

One-step synthesis of *N*-sulfonylazepines from sulfonylamides and benzene in the presence of XeF₂

Sergei V. Kovalenko,^a Valery K. Brel,^{*a} Nikolai S. Zefirov^a and Peter J. Stang^b

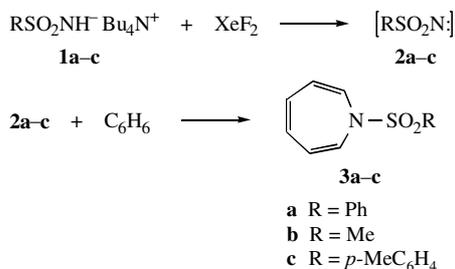
^a Institute of Physiologically Active Compounds, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax: +7 095 913 2113; e-mail: brel@ipac1.sherna.msk.su

^b Department of Chemistry, University of Utah, 84112 Salt Lake City, Utah, USA

Reaction of benzene and sulfonylnitrene, generated *in situ* from sulfonamide tetrabutylammonium salts and xenon difluoride, gives *N*-sulfonylazepines.

Xenon fluorides were discovered 35 years ago.¹ Xenon difluoride has proved to be one of the most useful fluorinating agents for organic substrates, including alkenes, acetylenes, aromatic and heteroaromatic compounds.^{2–4} In addition, XeF₂, being a strong oxidant, has been used for oxidative decarboxylation,⁵ fluorodeiodination⁶ and oxidation of organoelement compounds.⁷

In the course of our systematic studies of hypervalent compounds,⁸ we have unexpectedly found that reaction of XeF₂ with methyl-, *p*-tolyl-, and benzenesulfonamide tetrabutylammonium salts in benzene gives the corresponding *N*-sulfonylazepines (Scheme 1).[†]



Scheme 1

The reaction most probably proceeds *via* the intermediacy of sulfonylnitrenes, which rapidly react with the aromatic solvent to give *N*-sulfonylazepine.

The best results were obtained in boiling benzene. Addition of KF or CsF (to remove HF formed in the reaction) did not improve the yield of azepine. The use of sodium or potassium salts of the sulfonamide (instead of the tetrabutylammonium salt) did not result in the formation of azepine, presumably due to the low solubility of these salts in benzene. Indeed, the addition of one equivalent of [18]-crown-6 for the case of benzenesulfonamide gave *N*-sulfonylazepine in a yield of 17% at 25 °C or 25% at 80 °C. The yields of azepines for various substituents R and various reaction temperatures are summarised in Table 1.

Thus, the present reaction provides a new approach to the generation of sulfonylnitrenes and permits one to obtain *N*-sulfonylazepines in the reaction with aromatic compounds.

Table 1 Yields of azepines (%).

T/°C	3a	3b	3c
10	22	17	20
25	24	16	20
80	47	41	42

[†] Typical procedure: small portions of XeF₂ (0.338 g, 2 mmol) were added to a solution of sulfonamide tetrabutylammonium salt (2 mmol) in refluxing benzene (5 ml) over a period of 1 h (xenon evolution was observed). The mixture was cooled to room temperature, washed with water and dried (Na₂SO₄), then the solvent was evaporated. The azepines were isolated by column chromatography on silica gel with an ethyl acetate–hexane (1:3) mixture serving as the eluent. The spectral data obtained for azepines are in agreement with published data.^{9,10}

Although the yields of the products are modest, the synthesis of azepines is a one-step process, unlike the previously reported approaches⁹ which involve multi-step synthetic sequences. Applications of this methodology to other aromatic systems are in progress.

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