

that in the biosynthesis of the growing polyhydroxy fatty acid chain,  $\beta$ -ketoacyl CoA reduction can occur with either stereochemistry. For the moment no information is available as to how the secondary methyl stereochemistry at C-2, C-4, C-6, and C-24 is set.<sup>26</sup> While further experiments, now in progress, will be required to determine directly the origins of the three remaining ether oxygens as well as that of the C-26 hydroxyl, it is likely that all four atoms are derived from molecular oxygen. Extending the original suggestion of Westley,<sup>7</sup> it is therefore interesting to speculate that the first formed polyfunctional fatty acid would be the all-(*E*)-triene **6**<sup>27</sup> which could undergo epoxidation to give the (12*R*,13*R*,16*R*,17*R*,20*S*,21*S*)-triopoxide **7** (Scheme III). Attack of the C-5 hydroxyl of **7** at the C-9 carbonyl carbon would initiate a cascade of ring closures to generate all five ether rings of monensin. These results are also in accord with similar findings by Hutchinson et al. on the biosynthesis of the aromatic polyether lasalocid, reported in the accompanying communications.<sup>29</sup>

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(26) The methyl group stereochemistry at C-18 and C-22 is presumably determined as a consequence of the reduction of  $\alpha$ -methyl,  $\alpha,\beta$ -unsaturated-acyl-CoA intermediates, analogous to those of normal fatty acid biosynthesis: F. Lynen, *Biochem. J.*, **102**, 381 (1967); K. Bloch and D. Vance, *Annu. Rev. Biochem.*, **46**, 263 (1977); B. Sedgwick and J. W. Cornforth, *Eur. J. Biochem.*, **75**, 465 (1977); B. Sedgwick, J. W. Cornforth, S. J. French, R. T. Gray, E. Kelstrup, and P. Willadsen, *ibid.*, **75**, 481 (1977); B. Sedgwick, C. Morris, and S. J. French, *J. Chem. Soc., Chem. Commun.*, 193 (1978).

(27) Each (*E*)-olefin could be formed by either syn dehydration of an erythro- $\alpha$ -alkyl- $\beta$ -hydroxyacyl-CoA or anti dehydration of the corresponding threo- $\alpha$ -alkyl- $\beta$ -hydroxyacyl-CoA. In the latter regard we note the three relationship of the C-2, -3, C-4, -5, and C-6, -7 centers of monensin itself. The same three stereochemistry is prevalent in all known macrolides, as summarized by Celmer's rules.<sup>28</sup>

(28) W. D. Celmer, *Pure Appl. Chem.*, **28**, 413 (1971); W. D. Celmer, *J. Am. Chem. Soc.*, **87**, 1801 (1965).

(29) C. R. Hutchinson, M. M. Sherman, J. C. Vederas, and T. T. Nakashima, *J. Am. Chem. Soc.*, first paper in this series; C. R. Hutchinson, M. M. Sherman, J. C. Vederas, A. G. McInnes, and J. A. Walters, *ibid.*, second paper in this series.

## Reaction of Alkoxides with (Phenylthio)carbene: A Novel Oxyanionic Substituent Effect on the C-H Insertion of Carbenes

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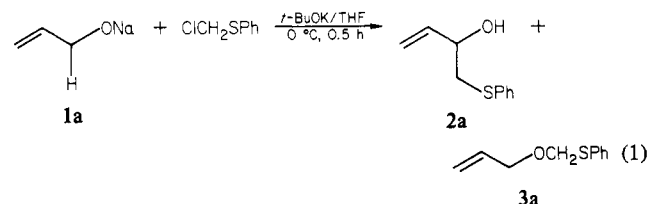
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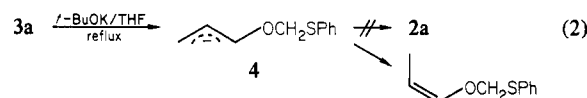
While the addition of carbenes to alkenes has been utilized as an efficient tool for C-C bond formation in organic synthesis, the insertion of carbenes has been overlooked owing to its less selective nature.<sup>1</sup> An activation of a particular C-H bond seems to be a requisite for the selective insertion to occur. For example, Seyferth et al. have reported that the  $\alpha$ -C-H bond of tetrahydrofuran shows enhanced reactivity toward dichlorocarbene

generated from  $\text{PhHgCCl}_2\text{Br}$  to give the insertion product in high yield.<sup>2</sup> In connection with the current interest in oxyanionic substituent effects,<sup>3</sup> we have examined the reactivity of carbenes toward alkoxide anions. Herein we wish to report a novel effect of oxyanion substituent which greatly facilitates the insertion of (phenylthio)carbene<sup>4</sup> into the  $\alpha$ -C-H bond of alkoxide anions.<sup>5</sup>

To a mixed suspension of sodium allylalkoxide (**1a**, 2.5 equiv) and *t*-BuOK (2.5 equiv) in THF was added a THF solution of chloromethyl phenyl sulfide, and the total mixture was stirred for 0.5 h at 0 °C. After aqueous workup followed by column chromatography, 1-(phenylthio)-3-buten-2-ol (**2a**) and allyl (phenylthio)methyl ether (**3a**) were isolated in 29% and 64% yield, respectively (eq 1). The formal insertion product **2a** could be

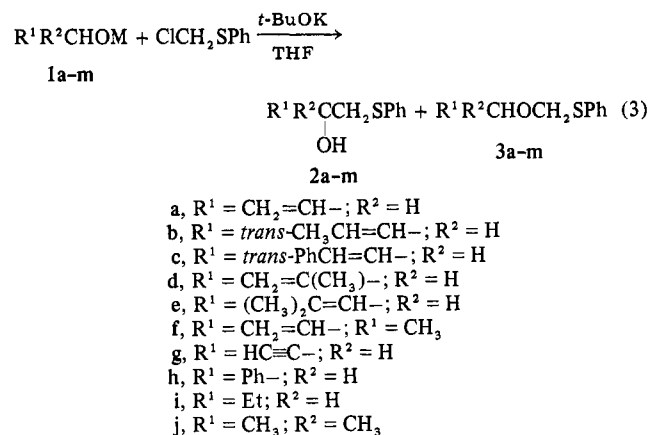


produced via a Wittig rearrangement of the first formed ether **3a** as shown in eq 2. However, the possibility is ruled out as



follows: **3a** slowly isomerized to *cis*-1-propenyl (phenylthio)methyl ether without the formation of **2a** when treated with *t*-BuOK (1.25 equiv) in refluxing THF.<sup>8</sup> Thus, under these reaction conditions allylic carbanion **4**, if formed, cannot be rearranged to give **2a**.

Not only other allylic alkoxides but also propargylic, benzylic, and even simple alkyl alkoxides undergo C-H insertion reaction to give  $\beta$ -phenylthio alcohols **2a-m** besides forming the corresponding ether **3a-m** (eq 3). These results are summarized in Table I.



While a small amount of olefin addition product **5** (13%) was obtained in addition to the insertion product **2e** in the reaction

(2) Seyferth, D.; Mai, V. A.; Gordon, M. E. *J. Org. Chem.* **1970**, *35*, 1993.

(3) (a) Evans, D. A.; Baillargeon, D. J. *Tetrahedron Lett.* **1978**, 3315 and 3319, and references cited therein. (b) Steigerwald, M. L.; Goddard, W. A., III; Evans, D. A. *J. Am. Chem. Soc.* **1979**, *101*, 1994.

(4) (a) For organosulfur carbenes and carbenoids see, for example: Block, E. "Reaction of Organosulfur Compounds"; Academic Press: New York, 1978. (b) Schöllkopf, U.; Lehmann, G. J.; Paust, J.; Härtl, H.-D. *Chem. Ber.* **1964**, *97*, 1527. (c) Boche, G.; Schneider, D. R. *Tetrahedron Lett.* **1975**, 4247.

(5) Under the reaction conditions of the Williamson synthesis, observations of complex reactions have sometimes been reported. For example, Corey et al. have noted a complex reaction between iodomethyl methylsulfide and secondary or tertiary sodium alkoxides.<sup>6</sup> Carig et al. have detected the C-H insertion product of vinylidenecarbene when they treated 1-bromoalk-1-ynes or 1-bromo 1,2-dienes with sodium alkoxides.<sup>7</sup>

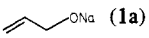

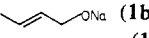
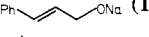
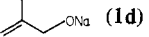
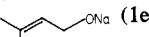
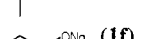
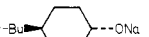
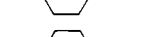
(6) Corey, E. J.; Bock, M. G. *Tetrahedron Lett.* **1975**, 3269.

(7) (a) Craig, J. C.; Beard, C. D. *Chem. Commun.* **1971**, 693. (d) *J. Am. Chem. Soc.* **1974**, *96*, 7950.

(8) Price, C. C.; Snyder, W. H. *J. Am. Chem. Soc.* **1961**, *83*, 1773.

(1) (a) Kirmse, W. "Carbene Chemistry", 2nd ed.; Academic Press: New York, 1971. (b) Parham, E. P.; Schweizer, E. E. *Org. React.* **1963**, *13*, 55. (c) Burke, S. D.; Grieco, P. A. *Ibid.* **1971**, *26*, 361. (d) Simmons, H. E.; Cairns, T. L.; Vladuchick, S. A.; Hoiness, C. M. *Ibid.* **1973**, *20*, 1.

Table I. Reaction of Alkoxides with (Phenylthio)carbene<sup>a</sup>

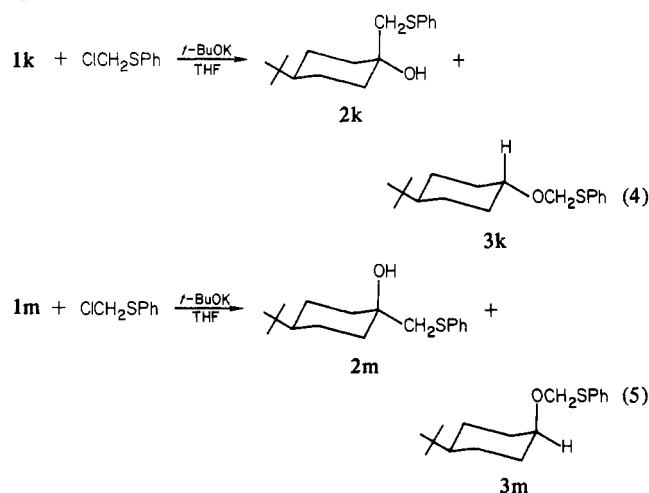
entry	alkoxides	(amount, equiv)	time, h	product <sup>b</sup> (yield, %) <sup>c</sup>	
				C-H insertion	C-M insertion
1	 (1a)	(2.5)	0.5	2a <sup>d</sup> (29)	3a <sup>d</sup> (64)
2 <sup>e</sup>	 (1b)	(2.5)	0.5	2a (26)	3a (30)
3	 (1c)	(2.5)	0.5	2b <sup>d</sup> (43)	3b <sup>d</sup> (38)
4	 (1c)	(2.5)	0.5	2c <sup>d</sup> (45)	3c <sup>d</sup> (43)
5	 (1d)	(2.5)	0.5	2d (42)	3d (40)
6	 (1e)	(2.5)	0.5	2e (38) 5 <sup>f</sup> (13)	3e (34)
7	 (1f)	(1.25)	0.5	2f (41)	3f (23)
8	HC≡CCH <sub>2</sub> ONa (1g)	(2.5)	0.5	2g (22)	3g (22) 6 <sup>g</sup> (39)
9	PhCH <sub>2</sub> OLi <sup>h</sup> (1h)	(1.25)	1.0	2h <sup>d</sup> (48)	3h <sup>d</sup> (22)
10	<i>n</i> -PrONa (1i)	(1.25)	0.5	2i (9)	3i (91)
11	<i>i</i> -PrOLi <sup>h</sup> (1j)	(1.25)	1.0	2j (12)	3j (36)
12	 (1k)	(1.25)	0.5	2k <sup>d</sup> (6)	3k <sup>d</sup> (27)
13	 (1m)	(1.25)	0.5	2m <sup>d</sup> (22)	3m (18)

<sup>a</sup> Unless otherwise noted, sodium alkoxides (1.25–2.5 equiv) prepared in situ from the corresponding alcohols with NaH in THF were allowed to react with ClCH<sub>2</sub>SPh (1 equiv) and *t*-BuOK (equivalent to alkoxides) for the period indicated. <sup>b</sup> All products showed satisfactory spectral data (IR, <sup>1</sup>H NMR, and mass). <sup>c</sup> Yields refer to the isolated yield based on ClCH<sub>2</sub>SPh. <sup>d</sup> Satisfactory analytical results were obtained for these compounds. <sup>e</sup> *t*-BuONa (2.5 equiv) was employed in place of *t*-BuOK. <sup>f</sup> 5; [3,3-dimethyl-2-(phenylthio)cyclopropyl]-methanol (mixture of isomers). <sup>g</sup> 6; CH<sub>2</sub>=C=CHOCH<sub>2</sub>SPh. <sup>h</sup> Lithium alkoxide prepared in situ from the corresponding alcohol with BuLi was used.

of sodium prenyl alkoxide (entry 6), no addition product was detected in other series of allylic alkoxides. These results present a remarkable contrast to the reported addition of dihalocarbene to allylic ethers and alcohols.<sup>9</sup> Seyferth et al. have reported that dichlorocarbene generated from PhHgCCl<sub>2</sub>Br reacts with allyl ethyl ether to give both the addition and the C–H insertion product in 82% and 14% yield, respectively.<sup>9a</sup> Exclusive addition of dihalocarbenes generated under phase-transfer conditions to allylic alcohols, such as methallyl alcohol and prenyl alcohol, was also reported.<sup>9d,e</sup> To ascertain that the present characteristic reactivity of the α-C–H bond of alkoxides is not due to the reactivity of (phenylthio)carbene but to an oxyanionic substituent effect, the following experiments were performed. (Phenylthio)carbene, generated under phase-transfer conditions (CH<sub>2</sub>Cl<sub>2</sub>–aqueous 50% NaOH using BzNEt<sub>3</sub><sup>+</sup>Cl<sup>–</sup> as a catalyst),<sup>4c</sup> was allowed to react with prenyl alcohol to give olefin adduct **5** (3.8%) together with prenyl (phenylthio)methyl ether **3e** (41%).<sup>10</sup> The insertion product **2e** could not be detected after thorough examination of the reaction mixture by means of column chromatography. Moreover, the reaction of methallyl methyl ether with (phenylthio)carbene under similar conditions only gave an olefin adduct, 2-methyl-2-(methoxymethyl)-1-(phenylthio)cyclopropane (36%).

The present oxyanionic substituent effect which facilitates the C–H insertion seems to be based on (1) the decrease in the C–H bond energy of alkoxides<sup>3b</sup> and (2) the stabilization of the polar transition state **7** by electron-donating substitution.<sup>11</sup> The ste-

reospecificity of the reaction as demonstrated below supports the validity of this concerted mechanism of the C–H insertion. Thus, the sodium alkoxides of *trans*- and *cis*-4-*tert*-butylcyclohexanol in the reaction with (phenylthio)carbene stereospecifically<sup>14</sup> gave the axial (**2k**) and equatorial C–H insertion product (**2m**), respectively (entry 12 and 13, eq 4 and 5).<sup>15</sup> As shown in Table



(9) (a) Seyferth, D.; Burlitch, J. M.; Minasz, R. J.; Mui, J. Y.-P.; Simmons, H. D., Jr.; Treiber, A. J. H.; Dowd, S. R. *J. Am. Chem. Soc.* **1965**, *87*, 4259. (b) Seyferth, D.; Mai, V. A. *Ibid.* **1970**, *92*, 7412 and references cited therein. (c) Hirano, S.; Hiyama, T.; Nozaki, H. *Tetrahedron* **1976**, *32*, 2381. (d) Hiyama, T.; Tsukamoto, M.; Nozaki, H. *J. Am. Chem. Soc.* **1976**, *98*, 3713. (e) Kleveland, K.; Skattebøl, L.; Sydnæs, L. K. *Acta Chem. Scand. Ser. B* **1977**, *B31*, 463.

(10) **3e** might be formed either by O–H insertion of (phenylthio)carbene or by S<sub>N</sub>2 displacement reaction.

(11) The insertion may occur by attack either on the electrons of the C–H bond (7)<sup>12</sup> or on the hydrogen atom via the transition state with a linearly arranged PhSCH<sub>2</sub>–H–C(O<sup>–</sup>) conformation.<sup>13</sup>

(12) (a) Doering, W. von E.; Prinzbach, H. *Tetrahedron* **1959**, *6*, 24. (b) Skell, P. S.; Woodworth, R. C. *J. Am. Chem. Soc.* **1956**, *78*, 4496. (c) Reference 2. (d) Gutsche, C. D.; Bachman, G. L.; Udell, W.; Bauerlein, S. *J. Am. Chem. Soc.* **1971**, *93*, 5172.

(13) (a) Benson, S. W.; DeMore, W. B. *Adv. Photochem.* **1964**, 219. (b) Dobson, R. C.; Hayes, D. M.; Hoffman, R. *J. Am. Chem. Soc.* **1971**, *93*, 6188. (c) Bodor, N.; Dewar, M. J. S.; Wasson, J. S. *Ibid.* **1972**, *94*, 9095.

(14) In each reaction, the other stereoisomer could not be detected by VPC analysis of the reaction mixtures.

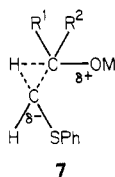
(15) Structures of isomeric alcohols **2k** and **2m** are determined after the desulfurization of one isomer **2m** to the known *cis*-4-*tert*-butyl-1-methylcyclohexanol (mp 69–70 °C, lit. 69–70 °C,<sup>16</sup> 70.5–71 °C<sup>17</sup>) using Raney nickel in refluxing ethanol (94% yield). Structures of **3k** and **3m** were determined by means of <sup>1</sup>H NMR spectral analysis of their C(1) protons: the axial proton of **3k** resonates as a broad multiplet (ca. 40 Hz) centered at δ 3.55, while the equatorial proton of **3m** resonates as a multiplet (ca. 16 Hz) at δ 4.00.<sup>18</sup>

(16) Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1965**, *87*, 1353.

(17) Depuy, C. H.; King, R. W. *J. Am. Chem. Soc.* **1961**, *83*, 2743.

(18) Jackman, L. M.; Sternhell, S. "Application of Nuclear Magnetic Resonance in Organic Chemistry, 2nd ed.; Pergamon Press: 1969; Chapter 4-1.

In the ratio of the C-H insertion to the formal C-Metal insertion rises with the increase of electron-donating substitution at the olefin or  $\alpha$ -carbon site, and this validates the second factor for facilitating the C-H insertion (vide supra).



As to the formation of ether **3**, there are two possible mechanisms: (1)  $S_N2$  attack of alkoxide anion on  $\text{ClCH}_2\text{SPh}$  and (2) the insertion of (phenylthio)carbene into the oxygen-metal bond and subsequent protonation. In the absence of *t*-BuOK, sodium allylalkoxide reacts with  $\text{ClCH}_2\text{SPh}$  very slowly at  $0^\circ\text{C}$ , and only a trace amount of **3a** is produced together with the almost quantitative recovery of  $\text{ClCH}_2\text{SPh}$  after reacting for 1 h. While this result suggests mechanism 2, there still remains at present a possibility of mechanism 1 where the addition of *t*-BuOK provides the corresponding potassium alkoxide as an active nucleophile. A reaction using *t*-BuONa in place of *t*-BuOK was performed, giving rise to the formation of **2a** and **3a** in 26% and 30% yield, respectively (entry 2, Table I). Thus, at least in this reaction, it is apparent that the formation of **3a** proceeds via the insertion of (phenylthio)carbene into the oxygen-sodium bond.

Work is in progress to disclose more precisely the nature and the synthetic potential of the present reaction.

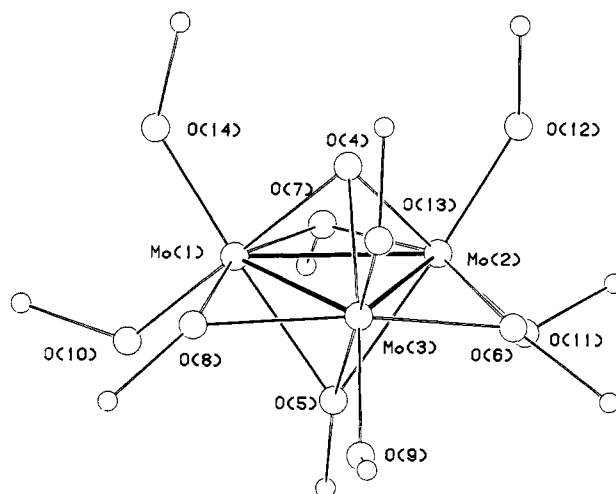
### Oxotrimolybdenum(IV) Alkoxides, $\text{Mo}_3(\mu_3\text{-O})(\mu_3\text{-OR})(\mu_2\text{-OR})_3(\text{OR})_6$ ( $\text{R} = \text{CH}(\text{CH}_3)_2$ and $\text{CH}_2\text{C}(\text{CH}_3)_3$ ). Synthetic Considerations

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Recently a large class of *triangulo*- $\text{M}_3$  complexes of molybdenum and tungsten have been discovered.<sup>1</sup> Some of these have involved 8-4 cluster electrons, though most commonly the number is 6. As yet little is known about the reaction pathways leading to these compounds, though they do appear to form very readily with a variety of ligands. For example, Bino, Cotton, and Dori recently reported<sup>2</sup> their characterization of six compounds of formula  $[\text{Mo}_3(\mu_3\text{-X})(\mu_3\text{-Y})(\text{OAc})_6(\text{H}_2\text{O})_3]_x \cdot y\text{H}_2\text{O}$ , where  $\text{X} = \text{Y} = \text{O}$ ,  $\text{X} = \text{Y} = \text{CCH}_3$ , and  $\text{X} = \text{O}$ ,  $\text{Y} = \text{CCH}_3$ . All of these were formed in the reaction between  $\text{Mo}(\text{CO})_6$ ,  $\text{AcOH}$ , and  $(\text{AcO})_2\text{O}$ , which also yields the well-known dinuclear compound  $\text{Mo}_2(\text{OAc})_4$  ( $\text{M}^4\text{-M}$ ). We wish here to report our discovery of oxotrimolybdenum(IV) alkoxides of formula  $\text{Mo}_3(\mu_3\text{-O})(\mu_3\text{-OR})(\mu_2\text{-OR})_3(\text{OR})_6$ , where  $\text{R} = \text{isopropyl (i-Pr)}$  and neopentyl (Ne), and furthermore to show that these compounds can be prepared in high yields by rational syntheses based on known reactivity patterns of metal-metal bonds.

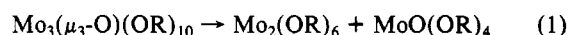
During the course of studies of the reactions between  $\text{Mo}_2(\text{OR})_6$  compounds and molecular oxygen, which lead ultimately to  $\text{MoO}_2(\text{OR})_2$  compounds with cleavage of the  $\text{Mo}\equiv\text{Mo}$  bond,<sup>3</sup> we noted the formation of green intermediates when  $\text{R} = \text{i-Pr}$  and



**Figure 1.** ORTEP view of the central  $\text{Mo}_3\text{O}(\text{OC})_{10}$  skeleton of the  $\text{Mo}_3\text{O}(\text{ONe})_{10}$  molecule. All atoms are assigned arbitrary thermal parameters. Each molybdenum atom is in a distorted octahedral environment with respect to six directly bonded oxygen atoms. Pertinent bond distances in Å (averaged) are  $\text{Mo-Mo} = 2.529$  (9),  $\text{Mo}-\mu_3\text{O}(\text{oxo}) = 2.03$  (3),  $\text{Mo}-\mu_3\text{OR} = 2.21$  (3),  $\text{Mo}-\mu_2\text{OR} = 2.02$  (3),  $\text{Mo-OR}(\text{terminal})$  trans to  $\text{O}(4) = 1.94$  (2),  $\text{Mo-OR}(\text{terminal})$  trans to  $\mu_3\text{-OR} = 1.85$  (3).

Ne ( $\text{Ne} = \text{CH}_2\text{CMe}_3$ ). Indeed, from reactions involving  $\text{Mo}_2(\text{ONe})_6$  and  $\text{O}_2$ , we were able to isolate the green crystalline compound  $\text{Mo}_3\text{O}(\text{ONe})_{10}$ , which was fully characterized by an X-ray study.<sup>4</sup> An ORTEP view of the central  $\text{Mo}_3\text{O}(\text{OC})_{10}$  skeleton of the molecule is shown in Figure 1 along with some pertinent bond distances.

A retrosynthetic analysis suggested that the *triangulo*- $\text{Mo}_3(\mu_3\text{-O})$  unit could be constructed by the addition of an oxomolybdenum (6+) unit across the  $\text{Mo}\equiv\text{Mo}$  bond as in reaction 1. This bears analogy with the approach to cluster synthesis adopted by Stone and co-workers involving  $\text{M}=\text{CR}_2$  and  $\text{M}\equiv\text{CR}$  groups.<sup>5</sup>



The oxomolybdenum(6+) alkoxides,  $\text{MoO}(\text{OR})_4$ , which were unknown, were viewed as the products of a simple replacement of a  $\text{Mo}\equiv\text{Mo}$  bond<sup>6</sup> by two  $\text{Mo}=\text{O}$  bonds in the oxygenolysis reaction (2). Previously it had been shown<sup>7</sup> that the three electron



ligand, NO, readily cleaves the  $\text{Mo}\equiv\text{Mo}$  bond to give two  $\text{Mo-NO}$  bonds, which may be formally viewed as  $\text{M}\equiv\text{N}-\text{O}$ .<sup>7</sup>

This synthetic strategy was successful:  $\text{Mo}_2(\text{OR})_8$  and molecular oxygen react to yield  $\text{MoO}(\text{OR})_4$  compounds which, in turn, react with  $\text{Mo}_2(\text{OR})_6$  compounds to yield  $\text{Mo}_3\text{O}(\text{OR})_{10}$  compounds in essentially quantitative reactions.<sup>8</sup>

(4) Crystals suitable for X-ray work were grown from methylene chloride. Crystal data, collected at  $-161^\circ\text{C}$ , using  $\text{Mo K}\alpha$  radiation, gave the following:  $a = 35.56$  (2),  $b = 18.97$  (1),  $c = 19.34$  (1) Å; space group *Pbcn*;  $Z = 8$ ;  $d_{\text{calc}} = 1.295 \text{ g cm}^{-3}$ . Of the 10379 reflections measured in the range  $6 \leq 2\theta \leq 40^\circ$ , 6102 were unique. Only 55% of the unique data were observed using the criteria  $F \geq 2.33\sigma(F)$ . In retrospect, this was proven to be caused by loss of a solvent molecule ( $\text{CH}_2\text{Cl}_2$ ) and disorder of one of the ONe ligands [O(5) in Figure 1] and high thermal motions of all the neopentyl groups. The structure was readily solved by direct methods and Fourier techniques and refined by full-matrix least squares. Only the largest 1500 reflections were used in the refinement. Molybdenum atoms were assigned anisotropic thermal parameters, and all other atoms were assigned isotropic parameters. Two peaks that occurred in a void in the crystal were assigned as chlorine atoms, whose occupancy refined to 0.33. The carbon of the  $\text{CH}_2\text{Cl}_2$  molecule was not discernible. Final residuals are  $R(F) = 0.0752$  and  $R_w(F) = 0.0759$ .

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