difference between the constants of free fullerenyl radicals and those bound into a complex.

We studied the effect of fluorine-containing alcohols on the parameters of the spin-adducts of C_{60} in a saturated toluene solution of $Hg[P(O)(OPr^i)_2]_2$ under standard conditions of formation of adducts of the multiple addition of the phosphoryl radicals to C_{60}.[10] However, when alcohols **2** or **3** (5 vol.%) are added, even prolonged photolysis (~30 min) results in the formation of the monoadducts only.

It can be assumed that alcohol forms a hydrogen bond directly with the phosphoryl radical and decreases the rate of its addition to fullerene. Since the photochemical generation of spin-adducts is a reversible process, the decrease in the rate of addition of the phosphoryl radicals to C_{60} shifts the equilibrium toward the monoadduct.

Thus, we observed the effect of fluorine-containing alcohols on the magnetic resonance parameters of phosphorylfullerenyl radicals, which can be useful in analysis of ESR spectra of spin-adducts of phosphoryl radicals with fullerene derivatives,[7] especially in the case where the ESR spectra of several isomers are imposed.

This work was performed within the framework of the Russian Scientific Technical Program "Urgent Problems in Condensed Matter Physics" (direction "Fullerenes and Atomic Clusters," Grant 98078) and was financially supported by the International Scientific Technical Center (Grant 079/B) and the Russian Foundation for Basic Research (Project No. 98-03-033016a).

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Received January 21, 1998;
in revised form February 13, 1998

Oxidation of aryl vinyl sulfides in the Bu^tOOH—$Ti(OPr^i)_4$—(*R*,*R*)-diethyl tartrate system

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Oxidation of aryl vinyl sulfides into aryl vinyl sulfoxides in the Bu^tOOH—$Ti(OPr^i)_4$—(*R*,*R*)-diethyl tartrate system was studied. The process afforded low optical yields (no more than 5%). A model of the oxidation was proposed that allows interpreting the dependence of the reaction enantioselectivity on the structure of a substrate.

Key words: aryl vinyl sulfides, enantioselective oxidation; Sharpless system; aryl vinyl sulfoxides.

Optically active alkenyl sulfoxides can be obtained by the reaction of (−)-menthyl aryl sulfinates with alkenylmagnesium bromides (the Andersen synthesis),[1–5] the reaction of carbonyl compounds with lithium salts of

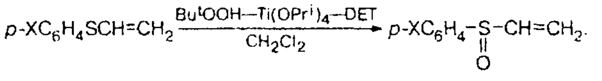
Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 9, pp. 1872—1873, September, 1998.

1066-5285/98/4709-1825 $20.00 © 1998 Plenum Publishing Corporation

(dimethoxyphosphoryl)methyl aryl sulfoxides (according to the Horner—Wittig reaction),[6,7] or biochemical oxidation of the corresponding sulfides.[8—10] About ten years ago it was claimed that chiral catalysis in the oxidation of sulfides into sulfoxides had not been described,[11] but almost immediately after this there appeared examples (although not numerous) of chemical oxidation that use chiral oxaziridines or modified Sharpless system.[10,12]

Optically active aryl vinyl sulfoxides $ArS(O)CH=CH_2$ with the unsubstituted vinyl group have been obtained only by the first approach (Ar = Ph or p-MeC_6H_4).[1,4] At the same time, it is known that Sharpless oxidation affords high optical yields for a series of sulfides, including unsaturated ones.[10,12,13]

In connection with this, it appeared interesting to study the possibility of enantioselective oxidation of aryl vinyl sulfides with the use of diethyl tartrate (DET), an available chiral additive, according to the equation



$$p\text{-}XC_6H_4SCH=CH_2 \xrightarrow[CH_2Cl_2]{Bu^tOOH-Ti(OPr^i)_4-DET} p\text{-}XC_6H_4-\underset{\underset{O}{\|}}{S}-CH=CH_2$$

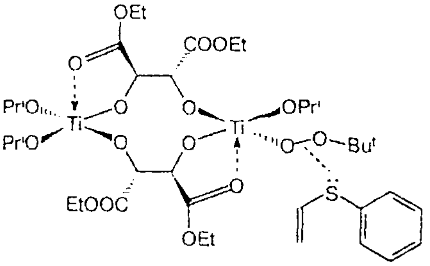
1a—c **2a—c**

X = Me (**a**), H (**b**), Cl (**c**)

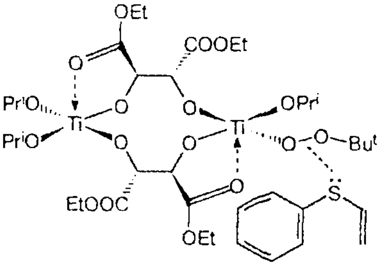
Aryl vinyl sulfides p-$XC_6H_4SCH=CH_2$ (**1**) were synthesized by addition of the corresponding thiophenols to acetylene.[14] Oxidation of sulfides in the $Bu^tOOH-Ti(OPr^i)_4$—DET system was carried out according to the known procedure[13] with a deficiency of the oxidant for the purpose of preventing sulfone from forming. According to the ^1H NMR spectrum, the reaction mixture obtained contained diethyl tartrate, unreacted vinyl sulfide **1**, diaryl disulfide, and vinyl sulfoxide **2**. The products were separated by column chromatography. The enantioselectivity of the process was estimated by comparison of our experimental $[\alpha]_D$ value with the known value for compound **2a**: $[\alpha]_D$ = +390.4° (c 1.2, acetone)[1]; +396° (c 1, EtOH)[4]. For sulfoxides **2a**, **2b**, and **2c** obtained by reaction (1), $[\alpha]_{546}$ = +21.3° (c 1, EtOH), +20° (c 1, EtOH), and +18° (c 1, EtOH), respectively, *i.e.*, the *ee* value amounts to only ~5%.

To understand the reasons for such sharp differences in the oxidation of various sulfides and predict the stereoselectivity of oxidation, it is necessary to consider transition-state structures, *viz.*, a complex of a chiral catalyst, an oxidant, and a substrate. Since such complexes have not been discussed for the case of oxidation of sulfides, the structures given below were constructed by us by analogy with the structure of a chiral catalyst and its complex with a substrate for epoxidation processes in the $Bu^tOOH-Ti(OPr^i)_4$—DET system.[11]

Complexes **A** and **B**, which lead to the formation of enantiomeric sulfoxides, differ in the orientation of the vinyl and aryl groups with respect to the $Bu^tOOH-Ti(OPr^i)_4$—DET complex. Taking into account the possible rotation around both S—C(sp^2) bonds, the energies of complexes **A** and **B** should probably be rather close to each other, which results in very low enantioselectivity of oxidation of compounds **1**. Benzo[*d*]dithiynes, in which the β-C atom of the vinyl group and the *ortho* position of the benzene ring are linked through the S atom, exhibit a very high enantioselectivity during oxidation,[12] which is likely due to the rigidity of the molecule and the impossibility of free rotation.



A



B

Experimental

^1H NMR spectra were recorded on a Jeol FX 90Q spectrometer (90 MHz) in $CDCl_3$ (HMDS as the internal standard). Optical rotation was measured on a Polamat A instrument at λ = 546 nm in a cuvette 1 dm long. Purity of substances and the course of reactions were monitored by TLC on Silufol UV 254 plates in the indicated eluent systems; spots were visualized with iodine vapors.

Aryl vinyl sulfides (1a—c) were obtained by addition of the corresponding thiophenols to acetylenes in DMSO in the presence of KOH under pressure[13]; physicochemical constants and parameters of ^1H NMR spectra correspond to literature data.

***p*-Tolyl vinyl sulfoxide (2a).** After the reaction mixture was worked up and the solvent evaporated, the residue was eluted with the CH_2Cl_2—petroleum ether (1 : 3) system on a column filled with silica gel 60 A (Biomedicals). Disulfide and unreacted sulfide were eluted, and sulfoxide **2a** that remained in the column was further eluted with AcOEt and re-chromatographed with the AcOEt—petroleum ether (1 : 1) system as an eluent. B.p. 95 °C (0.1 Torr) (Ref. 4: b.p. 88 °C (0.05 Torr)). ^1H NMR, δ: 2.38 (s, 3 H, CH_3); 5.85 (d, 1 H, H_β-*cis*, J = 9 Hz); 6.14 (d, 1 H, H_β-*trans*, J = 17 Hz); 6.58 (dd, 1 H, H_α); 7.35 (q, AB system, 4 H) (Ref. 4: ^1H NMR (CCl_4), δ: 2.32 (s, 1 H); 5.7—6.9 (m, 3 H); 7.1—7.6 (m, 4 H)).

Phenyl vinyl sulfoxide (2b). After the reaction mixture was worked up and the solvent evaporated, the residue was applied on a column filled with silica gel Chemapol 100/160 μm. Unreacted sulfide was eluted with the CH_2Cl_2—petroleum ether (1 : 3) system. Disulfide was eluted with the AcOEt—petroleum ether (1 : 1) mixture. Sulfoxide that remained in the column was eluted with AcOEt. ^{1}H NMR, δ: 5.85 (d, 1 H, H_β-*cis*, J = 9.3 Hz); 6.15 (d, 1 H, H_β-*trans*, J = 16.3 Hz); 6.62 (dd, 1 H, H_α); 7.50 (m, 5 H) (Ref. 15: ^{1}H NMR ($CHCl_3$), δ: 5.63—6.17 (m, 2 H); 6.44—6.87 (m, 1 H); 7.10—7.55 (m, 5 H)).

***p*-Chlorophenyl vinyl sulfoxide** (**2c**) was isolated by analogy with compound **2a** without repeated separation, but with subsequent distillation *in vacuo*. B.p. 140 °C (0.05 Torr). ^{1}H NMR, δ: 5.89 (d, 1 H, H_β-*cis*, J = 9 Hz); 6.15 (d, 1 H, H_β-*trans*, J = 17 Hz); 6.60 (dd, 1 H, H_α); 7.50 (q, AB system, 4 H).

This work was financially supported by the Russian Foundation for Basic Research (Project No. 96-03-33468a).

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Received February 16, 1998

A mechanism of the hydrogenation of the double bond in the synthesis of allyl chalcogenides in the hydrazine hydrate—potassium hydroxide system

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Allyl halides react with elemental selenium in the $N_2H_4 \cdot H_2O$—KOH system to give diallyl chalcogenides and allyl propyl chalcogenides. The latter form only in the presence of oxygen when unsaturated intermediates $CH_2{=}CHCH_2YK$ (Y = S and Se), which are soluble in hydrazine hydrate, are hydrogenated with diimide.

Key words: allyl chalcogenides, synthesis; hydrogenation, mechanism.

Symmetrical diorganyl chalcogenides R_2Y (Y = S, Se, or Te) can be readily synthesized by reaction of elemental chalcogens Y with the $N_2H_4 \cdot H_2O$—KOH system followed by alkylation of chalcogenide anions obtained with organyl halides.[1,2] Unsymmetrical organyl chalcogenides RYR' are formed as a result of generation of organyl chalcogenide anions from diorganyl dichalcogenides R_2Y_2 in the same system with subsequent alkylation with organyl halides.[3–5]

In some cases, reaction of allyl chloride with the Se—$N_2H_4 \cdot H_2O$—KOH system affords not only diallyl selenide but also allyl propyl selenide, the yield of which can be as large as 38%.[6] The authors of Ref. 6 have explained the formation of the latter by hydrogenation

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 9, pp. 1874—1876, September, 1998.

1066-5285/98/4709-1827 $20.00 © 1998 Plenum Publishing Corporation