Journal of Organometallic Chemistry, 307 (1986) C49–C51
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

TRANSITION METAL PROMOTED REACTIONS

XIV *. NOVEL REDUCTIVE COUPLING OF THIOKETALS WITH MOLYBDENUM HEXACARBONYL

CHI SANG WONG, WING SANG LEUNG, LAM LUNG YEUNG and TIEN-YAU LUH*
Department of Chemistry, The Chinese University of Hong Kong, Shatin, N.T. (Hong Kong)

(Received September 11th, 1985)

Summary

Thioketals of fluorenone, acetophenone, tetralone and indanone were treated with $Mo(CO)_6$ in chlorobenzene to give the corresponding dimeric olefins.

The carbon–sulfur bond cleavage reaction is important in both synthetic organic chemistry [2] as well as in coal and petroleum industries [3]. Metal carbonyls, such as $Fe(CO)_5$ [4], $Fe_3(CO)_{12}$ [5], $Os_3(CO)_{12}$ [6], $Mn_2(CO)_{10}$ [7], and $Co_2(CO)_8$ [4,8] are known to cleave the carbon–sulfur bond. We recently reported that $Mo(CO)_6$ in THF is a selective desulfurization reagent for the reduction of certain thiols and thioethers (eq. 1) [9]. The reaction may proceed via a radical-type mechanism [9]. If such a proposed mechanism is correct, we felt that compounds such as thioketals, where two sulfur functions are attached to a common carbon atom, may undergo this mechanism via a carbene-like intermediate which may be coupled to give dimeric olefins. We have tested this viewpoint and now describe our results.

$$Ar(CH_2)_nSR \xrightarrow{Mo(CO)_6} Ar(CH_2)_nH \qquad (1)$$

(R = H, alkyl, aryl; $n = 0, 1$)

Treatment of 9-fluorenone thioketal (I) with $Mo(CO)_6$ in THF under refluxing conditions gives fluorone (II) and bifluorenylidene (III) in 42 and 34% yield, respectively. II may be formed by hydrogen abstraction from the solvent (THF) by some kind of radical species. It is noteworthy that the α-hydrogen atom in an ethereal solvent is labile towards organic radicals [9–11]. Indeed, when chlorobenzene was employed as the solvent, only trace amounts of II were obtained, but the yield of III was not increased markedly.

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* For part XIII see ref. 1.

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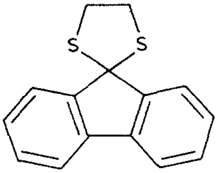
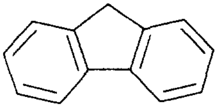
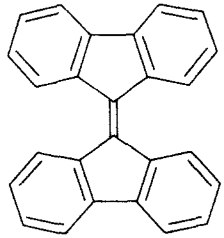


(I)



(II)



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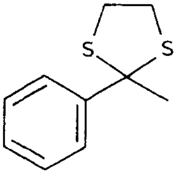
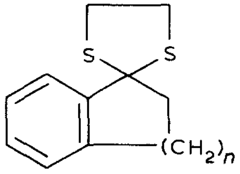


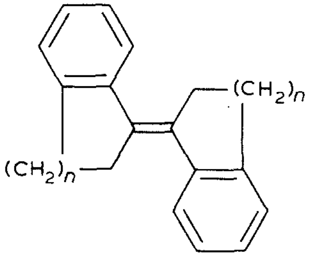
(IV)

$Ph(CH_3)C{=}C(CH_3)Ph$

(V, *E*-isomer ;
VI, *Z*-isomer)



(VII, *n* = 2 ;
VIII, *n* = 1)



(IX, *n* = 2 ;
X, *n* = 1)

Similarly, acetophenone thioketal (IV) was treated with $Mo(CO)_6$ in refluxing chlorobenzene to give an amount of *E*- and *Z*-dimethylstilbenes (V and VI) in 55% yield besides unidentified products. It is noteworthy that neither the reduced product, ethylbenzene, nor an intramolecular carbene-type insertion product, styrene, was obtained. Under the same conditions in chlorobenzene, thioketals of tetralone (VII) and indanone (VIII) behaved similarly to give the corresponding dimers, IX and X, respectively. It is interesting to note that both IX and X have *E* configurations which are less sterically crowded than the corresponding *Z* isomers. Again, neither tetralin nor dihydronaphthalene was detected among the reaction products from VII. Similarly, VIII did not yield indane or indene.

It is noteworthy that thioketones yielded the corresponding dimeric olefins upon treatment with $Co_2(CO)_8$ [4] or $Mn_2(CO)_{10}$ [7]. These reactions may occur via a carbene-like intermediate. Indeed, when thiocarbonate was treated with $Fe(CO)_5$, an carbeneiron complex was obtained [12]. The product distribution of the reaction with thioketals is similar to that observed with thioketones. Accordingly, it is not unlikely to suggest that the carbene or its molybdenum complex may be a possible intermediate which upon coupling give the corresponding dimeric olefin. However, the actual reaction mechanism remains to be clarified.

Thioketals of simple ketones did not react under these conditions. Thus, attempts to desulfurize adamantanone ethylene thioketal were unsuccessful and only the starting material was recovered. This finding is in agreement with our earlier results that simple aliphatic mercaptans or thioethers do not undergo desulfurization with $Mo(CO)_6$ under our conditions [9].

In summary, we have shown the first example of reductive coupling of thioketals to dimeric olefins. Further elaboration of the mechanism and the potential synthetic applications of this reaction is in progress.

References

1 M.-C. Chan, K.-M. Cheng, M.K. Li and T.-Y. Luh, J. Chem. Soc., Chem. Commun., (1985) 1610.
2 E.E. Bloch, Reactions of Organosulfur Compounds, Academic Press, New York, 1978.
3 P. Wiseman, An Introduction to Industrial Organic Chemistry, Applied Science, London, 1972.
4 H. Alper and H.-N. Paik, J. Org. Chem., 42 (1977) 3522.
5 H. Alper, F. Sibtain and J. Haveling, Tetrahedron Lett., (1983) 5329.
6 R.D. Adams, D.A. Katahira and L.W. Yang, Organometallics, 1 (1982) 235.
7 H. Alper, J. Organomet. Chem., 73 (1974) 359.
8 S.C. Shim, S. Antebi and H. Alper, J. Org. Chem., 50 (1985) 147.
9 T.-Y. Luh and C.S. Wong, J. Org. Chem., 50 (1985) 5413.
10 T.-Y. Luh and C.H. Lai, K.L. Lei and S.W. Tam, J. Org. Chem., 44 (1979) 641
11 S.J. Nelson, G. Detre, M. Tanabe, Tetrahedron Lett., (1973) 447.
12 J. Daub, G. Erhardt, K.H. Jogun, J. Kappler, A. Laumer, R. Pfiz and J.J. Stezowske, Chem. Ber., 115 (1982) 1787.