

Radical Reactions of 1,4-Bis(vinylsulfonyl)tetrafluorobenzene with Tetrahydrofuran

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Abstract—Homolytic addition of tetrahydrofuran at the vinylsulfonyl groups of 1,4-bis(vinylsulfonyl)tetrafluorobenzene in the absence of radical initiator at 20 and 55°C leads to formation of 1,4-bis[2-(2-tetrahydrofuryl)ethylsulfonyl]tetrafluorobenzene in 16 and 42% yield, respectively, and a mixture of telomers. The latter are formed as a result of opening of the tetrahydrofuran ring in the adduct.

We previously reported [1] on homolytic addition of tetrahydrofuran at the vinylsulfonyl groups of 1,4-bis(vinylsulfonyl)tetrafluorobenzene (**I**), which resulted in formation of 42% of 1,4-bis[2-(2-tetrahydrofuryl)ethylsulfonyl]tetrafluorobenzene (**II**) (Scheme 1). It was found that the reaction requires no radical initiator but is promoted by peroxides formed from tetrahydrofuran itself by the action of atmospheric oxygen. The main attention in [1] was given to determination of the product structure. The present work continues studying of this reaction.

We have found that vinylsulfonylfluorobenzene **I** reacts with tetrahydrofuran not only at 50–55°C in 8–10 h but also at 20–25°C; however, the reaction time increases to 10–14 days and the yield of **II** is only 16%. Both at 20–25°C and at 50–55°C, the addition process is accompanied by opening of the tetrahydrofuran ring in compound **II**, which leads to formation of a mixture of telomers as a dark brown thick material. Its IR spectrum contains strong broad carbonyl absorption bands at 1731–1773 cm⁻¹, a small

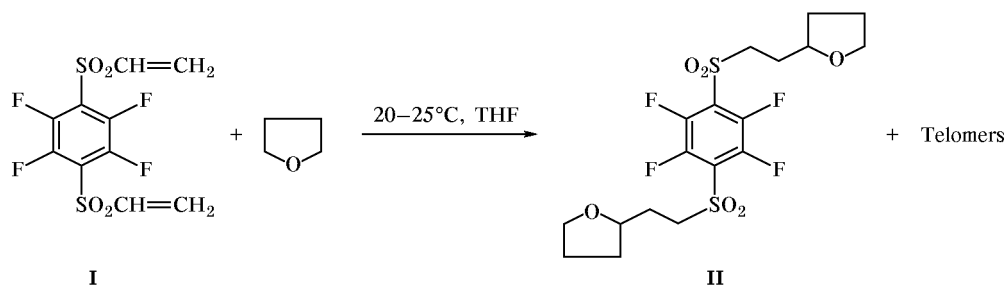
peak at 1645 cm⁻¹, and a broad band at 3397 cm⁻¹ (OH). These data suggest the presence of peroxy-carboxy, carboxy, and ketone groups in the telomers.

Opening of the tetrahydrofuran ring in adduct **II** with a conversion of ~70% was confirmed experimentally. When compound **II** was heated at 50–55°C in tetrahydrofuran (i.e., under conditions corresponding to the synthesis of **II**), identical telomer mixture was obtained. These data also explain the low yield of adduct **II**.

It is known [2] that the reaction of 1-octene with tetrahydrofuran, initiated by *tert*-butoxyl radicals at 135–150°C, gives a small amount of 2-octyltetrahydrofuran, while the major product is dodecan-4-one. According to the authors, it is formed by a process, the first stage of which is opening of α -tetrahydrofuryl radical with formation of a new radical species, CH₃CH₂CH₂Ċ(O).

Our results show that opening of the tetrahydrofuran ring in adduct **II** occurs under mild conditions (20–55°C). Probably, in the reaction of vinylsulfonyl

Scheme 1.



derivative **I** with tetrahydrofuran, ring opening in α -tetrahydrofuryl radical yields $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{O})$ [2], and the latter adds to vinylsulfonylfluorobenzene **I**. However, we failed to isolate such adducts as individual products.

Treatment of the telomer mixture with hot benzene and subsequent chromatography on aluminum oxide gave a fraction whose elemental composition (see Experimental) suggests that one molecule of vinylsulfonylfluorobenzene **I** takes up four molecules of tetrahydrofuran ring opening products. The IR spectrum of the isolated substance contains narrower peaks at 1148 ($\nu\text{S}=\text{O}$, sym.) and 1343 cm^{-1} ($\nu\text{S}=\text{O}$, asym.), which are typical of SO_2 group, and 1499 cm^{-1} ($\text{C}_{\text{arom}}-\text{F}$); carbonyl stretching vibrations appear as two bands at 1732 and 1773 cm^{-1} . We also isolated a thicker dark brown material which is insoluble in benzene but soluble in water. Its IR spectrum is characterized by a poorly resolved background absorption (a broad band at 1733 cm^{-1}).

Thus our results show that 1,4-bis(vinylsulfonyl)-tetrafluorobenzene (**I**) in the presence of peroxides under mild conditions is capable of undergoing radical addition and telomerization reactions.

EXPERIMENTAL

The IR spectra were recorded on a Bruker IPS-25 spectrometer from samples prepared as thin films or pelleted with KBr.

1,4-Bis[2-(2-tetrahydrofuryl)ethylsulfonyl]tetrafluorobenzene (II). A solution of 0.52 g of 1,4-bis(vinylsulfonyl)tetrafluorobenzene (**I**) in 50 ml of tetrahydrofuran was left to stand for two weeks on exposure to light. Excess tetrahydrofuran was removed under reduced pressure, and the residue (a dark brown material) was dried in a vacuum. The dry residue (0.6 g) was washed with ethanol to obtain 0.22 g of

a colorless substance which was washed with diethyl ether. We thus isolated 16% of compound **II** which was identical to the product described in [1]. Removal of the solvent from the ethanol fraction gave 0.33 g of a viscous dark brown material.

Reaction of 1,4-bis[2-(2-tetrahydrofuryl)ethylsulfonyl]tetrafluorobenzene (II) with tetrahydrofuran. A mixture of 0.5 g of compound **II** and 50 ml of tetrahydrofuran was stirred for 12 h at 50–55°C. The solvent was distilled off under reduced pressure, and the residue, a dark brown material, was washed with three portions of ethanol to obtain 0.16 g (30%) of a colorless substance. The latter was identified by IR and ^1H NMR spectroscopy as unreacted compound **II**. Removal of the solvent from the ethanol solution gave a viscous dark brown material (0.31 g). IR spectrum, ν , cm^{-1} : 1652–1773 ($\text{C}=\text{O}$), 1144 and 1337 (SO_2), 1482 ($\text{C}_{\text{arom}}-\text{F}$). The product was treated with hot benzene. The benzene solution was evaporated, and the residue was subjected to chromatography on aluminum oxide using ethanol as eluent to isolate 0.23 g of a narrower telomer fraction. Found, %: C 50.09; H 6.10; F 11.50; S 10.09. $\text{C}_{26}\text{H}_{34}\text{F}_4\text{O}_8\text{S}_2$. Calculated, %: C 50.80; H 5.57; F 12.36; S 10.43. *M* 614.

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