

Synthesis and structural characteristics of dicarboxylic acid silatranylmethyl ethers

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Abstract

Dicarboxylic acid silatranylmethyl ethers were synthesized by the equimolar reaction of chlormethyl-triethoxysilane with succinic acid and potassium hydrophthalate, following triethanolamine reetherification of corresponding intermediate alcoxyether. The adverse etherification reaction during triethanolamine reetherification (supporting released ethanol attack on carboxylic functional groups of succinic acid and hydrophthalate) was discovered. Diether synthesis complexity of succinic and phthalic acids due to low intermediate product solubility and high polymerization probability with siloxane bonding or even polymeric silicon dioxide isomers formation was shown. Salt synthesis method was shown to be unsuitable for etherification of aliphatic dicarboxylic acids due to corresponding alkali metal salts low solubility in utilized reaction mediums. The preferable method for these precursor types by triethylamine utilization without intermediate recovery was suggested. On the contrary sodium and potassium salt synthesis method was shown to be effective for aromatic dicarboxylic acid etherification in experiment trials.

Synthesized compound molecular structures were determined by X-ray structure analysis methods. It was shown, that the contained in silatranylmethyl ether structure acid properties affect in silatrane cycle molecular angle values and bond lengths due to dicarboxylic acid high electrostatic or field effects. These factors were found to lead in the high disorderliness in ratio 0.658 to 0.342 of carbon atom positions in N-C bonds inside silatrane cycles of aromatic dicarboxylic acid ethers compared to monocarboxylic ones. It was discovered, that unetherified by silatranylmethyl substituent carboxylic group steric orientation affects in O-Si-O angle values in silatrane cycle. The 1-ethylen-2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane fragment insertion into ether molecule was shown to identically affect in steric and chemical properties of carboxylic groups despite of precursor acid nature.

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