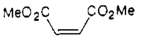
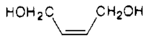
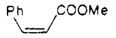
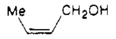
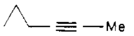
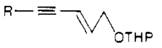
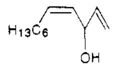
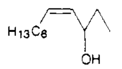
Table I. Stereoselective Hydrogenation of Alkynes, Enynes, and Dienes

entry	substrate	product	cis selectivity, % (cat. I)[a,b]
		Alkynes	
1	MeO_2C—≡—CO_2Me		97
2	Ph—≡—Ph		98
3	Me—≡—Ph		97
4	HOH_2C—≡—CH_2OH		97
5	Ph—≡—COOMe		95
6	Me—≡—CH_2OH		96
7			95
		Enynes	
8			
		a: R = CH_3	87[c] (86)[d]
		b: R = CH_2OTHP	85[c] (88)[d]
		Dienes	
9			85[c]
10			99
11			95

[a] Yields at 100% conversion. [b] Yields by GC/NMR. [c] Isolated yields. [d] Yields by Lindlar catalyst.

In contrast, analogous polymer-bound palladium(II) complex,[7] and Lindlar[8] and rhodium cationic complex catalysts[9] are sensitive to the nature of the systems and substituents present in those systems. Analogous polymer-bound palladium(II) complex displays cis selectivity as low as 50% for aromatic-substituted alkynes and high selectivity for simple alkynes.[7] The widely used Lindlar catalyst and recently reported Pd/W have shown 94% maximum cis selectivity in the semihydrogenation of triple bond in simple alkynes.[2,8,10] The striking failure of the Lindlar catalyst ($Pd/BaSo_4$) is evident in the semihydrogenation of methylphenylpropiolate (entry 5), which gave primarily totally hydrogenated product.[9] The cis selectivity in the semihydrogenation of conjugated enynes by the catalyst I is comparable with the Lindlar as described in the Table I.

Although rhodium cationic complex exhibited the cis selectivity as high as 99%, in most of the cases it shows poor selectivity in the hydrogenation of butynediol[9] (entry 4). Further, the recovery of this complex from the reaction medium is difficult.

The other striking feature of the present catalytic system is that unconjugated dienes are selectively hydrogenated without undergoing isomerization. The terminal double bond is preferentially hydrogenated in presence of hindered double bond (entry 9).

Thus the results of stereoselectivity described in this paper are demonstratively comparable and project the present catalytic system as practical and viable alternative to the Lindlar, rhodium cationic complex, polymer-anchored palladium(II) complex, and Pd/W for syntheses of various biologically active compounds.

The ^1H NMR data ($CDCl_3$, 300 MH_z) of the products for entries 8a, 8b, and 9 are as follows. 8a: δ 5.30–5.60 (m, 4 H), 5.05 (s, 1 H), 4.6 (d, 2 H), 3.9 (t, 2 H), 1.3–1.8 (m, 6 H), 1.58 (d, 3 H). 8b: δ 5.50–5.80 (m, 4 H), 4.90 (s, 2 H), 4.6 (d, 4 H), 3.50 (t, 2 H), 3.80 (t, 2 H), 1.2–1.8 (m, 12 H). 9: δ 5.25–5.7 (m, 2 H), 4.30 (m, 1 H), 2.10 (m, 2 H), 1.20–1.50 (m, 10 H), 0.9 (t, 6 H).

Acknowledgment. We thank P. Bharathi for the experimental assistance in the preliminary investigation and Dr. A. V. Rama Rao for his interest and encouragement for this work.

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Novel Alkylation with Tetrathiotungstates and Tetrathiomolybdates: Facile Synthesis of Disulfides from Alkyl Halides

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Summary: A novel reaction of alkyl halides with piperidinium tetrathiotungstate or piperidinium tetrathiomolybdate (MS_4^{2-}) has been found to afford disulfides in good to excellent isolated yields under very mild reaction conditions.

Sir: Interest in sulfur-containing compounds of molybdenum and tungsten has grown with respect to their implications in bioinorganic chemistry and catalysis.[1,2] Although these thioanions,[3] organic ligand complexes,[4] and polymeric heteronuclear clusters[5] have been the subject

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Table I. Reaction of Tetrathiotungstate 1a with Alkyl Halides

entry	substrate	product[a]	yield,[b] %
1	$PhCh_2Br$ **2a**	$PhCH_2S\text{-})_2$ **3a**	70
		$PhCH_2SH$ **4**	15
2	$PhCH_2Cl$	**3a**	67
		4	20
3	$PhCH_2I$ **2c**	**3a**	98
4	$p\text{-}O_2NC_6H_4CH_2Br$ **2d**	$p\text{-}O_2NC_6H_4CH_2S\text{-})_2$ **3d**	83
5	$p\text{-}NCC_6H_4CH_2Br$ **2e**	$p\text{-}NCC_6H_4CH_2S\text{-})_2$ **3e**	100
6	$p\text{-}ClC_6H_4CH_2Cl$ **2f**	$p\text{-}ClC_6H_4CH_2S\text{-})_2$ **3f**	73
7	$m\text{-}CH_3OC_6H_4CH_2Br$ **2g**	$m\text{-}CH_3OC_6H_4CH_2S\text{-})_2$ **3g**	82
		$m\text{-}CH_3OC_6H_4CH_2SH$ **5**	17
8	$m\text{-}CH_3OC_6H_4CH_2Cl$ **2h**	**3g**	76
		5	23
9	$CH_3CH_2CH_2CH_2Br$ **2i**	$CH_3CH_2CH_2CH_2S\text{-})_2$ **3i**	99
10	CH_3CH_2Br **2j**	$CH_3CH_2S\text{-})_2$ **3j**	40
11	$C_6H_{11}Br$ **2k**	$C_6H_{11}S\text{-})_2$ **35**	85
12	$(CH_3)_2CHBr$ **2l**	$[(CH_3)_2CHS\text{-}]_2$ **3l**	43
13	$CH_2{=}CHCH_2Br$ **2m**	$CH_2{=}CHCH_2S\text{-})_2$ **3m**	58

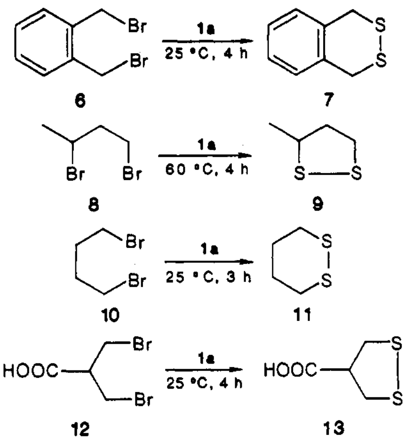
[a] All new compounds had satisfactory IR, NMR, mass spectral, and analytical data. [b] Yield refers to isolated products.

Table II. Reaction of Tetrathiomolybdate 1b with Alkyl Halides

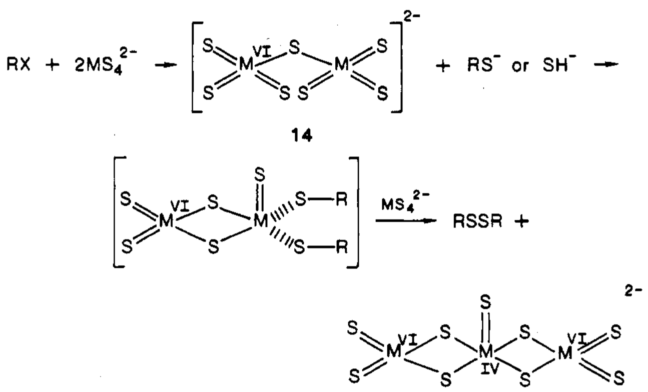
entry	substr	product[a]	yield,[b] %
1	**2a**	**3a**	90
2	**2d**	**3d**	59
3	**2e**	**3e**	65
4	**2f**	**3f**	99
5	**2g**	**3g**	73
6	**2i**	**3i**	97
7	**2k**	**3k**	76

[a] All new compounds had satisfactory IR, NMR, mass spectral, and analytical data. [b] Yield refers to isolated products.

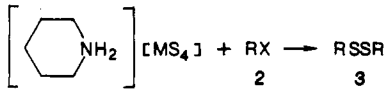
Scheme I



Scheme II



of study by theoretical and synthetic inorganic chemists, relatively few studies have been reported on reactivity with organic reagents.[6,7] Herein, we report our initial findings on a novel alkylation reaction of tetrathiometalates $[MS_4^{2-}]$ **1** of molybdenum and tungsten with alkyl halides. Reaction of piperidinium tetrathiotungstate (**1a**)[8] or piperidinium tetrathiomolybdate (**1b**)[8] with alkyl halides **2** in dimethylformamide at room temperature (25 °C) for 0.5–1.0 h gave after workup corresponding disulfides **3** in good to excellent yields.



1a, M = W; 1b, M = Mo

Although there are a number of methods available in the literature for the oxidation of thiols to disulfides,[9] the most commonly employed method for the direct conversion of alkyl halides to disulfides has been using Na_2S/S.[10] Unfortunately this transformation is usually effected at 70–90 °C for longer periods of time (20–30 h) to give moderate yields of the corresponding disulfides.

The results of sulfur transfer reactions on a variety of alkyl halides with **1a** and **1b** are summarized in Tables I and II, respectively. As the data in Table I indicate, benzyl chloride (**2b**) gave a slightly higher proportion of the minor product, thiol **4** (20%). On the other hand, benzyl iodide (**2c**) afforded the disulfide **3a** as the exclusive product in very high yield (98%). A similar trend was observed in the reaction of **2g** and **2h**. In all other cases disulfides were obtained in good yields without the formation of thiols. In the reaction of simple alkyl bromides with **1a**, it has been observed that primary bromides reacted faster to give better yields of the corresponding disulfides (entries 9–13, Table I). In all the reactions of alkyl halides with tetrathiomolybdate **1b** (Table II) disulfides **3** were the only

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products isolated in high yields.

This new methodology is equally effective for carrying out intramolecular reactions (Scheme I). Interestingly, reaction of **1a** with α,α'-dibromo-*o*-xylene (**6**)[11] afforded the cyclic disulfide **7**[12] as the sole product in excellent yield (94%).[13] Treatment of 1,3-dibromobutane (**8**) and 1,4-dibromobutane (**10**) with **1a** resulted in the formation of the corresponding cyclic disulfides **9** (61%) and **11**[14] (74%), respectively. Dibromo carboxylic acid **12** underwent a smooth alkylation at room temperature with **1a** to yield asparagusic acid (**13**) (77%), a naturally occurring 1,2-dithiolane.[15]

As a working hypothesis we propose a tentative mechanism for this novel alkylation which is outlined in Scheme II. The first step involves either an alkylation across the M–S bond to facilitate the departure of RS^- or protonation of WS_4^{2-} (from piperidinium cation) to help the departure of SH^- concomitant with dimerization to form intermediate $M_2S_7^{2-}$ ion **14**. This type of ion has previously been postulated[3e,16] that undergoes reduction of the metal with the oxidation of the ligand in an induced intramolecular electron-transfer pathway to form the disulfide. This suggestion is in support of an earlier observation that the alkylation of WS_4^{2-} bonds was a key feature of the mechanism of formation of $W_3S_9^{2-}$.[17a] It is likely that the alkyl chlorides tend to yield thiols as a minor product as a consequence of the first step of the mechanism envisaged.[17b]

The present methodology, apart from being novel as a sulfur transfer reaction from thiometalates, compares favorably with other methods of synthesis of disulfides.[9,10] Further synthetic and mechanistic studies involving the use of thiometalate complexes of molybdenum and tungsten with organic substrates are currently under investigation.

Typical Experimental Procedure for the Reaction of Tetrathiometalates with Alkyl Halides. To a stirred solution of tetrathiometalate **1a** or **1b** (2 mmol) in dimethylformamide (6 mL) was added slowly a solution of the alkyl halide (2 mmol) in dimethylformamide (4 mL) at room temperature (25 °C). The reaction mixture was stirred for 0.5–1.0 h and diluted with water (50 mL) and extracted with ether (3 × 40 mL). The ether extract was washed with water until the washings were colorless. The organic layer was dried ($MgSO_4$) and concentrated. The residue was purified by chromatography or recrystallization to reveal the product.

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Supplementary Material Available: Experimental details for the preparation of **1a** and **1b** and experimental data for **3a,d–g,i–m**, **5**, **7**, **9**, **11**, and **13** (3 pages). Ordering information is given on any current masthead page.

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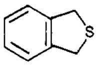
[13] Reaction of **6** with molybdenum persulfide complex $Mo_2S_{12}^{2-}$ has been shown to give the cyclic sulfide i as the only product (ref 7).



i

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