

## Behavior of 3,6-Bis(vinylsulfonyl)-1,2,4,5-tetrafluorobenzene in Homolytic Addition of Dialkyl Phosphites

S. V. Amosova, G. M. Gavrilova, T. I. Vakul'skaya,  
E. I. Biryukova, and V. G. Cherkashina

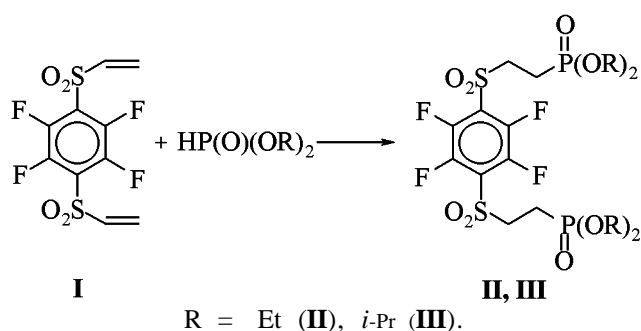
Faworsky Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences,  
Irkutsk, 664033 Russia

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**Abstract**—Reaction of 3,6-bis(vinylsulfonyl)-1,2,4,5-tetrafluorobenzene with dialkyl phosphites at thermal initiation (70°C) gives rise to 3,6-bis(dialkoxyphosphonoethylsulfonyl)-1,2,4,5-tetrafluorobenzenes in up to 45% yield. The formation of diethoxyphosphonyl radicals in the course of the reaction was observed with the use of ESR method applying spin trapping by 2-methyl-2-nitrosopropane. The use as initiator of the azo-bis-isobutyronitrile increased the yield of diadducts to 60%.

Vinylsulfones readily enter into nucleophilic addition reactions [1] but radical addition is not typical for this double bond [2, 3]. However we found formerly [4] that 3,6-bis(vinylsulfonyl)-1,2,4,5-tetrafluorobenzene (**I**) whose synthesis was described in [5] reacted with tetrahydrofuran under mild conditions (20–55°C) at both vinyl groups providing a product of homolytic addition.

In extension of the study on the discovered unusual reactivity of vinylsulfonyl groups in radical addition reactions we investigated the treatment of compound **I** with dialkyl phosphites resulting in formation of 3,6-bis(dialkoxyphosphonoethylsulfonyl)-1,2,4,5-tetrafluorobenzenes (**II**, **III**) in 38–60% yield.



The dialkyl phosphites are known to participate in reactions of homolytic addition across multiple bonds initiated by radical initiators or by UV irradiation [6, 7]. At the same time they readily react in the presence of alkali metal alcoholates with activated unsaturated compounds of electrophilic character, among them also with those containing vinylsulfonyl

groups [8, 9]. An addition of dialkyl phosphites to vinylsulfonyl fluoride was shown to occur without sodium alcoholate at 110°C [8] and was explained as caused by significantly increased reactivity of the double bond due to introduction of a fluorine atom into the molecule of vinylsulfonic acid. However the mechanism of this reaction was not discussed.

Since we presumed the radical mechanism of reaction between vinylsulfonylfluorobenzene **I** and dialkyl phosphites and took into consideration the relatively small chain transfer constant with dialkyl phosphites [10] and the dependence of the reaction rate and products composition on the reagents ratio [11], we performed the reaction at 10–20-fold excess of dialkyl phosphites. We studied the effect of temperature, radical initiation, and hydroquinone inhibition of this reaction.

The continuous monitoring of the reaction between compound **I** and excess diethyl phosphite was carried out with the use of isothermal calorimetry procedure for 7 h at 70°C. The reaction occurred in an ampule placed into the cell of the microcalorimeter; it was performed both after degassing of the reaction mixture or without gases removal, and also with addition of hydroquinone into the ampule.

It was demonstrated that under all these conditions the reaction occurred with heat evolution; therewith at degassing of the reaction mixture the heat quantity evolved is 1.7 times greater than in the run without gas removal (cf. Fig. 1, curves 1 and 2 respectively). The least amount of heat evolved in the run with hydroquinone addition (Fig. 1, curve 3).

The results obtained permit a conclusion that the reaction of vinylsulfonylfluorobenzene (**I**) with dialkyl phosphites occurs under thermal initiation. Therewith note that in the presence of air oxygen or hydroquinone the reaction is retarded, and the yield of product attains 38 and 27% respectively whereas the degassing of the reaction mixture leads to the yield of 45.5% within the same reaction time. At heating to 110°C a mixture of compound **I** with dialkyl phosphite in 1:20 ratio a temperature jump to 160°C was observed, and the yield of reaction product within 2 h was 45%. At the initiation of the reaction with the aza-bis-butyronitrile at 70–80°C the yield of diadduct **II** attained 60% within 6 h.

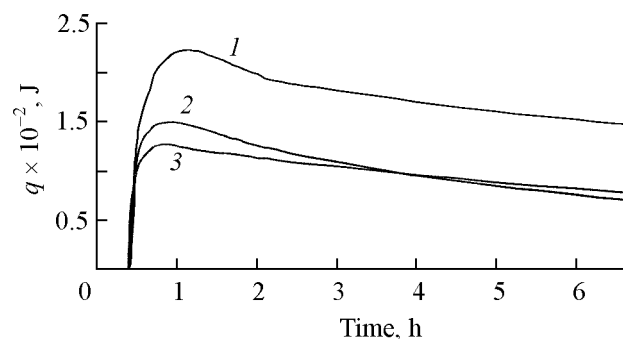
The data obtained testify to the homolytic character of the reaction between vinylsulfonylfluorobenzene **I** and dialkyl phosphites.

However the double bond in vinylsulfonylfluorobenzene **I** is known to be electrophilic, and so it is probable that in parallel with the homolytic process may occur nucleophilic addition of dialkyl phosphite [8, 9].

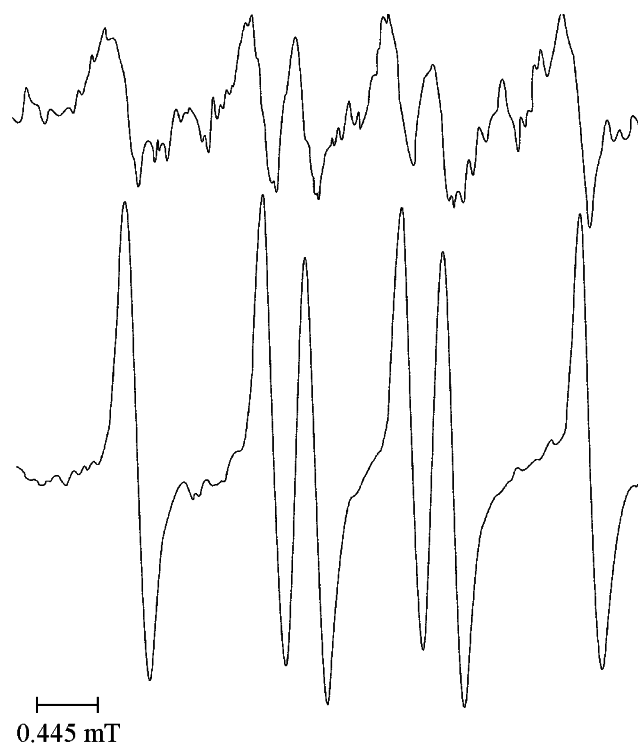
In some homolytic reactions proceeding with the use of radical initiators or under UV irradiation at low temperature dialkoxyphosphonyl radicals were registered and characterized by ESR method [12] although usually the lifetime of phosphonyl radicals is short, and they as a rule were not directly detected by ESR under ordinary conditions. Our attempt of direct observation of diethoxyphosphonyl radicals in the thermally initiated reaction of compound **I** with diethyl phosphite carried out in the probe of an ESR spectrometer also failed. Therefore we turned to the known and extensively used method of spin-trapping of the short-lived radicals with 2-methyl-2-nitrosopropane (*t*-BuNO) [13]. In particular, the parameters of ESR spectrum of just this spin trap adduct with a diethoxyphosphonyl radical in water were reported in [14].

We heated for 30 min the reaction mixture of compound **I** with 20-fold excess of diethyl phosphite in an ampule placed into the probe of ESR spectrometer. On cooling the reaction mixture the spin trap was added, and in 15 min an ESR signal appeared whose intensity within an hour increased more than ten-fold (Fig. 2).

The character (triplet of doublets) and hyperfine structure constants ( $a_N$  1.289 mT and  $a_P$  1.000 mT) indicate that the spectrum belongs to the spin adduct

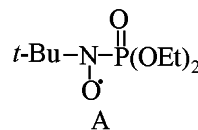


**Fig. 1.** Heat evolution in reaction of 3,6-bis(vinylsulfonyl)-1,2,4,5-tetrafluorobenzene (**I**) with diethyl phosphite: (1) after degassing of the reaction mixture; (2) without degassing of the reaction mixture; (3) with hydroquinone in the reaction mixture;  $q$ , J, is the heat amount liberated in reaction at the given time moment.



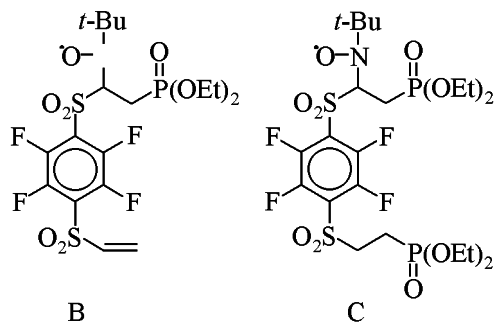
**Fig. 2.** ESR spectra of reaction mixture registered in the presence of *t*-BuNO in 15 min (top) and in 1 h (bottom) since the start of reaction.

A of the diethoxyphosphonyl radical with 2-methyl-2-nitrosopropane.

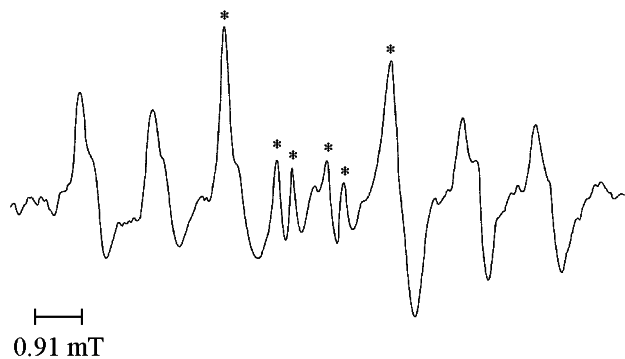
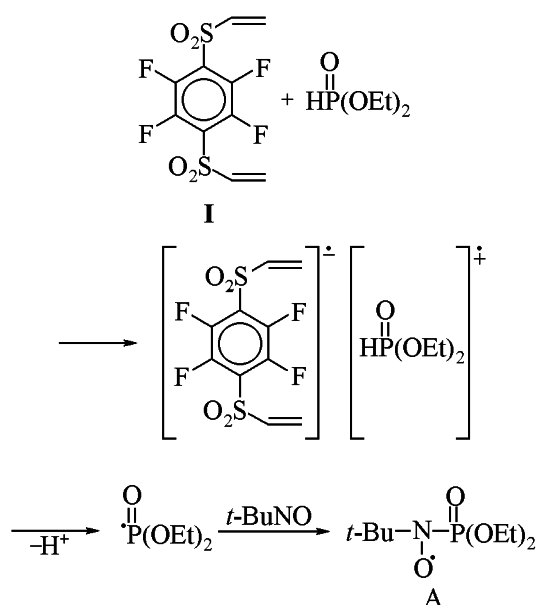


After 6 h in the ESR of the reaction mixture alongside the signal of adduct A appeared additional

signals, and their intensity grew in time. The ESR spectrum registered after 15 h of reaction is presented on Fig. 3. The spectrum shows superimposed on the signal of spin adduct A (marked with an asterisk) two doublets of triplets with different  $g$ -factors ( $\Delta g$  0.0015) and hyperfine structure constants about 6.0 and 1.4 mT respectively. The latter may be attributed to spin adducts of the trap to the radicals of mono- (B) and diaddition (C) of diethyl phosphite to vinylsulfonylfluorobenzene **I**.



It should be noted that in the blank experiment where the spin trap was added to diethyl phosphite within about 1 h was registered a weak ESR signal as a doublet of triplets with constants of hyperfine structure equal to  $a_N$  1.289 mT and  $a_P$  1.000 mT. Thus the spin trap behaved as acceptor with respect to diethyl phosphite. However on adding into the ampule of vinylsulfonylfluorobenzene **I** the intensity of this signal grew immediately nearly tenfold. This fact evidences more efficient redox-reaction of diethyl phosphite with vinylsulfonylfluorobenzene **I** than with the spin trap causing sharp increase in the yield of phosphoryl radicals.



**Fig. 3.** ESR spectrum of reaction mixture registered in the presence of *t*-BuNO in 15 h from the start of reaction (the lines of spin adduct **A** are marked with asterisk).

Thus the ESR data demonstrated that in the thermally initiated reaction of vinylsulfonylfluorobenzene **I** and diethyl phosphite arose diethoxyphosphonyl radicals which actively added to both vinylsulfonyl groups affording compound **II**.

Taking into account that ESR spectra revealed efficient redox-reaction of diethyl phosphite with vinylsulfonylfluorobenzene **I**, that the vinylsulfonyl groups of the latter compound possess considerable electron-acceptor character, and also that the reaction is decelerated with hydroquinone [15] we may assume in the reaction of homolytic character a stage of one-electron transfer giving rise to ion-radicals.

The structure of newly prepared compounds **II** and **III** was proved by IR,  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectroscopy.

## EXPERIMENTAL

IR spectra were recorded on spectrometer Bruker JPS 25 from samples pelletized with KBr.  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra were registered on JEOL FX 90Q instrument using as references HMDS for  $^1\text{H}$  spectra and  $\text{H}_3\text{PO}_4$  for  $^{31}\text{P}$  spectra. ESR spectra were measured on spectrometer SE/X-2547 (Radiopan, Poland). The reaction was investigated using the method of precision isothermal calorimetry on a microcalorimeter MKDP-2 equipped with signal converter "Terkon".

**3,6-Bis(diethoxyphosphonoethylsulfonyl)-1,2,4,5-tetrafluorobenzene (II).** A mixture of 0.06 g of 3,6-bis(vinylsulfonyl)-1,2,4,5-tetrafluorobenzene (**I**) and 0.5 g of diethylphosphite was heated in a flask to  $110^\circ\text{C}$ , and a temperature jump to  $160^\circ\text{C}$  was observed. On cooling in 2 h appeared a white fine crystalline precipitate that was separated, washed with ethyl ether ( $3 \times 10$  ml), and dried in a vacuum. We obtained 0.05 g (45%) of compound **II**, mp  $194^\circ\text{C}$

(from ethanol). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1147, 1344 ( $\text{SO}_2$ ); 1266 ( $\text{P}=\text{O}$ ), 1490 ( $\text{C}_{\text{Ar}}-\text{F}$ ).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.33 t (12H,  $4\text{CH}_3$ ), 2.27–2.23 m [4H,  $2\text{CH}_2\text{P}(\text{O})$ ], 3.62–3.58 m (4H,  $2\text{CH}_2\text{SO}_2$ ), 4.13–4.10 m (8H,  $4\text{OCH}_2\text{CH}_3$ ).  $^{31}\text{P}$  NMR spectrum,  $\delta$ , ppm: 25.18 s. Found, %: C 35.92; H 4.88; F 11.98; S 11.00; P 9.78.  $\text{C}_{18}\text{H}_{28}\text{F}_4\text{O}_{10}\text{S}_2\text{P}_2$ . Calculated, %: C 35.65; H 4.65; F 12.53; S 10.57; P 10.21.

**3,6-Bis(diisopropoxyphosphonoethylsulfonyl)-1,2,4,5-tetrafluorobenzene (III).** Compound III was prepared in a similar way. Yield 38%, mp 226–227°C (from ethanol). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1147, 1344 ( $\text{SO}_2$ ), 1266 ( $\text{P}=\text{O}$ ), 1490 ( $\text{C}_{\text{Ar}}-\text{F}$ ).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.33, 1.31 d (24H,  $4[\text{CH}(\text{CH}_3)_2]$ ), 2.25–2.16 m [4H,  $2\text{CH}_2\text{P}(\text{O})$ ], 3.61–3.55 m (4H,  $2\text{CH}_2\text{SO}_2$ ), 4.74–4.66 m (4H,  $4[\text{OCH}(\text{CH}_3)_2]$ ).  $^{31}\text{P}$  NMR spectrum,  $\delta$ , ppm: 22.85 s.

**Reaction of 3,6-bis(vinylsulfonyl)-1,2,4,5-tetrafluorobenzene (I) with diethyl phosphite in the presence of azo-bis-isobutyronitrile.** A mixture of 2 g of compound I, 10.5 g of diethyl phosphite, and catalytic amount of azo-bis-isobutyronitrile was heated to 70°C in a flask with stirring. The temperature rose to 120°C. The reaction mixture was maintained at 70–80°C for 6 h and left overnight. The separated white precipitate was washed with ethyl ether (3 × 50 ml), dried in a vacuum to afford 2.2 g (60%) of compound II. Ethyl ether and excess diethyl phosphite were evaporated in a vacuum to furnish 0.8 g of resinous residue.

**Investigation of reaction between compound I and diethyl phosphite using the method of precision isothermal calorimetry.** The reaction was carried out in an ampule placed into a cell of microcalorimeter. The composition of the reaction mixture was fixed for all runs: with degassing, without degassing, and with addition of catalytic amount of hydroquinone. The ratio of compound I to diethyl phosphite was 1:20, the reaction was carried out at 70°C for 7 h. The data were registered continuously and transferred to a computer with demonstration of numerical value of  $q$ , J (amount of heat liberated of a given moment), and of graphical data (efficiency of heat evolution, J per second, of a given moment). Proceeding from these data along a special program the thermal effect of the reaction was calculated. Maximum heat evolution was observed within 1 h, but the reaction did not completed even in 24 h. For comparison were used the data obtained within 7 h. The amount of heat liberated in reaction with degas-

sed mixture was  $4.04 \times 10^2$ , without degassing  $2.39 \times 10^2$ , and in the presence of hydroquinone  $2.17 \dots 10^2$  J.

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