

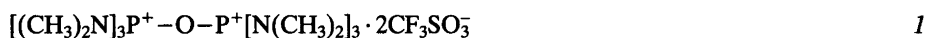
Short Communications

Intramolecular Cyclization Reaction of Diamides by Using Trifluoromethanesulfonic Anhydride

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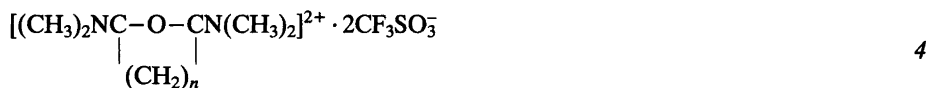
Previously we have reported^{1,2} that trifluoromethanesulfonic anhydride (Tf₂O) reacts with hexamethylphosphoramide and triphenylphosphine oxide to give the dication ether salts *1* and *2*, respectively:



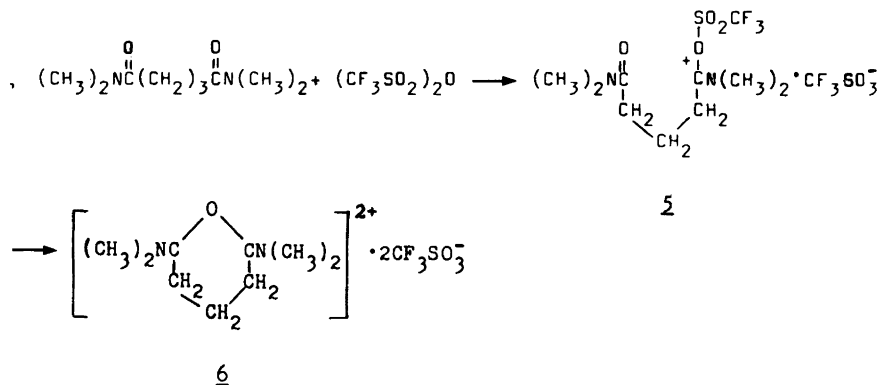
Later, similar reactions between various carbonyl compounds and Tf₂O have been shown^{3,4} to give novel dication ether salts of the type *3*:



To broaden the scope of our previous investigations, we here report a new intramolecular cyclization reaction of diamides by using Tf₂O. Hitherto the following, stable cyclic dication ether salts *4* have been prepared from *N,N'*-tetramethylsuccinamide (*n*=2), *N,N'*-tetramethylglutaramide (*n*=3) and *N,N'*-tetramethyladipamide (*n*=4):



The following reaction mechanism is proposed for the formation of the cyclic ether salts, exemplified by the reaction:



We believe that the first step in the reaction is the formation of a monocarbonium salt 5 which is rapidly attacked by the other carbonyl group in the same molecule to give the cyclic dication ether salt 6. The formation of the cyclic ether salt 6 and not the open monocalt 5 was confirmed by IR and NMR spectroscopy. The infrared spectra of the cyclic dication ether salts, performed in nujol, clearly showed the characteristic strong absorption of the CF_3SO_3^- ion in the 1250 cm^{-1} , 1179 cm^{-1} and 1045 cm^{-1} regions. Furthermore, the strong $\text{C}=\text{O}$ absorption at about 1630 cm^{-1} of the diamides disappeared on salt formation and a new band appeared at about 1690 cm^{-1} . These findings are in accordance with the results found for the dication ether salt formed by the reaction of Tf_2O with tetramethylurea⁴ and whose structure has been confirmed by X-ray crystallographic methods.⁵ The proton NMR spectra of the diamides and the corresponding cyclic ether salts in CD_3CN at room temperature showed, due to restricted rotation of the $\text{C}-\text{N}$ bond, two signals for the methyl groups ($n=2$: 2.984, 2.830 ppm and 3.700, 3.564 ppm; $n=3$: 2.959, 2.841 ppm and 3.331, 3.195 ppm; $n=4$: 2.959, 2.841 ppm and 3.289, 3.179 ppm, respectively for the diamides and the cyclic dication ether salts, downfield from TMS).

Experimental. In a typical experiment, trifluoromethanesulfonic anhydride (0.8508 g, 3 mmol) dissolved in dry CH_2Cl_2 (3 ml) was added dropwise with stirring to a solution of N,N' -tetramethylglutaramide (0.5623 g, 3 mmol) in CH_2Cl_2 (6 ml) at 0°C under dry nitrogen atmosphere. After completion of the addition, the mixture was stirred at 0°C for 30 min and the white crystals formed were filtered off and washed with dry CH_2Cl_2 (0.96 g, 68 % of 4 ($n=3$)). Found: C 27.98; H 3.81; S 13.79; equiv. 471.06. Calc. for $\text{C}_{11}\text{H}_{18}\text{O}_7\text{N}_2\text{S}_2\text{F}_6$: C 28.21; H 3.87; S 13.69; equiv. 468.38).

The same experimental procedure was used for the reaction between trifluoromethanesulfonic anhydride and N,N' -tetramethylsuccinamide (66 % yield of 4 ($n=2$)). Found: C 26.53; H 3.89; S 13.88; equiv. 455.01. Calc. for $\text{C}_{10}\text{H}_{16}\text{O}_7\text{N}_2\text{S}_2\text{F}_6$: C 26.44; H 3.55; S 14.11; equiv. 454.35) and between trifluoromethanesulfonic anhydride and N,N' -tetramethylpiperamide (82 % of 4 ($n=4$)). Found: C 29.66; H 4.33; S 13.19; equiv. 483.53. Calc. for $\text{C}_{12}\text{H}_{20}\text{O}_7\text{N}_2\text{S}_2\text{F}_6$: C 29.88; H 4.18; S 13.29; equiv. 482.40). The equivalent weight was determined by titration with aqueous sodium hydroxide.

Similar cyclization reactions using dicarbonyl compounds, diphosphoryl compounds and compounds containing both a $\text{P}=\text{O}$ and a $\text{C}=\text{O}$ group in the same molecule are under investigation.

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