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HOMOLYTIC ADDITION REACTION OF VINYLSULFONYLFLUOROBENZENE*

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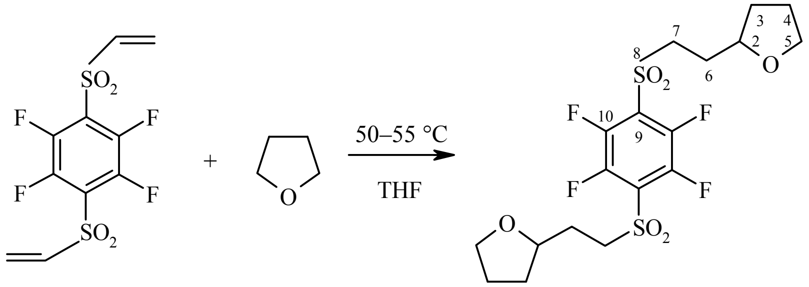
The reaction of 3,6-bis(vinylsulfonyl)-1,2,4,5-tetrafluorobenzene with a large excess of tetrahydrofuran at 50-55°C gives the homolytic addition product 3,6-bis[2-(2-tetrahydrofuryl)ethylsulfonyl]-1,2,4,5-tetrafluorobenzene. The reaction is effected by peroxides radical process initiators obtained by the autooxidation of tetrahydrofuran.

Keywords: vinylsulfonylfluorobenzene, tetrahydrofuran, homolytic addition, radical initiation.

In continuation of our investigations of the reactivity of 3,6-bis(vinylsulfonyl)-1,2,4,5-tetrafluorobenzene (**1**) [1, 2], we have discovered an unexpected addition reaction of tetrahydrofuran at both vinylsulfonyl groups to give the novel product 3,6-bis[2-(2-tetrahydrofuryl)ethylsulfonyl]-1,2,4,5-tetrafluorobenzene (**2**) in 42% yield.



1 **2**

There are literature reports of the 2-alkylation of tetrahydrofuran by 1-octene [3, 4] and maleic anhydride [5] under radical initiation conditions but not for the reaction of tetrahydrofuran with a vinylsulfonyl group.

The reaction of the vinylsulfonyltetrafluorobenzene **1** with tetrahydrofuran occurs at 50-55°C with a large excess of the latter which also acts as solvent. Compound **2** is a white, high melting powder, characterized by IR, ^{1}H, ^{13}C, and ^{19}F NMR spectroscopic data, and by elemental analysis which confirms its composition.

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* Dedicated to Academician M. G. Voronkov on his 80th Birthday.

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According to the evidence in the literature [3-5] the indicated reaction can be considered as a radical process, through which the fission of a hydrogen atom from the α-position of tetrahydrofuran gives an α-tetrahydrofuryl radicals which then add to the vinylsulfonyl group. The fission of the hydrogen atom most likely occurs through the action of peroxide radical process initiators, which can be formed from the tetrahydrofuran itself being prone to ready autooxidation in the presence of air.

It was found that compound **2** is also formed in the presence of benzoyl peroxide (in 33% yield) but with hydroquinone the reaction does not proceed and the starting compound **1** is recovered. The results confirm the homolytic nature of the reaction under discussion even though, according to literature data, the double bond in α-vinylsulfones readily takes part in nucleophilic addition [6] and a radical addition is not typical [7, 8].

The structure of the synthesized compound **2** was proved by ^{1}H and ^{13}C NMR spectroscopy with the use of COSY-90 [9] and HSQC [10] two dimensional (2D) experiments. In addition, the one dimensional (1D) traces of the ^{1}H–^{13}C HSQC spectrum at the carbon frequencies were analyzed and this permitted the resolution of the overall ^{1}H NMR spectrum into sub spectra corresponding to the proton resonances at the given carbon atom [11]. These spectra allowed one to carry out a full assignment of the signals in the ^{1}H and ^{13}C NMR spectra. The ^{1}H–^{1}H COSY-90 spectrum is shown in Fig. 1 and the HSQC 1D spectrum traces in Fig. 2. The ^{1}H and ^{13}C NMR spectroscopic parameters for compound **2** are given in Table 1.

The ^{13}C NMR spectrum shows six signals for aliphatic carbon atoms. Three signals (in the region 54-76 ppm) correspond to carbon atoms in the α-position relative to the S or O atoms and three signals (at 25-30 ppm) to carbon atoms not bonded to heteroatoms. The use of *J*-modulation in the ^{13}C NMR spectrum [12] showed one signal for the tertiary $C_{(2)}$ atom at 76.16 ppm. The HSQC spectrum allowed one to separate out the resonance for the H-2 proton (3.85 ppm, Fig. 2, b). In the COSY spectrum there is a cross peak between the H-2 signal and the signal at 1.47 ppm. The latter does not have cross peaks with the low field signals for H-5 and H-7 (Fig. 1), hence this signal is assigned to H-3. It has a cross peaks with the signals at 1.80 and 1.95 ppm. From the 1D traces of HSQC spectra at 25.3 and 30.5 ppm respectively (Fig. 2, g, e) it is apparent that the signal for H-3' is at 1.95 ppm and that two coincident signals for H-4 are at 1.80 ppm. Hence the chemical shifts of $C_{(4)}$ and $C_{(3)}$ are 25.27 and 30.53 ppm. The signal at 27.22 ppm is assigned to the $C_{(6)}$ atom since it is not bound to a

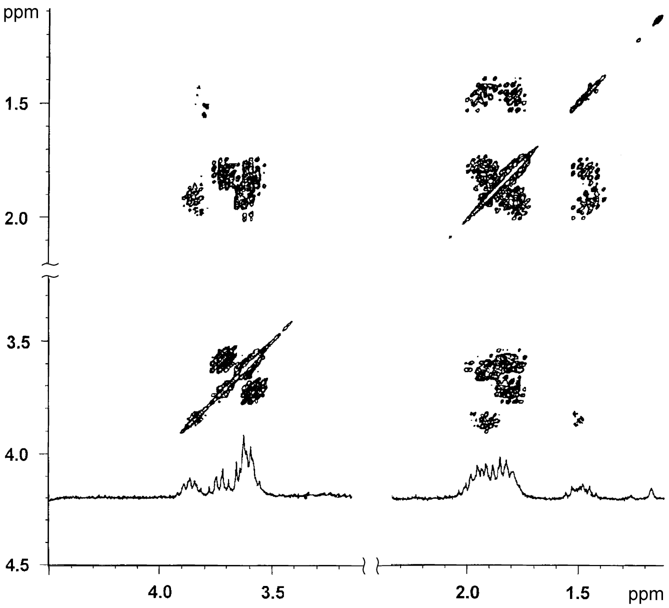

Figure 1. 2D (^{1}H–^{1}H) COSY spectrum of compound **2**.

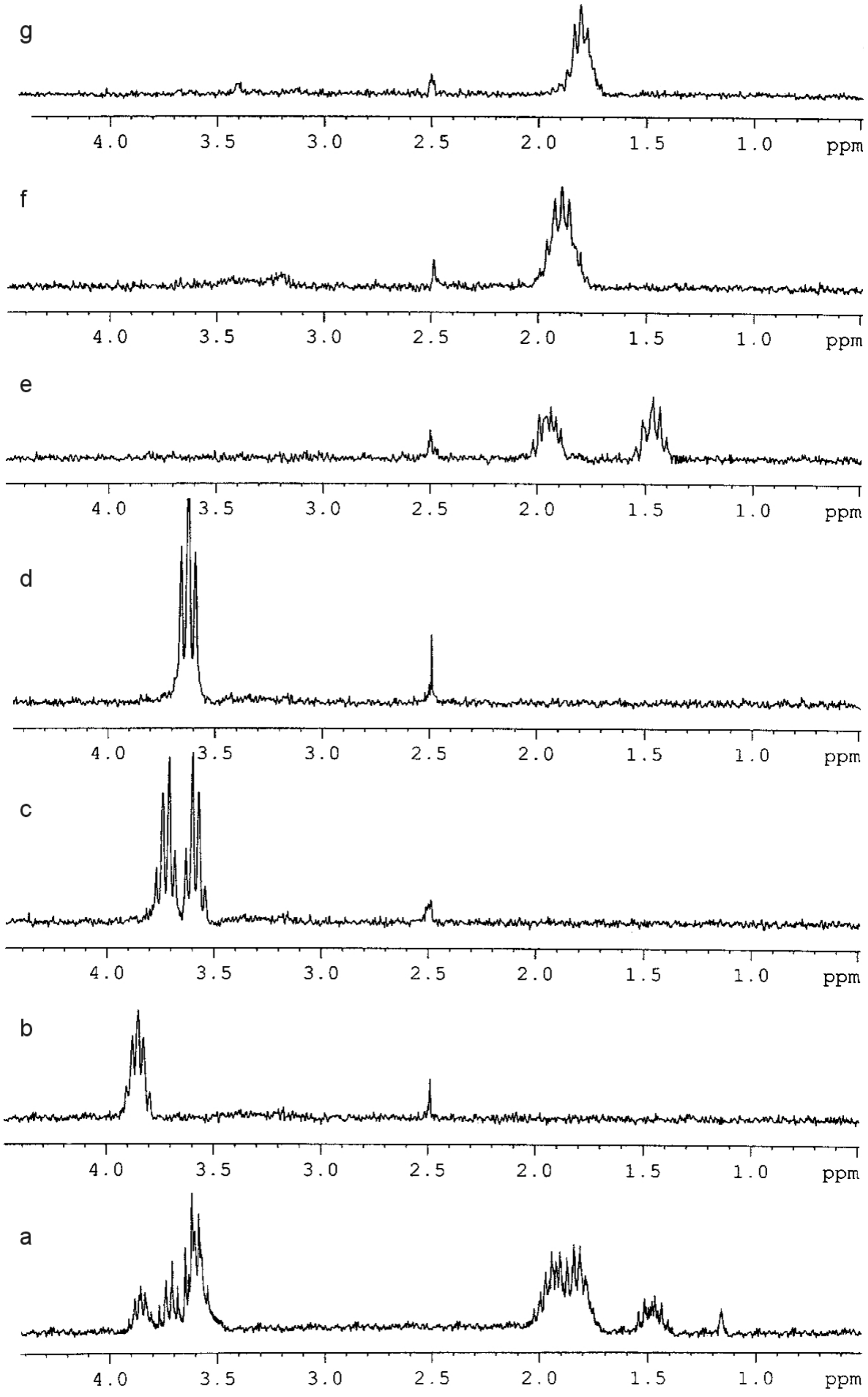

Figure 2. 1D (^{1}H) traces of the 2D HSQC (^{1}H–^{13}C) spectrum of compound **2**:
a – usual ^{1}H NMR spectrum; traces at 76.5 (b), 67.2 (c), 54.3 (d), 30.5 (e), 27.2 (f), and 25.3 ppm (g).

TABLE 1. ^1H and ^{13}C NMR Spectra of Compound **2***

H	Chemical shift, δ, ppm	C	Chemical shift, δ, ppm
H-2	3.85	$C_{(2)}$	76.16
H-3	1.47	$C_{(3)}$	30.53
H-3'	1.95	$C_{(4)}$	25.27
H-4	1.80	$C_{(5)}$	67.16
H-5	3.58	$C_{(6)}$	27.22
H-5'	3.72	$C_{(7)}$	54.29
H-6	1.89	$C_{(9)}$	130.65
H-7	3.63	$C_{(10)}$	145.08 ($^1J_{CF}$ = 256 Hz)

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* ^{19}F NMR spectrum, δ_F, ppm: -132.53 s

heteroatom. For the H-2 signal there is also a cross peak with the signal at 1.89 ppm. In the 1D trace of the HSQC spectrum at 27.2 ppm it can be seen that this is virtually coincident H-6 signals (Fig. 2, f). The signal at 3.72 ppm has a cross peaks with that at 3.58 ppm and the H-4 signal at 1.80 ppm (Fig. 1). From the HSQC trace at 67.2 ppm it follows that the protons H-5 and H-5' resonate at 3.58 and 3.72 ppm. The chemical shift of the $C_{(5)}$ atom is at 67.2 ppm. The remaining signal in the ^1H NMR spectrum at 3.63 ppm corresponds to the H-7 proton and the ^{13}C NMR signal at 54.3 ppm to the $C_{(7)}$ atom (Fig. 2, d). The ^{13}C NMR signals at 130.65 and 145.08 ppm are assigned to $C_{(9)}$ and $C_{(10)}$ respectively.

EXPERIMENTAL

IR spectra were recorded on a Bruker IPS 25 spectrometer. ^1H and ^{13}C NMR spectra were taken on a Bruker DPX-250 (250 MHz) instrument for $CDCl_3$ and DMSO-d_6 solutions with HMDS internal standard. ^{19}F NMR spectra were recorded on a JEOL FX 90Q instrument (84.25 MHz for ^{19}F) using $CF_3C_6H_5$ internal standard and with shifts calculated relative to $CFCl_3$.

3,6-Bis[2-(2-tetrahydrofuryl)ethylsulfonyl]-1,2,4,5-tetrafluorobenzene (2). A. A solution of compound **1** (1.5 g, 4.5 mmol) and tetrahydrofuran (50 ml) was held at 50-55°C with stirring for 8 h and then at room temperature for 48 h. The precipitated colorless powdery precipitate was filtered off and washed with ethanol and ether to give compound **2** (0.6 g). The filtrate was evaporated at reduced pressure and the solid precipitate was washed with ethanol and ether to give a further 0.3 g of compound **2**. Total yield 0.9 g (42%); mp 224-226°C. IR spectrum (KBr tablet), ν, cm^{-1}: 1142 and 1338 (SO_2), 1489 (C–F). Found, %: C 45.30; H 4.64; F 15.78; S 13.32. $C_{18}H_{22}F_4O_6S_2$. Calculated, %: C 45.56; H 4.67; F 16.00; S 13.51.

A similar reaction of compound **1** with tetrahydrofuran in the presence of hydroquinone (1% by weight) gave only recovered starting material **1**.

B. Benzoyl peroxide (0.02 g, 0.09 mmol) was added to a solution of compound **1** (1 g, 3 mmol) in tetrahydrofuran (50 ml). The reaction product was stirred for 8 h at 60-62°C and then held for about 16 h at room temperature. Work up of the reaction mixture as described in method A gave compound **2** (0.47 g, 33%). A mixed sample of compound **2** prepared by methods A and B did not show a depression of melting point.

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