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FLUORINATION WITH XENON DIFLUORIDE; PART IX. REACTION WITH PHENYLSUBSTITUTED SULPHIDES

MARKO ZUPAN

"Jozef Stefan" Institute and Department of Chemisty, University of Ljubljana,
61000 Ljubljana, Yugoslavia

SUMMARY

Fluorination of phenyl–methylsulphide with xenon difluoride yields phenyl–fluoromethylsulphide. Further fluorination leads to phenyl–difluoromethylsulphide. Reaction with cis–2,6–diphenyltetrahydro–1–thio–4–pyrone results in the dehydrogenated product 2,6–diphenyldihydro–1–thio–4–pyrone, while further reaction leads to 2,6–diphenyl–1–thio–4–pyrone; thiochroman–4–one yields thiochromen–4–one.
No evidence for precursors of the products isolated at room temperature was found.

INTRODUCTION

Filler and coworkers [1–5] have demonstrated the utility of xenon difluoride as a selective fluorinating agent for aromatic compounds in the liquid phase. Furthermore, Mackenzie and Fajer [6] have fluorinated aromatic compounds in the vapour phase, but only limited data are available on fluorine addition to olefins with this reagent [7]. We have shown that xenon difluoride readily adds fluorine to phenylsubstituted olefins [8,9], reacts with phenylacetylenes to form tetrafluoroproducts [10] and also reacts with phenanthrene to form 9–fluorophenanthrene, while the reaction with higher amounts of xenon difluoride results in 9,9,10–trifluoro–9,10–dihydro, 9,9,10,10–tetrafluoro–9,10–dihydro– and 9,10–difluorophenanthrene derivates [11]. We have also studied the oxidation properties of xenon difluoride, e.g. oxidation of 1,2– or 1,4–dihydroxybenzene derivates into corresponding quinones [12]. Gibson and Janzen [13] have shown that xenon difluoride reacts with organosilicon compounds, and they have also found that the reaction of methyliodine with xenon difluoride leads to methyliodine(III)difluoride [14]. We developed a similar method for preparation of a series of substituted aryliodine(III)difluorides [15]. In our continued interest in the reactions of xenon difluoride with organic molecules we found it reasonable to study its reactions with some phenylsubstituted sulphides.

We now report the reaction of xenon difluoride with phenyl–methylsulphide (1), phenyl–fluoromethylsulphide (2), cis–2,6–diphenyltetrahydro–1–thio–4–pyrone (4), 2,6–diphenyldihydro–1–thio–4–pyrone (5) and thiochroman–4–one (7).

RESULTS AND DISCUSSION

There has been considerable interest in sulphuranes in the past few years. Several have been isolated and a number have been postulated as reaction intermediates [16]. It has been shown that the reaction of trifluoromethyl hypofluorite with sulphides at low temperature yields difluorosulphuranes [16], while the reaction with an excess of the reagent results in tetrafluoropersulphurane [17]. The products are very unstable and decompose at room temperature.

We now report the reaction of xenon difluoride with some phenylsubstituted sulphides. In a typical experiment we dissolved 1 mmol of compound in methylene chloride anhydrous hydrogen fluoride (1 mmol) was introduced into the reaction mixture and under stirring at room temperature pure xenon difluoride (1 mmol) was added. The colourless solution turned orange and xenon gas was evolved. By fluorination of phenyl–methylsulphide (1) we have isolated phenyl–fluoromethylsulphide (2). The n.m.r. spectra of the product 2 showed a triplet signal at –185.3 ppm in ^{19}F n.m.r. spectra a doublet with a coupling constant of 60 Hz at 5.6 ppm in ^{1}H n.m.r. spectra.

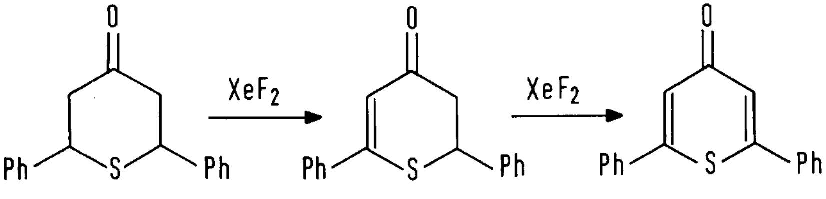
In order to detect the primarily formed products, we have taken n.m.r. spectra on the crude mixture, but no evidence for any other product was found. On the basis of the n.m.r., mass and i.r. spectral data, we have concluded that the product formed is phenyl–fluoromethylsulphide 2. Further reaction with 2 resulted in the formation of the product 3, which could be purified by preparative t.l.c. Tne n.m.r. spectra of the product 3 showed a doublet signal at δ –121 ppm in ^{19}F n.m.r. spectrum and a triplet signal at δ 6.5 ppm with a coupling constant 60 Hz in ^{1}H n.m.r. spectrum. On the basis of the spectral data we have assigned its structure as phenyl–difluoromethylsulphide (3).

The reaction with cis–2,6–diphenyltetrahydro–1–thio–4–pyrone (4) took place under similar conditions. The crude products showed no signal in the fluorine n.m.r. spectra, while the ^{1}H n.m.r. spectra showed a singlet signal at δ 6.6 ppm, corresponding to the olefinic proton, a doublet of doublet at 4.6 ppm with coupling constants 12 Hz and 6 Hz, corresponding to the proton, bonded to the same carbon atom as the phenyl group, and a multiplet signal at 3 ppm for two protons. The mass spectrum showed a molecular peak at m/e 266 which is two mass units lower than the starting material. In the i.r. spectra we observed a shift for carbonyl stretching from 1700 cm^{-1} to 1650 cm^{-1} for 5. On the basis of the data we have established that 2,6–diphenyldihydro–1–thio–4–pyrone (5) was formed. Further reaction of 5 with xenon difluoride resulted in the formation of 2,6–diphenyl–1–4–pyrone (6). The ^{1}H n.m.r. spectrum showed a singlet signal at δ 7.2 ppm for two olefinic protons. In the i.r. spectrum, carbonyl–group stretching was observed at 1590 cm^{-1}.

The reaction of thiochroman–4–one (7) with 1 mmol of xenon difluoride resulted in the formation of one product, which showed in its ^{1}H n.m.r. spectrum at δ 8.5 ppm a multiplet for one proton and a second multiplet at δ 7.5 ppm, corresponding the three aromatic protons and two doublets for two olefinic protons, the first at δ 7.2 ppm and the second at δ 7.8 ppm. In the i.r. spectrum the carbonyl stretching was shifted from 1680 cm^{-1} for 7 to 1625 cm^{-1} for 8, and the value of the molecular peak in the mass spectrum was diminished by two mass units from the starting compound 7. On the basis of the spectroscopic data mentioned above we have assigned the structure of the product as thiochromen–4–one (8).

All efforts to detect the precursors of the isolated products at room temperature were unsuccessful. However, in order to establish the reaction mechanism for fluorination

$$\underset{\underline{1}}{Ph{-}S{-}CH_3} \xrightarrow{XeF_2} \underset{\underline{2}}{Ph{-}S{-}CH_2F} \xrightarrow{XeF_2} \underset{\underline{3}}{Ph{-}S{-}CHF_2}$$



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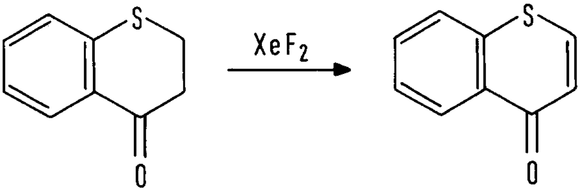

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of organic compounds with xenon difluoride in which we have been interested for some time, low temperature experiments, e.s.r. measurements and reactions with other organic sulphur compounds are in progress.

EXPERIMENTAL

I.r. spectra were recorded using a Perkin–Elmer 257 spectrometer, ^1H and ^{19}F n.m.r. spectra by a Jeol–JNM–PS–100 from CCl_4 solution with TMS or CCl_3F as internal reference. Mass spectra and high resolution measurements were taken on a CEC–21–110 spectrometer. Gas–liquid partition chromatography was carried out on a Varian Aerograph Model 1800 and t.l.c. on Merck–PSC–Fertigplatten F–254.

Materials

Pure samples of sulphides were prepared by known methods: phenyl–methylsulphide [18], cis–2,6–diphenyltetrahydro–1–thio–4–pyrone [19], thiochroman–4–one of Aldrich purity was used without further purification. Methylene chloride was purified [20] and stored over molecular sieves. Hydrogen fluoride of Fluka Purum Quality. was used. Xenon difluoride was prepared by photosynthetic methods [21] and its purity was better than 99.5 %.

Addition and isolation procedures

To a solution of 1 mmol of sulphide in methylene chloride (2ml) 1 mmol of xenon difluoride was added at 25°C and under stirring hydrogen fluoride was introduced into the reaction mixture (trace amounts). After a few seconds the colourless solution turned orange and xenon gas was quickly evolved. After 10 min. gas evolution had ceased, the reaction mixture was diluted with methylene chloride, washed with sodium hydrogencarbonate (5 %, 10 ml), water (10 ml, twice) and dried over anhydrous sodium sulphate. The solvent was evaporated in vacuo. The crude products were purified by preparative t.l.c. ^{19}F n.m.r. spectra were taken on the reaction mixture in teflon coated n.m.r. tubes. No evidence for S–F compounds at room temperature was found.

Phenyl–fluoromethylsulphide (2) nc:

Separation on SiO_2 (chloroform), yield 67 % of liquid product (decomposition by heating), mass spectrum: calcd. for C_7H_7FS m/e 142.0251, found m/e 142.0241, m/e: 142 (M^+, 26 %) 123 (100), 110 (20), 109 (70), 77 (32), 65 (30), 51 (31). N.m.r. spectrum: δ F–185.3 ppm (t), δ $C\underline{H}_2F$ 5.6 ppm (2H, d), δ Ph 7.3 ppm (5 H, m), $J(^{19}F-^1H)$= 60 Hz. Anal.: calcd. for C_7H_7FS C 59.2 %, H 5.0 %, found C 58.9 %, H 4.8 %.

Phenyl–difluoromethylsulphide (3) nc:

Separation on SiO_2 (chloroform), yield 58 % of liquid product (decomposition by heating), mass spectrum: calcd. for $C_7H_6F_2S$ m/e 160.0157, found m/e 160.0161, m/e: 160 (M^+, 74 %), 110 (100), 109 (70), 77 (80), 51 (80). N.m.r. spectrum: δ F–121 ppm (d), δ H 6.5 ppm (1 H, t), δ Ph 7.6 ppm (5 H, m). Anal.: calcd. for $C_7H_6F_2S$ C 52.5 %, H 3.8 %, found C 52.8 %, H 3.5 %.

2,6–diphenyldihydro–1–thio–4–pyrone (5)

Separation on SiO_2 (methanol: chloroform–1:9), crystallization from ethanol, yield 76 % of crystalline compound, mp: 65–66°C. N.m.r. spectrum: $\delta C\underline{H}$ 6.6 ppm (1H, s), δCH_2 3 ppm (2H, m), $\delta PhC\underline{H}$ 4.6 ppm (1H, dd), $J(^1H-^1H)$ = 12 Hz, 6 Hz, δPh 7.5 ppm (10 H, m). Mass spectrum: calcd. for $C_{17}H_{14}OS$ m/e 266.0762, found m/e 266.0750, m/e: 266 (M^+, 7 %), 162 (10), 124 (20), 104 (9), 86 (64), 84 (100).

2,6–diphenyl–1–thio–4–pyrone (6)

Separation on SiO_2 (Methanol: chloroform–1:9), crystallization from ethanol, yield 60 % of crystalline product, mp 128–129°C lit. (19) mp 132–133°C. N.m.r. spectrum: $\delta C\underline{H}$ 7.2 ppm (2H, s), δPh 7.7 ppm (10 H, m), mass spectrum m/e: 264 (M^+, 4 %), 140 (3), 107 (3), 106 (3), 88 (10), 86 (63), 84 (100).

Thiochromen–4–one (8)

Crystallization from water–ethanol, yield 65 % of crystalline compound, mp 74–75°C, lit. (22) mp 78°C. N.m.r. spectrum: olefinic protons: δH 7.2 ppm (1H, d), δH 7.8 ppm (1H, d); δH 8.5 ppm (1H, m), δH 7.5 ppm (3H, m).

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