POLY(ORTHOESTERS) BY THE ADDITION OF DIOLS TO A DIKETENE ACETAL

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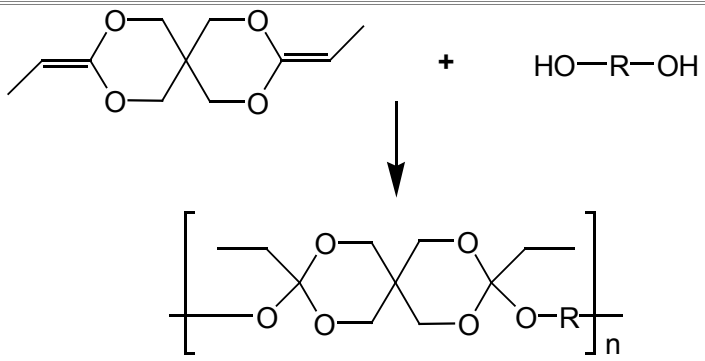
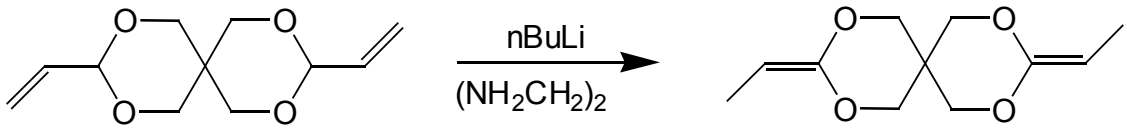


1. Procedure

a. Preparation of 3,9-bis(ethylidene-2,4,8,10-tetraoxaspiro[5,5]undecane)



In a 3 l three-necked flask fitted with a mechanical stirrer, argon inlet tube, thermometer and rubber septum is placed 1.2 l of ethylene diamine (Note 1). The flask is cooled with ice water and the contents kept at about 8°C (Note 2) under an argon atmosphere. A hexane solution of n-butyllithium (130 g, 2 mol, Note 3) is added via a stainless steel hypodermic U-tube pushed through the rubber septum using carefully controlled argon pressure over a period of 1 h. Next, a mixture of 3,9-bis(vinyl-2,4,8,10-tetraoxaspiro[5,5]undecane) (530 g, 2.5 mol, Note 4) and 0.5 l of ethylenediamine is cooled to 8°C and added to the three necked flask (Note 5). After stirring at 8°C for 3 h, the reaction mixture is poured into 3 l of ice-water with vigorous stirring. The aqueous mixture is extracted twice with 1 l portions of hexane. The combined hexane extracts are washed three times with 1 l portions of water, dried over anhydrous magnesium sulfate and filtered under suction. The filtrate is evaporated to dryness on a rotary evaporator to give crude material (413 g, 78%) containing 90% of 3,9-bis(ethylidene 2,4,8,10-tetraoxaspiro[5,5]undecane) (Note 6).

The crude product is dissolved in 2 l of hexane containing 10 ml of triethylamine (Note 7) and the solution placed in a 4 l filter flask, sealed and stored in a freezer at -20°C for two days (Note 8). The crystals thus formed are collected by basket centrifugation (Note 9) at -5°C under an argon atmosphere. Distillation of the brownish product (Note 10) through a 12 in vigreaux column at reduced pressure gives 3,9-bis-(ethylidene 2,4,8,10-tetraoxaspiro[5,5]undecane)(313 g, 61%, Note 11) as a colorless liquid, b.p. 82°C (0.1 torr) which crystallizes at room temperature, mp 30°C; characteristic IR band at 1700 cm^{-1}.

b. Preparation of Polymer

While maintaining anhydrous conditions, *trans*-cyclohexanedimethanol (89.57 g, 0.621 mol), 1,6-hexanediol (39.52 g, 0.334 mol) and 1.8 l of tetrahydrofuran distilled over calcium hydride are placed into a 5 l three necked flask equipped with an overhead stirrer, an argon inlet tube and a condenser on a trap (Note 12). The mixture is stirred until all solids have dissolved; then 3,9-bis(ethylidene 2,4,8,10-tetraoxaspiro[5,5]undecane) (206.75 g, 0.974 mol) is added. The polymerization is initiated by the addition of 0.5 ml of a 20 mg/ml solution of *p*-toluenesulfonic acid in tetrahydrofuran (Note 13).

The polymerization temperature rapidly rises to the boiling point of tetrahydrofuran and then gradually decreases. Stirring is continued for about 2 h, then 1 ml of triethylamine stabilizer is added and the reaction

mixture very slowly poured with vigorous stirring into about 5 gallons of methanol containing 10 ml of triethylamine.

The precipitated polymer is collected by vacuum filtration and dried in a vacuum oven at 60°C for 24 h to give 325 g (98.8% yd). Typical molecular weights are 50,000 to 100,000 as determined by light scattering.[3] The molecular weight can be controlled by skewing the reaction stoichiometry.[4]

c. Methods of Preparation

Although the superbase-catalyzed rearrangement of allyl ethers to propenyl ethers has been reported,[5,6,7] we are not aware of any work that describes the rearrangement of vinyl acetals to ketene acetals. We have found that this rearrangement proceeds readily and is thus an excellent alternative method for the synthesis of ketene acetals which are usually prepared by the dealcoholization of ortho esters.[8]

Poly(ortho esters) were first reported in a series of patents by the Alza Corporation and were prepared by a transesterification reaction between diethoxytetrahydrofuran and diols.[9,10,11,12] Another family of poly(ortho esters) also prepared by a transesterification reaction has recently been reported.[13] However, unlike both of these syntheses, which require long reaction times, the addition of alcohols to ketene acetals proceeds to completion virtually instantaneously.[14] Furthermore, because no small molecule by-products are produced, dense, crosslinked matrices can be produced by using varying proportions of diols and triols.[15]

2. Notes

1. Commercial ethylenediamine is used as received.
2. Ethylenediamine freezes at 5°C.
3. Hexane solutions of n-butyllithium of any practical concentration can be used.
4. 3,9-bis(vinyl-2,4,8,10-tetraoxaspiro[5,5]undecane) from Aldrich is purified by flash distillation with a short distillation head at 120°C and 0.5 torr. This compound can be prepared by reacting pentaerythritol with 20% excess of acrolein and catalytic amounts of acid using benzene as a drying solvent.[14]
5. The mixture can be added rapidly to the three-necked flask but the cooling capacity of the ice-bath must be adequate so that the reaction temperature does not rise above 8°C.
6. Analysis is conducted by GC on a 30 meter capillary column at an initial temperature of 40°C increasing to 225°C at a rate of 20°C/min.
7. Triethylamine is used as a stabilizer since 3,9-bis(ethylidene 2,4,8,10-tetraoxaspiro[5,5]undecane) is extremely unstable under acidic conditions. However, it is stable under basic conditions.
8. Seeding may be necessary.
9. Pressure filtration can be used but filtration under suction is not satisfactory.
10. Distillation removes high boiling and colored by-products.
11. One crystallization usually gives a product 98% pure. Because a purity better than 99% is required, a second crystallization is necessary.
12. All reagents must be handled under anhydrous conditions and should be at least 99% pure.
13. The polymerization is exothermic. A condenser on a trap to prevent the reaction mixture from boiling over should be used.

3. References

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