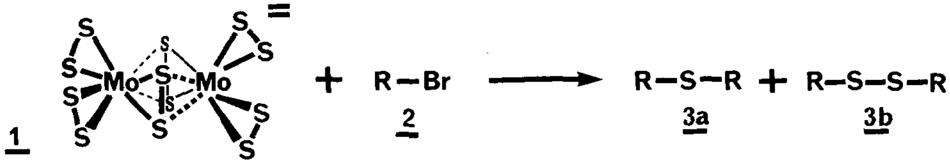
Tetrahedron Letters,Vol.25,No.7,pp 703-706,1984
Printed in Great Britain
0040-4039/84 $3.00 + .00

CHEMISTRY OF A MOLYBDENUM-PERSULFIDE COMPLEX: ALKYLATION AND OXIDATIVE COUPLING[1]

David N. Harpp* and J. Gavin MacDonald
Department of Chemistry, McGill University
Montreal, Quebec, Canada H3A 2K6

ABSTRACT: The reaction of alkyl halides, sulfinyl and sulfonyl chlorides with $(NH_4)_2[(S_2)_2Mo(S_2)_2Mo(S_2)_2]$ has been found to afford sulfides and disulfides in good-excellent isolated yield. The effect of solvent polarity and reaction time is discussed.

There is much current interest in the study of complexes containing molybdenum and sulfur[2], not least because of the coordination of molybdenum by a group of sulfur atoms in each of the molybdenum-containing enzymes such as nitrogenase, sulfite oxidase and xanthine oxidase[3]. Recent developments in molybdenum-sulfur chemistry serve to demonstrate the structural diversity possible for combination of these elements. Although these thioanions[4], organic-ligand complexes[5] and polymetallic heteronuclear clusters[6] continue to stimulate the interest of both theoretical and synthetic chemists, very few studies have been conducted to investigate the reactivity of these complexes with organic reagents[7]. We wish to report our initial findings on the chemistry of 1.

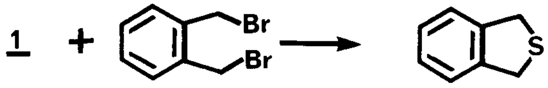


Reaction of $(NH_4)_2[Mo_2S_{12}]$ (1)[8] with benzyl bromide (2, R = $PhCH_2$-) in benzene in a sealed tube at 90°C gave after work-up, a 8:1 mixture of dibenzylsulfide (3a) to dibenzyldisulfide (3b) in 94% isolated yield[9]. Repeating the reaction with acetonitrile as solvent gave a 1:1 mixture of 3a to 3b in 95% overall yield. A series of alkyl bromides on treatment with reagent 1 with acetonitrile or benzene as solvent also gave a mixture of sulfides and disulfides (Table 1). It is of note that in benzene the more reactive benzyl bromide gave mainly sulfide whereas pentyl bromide gave mainly disulfide.

TABLE 1

Product	R	RSR:RSSR		Isolated Yield (%)	
		C_6H_6	CH_3CN	C_6H_6	CH_3CN
3a	$C_6H_5CH_2$-	8:1	1:1	94	95
3b	$CH_3(CH_2)_4$-	1:5	1:10	52	83
3c	cyclohexyl-	1:2	1:1	60	84

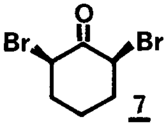
Interestingly, reaction of 1 with α,α'-dibromo-o-xylene (4) under similar conditions gave 1,3-dihydroisothianaphthene (5) as the sole product in good yield (67% in benzene and 70% in acetonitrile)[10]. Treatment of 2-bromo-2-methyl propane (6), 2,6-dibromocyclohexanone (7), or 1,3-dibromopropane (8) with sulfide reagent 1 in benzene or acetonitrile gave only starting materials even after prolonged heating.



4 5

$(CH_3)_3CBr$

6



7

$BrCH_2CH_2CH_2Br$

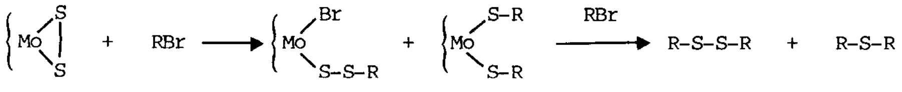
8

In order to help elucidate the mechanism of the alkylation reaction, a solvent/time study was undertaken using benzyl bromide. It can be seen from Table 2 that in a non-polar solvent, the longer the reaction time, the greater the ratio of sulfide to disulfide. This trend is not observed in the more polar solvent (acetonitrile) where a 1:1 ratio of sulfide and disulfide is formed[11].

TABLE 2

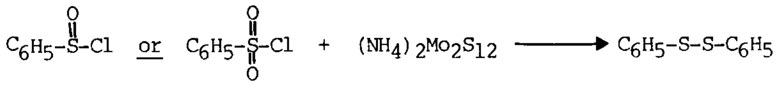
Solvent	Time(h)	Ratio (RSR:RSSR)	Yield (%)
C_6H_6	20	3:1	90
C_6H_6	34	5:1	95
C_6H_6	48	8:1	94
C_6H_6	96	10:1	98
CH_3CN	20	1:1	85
CH_3CN	34	1:1	95
CH_3CN	96	1:1	90
CH_3CN	116	1:1	87

As a working hypothesis, we propose that the alkylation reaction involves the addition of the alkyl bromide across both the Mo-S and S-S bonds to afford the molybdenum alkyl disulfide 9 and sulfide 10. These in turn would react with another molecule of alkyl bromide. Intermediates of type 10 are known and have been shown to react with alkyl halides to yield the sulfide[12].



9 10

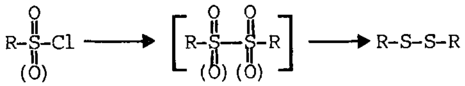
The solvent/reaction time study (Table 2) suggests a competition between the two pathways.



$$C_6H_5\text{-}\overset{O}{\overset{\|}{S}}\text{-}Cl \text{ or } C_6H_5\text{-}\underset{O}{\overset{O}{\overset{\|}{\underset{\|}{S}}}}\text{-}Cl + (NH_4)_2Mo_2S_{12} \longrightarrow C_6H_5\text{-}S\text{-}S\text{-}C_6H_5$$

11 12 1 13

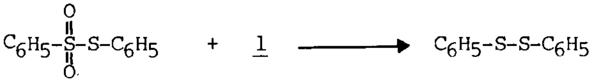
We also examined the reaction of the persulfide complex 1 with sulfinyl and sulfonyl chlorides. treatment of 1 with either benzenesulfinyl chloride (11) or benzene sulfonyl chloride (12), in refluxing acetonitrile under a nitrogen atmosphere for 8h gave a 68% and 90% yield, respectively, of diphenyl disulfide (13)[9].



$$R\text{-}\underset{(O)}{\overset{O}{\overset{\|}{\underset{\|}{S}}}}\text{-}Cl \longrightarrow \left[R\text{-}\underset{(O)}{\overset{O}{\overset{\|}{\underset{\|}{S}}}}\text{—}\underset{(O)}{\overset{O}{\overset{\|}{\underset{\|}{S}}}}\text{-}R\right] \longrightarrow R\text{-}S\text{-}S\text{-}R$$

11,(12) (13)

In similar fashion, reaction of toluenesulfonyl chloride with 1 gave a 67% yield of ditolyl disulfide. However, toluenesulfonic acid did not react and only starting material was recovered even after prolonged reflux (20h). Examples of this type of oxidative coupling are rare[13]. Although no intermediates have been isolated to date, it seems probable that the reaction pathway involves the formation of, in the sulfinyl case, an α-disulfoxide (which would be expected to rearrange to the thiosulfonate[14]) or, in the sulfonyl chloride system, the α-disulfone. These intermediates would then be reduced to the disulfide. Support for this pathway was obtained when a sample of benzenethiosulfonate (14) was refluxed in acetonitrile with 1 for 4h under a nitrogen atmosphere to yield 81% of diphenyl disulfide (13)[15].



$$C_6H_5\text{-}\underset{O}{\overset{O}{\overset{\|}{\underset{\|}{S}}}}\text{-}S\text{-}C_6H_5 + 1 \longrightarrow C_6H_5\text{-}S\text{-}S\text{-}C_6H_5$$

14 13

Further synthetic and mechanistic studies involving the use of molybdenum persulfide complexes are currently under investigation.

Acknowledgement: We gratefully acknowledge the Natural Sciences and Engineering Council of Canada for financial support of this work.

REFERENCES

1. Organic Sulfur Chemistry. Part 46. For part 45 see D. N. Harpp, T. Aida and T.H. Chan, Tetrahedron Lett., 5173 (1983).

2. W. Clegg, G. Christou, C.D. Gardiner and G.M. Sheldrick, Inorg.Chem., 20, 1562 (1981); "Molybdenum and Molybdenum Containing Enzymes", M. Coughlin, Ed., Pergamon Press: New York, 1980; A. Müller, and W. Jaegermann, Inorg. Chem., 18, 2631 (1979).

3. J. Bordas, R. C. Bray, C.D. Garner, S. Gutteridge and S. S. Hasnain, J. Biochem., 191, 499 (1980); S.P. Cramer, H.B. Gray and K. V. Rajagopalan, J. Am. Chem. Soc., 101, 2772 (1979); S. P. Cramer, K. O. Hodgson, L.E. Mortenson, E.I. Stiefel, J.R. Chrisnell, W.J. Brill and V.K. Shah, J. Am. Chem. Soc., 100, 3814 (1978).

4. W. H. Pan, M. E. Leonowicz and E. I. Stiefel, Inorg.Chem., 22, 672 (1983); A. Muller, W. O. Nolte and B. Krebs, Inorg. Chem., 19, 2835 (1980).

5. K. F. Miller, A. E. Bruce, J. L. Corbin, S. Wherland and E. I. Steifel, J. Am. Chem. Soc., 102, 5104 (1980) and references cited therin.

6. D. Coucouvanis, Accts. Chem. Res., 14, 201 (1981).

7. T. R. Halbet, W. H. Pan and E. I. Steifel, J. Am. Chem. Soc., 105, 5476 (1983).

8. A. Muller, W. O. Nolte and B. Krebs, Ang. Chem. Int. Ed. Eng., 17, 279 (1978).

9. The structures of the products were assigned on the basis of glc analysis and by comparison of their spectral and physical data with authentic samples. Glc analyses were conducted on a Varian Gas Chromatograph Model 3700 with Varian 4270 Integrator using a capillary column with appropriate standards.

10. PMR (60MHz, $CDCl_3$) 7.14 (s, 4H) and 4.20 (s, 4H); MS, m/e 136 (M^+); Anal. Calc'd for C_8H_8S: C, 70.54; H, 5.92; S, 23.54, Found: C, 70.44; H, 5.92; S, 23.64.

11. Authentic samples of dibenzyl disulfide and sulfide remained unchanged when heated in acetonitrile or benzene with 1 under "reaction" conditions for 50h.

12. Private communication: A. G. Shaver and G. Marmolejo, McGill University.

13. P. Kielbasinski, J. Drabowicz and M. Mikolajczyk, J. Org. Chem., 47, 4808 (1982); G. A. Olah, S. C. Narang, L. D. Field and G. F.Salem, J. Org. Chem., 45, 4792 (1980); T.H. Chan, J.P. Montillier, W.F. VanHorn and D. N. Harpp, J. Am. Chem. Soc., 92, 7224 (1970).

14. For example see: F. Freeman and C. N. Angeletakis, J. Am. Chem. Soc., 105, 4039 (1983).

15. The persulfide complex 1 does not appear to be a general reducing agent as treatment of 1 in acetonitrile with a variety of aralkyl and dialkyl sulfoxides and sulfones gave no trace of sulfide; starting materials were recovered even after prolonged reflux.

(Received in USA 9 November 1983)