Journal of Organometallic Chemistry, 54 (1973) 255–258
© Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE REACTION OF FERROCENE WITH TRICHLOROMETHANESULFONYL CHLORIDE

LEONARD P. MOTZ and ROBERT P. PINNELL*
Joint Science Department, Claremont Men's, Pitzer and Scripps Colleges, Claremont, California 91711 (U.S.A.)
(Received September 26th, 1972)

SUMMARY

Ferrocene reacts with sulfuryl and trichloromethanesulfonyl chlorides to give nearly quantitative yields of ferricinium tetrachloroferrate. A similar reaction is not observed with methane- or benzenesulfonyl chlorides. A free-radical mechanism is proposed based upon the known properties of the sulfonyl halides.

INTRODUCTION

The oxidation of ferrocene to the "ferricinium" cation is one of the more widely observed reactions of this species. On a preparative basis, such oxidation has been effected electrolytically and via a variety of inorganic and organic oxidants[1]. A particularly interesting reaction, mechanistically, is the reaction of ferrocene with elemental chlorine or sources of chlorine radicals.

Direct chlorination of ferrocene, at 0°, has been shown to result in complete destruction of the molecule[2]. Lowering the reaction temperature to −40° allowed the isolation of ferricinium tetrachloroferrate as the principal product.

$$2\,C_{10}H_{10}Fe+7\,Cl_2 \rightarrow C_{10}H_{10}Fe^+FeCl_4^- +2\,C_5H_5Cl_5$$

This derivative has also been prepared by ultraviolet or cobalt-60 irradiation of ferrocene in the presence of halocarbons[3–5] and by direct reaction with either triphenylmethyl chloride[5], sulfuryl chloride[2], or ferric chloride[5]. All but the last of these reactions have, in common, the possibility of oxidation of ferrocene by chlorine radicals. To further test this hypothesis, we have allowed ferrocene to react with two known sources of radical chlorine, sulfuryl and trichloromethanesulfonyl chlorides.

Both sulfuryl chloride and its trichloromethyl derivative have been shown to be highly selective chlorinating agents[6,7]. Although earlier reports[2] have indicated that reaction with sulfuryl chloride leads to significant destruction of the ferrocene moiety, it seemed reasonable that substitution of a trichloromethyl group for chlorine might moderate the reactivity of the reagent to permit simple oxidation of ferrocene to the ferricinium cation. To test the mechanism of the reaction, we also repeated the reaction of ferrocene with sulfuryl chloride and extended the range of sulfonyl halides used to include the methane and benzene derivatives.

---

* To whom correspondence should be addressed.

EXPERIMENTAL

Materials and analytical methods

Ferrocene (dicyclopentadienyliron) and methanesulfonyl chloride were purchased from Eastman Organic Chemicals. Benzenesulfonyl chloride, benzene (reagent grade), and sulfuryl chloride were purchased from Matheson, Coleman and Bell. Ferrocene was sublimed before use, all other reagents were used as received.

Elemental analyses were performed by Galbraith Laboratories. Infrared and visible-ultraviolet spectra were recorded on Beckman model IR-10 and DBG spectrophotometers, respectively.

Reaction of ferrocene with trichloromethanesulfonyl chloride

A solution of 4.36 g (0.02 mole) of trichloromethanesulfonyl chloride and 1.86 g (0.01 mole) of ferrocene in 50 ml of benzene was refluxed, with stirring, for a period of 5 h. A deep green precipitate formed rapidly. Evolved gases were entrained in a nitrogen stream and then passed into a trap containing a stoichiometric excess of standardized potassium triodide solution.

The original reaction mixture was filtered on a glass frit and the precipitate washed repeatedly with portions of benzene. Air drying of the precipitate yielded 1.82 g of ferricinium tetrachloroferrate (95% yield based upon ferrocene). (Found: C, 30.94; H, 2.77; Cl, 35.59. $C_{10}H_{10}Cl_4Fe_2$ calcd.: C, 31.30; H, 2.63; Cl, 36.96%.) The visible spectrum of the salt, as a solution in 0.25 *M* hydrochloric acid, exhibits intense absorption at 617 nm (ε 915), identical to the published spectrum[5].

When the benzene was distilled from the filtrate, a black tarry residue remained. All attempts at purification by chromatography, fractional crystallization or distillation failed to produce any characterizable products.

Back-titration of the iodine solution with standardized sodium thiosulfate solution revealed that 1.81 mmoles of sulfur dioxide had been evolved during the reaction (90% yield based upon ferrocene). The identity of the evolved gas was confirmed qualitatively by its characteristic odor and its infrared absorption at 1364 cm^{-1} (literature value[8], 1362 cm^{-1}, gas phase).

Similar reaction between ferrocene and trichloromethanesulfonyl chloride can be induced at room temperature using a 275-watt sunlamp at a distance of 50 cm for 12 h as a source of energy. This photocatalytic reaction produced a 96% yield of ferricinium tetrachloroferrate.

Reaction of ferrocene with sulfuryl chloride

In apparatus identical to that described above, 1.86 g (0.01 mole) of ferrocene was allowed to react with 1.34 g (0.01 mole) of sulfuryl chloride in 50 ml of benzene. After refluxing for 2 h, filtration yielded 1.87 g of ferricinium tetrachloroferrate (97% based upon ferrocene). Evolution of sulfur dioxide was confirmed qualitatively.

Attempted reactions of ferrocene with methane- and benzenesulfonyl chlorides

Solutions of ferrocene and benzenesulfonyl or methanesulfonyl chlorides were refluxed, or irradiated at room temperature, for periods of up to 12 h. Chromatography of the resulting reaction mixtures allowed recoveries of 90–95% unreacted ferrocene. Small amounts of tarry material were formed in each case. No evidence was found for evolution of sulfur dioxide or significant formation of ferricinium derivatives.

RESULTS AND DISCUSSION

Based upon the experimental data, the reactions of ferrocene with sulfuryl and trichloromethanesulfonyl chlorides appear to exhibit the following stoichiometry:

$$4\,Cl_3CSO_2Cl + 2\,C_{10}H_{10}Fe \rightarrow C_{10}H_{10}Fe^+FeCl_4^- + 4\,SO_2 + \text{polymer}$$
$$2\,SO_2Cl_2 + 2\,C_{10}H_{10}Fe \rightarrow C_{10}H_{10}Fe^+FeCl_4^- + 2\,SO_2 + \text{polymer}$$

No significant reaction was observed with either methane- or benzenesulfonyl chlorides.

Both trichloromethanesulfonyl and sulfuryl chlorides have been postulated to undergo homolytic cleavage to yield sulfinyl and chlorine radicals[6,7]. Chlorine atoms could then be expected to function as oxidants toward ferrocene, yielding ferricinium chloride. Ferricinium salts with small anion moieties have been found to be unstable, decomposing in the presence of halogen radicals to yield iron(III) chloride and substituted cyclopentadienyl species[9].

Based upon these earlier observations, the following mechanism is proposed for the reaction between ferrocene and trichloromethanesulfonyl chloride:

$$Cl_3CSO_2Cl \xrightarrow[\text{or } h\nu]{\Delta} Cl_3CSO_2^{\cdot} + Cl\cdot$$
$$Cl_3CSO_2^{\cdot} \rightarrow Cl_3C\cdot + SO_2$$
$$Cl\cdot + C_{10}H_{10}Fe \rightarrow C_{10}H_{10}Fe^+Cl^-$$
$$C_{10}H_{10}Fe^+Cl^- + 4\,Cl_3C\cdot + 2\,Cl\cdot \rightarrow FeCl_3 + 2\,C_5H_5(CCl_3)_2$$
$$n\,C_5H_5(CCl_3)_2 \rightarrow \text{polymer}$$
$$C_{10}H_{10}Fe^+Cl^- + FeCl_3 \rightarrow C_{10}H_{10}Fe^+FeCl_4^-$$

When the source of halogen atoms is sulfuryl chloride, two chlorine atoms are released per molecule of reactant and the stoichiometry is halved with respect to sulfuryl chloride.

Free-radical additions to olefins, yielding sulfonyl derivatives, have been observed for a number of organo-substituted sulfonyl halides[10]. However, substitution reactions, involving cleavage of carbon–hydrogen bonds, and elimination of sulfur dioxide, have been noted only for the sulfuryl and trichloromethanesulfonyl halides. It is significant that these are also the two reagents observed to oxidize ferrocene to ferricinium tetrachloroferrate. It is postulated that decomposition of the ferricinium salt to the tetrachloroferrate anion is dependent upon attack by both chlorine and significant concentrations of organo radicals for completion.

REFERENCES

1 M. Rosenblum, *Chemistry of the Iron Group Metallocenes*, Part 1, Wiley, New York, 1965, pp. 48–50.
2 A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya, T. V. Nikitina and N. S. Simonkova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, (1956) 739.
3 O. Traverso and F. Scandola, *Inorg. Chim. Acta*, 4 (1970) 493.
4 E. Koerner von Gustorf, H. Kronert, H. Koller, G. Tillmanna and G. O. Schenck, *Z. Naturforsch. B*, 19 (1964) 170.
5 I. J. Spilners, *J. Organometal. Chem.*, 11 (1968) 381.

6 G. A. Russell and H. C. Brown, *J. Amer. Chem. Soc.*, 77 (1955) 4031.
7 E. S. Huyser, H. Schinke and R. L. Burham, *J. Org. Chem.*, 28 (1963) 2141.
8 K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, 2nd. Ed., Wiley, New York, 1970 p. 89.
9 A. N. Nesmeyanov, L. P. Yur'eva, R. B. Materikova and B. Hetnarski, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 4 (1965) 731.
10 F. W. Stacey and J. F. Harris Jr., *Organic Reactions. Vol.* 13, Wiley, New York, 1963, pp. 200–204.