Tetrahedron Letters No.16, pp. 1239-1242, 1969. Pergamon Press. Printed in Great Britain.

# REACTION OF IRON PENTACARBONYL WITH SULFONYL CHLORIDES

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(Received in USA 23 January 1969; received in UK for publication 3 March 1969)

This communication reports a simple, rapid and convenient means of converting sulfonyl chlorides I to thiolsulfonate esters II using a 1:1 mixture of iron pentacarbonyl and boron trifluoride etherate in N,N-dimethylacetamide (DMAC) or tetramethylurea (TMU). A typical procedure follows.

$$\underset{\text{I}}{RSO_2Cl} \quad + \quad Fe(CO)_5 \quad \xrightarrow[\text{DMAC or TMU}]{BF_3\cdot(C_2H_5)_2O} \quad \underset{\text{II}}{RSSO_2R}$$

Boron trifluoride etherate (1.73 g., 12.2 mm.) and iron pentacarbonyl (1.64 ml., 12.2 mm.) were added to p-methoxybenzenesulfonyl chloride (2.23 g., 10.8 mm.) in anhydrous DMAC (11 ml.). The mixture was heated with stirring under a nitrogen atmosphere. At 63-65° a vigorous reaction took place. When the reaction had subsided (10-15 min.), the solution was warmed to 90-100° for 15 minutes, cooled and poured into 200 ml. of ice-water. The resulting precipitate was filtered, and recrystallized once from n-heptane to give white needles (0.68g., 41%) of II (R = p-$CH_3OC_6H_4$), m.p. 89.0-89.5°.

The reaction is applicable to a wide variety of sulfonyl chlorides giving thiolsulfonates in fair to good yields (Table I). The products were identified by comparison of melting points with those reported in the literature and by the appearance of intense bands in the infrared spectrum at 1340-1310 cm.$^{-1}$ and 1150-1130 cm.$^{-1}$ characteristic of thiolsulfonate esters (1, 2).

TABLE 1

Thiolsulfonates Obtained from Reaction of Sulfonyl Chlorides with Iron Pentacarbonyl and Boron Trifluoride Etherate in DMAC[a]

| Sulfonyl Chloride | Reaction Temperature (°C) | Yield of Thiolsulfonate (%) | Melting Point (°C) | Melting Point Lit. (°C) |
|---|---|---|---|---|
| Benzene[b] | 50 | 71 | 43.0-45.0 | 45[d] |
| p-Toluene | 58 | 48 | 75.5-77.0 | 76[e] |
| p-Methoxybenzene | 63-65 | 41 | 89.0-89.5 | 89-90[f] |
| p-Bromobenzene | 30 | 50 | 159.0-160.0 | 159-60[g] |
| m-Nitrobenzene | 0 | 66 | 122.0-123.0 | 124[f] |
| 2-Naphthalene | 60 | 45 | 104.5-106.5 | 106-108[g] |
| Methane | 63 | 36 | 117.0-119.0[c] | 119[h] |
| n-Hexadecane | 73-75 | 42 | 60.0-61.0 | 59-60[i] |
| Trichloromethane | -20 | -- | --- | --- |

[a] Approximately the same reaction temperatures and product yields were obtained using TMU as the solvent. In both DMAC and TMU, optimum yields resulted from 1.13-1.25:1.13-1.25:1 mole ratios of $Fe(CO)_5:BF_3\cdot(C_2H_5)_2O:RSO_2Cl$.

[b] Diphenyl disulfide, m.p. 59.0-60.0°, was obtained as a by-product in 4-6% yield.

[c] Boiling point at 15 mm.

[d] Reference 1.

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[f] G. Leandri and A. Tundo, Ann. Chim. (Rome) 44, 255 (1954).

[g] B.N. Trivedi, J. Indian Chem. Soc. 33, 359 (1956).

[h] Boiling point at 16 mm. H. Brintzinger and M. Langheck, Chem. Ber. 86, 557 (1953).

[i] P. Allen and J.W. Brook, J. Org. Chem. 27, 1019 (1962).

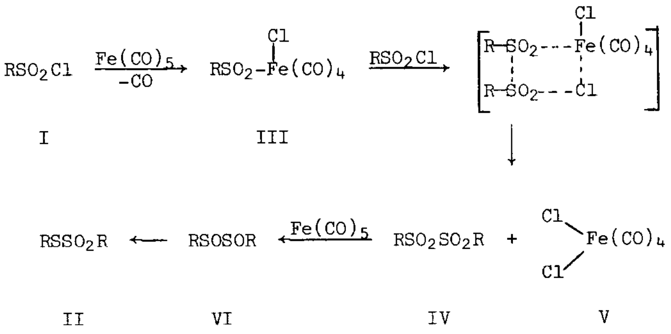
Thiolsulfonates were also obtained in the absence of (or in the presence of only a catalytic quantity of) boron trifluoride etherate, but the yields were substantially lower than those recorded in Table I. The sulfonyl chloride was recovered unchanged when no metal carbonyl was used (The reaction is not catalytic with respect to iron pentacarbonyl). Low yields of II resulted when the reaction was carried out in relatively non-polar solvents such as di-n-butyl ether or dioxane.

Aromatic nitro compounds are deoxygenated to azoxy, azo compounds or amines by iron pentacarbonyl depending upon reagent concentration (3). The conversion of m-nitrobenzenesulfonyl chloride to the corresponding thiolsulfonate ester indicates the selectivity of the metal carbonyl in reacting with the sulfonyl chloride group without affecting the nitro function.

The temperature at which the exothermic reaction began (Table I) varied substantially depending on the nature of the sulfonyl chloride. Aromatic sulfonyl chlorides having electron-releasing substituents required higher temperatures than the parent benzenesulfonyl chloride while m-nitrobenzenesulfonyl chloride readily reacted at 0°. Similar results were obtained for aliphatic sulfonyl chlorides - trichloromethanesulfonyl chloride was violently reactive even at temperatures of -20° to 0°.

A postulated mechanism for the reaction (Scheme 1) involves initial formation of a sulfur-iron σ-bonded complex III. A similar type of complex has been obtained by reaction of heptafluoropropyl iodide with iron pentacarbonyl (4). Complex III can then react with additional sulfonyl chloride to give the disulfone IV and the fairly unstable halogeno metal carbonyl V (5), possibly via a four-center transition state. Deoxygenation of IV with iron carbonyl produces the disulfoxide VI which is known to exist as the thiolsulfonate tautomer II (1). Some

Scheme 1



support for this mechanism was obtained by reaction of diphenyldisulfone (IV, R = $C_6H_5$) (6) with iron pentacarbonyl in DMAC giving II (R = $C_6H_5$) as the major product (65% yield) with a small amount (7%) of diphenyl disulfide (formed by deoxygenation of IV and/or II). The role of boron trifluoride etherate in increasing the yield of II is not clear.

A detailed investigation of the mechanism of the reaction is currently in progress.

## ACKNOWLEDGEMENT

We are grateful to the OTT Chemical Company for their generous gift of tetramethylurea.

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