

Synthesis of Hexakis(vinylthio)benzene

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Abstract—Exhaustive nucleophilic replacement of fluorine atoms in hexafluorobenzene by vinylthio groups was accomplished by the action of sodium ethenethiolate in dimethylformamide–liquid ammonia at -5 to 0°C .

Nucleophilic substitution of halogen by vinylthio group is the only possible method for introduction of that group into aromatic systems. The use of divinyl sulfide [1] as a source of vinylthio group opens the way to hitherto unknown polyfluoroaromatic compounds containing vinylthio groups [2, 3]. We showed in [2] that ethenethiolate ion can readily be generated by the action of sodium on divinyl sulfide in liquid ammonia; the reaction of ethenethiolate ion with hexafluorobenzene, depending on the reactant ratio and order of their mixing, yields highly reactive 1,2,4,5-tetrafluoro-3,6-bis(vinylthio)benzene and 1,4-difluoro-2,3,5,6-tetrakis(vinylthio)benzene. However, we failed to replace all fluorine atoms in hexafluorobenzene by carrying out the reaction in DMF at 20 – 30°C with a large excess of sodium ethenethiolate.

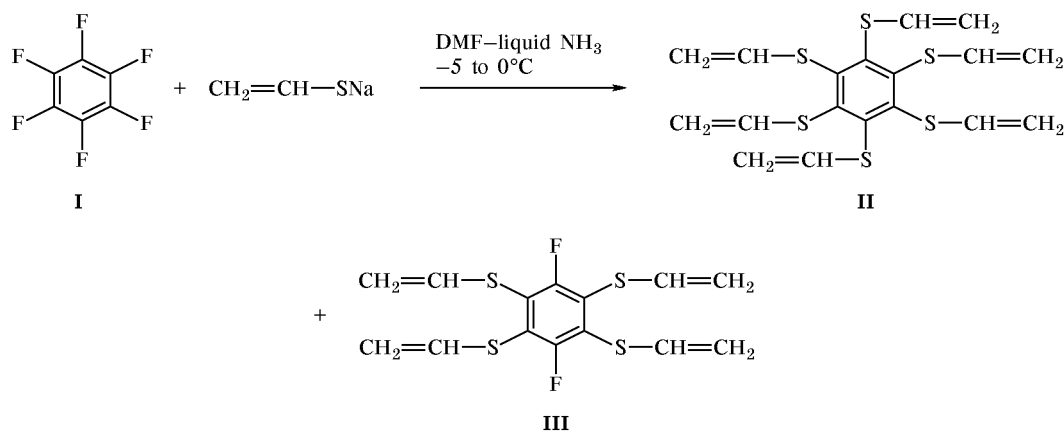
Testaferri *et al.* [4] synthesized hexakis(isopropylthio)benzene by reaction of hexachloro- or hexafluorobenzene with excess sodium 2-propanethiolate in HMPA at 20 or 0°C . Hexachlorobenzene is known [5]

to react with sodium alkanethiolates in polyethylene glycol ethers at 128°C , affording the corresponding hexakis(alkylthio)benzenes.

The present communication reports the results of our study on the synthesis of previously unknown hexakis(vinylthio)benzene. The target compound was obtained by reaction of hexafluorobenzene (**I**) with 6 equiv of sodium ethenethiolate which was generated by cleavage of divinyl sulfide with metallic sodium in liquid ammonia. The reaction was carried out in a mixture of DMF with liquid ammonia at -5 to 0°C (reaction time h). The yield of product **II** was 26% (calculated on the initial hexafluorobenzene); it was isolated as light yellow needles. Also, 1,4-difluoro-2,3,5,6-tetrakis(vinylthio)benzene (**III**) was obtained in 50% yield (Scheme 1).

We succeeded in raising the yield of sulfide **II** to 57% by increasing the reaction time to 3 days and adding hydroquinone. Compound **II** was also obtained by reaction of 1,4-difluoro-2,3,5,6-tetrakis(vinylthio)-

Scheme 1.



benzene (**III**) with sodium ethenethiolate in DMF–liquid ammonia at -5 to 0°C in the presence of hydroquinone; the reaction time was 20 h, and the yield of **II** was 58% on the reacted **III**.

The molecule of sulfide **II** contains six highly reactive vinylthio groups; therefore, it readily undergoes polymerization even at room temperature, and we failed to obtain this compound at 20 – 30°C [2]. On the other hand, sulfide **II** can be used as a new cross-linking agent.

The structure of sulfide **II** was proved by elemental analysis and IR and NMR spectroscopy. No fluorine signals were observed in the ^{19}F NMR spectrum of **II**, whereas the ^{13}C NMR spectrum contained only one aromatic carbon signal at δ 144.289 ppm. These data unambiguously indicate exhaustive replacement of the fluorine atoms by vinylthio groups. The carbon signals from the vinylthio groups [δ_{C} 132.218 (C^α) and 113.073 ppm (C^β)] differ from those in the spectra of bis(vinylthio)- (δ_{C} 128.39 and 116.81 ppm) and tetrakis(vinylthio)benzenes (δ_{C} 129.92 and 115.11 ppm). The ^1H NMR signals from vinylthio groups in **II** (δ 5.00, 5.28, and 6.30 ppm) appear more upfield relative to the corresponding signals from bis(vinylthio) (δ 5.32, 5.41, and 6.39 ppm) and tetrakis(vinylthio) derivatives (δ 5.21, 5.35, and 6.41 ppm) [2]. Unlike bis- and tetrakis(vinylthio)benzenes [2, 6, 7], proton signals of sulfide **II** are not split because of the lack of coupling with fluorine.

EXPERIMENTAL

The IR spectra were recorded on a Bruker IPS-25 spectrometer in KBr. The ^1H and ^{13}C NMR spectra were obtained on a Bruker DPX-400 instrument in CDCl_3 using HMDS as internal reference.

Hexakis(vinylthio)benzene (II). To a solution of 5.16 g of divinyl sulfide in 150 ml of liquid ammonia we added under stirring 2.76 g of metallic sodium in small portions. The mixture was stirred for 30 min, and 70 ml of ammonia was allowed to vaporize. The mixture was carefully diluted with 50 ml of dimethylformamide, and 0.05 g of hydroquinone was added. To the resulting solution at -25°C we added dropwise a solution of 1.85 g of hexafluorobenzene (**I**) in 5 ml

of DMF, and the mixture was stirred for 2 h at -5 to 0°C and was then kept for 3 days at -5°C . The mixture was allowed to warm up to room temperature, diluted with 100 ml of water, and extracted with diethyl ether. The ether extracts were washed with water, dried over MgSO_4 , and evaporated under reduced pressure. The residue, 3.5 g, contained (according to the ^1H NMR data) 2.44 g (57%) of sulfide **II** and 1.06 g (30%) of compound **III** (ratio 2.3:1). It was recrystallized from ethanol to obtain 2.3 g of compound **II** as light yellow needles with a small admixture of slightly colored plates. The light yellow crystals were separated manually. On heating to 200°C the crystals turned brown without melting. IR spectrum, ν , cm^{-1} : 1583 ($\text{SCH}=\text{CH}_2$), 1259 ($\text{Ar}-\text{S}$), 690 ($\text{C}-\text{S}$). ^1H NMR spectrum (CDCl_3), δ , ppm: 5.01 d.d, 5.28 d.d (2H, $=\text{CH}_2$), 6.30 q (1H, $=\text{CHS}$), $^3J_{\text{H,H-cis}} = 9.6$, $^3J_{\text{H,H-trans}} = 16.5$ Hz. ^{13}C NMR spectrum (CDCl_3), δ_{C} , ppm: 144.28 (C_{arom}), 132.218 (C^α), 113.07 (C^β). Found, %: C 50.53; H 4.29; S 45.22. $\text{C}_{18}\text{H}_{18}\text{S}_6$. Calculated, %: C 50.67; H 4.25; S 45.16.

In a similar way, sulfide **II** was obtained in 58% yield from compound **III**.

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