

## Fluorination with Xenon Difluoride. Part 18.† Reactivity of Diphenyl Sulphide and Substituted Thiochromanones

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The fluorination of diphenyl sulphide with 1 mol. equiv. of xenon difluoride resulted in formation of diphenyl sulphoxide, while reaction with 2 mol. equiv. of xenon difluoride gave diphenyl sulphone after hydrolysis. Reaction with 3-bromothiochroman-4-one resulted in the formation of 3-bromothiochromen-4-one, while fluorination of 3,3-dibromothiochroman-4-one yielded 3,3-dibromo-2-fluorothiochroman-4-one. The formation of di- and tetra-fluoropersulphuranes, which were not isolated, is suggested.

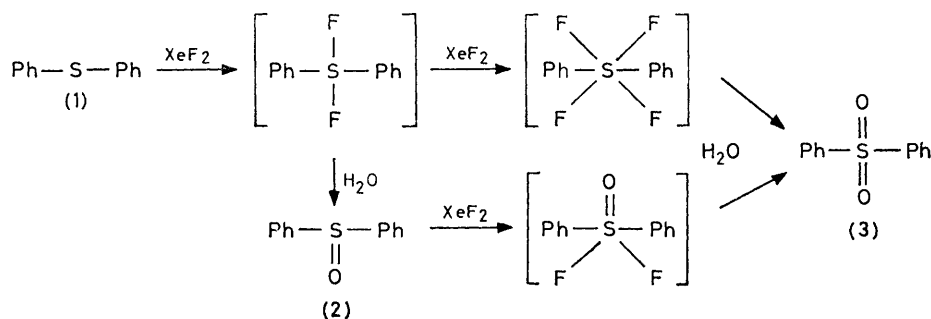
THERE has been a considerable interest in sulphuranes in the past few years. Several have been isolated and a number have been postulated as reaction intermediates.<sup>1</sup> Denney *et al.*<sup>1</sup> found that the reaction of trifluoromethyl hypofluorite with sulphides at low temperature yields difluorosulphuranes, while further reaction resulted in tetrafluoropersulphuranes.<sup>2</sup> They have shown that the products are stable at low temperature and that hydrolysis gave sulphoxides in high yield.<sup>1,2</sup>

Recently we have found that the reaction of xenon difluoride with phenyl-substituted sulphides<sup>3</sup> resulted in two types of products, depending on the structure of the

disubstituted thiochroman-4-one, where keto-enol tautomerism is impossible, as substrates.

### RESULTS AND DISCUSSION

In a typical experiment, diphenyl sulphide (1) (1 mmol) was dissolved in methylene chloride and hydrogen fluoride (trace) was introduced into the mixture and, with stirring at room temperature, pure xenon difluoride (1 mmol) was added. The <sup>19</sup>F n.m.r. spectrum of the crude mixture (measured at room temperature) showed no sharp signals. Further washing of the mixture with aqueous sodium hydrogencarbonate and water resulted



SCHEME 1

substrate. The formation of fluoromethyl phenyl sulphide by fluorination of methyl phenyl sulphide could be explained by the formation of intermediate difluorosulphuranes, elimination of hydrogen fluoride, followed by fluorine migration from the sulphur to the carbon atom. This reaction pathway could also account for the formation of dehydrogenated products, formed by the reaction of *cis*-2,6-diphenyltetrahydro-4-thiopyrone and thiochroman-4-one with xenon difluoride. However, the reaction could also proceed *via* fluorine addition to the enolic double bond, followed by further elimination of hydrogen fluoride. The reactions of xenon difluoride with ketones and diketones (acetylacetone, cyclopentanone, cyclohexanone, *etc.*) have recently been observed.<sup>4</sup> In order to obtain further information on the reaction pathways for the fluorination of sulphides, we chose diphenyl sulphide, where rearrangement is impossible, and 3,3-

in the formation of diphenyl sulphoxide (2) in high yield (Scheme 1). However, careful analysis of the crude reaction mixture by t.l.c. showed the presence of traces of diphenyl sulphone (3) as well. The reaction of diphenyl sulphide (1) with 2 mol. equiv. of xenon difluoride resulted in a crude mixture, whose <sup>19</sup>F n.m.r. spectrum also showed no sharp signals, while further hydrolysis under the conditions above led to the formation of diphenyl sulphone (3). The time needed for the completion of the reaction was much longer (15 h) in this case than when 1 mol. equiv. of xenon difluoride was used (1 h). In order to obtain further information about the intermediate in fluorination of diphenyl sulphide with 1 mol. equiv. of xenon difluoride, we also fluorinated diphenyl sulphoxide. The mixture, obtained by hydrolysis of the crude product after 21 h, showed that only

† Part 17, M. Zupan and B. Šket, *J. Org. Chem.*, 1978, **43**, 696.

<sup>1</sup> D. B. Denney, D. Z. Denney, and Y. F. Hsu, *J. Amer. Chem. Soc.*, 1973, **95**, 4064, and references cited therein.

<sup>2</sup> D. B. Denney, D. Z. Denney, and Y. F. Hsu, *J. Amer. Chem. Soc.*, 1973, **95**, 8191.

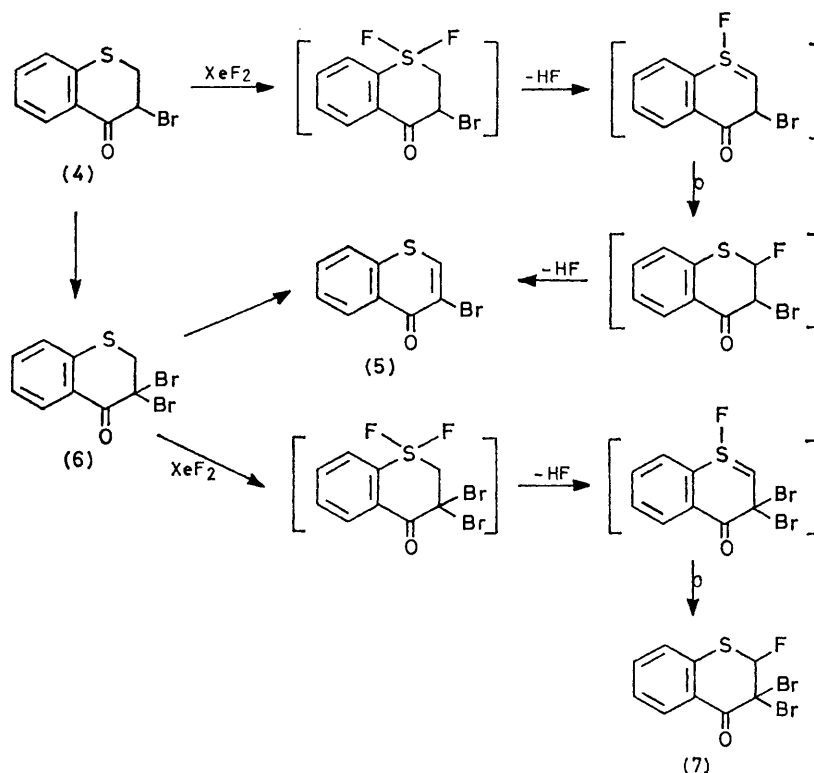
<sup>3</sup> M. Zupan, *J. Fluorine Chem.*, 1976, **8**, 305.

<sup>4</sup> M. Zupan, unpublished observations.

70% diphenyl sulphoxide was converted into diphenyl sulphone.

The fluorination of thiochroman-4-one with xenon difluoride resulted in the formation of thiochromen-4-one,<sup>3</sup> while the reaction with 3-bromothiochroman-4-one (4)

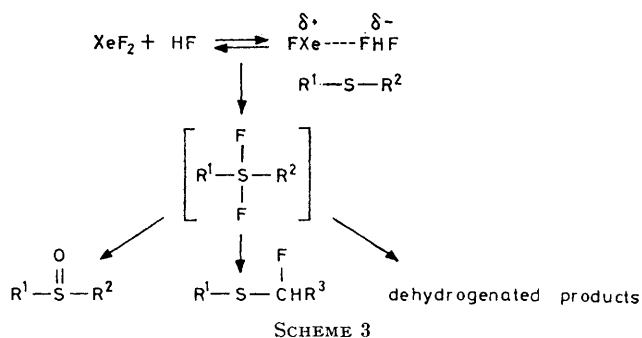
On the basis of these observations, the formation of difluorosulphuranes can be suggested (Scheme 3). Fluorination must involve catalysis by hydrogen fluoride since the reaction was very slow without it. It might be expected that, in the presence of hydrogen fluoride,



SCHEME 2

(Scheme 2) resulted in the formation of 3-bromothiochromen-4-one (5) in high yield, which was also prepared by elimination of hydrogen bromide from 3,3-dibromothiochroman-4-one (6), formed by bromination of 3-bromothiochroman-4-one (4). The fluorination of 3,3-dibromothiochroman-4-one (6) with xenon difluoride at

xenon difluoride would behave as an electrophile, as suggested by Filler *et al.*<sup>5</sup> for the fluorination of aromatic compounds. However, at the present time we are unable to suggest which type of Xe-F bond cleavage occurs, *i.e.* homolytic, heterolytic, or the formation of ion radicals. Difluorosulphuranes, which were not detected at room temperature, can lead to three types of products, depending on the structure of the sulphide: sulphoxides, dehydrogenated sulphides, or  $\alpha$ -fluoro-substituted sulphides. In the case of diphenyl sulphide, fluorination with 2 mol. equiv. of xenon difluoride also occurred, leading to the isolation of diphenyl sulphone, which could be explained by the formation of intermediate tetrafluoropersulphurane. On the other hand, the reaction of xenon difluoride with diphenyl sulphoxide, leading to diphenyl sulphone, was much slower than the above mentioned reaction.



SCHEME 3

room temperature resulted in 3,3-dibromo-2-fluorothiochroman-4-one (7) after 3 h (Scheme 2). The production of (7) reduced the possibility of the reaction path proceeding *via* addition of fluorine to the enol form of thiochroman-4-one; this was also taken into account in explaining the formation of thiochromen-4-one.

#### EXPERIMENTAL

I.r. spectra were recorded with a Perkin-Elmer 257 spectrometer, and <sup>1</sup>H and <sup>19</sup>F n.m.r. spectra with a JEOL-JNM-

<sup>5</sup> M. J. Shaw, J. A. Weil, H. H. Hyman, and R. Filler, *J. Amer. Chem. Soc.*, 1976, **92**, 5096; M. J. Shaw, H. H. Hyman, and R. Filler *ibid.*, p. 6498; *J. Org. Chem.*, 1971, **36**, 2917; S. P. Anand, L. A. Quarterman, H. H. Hyman, K. G. Migliorese, and R. Filler, *ibid.*, 1975, **40**, 807.

PS-100 instrument ( $\text{CCl}_4$  as solvent and  $\text{Me}_4\text{Si}$  or  $\text{CCl}_3\text{F}$  as internal reference). Mass spectra and high resolution measurements were obtained with a CEC-21-110 spectrometer. T.l.c. was carried out with Merck chromatoplates (PSC-Fertigplatten F-254).

**Materials.**—Pure samples of diphenyl sulphide,<sup>6</sup> diphenyl sulphoxide<sup>7</sup>, 3-bromothiochroman-4-one,<sup>8</sup> and 3,3-dibromothiochroman-4-one<sup>8</sup> were prepared by known methods. Methylene chloride was purified<sup>9</sup> and stored over molecular sieves. Xenon difluoride was prepared by photosynthetic methods<sup>10</sup> and its purity was >99.5%.

**Addition and Isolation Procedures.**—To a solution of diphenyl sulphide (1 mmol) in methylene chloride (2 ml) xenon difluoride (1 mmol) was added at 25 °C, and with stirring, hydrogen fluoride was introduced (trace amounts). The colourless solution turned orange and xenon gas was evolved. When gas evolution had ceased, the mixture was diluted with methylene chloride, washed with sodium hydrogencarbonate (5%; 10 ml), water (2 × 10 ml), and dried ( $\text{Na}_2\text{SO}_4$ ). The solvent was evaporated *in vacuo*. The crude products were purified by preparative t.l.c. <sup>19</sup>F N.m.r. spectra were taken in Teflon-coated n.m.r. tubes. No evidence for S-F compounds was found at room temperature.

**Diphenyl sulphoxide (2).** After a reaction time of 1 h, separation on  $\text{SiO}_2$  (chloroform), gave the crystalline compound (71%), m.p. 69–70.5 °C (lit.,<sup>7</sup> 70–71 °C). Spectroscopic data were in agreement with those of the independently synthesized diphenyl sulphoxide.<sup>7</sup>

**3-Bromothiochromen-4-one (5).** After a reaction time of 3 h, separation on  $\text{SiO}_2$  (chloroform), gave the crystalline product, m.p. 140–142 °C (lit.,<sup>8</sup> 142–143 °C) (Found: *m/e* 239.9170. Calc. for  $\text{C}_9\text{H}_5\text{BrOS}$ : *M*, 239.9245), 8.3 (1 H, s, CH), 7.5 (3 H, m, ArH), and 8.7 (1 H, m, ArH).

<sup>6</sup> F. Mauthner, *Ber.*, 1906, **39**, 3593.

<sup>7</sup> O. Hinsberg, *Ber.*, 1910, **43**, 289.

<sup>8</sup> F. Arndt, *Ber.*, 1925, **58**, 1612.

**2-Fluoro-3,3-dibromothiochroman-4-one (7).** After a reaction time of 3 h, separation on  $\text{SiO}_2$  (chloroform), gave the crystalline product (44.5%), m.p. 78–80 °C (Found: *m/e* 337.8413. Calc. for  $\text{C}_9\text{H}_5\text{Br}_2\text{FOS}$ : *M*, 337.8413), *m/e* 340 ( $M^+ + 2$ , 8%), 338 ( $M^+$ , 4), 180 (19), 136 (100), 108 (18), 76 (13), 69 (16), and 50 (12),  $\delta_{\text{F}}$  –154.5 p.p.m. ( $d, {}^2 J_{\text{FH}}$  48 Hz),  $\delta_{\text{H}}$  6.05 (1 H, d, CFH), 7.2 (3 H, m, ArH), and 8.05 (1 H, m, ArH) (Found: C, 32.15; H, 1.5. Calc. for  $\text{C}_9\text{H}_5\text{Br}_2\text{FOS}$ : C, 31.8; H, 1.5%).

**Fluorination of Diphenyl Sulphide (1) with 2 Mol. Equiv. of Xenon Difluoride.**—To a solution of diphenyl sulphide (1) (1 mmol) in methylene chloride (2 ml) xenon difluoride (2 mmol) was added at 25 °C, and with stirring, hydrogen fluoride (trace) was introduced. The colourless solution slowly turned orange. After 15 h the mixture was diluted with methylene chloride, washed with sodium hydrogencarbonate (5%; 10 ml), water (2 × 10 ml), and dried ( $\text{Na}_2\text{SO}_4$ ). The solvent was evaporated *in vacuo*. The crude product was purified by preparative t.l.c. ( $\text{SiO}_2$ ; chloroform) and the crystalline sulphone (59.2%), m.p. 122–123 °C (lit.,<sup>7</sup> 124 °C), was isolated. Spectroscopic data were in agreement with those of the independently synthesized diphenyl sulphone.

**Fluorination of Diphenyl Sulphoxide (2).**—Diphenyl sulphoxide (2) (1 mmol) was treated with xenon difluoride (1 mmol) and hydrogen fluoride (trace) as above. After 21 h work up as before gave the crystalline sulphone (51%), m.p. 122–123 °C.

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<sup>9</sup> 'Technique of Organic Chemistry. Vol. VII, Organic Solvents,' ed. A. Weissberger, Interscience, New York, 1955.

<sup>10</sup> S. M. Williamson, *Inorg. Synth.*, 1968, **11**, 147.