Photochemical Synthesis of Carbon-14 Labelled Dibenz[*a,h*]anthracene

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Carrier-free [5,12-^{14}C]dibenz[*a,h*]anthracene (DBA, **12***) has been prepared for the first time using [^{14}C]methyl iodide as the source of the label. The key step in this radiosynthesis consisted of the regiospecific photocyclization of 2',5'-divinyl-1,1':4',1''-terphenyl **10*** to 5,6,12,13-tetrahydro-DBA **11*** followed by dehydrogenation to **12*** with DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone). Divinylterphenyl **10*** was obtained from 2',5'-bis(bromomethyl)-1,1':4',1''-terphenyl **3** *via* the diformyl derivative **9** and its Wittig olefination with the triphenylphosphonium salt of $^{14}CH_3I$. Thus **12*** was synthesized with a radiochemical purity exceeding 99%. The chemical yield amounted to 58% from **9** in the case of **12*** with a specific activity of 391 MBq mmol^{-1} and to 12% in the case of carrier-free **12*** with a specific activity of 4.14 GBq mmol^{-1}. Wide applicability of this radiosynthetic approach to the preparation of many other carbon-14 labelled polycyclic aromatic hydrocarbons can be envisaged.

Lipophilic drugs and other xenobiotics entering the body must be enzymatically transformed to hydrophilic metabolites in order to be easily excreted. During this biotransformation biologically inactive metabolites can be formed but in some cases activation to cytotoxic, mutagenic or carcinogenic metabolites may also be encountered. Thus the study of biotransformation of foreign compounds is of great pharmacological and toxicological relevance.

For the investigation of a biotransformation, the substrate in question and its metabolites have to be traced in the body or in other complex biological systems with high selectivity and sensitivity. This has been achieved by applying radioactively labelled compounds containing tritium or carbon-14 in most cases.

These substrates and their metabolites are not only easily detected by liquid scintillation counting but can also be conveniently quantified, even in the case of metabolites of unknown structure, provided that the label is not lost during biotransformation. This can usually be prevented by introducing the radioactive isotope as part of a hydrocarbon moiety, but even under these circumstances tritium is sometimes enzymatically removed.[1] Thus substrates labelled with carbon-14 are generally preferred for the study of biotransformation.

Dibenz[*a,h*]anthracene (DBA, **12**) is a polycyclic aromatic hydrocarbon (PAH) of considerable carcinogenic activity[2] occurring in the environment as the result of incomplete combustion of organic matter.[3] Investigation concerning the biotransformation of DBA[4,5] and the covalent binding of its metabolites to DNA required the carbon-14 labelled PAH. Since it is not commercially available we have devised a suitable radiosynthesis.

[7-^{14}C]-DBA has been prepared in low yield and unknown isomeric purity from [*carbonyl*-^{14}C]-1-(2-naphthoyl)-2-methylnaphthalene by the Elbs reaction using barium [^{14}C]-carbonate as the source of the label.[6] In a further radiosynthetic approach [7-^{14}C]-DBA was obtained regioselectively in a fair yield by cyclization of [carbonyl-^{14}C]-2-(1-naphthylmethyl)-1-naphthoic acid followed by aromatization.[7] Neither radiosynthesis suited our needs because of the cumbersome work involving gaseous $^{14}CO_2$ and due to the fact that neither the radiochemical yield nor the specific radioactivity were impressively high. We therefore devised a synthetic pathway which overcame all three shortcomings in only three radioactive stages leading to carrier-free [5,12-^{14}C]-DBA **12***.†

Results and Discussion

The radiosynthesis of [^{14}C]-DBA had to meet three objectives: (i) regiospecific construction of the DBA skeleton, (ii) introduction of at least two carbon-14 atoms to obtain high specific activity, (iii) few radioactive steps with high radiochemical yields. For the introduction of the label we considered the use of K^{14}CN, $(^{14}CH_2O)_n$ and $^{14}CH_3I$ which are all carrier-free commercially available.

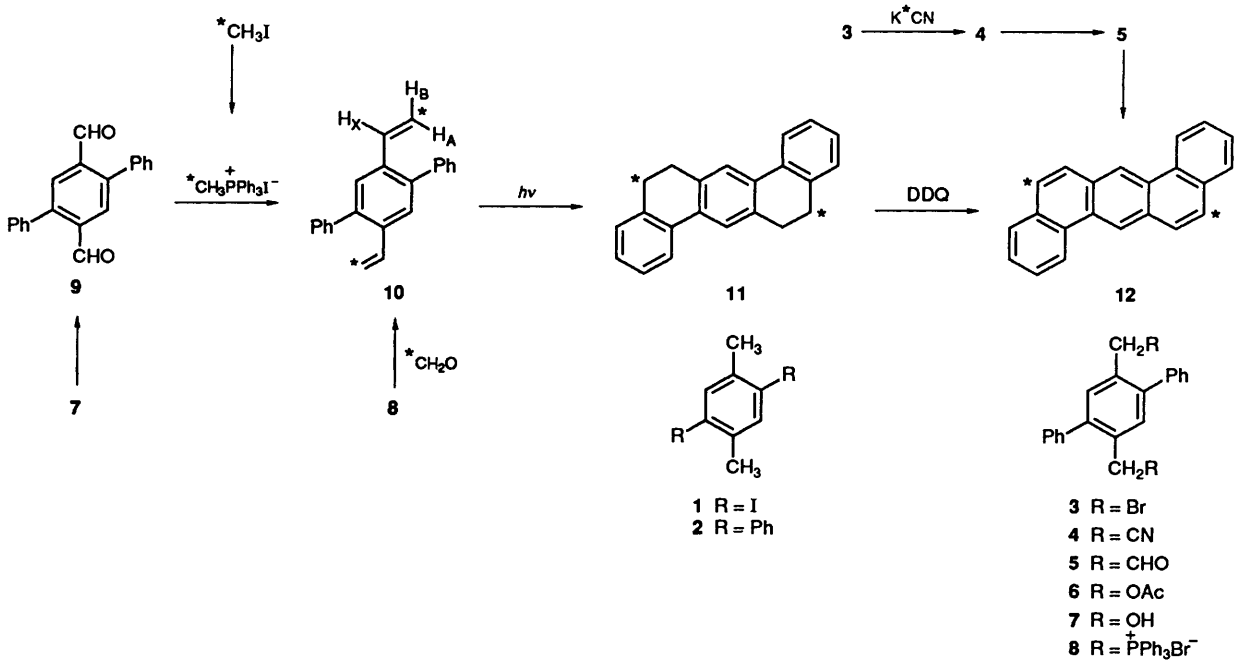
For the construction of the DBA skeleton two approaches were attempted; cyclodehydration of bisacetaldehyde **5** (*cf.* Scheme 1), a reaction also used for the synthesis of other PAH,[8] and photocyclization of divinylterphenyl **10** in a similar manner as previously applied for the formation of the 9,10-dihydrophenanthrene moiety.[9,10]

The starting compound for both synthetic routes is **3** which can be obtained from *p*-xylene in three steps *via* iodination to **1**,[11] coupling with the Grignard reagent of bromobenzene catalysed by a nickel salt[12] yielding **2** followed by NBS (*N*-bromosuccinimide) bromination. The product of the latter reaction contained not only bromomethyl groups but also variable amounts of dibromomethyl (5–15 mol%) and unsubstituted methyl groups (2–8 mol%) a situation that could not be changed reproducibly in favour of **3** by varying the ratio of the reactants. Purification of **3** by recrystallization resulted in considerable loss, however **3** could be employed for the subsequent reactions as the crude product.

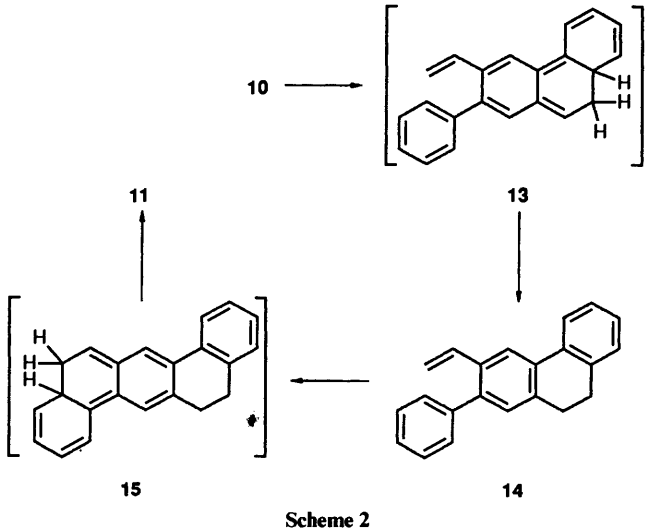
As a model reaction for introducing carbon-14 with K^{14}CN, **3** was transformed to **4** using the phase-transfer modification[8] of the Kolbe nitrile synthesis.[13] Reduction of the dinitrile to the dialdehyde **5** with diisobutylaluminium hydride and subsequent cyclodehydration with polyphosphoric acid, however, resulted in a very low yield (≈1%) of DBA making this pathway not feasible for the efficient synthesis of [5,12-^{14}C]-DBA.

Consequently $(^{14}CH_2O)_n$ was employed as source of the label. For this purpose **3** was quaternized to the bis(triphenylphosphonium) salt **8** which underwent a Wittig olefination[14] in high yield to **10** using the phase-transfer conditions introduced by Märkl and Merz.[15] The divinylterphenyl **10** as a solution in benzene was then irradiated with a 200 W lamp under anaerobic conditions for 6 d leading to **11** in 64% yield. The mechanism of

† Compound numbers marked with an asterisk designate carbon-14 labelling.



Scheme 1 Asterisks denote positions of carbon-14



Scheme 2

this photocyclization can be explained as outlined in Scheme 2:[9] successive intramolecular cycloaddition of the vinyl groups in **10** leading to the intermediates **13** and **15**, respectively, which are stabilized by a rapid 1,5-sigmatropic shift of their tertiary hydrogens resulting finally in **11**. 2-Phenyl-3-vinyl-9,10-dihydrophenanthrene **14** was not isolated, however GC analysis of the photocyclization furnished an indication of its formation: after short irradiation time the peak of **10** in the gas chromatogram had disappeared giving rise to a new peak which in turn disappeared very slowly being converted to the peak of tetrahydro-DBA **11**. Thus the photoreaction of divinylterphenyl **10** resembles the reported successive intramolecular cycloaddition of two vinyl groups in the biphenyl system.[16] Dehydrogenation of **11** with DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) produced DBA **12** in good yield.

Wittig olefination of **8** with [^{14}C]-paraformaldehyde (0.3 mmol), photocyclization and dehydrogenation as described above furnished [5,12-^{14}C]-DBA, however in very low yield (3.1%). Due to the rather high cost of $(^{14}CH_2O)_n$ the reason for this failure was not investigated further but the introduction of the label with $^{14}CH_3I$ *via* the triphenylphosphonium iodide and the dialdehyde **9** (*cf.* Scheme 1) was tried.

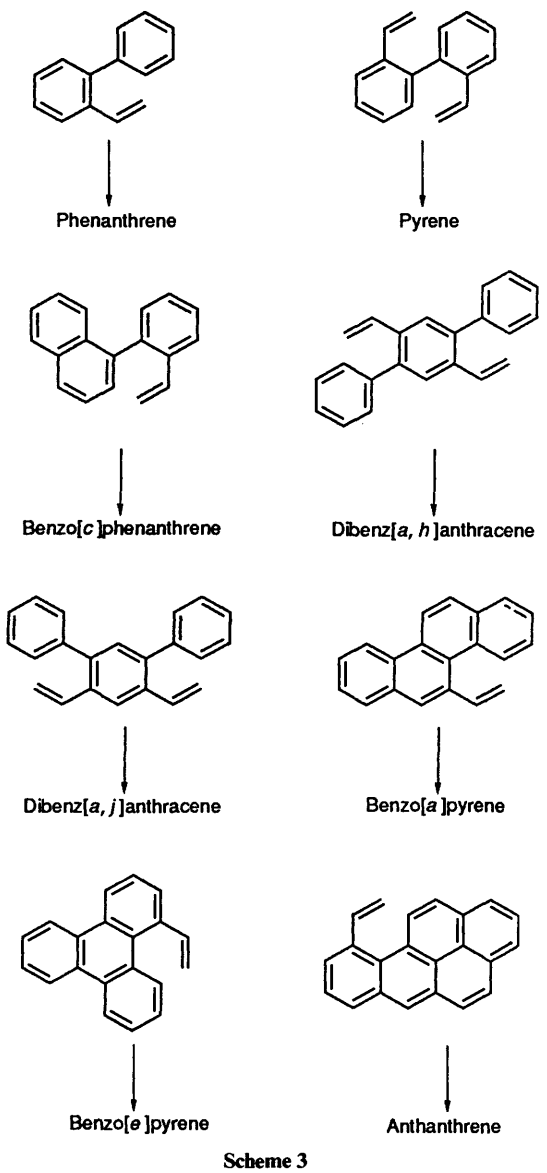
Dialdehyde **9** was first obtained from **3** by the Sommelet reaction[17] but with low and very variable yields; this might be caused by steric hindrance of the *ortho*-phenyl groups as has been reported in the case of 2,2′-bischloromethylbiphenyl.[18] Therefore an efficient synthetic detour was chosen: crude **3** was converted *via* the diacetate **6** into the dialcohol **7**. The dialcohol could be oxidized with NaOCl under phase-transfer conditions[19] to a mixture of the mono- and di-aldehyde **9** (1:2) in high yield. Complete conversion of **7** into **9** was achieved with pyridinium chlorochromate.[20]

Dialdehyde **9** was then transformed to the divinylterphenyl **10** with the phosphine alkylene from methyltriphenylphosphonium iodide. The convenient phase-transfer modification[15] of the Wittig olefination formerly used for the transformation of **8** into **10** was not very efficient in the latter case. This is probably due to the lower stability in aqueous solution of the triphenylphosphoranes as compared to benzylidenetriphenylphosphoranes.[15] However, by employing the classic conditions of the Wittig olefination[14] (phenyllithium, aprotic solvent) conversion of **9** into **10** was achieved in high yield.

Finally, the knowledge obtained with the unlabelled compounds could successfully be applied to the radiosynthesis of DBA: **12*** was obtained in radiochemical purity exceeding 99%; the chemical yield (from **9**) ranged from 58% in the case of **12*** with a specific activity of 391 MBq mmol^{-1} to 12% in the case of carrier-free **12*** (specific activity 4.14 GBq mmol^{-1}), the low yield in the latter case probably being the result of technical problems with the microscale reaction.

Carbon-14 labelled DBA **12*** thus obtained could successfully be applied for further studies concerned with the biotransformation of this PAH.[21] Moreover, **12*** was employed for investigations aiming towards elucidating the quantity and structure of DNA adducts of enzymatically activated DBA *in vitro*[22] and *in vivo*.

It can be envisaged that the radiosynthetic pathway reported here could easily be adapted to the synthesis of a large variety of other isotopic carbon labelled and unlabelled PAH containing the structural element of phenanthrene as depicted



Scheme 3

in Scheme 3. Since virtually all PAH besides the linearly annelated members of this class fulfil this requirement our synthetic approach can be expected to have a very general application.

Experimental

General Methods.—Bis(triphenylphosphine)nickel(II)chloride, pyridinium chlorochromate and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) were obtained from Aldrich (Steinheim, Germany). Aliquat 336 (trioctylammonium chloride) and phenyllithium in benzene–Et_2O (70:30) were supplied by Fluka (Neu-Ulm, Germany). [^{14}C]-Methyl iodide (specific activity: 2.072 GBq mmol^{-1}) and [^{14}C]-paraformaldehyde were purchased from Amersham Buchler (Braunschweig, Germany). All other chemicals used were of the highest commercial quality and were used without further purification.

^{1}H NMR spectra were obtained on a Varian EM 360 spectrometer at 60 MHz; chemical shifts (δ_H) are given in ppm downfield from $SiMe_4$ as an internal standard. *J* Values are given in Hz. Electron impact mass spectra were obtained with a Varian CH7A mass spectrometer at 70 eV. GC chromatograms were run with a Packard 427 chromatograph on a 2 m column with 3% OV-17 on Chromosorb WAW-DMCS as the stationary phase using FI-detection. HPLC separations were carried out with a Spectra Physics SP 8700/8750 LC system fitted to an LKB 2140 diode array detector. The radiochemical purity of **12*** was determined by HPLC as previously described;[23] it is given as the percentage of total radioactivity of a chromatographic run that is eluted within the same elution volume as the pure unlabelled compound. M.p. were determined in open capillary tubes with a Büchi 510 melting point apparatus and are uncorrected.

1,4-*Diiodo*-2,5-*dimethylbenzene* **1**.—Xylene (26.5 g, 0.25 mol), H_5IO_6 (22.8 g, 0.1 mol) and iodine (51.0 g, 0.2 mol) were added to a solution of conc. H_2SO_4 (15 cm^3) and water (100 cm^3) in glacial acetic acid (500 cm^3). The resulting purple solution was stirred at 70 °C for 3 h, then cooled to 0 °C and the precipitate isolated by filtration. Recrystallization (MeOH–$CHCl_3$) yielded compound **1** (66.3 g, 74%) as white needles, m.p. 103 °C (lit.,[11] 103–104 °C); δ_H($CDCl_3$) 2.25 (6 H, s, CH_3) and 7.52 (2 H, s, Ar H); *m/z* 358 (M^+, 100%), 231 (M − I, 26.2), 104 (M − 2 I, 72.1) and 77 (30.9).

2′,5′-*Dimethyl*-1,1′:4′,1″-*terphenyl* **2**.—Magnesium turnings (4.84 g, 0.2 mol) in dry Et_2O (20 cm^3) were treated with a solution (10 cm^3) of bromobenzene (31.6 g, 0.2 mol) in dry Et_2O (80 cm^3). After the exothermic start of the reaction the remainder of the above solution was added in such a way that gentle refluxing continued. The mixture obtained was heated to reflux for a further 2 h and then cooled to room temperature. $NiCl_2(Ph_3P)_2$ (1.2 g, 1.8 mmol) was added, followed by the addition of a solution of **1** (28.8 g, 80 mmol) in dry Et_2O (200 cm^3) under reflux which was maintained for an additional 16 h. The resulting suspension was poured on ice (1 kg) and acidified with a mixture of water (100 cm^3) and conc. HCl (100 cm^3). The ethereal phase was separated and the aqueous phase extracted with Et_2O (3 × 200 ml). The combined organic phases were washed neutral with water and dried ($MgSO_4$). Removal of the drying agent by filtration, evaporation of the filtrate under reduced pressure and recrystallization of the residue from EtOH yielded compound **2** (14.3 g, 69%) as colourless crystals, m.p. 183 °C (lit.,[24] 182–184 °C); δ_H($CDCl_3$) 2.24 (6 H, s, CH_3), 7.10 (2 H, s, 3′,6′-H) and 7.33 (10 H, s, ArH); *m/z* 258 (M^+, 100%), 243 (M − CH_3, 13.9), 241 (10.7) and 228 (M − 2 CH_3, 6.2).

2′,5′-*Bis*(*bromomethyl*)-1,1′:4′,1″-*terphenyl* **3**.—A suspension of **2** (10.3 g, 40 mmol), *N*-bromosuccinimide (NBS) (14.2 g, 80 mmol) and benzoyl peroxide (100 mg) in CCl_4 (150 cm^3) was heated to reflux for 3 h and then cooled to room temperature. The precipitate (succinimide) was isolated by filtration and the filtrate concentrated to *ca.* 50 cm^3 under reduced pressure. Stirring overnight at 0 °C led to a white precipitate which was isolated by filtration yielding crude **3** (13.5 g) as a white crystalline powder, m.p. 160–162 °C; ^{1}H NMR spectroscopic analysis revealed the molar ratio of methyl:bromomethyl:dibromomethyl to be 5:85:10. After several recrystallizations from CCl_4, resulting in considerable loss, the pure *title compound* **3** was obtained as white crystals, m.p. 165 °C (Found: C, 57.5; H, 3.8; Br, 37.9. $C_{20}H_{16}Br_2$ requires C, 57.72; H, 3.88; Br, 38.40%); δ_H($CDCl_3$) 4.40 (4 H, s, CH_2Br) and 7.2–7.5 (12 H, m, Ar H); *m/z* 418 (M^+[^{81}Br,^{81}Br], 1.5%), 416 (M^+[^{79}Br,^{81}Br], 3.0), 414 (M^+[^{79}Br,^{79}Br], 1.5), 337 (M[^{81}Br,^{81}Br] − ^{81}Br; M[^{79}Br,^{79}Br] − ^{79}Br, 6.5) and 335 (M[^{79}Br,^{81}Br] − ^{81}Br; M[^{79}Br,^{79}Br] − ^{79}Br, 6.0).

2′,5′-*Bis*(*cyanomethyl*)-1,1′:4′,1″-*terphenyl* **4**.—A solution of crude **3** (8.3 g) in benzene (300 cm^3) was added to a solution of KCN (3.9 g, 60 mmol) and Aliquat 336 (1.5 g) in water (200 cm^3). The resulting mixture was stirred under reflux for 3 h and then cooled to room temperature. Following separation of the

organic phase the aqueous phase was extracted twice with benzene (100 cm^3). The combined organic phases were washed with water (5 × 100 cm^3), dried ($MgSO_4$) and the solvent was evaporated under reduced pressure. Chromatographic purification of the brown residue on silica gel eluting with $CHCl_3$–light petroleum (4:1) afforded the *title compound* **4** (2.7 g, 36% from **2**) as yellowish solid, m.p. 156 °C (Found: C, 85.8; H, 5.3; N, 8.95. $C_{22}H_{16}N_2$ requires C, 85.69; H, 5.23; N, 9.08%); $\delta_H(CDCl_3)$ 3.73 (4 H, s, CH_2CN) and 7.3–7.7 (12 H, m, ArH).

2′,5′-*Bis*(*acetoxymethyl*)-1,1′:4′,1″-*terphenyl* **6**.—A mixture of crude **3** (10.0 g) and dry sodium acetate (8.2 g, 0.1 mol) in glacial acetic acid (75 cm^3) was stirred under reflux for 22 h. After cooling to room temperature the reaction mixture was poured into water (400 cm^3) and the precipitate isolated by filtration. Chromatography on silica gel eluting with CH_2Cl_2 yielded the *title compound* **6** (6.9 g, 62% from **2**) as off-white solid, m.p. 125–126 °C (Found: C, 77.1; H, 6.0. $C_{24}H_{22}O_4$ requires C, 76.99; H, 5.92%); $\delta_H(CDCl_3)$ 2.00 (6 H, s, acetate CH_3), 5.05 (4 H, s, CH_2OAc) and 7.36 (12 H, s, ArH); *m*/*z* 374 (M^+, 34.0%), 272 (M − CH_3CO_2H − CH_2CO, 100) and 254 (43.5).

2′,5′-*Bis*(*hydroxymethyl*)-1,1′:4′,1″-*terphenyl* **7**.—A suspension of **6** (6.7 g, 17.9 mmol) in a mixture of MeOH (130 cm^3) and 15% (w/v) NaOH (18 cm^3) was stirred at 50 °C for 6 h. The reaction mixture was cooled to room temperature, poured into water (400 cm^3), the precipitate isolated by filtration, washed neutral with water and dried ($MgSO_4$). Recrystallization from CH_2Cl_2 afforded the *title compound* **7** (4.5 g, 87%) as a white solid, m.p. 180 °C (Found: C, 82.65; H, 6.2. $C_{20}H_{18}O_2$ requires C, 82.73; H, 6.25%); $\delta_H([^2H_8]$-dioxane) 3.58 (2 H, br s, OH), 4.58 (4 H, s, CH_2) and 7.4–7.7 (12 H, m, ArH); *m*/*z* 290 (M^+, 100%), 259 (12.3) and 241 (43.4).

1,1′:4′,1″-*Terphenyl*-2′,5′-*dicarbaldehyde* **9**.—A solution of **7** (14.5 g, 50 mmol) in CH_2Cl_2 (120 cm^3) was added to a suspension of pyridinium chlorochromate (23.7 g, 110 mmol) in CH_2Cl_2 (150 cm^3) and stirred for 2 h at room temperature. The reaction mixture was washed with water (3 × 200 cm^3) and dried ($MgSO_4$). Removal of the drying agent by filtration, evaporation of the filtrate under reduced pressure and purification of the residue by chromatography over neutral alumina (activity II–III) with CH_2Cl_2 yielded the *title compound* **9** (6.9 g, 48%) as yellowish solid, m.p. 191 °C (Found: C, 83.6; H, 5.15. $C_{20}H_{14}O_2$ requires C, 83.90; H, 4.92%); $\delta_H(CDCl_3)$ 7.46 (10 H, s, ArH), 8.06 (2 H, s, 3′,6′-H) and 10.04 (2 H, s, CHO); *m*/*z* 286 (M^+, 100%), 257 (M − CHO, 38.4) and 228 (M − 2 CHO, 28.7).

2′,5′-*Divinyl*-1,1′:4′,1″-*terphenyl* **10**.—*From* **3**. A solution of **3** (1.25 g, 3 mmol) and triphenylphosphine (1.57 g, 6 mmol) in DMF (*N*,*N*-dimethylformamide) (30 cm^3) was stirred at 90 °C for 2 h and at room temperature for a further 16 h. The resulting white suspension was diluted with Et_2O (40 cm^3); the precipitate was isolated by filtration, washed with $CHCl_3$ (40 cm^3) and Et_2O (20 cm^3) and dried ($MgSO_4$), yielding bis(triphenylphosphonium) salt **8** (2.77 g, 98%) as a white solid.

A mixture of **8** (940 mg, 1 mmol), paraformaldehyde (113 mg, 3.8 mmol), CH_2Cl_2 (25 cm^3), 50% (w/w) aqueous KOH (2.5 cm^3) was vigorously stirred at room temperature under nitrogen for 40 min. During this time the orange suspension turned to a clear yellow solution. Water (40 cm^3) and CH_2Cl_2 (40 cm^3) were added. The aqueous phase was extracted with CH_2Cl_2 (4 × 60 cm^3). The combined organic phases were washed neutral with water, then dried ($MgSO_4$) and brought to dryness under reduced pressure. Purification of the residue by chromatography over neutral alumina (activity II–III) with hexane yielded the *title compound* **10** (232 mg, 82%) as a yellowish solid, m.p. 115 °C (Found: C, 93.4; H, 6.55. $C_{22}H_{18}$ requires C, 93.58; H, 6.42%); $\delta_H(CCl_4)$ 5.09 (2 H, dd, J_{BX} 10.8, J_{BA} 1.4, vinyl-H_B), 5.60 (2 H, dd, J_{AX} 16.9, J_{AB} 1.4, vinyl-H_A), 6.69 (2 H, dd, J_{XA} 16.9, J_{XB} 10.8, vinyl-H_X), 7.30 (10 H, s, ArH) and 7.45 (2 H, s, 3′,6′-H); *m*/*z* 282 (M^+, 100%), 265 (32.3) and 252 (17.7).

2′,5′-*Divinyl*-1,1′:4′,1″-*terphenyl* **10**.—*From* **9**. A solution of methyl iodide (9 mm^3, 144.6 μmol) and triphenylphosphine (50 mg, 190.6 μmol) in dry Et_2O (2 cm^3) was kept at room temperature for one week with occasional shaking. The white precipitate was isolated by filtration, washed with Et_2O and dried ($MgSO_4$) yielding methyltriphenylphosphonium iodide (38.4 mg, 66%). A suspension of methyltriphenylphosphonium iodide (33.8 mg, 83.6 μmol) in absolute THF (tetrahydrofuran) (2 cm^3) cooled under argon to −70 °C was treated over 1 h with a 2 mol dm^{-3} solution of phenyllithium in benzene–Et_2O (100 mm^3, 200 μmol) by means of a syringe through a rubber septum. This was followed by the slow addition under stirring of a solution of **9** (11.4 mg, 39.8 μmol) in absolute THF (2 cm^3) within 2 h at −50 °C. Then the temperature of the cooling bath was raised to −10 °C within an additional hour. Unchanged phenyllithium was quenched with a few drops of EtOH and the solvent removed under reduced pressure. Purification of the residue was achieved as described above yielding the *title compound* **10** (7.5 mg, 67%) as yellowish solid, m.p. 114 °C (Found: C, 93.25; H, 6.3. $C_{22}H_{18}$ requires C, 93.58; H, 6.42%). This material was spectroscopically identical with the previous sample of **10**.

5,6,12,13-*Tetrahydrodibenz*[a,h]*anthracene* **11**.—A solution of **10** (8.0 mg, 28.3 μmol) in benzene (120 cm^3) was irradiated under argon with a conventional light bulb (200 W, Osram). The cyclization reaction was monitored by GC using a linear temperature gradient from 250–330 °C in 10 min (t_R, **10**: 68 sec; **11**: 239 sec). After *ca.* 6 d the solvent was removed under reduced pressure and the residue was subjected to chromatography over neutral alumina (activity II–III) with light petroleum–$CHCl_3$ (4:1) yielding the *title compound* **11** (5.1 mg, 64%) as white crystals, m.p. 187 °C (Found: C, 93.45; H, 6.4. $C_{22}H_{18}$ requires C, 93.58; H, 6.42%); $\delta_H(CDCl_3)$ 2.90 (8 H, s, 5,6,12,13-H), 7.12–7.44 (6 H, m, 2,3,4,9,10,11-H), 7.60 (2 H, s, 7,14-H) and 7.65–7.94 (2 H, m, 1,8-H); *m*/*z* 282 (M^+, 100%) and 265 (23).

Dibenz[a,h]*anthracene* **12**.—A solution of **11** (5.0 mg, 17.7 μmol) in benzene (10 cm^3) was treated with DDQ (40 mg, 176 μmol) under reflux for 48 h. The dark reaction mixture was percolated through basic alumina (activity I) eluting with boiling benzene. The extract was brought to dryness under reduced pressure and the residue recrystallized from acetone yielding DBA **12** (3.7 mg, 75%) as silver leaflets, m.p. 260 °C (lit.,[25] 262 °C); $\delta_H(CDCl_3)$ 7.4–8.0 (10 H, m, 2,3,4,5,6,9,10,11,12,13-H), 8.65–9.0 (2 H, m, 1,8-H) and 9.08 (2 H, s, 7,14-H); *m*/*z* 278 (M^+, 100%) and 139 (M^{2+}, 31).

[5,12-^{14}C]*Dibenz*[a,h]*anthracene* **12***.—An ampoule containing [^{14}C]-methyl iodide (296 mBq, specific activity: 2.072 GBq $mmol^{-1}$, 0.143 mmol) was cooled with liquid N_2 and opened. Methyl iodide (82 mm^3, 1.317 mmol) in Et_2O (500 mm^3) was added followed by the addition of triphenylphosphine (530 mg, 2.021 mmol) dissolved in Et_2O (4.5 cm^3). The ampoule was stoppered and the solution stirred by means of a magnetic stirrer at room temperature for 4 d. The white precipitate was isolated by filtration and washed with Et_2O (50 cm^3) yielding [*methyl*-^{14}C]methyltriphenylphosphonium iodide (529

mg, 1.309 mmol). The entire amount of the phosphonium salt was suspended under argon in absolute THF (30 cm^3). The stirred mixture was cooled to −70 °C and a 2 mol dm^{-3} solution of phenyllithium in benzene–Et_2O (1.3 cm^3, 2.60 mmol) was added, with a syringe through a rubber septum over 1 h. The reaction temperature was raised to −50 °C and a solution of **9** (185 mg, 0.646 mmol) in absolute THF (20 cm^3) was added within 2 h bringing the temperature to −30 °C. Then the reaction mixture was stirred at −10 °C for 1 h and at room temperature for additional 1.5 h. The solvent was removed under reduced pressure and the residue was purified by chromatography over neutral alumina (activity II–III) with hexane yielding a solution of **10***. The solvent was evaporated under reduced pressure, benzene (800 cm^3) added and the solution irradiated with a conventional light bulb (200 W) for 6 d. The volume of the resulting solution was reduced to 1/20 under reduced pressure. Then DDQ (500 mg, 2.20 mmol) was added and the suspension was refluxed for 48 h. The dark reaction mixture was percolated through basic alumina (activity I) eluting with boiling benzene. The extract was brought to dryness under reduced pressure and purified by HPLC using Polygosil 60-5 C 18 (5 μm, 250 × 16 mm; Macherey-Nagel, Düren, Germany) as stationary and methanol (4 cm^3 min^{-1}) as mobile phase. The fraction eluting after 21.5 min yielded the pure *title compound* **12*** (104 mg, 58% from **9**) as white solid; specific activity: 391 MBq $mmol^{-1}$; radiochemical purity, 99.7%.

Carrier-free [5,12-^{14}C]dibenz[*a*,*h*]anthracene **12*** was prepared as described above by scaling down the reaction by a factor of ten using undiluted [^{14}C]-methyl iodide (296 MBq, specific activity: 2.072 GBq $mmol^{-1}$, 143 μmol). Purification by preparative HPLC furnished **12*** (2.1 mg, 12% from **9**); specific activity: 4.14 GBq $mmol^{-1}$; radiochemical purity: 99.8%.

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