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Synthesis of a Star-Shaped Tris(Reissert compound)

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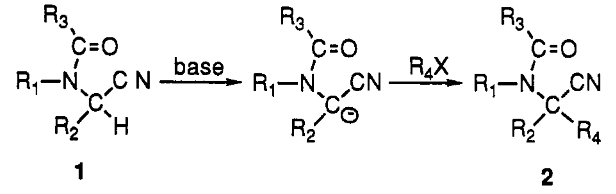
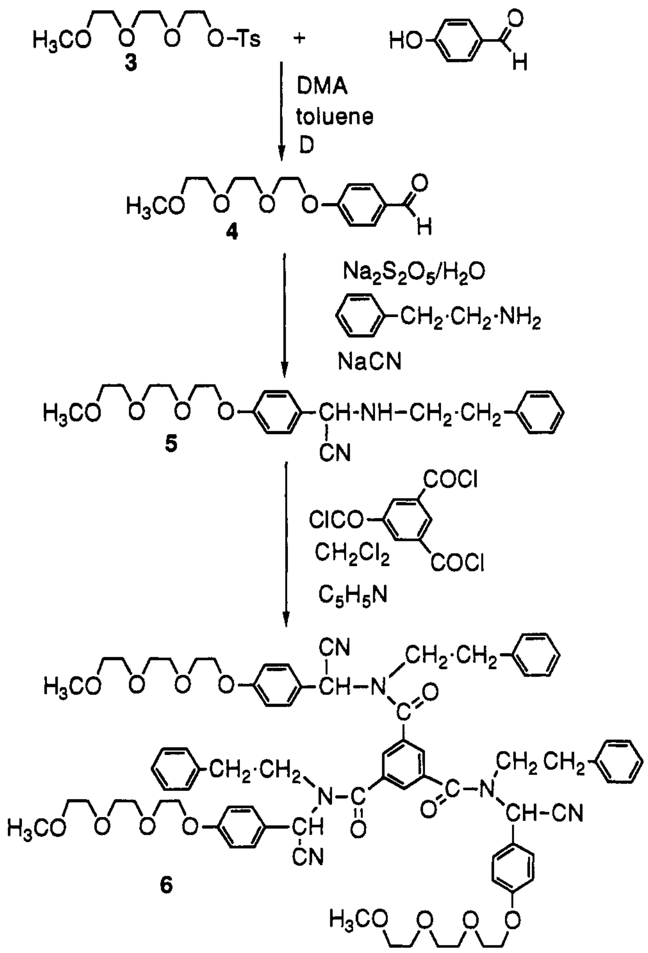
An especially attractive feature of acyclic Reissert compounds 1 (α-acylamino nitriles)[1] resides in their structural versatility. Indeed, one can select various amines (R_1NH_2), aldehydes (R_2CHO), and acyl halides (R_3COCl) for the preparation of 1.[1-8] The methine proton of 1 can be abstracted with a base to generate the conjugate anion which can undergo electrophilic attack by an alkyl halide R_4X to produce the alkylated Reissert compound 2.[1]



As a model compound for poly(ethylene glycol) monomethyl ethers, triethylene glycol monomethyl ether tosylate (3) was converted to the aldehyde-terminated analog 4 (Scheme 1). We preferred potassium carbonate as the base to generate *p*-formylphenoxide using a technique similar to that used for poly(arylene ether)s[9] rather than the method used by Harris on higher molecular weight poly(ethylene glycol)s, which involved the use of potassium.[10] Conversion of the aldehyde to the α-amino nitrile 5 was readily achieved by a modified Strecker procedure.[11] The oily amino nitrile could not be purified by column chromatography on neutral alumina, and thus was directly acylated with 1,3,5-benzenetricarbonyl trichloride to yield the star-shaped tris(Reissert compound) 6 comprising a hydrophobic core fitted with hydrophilic arms. We believe this to be the first tris(Reissert compound). Compound 6 is a very viscous oil which formed stable water/dichloromethane emulsions. These observations demonstrate the wetting properties of 6 and a potential use of the acyclic Reissert compounds as nonionic wetting agents.

Scheme 1



Experimental Section

Chemicals were used as received, except triethylene glycol monomethyl ether, which was distilled under vacuum, and its purity was checked by GC.[12] ^1H NMR spectra were recorded using TMS as the reference and $CDCl_3$ as the solvent. Elemental analysis was performed by Atlantic Microlab, Inc., Norcross, GA.

Triethylene glycol monomethyl ether tosylate (3) was obtained by tosylation of triethylene glycol monomethyl ether in $THF/H_2O/NaOH$ and was purified on a silica gel column (dichloromethane) as an oil.[13]

***p*-(1,4,7,10-Tetraoxaundecyl)benzaldehyde (4).** A mixture of triethylene glycol monomethyl ether tosylate (3) (63 g, 0.198 mol), *p*-hydroxybenzaldehyde (24.39 g, 0.200 mol), and potassium carbonate (34.94 g, 0.253 mol) in 50 mL of anhydrous DMA and 100 mL of anhydrous toluene was refluxed for 18 h under nitrogen in a flask equipped with a Dean-Stark trap. After filtration, the solvent was evaporated to give an oil which was filtered through a silica gel column using ethyl acetate as the eluant (49.4 g, 63%). A colorless oil as reported[14] was obtained by treatment of the crude oil with sodium metabisulfite in water, followed by filtration, acidification of the filtrate with aqueous HCl, extraction with CH_2Cl_2 (4 times), drying over sodium sulfate, and evaporation: ^1H NMR δ 9.89 (s, 1H), 7.83 (d, J = 9 Hz, 2H), 7.02 (d, J = 9 Hz, 2H), 4.22 (t, J = 5 Hz, 2H), 3.90 (t, J = 5 Hz, 2H), 3.74 (m, 2H), 3.68 (m, 4H), 3.55 (t, J = 5 Hz, 2H), 3.38 (s, 3H).

α-Cyano-*N*-(2-phenethyl)-*p*-(1,4,7,10-tetraoxaundecyl)-benzylamine (5). A mixture of 4 (12.80 g, 47.7 mmol) and sodium metabisulfite (4.85 g, 25.5 mmol) was stirred in 200 mL of water

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for 2 h. The reaction can be performed with crude aldehyde 4, the insoluble particles contained in the bisulfite solution being filtered out. Phenethylamine, (6.0 mL, 48 mmol) was then added and the mixture was stirred for 4 h. NaCN (2.42 g, 49.4 mmol) was added and the mixture was stirred for 3 h and extracted with 200 mL of CH_2Cl_2. The organic phase was washed with 100 mL of water, dried over Na_2SO_4, and evaporated to give 18.2 g (96%) of a yellow oil: IR (neat) 3316, 3064, 3031, 2931, 2878, 2227 (v weak), 1609, 1510, 1251, 1111; ^{1}H NMR δ 7.37 (d, J = 9 Hz, 2H), 7.25 (m, 5H), 6.91 (d, J = 9 Hz, 2H), 4.74 (s, 1H), 4.13 (t, J = 5 Hz, 2H), 3.85 (t, J = 5 Hz, 2H), 3.68 (m, 6H), 3.55 (m, 2H), 3.38 (s, 3H), 3.15–2.9 (m, 2H), 2.85 (m, 2H), 1.49 (bs, 1H).

***N,N′,N″*-Tris[*p*-(1,4,7,10-tetraoxaundecyl)-*α*-cyanobenzyl]-*N,N′,N″*-tris(2-phenethyl)-1,3,5-benzenetricarboxamide (6).** To a mixture of *α*-cyano-*N*-(2-phenethyl)-[*p*-(1,4,7,10-tetraoxaundecyl)]benzylamine (5) (37.23 g, 93.4 mmol) in 100 mL of CH_2Cl_2 cooled in an ice bath was added 7.80 g (29.4 mmol) of 1,3,5-benzenetricarbonyl trichloride. The mixture was stirred overnight, after which 7.3 mL (90 mmol) of pyridine was added. Stirring was continued for 2 h. CH_2Cl_2 (100 mL) was added and the mixture was washed with 100 mL of water and 100 mL of dilute HCl. Evaporation of the solvent afforded 50.8 g of a viscous orange oil. Purification was performed by chromatography on a silica gel column (ethyl acetate) to give 27.82 g (66%) of a pale yellow viscous oil: IR (neat) 3064, 3028, 2926, 2880, 2242, 1653, 1252, 1154, 1127 cm^{-1}; ^{1}H NMR δ 7.49 (bs) + 7.35 (bs) + 7.10 (s) + 7.03 (d, J = 8 Hz), + 6.80 (bs) (33H), 4.17 (t, J = 5 Hz, 6H), 3.88 (t, J = 5 Hz, 6H), 3.74 (m, 6H), 3.70–3.64 (m, 12H), 3.55 (m, 6H), 3.38 (s, 9H), 3.50 (bs) + 3.35 (bs) (6H), 2.75 (bs) + 2.54 (bs) (6H). Anal. Calcd for $C_{78}H_{90}N_6O_{15}$: C, 69.31; H, 6.71; N, 6.22. Found: C, 69.37; H, 6.73; N, 6.16.

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