Pergamon

Tetrahedron, Vol. 53, No. 18, pp. 6377-6390, 1997

0040-4020/97 $17.00 + 0.00

PII: S0040-4020(97)00297-4

Different Synthetic Routes towards Efficient Organogelators: 2,3-Substituted Anthracenes

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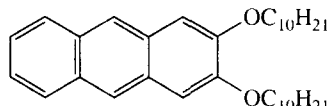
Abstract: Three synthetic approaches towards 2,3-substituted anthracenes are reported and discussed in terms of selectivity and viability. This allowed us to introduce a variety of substituents as sidearms. Promising results have been found using a tandem Diels-Alder aromatization reaction using 2,3-dimethoxybutadiene **9** as a key intermediate. However, for multigram preparations the Friedel-Crafts approach is preferred. © 1997 Elsevier Science Ltd.

Gelation of organic solvents by small organic molecules has received increasing attention during the last few years. [1,2] Several low-molecular-weight molecules of diverse structures have been reported [3-10], each of them forming a gel with a specific range of solvents. These gels may have a wide range of potential applications *e.g.* as hardeners of spilled toxic solvents, in environmental clean-up or as medicinal drug-delivery systems. Among the reported structures, 2,3-di-n-decyloxyanthracene **1** (denoted DDOA for convenience) forms thermoreversibly gels with alcohols and to a lesser extent with amines and alkanes. [10] This gelator can bind a considerable number of solvent molecules at very low concentrations (*ca* 5.10^{-3} mol/l); related anthraquinones display similar properties.



1 (DDOA)

Although numerous systems that aggregate and form gels have been designed, examples are quite rare that involve only van der Waals and dipole-dipole interactions as the driving forces for gel formation as is the case of DDOA in non protic solvents. In this series, we have carried out several structural modifications [10] which have shown that the gelling agent requires three linearly fused rings *i.e.* anthracene or anthraquinone nuclei and two long chain alkoxy substituents located on positions 2 and 3. According to our observations, the gelling abilities can be tuned by varying the length of the chains. In order to investigate more precisely the role of substitution pattern, we needed substantial amounts of several disubstituted anthraquinones and anthracenes. We here report the results of different synthetical approaches towards the desired organic gelators.

RESULTS AND DISCUSSION

We first reasoned that 2,3-dihydroxy-9,10-anthraquinone could be a good starting point for such targets.

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As further reduction would lead to the desired anthracenes, therefore this compound seems to be a key synthetic intermediate as outlined in a retrosynthetic analysis (figure 1). We describe in detail two general approaches *via* a Friedel-Crafts reaction and a Diels-Alder cycloaddition respectively.

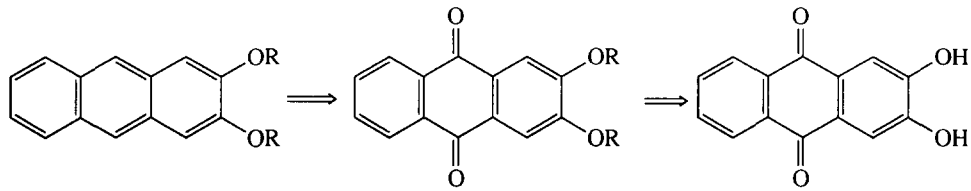


Figure 1

Friedel-Crafts route

As the first tested method to build the conveniently substituted anthraquinone moiety, we re-examined the previously described approach which was based on a intermolecular Friedel-Crafts acylation of 1,2-dihydroxybenzene (catechol) with phthalic anhydride. [11]

The best solvent for this step was found to be an eutectic mixture of aluminum chloride (13 molar equivalents) and sodium chloride (6 molar equivalents) melting at 140°C. The careful addition of reactants prevented the formation of an intractable residue. The resulting keto-acid isomers **2** (2-(3',4'-dihydroxybenzoyl) benzoic acid and 2-(2',3'-dihydroxybenzoyl) benzoic acid) could not be fully characterized due to their very low solubilities. This represented the initial difficulty using this approach. After work-up, the crude mixture was then refluxed in 95% sulfuric acid to afford anthraquinone derivatives by an intramolecular Friedel-Crafts reaction.

This strategy suffered from several disadvantages such as tedious work-up and drastic conditions which would presumably preclude the direct introduction of sensitive functions. Furthermore, this synthetic sequence is not specific and lead to a mixture of anthraquinones. In contrast with previous results [11], the ratio between hystazarone **3** (2,3-dihydroxy-9,10-anthraquinone) and alizarin **4** (1,2-dihydroxy-9,10-anthraquinone) was found to be 85:15 instead of 90:10. This was unambiguously determined on the basis of ^{1}H nmr data of the crude mixture and by direct comparison with the assignments for each pure isomer in deuteriated dimethylsulfoxide.

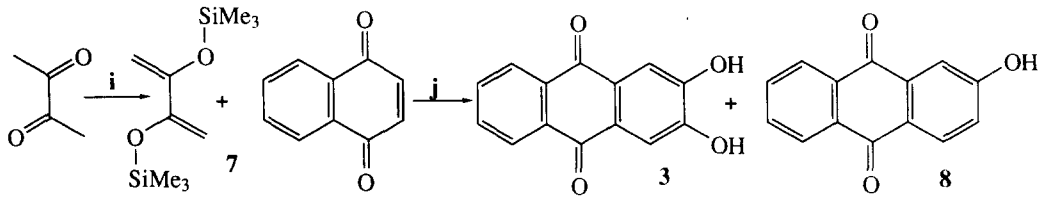
Although restricted to laboratory scale, the purification of 2,3-dihydroxy-9,10-anthraquinone **3** could be achieved by sublimation in poor yield. However on a larger scale, the unwanted isomer was difficult to remove. In the present work, the major isomer was only isolated in pure manner after a fastidious acetylation, selective crystallization and deacetylation sequence. The minor isomer has been successfully extracted from the filtrate after the aforementioned crystallization of 2,3-diacetyloxy-9,10-anthraquinone **5**. Further purification has been realized by several chromatographies on column and then subsequent deacetylation of compound **6** (1,2-diacetyloxy-9,10-anthraquinone) to afford alizarin **4**. Despite the fact that this synthetic approach could be realized on a large scale (greater than 10 grams) with an overall yield of 33% in **3**, (starting from phthalic anhydride), we examined other routes avoiding the lack of selectivity in the cycloacylation of benzoylbenzoic acid to anthraquinone and such cumbersome set-up and work-up.

Diels-Alder routes

Alternatively, the extended linear aromatics could be prepared using the tandem Diels-Alder aromatization reaction. In our case, this route to anthracene involved 1,4-naphthoquinone and 2,3-disubstituted diene as

precursors. This would be followed by subsequent aromatization to anthraquinone and the aforementioned reduction to anthracene.

The 2,3-disilyloxybuta-1,3-diene route. In order to prepare a general synthetic approach to 2,3-dialkoxyanthracenes and considering that silyloxy substituted buta-1,3-dienes have found increasing use in Diels-Alder reaction [12], 2,3-disilyloxybutadiene appeared to be appropriate to reach our synthetic target. In fact, the easily hydrolyzable trimethylsilyloxy groups have the potential of generating 1,2-diones, diols, quinone or ortho diphenol under mild and selective conditions. A synthesis of 2,3-bis-trimethylsilyloxybuta-1,3-diene **7** has been reported from cyclobutene. [13] This compound could also be obtained in good yield by treating 2,3-butadione (biacetyl), with lithium bromide and chlorotrimethylsilane in dry tetrahydrofuran followed by the addition of triethylamine; the lithium salt (which could be replaced by sodium bromide without affecting the yield) producing *in situ* the more reactive bromotrialkylsilane. [14] This oxygenated diene underwent facile cycloaddition with 1,4-naphthoquinone in refluxing toluene under an inert atmosphere (scheme 1).



i) NEt_3, $ClSiMe_3$, LiBr, 45°C j) refluxing toluene

Scheme 1

The Diels-Alder adduct was never observed, presumably owing to a very fast transformation to the anthraquinone. This result was found to be repeatable even after a shorter reaction time, which consequently had a lower conversion rate. T.L.C. analysis carried out over the reaction showed complete removal of the silyl groups. Amazingly, evaporation of the solvent gave a gum which on trituration with methanol afforded directly a mixture of hystazarone **3** and 2-hydroxyanthraquinone **8**. The formation of this latter compound is not currently fully understood, but clearly is a facile method for the preparation of 2-hydroxyanthraquinone **8** and hence 2-substituted anthracenes where other known procedures [15,16] appear to be less convenient.

Although this second synthetic pathway offers the advantage of being an easily carried out one step method, the yield of disubstituted isomer **3** had to be increased. Several attempts to modify the ratio between the two isomers, varying the solvent polarity and reaction time, using elevated temperatures and a greater excess of diene, failed to afford the desired anthraquinonic compound in increased yield. Unfortunately, all experiments yielded about 66% of monosubstituted derivative **8** and 33% of the desired compound **3**. Large scale experiments were found to have little effect on the time of the reaction and the nature of the products. These findings encouraged us to adopt a different route to the desired structures. As we were mainly interested in hystazarone derivatives, we isolated the monosubstituted derivative by specific crystallization. It was further alkylated with various subtituents and then the products were reduced into the corresponding anthracenes.

The 2,3-dimethoxybuta-1,3-diene route. As the disilylated dienophile was not fully successful, we thought it better to use 2,3-dimethoxybutadiene **9**. This diene was prepared by reaction of 2,3-butadione (biacetyl) and trimethylorthoformate to give initially the bisacetal by transetherification, which was converted into diene **9** in 73% isolated yield *via* distillation in the presence of hydroquinone and ammonium

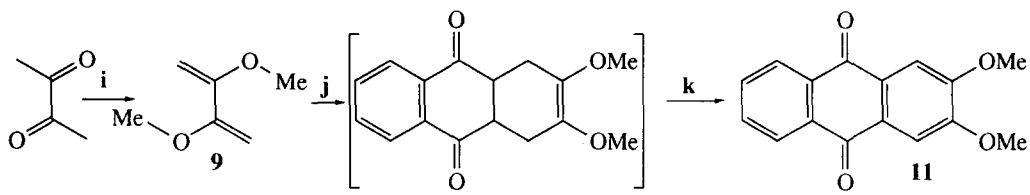
dihydrogenophosphate. The analogous 2,3-diethoxy compound **10** was prepared in the same manner using ethanol and triethylorthoformate albeit in markedly lower yield. This was mainly due to the difficult elimination of unreacted material; therefore the methyl derivative was preferred.

Table 1. Reaction conditions and yield for the tandem Diels-Alder aromatization reaction

entry	solvent	molar ratio[a]	reaction time (h)	yield (%) [b]
1	Toluene	2:1	48	23
2	Toluene	3:1	30	37
3	Toluene	4:1	30	57
4	Toluene	4:1	20	61 (19[c])
5	Ethanol	4:1	40	3

[a] molar ratio between 2,3-dimethoxybutadiene **9** and 1,4-naphthoquinone. [b] yield in pure isolated compound based on 1,4-naphthoquinone (2.28g, 14.4 mmol). [c] This value refers to yield when performed on a larger scale (1,4-naphthoquinone, *ca.* 10-15g).

2,3-Dimethoxy-9,10-anthraquinone **11** was obtained by direct oxidation of the unstable adduct arising from the Diels-Alder reaction of the former diene with 1,4-naphthoquinone. This could be simply achieved by oxidative aeration of the adduct solution in aqueous potassium hydroxide. In order to optimize the reaction conditions, the ratio between the different reagents was varied monitoring the cycloaddition by T.L.C. (aeration and basic hydrolysis of an aliquot) and by liquid chromatography. We also examined the influence of medium polarity as summarized in Table 1. The best yields were achieved using four molar equivalents of diene in excess with respect to 1,4-naphthoquinone in freshly distilled toluene (entry 4), as well as the shortest reaction time (compare entries 1, 2). Unsatisfactorily, this method lead to lower yields when it was applied to larger scales (to obtain multigram quantities of **11**). This could be explained by the competition with the self-polymerization reaction of the butadiene reactant and with the tedious work-up due to the formaztion of an intractable residue in the polymerization reaction. Indeed, several runs were required in order to prepare **11** in gram quantities.

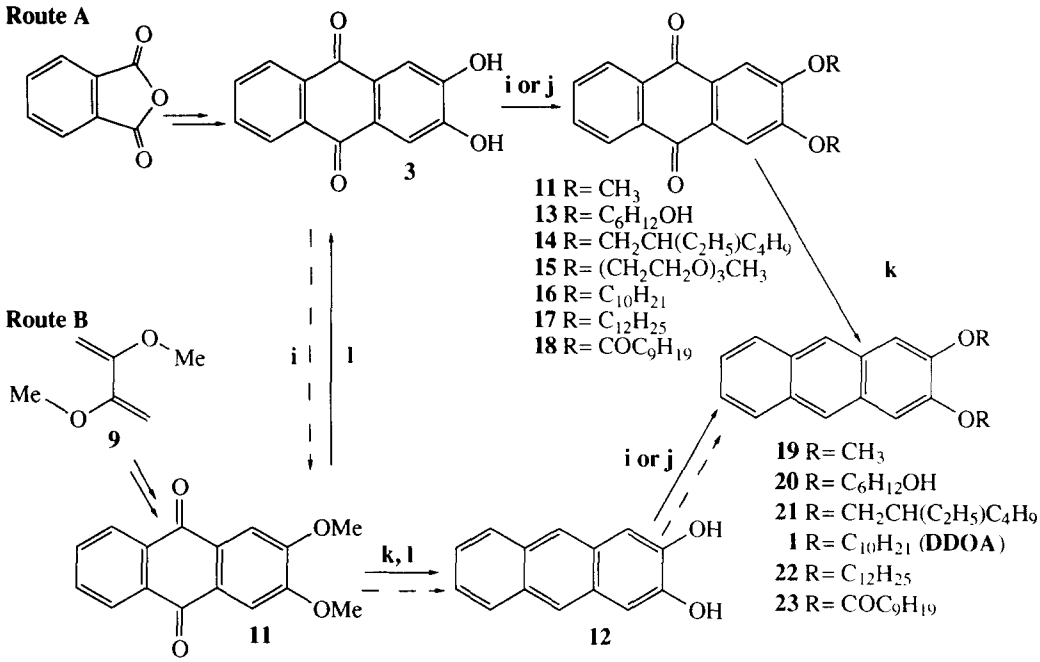


i) $HC(OMe)_3$ j) 1,4-naphthoquinone k) CH_2Cl_2, MeOH, KOH, Air bubbling

Scheme 2

Comparison of the different routes towards the 2,3-disubstituted anthracenes

No marked difference in terms of yield within the synthesized series was observed between alkylation of anthraquinone (**3**, **4**, **8**) and anthracene (**12**) derivatives (scheme 3). This reflected the weak difference of both acidities and nucleophilicities between the tested phenols.



i) RX, K_2CO_3, DMF, 160°C j) RX (R= R'CO), NEt_3, DMAP, CH_2Cl_2, r.t.
k) $NaBH_4$, isopropanol, 85°C then HCl 35% (Twice) l) BBr_3, CH_2Cl_2

Scheme 3

Alkylation was achieved according to the classical procedure using potassium carbonate as a base and alkyl halides in refluxing dimethylformamide. A typical experiment was based on 1:5:4.5 molar ratio between diphenols, base and alkyl halides respectively. More precise experimental data are reported in the experimental section and some corresponding yields are listed in Table 2. Esterification of the 2,3-diphenols was achieved using an acid chloride in the presence of triethylamine and DMAP. [17] The corresponding yields, as reported in Table 2, do not show any correlation with the nature of the starting phenol. As outlined in scheme 3, we used routes **A** and **B**.

The conversion of anthraquinone to anthracene by a three-step procedure involving two reduction-dehydration has been reported to be efficient. [18,19] The reduction by sodium borohydride in alcohols such as methanol or 2-propanol, proceeds *via* successive formation of 9,10-dihydroxy-9,10-dihydro intermediates, anthrone and 9-hydroxy-9,10-dihydroanthracene derivatives. In the present work, this step was found to be of crucial importance. The low yields observed in the reduction of anthraquinones, especially **16** and **17**, (see scheme 3 and table 2) should be ascribed to the ability of the starting materials and the products to form aggregates in alcohols. Indeed, these latter anthraquinones and the corresponding anthracenes **1** and **22** have been shown to form gels in alcohols. [10]

Furthermore, we found that route **A** has limitations in terms of chemical structure of the side chain since the ester groups were converted to hydroxyl groups even when the less reactive sodium cyanoborohydride was used as reducing reagent. The action of sodium borohydride on anthraquinones having $(ethyleneoxy)_n$ sidearms led to complex mixtures. These derivatives (such as **15**) must also be easily cleaved and undergo direct nucleophilic displacement since alkoxide derivatives were generated *in situ* as observed by Gokel in similar cases. [20]

Table 2: Alkylation, esterification and reduction % yields observed using routes A and B.

	Route A				Route B		
2- or 2,3-substituents	alkylation or esterification [a]	reduction	overall yield [b]	compounds [d]	reduction	alkylation or esterification [e]	overall yield [f]
OCH_3	-	85	-	**19**	85		52
$OC_6H_{12}OH$	45	52	8 (10.5) [c]	**20**			
$OCH_2CH(C_2H_5)C_4H_9$	56	56	10 (12.5) [c]	**21**			
$OC_{10}H_{21}$	84	37	10 (14) [c]	**1**		82	41 (33) [c]
	91 [g]	44 [g]	- (18) [c]	**25** [g]			
$OC_{12}H_{25}$	86	34	9.5 (13) [c]	**22**			
$OCOC_9H_{19}$	69	0	- (0) [c]	**23**		74	37 (59) [c]

[a] yield of the Williamson reaction or esterification of the sidearms based on 2,3-dihydroxy-9,10-anthraquinone **3**. [b] yield in pure isolated product based on phthalic anhydride. [c] values in parenthesis refer to yield based on alkyl bromides or acyl chloride. [d] anthracene derivatives (see Scheme 3 or experimental part). [e] refer to yield of the Williamson reaction or esterification of the sidearms based on 2,3-dihydroxyanthracene **12**. [f] based on 1,4-naphthoquinone. [g] refer to monosubstituted derivatives.

Demethylation using BBr_3 was found to be nearly quantitative. Using synthetic route **B**, a lesser amount of starting material for the chain is required according to experimental data, the yields based on alkyl bromides or acyl chlorides increasing up to four times (table 2). Although the cycloaddition step, reflecting the balance between reactivity of 2,3-dimethoxybutadiene **9** towards the dienophile and selfpolymerization, restricts this strategy to the gram scale, it seems to have no structural limitations, affording both anthracenes and anthraquinones.

Finally, route **C** (scheme 3) combining the advantages of an efficient preparation of 2,3-dihydroxyanthraquinone **3** and the smooth reduction of 2,3-dimethoxyanthraquinone **11** followed by dealkylation into 2,3-dihydroxyanthracene **12** seems to be more convenient for a multigram synthesis.It is therefore clear that the 2,3-disubstituted anthracenes (diether, diester) can be successfully prepared by two different ways:

The Friedel-Crafts approach, a multigram synthesis starting from phthalic anhydride. DDOA **1** for instance was obtained in five steps (*ca* 15% overall yield). Thus, it is possible to obtain *ca* 18 g of DDOA **1** from 20g of 2,3-dihydroxy-9,10-anthraquinone **3** provided from 37.5 g of phthalic anhydride.

The Diels-Alder approach, starting from naphthoquinone, DDOA **1** was prepared in five steps (*ca* 40% overall yield). The preparation is easier to handle, but was found to be limited to small scale synthesis (< 1g). 2,3-Dimethoxy-9,10-anthraquinone **11** was isolated in 60% yield. From 1g of **11**, it is possible to obtain *ca* 1.1g of **1**.

This work describes in detail and complements the first publication by Etienne and Bourdon. [11] It opens the way to the synthesis of a series of 2,3-disubstituted anthracenes endowed with gelling properties for organic solvents, and to the introduction of a variety of other fragments (mesogenic, chiral, ...). In addition, although the

Diels-Alder approach using 2,3-disilyloxybuta-2,3-diene proved inadequate for the preparation of 2,3-disubstituted anthracenes, it provides an easy access to 2-substituted anthrylethers.

ACKNOWLEDGMENTS

We thank the Ministère de l'Education Nationale for a thesis grant to Gilles M. Clavier. We are indebted to CESAMO (U. Bordeaux I) for recording the mass spectra and to the 'Region Aquitaine' for financial assistance.

EXPERIMENTAL

General Information

All reactions were performed in a nitrogen atmosphere, unless otherwise stated. M.p.s. were determined in capillary tubes on a Buchi 510 apparatus and are uncorrected. Fourier Transform infrared spectra were recorded on a Perkin Elmer Paragon 1000 spectrophotometer and refer to KBr disks. ^{1}H n.m.r. and ^{13}C spectra were recorded respectively at 250 and at 62.5 MHz on a Bruker AC 250 instrument. UV-Visible spectra were recorded on a Hitachi U-3300 on ethanolic solutions (Carlo Erba, ACS quality). Flash chromatography separations were performed on Merck silicagel 60H (5-40 μm). Mass spectra were obtained on an AutoSpeq EQ spectrometer. Elemental analyses were performed by the Microanalytical Service, University Bordeaux I.

2-(3',4'-Dihydroxybenzoyl)benzoic acid (2a), 2-(2',3'-Dihydroxybenzoyl) benzoic acid (2b)

Aluminum chloride (400g, 3.3 mol) and sodium chloride (46.5g, 1.71mol) were introduced in a 3l flask equipped with a condenser and a mechanical stirrer. The mixture was then heated to 110°C. From this temperature, an eutectic mixture was formed which was raised to 140°C. 1,2-Dihydroxybenzene (32.7g, 297mmol) and phthalic anhydride (33.3g, 225mmol) were added by portions within 30 mn and heating was continued for a further 2 h. The reaction mixture was cooled, then hydrolyzed with cold water (400 ml). Hydrochloric acid (600 ml) was added to the suspension which was dissolved by boiling for 2 h. On cooling, a brown solid precipitated which was filtered and dried for 3 days *in vacuo*. Concentration under reduced pressure afforded the keto acids **2** which were used without further purification. (44.1g, 76%), m.p. 212°C (lit [11] m.p. 210°C).

2,3-Diacetoxy-9,10-anthraquinone (5)

The keto acids **2** (44.1g, 171mmol) were dissolved in sulfuric acid 95% (860ml) in a 3l three-necked flask equipped with a condenser and a mechanical stirrer. The reaction mixture was heated under reflux for 3 h. The solution was cooled, then cold water added (2l) and the resulting brownish precipitate filtered off and dried overnight *in vacuo* over diphosphorous pentoxide. The remaining water was eliminated by azeotropic distillation with toluene. The resulting mixture of 2,3-dihydroxy-9,10-anthraquinone **3** and 1,2-dihydroxy-9,10-anthraquinone **4** was reacted with acetic anhydride (400ml), a few drops of sulfuric acid 95% was added. Excess of reagent was removed under reduced pressure. 2,3-Diacetoxy-9,10-anthraquinone **5** was purified by several recrystallizations from glacial acetic acid. (24.4g, 49%), m.p. 199°C (lit [11] m.p. 212°C); ^{1}H n.m.r. ($CDCl_3$): δ 8.25, m, H5 and H8; 8.14, s, H1 and H4; 7.80, m, H6 and H7; 2.38, s, $OCOCH_3$. υ_{max} 3030, 3010, 2910, 1750, 1670, 1580, 1480, 1420, 1365, 1335, 1300, 1190, 1155, 1100, 1075, 1010, 900, 865, 780, 700 cm^{-1}.

1,2-Diacetoxy-9,10-anthraquinone (6)

The filtrates of former recrystallizations were concentrated to afford a brownish solid which was purified by chromatography using a mixture of ethyl acetate and methanol as eluent (70:30). Desired fractions were concentrated under reduced pressure to afford a yellow solid (3.5g, 7%); m.p. 178°C (from methanol); ^{1}H n.m.r. ($CDCl_3$): δ 8.35, m, H5; 8.13, m, H8; 7.96, d, J8Hz, H4; 7.79, m, H6 and H7; 7.34, d, J8Hz, H3; 2.36, s, $OCOCH_3$. $\bar{\upsilon}_{max}$ 3030, 3015, 2920, 1750, 1675, 1580, 1490, 1420, 1365, 1300, 1160, 860, 785, 690 cm^{-1}.

2,3-Dihydroxy-9,10-anthraquinone (hystazarone) (3)

2,3-Diacetoxy-9,10-anthraquinone **5** was dissolved in sulfuric acid 95% (300ml). The solution was stirred for 1 h at room temperature then hydrolyzed with water (500ml). The yellowish precipitate was filtered off, washed twice with water and dried overnight *in vacuo* over diphosphorous pentoxide. Any remaining water was eliminated by azeotropic distillation with toluene. Concentration under reduced pressure yielded 2,3-hydroxy-9,10-anthraquinone **3** (17.8g, 87%), m.p.>260°C (lit [11] 393-394°C) . ^{1}H n.m.r. [$(CD_3)_2SO$]: δ 10.65, OH; 8.18, m, H5 and H8; 7.90, m, H6 and H7; 7.57, s, H1 and H4. ^{13}C n.m.r. [$(CD_3)_2SO$]: δ 182.1, C9 and C10; 153.2, C2 and C3; 134.5, C6 and C7; 133.9, C8a and C10a; 127.5, C4a and C9a; 127.0, C5 and C8; 114.2, C1 and C4. $\bar{\upsilon}_{max}$ 3430, 3200, 1760, 1660, 1570, 1510, 1405, 1325, 1180, 1150, 1080, 945, 875, 775, 700, 600 cm^{-1}.

1,2-Dihydroxy-9,10-anthraquinone (alizarin) (4)

An identical deacetylation procedure was used for this compound. m.p.>260°C. ^{1}H n.m.r. [$(CD_3)_2SO$]: δ 10.35, OH; 8.19, m, H5; 8.04, m, H8; 7.96, d, J8.5Hz, H4; 7.65-7.60, m, H6 and H7; 7.28, d, J8.5Hz, H3. $\bar{\upsilon}_{max}$ 3420, 3180, 1760, 1665, 1580, 1510, 1410, 1315, 1180, 955, 775, 720 cm^{-1}.

2,3-Bis(trimethylsilyloxy)buta-1,3-diene (7)

Dry lithium bromide (8.68g, 100mmol) was placed in a 125 ml three-necked flask equipped with a condenser. The flask was heated to *ca.* 300°C with an electric heat gun. Anhydrous tetrahydrofuran (30 ml) was added. The mixture became pale yellow and was stirred until complete dissolution of the lithium bromide occurred, then was cooled to -15°C. Successively chlorotrimethylsilane (9.70 ml, 75 mmol), 2,3-butadione (9.70 ml, 25 mmol) and triethylamine (10.61ml, 75 mmol) were added by needle transfer. The reaction mixture was warmed to 45°C and vigorously stirred for 48 h. Then, the flask being cooled to -10°C, cold pentane (25ml) was added and the mixture was poured into a separatory funnel charged with saturated sodium chloride solution (25 ml), saturated hydrogen carbonate solution (25 ml) and crushed ice (25 g). The aqueous layer was immediately extracted with cold pentane (5x70ml). The organic layers were combined, concentrated and dried ($MgSO_4$). The yellow residue was purified by distillation under reduced pressure to yield **7** as a colorless liquid (4.61g, 79%), $Eb_{3.5}$ =60-61°C. ^{1}H n.m.r. ($CDCl_3$): δ 4.81, s, 2H; 4.31, s, 2H; 0.19, s, $OSi(CH_3)_3$ ^{13}C n.m.r. ($CDCl_3$): δ 153.2, 92.6, -0.12.

2,3-Dihydroxy-9,10-anthraquinone (3) and 2-hydroxy-9,10-anthraquinone (8)

1,4-Naphthoquinone (2.63g, 16.5mmol) was dissolved in anhydrous toluene (30ml) in a 100ml three necked flask. 2,3-Bis(trimethylsilyloxy)buta-1,3-diene **7** (4.03g, 17.5mmol) was added by needle transfer. The solution was heated to reflux for 24 h. After cooling, the solvent was removed under reduced pressure to afford a gum. Trituration with methanol yielded a brownish solid which consisted of a mixture of 2-hydroxy-9,10-

anthraquinone **8** and 2,3-dihydroxy-9,10-anthraquinone **3** (respectively 66% and 33%). The isomers were purified by flash chromatography with a mixture 1:3 of ethyl acetate-dichloromethane as the eluent.

2-Hydroxy-9,10-anthraquinone (8)

(1.99g, 8.91mmol, 54%); m.p.>260°C. ^{1}H n.m.r. [$(CD_3)_2SO$]: δ 10.20 OH; 8.51, d, J8.7Hz, H4; 8.30-8.25, m, H5 and H8; 7.96, d, J2.3Hz, H1; 7.82-7.78, m, H6 and H7; 7.42, dd, J8.7 and J2.3Hz, H3. υ_{max} 3355, 2963, 2926, 1668, 1575, 1513, 1465, 1335, 1310, 1220, 1100, 1090, 715, 620 cm^{-1}.

2,3-Dimethoxybuta-1,3-diene (9)

2,3-Butanedione (14.3ml, 0.16mol), trimethylorthoformate (54.1ml, 0.49mol) and absolute methanol (42ml) were stirred at room temperature and degassed by bubbling nitrogen through the solution. A few drops of sulfuric acid were added and the solution was refluxed for 12 h. The excess of reagents distilled off. Ammonium dihydrogenophophate (20mg, 0.24mmol) and hydroquinone (25mg) were added before distillation of the remaining liquid under vacuum. Residual methanol and orthoformate along with methyl formate were slowly distilled, then 2,3-dimethoxybuta-1,3-diene **9** (13.31g, 0.12mol, 73%) was obtained as a colorless liquid. Eb_{760}=133-134°C (lit [13] Eb_{760}=132-132.5°C). ^{1}H n.m.r. ($CDCl_3$): δ 4.57, d, J1.5Hz, H*olefinic*; 4.02, d, J1.5Hz, H*olefinic*; 3.57, s, OCH_3. $\bar{\upsilon}_{max}$ 2830, 1627, 1215, 1035 cm^{-1}.

2,3-Diethoxybuta-1,3-diene (10)

2,3-Butanedione (10ml, 0.112mol), triethylorthoformate (37.8ml, 0.34mol) and absolute ethanol (56ml) were placed in a flask under argon. A few drops of sulfuric acid were added and the solution was refluxed overnight. The excess of reagents distilled off. Ammonium dihydrogenophophate (20mg, 0.24mmol) and hydroquinone (25mg) were added before distillation of the remaining liquid under vacuum. Residual ethanol and orthoformate along with ethyl formate were slowly distilled, then 2,3-diethoxybuta-1,3-diene **10** (10.65g, 75mmol, 67%) was obtained as a colorless liquid (Eb_{20}=33-34°C). m.p. 31°C. ^{1}H n.m.r. ($CDCl_3$): δ 4.56, d, J1.5Hz, H *olefinic*; 4.04, d, J1.5Hz, H *olefinic*; 3.97, q, *J*6.8Hz, *OCH_2*; 1.97, t, *J*6.8Hz, *CH_3*. $\bar{\upsilon}_{max}$ 2825, 1630, 1220, 1040 cm^{-1}.

2,3-Dimethoxy-9,10-anthraquinone (11)

In a 50ml three necked flask, 1,4-naphthoquinone (2.28g, 14.4mmol) and the diene **9** (6.61g, 58mmol) were warmed in toluene (5ml) until dissolution occurred and then the mixture was refluxed for 20 h. The brownish solid, obtained after concentration, was used without further purification and was dissolved in a mixture of dichloromethane and methanol (13 ml, 50/50 v/v), then a saturated potassium hydroxide solution was added. The mixture was stirred vigorously at room temperature for 2 h under air bubbling. The solution was extracted three times with dichloromethane (50ml). The organic layers were combined , washed with water dried ($MgSO_4$). The resulting brown solid was recrystallized from methanol to yield 2,3-dimethoxy-9,10-anthraquinone **11**, as yellowish solid (2.35g, 61%), m.p. 235-236°C (lit 235°C). ^{1}H n.m.r. ($CDCl_3$): δ 8.20, m, H5 and H8; 7.70, m, H6 and H7; 7.66, s, H1 and H4; 4.01, s, OCH_3. ^{13}C n.m.r. ($CDCl_3$): δ 182.5, C9 and C10; 154.9, C2 and C3; 133.7, C6 and C7; 129.5, C8a and C10a; 128.9, C4a and C9a; 127.0, C5 and C8; 108.4, C1 and C4; 56.6, OCH_3.

General procedure for alkylation of hydroxy-9,10-anthraquinones

In a three-necked flask, anthraquinone and potassium carbonate (2.5 equivalents per hydroxy group) were dispersed in freshly distilled DMF (10ml per mmol). The solution was warmed until complete dissolution

occurred. The alkyl bromide (2.25 equivalents per hydroxy group) was then added over 20 minutes. The reaction mixture was refluxed for 12 h and slowly allowed to cool. The solvent was evaporated under reduced pressure. The remaining solid was hydrolyzed with water and the aqueous layer was extracted continuously with dichloromethane. The organic layers were combined, dried ($MgSO_4$) and then filtered. Subsequent elution from silica with petroleum ether-dichloromethane as the eluent [percentage of dichloromethane, solvent system **A**: 20%, **B**: 40%, **C**: 50%] gave the desired product. After concentration, the crystalline residue was recrystallized from the appropriate solvent.

2,3-Di-6'-hydroxyhexyloxy-9,10-anthraquinone (13)

[solvent system **C**] (45%); m.p. 127°C (from heptane-benzene). (Found: C, 70.77; H, 7.40 $C_{26}H_{32}O_6$ requires C, 70.88; H, 7.33; O, 21.79%). ^{1}H n.m.r. ($CDCl_3$): δ 8.17, m, H5 and H8; 7.68, m, H6 and H7; 7.58, s, H1 and H4; 4.08, t, J6.3Hz, ArO*CH*$_2$; 3.69, t, J6.2Hz, *CH*$_2$OH; 1.90-1.80, m, OCH$_2$*CH*$_2$ and *CH*$_2$CH$_2$OH; 1.60-1.30, m, H3' and H4'. ^{13}C n.m.r. ($CDCl_3$): δ 184.5, C9 and C10; 153.7, C2 and C3; 133.7, C6 and C7; 133.6, C8a and C10a; 128.1, C4a and C9a; 127.0, C5 and C8; 109.3, C1 and C4; 69.2, ArO*CH*$_2$; 62.8, *CH*$_2$OH; 32.7, t; 28.9, t; 25.9, t; 25.5, t. $\bar{\upsilon}_{max}$ 3497, 3355, 2930, 2858, 1665, 1578, 1331, 1310 cm^{-1}.

2,3-Di-2'-ethylhexyloxy-9,10-anthraquinone (14)

[solvent system **B**] (56%). m.p. 56°C. ^{1}H n.m.r. ($CDCl_3$): δ 8.14, m, H5 and H8; 7.83, m, H6 and H7; 7.5, s, H1 and H4; 4.09, d, J6.6Hz, O*CH*$_2$; 1.75, m, OCH2*CH*; 1.42-1.19, m, *CH*$_2$; 0.91, t, J6.7Hz, CH_3; 0.89, t, J6.8Hz, CH_3. ^{13}C n.m.r. ($CDCl_3$): δ 181.6, C9 and C10; 153.4, C2 and C3; 134.1, C6 and C7; 132.9, C8a and C10a; 127.5, C4a and C9a; 126.5, C5 and C8; 108.7, C1 and C4; 70.9, O*CH*$_2$; 30.0, OCH$_2$*CH*; 28.5, t; 23.4, t; 22.5, t; 13.9, CH_3; 11.1, CH_3. $\bar{\upsilon}_{max}$ 3060, 2960, 2920, 1730, 1670, 1580, 1520, 1470, 1380, 1310, 1220, 1090, 1010, 970, 790, 720, 620 cm^{-1}. FAB$^+$ m/z: 464.3(M, 52%); 240.0(100); 57.1(35).

2,3-Di-3',6',9'-trioxodecyloxy-9,10-anthraquinone (15)

10-Tosyl-2,5,8-trioxodecane was used in the place of alkyl bromide. (19%) [solvent system **C**]; m.p. 43-44°C (from methanol). ^{1}H n.m.r. ($CDCl_3$): δ 8.49, m, H5 and H8; 8.02, m, H6 and H7; 7.97, s, H1 and H4; 4.59, t, H1'; 4.22, t, H2'; 4.05, t, H4'; 3.92, t, H5'; 3.88-3.80, m, H6' and H7'; 3.69, s, H9'. ^{13}C n.m.r. ($CDCl_3$): δ 182.2, C9 and C10; 153.3, C2 and C3; 133.6, C6 and C7; 133.4, C8a and C10a; 128.2, C4a and C9a; 126.8, C5 and C8; 109.6, C1 and C4; 72.8, C1'; 70.9, C7'; 69.8, t; 69.4, t; 69.0, t; 68.6, t; 58.7, C9'. $\bar{\upsilon}_{max}$ 3075, 2953, 2927, 1668, 1576, 1513, 1465, 1375, 1333, 1219, 1087, 713 cm^{-1}. FAB$^+$ m/z: 532.4 (M, 26%), 240.0 (100).

2,3-Di-n-decyloxy-9,10-anthraquinone (16)

[solvent system **B**] (84%); m.p. 101°C (from methanol). (Found: C, 78.57; H, 9.40 $C_{34}H_{48}O_4$ requires C, 78.42; H, 9.29; O, 12.29%). ^{1}H n.m.r. ($CDCl_3$): δ 8.15, m, H5 and H8; 7.65, m, H6 and H7; 7.58, s, H1 and H4; 4.11, t, J6.4Hz, O*CH*$_2$; 1.83, m, OCH$_2$*CH*$_2$; 1.49, m, OCH$_2$CH$_2$*CH*$_2$; 1.25-1.20, 24H, m, CH_2; 0.88, t, J6.8Hz, CH_3. ^{13}C n.m.r. ($CDCl_3$): δ 182.5, C9 and C10; 154.9, C2 and C3; 133.8, C6 and C7; 129.5, C8a and C10a; 128.9, C4a and C9a; 127.1, C5 and C8; 108.4, C1 and C4; 68.8 O*CH*$_2$; 32.0, *CH*$_2$CH$_2$CH$_3$; 29.7,

OCH_2CH_2; 29.6, t; 29.4, t; 29.0, t; 25.9, t; 25.8, t; 22.7, CH_2CH_3; 14.1, CH_3. $\bar{\upsilon}_{max}$ 3078, 2921, 2851, 1670, 1577, 1514, 1467, 1379, 1332, 1219, 1089, 712 cm^{-1}. FAB^+ *m/z* 520.3(M, 85%), 380.2(37), 240.1(100).

2,3-Di-n-dodecyloxy-9,10-anthraquinone (17)

[solvent system **B**] (85%); m.p. 95°C. ^1H n.m.r. ($CDCl_3$): δ 8.16, m, H5 and H8; 7.64, m, H6 and H7; 7.58, s, H1 and H4; 4.15, t, J6.2Hz, OCH_2; 1.83, m, OCH_2CH_2; 1.42, m, $OCH_2CH_2CH_2$; 1.15, m, CH_2; 0.80, t, J6.7Hz, CH_3. ^{13}C n.m.r. ($CDCl_3$): δ 182.5, C9 and C10; 153.7, C2 and C3; 133.6, C6 and C7; 133.5, C8a and C10a; 128.0, C4a and C9a; 126.9, C5 and C8; 109.2, C1 and C4; 69.3, OCH_2; 32.0, $CH_2CH_2CH_3$; 29.8, t; 29.7, t; 29.6, t; 29.4, t; 28.9, t; 26.0, t, 2C; 22.7, CH_2CH_3; 14.1, CH_3. $\bar{\upsilon}_{max}$ 3074, 2960, 2855, 1672, 1580, 1475 cm^{-1}. FAB^+ *m/z*: 576.5(42%), 240.1(100), 57(23).

2,3-Didecanoyloxy-9,10-anthraquinone (18)

Compound (**18**) was prepared according to a previously described procedure [17], [solvent system **C**] (69%); m.p. 72°C (from methanol). (Found: C, 74.57; H, 8.17 $C_{34}H_{44}O_6$ requires C, 74.42; H, 8.09; O, 17.49%). ^1H n.m.r. ($CDCl_3$): δ 8.23, m, H5 and H8; 8.04, s, H1 and H4; 7.73, m, H6 and H7; 2.52, t, J7.1Hz, $OCOCH_2$; 1.69, m, $OCOCH_2CH_2$; 1.40-1.10, m, 12H, CH_2 aliphatics; 0.82, t, J6.8Hz, CH_3. ^{13}C n.m.r. ($CDCl_3$): δ 182.1, C9 and C10; 170.4, $ArOCOCH_2$, 147.8, C2 and C3; 134.3, C6 and C7; 133.9, C8a and C10a; 133.2, C4a and C9a; 127.4, C5 and C8; 122.9, C1 and C4; 34.1 $OCOCH_2$; 31.9, t; 29.5, t; 29.3, t; 29.2, t; 24.9, t; 22.7, CH_2CH_3; 14.1, CH_3. $\bar{\upsilon}_{max}$ 2954, 2921, 2853, 1774, 1674, 1594, 1488, 1467, 1331, 1102, 713 cm^{-1}.

2-n-Decyloxy-9,10-anthraquinone (24)

2-Hydroxy-9,10-anthraquinone **8** was used in the place of hystarazone **3**.[solvent system **A**] (91%); m.p. 136°C (from petroleum ether). (Found: C, 79.37; H, 7.80 $C_{24}H_{28}O_3$ requires C, 79.09; H, 7.74; O, 13.17%). ^1H n.m.r. ($CDCl_3$): δ 8.15, m, H5 and H8; 8.10, d, J8.7Hz, H4; 7.64, m, H6 and H7; 7.55, d, J2.5Hz, H1; 7.12, dd, J8.7 and J2.6Hz, H3; 4.01, t, J6.5Hz, OCH_2; 1.81, m, OCH_2CH_2; 1.41, m, CH_2; 1.25, m, CH_2; 0.85, t, J6.8Hz, CH_3. ^{13}C n.m.r. ($CDCl_3$): δ 183.6 and 181.7, C9 and C10; 159.9, C2; 135.1, s; 134.1, s; 133.7, s; 133.0 and 132.4, C6 and C7; 127.6, C4; 126.9 and 126.5, C5 and C8; 125.3, C4a; 120.4, C1; 116.3, C3; 68.6, OCH_2; 31.7, $CH_2CH_2CH_3$; 29.5, OCH_2CH_2; 29.1, t; 29.0, t; 28.8, t; 26.1, t; 25.8, t; 22.7, CH_2CH_3; 13.9, CH_3. $\bar{\upsilon}_{max}$ 2920, 2846, 1673, 1590, 1570, 1469, 718 cm^{-1}.

General procedure for the reduction of 9,10-anthraquinones

In a three-necked flask, anthraquinone was placed in isopropanol (20ml per mmol). Solid sodium borohydride (23 molecular equivalents) was added in small portions at such a rate as to prevent a rapid temperature rise. Then the mixture was refluxed for 3 h. After cooling, the mixture was hydrolyzed with hydrochloric acid (35%) and crushed ice, and then extracted several times with dichloromethane. The organic layers were combined, washed with a sodium hydroxide solution, dried ($MgSO_4$) and then filtered. After concentration, the crystalline residue was dissolved in isopropanol (20ml per mmol). Portions of sodium borohydride (19 molecular equivalents) were carefully added. Under an inert atmosphere, the solution was refluxed overnight. The mixture was hydrolyzed with hydrochloric acid (35%) and crushed ice. The reaction mixture was extracted several times with

dichloromethane. The organic layers were combined and dried ($MgSO_4$). Subsequent elution from silica with petroleum ether- dichloromethane as the eluent [percentage of dichloromethane, solvent system **D**: 10%, **E**: 30%] gave the desired product. After concentration, the residue was recrystallized from the appropriate solvent.

2,3-Dimethoxyanthracene (19)

[solvent system **E**] (85%); (1,07g, 4.5 mmol); m.p. 133°C (from cyclohexane). (Found: C, 80.71; H, 5.86; $C_{16}H_{14}O_2$ requires C, 80.65; H, 5.92; O, 13.43%). ^{1}H n.m.r. ($CDCl_3$): δ 8.21, s, H9 and H10; 7.93, m, H5 and H8; 7.42, m, H6 and H7; 7.18, s, H1 and H4; 4.04, s, OCH_3. ^{13}C n.m.r. ($CDCl_3$): δ 150.1, C2 and C3; 130.9, C8a and C10a; 128.6, C4a and C9a; 127.7, C5 and C8; 124.6, C6 and C7; 124.0, C9 and C10; 104.9, C1 and C4; 55.9, OCH_3. $\bar{\upsilon}_{max}$ 3051, 2920, 2850, 1630, 1565, 1470, 1400, 840, 760 cm^{-1}.

2,3-Di-6'-hydroxyhexyloxyanthracene (20)

[solvent system **E**] (45%); m.p. 116°C (from heptane-benzene). (Found: C, 75.97; H, 8.40 $C_{26}H_4O_4$ requires C, 76.06; H, 8.35; O, 15.59%). ^{1}H n.m.r. ($CDCl_3$): δ 8.24, s, H9 and H10; 7.93, m, H5 and H8; 7.44, m, H6 and H7; 7.16, s, H1 and H4; 4.09, t, J6.3Hz, ArOCH_2; 3.71, t, J6.2Hz, CH_2OH; 1.90-1.80, m, OCH_2CH_2 and CH_2CH_2OH; 1.60-1.30, m, H3' and H4'. ^{13}C n.m.r. ($CDCl_3$): δ 150.1, C2 and C3; 130.7, C8a and C10a; 128.8, C4a and C9a; 127.6, C5 and C8; 124.4, C6 and C7;123.8 C9 and C10; 105.9 C1 and C4; 68.5, ArOCH_2; 62.6, CH_2OH; 32.7, t; 29.4, t; 26.1, t; 25.6, t. $\bar{\upsilon}_{max}$ 3430, 3050, 2916, 2850, 1630, 1570, 1490, 1470, 1390, 1290, 1225, 1195, 880, 730 cm^{-1}.

2,3-Di-2'-ethylhexyloxyanthracene (21)

[solvent system **E**] (56%); oil. (Found C, 82.98; H, 9.80; $C_{30}H_{42}O_2$ requires C, 82.90; H, 9.74; O, 7.36%).^{1}H n.m.r. ($CDCl_3$): δ 8.36, s, H9 and H10; 8.08, m, H5 and H8; 7.57, m, H6 and H7; 7.35, s, H1 and H4; 4.21, d, J6.5Hz, OCH_2; 2.09, m, OCH_2CH; 1.73-1.55, m, CH_2; 1.11, t, CH_3; 1.08, t, CH_3. ^{13}C n.m.r. ($CDCl_3$): δ 150.5, C2 and C3; 131.1, C8a and C10a; 129.2, C4a and C9a; 127.9, C5 and C8; 124.7, C6 and C7; 124.0, C9 and C10; 105.9, C1 and C4; 71.4, OCH_2; 39.6, OCH_2CH; 30.2, t; 29.2, t; 24.5, t; 23.1, t; 14.5, CH_3; 11.7, CH_3. $\bar{\upsilon}_{max}$ 3040, 2925, 2855, 1630, 1567, 1492, 1402, 1376, 1285, 1170, 830, 740 cm^{-1}. FAB$^+$ m/z: 434.3(M, 64%); 322.2(8); 210.1(100); HRMS MH$^+$ calcd 435.3263, found 435.3292.

2,3-Di-n-dodecyloxyanthracene (22)

[solvent system **D**] (34%); m.p. 74°C (from pentane). (Found C, 82.98; H, 10.80; $C_{38}H_{58}O_2$ requires C, 83.46; H, 10.69; O, 5.85%).^{1}H n.m.r. ($CDCl_3$): δ 8.29, s, H9 and H10; 7.94, m, H5 and H8; 7.40, m, H6 and H7; 7.17, s, H1 and H4; 4.14, t, J6.5Hz, OCH_2; 1.93, m, OCH_2CH_2; 1.49, m, $OCH_2CH_2CH_2$; 1.35-1.30, m, CH_2; 0.93, t, J6.7Hz, CH_3. ^{13}C n.m.r. ($CDCl_3$): δ 150.1, C2 and C3; 130.7, C8a and C10a; 128.8, C4a and C9a; 127.6, C5 and C8; 124.4, C6 and C7;123.8 C9 and C10; 105.9 C1 and C4; 68.7, O CH_2; 32.0, C10'; 29.8, t; 29.7, t; 29.5, t; 29.4, (t, 2C); 29.1, t; 26.2, (t, 2C); 22.8, CH_2CH_3; 14.2, CH_3. $\bar{\upsilon}_{max}$ 3045, 2916, 2849, 1633, 1569, 1490, 1467, 1395, 1288, 1222, 1195, 1164, 880, 730 cm^{-1}. FAB$^+$ *m/z* 546.4(100%), 378.3(24), 210.1(44); HRMS MH$^+$ calcd 547.4515, found 547.4522.

2-n-Decyloxyanthracene (25)

[solvent system **D**] (44%); m.p. 113°C (from heptane); (Found: C, 86.34; H, 8.96; $C_{24}H_{30}O$ requires C, 86.18; H, 9.04; O: 4.78%). ^{1}H n.m.r. ($CDCl_3$): δ 8.34, s, H9; 8.22, s, H10; 7.95-7.85, m, H4 ,H5 and H8; 7.40-7.35, m, H6 and H7; 7.17, m, H3; 7.13, d, J2.3Hz, H1; 4.07, t, J6.2Hz, OCH_2; 1.90, m, OCH_2CH_2; 1.37, m, CH_2; 1.25-1.20, m, CH_2; 0.92, t, J6.8Hz, CH_3. ^{13}C n.m.r. ($CDCl_3$): δ 156.9, C2; 133.4 and 132.7, C8a and C9a; 130.0 and 129.1, C4a and C10a; 128.9, C4; 128.0 and 127.7, C5 and C8; 126.3 and 125.9, C9 and C10; 124.6 and 124.4, C6 and C7; 121.0, C3; 107.0, C1; 68.6, OCH_2; 32.0, C8'; 29.7, t; 29.4, t; 29.3, t; 29.1, t; 28.8, t; 26.0, t; 22.9, CH_2CH_3; 13.8, CH_3. $\bar{\upsilon}_{max}$ 2955, 2917, 2850, 1634, 1579, 1471, 1305, 1211, 1166, 886, 738 cm^{-1}. FAB$^+$ *m/z* 334.2(100%), 210(16).

2,3-Dihydroxyanthracene (12)

Boron tribromide 1M in dichloromethane (3.15ml, 3.15mmol) was added dropwise to a solution of 2,3-dimethoxyanthracene (300mg, 1.26mmol) in dichloromethane (20ml) below 0°C with an ice-salt bath. The solution was slowly warmed to room temperature and then refluxed for 2 hours. After cooling, the crude reaction mixture was hydrolyzed with hydrochloric acid (0.1 N, 30ml). The aqueous layer was extracted twice with diethyl ether (2x10 ml) and twice with dichloromethane (2x10 ml). The organic layers were combined, washed with water until pH became neutral, dried ($MgSO_4$) and evaporated under reduced pressure to yield 2,3-dihydroxyanthracene **12** (256mg, 97%); m.p.>260°C. ^{1}H n.m.r. ($CDCl_3$): δ 8.11, s, H9 and H10; 7.94, m, H5 and H8; 7.35, m, H6 and H7; 7.06, s, H6 and H7; 5.96, OH.

2,3-Di-n-decyloxyanthracene (DDOA) (1)

In a three-necked flask, 2,3-dihydroxyanthracene (210mg, 1mmol) and potassium carbonate (690mg, 5mmol) were dispersed in freshly distilled DMF (5ml). The solution was warmed till complete dissolution occurred. Decylbromide (1g, 4.5mmol) in tetrahydrofuran (5ml) was added over 5 minutes. The reaction mixture was refluxed overnight and then allowed to cool. The solvent was evaporated under reduced pressure. The remaining solid was hydrolyzed with water. The aqueous layer was extracted several times with dichloromethane. The organic layer was dried ($MgSO_4$) and then filtered. Subsequent elution from silica with petroleum ether-dichloromethane (70/30 v/v) as the eluent gave the anthracenic fraction. After concentration, the crystalline residue was recrystallized from pentane. (382mg, 78%); m.p. 84°C (from pentane). (Found: C, 83.48; H, 10.1; $C_{34}H_{50}O_2$ requires C, 83.21; H, 10.27; O, 6.52%). ^{1}H n.m.r. ($CDCl_3$): δ 8.25, s, H9 and H10; 7.98, m, H5 and H8; 7.45, m, H6 and H7; 7.23, s, H1 and H4; 4.20, t, J6.4Hz, OCH_2; 2.00, m, OCH_2CH_2; 1.55, m, $OCH_2CH_2CH_2$; 1.37, m, CH_2; 0.98, t, J6.8Hz, CH_3. ^{13}C n.m.r. ($CDCl_3$): δ 149.9, C2 and C3; 130.6, C8a and C10a; 128.7, C4a and C9a; 127.5, C5 and C8; 124.3, C6 and C7; 123.7, C9 and C10; 105.8, C1 and C4; 68.6, OCH_2; 32.0, C8'; 29.6, t; 29.5, t; 29.4, t; 29.3, t; 29.0, t; 26.1, t; 22.7, CH_2CH_3; 14.1, CH_3. υ_{max} 3040, 2920, 2850, 1632, 1569, 1490, 1468, 1400, 1390, 1290, 1225, 1195, 1170, 880, 730 cm^{-1}. FAB$^+$ *m/z* 490(M, 62%), 350(12), 222(22), 210.1(100).

2,3-Didecanoyloxyanthracene (23)

The preparation was achieved using a well-established procedure starting from 2,3-dihydroxyanthracene, decanoyl chloride, triethylamine and DMAP [17]. It was purified by flash chromatography with petroleum ether-

dichloromethane (80/20 v/v) as the eluent. After concentration of the anthracenic fraction, the crystalline residue was recrystallized as a pale yellow solid. (78%); m.p. 94°C (from pentane). (Found: C, 78.83; H, 8.87 $C_{34}H_{46}O_4$ requires C, 78.72; H, 8.94; O, 12.34%). ^{1}H n.m.r. ($CDCl_3$): δ 8.26, s, H9 and H10; 7.87, m, H5 and H8; 7.72, s, H1 and H4; 7.38, m, H6 and H7; 2.55, t, J6.2Hz, OCO*CH*$_2$; 1.73, m, OCOCH$_2$*CH*$_2$; 1.40-1.10, m, 12H, CH_2 aliphatics; 0.85, t, J6.4Hz, CH_3. ^{13}C n.m.r. ($CDCl_3$): δ 171.5 ArO*C*O, 141.3, C2 and C3; 131.8, C8a and C10a; 129.6, C4a and C9a; 128.0, C5 and C8; 126.0, C9 and C10; 125.7 C6 and C7; 120.5 C1 and C4; 34.3 ArOCO*CH*$_2$; 32.0, t; 29.5, t; 29.4, (t, 2C); 29.3, t; 25.0, t; 22.8, *CH*$_2$CH$_3$; 14.2, CH_3. υ_{max} 3033, 2953, 2919, 2849, 1762, 1654, 1444, 1285, 1210, 1130, 913, 754 cm^{-1}.

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(*Received in Belgium* 10 *January* 1997; *accepted* 18 *March* 1997)