

DEOXYGENATION OF SULFOXIDES BY IRON PENTACARBONYL

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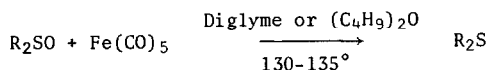
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Iron pentacarbonyl is a versatile reagent in organic chemistry capable of effecting: (a) formation of thioisulfonate esters from sulfonyl chlorides<sup>2a</sup>; (b) conversion of amides and thioamides to nitriles<sup>2b</sup>; (c) regeneration of carbonyl compounds from oximes<sup>2c</sup>; (d) isomerization of transoid steroid dienes to their thermodynamically less stable homoannular cisoid isomers<sup>2d</sup>; (e) formation of tetraarylethylenes from dihaloarylmethanes<sup>2e</sup>; and (f) carbonyl insertion in reaction with diazonium chlorides<sup>2f</sup>. We now wish to report that the metal carbonyl is an excellent reagent for the deoxygenation of sulfoxides to sulfides.

Reaction of sulfoxides with iron pentacarbonyl in either diglyme or di-n-butyl ether under remarkably simple conditions results in the formation of sulfides in fair to excellent yields.



This facile reaction is applicable to a wide variety of dialkyl, diaryl and heterocyclic sulfoxides as well as disulfoxides (Table I). Other solvents which can be used for this deoxygenation include 2-butanone and tetramethylurea but yields are substantially lower. The reaction is not catalytic in the metal carbonyl and addition of boron trifluoride etherate did not improve

TABLE I  
 Yields of Sulfides Obtained from Reaction of Sulfoxides  
 with Iron Pentacarbonyl<sup>a</sup>

Sulfoxide	Reaction Time, hr	Solvent <sup>b</sup>	% RSR <sup>c</sup>
( <u>n</u> -C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> SO	3	D	62
( <u>n</u> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> SO	3	D	96
( <u>n</u> -C <sub>6</sub> H <sub>13</sub> ) <sub>2</sub> SO	3	D	70
(C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> ) <sub>2</sub> SO	3	B	48
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> SO	8	B	91
( <u>p</u> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>2</sub> SO	3	D	89
β-CH <sub>3</sub> SOCH <sub>2</sub> CH <sub>2</sub> SOCH <sub>3</sub>	4	D	74
CH <sub>3</sub> SO(CH <sub>2</sub> ) <sub>3</sub> SOCH <sub>3</sub>	4	D	84
Tetramethylene sulfoxide	3	D	57
Phenoxymethyl penicillin sulfoxide methyl ester	3	D	12 <sup>d</sup>

<sup>a</sup> A 1.1/1.0 mole ratio of metal carbonyl to sulfoxide was used for monosulfoxides while the deoxygenation of disulfoxides to disulfides was effected by the use of a 2.2/1.0 mole ratio of metal carbonyl to reactant. <sup>b</sup> B ≡ Di-n-butyl ether and D ≡ diglyme. <sup>c</sup> Yields indicated are of products purified by recrystallization or distillation.

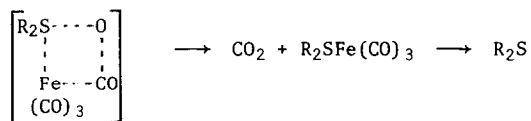
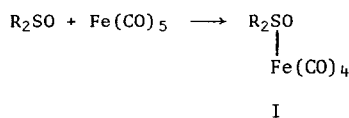
<sup>d</sup> Methyl α-isopropenyl-4-phenoxyacetamido-3-isothiazolone-2-acetate and methyl 3-methyl-7-(2-phenoxyacetamido)-3-cephem-4-carboxylate were two of the by-products of the reaction. The low yield of deoxygenated product is not unexpected as phenoxymethyl penicillin sulfoxide methyl ester readily undergoes rearrangement and ring-opening reactions (R.B. Morin, B.G. Jackson, R.A. Mueller, E.R. Lavagino, W.B. Scanlon and S.L. Andrews, J. Am. Chem. Soc. **91**, 1401 (1969)).

the yield as it did in the reaction of iron pentacarbonyl with sulfonyl chlorides<sup>2a</sup>. Reaction of molybdenum hexacarbonyl with di-n-propyl or diphenyl sulfoxide gave recovered starting material.

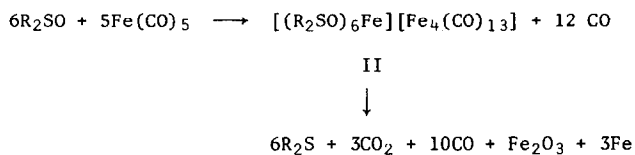
The following procedure for the conversion of di-n-butyl sulfoxide to di-n-butyl sulfide is typical of the general method used. In a three-necked 100 ml. flask equipped with a nitrogen inlet, reflux condenser, stopper and magnetic stirrer was placed di-n-butyl sulfoxide (5.67 g., 34.9 mm.), iron pentacarbonyl (5.17 ml., 38.4 mm.) and diglyme (20 ml.). The reaction mixture was heated at 130-135° with stirring under nitrogen for three hours. The solution was cooled and filtered through celite to remove inorganic material. The filtrate was added to water (300 ml.) and the sulfide was extracted with two 50 ml. portions of n-pentane. The pentane extract was washed five times with 100 ml. of water and then dried over magnesium sulfate. The pentane was removed by distillation at atmospheric pressure and the residue was distilled at 0.7 mm. to give 4.87 g. (96%) of di-n-butyl sulfide, b.p. 26°, identical with an authentic sample.

Preliminary mechanistic investigations indicate that the deoxygenation reaction may occur via substitution or disproportionation complexes of the type obtained by photolysis of sulfoxides and the metal carbonyl. Strohmeier and co-workers<sup>3</sup> prepared I (R=CH<sub>3</sub>, (CH<sub>2</sub>)<sub>4</sub>, Scheme 1) by photolysis of sulfoxides and iron pentacarbonyl at room temperature. The conversion of I to the sul-

Scheme 1



Scheme 2



fide can be visualized as proceeding via a four-center transition state. Hieber and Lipp<sup>4</sup> obtained II, R=CH<sub>3</sub> (Scheme 2), by photolysis of a mixture of the sulfoxide and iron pentacarbonyl in benzene at 80°. We prepared I and II,<sup>5</sup> R=tetramethylene, and heated each complex in diglyme at 130-135° for 0.5 hours. Tetramethylene sulfide was formed in each instance along with carbon dioxide (detected by bubbling the evolved gases through a solution of barium hydroxide). However, the results obtained thus far do not distinguish between Schemes 1 and 2 since the rate of Fe(CO)<sub>3</sub> (Scheme 1) remains uncertain.

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#### References

1. National Science Foundation Undergraduate Research Participant.
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3. W. Strohmeier, J.F. Guttenberger, and G. Popp, *Chem. Ber.* 98, 2248 (1965).
4. W. Heiber and A. Lipp, *Ibid.* 92, 2085 (1959).
5. II was obtained as red-black crystals. Anal. calcd. for C<sub>37</sub>H<sub>40</sub>O<sub>19</sub>S<sub>6</sub>Fe<sub>5</sub>: C, 35.04; H, 3.81; S, 15.16. Found: C, 35.37; H, 3.62; S, 14.99.