was recondensed, cyclopentadiene (0.4 g, 6 mmol) in 20 mL of THF was added to the residue, and the mixture was kept for 48 h at ~20 °C. The unreacted cyclopentadiene (5.4 mmol) was found by GLC in the volatile fraction. The solvent was removed from the reaction mixture *in vacuo*, and the solid residue was extracted with pentane. Cooling to −25 °C resulted in the precipitation of violet-brown crystals of $(Me_3SiCH_2)_3V \cdot PEt_3$ (1.83 g, yield 71%). Found (%): C, 49.86; H, 11.06; V, 11.35. $C_{18}H_{48}PSi_3V$. Calculated (%): C, 50.23; H, 11.16; V, 11.86.

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Separation of C_{60} and C_{70} fullerenes on silica modified by polyaromatic and π-acid aromatic compounds

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Separation of C_{60} and C_{70} fullerenes by HPLC was studied using sorbents synthesized by reaction of perylenedicarboxylic anhydride, dimethoxyviolanthrene, the tetramer of chromotropic acid with formaldehyde (TCA), trinitrobenzoyl chloride, or chlorotrinitrobenzene with γ-aminopropyl silica. These sorbents possess satisfactory chromatographic properties. The sorbent based on TCA is effective for separation of preparative amounts of fullerenes.

Key words: fullerenes, HPLC, sorbents.

The sorbents used currently for the separation of fullerenes by liquid chromatography are materials based on polyaromatic compounds bound to silica gel,[1] materials based on aromatic π-acids,[2] and sorbents based on porphyrins and phthalocyanines bound to silica gel.[3,4] A sorbent containing ethylpyrene linked to silica gel by covalent bonds belongs to the first group. Sorbents with grafted π-acids have been synthesized using dinitrofluorobenzene, which is a weak π-acid. In order to extend the range of materials suitable for separation of C_{60} and C_{70}, we prepared sorbents by reaction of various compounds with γ-aminopropyl silica gel (γ-APS). These compounds include stronger π-acids, *viz.*, trinitrobenzoyl chloride (sorbent **1**) and chlorotrinitrobenzene (sorbents **2** and **3**), and also substances characterized by larger effective areas of molecules than pyrene, *viz.*, perylenedicarboxylic acid anhydride (sorbent **4**), dimethoxyviolanthrene (sorbent **5**), and the tetramer of chromotropic acid with formaldehyde (TCA) (sorbent **6**).

Experimental

Sorbents **1**—**6** were synthesized using Separon-NH_2 γ-APS and poly-γ-APS; the latter was prepared by refluxing a dry sample of Separon-SGX silica gel with 15% γ-aminopropyltriethoxysilane and 15% water in toluene for 6 h followed by washing with isopropyl alcohol and drying *in vacuo*.

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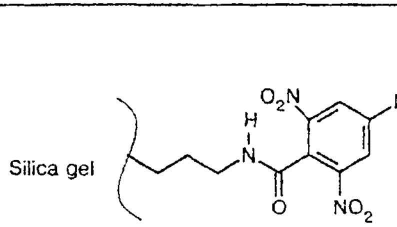

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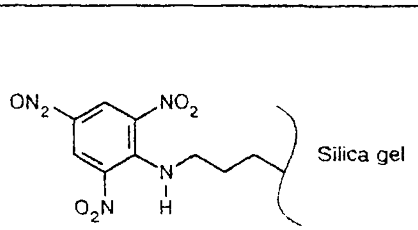

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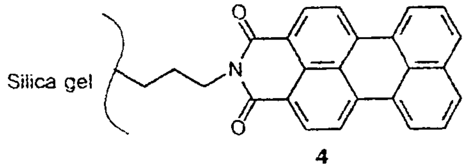

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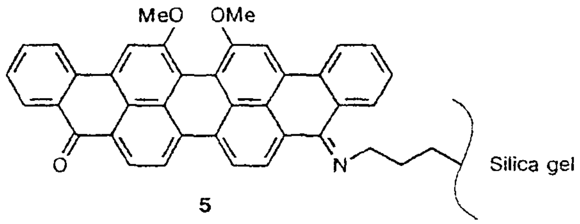

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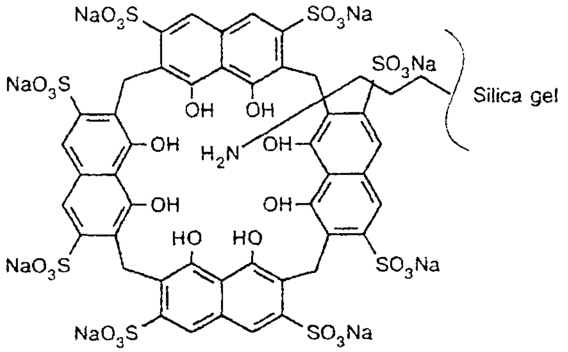

6

Sorbents 1—3. γ-APS (Separon-NH_2 for sorbents **1** and **2** or poly-γ-APS for sorbent **3**) (160 mg) was added to a solution of trinitrobenzoyl chloride or chlorotrinitrobenzene (35 mg) in dry CH_2Cl_2, and the mixture was stirred at 25 °C for 12 h; the resulting material was washed with acetone and dried *in vacuo* at 70 °C.

Sorbents 4 and 5. Dimethoxyviolanthrene or perylenedicarboxylic anhydride (35 mg) prepared by a known procedure[5] was dissolved at 100 °C in dry nitrobenzene, dry Separon-NH_2 silica gel (160 mg) was added, and the mixture was stirred for 5 h at the same temperature. The material was washed with nitrobenzene and dried *in vacuo* at 70 °C.

Sorbent 6. Separon-NH_2 silica gel (160 mg) was added to a solution of TCA (35 mg) prepared by a known procedure[6] in MeOH, and the mixture was stirred for 5 h. The material was washed with MeOH and water. This yielded a stable complex of TCA with γ-APS.

Table 1. Retention factors (k) and selectivities (α) of the separation of C_{60} and C_{70} fullerenes on sorbents **1—6**

Sorbent	Mobile phase	$k(C_{60})$	$k(C_{70})$	$\alpha(C_{60}/C_{70})$
1	Toluene—hexane (1 : 1)	0.25	0.45	1.9
	Toluene—hexane (1 : 2)	0.83	1.67	2.0
2	Toluene—hexane (1 : 1)	0.67	1.13	1.7
3	Toluene—hexane (1 : 1)	1.20	2.67	2.2
4	Toluene—hexane (1 : 1)	0.60	1.37	2.3
	Toluene—hexane (1 : 2)	1.33	3.33	2.5
5	Toluene—hexane (1 : 1)	2.10	5.46	2.6
	Toluene	0.31	0.62	2.0
6	Toluene—hexane (1 : 1)	0.47	1.13	2.4
	Toluene—hexane (1 : 4)	2.67	7.47	2.8

Packing of columns for HPLC. A sample of a sorbent was suspended in 10 mL of toluene, the suspension was placed in a setup for packing HPLC columns (60 mm×2 mm), and the columns were packed by pumping toluene from bottom to top at a pressure of 30 MPa.

HPLC was carried out on a Millichrom chromatograph with a UV detector (330 nm). The flow rate of the mobile phase was 0.2 mL min^{-1}, and the temperature of the column was 20 °C; 2-μL samples of a toluene solution containing 1 mg mL^{-1} of a mixture of C_{60} and C_{70} fullerenes were subjected to analysis. The dead retention volumes of the columns packed with sorbents **1—6** (V_0) needed to calculate the retention factors (k) were determined by eluting a sample of C_{60} with 1-methylnaphthalene. The V_0 values for all of the columns were 0.14—0.16 mL.

Results and Discussion

Chromatographic characteristics of the sorbents are listed in Table 1. Comparison of the retention factors and selectivities of sorbents **1—3**, containing a trinitrobenzene fragment as the π-acid, with the published data[1] for sorbents based on dinitrobenzene indicates that they do not differ markedly from one another. The retention of C_{60} and C_{70} on sorbent **3** based on γ-APS and synthesized with polymeric coating of the surface with γ-aminopropyltriethoxysilane is approximately twice that on sorbent **2**.

The chromatographic characteristics of sorbents **4** and **5** based on polyaromatic compounds are comparable with those reported in the literature for the separation of fullerenes on [2-(1-pyrenyl)ethyl]silyl silica gel.[2]

It should be noted that the capacities of the obtained sorbents with respect to C_{60} and C_{70} proved to be low. When the quantity of the fullerenes introduced increases, chromatographic peaks become asymmetrical, except for those on the sorbent based on TCA (sorbent **6**). The latter exhibited a high capacity, although the retention factors (*k*) attained on this sorbent are relatively low. In our opinion, this is due to the fact that TCA in sorbent **6**, unlike the grafted compounds in sorbents **1**—**5**, is arranged flatly with respect to the silica gel surface. This ensures high density of the grafted TCA (10—12 % (w/w)) and, perhaps, more favorable conditions for the sorption of C_{60} and C_{70}.

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Acid-catalyzed decomposition of cyclohexanespiro-2-oxazolidine

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Heating cyclohexanespiro-2-oxazolidine at 160—200 °C in the presence of protic acids results in its decomposition to give *N*-(2-hydroxyethyl)cyclohexylamine, *N*-(2-hydroxyethyl)-4,5,6,7-tetrahydroindole, and 2-cyclohexylidenecyclohexanone. The possible pathways leading to these compounds are discussed.

Key words: cyclohexanespiro-2-oxazolidine, *N*-(2-hydroxyethyl)cyclohexylamine, *N*-(2-hydroxyethyl)-4,5,6,7-tetrahydroindole, 2-cyclohexylidenecyclohexanone, acid catalysis.

The outcome of acid-catalyzed transformations of oxazolidines depends markedly on the structure of the oxazolidine itself and on the nature of the catalyst. For example, heating *N*-phenyloxazolidines in the presence of TsOH or $R_3N \cdot HCl$ leads to low-molecular-weight poly(aminoethers);[1] *N*-alkyloxazolidines do not polymerize under these conditions. When *N*-propyloxazolidine is heated to 130 °C in the presence of HCl or H_2SO_4, it is partly reduced to *N*-methyl-*N*-propylaminoethanol and it partly polymerizes.[2] Upon heating with polyphosphoric acid, *N*-substituted cyclohexanespiro-2-oxazolidines are cleaved to give cyclohexanone and *N,N'*-disubstituted piperazines.[3]

In conformity with published data,[3] we expected that cyclohexanespiro-2-oxazolidine (**1**) would be converted under similar conditions into cyclohexanone and piperazine or their derivatives. However, it was found that at 160—200 °C in the presence of polyphosphoric acid, oxazolidine **1** decomposes with elimination of ammonia and water to give a complex mixture of products (12 components, GLC). *N*-(2-Hydroxyethyl)cyclohexylamine (**2**), *N*-(2-hydroxyethyl)-4,5,6,7-tetrahydroindole (**3**), and 2-cyclohexylidenecyclohexanone (**4**) formed as the major products and were isolated preparatively (Scheme 1). In addition, GLC analysis showed that the reaction mixture contained the initial oxazolidine **1**, cyclohexanone, 2-aminoethanol, and contained no piperazine and no products of the reduction of cyclohexanone and ketone **4**, *viz.*, cyclohexanol or 2-cyclohexylidenecyclohexanol.

This reaction outcome, which differs fundamentally from that of the acid-catalyzed cleavage of *N*-substituted cyclohexanespiro-2-oxazolidines, is apparently due to the fact that oxazolidine **1** is able[4] to undergo tautomeric transformation into *N*-cyclohexylideneaminoethanol (**1a**).

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