

REDUCTIVE DEHALOGENATION IN $\text{Fe}(\text{CO})_5$ -MEDIATED PHOTOLYSIS OF 3-HALO- AND 3,4-DIHALO-2,5-DIMETHYLTHIOPHENE 1,1-DIOXIDES

VARDA USIELI

Department of Pharmaceutical Chemistry, The Hebrew University School of Pharmacy, Jerusalem (Israel)

SALO GRONOWITZ and INGRID ANDERSSON

Division of Organic Chemistry 1, Chemical Center, University of Lund, Lund (Sweden)

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Summary

Irradiation of 3,4-dibromo-, 3,4-dichloro- and 3-chloro-2,5-dimethylthiophene 1,1-dioxide in the presence of pentacarbonyliron caused successive reductive dehalogenation of the substrates, and π -complexation of the parent compounds and of the reduced products to tricarbonyliron. A mechanism for the dehalogenation is suggested. The mass spectral fragmentation patterns of the thiophene dioxides and of the complexes are discussed.

As part of a study aimed at preparing cyclobutadiene systems, some substituted thiophene 1,1-dioxides were photolysed in the presence of pentacarbonyliron.

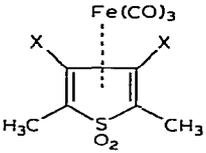
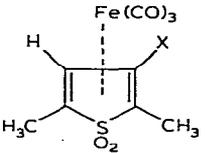
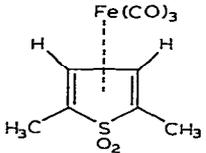
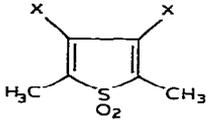
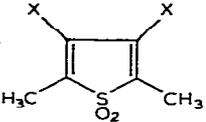
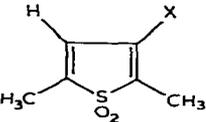
When 3,4-dibromo-2,5-dimethylthiophene 1,1-dioxide (I) and an excess of $\text{Fe}(\text{CO})_5$ were irradiated in dichloromethane solution a mixture of products was obtained, from which three main components were isolated by preparative thin layer chromatography. The product of highest R_f value was identified as the tricarbonyliron complex of the parent compound (II) on the basis of its IR, NMR and mass spectral data. The other two exhibited IR spectra very similar to that of II both in shape and in positions of peaks, and all three showed a common pattern of mass spectral fragmentation. Mass spectral analysis of the organometallic products having lower R_f values indicated that the one of lowest R_f value was of formula $\text{C}_9\text{H}_8\text{O}_5\text{SFe}$, and the other of formula $\text{C}_9\text{H}_7\text{O}_5\text{SBrFe}$, both representing reductively-debrominated products coordinated to metal. The $\text{C}_9\text{H}_7\text{O}_5\text{SBrFe}$ compound was assigned the 2,5-dimethyl-3-bromo-1,1-dioxothiophenetricarbonyliron structure (III) on the basis of its spectral data. The $\text{C}_9\text{H}_8\text{O}_5\text{SFe}$ product was found to be identical with the known 2,5-dimethylthiophene-1,1-dioxidetricarbonyliron π -complex (IV) previously described by Chow, Fossey and Perry [1].

These findings clearly indicate that under the photochemical conditions employed the substrate I undergoes two distinctly different types of reaction: (a) successive reductive debrominations; (b) coordination of the dienic moiety of the 1,1-dioxothiophene systems in II–IV to the metal carbonyl residue $[\text{Fe}(\text{CO})_3]$.

In order to determine the scope of the reaction, 2,5-dimethyl-3,4-dichlorothiophene-1,1-dioxide V was subjected to the action of $\text{Fe}(\text{CO})_5$ under the same conditions. Significantly, compound IV and the π -complexes of structures VI and VII, which are analogous to compounds II and III, were obtained. However, the overall yield was only 50% and the ratio of the products changed markedly (see Table 1). The scope of this reaction was further demonstrated by the $\text{Fe}(\text{CO})_5$ -mediated photolysis of 2,5-dimethyl-3-chlorothiophene 1,1-dioxide (VIII), which yielded a 5/3-mixture of VII and IV, respectively, in 69% overall yield.

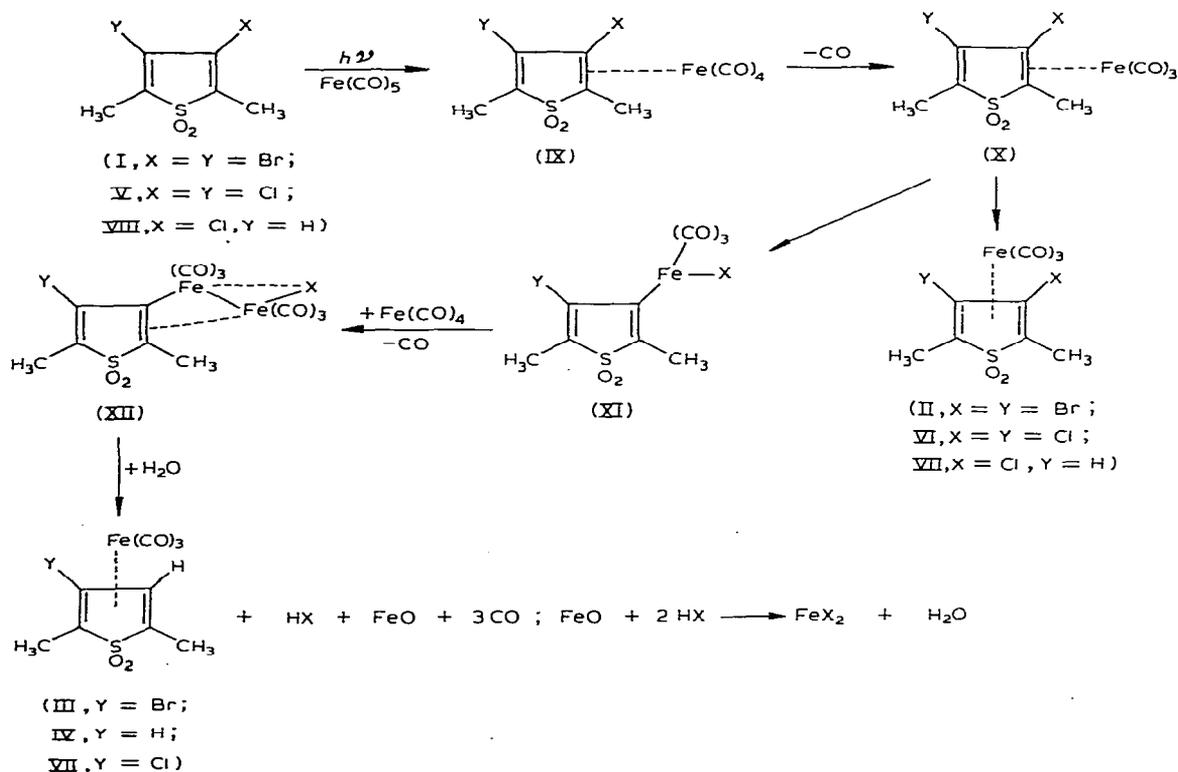
Consideration of the mechanism of the reductive dehalogenation must take

TABLE 1
PRODUCTS OBTAINED FROM PHOTOLYSIS OF HALOGEN-SUBSTITUTED THIOPHENE 1,1-DIOXIDES AND $\text{Fe}(\text{CO})_5$ (Yields in %)

Thiophene 1,1-dioxide	Products		
			
 (I, x = Br)	23	25	15
 (V, x = Cl)	33	14	3
 (VIII, x = Cl)	—	43	26

account of the role of the metal and the source of protons for this reaction. This source could conceivably be external, probably the small quantities of water usually present in solvents and in $\text{Fe}(\text{CO})_5$. Consequently, the reductive dehalogenation of 2,5-dimethyl-3-halo- and 2,5-dimethyl-3,4-dihalo-thiophene 1,1-dioxides in the course of $\text{Fe}(\text{CO})_5$ -mediated photolysis could be visualized as resulting from a multi-stage process initiated by an oxidative metal insertion into the carbon-halogen bond followed by displacement of the metal by a proton and final coordination to zerovalent metal. Scheme 1 delineates in outline the various phases of this process.

SCHEME 1



The stoichiometry of this reaction is given by equation 1. It implies that FeX_2 $2[\text{S}-\text{X}] + 4 \text{Fe}(\text{CO})_5 + \text{H}_2\text{O} \rightarrow 2[\text{S}-\text{H}] \cdots \text{Fe}(\text{CO})_3 + \text{FeX}_2 + \text{FeO} + 14 \text{CO}$ (1) ($\text{S} = 2,5$ -dimethyl-1,1-dioxothiophenyl)

is produced in the course of the reaction. Indeed, this was verified by analysis of the residue left after filtration of the reaction mixture.

The formation of halovinylbis(tricarbonyliron) complexes from $\text{Fe}(\text{CO})_5$ -mediated photolysis of vinyl halides [2] has a direct bearing on the above reductive dehalogenation reaction. It is known that thermal reactions of $\text{Fe}(\text{CO})_5$ with organic halides lead in some cases to reductive dehalogenation products. Bruce was able to isolate a small amount of bis(pentafluorophenyl)methane from the reaction of decafluorobenzhydryl bromide with $\text{Fe}(\text{CO})_5$, which

yielded the dimeric species as the major product [3]. Also, in the reaction of $\text{Fe}(\text{CO})_5$ with $\alpha, \alpha', \alpha', \alpha'$ -tetrabromo-*o*-xylene minor amounts of α, α' -dibromo-*o*-xylene were isolated by Victor [4]. Alper and Keung found that the thermal reaction of α -haloketones with $\text{Fe}(\text{CO})_5$ followed by hydrolysis leads to the formation of the coupled 1,4-diketones and the reduced monoketones [5]. Unlike the $\text{I} \rightarrow \text{II} + \text{III} + \text{IV}$ and $\text{V} \rightarrow \text{VI} + \text{VII} + \text{IV}$ conversions, the examples in the literature relate to halides residing on saturated carbons.

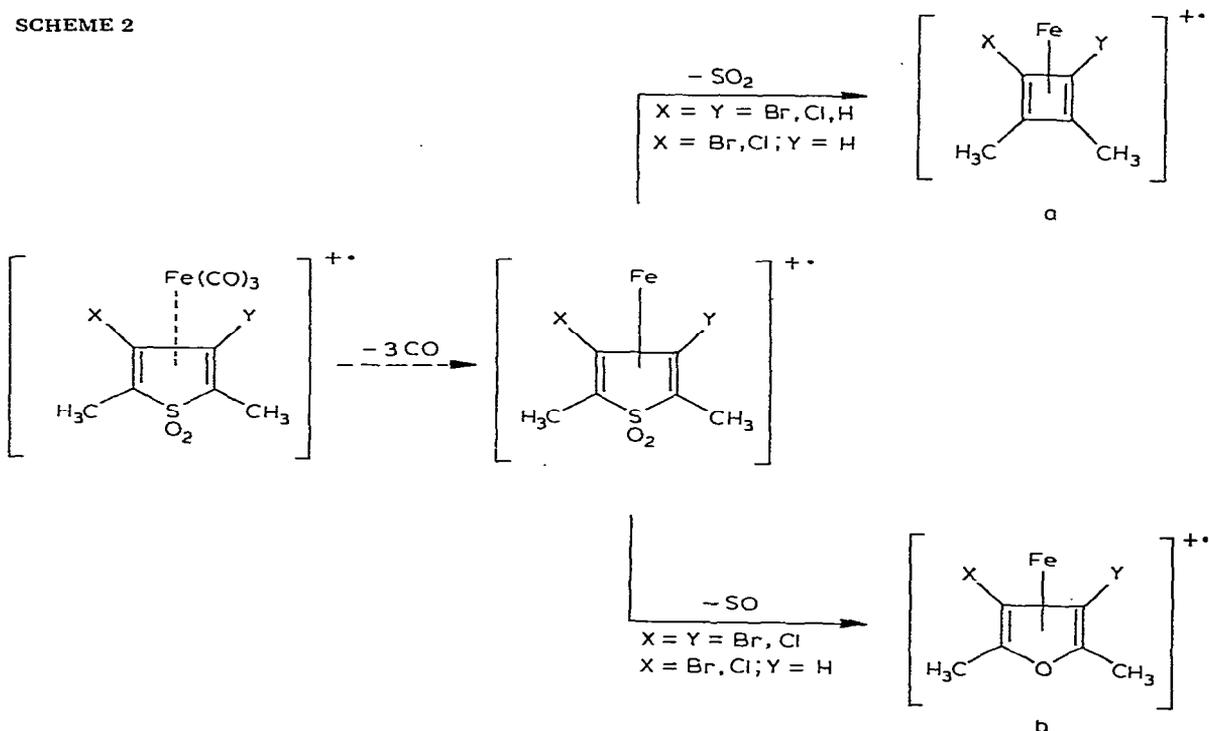
Examples of reductive carbonylation of saturated nitro compounds [6] and of oxygen extrusion from 1,2-oxazines [7] mediated by carbonyliron compounds and protonic species have been recorded.

Mass spectra of thiophene dioxides and of the respective tricarbonyliron complexes

The mass spectra of thiophene dioxides I, V and VIII exhibit a common fragmentation pattern featuring an initial ejection of a SO group from the molecular ion to yield the base peak, $[M - 48]^{+\bullet}$. The observed preference for the extrusion of SO rather than of a SO_2 entity from thiophene dioxides has been observed previously in the cases of 2,5-dimethyl-, 2,5-diphenyl- and 3,4-diphenyl-thiophene dioxides, and discussed in terms of product ion stability [8]. In contrast to the latter halogen-free thiophene dioxides which exhibit low abundance of $M - \text{SO}_2$ ions in their mass spectra, these ions were absent in the respective spectra of the halogenated species I, V and VIII.

The principal mass spectral cracking of complexes II, III, VI and VII is characterized by successive losses of three CO groups followed by ejection of a SO_2 unit to yield the corresponding cyclobutadienyliron ion species a (see Scheme 2). This is in consonance with the fragmentation path described for the

SCHEME 2



tricarbonyliron complexes of 2,5-dimethylthiophene dioxide (IV), tetraphenylthiophene dioxide and the unsubstituted thiophene dioxide [1]. Loss of a SO unit, which gives rise to ion b, was noted in low intensity only in the spectra of II, III, VI and VII, but not in the spectrum of IV.

The data presented here strongly suggest that the tendency to lose SO₂ upon electron impact decreases on inclusion of halogen into the thiophene dioxide molecule, possibly because the stability of the cyclobutadiene species produced is decreased by the electron demand of the halogen substituent.

Experimental

All melting points are uncorrected. The NMR spectra were recorded on a Varian A60 and a JEOL MH 100 NMR spectrometer (CDCl₃ solution, TMS standard). The mass spectra were recorded on an LKB A900 spectrometer and a MAT CH-5 spectrometer. IR spectra were measured on a Perkin-Elmer 237 Grating Infrared Spectrophotometer.

3,4-Dibromo-2,5-dimethylthiophene was prepared according to Melles and Backer [9].

3,4-Dichloro-2,5-dimethylthiophene was prepared according to Gronowitz and Frejd [10].

3-Chloro-2,5-dimethylthiophene. To a solution of 11.2 g (0.1 mol) of 2,5-dimethylthiophene in 50 ml of carbon tetrachloride and 50 ml of acetic acid was added 13.3 g (0.1 mol) of *N*-chlorosuccinimide. After stirring for 2 h at room temperature the mixture was poured into water and ether was added. The water phase was extracted three times with ether and the combined organic phases were washed with NaHCO₃ solution until neutral reaction. The ether phase was dried over MgSO₄, evaporated and distilled to give 4.6 g (32%) of 3-chloro-2,5-dimethylthiophene, b.p. 67–71°C/16 mmHg.

3,4-Dibromo-2,5-dimethylthiophene 1,1-dioxide (I) was synthesized according to Melles and Backer [9].

3,4-Dichloro-2,5-dimethylthiophene 1,1-dioxide (V). *Method A.* A mixture of 7.4 g (0.04 mol) of 3,4-dichloro-2,5-dimethylthiophene, 16 ml of 30% H₂O₂ and 100 ml of acetic acid was refluxed for 4 h at 90°C. The mixture was poured into water. The solid was filtered off and recrystallized to yield 3.2 g (38%) of 3,4-dichloro-2,5-dimethylthiophene 1,1-dioxide, m.p. 70–72°C. ¹H NMR: δ 2.17(s) ppm; mass spectrum, *m/e* 216, 214, 212 (*M*⁺), 168, 167, 166, 165, 164 (100%), 163, 131, 129. Analysis: Found: C, 33.8; H, 2.77. C₆H₆Cl₂O₂S calcd.: C, 33.8; H, 2.84%.

Method B. To a solution of 1.1 g (0.006 mol) of 3,4-dichloro-2,5-dimethylthiophene in 50 ml of methylene chloride was added 3.1 g (0.018 mol) of *m*-chloroperbenzoic acid. The mixture was stirred at room temperature for 27 h. The solid was removed by filtration. The filtrate was washed with a saturated NaHCO₃ solution, then water, and dried (MgSO₄) and evaporated to yield 1.6 g of 3,4-dichloro-2,5-dimethylthiophene 1,1-dioxide.

3-Chloro-2,5-dimethylthiophene 1,1-dioxide (VIII). A mixture of 29.2 g (0.2 mol) of 3-chloro-2,5-dimethylthiophene, 80 ml of 30% H₂O₂ and 500 ml of acetic acid was refluxed for 1 h at 90°C. The mixture was poured into water. The solid was filtered off and recrystallized to yield 5.0 g (33%) of 3-chloro-2,5-

dimethylthiophene 1,1-dioxide, m.p. 81–83°C. $^1\text{H NMR}$: δ 2.16 and 2.20 (6H, two overlapping singlets), 6.28 ppm (1H, s); mass spectrum, m/e 180, 178 (M^+), 132, 131, 130 (100%), 129, 115, 95, 77. Analysis: Found: C, 40.2; H, 3.87; Cl, 20.1; S, 17.8. $\text{C}_6\text{H}_7\text{ClO}_2\text{S}$ calcd.: C, 40.3; H, 3.95; Cl, 19.8; S, 17.9%.

Standard procedure for photochemical reactions of 3-halo- or 3,4-dihalo-2,5-dimethylthiophene 1,1-dioxides. A solution of 0.5 mmol of the substituted thiophene 1,1-dioxide and 0.5 ml (3.7 mmol) of $\text{Fe}(\text{CO})_5$ in 100 ml of dichloromethane was irradiated for 2–2.5 h under nitrogen. A Philips HPK-125 lamp in a water-cooled Pyrex immersion vessel was used.

The product mixture was filtered through Celite and the precipitate gave a positive test for bromide (or chloride) ions. The filtrate was evaporated on a rotary evaporator and the brown residue was chromatographed on silica gel preparative plates with a 2/1 mixture of petroleum ether 40–60: ether as developing solvent. The 3,4-dihalo-, 3-monohalo-, and unhalogenated 2,5-dimethylthiophene 1,1-dioxide tricarbonyliron complexes showed a decreasing order of R_f values. After elution with chloroform and evaporation, the products were recrystallized from hexane or from ether.

3,4-Dibromo-2,5-dimethylthiophene 1,1-dioxide tricarbonyliron (II). Yellow needles (hexane), m.p. 183–184°C; IR (hexane), 2083, 2031, 2011 cm^{-1} (metal CO); $^1\text{H NMR}$: δ 1.90(s); mass spectrum, m/e 444, 442, 440 in a 1/2/1 ratio (M^+), 416, 414, 412 [$(M - \text{CO})^+$], 388, 386, 384 [$(M - 2 \text{CO})^+$], 360, 358 356 [$(M - 3 \text{CO})^+$], 296, 294, 292 [$(M - 3 \text{CO} - \text{SO}_2)^+$]. Analysis: Found: C, 24.29; H, 1.23. $\text{C}_9\text{H}_6\text{Br}_2\text{FeO}_5\text{S}$ calcd.: C, 24.43; H, 1.35%.

3-Bromo-2,5-dimethylthiophene 1,1-dioxide tricarbonyliron (III). Yellow plates (hexane), m.p. 134–135°C; IR (hexane), 2080, 2030, 2006 cm^{-1} (metal CO); $^1\text{H NMR}$: δ 1.75 (3H, s), 1.84 (3H, s), 5.79 (1H, s) ppm; mass spectrum, m/e 364, 362 in a 1/1 ratio (M^+), 336, 334 [$(M - \text{CO})^+$], 308, 306 [$(M - 2 \text{CO})^+$], 280, 278 [$(M - 3 \text{CO})^+$], 216, 214 [$(M - 3 \text{CO} - \text{SO}_2)^+$]. Analysis: Found: C, 29.60; H, 1.65. $\text{C}_9\text{H}_7\text{BrFeO}_5\text{S}$ calcd.: C, 29.75; H, 1.93%.

3,4-Dichloro-2,5-dimethylthiophene 1,1-dioxide tricarbonyliron (VI). Yellow needles (hexane), m.p. 159°C; IR (hexane), 2091, 2041, 2023 cm^{-1} (metal CO); $^1\text{H NMR}$: δ 1.86(s) ppm; mass spectrum, m/e 356, 354, 352 in a 1 : 6 : 9 ratio [M^+], 328, 326, 324 [$(M - \text{CO})^+$], 300, 298, 296 [$(M - 2 \text{CO})^+$], 272, 270, 268 [$(M - 3 \text{CO})^+$], 208, 206, 204 [$(M - 3 \text{CO} - \text{SO}_2)^+$]. Analysis: Found: C, 30.79; H, 1.61. $\text{C}_9\text{H}_6\text{Cl}_2\text{FeO}_5\text{S}$ calcd.: C, 30.59; H, 1.70%.

3-Chloro-2,5-dimethylthiophene 1,1-dioxide tricarbonyliron (VII). Yellow plates, m.p. 105–107°C; IR (hexane), 2083, 2035, 2011 cm^{-1} (metal CO); $^1\text{H NMR}$: δ 1.71 (3H, s), 1.82 (3H, s), 5.74 (1H, s) ppm; mass spectrum, m/e 320, 318 in 1/3 ratio (M^+) 292, 290 [$(M - \text{CO})^+$], 264, 262 [$(M - 2 \text{CO})^+$], 236, 234 [$(M - 3 \text{CO})^+$], 172, 170 [$(M - 3 \text{CO} - \text{SO}_2)^+$]. Analysis: Found: C, 34.12; H, 2.22. $\text{C}_9\text{H}_7\text{ClFeO}_5\text{S}$ calcd.: C, 33.91; H, 2.20%.

2,5-Dimethylthiophene 1,1-dioxide tricarbonyliron (IV). Yellow needles (ether), m.p. 146–148°C (lit. [1], 146–148°C); IR (hexane), 2079, 2023, 2001 cm^{-1} (metal CO); $^1\text{H NMR}$: δ 1.76 (6H, s), 5.41 (2H, s) (lit. [1], 1.75 and 5.38, respectively); mass spectrum, m/e 284 (M^+), 256 [$(M - \text{CO})^+$], 228 [$(M - 2 \text{CO})^+$], 200 [$(M - 3 \text{CO})^+$], 136 [$(M - 3 \text{CO} - \text{SO}_2)^+$]. Analysis: Found: C, 38.07; H, 2.67. $\text{C}_9\text{H}_8\text{FeO}_5\text{S}$ calcd.: C, 38.03; H, 2.82%.

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