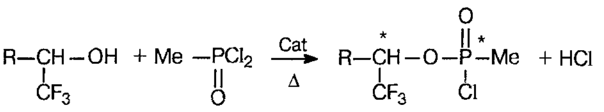
Table 1. Composition of the products of the catalytic phosphorylation of compounds **1a—d**

Compound	R	Diastereomers ratio determined by ^{31}P NMR
2a	Bu^n	50 : 50
2b	Bu^t	52 : 48
2c	n-C_6H_{13}	50:50
2d	$PhCH_2$	64:36

Note. LiCl was used as the catalyst.

α-(polyfluoroalkyl)benzyl alcohols.[3—5] To continue these studies, we prepared a number of methylphosphonochloridates starting from secondary 1-(trifluoromethyl)alkanols.



$$R-\underset{CF_3}{CH}-OH + Me-\underset{O}{\overset{}{P}}Cl_2 \xrightarrow[\Delta]{Cat} R-\overset{*}{\underset{CF_3}{CH}}-O-\overset{O}{\underset{Cl}{P^*}}-Me + HCl$$

1a—d **2a—d**

R = Bu^n (**a**), Bu^t (**b**), n-C_6H_{13} (**c**), $PhCH_2$ (**d**)

Thus, for example, heating compounds **1a—d** with methylphosphonic dichloride without a solvent at 120—160 °C for 1—3 h in the presence of 1—5 mol. % LiCl or $MgCl_2$ as a catalyst affords the corresponding chlorophosphonates **2a—d** in 70—84 % yield. It should be noted that this reaction is the first example of catalytic phosphorylation of secondary alkyl(trifluoromethyl)carbinols with methylphosphonic dichloride. According to ^{31}P NMR spectroscopy and GLC, the resulting *O*-(1-trifluoromethylalkyl)methylphosphonochloridates **2a—d** are mixtures of diastereomers (Table 1).

It should be noted that in the case of **2d**, the ratio between the diastereomers obtained in the reaction noticeably deviates from the statistical value. The diastereomeric excess amounts to 28 %, according to ^{31}P NMR, and 30 and 34 %, according to the data of GLC and GC—MS, respectively. Previously, the predominant formation of one of the diastereomers has been observed only in the catalytic phosphorylation of α-(polyfluoroalkyl)benzyl alcohols with methylphosphonic dichloride.[4—6]

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The use of XeF_2 for preparation of azepins

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In recent years, apart from the traditional use of xenon difluoride (XeF_2) as a mild fluorinating agent, the increasing attention has been attracted to methods based on the generation of other highly reactive reagents using

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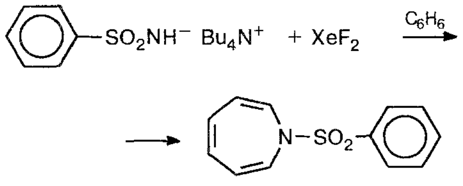
XeF_2. For example, reactions carried out with XeF_2 + HOR mixtures (where R is C(O)Alk, $C(O)R_f$, Alk) have made it possible to develop efficient methods for trifluoroacetoxylation,[2] alkylation,[3–5] and fluoroalkoxylation[6–8] of unsaturated and aromatic compounds, and insertion of SO_3 into the Xe—F bond has resulted in the formation of fluorosulfonating reagents.[7]

We showed for the first time that XeF_2 can be used for the synthesis of nitrogen-containing heterocyclic compounds. We prepared *N*-benzenesulfonylazepine (**1**) by the reaction of XeF_2 with the tetrabutylammonium salt of benzenesulfamide in benzene.



1

Compound **1** was isolated in the individual state by chromatography on silica gel. The structure of azepine **1** was confirmed by the data of IR and ^1H NMR spectroscopy and mass spectrometry.

XeF_2 (0.17 g, 1.0 mmol) was added to a stirred solution of the tetrabutylammonium salt of benzenesulfamide (0.398 g, 1.0 mmol) in 3 mL of abs. benzene over a period of 15 min. The reaction mixture was stirred for 3 h and washed with water, and the organic layer was separated, dried, and concentrated *in vacuo* to give 0.052 g (22 %) of azepine **1**, m.p. 130—132 °C (benzene—hexane) (see Ref. 7, 132—133 °C). The spectroscopic characteristics of compound **1** obtained coincide with those given in the literature for *N*-benzenesulfonylazepine.[8]

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