N-Allenyl-N-benzyltrifluoromethanesulfonamide

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Abstract—First N-allenyl-substituted triflamides CF$_3$SO$_2$N(Bn)CH=CH$_2$ were synthesized from N-allyl triflamides by successive reactions of bromination, N-alkylation, and dehydrobromination. Isomeric N-propargyl triflamide CF$_3$SO$_2$N(Bn)CH$_2$C≡CH is present in the reaction products as a minor admixture.

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N-allenylsulfonamides are insufficiently studied compounds. They are generated along with the N-propargylsulfonamides by a reaction of the lithium salts of the substituted tosylamides with propargyl carbonate [1]. Reactions of [2+2]-cycloaddition of substituted styrenes [2] and vinyl ethers [3] are known, catalyzed by the gold complexes. When the alkynyl group is present in the ortho-position of the benzene ring in the N-aryl-N-allenyltosilamide molecule the intermolecular cyclization into benzazepines occurs, as well as elimination of the allenyl group and its isomerisation into propenyl one [4].

N-propargylsulfonamides isomeric to N-allenylsulfonamides are obtained by interaction of propargylamines with sulfonyl chlorides [5]; recently their synthesis with high yield by the InCl$_3$-catalyzed nucleophilic substitution of the acetate group in propargyl acetates with tosylamide residue [6] have been described. However, neither fluorine-containing N-allenylsulfonamides, nor their isomeric propargylsulfonamides were known until present time.

The first N-alkenyl derivatives of triflamides [7–9] were synthesized recently, including also the first allyl derivatives of triflamides I, III [9] (Scheme 1), and some of their properties were investigated.

An attempt of further dehydrobromination of compound III aiming to obtain an acetylene derivative (N-propargyl triflamide), or its allenyl isomere (N-allenyl triflamide) was not successful. Apparently it is due to the high NH-acidity of the substrate III that gives triflamide salt with sodium alcoholate. That, in its turn, makes dehydrobromination difficult because of disadvantageous interaction of two anions: triflamidic and alkoxylic. That does not interfere with the reaction of dehydrobromination of dibromide II, obviously, due to easier of elimination of HBr from the polybrominated fragment. To overcome these difficulties, we decided to insert a protective group to the nitrogen atom in adduct II at the start and then the N-protected product, unable to generate the amide anion, would be brought in the dehydrobromination reaction.

The alkylation of N-(2,3-dibrompropyl) triflamide (II) with benzylbromide was carried out in dipolar aprotic solvents (DMSO, DMF) at heating. The reaction in DMSO goes well, however the process does not stop at the alkylation.
tion stage, but it is followed by dehydrobromination of the intermediate N-benzyl-N-(2-bromopropyl)-triflamide (IV) with the formation of N-benzyl-N-(2-bromoallyl) triflamide (V) (Scheme 2). The structure of compound V was established by $^1$H, $^{13}$C, and $^{19}$F NMR spectroscopy and was proved by the elemental analysis. The assignment of the methylene groups signals in the benzyl and allyl fragments was performed using the $^1$H–$^{13}$C HSQC spectrum, and the presence of the carbon atom of the terminal vinyl group $=$CH$_2$, with the help of the $^j$-modulated $^{13}$C NMR spectrum.

The observed regioselective dehydrobromination of the intermediate dibromide IV is similar to the formation of 1-(2-bromoallyl)isatin at the alkylation of isatin with 1,2,3-tribromopropane in DMF in the presence of potassium carbonate [10].

The reaction in DMF goes in the similar way, but with the lower yield, and up to 30% of side product dimethylbenzylammonium bromide Me$_2$Bn$_2$NBr was isolated, identified by comparing $^1$H and $^{13}$C NMR spectra to the spectra of the authentic sample. The generation mechanism of such salt is not clear; the reaction corresponds the formal scheme:

$$\text{Me}_2\text{NCHO} + 2\text{BnBr} \rightarrow \text{Me}_2\text{Bn}_2\text{NBr} + \text{HBr} + \text{CO}$$

The easier dehydrobromination of the dibromide IV (yield 65% in presence of K$_2$CO$_3$ in process of the alkylation) compared to dehydrobromination of its N-unsubstituted analog II (yield ~40% with stronger base EtO$^-$, and the analytically pure product cannot be isolated [9]) proves that the strategy of preliminary protection of the triflamide NH group is adequate.

The dehydrobromination of compound V can lead either to acetylene, or to allene product. Higher stability of the conjugated carbanion A compared to unconjugated terminal carbanion B allows to assume the easier formation of allene VI than of acetylene VII (Scheme 3).

However, considering the possibility of the acetylene-allene rearrangement, the ratio of the products VI and VII can be defined not only, and not as much by the ease of their formation, as by their comparative stability. As a result we have made calculations of the molecules of the compounds VI and VII in the approximation of B3LYP/6-311G(d,p), including the force problem, and calculated the difference of the total energies $\Delta E$ and the difference of the free energies $\Delta G^0$ of the isomers VI and VII. The difference of the total energies for the acetylene-allene isomerisation (VII) $\rightarrow$ (VI) (Fig. 1) is $\Delta E$ 2.5 kcal mol$^{-1}$, the difference of free energies is $\Delta G^0$ 3.2 kcal mol$^{-1}$ (298 K). Hence, the formation of the allene isomer VI must be preferential to the formation of the acetylene isomer VII kinetically, as well as thermodynamically.

According to the data of the $^1$H, $^{13}$C NMR and IR spectroscopy, the N-benzyl-N-allenyltriflamide (VI) is actually generated. It is proved by the presence of the doublet at $\sim$5.4 ppm and the triplet at $\sim$6.6 ppm in the $^1$H NMR spectrum, and of signals at 202, 98 and 89 ppm in the $^{13}$C NMR spectrum, typical of the allenyl, but not the propargyl fragment. In the IR spectrum a doublet band