ducts is in striking contrast to that of the adducts with Vaska's compound and bis(triphenylphosphine)platinum(0). We find that even in boiling chloroform–water mixtures, these latter adducts are recovered unchanged.[14] The driving force for hydrolysis may be the formation of stable products. For molybdenum the *cis*-dioxomolybdenum(VI) species fits this criterion perfectly, while for iridium or platinum the appropriate oxo species is unknown and its production probably unfavorable,

Oxidative addition of the nitrogen–nitrogen multiple bond and hydrolysis of the resultant complex, occurring only for molybdenum, has an obvious analogy with the interaction of dinitrogen with nitrogenase. Further, this system may elucidate the possible role of molybdenum in other redox-active molybdoenzymes. The results detailed above suggest that the mode of reaction proposed herein for dinitrogen and its other substrates[15] with nitrogenase may be common to all redox-active molybdoenzymes, *e,g*,, nitrate reductase,[16] sulfite,[17] aldehyde,[18] and xanthine[19] oxidases. The interactions of all these enzyme systems may be interrelated through similar electronic and structural requirements for the active metal atom, *viz*., molybdenum, For the oxidases, the "reverse" process of transfer of an oxo ligand from molybdenum(VI) to the substrate occurs causing a two-electron reduction to molybdenum(IV). This mode of action for the oxidases finds support in the reaction[20] of triphenylphosphine with *cis*-dioxobis(*N*,*N*-diethyldithiocarbamato)molybdenum(VI) to produce triphenylphosphine oxide and oxobis(*N*,*N*-diethyldithiocarbamato)molybdenum(IV). These reactions may all be related to the recently proposed principle of metal ion promoted atom-transfer redox reactions,[21]

Although these oxobis(*N*,*N*-dialkyldithiocarbamato)molybdenum(IV) complexes react only with highly activated multiple bonds, they do resemble the suggested structures of the active sites of molybdoenzymes,[22] *i.e*,, the involvement of sulfur ligands at the metal, more closely than previous models (*e.g*,, a platinum(II)–phosphine complex[23] for the nitrogenase active site). Therefore, we suggest that these coordinatively unsaturated molybdenum(IV) complexes and the related oxomolybdenum(VI) complexes constitute valuable probes for investigating the mode(s) of reaction of the various molybdoenzymes,

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[14] The isolation of **9** from mixtures of **2** and tetrakis(methyldiphenylphosphine)platinum(0) has been ascribed to hydrogen abstraction from the methyl group of the phosphine coordinated to platinum,[13] However, we find that **9** is not produced when water is excluded and that **2** interacts with methyldiphenylphosphine alone, the adduct so formed hydrolyzing on addition of water to produce **9** and methyldiphenylphosphine oxide. Therefore it appears that liberated methyldiphenylphosphine, not the platinum(0) complex, is responsible for the formation of **9**,

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[21] J. P. Collman, M. Kubota, and J. W, Hosking, *J. Amer. Chem, Soc*., **89**, 4809 (1967).

[22] See *e.g*., J. T, Spence, *Coord. Chem. Rev*., **4**, 475 (1969).

[23] G. W. Parshall, *J. Amer. Chem. Soc*., **89**, 1822 (1967),

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## Convenient Synthesis of 1,4-Diketones. Application to the Synthesis of Dihydrojasmone

*Sir:*

A variety of synthetic routes for the preparation of 1,4-diketones, valuable intermediates for syntheses of cyclopentenones and furans, have been developed;[1] however, there remains room for improvement. We wish to report a convenient route for synthesis of 1,4-diketones from diphenylthioacetals and conjugated enones and to illustrate its utility in a synthesis of dihydrojasmone.

Alkylcopper reagents react with conjugated enones to give 1,4-addition products,[2] but the reaction of conjugated enones with metalated ($Mg-Cu^I$) 1,3-dithiane, which is synthetically equivalent to carbonyl function, leads only to 1,2 addition to conjugated enones.[3]

We found that lithium di[bis(phenylthio)methyl]copper (I, $R^1 = H$), which is prepared from bis(phenylthio)methyllithium and 0,5 equiv of CuI, reacts with methyl vinyl ketone (MVK) at −78° to afford the 1,4-addition product IIIa (50%) along with the 1,2-addition product IVa (23%), On the other hand, when the reaction of lithium bis[tris(phenylthio)methyl]copper (I, $R^1 = C_6H_5S$) with MVK was carried out under the same condition, the 1,4-addition product, 1-tris(phenylthio)pentan-4-one (IIIb), was selectively obtained in 70% yield,

From these results, it was expected that substituted diphenylthioacetals (I, $R^1$ = alkyl) would react with conjugated enones to yield 1,4-addition products exclusively, In fact, the treatment of lithium [$\alpha$,$\alpha$-bis(phenylthio)benzyl]copper (I, $R^1 = C_6H_5$) with MVK afforded 1-phenyl-1-bis(phenylthio)pentan-4-one (IIIc) in 94% yield according to the following procedure. To 70 ml of a dry tetrahydrofuran (THF) solution of benzaldehyde diphenylthioacetal (10 mmol) was added 6.45 ml of an *n*-hexane solution of *n*-BuLi (10 mmol) at −78° under an argon atmosphere, and the mixture was stirred for 1 hr, Cuprous iodide (5 mmol) was then added at once and the mixture was kept stirring for 1 hr at −78°, Fifteen milliliters of a THF solution of MVK (5 mmol) was added slowly at −78° and the mixture, after being stirred for 2 hr at −78°, was quenched at −78° by the addition of water, and allowed to warm to

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[1] G. Stork and R. Borch, *J. Amer. Chem. Soc*., **86**, 935 (1964); G. Büchi and H. Wüest, *J. Org. Chem*,, **31**, 977 (1966); E. J. Corey and L. S. Hegedus, *J. Amer. Chem. Soc*., **91**, 4926 (1969); E. Wenkert, R. A. Mueller, E, J. Reardon, Jr,, S. S. Sathe, D. J. Scharf, and G. Tosi, *ibid*., **92**, 7428 (1970); J. E. McMurry and T. E. Glass, *Tetrahedron Lett*., 2575 (1971); J. E, McMurry and J. Melton, *J. Amer. Chem. Soc*., **93**, 5309 (1971),

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[3] D. Seebach and H. F. Leits, *Angew. Chem*., **81**, 1047 (1969).

room temperature. The resulting precipitate was filtered off and after THF was evaporated under reduced pressure, the organic layer was extracted with ether. The extract was dried with $Na_2SO_4$ and concentrated. Separation by silica gel column chromatography from impurities gives IIIc, homogeneous by tlc and having ir and pmr spectra and elemental analysis in accord with the assigned structure [pmr $\tau$ 2.49–3.03 (m, 15 H), 7.28 (m, 2 H), 7.66 (m, 2 H), 8.06 (s, 3 H)].

The generality of the reaction between copper reagents of thioacetal (I) and conjugated enone is apparent from the results summarized in Scheme I and Table I.

**Scheme I**

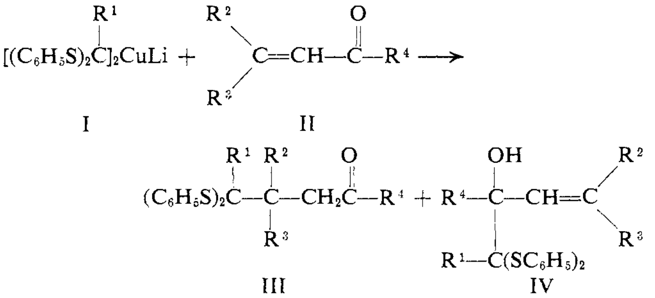
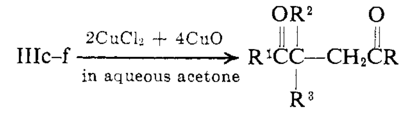


**Table I**

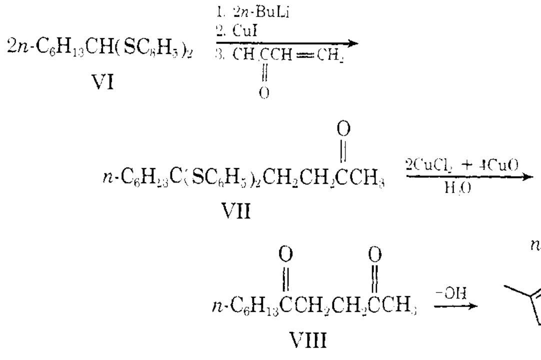
| | I | ——— | II | ——— | Yield, % | |
|---|---|---|---|---|---|---|
| | $R^1$ | $R^2$ | $R^3$ | $R^4$ | III | IV |
| a | H | H | H | $CH_3$ | 50 | 23 |
| b | $C_6H_5S$ | H | H | $CH_3$ | 70 | |
| c | $C_6H_5$ | H | H | $CH_3$ | 94 | |
| d | $C_6H_5$ | $CH_3$ | $CH_3$ | $CH_3$ | 82 | |
| e | $C_6H_5$ | $C_6H_5$ | H | $CH_3$ | 94 | |
| f | $C_6H_5$ | $C_6H_5$ | H | $C_6H_5$ | 94 | |
| g | $CH_3$ | H | H | $CH_3$ | 73 | 4 |
| h | $n$-$C_5H_{11}$ | H | H | $CH_3$ | 73 | |

In order to obtain 1,4-diketone from $\gamma$-ketothioketal (III), there is a necessity to establish a convenient method for hydrolysis of thioacetal which is carried out under mild conditions, because 1,4-diketone is easily converted to furan or cyclopentenone by the treatment under acidic or basic condition or on heating. Previously, it was found in our laboratory that $CuCl_2$ is effective for the activation of the carbon–sulfur bond.[4] Therefore, we investigated the hydrolysis of $\gamma$-ketothioketal using $CuCl_2$ and CuO. 1-Phenyl-1-bis(phenylthio)pentan-4-one (IIIc) was treated with 2 equiv of $CuCl_2$ and 4 equiv of CuO in aqueous 99% acetone at room temperature for 1 hr. After purification by silica gel column chromatography and distillation, 1-phenylpentane-1,4-dione (Vc) was obtained in 91% yield [bp 127° (2 mm); pmr $\tau$ 2.03–2.83 (m, 5H), 6.90 (m, 2 H), 7.33 (m, 2 H), 8.95 (s, 3 H)]. Similarly, the other $\gamma$-ketothioketals (IIId–f) were converted into the corresponding 1,4-diketones (Vd–f) in more than 90% yields.



Vc–f

As an example of a synthetic utility of this method, we carried out a simple synthesis of dihydrojasmone according to the following procedure. Heptanal diphenylthioacetal (VI) was treated with 1 equiv of $n$-BuLi in THF at −40 to − 30° for 1 hr under an argon atmosphere and 0.5 equiv of CuI was added at once at −78°. After being stirred for 1 hr, a THF solution of MVK was added dropwise to the reaction mixture and stirred for 2 hr at −78°. The corresponding $\gamma$-ketothioketal (VII) was isolated in 80% yield [pmr $\tau$ 2.25–2.86 (m, 10 H), 7.04–7.45 (m, 2 H), 7.97 (s, 3 H), 8.00–9.33 (m, 15 H). *Anal.* Calcd for $C_{23}H_{30}OS_2$: C, 71.48; H, 7.82; S, 16.56. Found: C, 71.75; H, 7.66; S, 16.40]. The treatment of VII with 2 equiv of $CuCl_2$ and 4 equiv of CuO in aqueous 99% acetone gave corresponding 1,4-diketone VIII in 90% yield [bp 93–94° (0.5 mm); lit.[5] bp 141° (14 mm); pmr $\tau$ 7.45 (s, 4 H), 7.66 (t, 2 H), 7.96 (s, 3 H), 8.33–9.33 (m, 11 H)]. According to Hunsdiecker's method,[6] VIII was converted into dihydrojasmone (IX) in 94% yield by refluxing for 6 hr with 2% aqueous NaOH and ethanol [bp 129–131° (19 mm); lit.[6] bp 122–124° (12 mm); homogeneous by tlc and vpc and having pmr and ir spectra and elemental analysis in accord with IX].



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## Reaction of Sulfur Dioxide with Enol Ethers

*Sir:*

Sulfur dioxide readily undergoes 1,4-cycloaddition reactions with a variety of conjugated dienes to give the corresponding 2,5-dihydrothiophene 1,1-dioxides.[1] On the other hand, while sulfur dioxide reacts with

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(1) S. D. Turk and R. L. Cobb in "1,4-Cycloaddition Reactions," J. Hamer, Ed., Academic Press, New York, N. Y., 1967, p 13.