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Transition metal promoted reactions

XXXV *. On the mechanism of the $W(CO)_6$ -mediated C–S bond cleavage reaction

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Abstract

The reaction of 2-naphthylmethyl mercaptan (I) with $W(CO)_6$ in refluxing chlorobenzene was monitored by 1H NMR. The formation of 2-methylnaphthalene (II) occurs via the hydrogen abstraction from the mercaptan (I) by the intermediate 2-naphthylmethyl radical (VI) while IV is not formed directly from I but from the intermediate compound bis(2-naphthylmethyl)sulfide(III).

Metal carbonyls are useful in the cleavage of C–S bonds [1–6]. We recently reported that group 6 metal carbonyls are selective reagents for the reduction of C–S bonds [2,3] and for the desulfurdimerization of thioethers and dithioacetals [2,4–6]. A free radical mechanism has been suggested on the basis of deuterium labelling experiments, complete racemization in the products using optically active substrates, isolation of disproportionation products, as well as novel fragmentation process of dithiolanes [2,4–6]. It is noted that the reaction of $W(CO)_6$ with benzylic mercaptans in refluxing chlorobenzene afforded not only reduced products but a significant amount of dimers as byproducts (eq. 1) [4].



The former product may be formed by hydrogen abstraction from the radical, and the latter by dimerization of the radical. It is well documented that the rate of the hydrogen abstraction reaction of a radical species is in the order of 10^6 to $10^7 M^{-1} s^{-1}$ [7] and that of the coupling process of radical moieties is nearly diffusion

* For Part XXXIV see ref. 12.

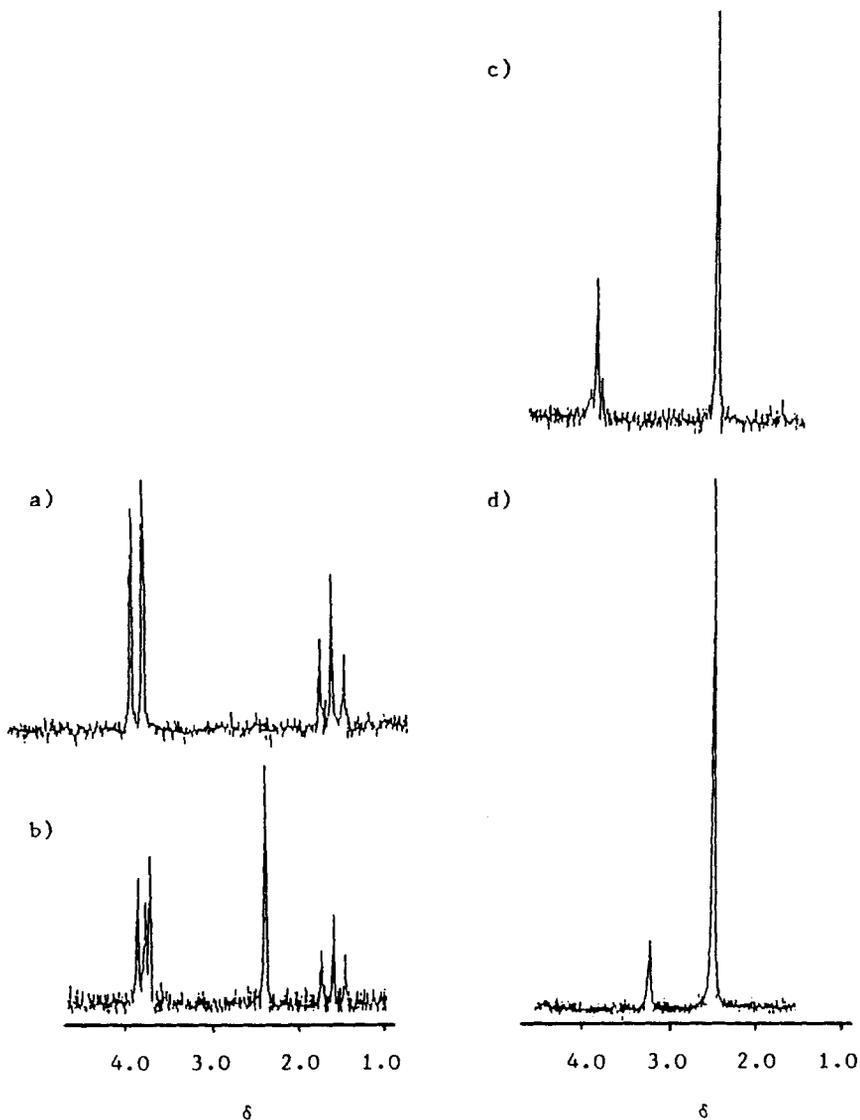
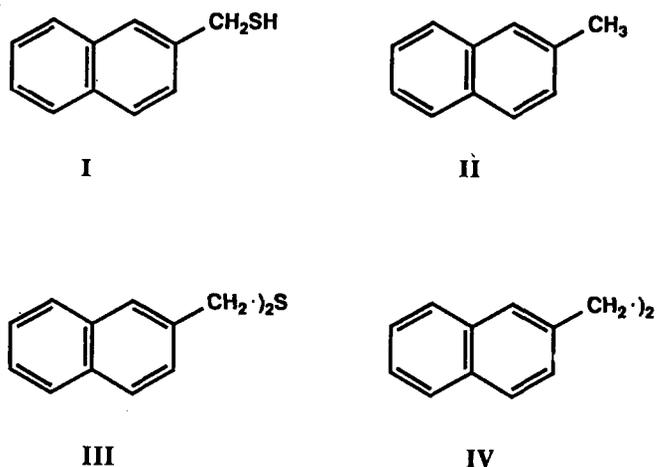


Fig. 1. ^1H NMR spectra of the reaction of 1 with $\text{W}(\text{CO})_6$ in chlorobenzene at (a) $t=0$, (b) $t=6$ h, (c) $t=16$ h, (d) $t=36$ h.

controlled [8]. These rate data suggest that the two pathways are competitive and it is therefore highly desirable to determine at which stage the product is formed in this $\text{W}(\text{CO})_6$ -mediated desulfurization reaction. In this paper, we describe a complementary investigation using ^1H NMR spectroscopy to monitor such a reaction to further support the radical mechanism and provide a useful evidence on the actual mode of the metal carbonyl-promoted desulfurization.

A mixture of 2-naphthylmethanethiol (I) and an equimolar amount of tungsten hexacarbonyl in chlorobenzene was immersed in an oil bath preheated to 170°C . During the course of the reaction, aliquots were withdrawn from time to time and

subjected to H NMR analysis. The spectra are shown in Fig. 1. Figure 1a shows the NMR spectrum at $t = 0$. During the course of the reaction, the intensity of the signals at δ 1.76 and 3.78 gradually decreased and a new singlet at δ 2.47 progressively appeared. The latter signal is due to the absorption of the methyl group of the reduced product, 2-methylnaphthalene (II). In addition, a new singlet at δ 3.77 appeared at the very beginning of the reaction. However, the change in intensity of this signal was very slow, as can be seen from Fig. 1. This signal is attributed to the absorption of the CH_2 group of bis(2-naphthylmethyl) sulfide (III). At $t = 16$ h (Fig. 1c), I was almost consumed, and II and III were the only organic products at this stage. Further reaction led to the disappearance of the signal at δ 3.77 and appearance of a new singlet at δ 3.20 (Fig. 1d). This new absorption is due to the methylene group of IV. The ratio of II and IV in the final mixture was 5 to 1.

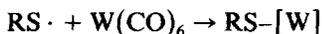
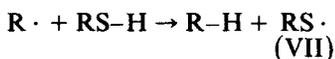
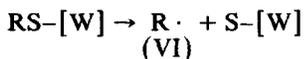
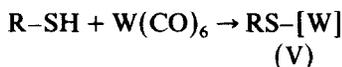


In order to show that thioether III was indeed the intermediate in this transformation, the reaction was stopped after 6 h of reflux and III was isolated in 3% yield. In addition, the reaction of III under the same conditions afforded IV and II in 54% and 15% yields, respectively*.

On the basis of these results, a plausible mechanism is proposed (Scheme 1). Mercaptan I will first associate with the tungsten moiety to give a thiolato complex V [9,10] in which the carbon-sulfur bond is activated [11]. Homolytic cleavage of the carbon-sulfur bond of V will generate the radical VI, which will rapidly abstract the hydrogen atom from I yielding II and VII. The sulfur radical VII will then react with tungsten carbonyl to give again a thiolato species similar to V which furnishes the chain propagation process. Coupling of VI and VII will give III.

Our results indicate that the rate of the hydrogen abstraction by VI under the reaction conditions would be much faster than that of the dimerization of VI as long as a hydrogen source, or SH moiety, is available. Sulfide III can also undergo C-S bond cleavage under the reaction conditions [2-4] and, therefore, the growth of the intensity of the peak at δ 3.77 was found to be slow.

* The origin of the hydrogen source for the formation of II is not clear. It may arise from the hydrogen abstraction from the benzylic hydrogen of III or the like by VI.



Scheme 1. (R = 2-naphthylmethyl).

In conclusion, we have provided further evidence to support that W(CO)_6 -mediated C-S bond cleavage occurs via a free radical mechanism. In the desulfurization of mercaptans, the dimeric product is not from mercaptans but from thioethers generated *in situ* during the course of the reaction.

Experimental section

NMR study of the desulfurization of naphthylmethanethiol (I). A mixture of I (290 mg, 1.7 mmol) and tungsten hexacarbonyl (560 mg, 1.7 mmol) in chlorobenzene (20 mL, freshly distilled from P_2O_5) was frozen in liquid nitrogen bath, evacuated and flushed with nitrogen. After warming to room temperature, the flask was then immersed in an oil bath preheated to 170°C. The mixture was heated under reflux and the color of the solution turn into yellow then black. Aliquots were withdrawn at different time intervals and subjected to ^1H NMR analysis on a JEOL PMX-60 NMR spectrometer. The results are shown in Fig. 1.

Isolation of III from the reaction of I with W(CO)_6 . The reaction was carried out as described above. A mixture of I (290 mg, 1.7 mmol) and tungsten hexacarbonyl (560 mg, 1.7 mmol) in chlorobenzene (20 mL) was heated under reflux for 6 h. After cooling to room temperature, chlorobenzene was removed by vacuum distillation and the residue was washed with diethyl ether. The organic solution was filtered and the filtrate was carefully evaporated to give a residue which was chromatographed on silica gel using hexane as eluent to yield II (60 mg, 25%), III (8 mg, 3%), and recovered I (142 mg, 48%). No IV was detected.

Acknowledgment

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