Selective preparation of polycyclic aromatic hydrocarbons. Part 4.[1] New synthetic route to anthracenes from diphenylmethanes using Friedel–Crafts intramolecular cyclization

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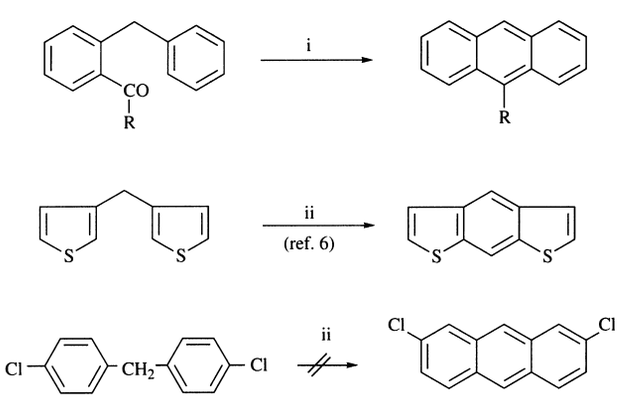
Preparation of several anthracenes from diphenylmethanes by direct Bradsher-type reaction, which incorporates formylation of a hydrocarbon followed by Friedel–Crafts intramolecular cyclization, is presented. The present method involving the action of Cl_2CHOMe and $TiCl_4$ on a variety of diphenylmethanes (constructed such that electrophilic substitution occurs *ortho* to the biphenyl linkage) offers a convenient, mild, one-pot synthesis of substituted anthracenes.

Introduction

Anthracenes can be obtained by a number of synthetic processes; the yields, however, are usually not very satisfactory and the methods were chiefly important as confirming the structure of the hydrocarbon. The most familiar routes are the Friedel–Crafts reaction,[2] Fittig (Wurtz–Fittig) reaction,[3] Elbs reaction[4] and so on. The Bradsher reaction,[5] involving the acid-catalysed cyclodehydration of *o*-acyldiarylmethanes, offers a useful alternative to the Elbs reaction as a primary synthetic route to specially substituted anthracenes. However, the preparation of the starting materials frequently presents difficulty. Later, Meth-Cohn and his co-workers reported[6] the formylation of diarylmethanes to afford anthracenes by direct Bradsher-type reactions. However, the reaction's scope was limited to the preparation of benzothiophene derivatives.[6] Thus, the action of Cl_2CHOMe, in the presence of $SnCl_4$, on dithienylmethanes led to Bradsher-type reactions to afford benzothiophenes, but in the case of 4,4′-dichlorodiphenylmethane only resulted in the recovery of starting compound. These results (Scheme 1) probably reflect the highly activated character of thiophene rings, which permits a Bradsher-type reaction to occur.



Scheme 1 *Reagents and conditions:* i, H^+; ii, Cl_2CHOMe, $SnCl_4$

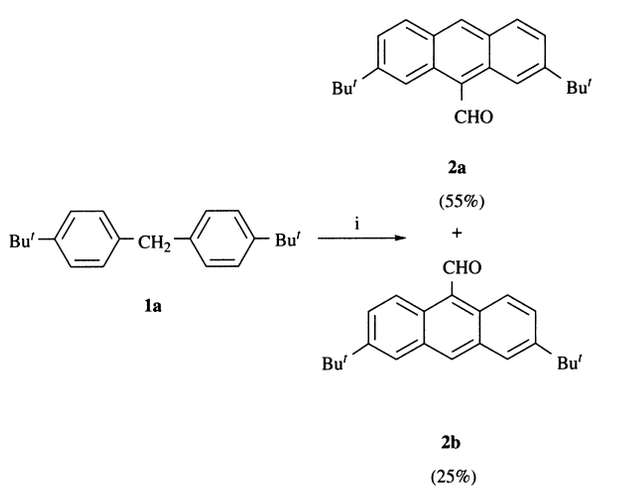
Recently, we reported[7] the first successful formation of the fluorene skeleton *via* Friedel–Crafts intramolecular benzylation during the action of $ClCH_2OMe$ and $TiCl_4$ on highly activated biphenyls, which are constructed such that electrophilic substitution occurs *ortho* to the biphenyl linkage. This strategy was then applied to the preparation of anthracene derivatives.

We describe here a highly efficient and mild, one-pot procedure for the preparation of anthracenes from diphenylmethanes by direct Bradsher-type reaction using dichloromethyl methyl ether.[8] This reaction incorporates formylation of a hydrocarbon followed by Friedel–Crafts intramolecular cyclization.

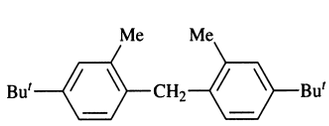
Results and discussion

In order to accomplish the formation of the anthracene skeleton *via* Friedel–Crafts intramolecular cyclization under the formylation conditions, the starting material 4,4′-di-*tert*-butyldiphenylmethane **1a** was designed such that electrophilic substitution occurs at the *ortho* position, thus leading to the diphenylmethane linkage.

The preparation of substrate **1a** was carried out as previously reported.[9] Treatment of compound **1a** with 5.4 mol equiv. of Cl_2CHOMe in the presence of $TiCl_4$ at room temperature for 1 h gave a mixture of 2,7-di-*tert*-butyl-9-formylanthracene **2a** and 2,7-di-*tert*-butyl-10-formylanthracene **2b** in 55 and 25% yield, respectively (Scheme 2).

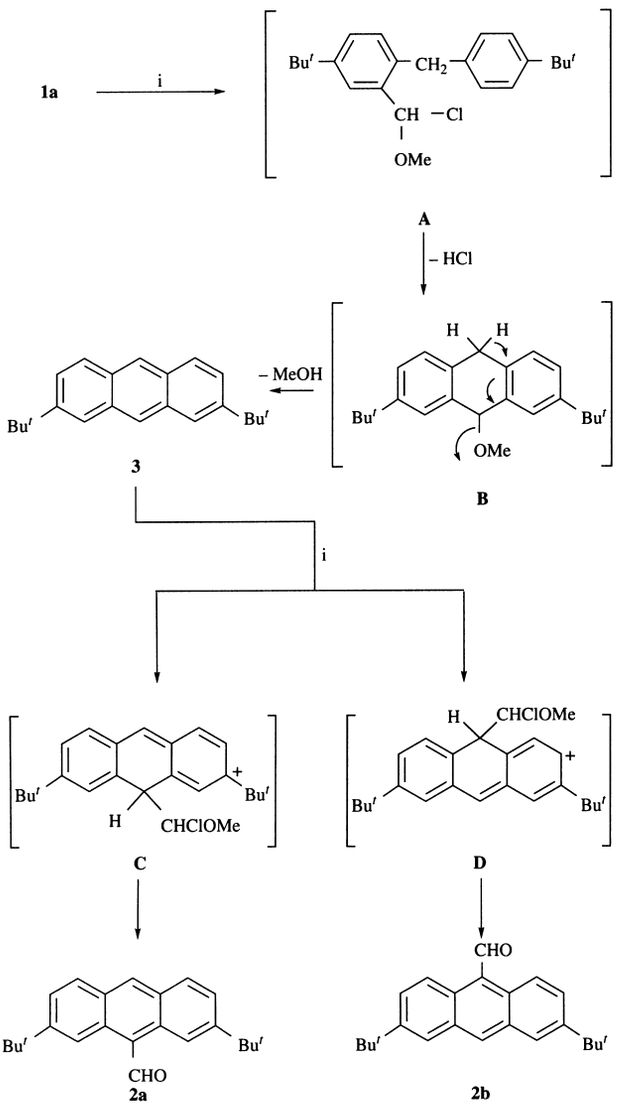


Scheme 2 *Reagents and conditions:* i, Cl_2CHOMe, $TiCl_4$, CH_2Cl_2, room temperature, 1 h



1b

The reaction pathway of formation of anthracenes **2a** and **2b** is shown in Scheme 3. As expected, the electrophilic substitu-

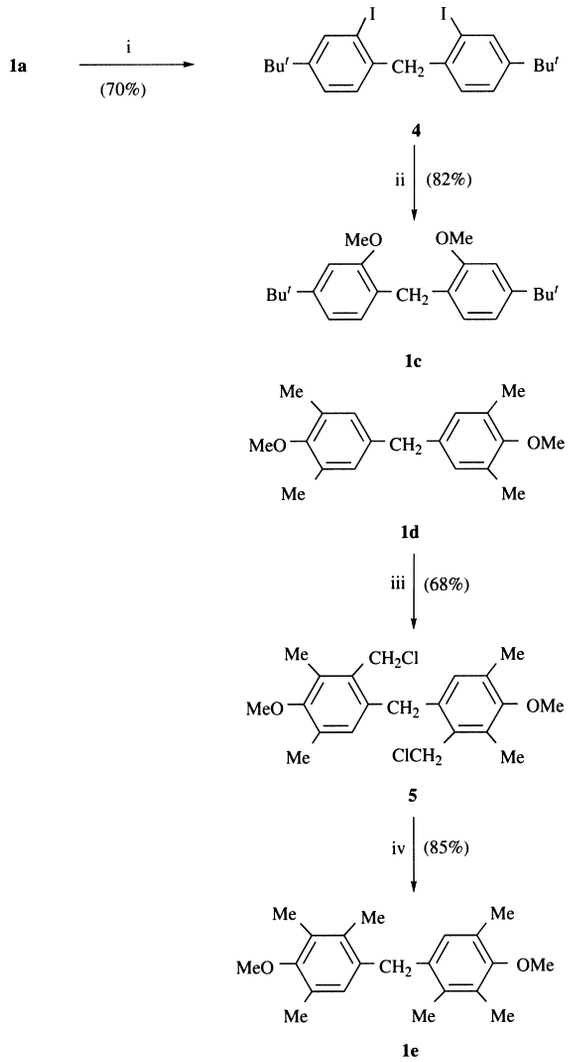


Scheme 3 *Reagent:* i, Cl_2CHOMe

tion with Cl_2CHOMe occurs at the *ortho* position to form intermediate **A** from which the Bradsher-type Friedel–Crafts intramolecular cyclization afforded 2,7-di-*tert*-butylanthracene **3** *via* intermediate **B**. Further competitive formylation at positions 9 and 10 afforded the final products **2a** and **2b**. Interestingly, the yield of isomer **2a** was superior to that of regioisomer **2b**. The relative rate of formylation at positions 9 and 10 of hydrocarbon **3** might depend on the relative stabilities of the corresponding σ-complex intermediates **C** and **D**. The former complex might be more stable than the latter (tertiary *versus* secondary carbenium ions).

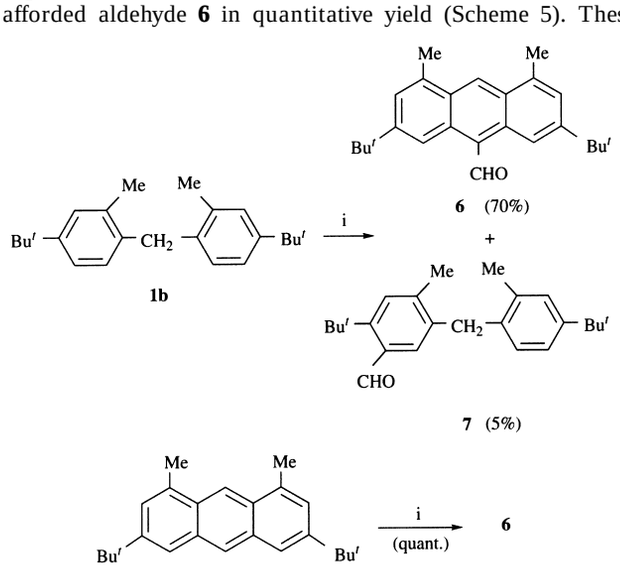
We have prepared various diphenylmethanes **1b–f** in order to study the scope and limitations of the present method. 4,4′-Di-*tert*-butyl-2,2′-dimethyldiphenylmethane **1b** was easily prepared in three steps from diphenylmethane by using the *tert*-butyl group as a positional protective group on the aromatic ring.[10] The preparation of compounds **1c** and **1e** is shown in Scheme 4. 4,4′-Dimethoxy-3,3′,5,5′-tetramethyldiphenylmethane **1d** and 3,3′,4,4′-tetramethoxydiphenylmethane **1f** were prepared as previously reported.[11]

When 4,4′-di-*tert*-butyl-2,2′-dimethyldiphenylmethane **1b** was treated with Cl_2CHOMe in methylene dichloride in the presence of $TiCl_4$ at room temperature for 3 h, the desired product, 3,6-di-*tert*-butyl-10-formyl-1,8-dimethylanthracene **6** was obtained as pale yellow prisms in 50% yield along with 4,4′-



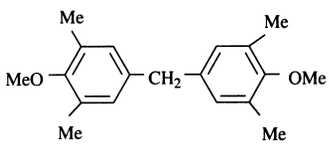
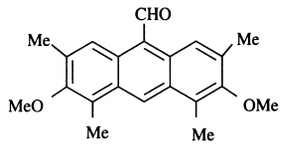
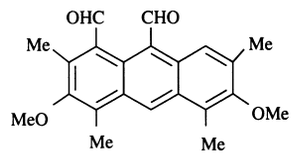
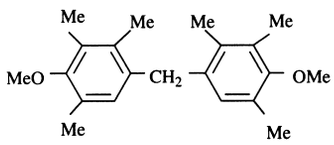
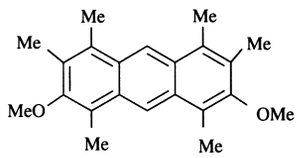
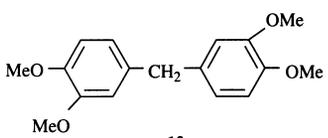
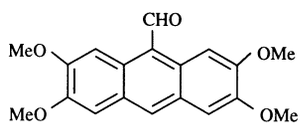
Scheme 4 *Reagents and conditions:* i, HIO_4, I_2, H_2SO_4–AcOH, 80 °C, 12 h; ii, NaOMe, CuI, MeOH–DMF, reflux, 24 h; iii, $ClCH_2OMe$, $TiCl_4$, CS_2, 0 °C, 30 min; iv, $LiAlH_4$, THF, reflux, 1 h

di-*tert*-butyl-5-formyl-2,2′-dimethyldiphenylmethane **7** in 7% yield. The yield of compound **6** was increased to 70% by prolonging the reaction time to 12 h. It was also found that treatment of 1,8-dimethyl-3,6-di-*tert*-butylanthracene **8** with Cl_2CHOMe under the same conditions as described above afforded aldehyde **6** in quantitative yield (Scheme 5). These



Scheme 5 *Reagents and conditions:* i, Cl_2CHOMe, $TiCl_4$, CH_2Cl_2, room temperature, 12 h

Table 1 Reaction of diphenylmethanes **1d–f** with Cl_2CHOMe in the presence of $TiCl_4$[a]

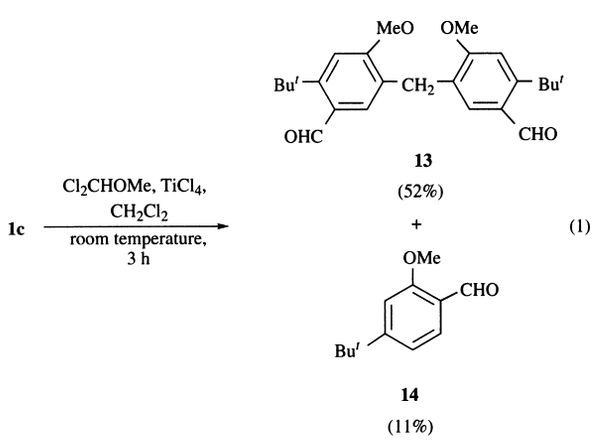
Substrate	Time (*t*/h)	Products	Yield (%)[b]
 **1d**	1	 **9**	77
		 **10**	10
 **1e**	3	 **11**	40
 **1f**	0.5	 **12**	27

[a] The reaction temperature was 20 °C; Cl_2CHOMe : $TiCl_4$: **1** 5.4 : 3.7 : 1. [b] The isolated yield is shown.

results suggested that compound **8** was an intermediate in the formation of aldehyde **6**.

The currently developed method was further applied to other substituted diphenylmethanes. The reaction was carried out under the same conditions and our results are compiled in Table 1.

The intramolecular Bradsher-type reaction to form the anthracene skeleton can be attributed to the highly activated character of the aryl ring. It is noted that further formylation at positions 9 and 10 of the anthracene ring was found to be disturbed by the steric hindrance of the methyl groups at positions 1 and 8. Interestingly, in the case of 4,4′-di-*tert*-butyl-2,2′-dimethoxydiphenylmethane **1c**, the desired anthracene was not obtained. Only 4,4′-di-*tert*-butyl-5,5′-diformyl-2,2′-dimethoxydiphenylmethane **13** was obtained, in 52% yield, along with the cleavage product, 5-*tert*-butyl-2-formylanisole **14** arising from *ipso*-attack at the benzylic position, in 11% yield. This result



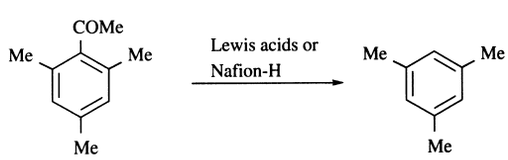
(1)

is the same as that from the nitration of polymethyldiphenylmethanes which mainly afford products from cleavage at the diphenylmethane linkage.[12]

In order to study the present novel cyclobenzylation, which affords anthracene derivatives, in more detail, we attempted to prepare further methylene-substituted diphenylmethanes **1g** and **1h** and react them with Cl_2CHOMe under the same conditions as described above. Preparative routes to compounds **1g** and **1h** are shown in Scheme 6.

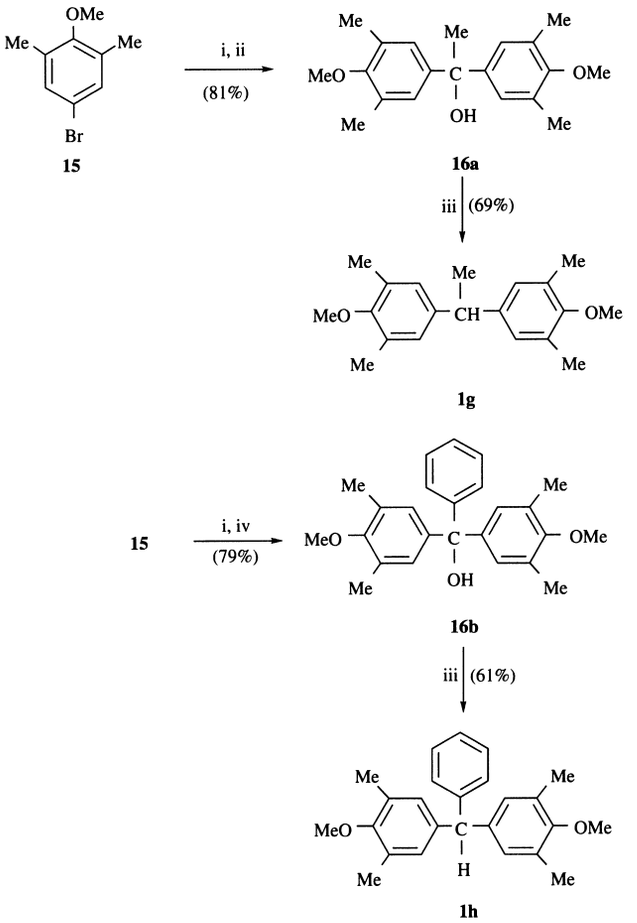
When compounds **1g** and **1h** were treated with Cl_2CHOMe in methylene dichloride in the presence of $TiCl_4$ at room temperature for 3 h, the desired anthrathenes **17a** and **17b** were obtained in 44 and 50% yield, respectively (Scheme 7).

Transacetylation of aromatic ketones and the notion of reversibility of acetylation under Friedel–Crafts conditions is a subject of continuing interest.[13,14] Baddeley and Pendleton reported[13] deacetylation of 2,6-dimethylacetophenone and acetylmesitylene by Lewis acids and protic acids. Olah *et al.* also reported[15] the deacetylation of aromatic compounds catalysed by Nafion-H (a perfluorinated resinsulfonic acid).[16,17] This reaction, however, appeared to be of synthetic value only in the case of activated aryl methyl ketones. The reaction proceeds *via ipso* protonation of the substrate followed by deacetylation [eqn. (2)].

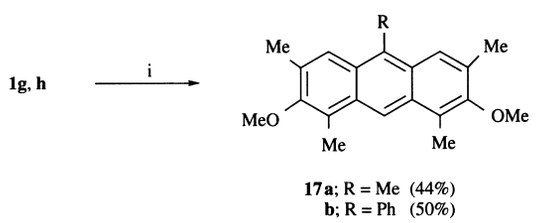


(2)

Although Olah *et al.* reported[15] the Nafion-H-catalysed deacetylation of 9-acetylanthracene under toluene reflux, no deformylation of 9-formylanthracene derivatives was reported.



Scheme 6 *Reagents and conditions:* i, Mg, THF, reflux, 3 h; ii, $MeCO_2Et$, reflux, 12 h; iii, $LiAlH_4$, $AlCl_3$, Et_2O, reflux, 3 h; iv, $PhCO_2Et$, reflux, 12 h



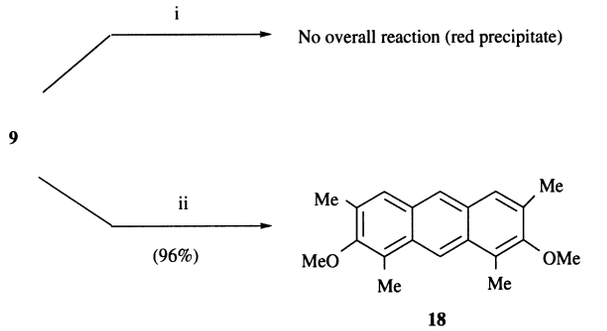
Scheme 7 *Reagents and conditions:* i, Cl_2CHOMe, $TiCl_4$, CH_2Cl_2, room temperature, 3 h

Attempted $AlCl_3$–$MeNO_2$-catalysed deformylation of the 9-formylanthracene **9** under toluene reflux failed. Only the starting compound was recovered. The immediate formation of a red precipitate, which might come from complexation between the anthracene moiety and Lewis acid, was observed after the addition of $AlCl_3$–$MeNO_2$ catalyst.

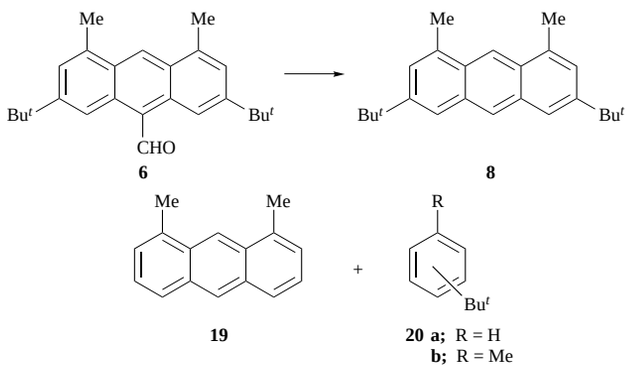
In contrast, deformylation of compound **9**, in the presence of Nafion-H as a catalyst, was carried out in boiling toluene to afford the desired deformylated anthracene **18** in 96% yield (Scheme 8). However, formyltoluene was not detected. Thus the formyl group might be removed as carbon monoxide after the *ipso* protonation of the substrate. In the anthracene skeleton, not only the highly increased π-density but also favourable *peri* interactions might provide the driving force for the deformylation.

Selective deformylation of compound **6** was accomplished by using 200 wt% of Nafion-H under the conditions of refluxing benzene for 24 h to afford 3,6-di-*tert*-butyl-1,8-dimethylanthracene **8** in 75% yield (Scheme 9).

Deformylation and *trans*-*tert*-butylation of compound **6**, in the presence of Nafion-H (200 wt%) as a catalyst, was carried out in boiling toluene to afford the desired 1,8-dimethyl-



Scheme 8 *Reagents and conditions:* i, $AlCl_3$, $MeNO_2$, toluene, reflux, 3 h; ii, Nafion-H (200 wt%), toluene, reflux, 3 h



Scheme 9 (see Table 2) *Reagents and conditions:* i, Nafion-H, ArH, reflux

Table 2 Nafion-H-catalysed deformylation and de-*tert*-butylation of 3,6-di-*tert*-butyl-10-formyl-1,8-dimethylanthracene **6** [a]

Run	Solvent	Amount of Nafion-H (wt%)	Time (*t*/h)	Product (%) [a]		Recovery of substrate **6**
				8	**19**	
1	Benzene	100	24	83 (73) [b]	0	8
2	Benzene	200	7	81	0	13
3	Benzene	200	24	86 (75) [b]	8	0
4	Toluene	100	3	70	9	8
5	Toluene	200	3	4	82 (70) [b]	0

[a] Yields are determined by GLC analysis. [b] Isolated yields are shown in parentheses.

anthracene **19** in 70% yield along with *tert*-butyltoluene **20b**. Depending on the amount of Nafion-H and the presence of an acceptor for the *tert*-butyl group, *i.e.* benzene and toluene, selective deformylation and *trans*-*tert*-butylation were found to be possible. As shown in Table 2, the present method provides good yields, easy isolation of the products, and no concomitant demethylation under the reaction conditions. Furthermore, ready regeneration of the catalyst without the loss of catalytic activity offers advantages over previously reported methods.

Conclusions

In conclusion, the method described herein employing formylation of diphenylmethanes offers a convenient, mild, one-pot synthesis of substituted anthracenes. We are now developing the present method for the preparation of a wide range of substituted anthracenes. Our results will open up new preparative aspects for polycyclic aromatic hydrocarbon chemistry. Further studies on the Friedel–Crafts intramolecular cyclization are now in progress.

Experimental

All mps and bps are uncorrected. Mps were measured on a Yanagimoto MP-S1 instrument. NMR spectra were determined at 270 MHz with a Nippon Denshi JEOL FT-270 NMR

spectrometer with $SiMe_4$ as internal reference: *J*-values are given in Hz. IR spectra were measured for samples as KBr pellets or a liquid film on NaCl plates in a Nippon Denshi JIR-AQ2OM spectrophotometer. Mass spectra were obtained on a Nippon Denshi JMS-01SA-2 spectrometer at 75 eV using a direct-inlet system through GLC. Vapour phase chromatographic (VPC) analyses were performed by a Shimadzu gas chromatograph, GC-14A with Silicone OV-1, 2 m; programmed temperature rise, 12 °C min^{-1} carrier gas nitrogen, 25 cm^3 min^{-1}.

Materials

Preparation of 4,4′-di-*tert*-butyldiphenylmethane **1a**,[9] 4,4′-di-*tert*-butyl-2,2′-dimethyldiphenylmethane **1b**,[9] 4,4′-dimethoxy-3,3′,5,5′-tetramethyldiphenylmethane **1d**[11] and 3,3′,4,4′-tetramethoxydiphenylmethane **1f**[11] were previously described.

Nafion-H catalyst was prepared from commercially available (DuPont) Nafion-K resin, as previously described.[16,17]

Preparation of 4,4′-di-*tert*-butyl-2,2′-dimethoxydiphenylmethane 1c

To methanol (24 cm^3) was added sodium (730 mg, 31.7 mmol), and then a mixture of CuI (240 mg) and 4,4′-di-*tert*-butyl-2,2′-diiododiphenylmethane **4**[18] (673 mg, 1.88 mmol) in dimethylformamide (DMF) (3 cm^3) was added. After the reaction mixture had been refluxed for 24 h, it was poured into a large amount of ice–water and was extracted with CH_2Cl_2 (20 cm^3 × 3). The extract was washed with water (20 cm^3 × 2), dried over Na_2SO_4, and concentrated *in vacuo*. The residue was recrystallized from ethanol to afford the *title compound* **1c** (500 mg, 82%) as prisms, mp 78–79 °C; $\delta_H(CDCl_3)$ 1.31 (18 H, s), 3.63 (6 H, s), 3.89 (2 H, s), 6.86 (2 H, dd, *J* 7.8 and 2.0), 6.88 (2 H, d, *J* 2.0) and 6.96 (2 H, d, *J* 7.8); *m*/*z* 340 (M^+) (Found: C, 81.42; H, 9.45. $C_{23}H_{32}O_2$ requires C, 81.13; H, 9.47%).

Preparation of 2,2′-bis(chloromethyl)-4,4′-dimethoxy-3,3′,5,5′-tetramethyldiphenylmethane 5

To a solution of 4,4′-dimethoxy-3,3′,5,5′-tetramethyldiphenylmethane **1d**[11] (842 mg, 2.96 mmol) and $ClCH_2OMe$ (1.28 cm^3, 16.9 mmol) in carbon disulfide (16 cm^3) at 0 °C was gradually added titanium tetrachloride (0.88 cm^3). After the reaction mixture had been stirred at 0 °C for 30 min, the reaction was quenched with a large amount of ice–water and the mixture was extracted with CH_2Cl_2 (10 cm^3 × 3). The extract was washed with water (100 cm^3 × 2), dried over Na_2SO_4, and concentrated *in vacuo*. The residue was chromatographed over silica gel (Wako, C-300; 50 g) with benzene as eluent to give a solid, which was recrystallized from hexane to afford the *title compound* **5** (767 mg, 68%) as prisms, mp 134–136 °C; ν_{max}(KBr)/cm^{-1} 2997, 2944, 1405, 1262, 1255, 1231, 1218, 1094, 1002, 730, 665 and 621; $\delta_H(CDCl_3)$ 2.21 (6 H, s), 2.39 (6 H, s), 3.71 (6 H, s), 4.11 (2 H, s), 4.60 (4 H, s) and 6.59 (2 H, s); *m*/*z* 380, 382 and 384 (M^+) (Found: C, 66.32; H, 6.77. $C_{21}H_{26}Cl_2O_2$ requires C, 66.14; H, 6.87%).

Preparation of 4,4′-dimethoxy-2,2′,3,3′,5,5′-hexamethyldiphenylmethane 1e

To a suspension of lithium aluminium hydride (150 mg, 3.96 mmol) in tetrahydrofuran (THF) (10 cm^3) was added a solution of dichloride **5** (500 mg, 1.31 mmol) in THF (10 cm^3) under gently refluxing conditions. After the reaction mixture had been refluxed for an additional 1 h, it was poured into a large amount of stirred ice–water containing 10% H_2SO_4 (20 cm^3) and was extracted with diethyl ether (30 cm^3 × 3). The ether solution was washed with water (30 cm^3), dried over Na_2SO_4, and concentrated. The residue was chromatographed over silica gel (Wako, C-300; 50 g) with benzene as eluent to give a solid, which was recrystallized from hexane to afford the *title compound* **1e** (350 mg, 85%) as prisms, mp 80–82 °C; ν_{max}(KBr)/cm^{-1} 2988, 2943, 1479, 1452, 1230, 1218, 1092 and 1005; $\delta_H(CDCl_3)$ 2.12 (6 H, s), 2.19 (6 H, s), 2.24 (6 H, s), 3.69 (6 H, s), 3.80 (2 H, s) and 6.53 (2 H, s); *m*/*z* 312 (M^+) (Found: C, 80.73; H, 9.03. $C_{21}H_{28}O_2$ requires C, 80.52; H, 8.87%).

Preparation of 1,1-bis(4-methoxy-3,5-dimethylphenyl)ethanol 16a

To a solution of 4-methoxy-3,5-dimethylphenylmagnesium bromide [prepared from 4-bromo-2,6-dimethylanisole **15** (10 g, 47 mmol) and magnesium (1.7 g, 70 mmol)] in THF (20 cm^3) was added a solution of 1.32 g (15 mmol) of ethyl acetate in THF (10 cm^3) dropwise under gentle refluxing. After the reaction mixture had been refluxed for an additional 12 h, it was quenched with 10% aq. ammonium chloride (50 cm^3) and extracted with CH_2Cl_2 (40 cm^3 × 3). The extract was washed with water (30 cm^3 × 2), dried over Na_2SO_4, and concentrated *in vacuo*. The residue was recrystallized from hexane–benzene (1:1) to afford the *title compound* **16a** (3.8 g, 81%) as prisms, mp 150–152 °C; ν_{max}(KBr)/cm^{-1} 3470 (OH), 2983, 2936, 1488, 1457, 1376, 1307, 1225, 1184, 1152, 1003, 868 and 657; $\delta_H(CDCl_3)$ 1.84 (3 H, s), 2.22 (12 H, s), 2.54 (1 H, s), 3.67 (6 H, s) and 7.00 (4 H, s); *m*/*z* 314 (M^+) (Found: C, 76.70; H, 8.42. $C_{20}H_{26}O_3$ requires C, 76.40; H, 8.33%).

Preparation of 1,1-bis(4-methoxy-3,5-dimethylphenyl)ethane 1g

To a suspension of chlorodihydroalane (AlH_2Cl) [prepared from $LiAlH_4$ (695 mg, 18.3 mmol) and $AlCl_3$ (2.44 g, 18.3 mmol)] in diethyl ether (15 cm^3) was added a solution of the alcohol **16a** (1.67 g, 5.3 mmol) in diethyl ether (10 cm^3) dropwise under gentle refluxing. After the reaction mixture had been refluxed for an additional 3 h, it was poured into a large amount of stirred ice–water containing 10% H_2SO_4 (10 cm^3) and was extracted with diethyl ether (30 cm^3 × 3). The ether solution was washed with water (30 cm^3 × 2), dried over Na_2SO_4, and concentrated. The residue was chromatographed over silica gel (Wako, C-300; 50 g) with benzene as eluent to give a solid, which was recrystallized from hexane to afford the *title compound* **1g** (1.09, 69%) as prisms, mp 35–37 °C; ν_{max}(KBr)/cm^{-1} 2870, 2830, 1484, 1454, 1222, 1141, 1013, 865 and 768; $\delta_H(CDCl_3)$ 1.54 (3 H, d, *J* 6.8), 2.24 (12 H, s), 3.69 (6 H, s), 3.90 (1 H, q, *J* 6.8) and 6.84 (4 H, s); *m*/*z* 298 (M^+) (Found: C, 80.33; H, 8.88. $C_{20}H_{26}O_2$ requires C, 80.50; H, 8.78%).

Preparation of 1,1-bis(4-methoxy-3,5-dimethylphenyl)-1-phenylmethanol 16b

To a solution of 4-methoxy-3,5-dimethylphenylmagnesium bromide [prepared from bromide **15** (10 g, 47 mmol) and magnesium (2.5 g, 61 mmol)] in THF (20 cm^3) was added a solution of ethyl benzoate (2.25 g, 15 mmol) in THF (10 cm^3) dropwise under gentle refluxing. After the reaction mixture had been refluxed for an additional 12 h, it was quenched with 10% aq. ammonium chloride (50 cm^3) and extracted with CH_2Cl_2 (40 cm^3 × 3). The extract was washed with water (30 cm^3 × 2), dried over Na_2SO_4, and concentrated *in vacuo*. The residue was recrystallized from hexane–benzene (1:1) to afford the *title compound* **16b** (4.44 g, 79%) as prisms, mp 153 °C; ν_{max}(KBr)/cm^{-1} 3428 (OH), 2947, 1481, 1448, 1298, 1231, 1131, 1048, 1003, 889, 763, 747 and 706; $\delta_H(CDCl_3)$ 2.19 (12 H, s), 3.02 (1 H, s), 3.68 (6 H, s), 6.87 (4 H, s) and 7.26 (5 H, s); *m*/*z* 376 (M^+) (Found: C, 80.13; H, 7.27. $C_{25}H_{28}O_3$ requires C, 79.76; H, 7.50%).

Preparation of 1,1-bis(4-methoxy-3,5-dimethylphenyl)-1-phenylmethane 1h

To a suspension of chlorodihydroalane [prepared from $LiAlH_4$ (695 mg, 18.3 mmol) and $AlCl_3$ (2.44 g, 18.3 mmol)] in diethyl ether (15 cm^3) was added a solution of the alcohol **16b** (2.26 g, 6.0 mmol) in diethyl ether (10 cm^3) dropwise under gentle refluxing. After the reaction mixture had been refluxed for an additional 3 h, it was poured into a large amount of stirred ice–water containing 10% H_2SO_4 (10 cm^3) and was extracted with

diethyl ether (30 cm^3 × 3). The ether solution was washed with water (30 cm^3 × 2), dried over Na_2SO_4, and concentrated. The residue was chromatographed over silica gel (Wako, C-300; 50 g) with benzene as eluent to give a solid, which was recrystallized from hexane to afford the *title compound* **1h** (1.32, 61%) as prisms, mp 88–90 °C; ν_{max}(KBr)/cm^{-1} 2998, 2935, 1479, 1452, 1220, 1144, 1134, 1010, 883 and 727; δ_H($CDCl_3$) 2.20 (12 H, s), 3.66 (6 H, s), 5.30 (1 H, s), 6.74 (4 H, s) and 7.08–7.23 (5 H, m); *m*/*z* 360 (M^+) (Found: C, 83.27; H, 7.82. $C_{25}H_{28}O_2$ requires C, 83.29; H, 7.83%).

Reaction of diphenylmethanes 1 with Cl_2CHOMe in the presence of $TiCl_4$

Typical procedure. To a solution of 1.0 g (3.57 mmol) of **1a** and dichloromethyl methyl ether (1.7 cm^3, 19.2 mmol) in CH_2Cl_2 (50 cm^3) was added a solution of $TiCl_4$ (1.45 cm^3, 13.2 mmol) in CH_2Cl_2 (5 cm^3) at 0 °C. The reaction mixture was kept at room temperature for 1 h before the addition of cold water (20 cm^3) and extraction with CH_2Cl_2 (30 cm^3 × 3). The extract was washed with water (30 cm^3 × 2), dried over Na_2SO_4, and concentrated. The residue was chromatographed over silica gel (Wako, C-300; 100 g) with hexane–benzene (1 : 1) as eluent. The first fraction afforded a pale yellow solid, which was recrystallized from hexane to give 2,7-*di*-tert-*butyl*-9-*formylanthracene* **2a** (627 mg, 55%) as pale yellow prisms, mp 107–110 °C; ν_{max}(KBr)/cm^{-1} 1676 (C=O); δ_H($CDCl_3$) 1.47 (18 H, s), 7.61 (2 H, dd, *J* 9.2 and 1.8), 7.95 (2 H, d, *J* 9.2), 8.54 (1 H, s), 8.93 (2 H, d, *J* 1.8) and 11.54 (1 H, s); *m*/*z* 318 (M^+) (Found: C, 86.68; H, 8.22. $C_{23}H_{26}O$ requires C, 86.75; H, 8.23%).

The second fraction afforded 2,7-*di*-tert-*butyl*-10-*formylanthracene* **2b** (285 mg, 25%) as a pale yellow oil; ν_{max}(NaCl)/cm^{-1} 1679 (C=O); δ_H($CDCl_3$) 1.45 (18 H, s), 7.76 (2 H, dd, *J* 9.1 and 1.8), 7.90 (2 H, d, *J* 1.8), 8.64 (1 H, s), 8.94 (2 H, d, *J* 9.1) and 11.48 (1 H, s); *m*/*z* 318 (M^+) (Found: C, 86.50; H, 8.32%).

Compounds **6**, **7** and **9**–**12** were also obtained from substrates **1b** and **1d**–**f** under various conditions (see Scheme 5 and Table 1).

3,6-*Di*-tert-*butyl*-10-*formyl*-1,8-*dimethylanthracene* **6** was obtained as pale yellow prisms (from hexane), mp 225–227 °C; ν_{max}(KBr)/cm^{-1} 1677 (C=O); δ_H($CDCl_3$) 1.46 (18 H, s), 2.85 (6 H, s), 7.46 (2 H, s), 8.71 (2 H, s), 8.84 (1 H, s) and 11.53 (1 H, s); *m*/*z* 346 (M^+) (Found: C, 86.25; H, 8.71. $C_{25}H_{30}O$ requires C, 86.66; H, 8.73%).

4,4′-*Di*-tert-*butyl*-5-*formyl*-2,2′-*dimethyldiphenylmethane* **7** was obtained as a pale yellow oil; ν_{max}(NaCl)/cm^{-1} 1677 (C=O); δ_H($CDCl_3$) 1.30 (9 H, s), 1.51 (9 H, s), 2.30 (6 H, s), 3.88 (2 H, s), 6.73 (1 H, d, *J* 8.0), 7.09 (1 H, dd, *J* 8.0 and 1.0), 7.24 (1 H, d, *J* 1.0), 7.27 (1 H, s), 7.58 (1 H, s) and 10.70 (1 H, s); *m*/*z* 336 (M^+) (Found: C, 85.81; H, 9.58. $C_{24}H_{32}O$ requires C, 85.66; H, 9.59%).

10-*Formyl*-2,7-*dimethoxy*-1,3,6,8-*tetramethylanthracene* **9** was obtained as pale yellow prisms [from hexane–benzene (5 : 1)], mp 192–195 °C; ν_{max}(KBr)/cm^{-1} 1671 (C=O); δ_H($CDCl_3$) 2.54 (6 H, s), 2.76 (6 H, s), 3.84 (6 H, s), 8.60 (2 H, s), 8.78 (1 H, s) and 11.43 (1 H, s); *m*/*z* 322 (M^+) (Found: C, 78.65; H, 6.89. $C_{21}H_{22}O$ requires C, 78.23; H, 6.88%).

1,9-*Diformyl*-3,6-*dimethoxy*-2,4,5,7-*tetramethylanthracene* **10** was obtained as pale brown prisms [from hexane–benzene (1 : 3)], mp 226–228 °C; ν_{max}(KBr)/cm^{-1} 1680 and 1664 (C=O); δ_H($CDCl_3$) 2.78 (6 H, s), 2.79 (6 H, s), 3.82 (6 H, s), 8.51 (1 H, s), 10.49 (1 H, s) and 11.05 (2 H, s); *m*/*z* 350 (M^+) (Found: C, 75.21; H, 6.32. $C_{22}H_{22}O_4$ requires C, 75.41; H, 6.33%).

2,7-*Dimethoxy*-1,3,4,5,6,8-*hexamethylanthracene* **11** was obtained as pale yellow prisms (from hexane), mp 215 °C; δ_H($CDCl_3$) 2.48 (6 H, s), 2.73 (6 H, s), 2.74 (6 H, s), 3.79 (6 H, s), 8.46 (1 H, s) and 8.62 (1 H, s); *m*/*z* 322 (M^+) (Found: C, 81.75; H, 7.76. $C_{22}H_{26}O_2$ requires C, 81.95; H, 8.13%).

9-*Formyl*-2,3,6,7-*tetramethoxyanthracene* **12** was obtained as yellow prisms (from benzene), mp 260–262 °C (decomp.); ν_{max}(KBr)/cm^{-1} 1661 (C=O); δ_H($CDCl_3$) 4.05 (6 H, s), 4.10 (6 H, s), 7.16 (2 H, s), 8.28 (1 H, s), 8.38 (2 H, s) and 11.37 (1 H, s); *m*/*z* 326 (M^+) (Found: C, 69.72; H, 5.45. $C_{19}H_{18}O_5$ requires C, 69.93; H, 5.56%).

An attempted reaction of 4,4′-di-*tert*-butyl-2,2′-dimethoxydiphenylmethane **1c** with Cl_2CHOMe under the same conditions as with compound **1b** to afford the corresponding anthracene derivatives failed. Only compounds **13** and **14** were obtained, in 52 and 11% yield, respectively.

4,4′-*Di*-tert-*butyl*-5,5′-*diformyl*-2,2′-*dimethoxydiphenylmethane* **13** was obtained as a pale yellow oil; ν_{max}(KBr)/cm^{-1} 1677 (C=O); δ_H($CDCl_3$) 1.51 (18 H, s), 3.91 (2 H, s), 3.92 (6 H, s), 6.92 (2 H, s), 7.78 (2 H, s) and 10.68 (2 H, s); *m*/*z* 396 (M^+) (Found: C, 75.81; H, 8.18. $C_{25}H_{32}O_4$ requires C, 75.73; H, 8.13%).

4-tert-*Butyl*-2-*methoxybenzaldehyde* **14** was obtained as a pale yellow oil; ν_{max}(KBr)/cm^{-1} 1677 (C=O); δ_H($CDCl_3$) 1.34 (9 H, s), 3.93 (3 H, s), 6.98 (1 H, d, *J* 1.0), 7.05 (1 H, dd, *J* 8.0 and 1.0), 7.75 (1 H, d, *J* 8.0) and 10.41 (1 H, s); *m*/*z* 192 (M^+) (Found: C, 75.18; H, 8.28. $C_{12}H_{16}O_2$ requires C, 74.97; H, 8.39%).

Reaction of 1,1-bis(4-methoxy-3,5-dimethylphenyl)ethane 1g with Cl_2CHOMe in the presence of $TiCl_4$

To a solution of 250 mg (0.84 mmol) of compound **1g** and dichloromethyl methyl ether (0.4 cm^3, 4.52 mmol) in CH_2Cl_2 (4 cm^3) was added a solution of $TiCl_4$ (0.34 cm^3, 3.10 mmol) in CH_2Cl_2 (1 cm^3) at 0 °C. The reaction mixture was kept at room temperature for 3 h before the addition of cold water (10 cm^3) and extraction with CH_2Cl_2 (20 cm^3 × 3). The extract was washed with water (10 cm^3 × 2), dried over Na_2SO_4, and concentrated. The residue was chromatographed over silica gel (Wako, C-300; 50 g) with hexane–benzene (1 : 1) as eluent. The first fraction afforded a pale yellow solid, which was recrystallized from hexane to give 2,7-*dimethoxy*-1,3,6,8,10-*pentamethylanthracene* **17a** (115 mg, 44%) as pale yellow prisms, mp 207 °C; δ_H($CDCl_3$) 2.57 (6 H, s), 2.73 (6 H, s), 3.01 (3 H, s), 3.82 (6 H, s), 7.93 (2 H, s) and 8.36 (1 H, s); *m*/*z* 308 (M^+) (Found: C, 82.04; H, 7.70. $C_{21}H_{24}O_2$ requires C, 81.78; H, 7.84%).

Compound **17b** was prepared according to the method described above in 50% yield.

2,7-*Dimethoxy*-1,3,6,8-*tetramethyl*-10-*phenylanthracene* **17b** was obtained as pale yellow prisms (from hexane), mp 126 °C; δ_H($CDCl_3$) 2.34 (6 H, s), 2.77 (6 H, s), 3.80 (6 H, s), 7.23 (2 H, s), 7.34–7.59 (5 H, m) and 8.51 (1 H, s); *m*/*z* 370 (M^+) (Found: C, 84.52; H, 7.11. $C_{26}H_{26}O_2$ requires C, 84.29; H, 7.07%).

Nafion-H-catalysed deformylation

Typical procedure. A mixture of compound **9** (100 mg, 0.31 mmol) and Nafion-H (200 mg) in toluene (4 cm^3) was refluxed until completion of the reaction as monitored by GLC (3 h). The filtrate was evaporated under vacuum to leave a residue. The residue was chromatographed over silica gel (Wako, C-300; 50 g) with hexane–benzene (1 : 1) as eluent to give a pale yellow solid, which was recrystallized from hexane to afford 2,7-*dimethoxy*-1,3,6,8-*tetramethylanthracene* **18** (91.1 mg, 96%) as pale yellow prisms, mp 158–160 °C; δ_H($CDCl_3$) 2.48 (6 H, s), 2.73 (6 H, s), 3.83 (6 H, s), 7.26 (2 H, s), 7.14 (1 H, s) and 8.41 (1 H, s); *m*/*z* 294 (M^+) (Found: C, 81.90; H, 7.64. $C_{20}H_{22}O_2$ requires C, 81.60; H, 7.53%).

Nafion-H-catalysed deformylation and de-*tert*-butylation

Typical procedure. A mixture of aldehyde **6** (100 mg, 0.29 mmol) and Nafion-H (200 mg) in benzene (4 cm^3) was refluxed for 24 h. The filtrate was evaporated under vacuum to leave a residue. The residue was chromatographed over silica gel (Wako, C-300; 50 g) with hexane as eluent to give a pale yellow solid, which was recrystallized from methanol to afford 3,6-*di*-tert-*butyl*-1,8-*dimethylanthracene* **8** (67.3 mg, 73%) as pale yellow prisms (from methanol), mp 184–186 °C; δ_H($CDCl_3$)

1.44 (18 H, s), 2.82 (6 H, s), 7.37 (2 H, s), 7.72 (2 H, s), 8.32 (1 H, s) and 8.47 (1 H, s); *m*/*z* 318 (M^+) (Found: C, 90.51; H, 9.49. $C_{24}H_{30}$ requires C, 90.51; H, 9.49%).

The formation of *tert*-butylbenzene **20a** and *tert*-butyltoluene **20b** was confirmed by GLC.

Compound **19** was also obtained from substrate **6** in 70% yield under the conditions as shown in Table 2, run 5.

1,8-Dimethylanthracene **19**. Pale yellow prisms (from methanol), mp 133–134 °C (lit.,[19] 130–131 °C).

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