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BOOK OF ABSTRACTS

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PB-26

SYNTHESIS OF NOVEL SULFUR CONTAINING SUGAR-ISOXAZOLE CONJUGATES

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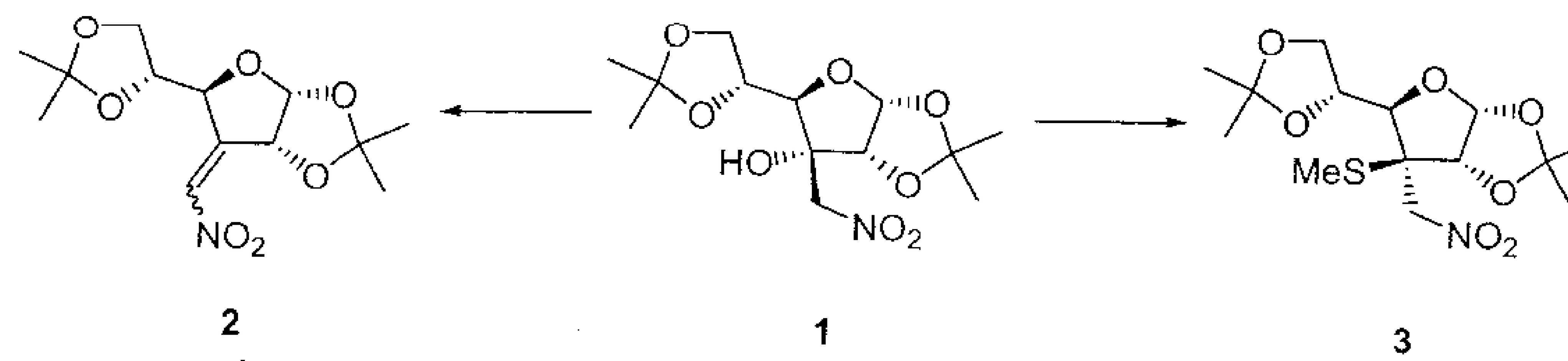
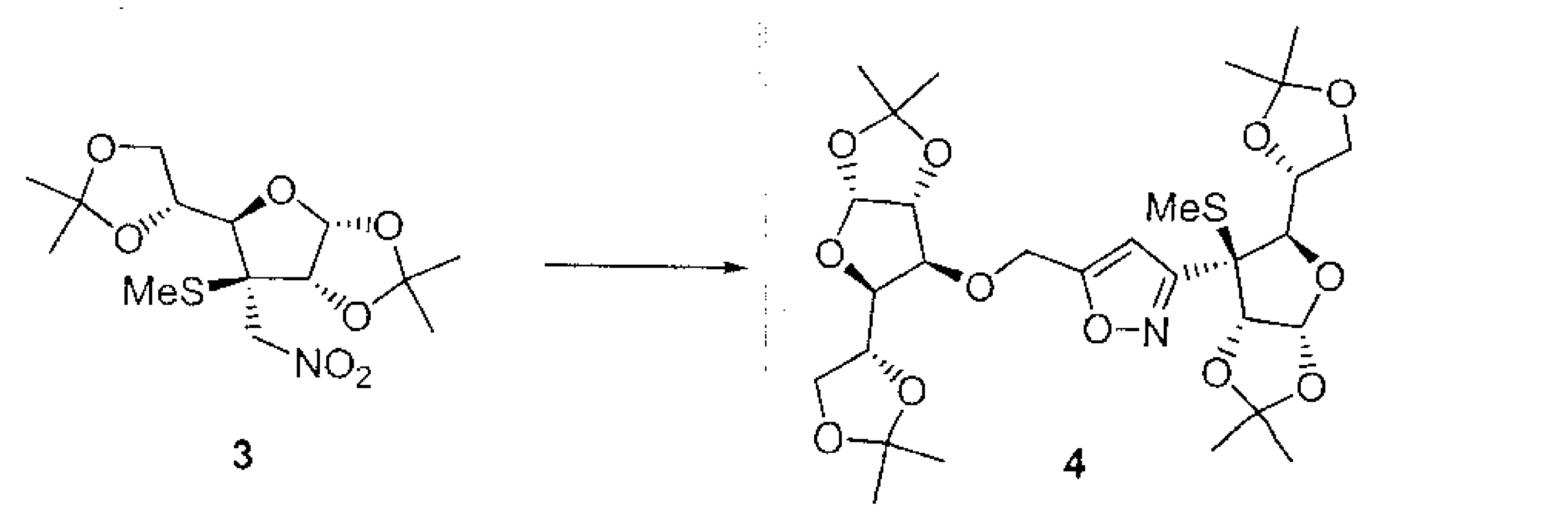
In a dehydration reaction of tertiary alcohol **1** with acetic anhydride and dimethylsulfoxide accordingly to previously reported method[1] we isolated a methyl sulfide group containing side product **3** along with the expected compound **2**. Recently, products arising from methyl thiolate addition have been isolated in Swern oxidation.[2]



Product **3** most probably originates from the Pummerer rearrangement that takes place during basic work-up generating methyl thiolate anion, which undergoes consecutive Michael addition to the activated double bond in compound **2**.

After optimization of the work-up procedure we established conditions for selective synthesis of either dehydratation product **2** or the adduct **3**. Further, thiolate adduct **3** was successfully used as a substrate for the synthesis of sugar-isoxazole conjugates.[3] A representative example of the latter (dimer **4**) is shown below:



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PA-32

VOGEL'S SILYL SULFINATE IN SULFOXIDE SYNTHESIS AND GAS CHROMATOGRAPHIC ANALYSIS OF POLYHYDROXYLATED COMPOUNDS

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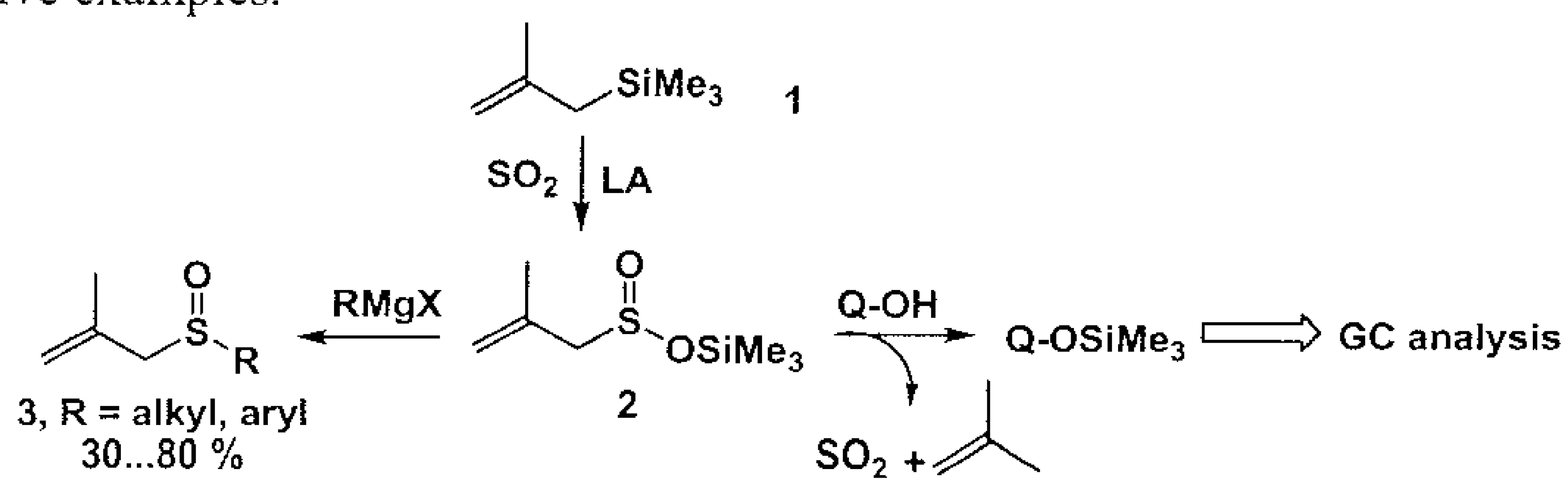
In 2002, new metallo-ene reaction of allylsilanes with sulfur dioxide was reported.[1] Obtained silyl allylsulfinates were used as valuable precursors of sulfones and sulfonamides,[2] and powerful silylating agents.[3]
Here, we report their use as good starting materials in the synthesis of allylsulfoxides. In a typical sulfoxide synthesis, trimethylsilyl methallylsulfinate **2** worked as a good electrophile with Grignard reagents and provided products **3** in moderate to good yields.
On the other hand, trimethylsilyl methallylsulfinate **2** can be viewed as an equivalent competitor for contemporarily used commercial silylating reagents. The main advantage of silylation with silyl sulfinate **2** is the formation of volatile byproducts: sulfur dioxide and isobutene. The silylation procedure with **2** does not require additional reagents (e.g., bases or acids) that are usually added along with other silylating agents.[4]
In a common silylation experiment, corresponding alcohols, polyols, phenols, carboxylic acids, monosaccharides and/or their mixtures were mixed with silyl sulfinate **2** and analyzed by GC-MS and/or GC-FID. The new conditions of silylation can be used in both, qualitative and quantitative analysis. Examples including silylation and analyses of glycerol, 2-ethyl-2-(hydroxymethyl)-1,3-propanediol, 2,2-dimethyl-1,3-propanediol, pentaerythritol, tartaric, mandelic, malic, citric acids and other polyhydroxylated compounds will be discussed. One of the perspectives is GC-MS analysis of derivatized sugar samples which will be demonstrated on mannose and ribose as representative examples.



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