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A NEW ACCESS TO THE ANTHRACENE CORE

SYNTHESIS OF TWO WATER SOLUBLE SINGLET OXYGEN TRAPS DERIVED FROM 1,3-DIPHENYLISOBENZOFURAN AND 9,10-DIPHENYLANTHRACENE

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Abstracts—Two water soluble $^1O_2$ traps: dipotassium 1,3 - diphenylisobenzofuran - 5,6 - dicarboxylate and tetrapotassium 9,10 - diphenylanthracene - 2,3,6,7 - tetracarboxylate have been prepared in good yields and a new access to the anthracene skeleton is described. The key-step of this synthesis consists of a cycloaddition between 1,3 - diphenylisobenzofurans and dimethyl 7 - oxabicyclo[2.2.1] - 5 - heptene - 2,3 - dicarboxylate; the adducts thus obtained undergo dehydration to afford the corresponding anthracenes.

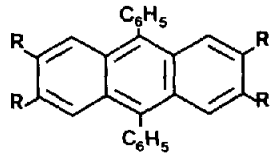
The possible production of $^1O_2$ in aqueous media by biochemical,[1] inorganic,[2] and photochemical[3] processes has been intensively investigated in the past few years. In some cases, however, the results remained ambiguous chiefly for lack of specific water soluble $^1O_2$ traps; this peculiar problem arose our interest and prompted us to design new trapping agents. We selected them among the polycyclic aromatic hydrocarbons which are known to react specifically with $^1O_2$ to form stable endoperoxides.[4] The solubility challenge was readily overcome by introducing several carboxylate groups which were located far from the reaction center and achieved a high solubility in neutral to basic aqueous solutions.

We have already reported the synthesis of such a compound: tetrapotassium rubrene - 2,3,6,7 - tetracarboxylate.[5] In the presence of $^1O_2$, this highly reactive red compound yields a colourless endoperoxide and thus provides a useful test for $^1O_2$ in aqueous medium.

It was necessary, however, to synthesise other specific models, thus an anthracenic compound showing little or no absorption in the visible spectrum would permit one to study the photosensitising properties of various coloured materials present in natural waters,[6] a simple structure would be a further advantage in allowing an easy identification of the oxidation products by NMR.

The hygroscopic sodium salt of anthracene - 9,10 - bisethanesulphonic acid,[23] the sparingly soluble salts of 9,10 - diphenylanthracene - 2,3 - dicarboxylic acid[24-27] and 9,10 - anthracenedipropionic acid,[27,28] and the readily water-soluble tetrapotassium 9,10 - diphenylanthracene - 2,3,6,7 - tetracarboxylate[7-9] **1d** meet the preceeding requirements and we report here a new access to this latter compound.

Three preparations of the methyl ester **1a** are already known; they all proceed through a cycloaddition step on the 1,4 position of an anthracene involving the following pairs: 9,10 - diphenylanthracene/dimethyl acetylenedicarboxylate (6 steps, 5%);[7] 9,10 - diphenyl - 2,3,6,7 - tetramethoxyanthracene/dimethyl acetylenedicarboxylate (1 step, 19%)[8] and 9,10-diphenylanthracene/dicyanoacetylene (4 steps, 35%).[9] However, these methods proved inappropriate for preparing **1a** on a large scale: the first two preparations require tedious chromatographic separations whereas the last one uses dicyanoacetylene, a compound rather hazardous to prepare.[10]



1a R = CO_2CH_3

1d R = CO_2K

In the new approach reported here, we propose to build the anthracene core from synthons already carrying the carboxylic functions using as key-step a cycloaddition between dimethyl 1,3 - diphenylisobenzofuran - 5,6 - dicarboxylate **2a** and dimethyl *cis* - *exo* - 7 - oxabicyclo[2.2.1] - 5 - heptene - 2,3 - dicarboxylate **3** (Scheme 1).

The readily available dienophile **3**,[11] is a synthon equivalent to dimethyl phthalate which offers a convenient route to various substituted anthracenes **1** by reaction with an appropriate 1,3 - diphenylisobenzofuran **2** and subsequent double dehydration. Furthermore, dimethyl 1,3 - diphenylisobenzofuran - 5,6 - dicarboxylate **2a** has never been prepared before and we expect the corresponding potassium salt also to be a valuable $^1O_2$ trap highly reactive but non specific by analogy with the parent compound **2b**.[12] Nevertheless, this compound should prove particularly useful in kinetic studies where $^1O_2$ is known to be the sole oxidising species.

Access to dimethyl - 1,3 - diphenylisobenzofuran - 5,6 - dicarboxylate

The ester **2a** was prepared in good overall yield (77%) from 1,2 - dibenzoyl - 4,5 - dimethylbenzene **5** by the sequence illustrated in Scheme 2.

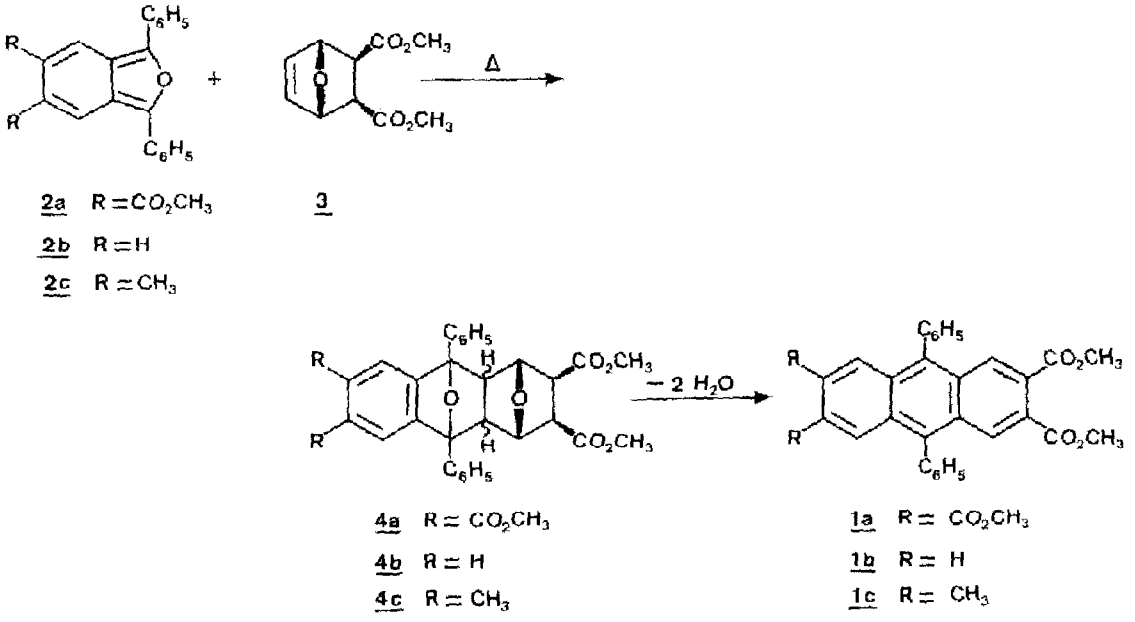
In the first step (Scheme 2), the aromatic methyls of **5** were oxidised to carboxylic acid groups. Dilute nitric acid at 170°C which has often been used in similar cases[13] was first tried as an oxidant. The moderate yields we obtained (40%), just as the difficulty we encountered in finding optimum conditions, led us to prefer the method of Friedman.[14] In this process, aqueous sodium

dichromate at 250°C is used as an oxidant:

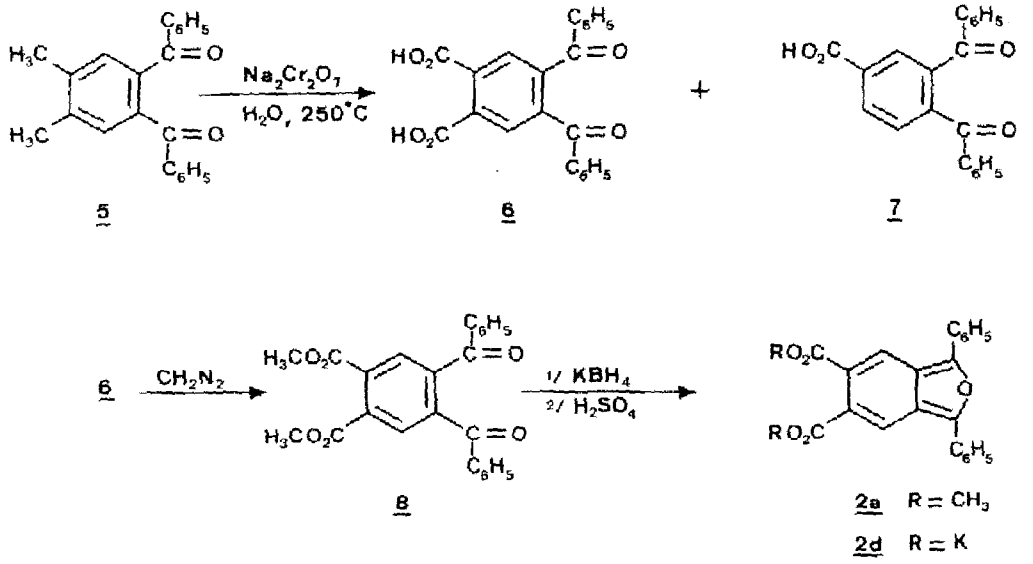
$$ArCH_3 + Na_2Cr_2O_7 \longrightarrow ArCO_2Na + NaOH + Cr_2O_3 + H_2O.$$

Sodium hydroxide is produced and reacts with sodium dichromate to yield sodium chromate a milder oxidant which slows down the oxidation process. The reaction is therefore better performed in the presence of a buffer such as sodium dihydrogenophosphate or carbon dioxide. In these conditions, two compounds, the diacid **6** (85%) besides its monodecarboxylation product **7** (10%), were formed. The former was readily purified by recrystallization of its methyl ester **8** prepared by treatment of crude **6** with diazomethane.

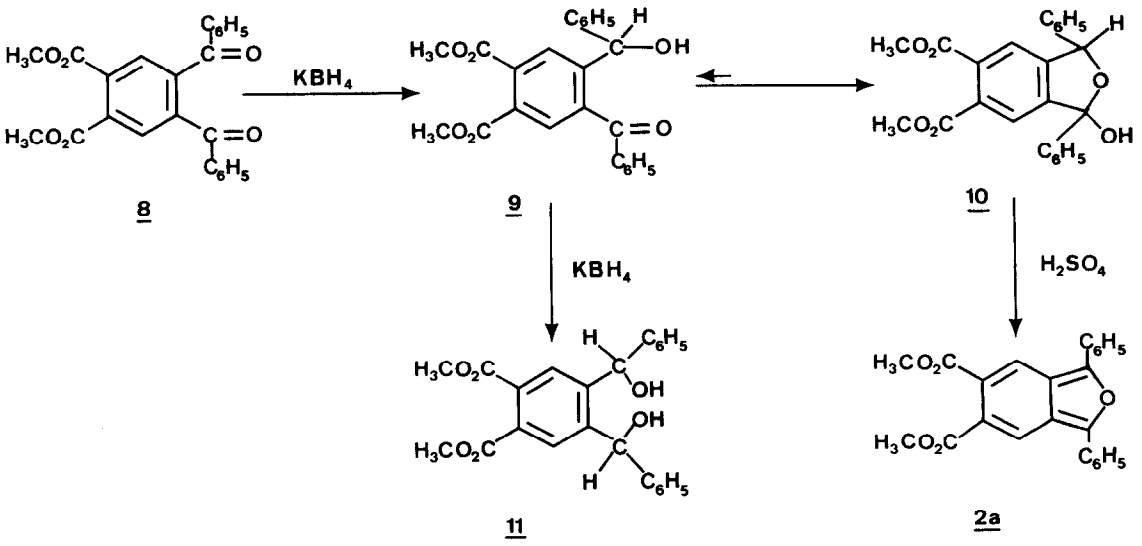
In the following steps (Scheme 3) the diketone **8** is partially reduced to keto-alcohol **9** which is then dehydrated to furan **2a**. Both steps can be performed by reduction of 1,2 - dibenzoylbenzenes with zinc followed by dehydration in acetic acid.[15] This method which generally gives poor and irreproducible results could not be used in our case owing to the possible hydrolysis of the methoxycarbonyl groups. Instead, we adapted the more recent procedure developed by Cava:[16] the diketone **8** was first partially reduced by methanolic potassium borohydride to the keto-alcohol **9** which underwent rapid



Scheme 1.



Scheme 2.



Scheme 3.

equilibration to the "phthalan" **10**; this latter was then dehydrated by methanolic sulfuric acid to afford the furan **2a** (Scheme 3).

The reduction step must be performed quickly (1 min) to avoid the accumulation of **9** which could, in its turn, undergo reduction to the diol **11**; thus the sequence illustrated in Scheme 3 must be repeated several times until **8** has been completely transformed to **2a**. Return to the basic conditions, needed to perform reductions, was achieved by adding methanolic sodium methoxide. In these conditions, little or no hydrolysis occurred and furan **2a** was obtained in high yield (90%).

Treatment of this latter compound with methanolic potassium hydroxide afforded the corresponding potassium salt **2d** in quantitative yield.

Access to 6,7 - *dimethyl* -, 6,7 - *dimethoxycarbonyl* - *and unsubstituted* 9,10 - *diphenyl* - 2,3 - *dimethoxycarbonyl anthracenes* **1a**, **1b** *and* **1c**

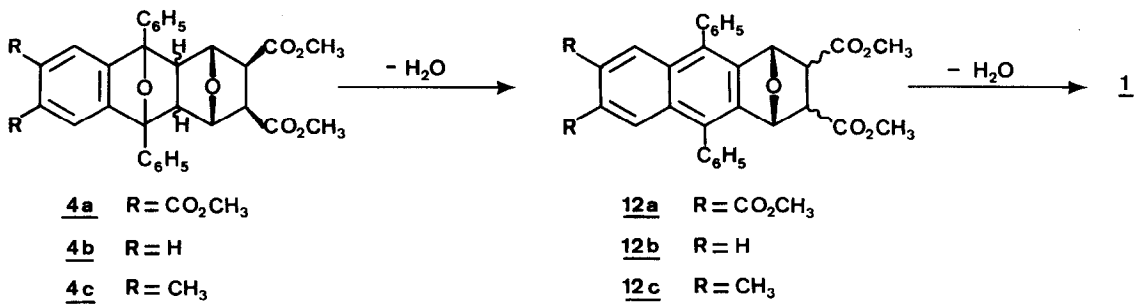
The second part of this synthesis, illustrated in Scheme 1, is concerned with the construction of the anthracene skeleton itself by the new method starting with the cycloaddition of 1,3 - diphenylisobenzofurans **2** with the dienophile **3**. Oxabenzonorbornadiene,[17] like norbornadiene,[18] shows, in cycloaddition reactions with activated dienes such as 1,3 - diphenylisobenzofuran, an unexpected reactivity which has generally been attributed to the five-membered ring strain. Dimethyl *cis* - *exo* - 7 - oxabicyclo[2.2.1] - 5 - heptene - 2,3 - dicarboxylate **3** behaved similarly and was found to react slowly (two days) in refluxing chloroform with the substituted 1,3 - diphenylisobenzofurans **2a–2c** to afford the adducts **4a** (90%), **4b** (92%) and **4c** (89%) as a mixture of stereoisomers,† the separation of which was not needed to complete the synthesis.

This reaction is necessarily performed at a relatively low temperature since above 80°C **3** starts dissociating to produce furan and dimethyl maleate, a highly reactive dienophile which could also react with **2**.

The preceeding temperature requirement limits the synthetic applications of **3** and thus only very electron-rich or very electron-deficient[19] dienes can be expected to react with this unactivated dienophile at reasonable rates.[20] With other less reactive dienes, cycloaddition is less likely, but should still be attainable using high pressure devices.[21] The aromatisation to the anthracenes **1a–1c** was effected by a two steps dehydration of the adducts **4a–4c** as illustrated in Scheme 4.

The first step leading to monoepoxides **12** was readily performed under a wide range of conditions including CH_3OH/HCl at 70°C or P_2O_5 in CH_2Cl_2 (86–93%) at room temperature; during this latter process a partial epimerisation of the methoxycarbonyls occurred.[22] On

†See experimental part.



Scheme 4.

the other hand the second step proved impossible to achieve under the previous conditions: a possible explanation would be that the intermediate carbonium ion did not benefit by the stabilizing effect of the phenyl groups which was operative previously.

Yet, under more drastic conditions, such as concentrated sulfuric acid in methylene chloride at 0°C, it has been possible to obtain the anthracenes **1a–1c** in fair yields (65–80%) directly from **4**.

In another attempt to dehydrate the adducts **4a**, we used hydrobromic acid in boiling acetic acid; in this case, we observed a rapid hydrolysis of the methoxycarbonyl groups and the formation of a by-product **13** in 20% yield.

This phenomenon which has already been observed in similar cases can be explained in terms of an epoxy cleavage assisted decarboxylation[22] (Scheme 5).

Treatment of the tetraester **1a** with methanolic potassium hydroxide afforded the corresponding potassium salt **1d** in quantitative yield.

CONCLUSION

The present synthetic work outlines a new access to aromatic hydrocarbon derivatives bearing methoxycarbonyl groups using a readily available synthon dimethyl 7 - oxabicyclo[2.2.1] - 5 - heptene - 2,3 - dicarboxylate.

This methodology proved highly useful and enabled us to prepare two water soluble $^1O_2$ traps namely dipotassium 1,3 - diphenylisobenzofuran - 5,6 - dicarboxylate and tetrapotassium 9,10 - diphenylanthracene - 2,3,6,7 - tetracarboxylate without any chromatographic separation.

EXPERIMENTAL

The IR spectra were recorded on a Perkin–Elmer 297 spectrophotometer; NMR spectra were determined on a Varian EM 390 spectrometer in $CDCl_3$ soln. (unless specified otherwise) with chemical shifts reported in δ units downfield from internal TMS. Mass spectra were determined on a AEI MS 30 spectrometer. All m.ps are uncorrected and were determined on a Maquenne bloc.

Dimethyl *cis* - *exo* - 7 - oxabicyclo[2.2.1] - 5 - heptene - 2,3 - dicarboxylate **3** was prepared in two steps starting from furan and maleic anhydride according to Jolivet,[11] m.p. 119°C with decomposition. 1,2 - Dibenzoyl - 4,5 - dimethylbenzene **5** was prepared in two steps, starting from 2,3 - dimethyl - 1,3 - butadiene and *trans* - dibenzoylethylene according to Adams,[15] m.p. 144°C. 5,6 - Dimethyl - 1,3 - diphenylisobenzofuran **2c** was prepared in 86% yield by reduction of **5** according to Cava's procedure,[16] m.p. 188°C, and 1,3 - diphenylisobenzofuran **2b** was the commercially available reagent. In all cases, we obtained the yields previously reported.

4,5 - Dibenzoylphthalic acid **6**

12.6 g (0.04 mole) of finely powdered **5**[15] were added to a stirred soln of 23.5 g (0.082 mole) of $Na_2Cr_2O_7$, 2 H_2O in 125 cm^3 water buffered with 15.5 g (0.1 mole) of NaH_2PO_4. 2 H_2O. The suspension thus obtained was quickly introduced in a stainless steel autoclave (P_{max} = 300 atm.) of 250 cm^3. The vessel was then heated to 240°C (P = 60 atm.) for 15 hr under rocking. After cooling to room temperature, the reaction mixture was treated with excess aqueous NaOH, with charcoal and filtered. Upon evaporation of water *in vacuo*, the filtrate yielded a yellow syrup which deposited tiny crystals on acidification with conc. HCl.

After washing with cold water and drying 14.25 g (95%) of crude **6** containing up to 10% of **7** were obtained. An analytical sample of **6** was prepared by recrystallisation from acetic acid. m.p. 228–230°C; IR (KBr) ν_{max} 3450–2750, 1700, 1650, 1275 cm^{-1}. NMR (DMSO) δ 7.93 (s, 2H, on carbons 3,6); 7.35–7.85 (m, 10H, aromatic). (Found: C, 70.44; H, 3.89. Calc. for $C_{22}H_{14}O_6$: C, 70.58; H, 3.77%).

Dimethyl 4,5 - *dibenzoylphthalate* **8**

5 g of crude **6** were treated with excess diazomethane. After evaporation *in vacuo*, the residue was crystallised in cyclohexane containing 5% of $CHCl_3$. The precipitate 4.8 g (90%) was recrystallised twice from methanol to yield an analytical sample. m.p. 138°C; IR (KBr) ν_{max} 2950, 1725, 1655, 1250, 1120, 715 cm^{-1}. NMR δ 7.95 (s, 2H, on carbons 3,6); 7.3–7.8 (m, 10H, aromatic); 3.95 (s, 6H, OCH_3). (Found: C, 71.59; H, 4.62. Calc. for $C_{24}H_{18}O_6$: C, 71.64; H, 4.51%).

Methyl 3,4 - *dibenzoylbenzoate*

It remains in the preceeding mother liquors from which it can be separated through chromatography over silica gel using CH_2Cl_2 - Et_2O (9.5/0.5) as eluent. m.p. 135°C; IR (KBr) ν_{max} 2950, 1720, 1430, 1250, 1115, 700 cm^{-1}. NMR δ 8.2–8.3 (m, 2H, aromatic); 7.2–7.8 (m, 11H, aromatic); 3.95 (s, 3H, OCH_3); *m/e* 344 (M^+).

Dimethyl 1,3 - *diphenylisobenzofuran* - 5,6 - *dicarboxylate* **2a**

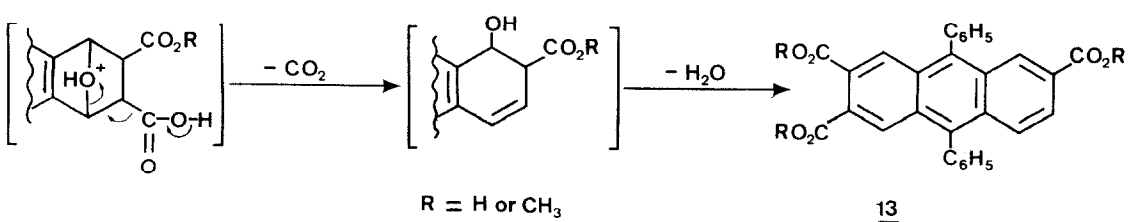
1.5 g of **8** (3.7 mmol) in 80 ml refluxing anhydrous MeOH were treated with 10 ml of a 0.5% KBH_4 soln in MeOH. After 1 min, excess borohydride was destroyed by the addition of 4.5 *N* H_2SO_4 in MeOH (1 ml). After stirring and refluxing the soln for 10 min, the reaction mixture was made basic by the addition of 4.5 *N* CH_3ONa in MeOH (1 ml) and a second 10 ml portion of borohydride soln was added. Reduction was again allowed to proceed for 1 min and then stopped as before. The entire cycle was repeated several times (10 times) until **8** had disappeared by tlc. Most of the methanol was then removed *in vacuo* and the chilled reaction mixture was poured onto ice-water. The precipitate was filtered with suction and washed several times with water (to remove Na_2SO_4).

The product was dried *in vacuo* over P_2O_5 to give 1.3 g (91%) of yellow crystals: m.p. 180°C; IR (KBr) ν_{max} 2950, 1715, 1245, 685 cm^{-1}. NMR δ 8.23 (s, 2H, on carbons 4,7); 7.3–8.0 (m, 10H, aromatic); 3.90 (s, 6H, OCH_3). (Found: C, 74.48; H, 4.79. Calc. for $C_{24}H_{18}O_5$: C, 74.60; H, 4.70%).

Dipotassium 1,3 - *diphenylisobenzofuran* - 5,6 - *dicarboxylate* **2d**

A solution of 185 mg (0.48 mmol) of **2a** in 5 ml of tetrahydrofuran free of peroxide and 28 ml of methanolic potassium hydroxide (1 *M*) was refluxed under argon, in the dark, for 30 min. The precipitate was collected and washed with absolute methanol leading quantitatively to potassium salt **2d**. IR (KBr) ν_{max} 1550, 1390, 800, 760, 750 cm^{-1}. NMR δ (D_2O/DSS)† 7.87 (s, 2H, aromatic); 7.2–7.7 (m, 10H, aromatic).

†DSS = Sodium 4,4 - dimethyl - 4 silapentanesulfonate.



R = H or CH_3 13

Scheme 5.

Tetramethyl 9,10 - *diphenyl* - 1,4;9,10 - *diepoxy* - 1,2,3,4,-4*a*,9,9*a*,10 - *octahydroanthracene* - 2,3,6,7 - *tetracarboxylate* **4a** *and related compounds* **4b** *and* **4c**

A soln of 773 mg of **2a** (2 mmol) and 450 mg of **3** (2.1 mmol) in chloroform was refluxed under N_2. After 2 days, the green fluorescence had disappeared and the solvent was removed *in vacuo*. Further treatment with diisopropyl oxide induced precipitation; filtration and washing with pentane yielded a white powder 1.08 g (90%). **4a**: m.p. of the mixture (decomp.) 265°C; IR (KBr) ν_{max} 2950, 1730, 1430, 1275, 1010, 705 cm^{-1}. (Found: C, 68.40; H, 4.89. Calc. for $C_{34}H_{30}O_{10}$: C, 68.22; H, 5.05%).

NMR, two isomers 80/20.

1*st Isomer*; δ 7.2–7.8 (m, 12 H, aromatic); 4.60 (s, 2H, bridgehead proton); 3.85 (s, 6H, aromatic methoxycarbonyl); 3.53 (s, 6H, methoxycarbonyl); 2.88 (s, 2H, α of methoxycarbonyl); 2.55 (s, 2H, on carbons 4a and 9a).

2*nd Isomer*. δ 7.2–7.8 (m, 12H, aromatic); 4.65 (s, 2H, bridgehead proton; 3.90 (s, 6H, aromatic methoxycarbonyl); 3.63 (s, 6H, methoxycarbonyl); 3.07 and 3.00 (2s, 2H α of methoxycarbonyl and 2H on carbons 4a and 9a).

4b and **4c** were prepared in the same way from **2b** and **2c** in 92% and 89% yield, respectively. They are both thermally unstable and dissociate above 150°C.

4b: m.p. of the mixture (decomp.) 273°C; IR (KBr) ν_{max} 2950, 1725, 1270, 1170, 1020 cm^{-1}. (Found: C, 74.43; H, 5.69. Calc. for $C_{30}H_{26}O_6$: C, 74.67; H, 5.43%).

NMR, two isomers 85/15

1*st Isomer*. δ 7.4–7.8 (m, 10H, aromatic); 7.10 (s, 4H, on carbons 5,6,7,8); 4.57 (s, 2H, bridgehead proton); 3.53 (s, 6H, methoxycarbonyl); 2.87 (s, 2H, α of methoxycarbonyl); 2.55 (s, 2H, on carbons 4a and 9a).

2*nd Isomer*. δ 7.4–7.8 (m, 10H, aromatic); 7.10 (s, 4H, on carbons 5,6,7,8); 4.62 (s, 2H, bridgehead proton); 3.60 (s, 6H, methoxycarbonyl); 2.99 and 2.96 (2s, 2H in α of methoxycarbonyl and 2H on carbons 4a and 9a).

4c: m.p. of the mixture (decomp.) 280°C; IR (KBr) ν_{max} 2950, 1720, 1160, 1015, 755, 705, 695 cm^{-1}. (Found: C, 75.41; H, 6.05. Calc. for $C_{32}H_{30}O_6$: C, 75.27; H, 5.92%).

NMR, two isomers 60/40

1*st Isomer*. δ 7.3–7.8 (m, 10H, aromatic); 6.83 (s, 2H, carbons 5,8); 4.50 (s, 2H, bridgehead proton); 3.47 (s, 6H, methoxycarbonyl); 2.80 (s, 2H, α of methoxycarbonyl); 2.50 (s, 2H, on carbons 4a and 9a); 2.10 (s, 6H, aromatic methyl).

2*nd Isomer*. δ 7.3–7.8 (m, 10H, aromatic); 6.60 (s, 2H, on carbons 5,8); 4.57 (s, 2H, bridgehead proton); 3.57 (s, 6H, methoxycarbonyl); 2.90 and 2.87 (2s, 2H α of methoxycarbonyl and 2H, on carbons 4a and 9a); 2.07 (s, 6H, aromatic methyl).

Tetramethyl 9,10 - *diphenyl* - 1,4 - *epoxy* - 1,2,3,4 - *tetrahydroanthracene* - 2,3,6,7 - *tetracarboxylate* **12a** *and related compounds* **12b** *and* **12c**

A soln of 1.10 g of the adduct **4a** in dichloromethane (50 ml) was stirred at room temperature with 0.3 g P_2O_5. After 5 hr, the adduct **4a** was totally transformed into the epoxyanthracene **12a** (two isomers). The reaction mixture was treated cautiously with methanol, washed with aqueous $NaHCO_3$, with water and dried. Evaporation afforded white crystals of **12a**, 0.96 g (86%) which were recrystallised from methanol. **12a**: m.p. of the mixture 264°C; IR (KBr) ν_{max} 2950, 1720, 1430, 1280, 1050, 700 cm^{-1}. (Found: C, 70.22; H, 5.00. Calc. for $C_{34}H_{28}O_9$: C, 70.34; H, 4.86%).

NMR, two isomers 60/40

1*st Isomer*. δ 8.2 (s, 2H, on carbons 5,8); 7.3–7.6 (m, 10H, aromatic); 5.6 (s, 2H, bridgehead proton); 3.8 (s, 6H, aromatic methoxycarbonyl); 3.65 (s, 6H, methoxycarbonyl); 3.2 (s, 2H, α of methoxycarbonyl).

2*nd Isomer*. δ 8.17 (d, 2H, on carbons 5,8); 7.3–7.6 (m, 10H, aromatic); 4.55–4.65 (m, 2H, bridgehead proton); 3.60–3.80 (m, 12H, methoxycarbonyl); 2.95–3.10 (m, 2H, α of methoxycarbonyl).

12b and **12c** were obtained in the same way from **4b** and **4c** in 93% and 90% yield, respectively.

12b: m.p. of the mixture 204°C; IR (KBr) ν_{max} 2950, 1720, 1430, 1270, 1190, 1015, 770, 745, 700 cm^{-1}. (Found: C, 77.42; H, 5.15. Calc. for $C_{30}H_{24}O_5$: C, 77.57; H, 5.20%).

NMR, two isomers 60/40

1*st Isomer*. δ 6.8–7.9 (m, 14H, aromatic); 5.58 (s, 2H, bridgehead proton); 3.68 (s, 6H, methoxycarbonyl); 3.22 (s, 2H, α of methoxycarbonyl).

2*nd Isomer*. δ 6.8–7.9 (m, 14H, aromatic); 4.63 (s, 2H, bridgehead proton); 3.63 (s, 6H, methoxycarbonyl); 3.00 (d, 2H, α of methoxycarbonyl).

12c: m.p. of the mixture 214°C; IR (KBr) ν_{max} 2950, 1725, 1270, 1165, 695 cm^{-1}. (Found: C, 78.03; H, 5.69. Calc. for $C_{32}H_{28}O_5$: C, 78.03; H, 5.73%).

NMR, two isomers 70/30

1*st Isomer*. δ 7.3–7.7 (m, 12H, aromatic); 5.53 (s, 2H, bridgehead proton); 3.67 (s, 6H, methoxycarbonyl); 3.19 (s, 2H, α of methoxycarbonyl); 2.27 (s, 6H, aromatic methyl).

2*nd Isomer*. δ 7.3–7.7 (m, 12H, aromatic); 4.60 (s, 2H, bridgehead proton); 3.62 (s, 6H, methoxycarbonyl); 2.93 (s, 2H, α of methoxycarbonyl); 2.12 (s, 6H, aromatic methyl).

Tetramethyl 9,10 - *diphenylanthracene* - 2,3,6,7 - *tetracarboxylate* **1a** *and related compounds* **1b** *and* **1c**

A soln of 1.10 g of the adduct **4a** in dichloromethane (40 ml) containing 0.4 g sulfuric acid was stirred under ultrasonic agitation at a temperature below 10°C. After 6 hr, the fluorescent soln was treated with methanol, washed with aqueous $NaHCO_3$, with water, and dried. Evaporation yielded a yellow syrup which crystallised in methanol. Two recrystallisations afforded **1a** in 65% yield.

1a: m.p. 361°C (melting point is not depressed by mixing with an authentic sample[7]); IR (KBr) ν_{max} 2950, 1710, 1425, 1260, 1120, 1040, 810, 780, 695 cm^{-1}. NMR δ 8.20 (s, 4H, on carbons 1,4,5,8); 7.43–7.83 (m, 10H, aromatic); 3.85 (s, 12H, methoxycarbonyl).

The dehydration reaction proceeded more readily with **4b** and **4c** to afford the anthracenes **1b** and **1c** in 80% and 76% yield respectively.

1b: m.p. 199°C (melting point is not depressed by mixing with an authentic sample[24]); IR (KBr) ν_{max} 2940, 1720, 1265, 1125, 775, 700 cm^{-1}. NMR δ 8.17 (s, 2H, on carbons 1,4); 7.35–7.85 (m, 14H, aromatic); 3.85 (s, 6H, methoxycarbonyl).

1c: m.p. 265°C; IR (KBr) ν_{max} 2940, 1715, 1265, 1120, 760, 695 cm^{-1}. NMR δ 8.08 (s, 2H, on carbons 1,4); 7.37–7.75 (m, 12H, aromatic); 3.82 (s, 6H, methoxycarbonyl); 2.32 (s, 6H, methyl). (Found: C, 80.95; H, 5.42. Calc. for $C_{32}H_{26}O_4$: C, 80.99; H, 5.52%).

Trimethyl 9,10 - *diphenylanthracene* - 2,3,6 - *tricarboxylate* **13**

The adduct **4a** (100 mg) was treated with 2 ml acetic acid containing 0.5 ml fuming hydrobromic acid. After refluxing for 1 hr, the solution was chilled, treated cautiously with aqueous $NaHCO_3$, extracted with ether, dried over $MgSO_4$ and treated with excess diazomethane. Usual treatment yielded a yellow syrup which was chromatographed over silica gel to afford **4a** (30%), **12a** (25%) and **13** (20%), m.p. 238°C; IR (KBr) ν_{max} 2940, 1710, 1430, 1255, 1125, 780, 760, 750, 700 cm^{-1}. NMR δ 7.3–8.5 (m, 15H, aromatic); 3.87 (s, 3H, methoxycarbonyl on carbon 6); 3.83 (s, 6H, methoxycarbonyls on carbons 2,3). m/e = 504 (M^+).

Tetrapotassium 9,10 - *diphenylanthracene* - 2,3,6,7 - *tetracarboxylate* **1d**

A soln of 200 mg (0.36 mmol) of **1a** in 5 ml of dioxane and 30 ml of methanolic potassium hydroxide (1 *M*) was refluxed for 30 min. The precipitate was collected and washed with absolute methanol leading quantitatively to potassium salt **1d**. IR (KBr) ν_{max} 1550, 1450, 1430, 1360, 820, 700 cm^{-1}. NMR δ (D_2O/DSS) 7.85 (s, 4H, on carbons 1,4,5,8); 7.50–7.85 (m, 10H, aromatic).

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