

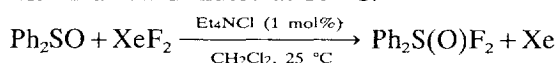
Oxidative fluorination of sulfur(IV) compounds by XeF₂

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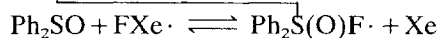
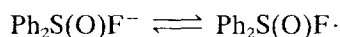
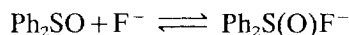
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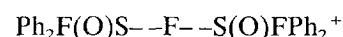
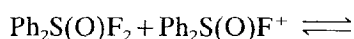
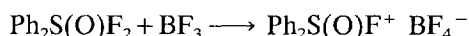
The oxidative fluorination of sulfur(IV) compounds such as diphenyl sulfoxide or diphenylsulfur difluoride occurs under mild conditions in the presence of xenon difluoride and catalytic amounts of chloride ion (~1 mol%). In the case of Ph₂SO, the sulfur(VI) product Ph₂S(O)F₂ is formed in essentially quantitative yield within a few minutes at 25 °C.



Chloride ion reacts with XeF₂ to produce fluoride ion, and a mechanism of oxidative fluorination is proposed which involves fluorosulfur(IV) anions and fluorosulfur(V) radicals.



In the presence of Lewis acids such as BF₃, fluorosulfur(VI) cations are formed, i.e. Ph₂S(O)F⁺ [1], and these cations undergo rapid intermolecular fluorine exchange with Ph₂S(O)F₂, presumably via fluorine-bridged intermediates [2].



This equilibrium has been studied by dynamic ¹⁹F and ¹³C NMR spectroscopy. Rapid halogen exchange is also observed when chloride ion is added to cationic Ph₂S(O)F⁺, but an excess of chloride ion slows down exchange as Ph₂S(O)F₂ and Ph₂S(O)Cl₂ are produced, as confirmed by ¹³C NMR.

In the above synthetic and fluorine-exchange studies, the ¹³C NMR spectrum of Ph₂S(O)F₂ was used to monitor the purity of reagents and solvent. A trace of moisture immediately produces Ph₂SO₂, while contact with glass apparatus converts the C(1) triplet into a broadened single peak, presumably because reaction with glass liberates the Lewis acids BF₃ and SiF₄, which in turn produce the cation Ph₂S(O)F⁺. Ab initio MO calculations (3-21G*) were carried out of the proposed anionic, radical and cationic intermediates.

References

- [1] I. Ruppert, *Chem. Ber.*, 113 (1980) 1047.
- [2] A.F. Janzen, *Coord. Chem. Rev.*, 130 (1994) 355.

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