Journal of Organometallic Chemistry, 285 (1985) 225–229
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

DESULFURIZATION OF BENZYLIC MERCAPTANS BY TRIIRON DODECACARBONYL UNDER ACIDIC AND BIPHASIC CONDITIONS

HOWARD ALPER* and FAZLE SIBTAIN

Ottawa-Carleton Institute for Research and Graduate Studies in Chemistry, Department of Chemistry, University of Ottawa, Ottawa, Ontario K1N 9B4 (Canada)

(Received June 22nd, 1984)

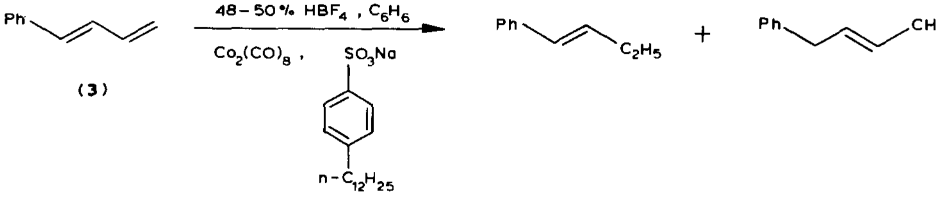
Summary

The biphasic reaction of benzylic mercaptans with triiron dodecacarbonyl, 48–50% tetrafluoroboric acid, and benzene affords desulfurized products in good to excellent yields. This reaction is superior to that effected in the presence of sodium dodecylbenzenesulfonate, a phase transfer agent for acidic processes.

The desulfurization of benzylic mercaptans by means of basic phase transfer catalysis has been reported recently [1]. Hydrocarbons (**2**) were obtained as the principal or only products by the reaction of a mercaptan (**1**) with triiron dodecacarbonyl, tetrabutylammonium hydrogen sulfate as the phase transfer agent, and benzene/5 *N* NaOH as the two-phase system.

$$\underset{(\mathbf{1})}{R^1R^2R^3CSH} + Fe_3(CO)_{12} \xrightarrow[(C_4H_9)_4N^+\ HSO_4^-]{5\ N\ NaOH,\ C_6H_6,\ 60°C} \underset{(\mathbf{2})}{R^1R^2R^3CH}$$

Acidic phase transfer catalysis has been little investigated up to the present time [2–6]. In 1983, one of us described the first examples of organometallic phase transfer catalysis under acidic conditions [5]. Diarylethylenes and other activated olefins are hydrogenated in high yields on reaction with cobalt carbonyl, using sodium 4-dodecylbenzenesulfonate as the phase transfer catalyst, with benzene and 48–50% aqueous tetrafluoroboric acid as the two phases. This reaction, which is also applicable to styrenes and arylbutadienes (e.g., **3**), may occur via the intermediacy of hydridotetracarbonylcobalt [6].

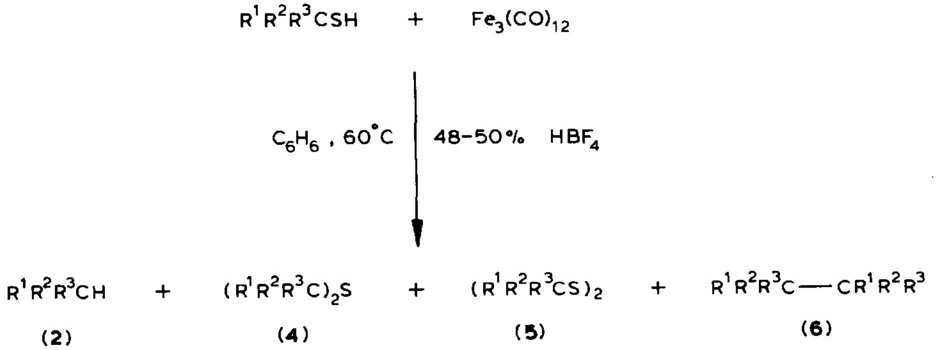


0022-328X/85/$03.30

There have been no reports on acidic phase transfer catalyzed reactions involving iron carbonyls as reagents. This publication is concerned with the interesting results obtained on attempted desulfurization of benzylic mercaptans by triiron dodecacarbonyl under acidic phase transfer conditions.

Results and discussion

When *p*-chlorobenzyl mercaptan (**1**, $R^1 = p\text{-ClC}_6H_4$, $R^2 = R^3 = H$) was treated with an equimolar amount of triiron dodecacarbonyl in benzene, 48–50% tetrafluoroboric acid, sodium dodecylbenzenesulfonate as the phase transfer catalyst, at 60°C and 1 atmosphere, *p*-chlorotoluene (**2**) was obtained in only 6% yield, the main product (40% yield) being the disulfide (**5**, $R^1 = p\text{-ClC}_6H_4$, $R^2 = R^3 = H$). However, if the reaction is conducted in an identical manner, except without the phase transfer agent, the amount of *p*-chlorotoluene formed increased significantly (44% yield). No reaction occurs in the absence of $Fe_3(CO)_{12}$. Additional evidence that the desulfurization reaction is a biphasic and not a phase transfer process comes from the results obtained with *p*-methoxybenzyl mercaptan and *o*-methylbenzyl mercaptan where the yields of **2** are considerably higher when the reaction is effected in the absence than in the presence of sodium dodecylbenzenesulfonate (reaction products and yields are listed in Table 1). While no products of desulfurization were obtained when *p*-methylbenzyl mercaptan was employed as the reactant under phase transfer conditions (except for 2% *p*-tolualdehyde), a combined yield of 64% for **2** and **6** resulted in the absence of the phase transfer agent. One case was found, that of 2,4-dichlorobenzyl mercaptan, where the presence of the phase transfer catalyst did not have a detrimental effect on the desulfurization reaction.



The desulfurization reaction is not catalytic with respect to $Fe_3(CO)_{12}$; however, sulfides are formed in good yields by use of a catalytic amount of the metal carbonyl. The use of lower concentrations of tetrafluoroboric acid results in reduced product yields, e.g., 2,4-dichlorotoluene was obtained in 41% yield when the biphasic reaction was run using 25% HBF_4 as the aqueous phase (compared with a yield of 74% for 48–50% HBF_4). No desulfurization occurred when the mercaptan $Fe_3(CO)_{12}$ reaction was effected under homogeneous conditions (i.e., HBF_4/ether in place of 48–50% HBF_4); rather, *o*-methylbenzyl ethyl thioether was formed from *o*-methylbenzyl mercaptan. Use of a carbon monoxide instead of a nitrogen atmosphere for the acidic-biphasic reaction has little influence on the product yield (e.g., **1**, $R^1 = R^2$

TABLE 1

PRODUCTS OBTAINED FROM THE BIPHASIC AND PHASE TRANSFER CATALYZED REACTIONS OF MERCAPTANS WITH $Fe_3(CO)_{12}$ AND 48–50% HBF_4

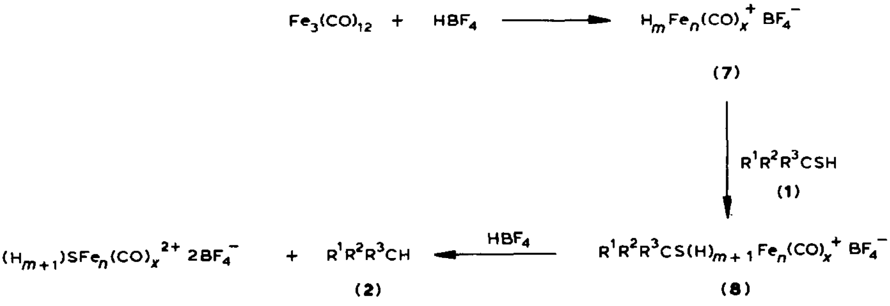
1			Products [a]	Yield (%)	
R^1	R^2	R^3		Phase transfer	Biphasic
p-ClC_6H_4	H	H	p-$ClC_6H_4CH_3$	6	44
			$(p$-$ClC_6H_4CH_2)_2S$	11	19
			$(p$-$ClC_6H_4CH_2S)_2$	40	6
p-$CH_3OC_6H_4$	H	H	p-$CH_3OC_6H_4CH_3$	10	72
			$(p$-$CH_3OC_6H_4CH_2)_2S$	7	4
o-$CH_3C_6H_4$	H	H	o-xylene	20	36
p-$CH_3C_6H_4$	H	H	p-xylene	0	15 [b]
			$(p$-$CH_3C_6H_4CH_2)_2$	0	49
			$(p$-$CH_3C_6H_4CH_2)_2S$	2	28
			$(p$-$CH_3C_6H_4CH_2S)_2$	90	0
			p-$CH_3C_6H_4CHO$	2	3
2,4-$Cl_2C_6H_4$	H	H	2,4-$Cl_2C_6H_3CH_3$	73	74 [c]
			(2,4-$Cl_2C_6H_3CH_2)_2$	5	10
			(2,4-$Cl_2C_6H_3CH_2)_2S$	2	2
			2,4-$Cl_2C_6H_3CHO$	3	3
p-$CH_3C_6H_4$	p-$CH_3C_6H_4$	H	$(p$-$CH_3C_6H_4)_2CH_2$	– [d]	94 [e]
Ph	Ph	H	Ph_2CH_2	– [d]	84
			$(Ph_2CH)_2S$		8

[a] Products were identified by comparison of data (IR, NMR(^1H,^{13}C), MS, GC) with those for authentic materials. [b] Use of a catalytic quantity of $Fe_3(CO)_{12}$ (i.e., 10/1 : 1/$Fe_3(CO)_{12}$) gave p-xylene (3%), $(p$-$CH_3C_6H_4CH_2)_2$ (15%), $(p$-$CH_3C_6H_4CH_2)_2S$ (70%), and p-$CH_3C_6H_4CHO$ (1%). [c] Use of 25% HBF_4 as the aqueous phase resulted in 41% 2,4-dichlorotoluene, 32% (2,4-$Cl_2C_6H_3CH_2)_2S$ and 3% 2,4-$Cl_2C_6H_3CHO$. [d] Not done. [e] The yield was 90% when a carbon monoxide atmosphere was used.

$= p$-$CH_3C_6H_4$, $R^3 = H$ gave 90% hydrocarbon under carbon monoxide; 94% under nitrogen).

The desulfurization reaction may possibly proceed via the binuclear complexes, $[R^1R^2R^3CSFe(CO)_3]_2$ [7]. However, only traces of toluene were formed on attempted reaction of $[PhCH_2SFe(CO)_3]_2$ [8] with 48–50% HBF_4. It is also known that exposure of $[R^1R^2R^3CSFe(CO)_3]_2$ to concentrated nitric acid gives a sulfonic acid rather than the hydrocarbon [8].

Another pathway (Scheme 1) may involve the generation of a cationic iron hydride 7 by reaction of the metal carbonyl with 48–50% HBF_4. Several neutral iron



SCHEME 1

cluster hydrides are known [9]. Reaction of **7** with **1** may give **8** which is convertible to the desulfurized product by exposure to additional HBF_4. We have been unsuccessful in attempting to isolate an organometallic by-product in these reactions.

It is believed that H_3O^+-p-$C_{12}H_{25}C_6H_4SO_3^-$ is transferred to the organic phase in acidic phase transfer reactions involving sodium dodecylbenzenesulfonate [6]. The sulfonate anion may induce disproportionation of triiron dodecacarbonyl to a mixture of carbonylferrates [10]. The latter reaction would account for the particularly significant differences in behaviour usually observed when one compares the biphasic and phase transfer processes.

In conclusion, mercaptans undergo desulfurization in good to excellent yields by reaction with $Fe_3(CO)_{12}$ in an acidic biphasic but not a phase transfer system. While several useful acidic biphasic reactions have been observed in organic chemistry [11], the above system is, to our knowledge, the first example of such a reaction using organometallic reagents.

Experimental

The following instrumentation was used to record spectra of products: IR: Perkin–Elmer 783; NMR: Varian EM-360 or T-60(^1H), FT-80(^{13}C); MS: VG Micromass 7070E. Gas chromatographic analysis was carried out using a Varian Vista 6000 chromatograph.

Tetrafluoroboric acid and most of the mercaptans were commercially available, and used as received. Compound **1**, $R^1 = R^2 = Ph$, $R^3 = H$ and **1**, $R^1 = R^2 = p$-$CH_3C_6H_4$, $R^3 = H$ were prepared by sodium borohydride reduction of the corresponding thioketones [12]. Triiron dodecacarbonyl, a commercial material containing 5–10% methanol, was thoroughly dried prior to use. The sulfur-iron complex $[PhCH_2SFe(CO)_3]_2$ was prepared from benzyl disulfide according to literature procedures [8,13].

General procedure for the desulfurization of mercaptans under acidic and biphasic conditions

Nitrogen gas was bubbled for 30 minutes through a mixture of benzene and 48–50% HBF_4 (25 ml each). Triiron dodecacarbonyl (2.0 mmol) was added and the reaction mixture was stirred under nitrogen for 4 h at room temperature. The mercaptan (2.0 mmol) was then added and the mixture was stirred overnight at 60°C (N_2). The reaction mixture was cooled to room temperature, the phases were separated, and the organic phase was washed with aqueous sodium hydroxide, followed by water (2–3 times). After drying ($MgSO_4$) and concentration by rotary evaporation, the residue was dissolved in hexane and purification was achieved by chromatography with silica gel using hexane as eluant.

General procedure for the phase transfer catalyzed reaction of mercaptans with triiron dodecacarbonyl

The reaction and work-up procedure used was identical to the previous one, except that 1.0 mmol of sodium dodecylbenzenesulfonate was added just prior to addition of triiron dodecacarbonyl.

Reaction of $[PhCH_2SFe(CO)_3]_2$ with 48–50% HBF_4 under biphasic conditions

Treatment of $[PhCH_2SFe(CO)_3]_2$ with 48–50% HBF_4 and benzene (25 ml. each) at 60°C, as described above for the biphasic reaction, afforded only trace quantities of toluene as determined by gas chromatographic analysis.

Acknowledgement

We are indebted to the Natural Sciences and Engineering Research Council of Canada for support of this research.

References

1 H. Alper, F. Sibtain and J. Heveling, Tetrahedron Lett., 24 (1983) 5329.
2 W. Tagaki, N. Iwamoto, K. Suzuki, and S. Tamagaki, Tetrahedron Lett., 22 (1981) 5213.
3 H. Iwamoto, M. Yoshimura, T. Sonoda, and H. Kobayashi, Bull. Chem. Soc. Japan, 56 (1983) 796.
4 M. Ellwood and J. Griffiths, J. Chem. Soc., Chem. Commun., (1980) 181.
5 H. Alper and J. Heveling, J. Chem. Soc., Chem. Commun., (1983) 365.
6 V. Galamb, S.C. Shim, F. Sibtain and H. Alper, Isr. J. Chem., in press.
7 L. Marko and B. Marko-Monostory, in E.A. Koerner von Gustorf, F.W. Grevels, and I. Fischler (Eds.), The Organic Chemistry of Iron, Academic Press, New York, Vol. 2, 1981, p. 283–332.
8 N.S. Nametkin, V.D. Tyurin and M.A. Kukina, J. Organomet. Chem., 149 (1978) 355.
9 W. Hieber and R. Werner, Chem. Ber., 90 (1957) 286.
10 F. Calderazzo, R. Ercoli and G. Natta, in I. Wender and P. Pino (Eds.), Organic Syntheses via Metal Carbonyls, J. Wiley and Sons, New York, vol. 1, 1968, p. 99–109.
11 e.g., H.M.R. Hoffmann, Angew. Chem. Int. Ed., 23 (1984) 1.
12 D. Paquer, Int. J. Sulfur Chem., 8 (1973) 173; R. Mayer, J. Morgenstern, and J. Fabian, Angew. Chem., 76 (1964) 157.
13 R.B. King, Organomet. Syn., 1 (1965) 180.