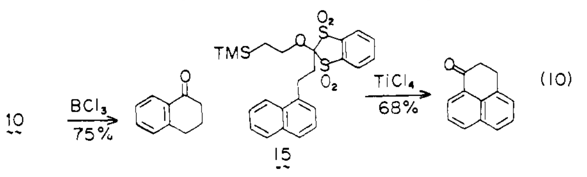
can be employed (cf. eq 7), but trichloroethanol failed.



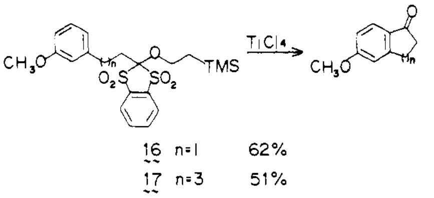
Direct amide formation proceeds equally well. For example, reacting **12** or **13** with boron trichloride (2.4 equiv) followed by excess amine led to the amides as in eq 8 and 9.



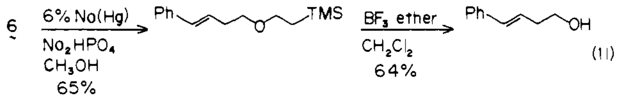
The question of intramolecular trapping by carbon nucleophiles was of special interest. To explore this point, **10** was exposed to boron trichloride (2.4 equiv) at −78 °C (1 h) in methylene chloride and then allowed to warm to 0 °C over 15 min and kept there for 40 min. Addition of methanol then led to a 70:30 mixture of the methyl ester **11** and tetralone in quantitative yield. On the other hand, a 75% yield of tetralone is obtained if the reaction is stirred at room temperature for 17 h before quenching (eq 10).



The use of 2–4 equiv of titanium tetrachloride, initially at −78 °C and then at −10 to 0 °C, led to 5-, 6-, and 7-membered rings from **15–17**. While quantitative data do not exist, the ease of cyclization appears to follow the order 6 > 5 > 7. Thus, for example, use of the boron catalyst with **16** led to the indanone in only 14% yield in contrast to the 75% yield of eq 10. Furthermore, cyclization of **15** produced the peri-bridged six-membered ring in great predominance (68% yield) over the angularly fused five-membered ring (1% isolated yield). Cyclization times for **16** and **17** were approximately 3.5 and 18 h, respectively. The high regioselectivity of this cyclization reaction is noteworthy.[12]

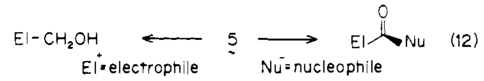


One additional application of these new nucleophiles is their ability to undergo desulfonylation[13] so that they serve as a synthon for a hydroxymethyl anion[14] as shown in eq 11. It is conceivable



to also employ a monosulfonylalkoxymethane[15] in a similar sequence with simple electrophiles; however, the carbanions derived from such a monosulfonyl species fail to serve as a nucleophile in palladium- catalyzed reactions.

It does appear that **5** has the functional equivalence of a carbonyl 1,1-dipole as well as a hydroxymethyl carbanion so that the transformations summarized in eq 12 are possible. While the



details of the unmasking have yet to be elucidated, it would seem likely that acyl sulfones are indeed intermediates although it cannot be ascertained whether they are the actual species undergoing the final acylation.

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(12) Cf.: Johnson, W. S. *Org. React.* **1944**, *2*, 114. Sethna, S. *Friedel–Crafts Relat.* **1964**, *pt. 2, 3*, 911.

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Direct Observation and Chemistry of Triplet 1,6-Biradicals in the Norrish I Reaction

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The familiar Norrish I (α-cleavage) photoreaction of cycloalkanones occurs dominantly from the triplet state of the ketone and follows the mechanism depicted in Scheme I.[1] The transients in this reaction, particularly the biradicals, have not hitherto been observed. We now report the observation and the lifetime of two such biradicals. Deuterium isotope effects for one are consistent with the familiar triplet biradical → singlet biradical → product mechanism.

The photochemistry of **1a** has already been reported;[2] the aldehyde **3a** is the only significant product, requiring $k_{\mathrm{A}} >> k_{\mathrm{K}}$. The multiplicity is largely or exclusively triplet.[2b] For **1b**, we observe (in methanol solvent) only aldehyde **3b** accompanied by three small GC peaks totalling ≤2% of the area for **3b**. There is no detectable methyl ester peak in the NMR as would have been expected from methanolysis of any ketene formed via k_{K}. Clearly, $k_{\mathrm{A}} >> k_{\mathrm{K}}$ for **2b** also.

Irradiation with either a mode-locked or a Q-switched Nd-YAG laser at ca. 10 mJ/pulse (10-ns fwhm, 266-nm fourth harmonic) affords a moderately strong transient for **1a**, $\lambda_{\max} \leq 310$ nm, and a very strong transient for **1b**, $\lambda_{\max}$ 330 nm in heptane and 335 nm in methanol (Figure 1). The transient lifetimes (nanoseconds) in heptane (methanol) are, for **2a**, 49 (50) ± 5%, for **2b**, 56.2 (66.7) ± 2%, and for **2c**, 57.1 (67.6) ± 2%. Mass spectrometric analysis of **2c** showed $d_0 < 1\%$, $d_1 = 10\%$, $d_2 = 79\%$, and $d_3 = 10\%$; NMR showed 0.1 H at δ 2.59 (H-3) and 1.8 H at δ 2.51 (H-6).

Three assignments are possible for the transient according to Scheme I: S_1 of the ketone, T_1 of the ketone, or the triplet biradical. Since the fluorescence of **1b** (3.3 ± 0.3 ns) is much faster than decay of the transient absorption, the transient from **1b** at least is not the ketone singlet. The transients are affected

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[†] On leave from the Department of Chemistry, University of Tsukuba, Japan.

(1) Weiss, D. S. In "Organic Photochemistry", Padwa, A., Ed.; Marcel Dekker: New York, 1981; Vol. 5, pp 347ff. Provides a good recent review.

(2) (a) Baum, A. *Tetrahedron Lett.* **1972**, 1817. (b) Wagner, P. J.; Stratton, T. J. *Tetrahedron* **1981**, *37*, 3317.

0002-7863/84/1506-2471$01.50/0