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SYNTHESIS AND APPLICATION OF PRECURSORS OF HETERO-ANTHRACENES

2-HALO- AND 2,2'-DIHALODIPHENYLMETHANES AND METHINE SUBSTITUTED DERIVATIVES

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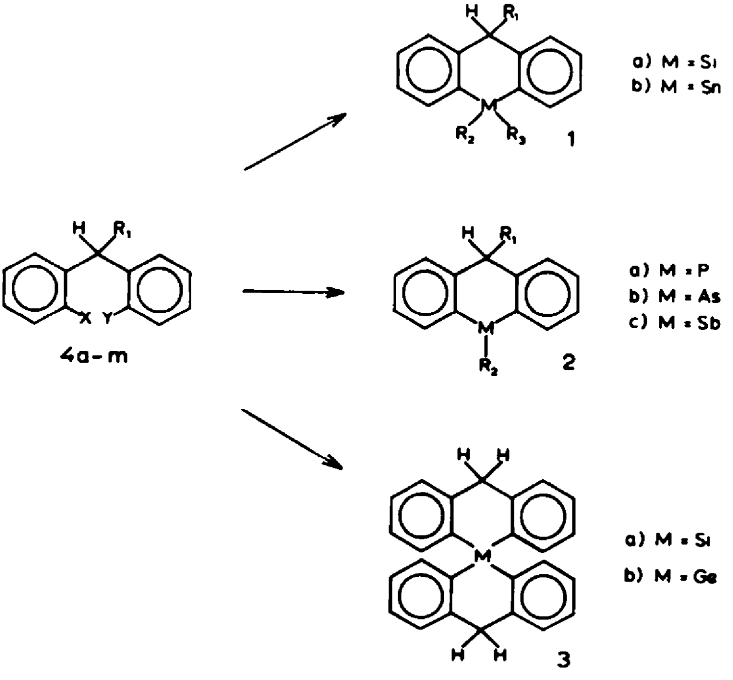
Abstract—In the diphenylmethane series, the synthesis of 2,2' - diiododiphenylmethane (**4g**) and the improved synthesis of 2,2' - dibromodiphenylmethane (**4e**) are reported. The triphenylmethane derivatives, 2-bromo-, 2-iodo-, 2,2'-dichloro-, 2,2'-dibromo- and 2,2'-diiodotriphenylmethane (**4f**, **4h**, **4i**, **4j** and **4k**, respectively) have been prepared. Via an entirely different approach, 1-(2-bromophenyl)- and 1 - (2 - chlorophenyl) - 1 - phenyl - 2,2 - dimethylpropane (**4m** and **4l**) were obtained as derivatives of t-butyldiphenylmethane. Examples are given for the application of the new compounds in the synthesis of 9,10 - dihydro - 9 - heteroanthracenes (**1**, **2** and **3**) via the formation of the corresponding organometallic derivatives.

INTRODUCTION

In the course of our investigations on heteroaromatic compounds of the anthracene type[1] we needed 9,10 - dihydroanthracenes with the heteroatom in position 9. These compounds (**1** and **2**) could in principle be obtained via organometallic reactions starting from 2-halo- and 2,2' - dihalo - substituted diphenylmethanes (**4a–m**). Similarly, spiro compounds of type **3** could be obtained.

Phosphorus[2–4] and arsenic[5] have been introduced via the organometallic derivatives (MgX, Li) obtained from the monohalodiphenylmethanes by reaction with bisdiethylaminochlorophosphine or the corresponding arsine and Friedel Crafts ring closure[2–4,6] or alternatively, from the dimetallic diphenylmethane derivatives with diethylaminodichlorophosphine[2,7] or arsine, respectively. It was observed that in the arsenic case the direct ring closure by



	4a	4b	4c	4d	4e	4f	4g	4h	4i	4j	4k	4l	4m
R₁	H	H	H	H	H	C_6H_5	H	C_6H_5	C_6H_5	C_6H_5	C_6H_5	$(CH_3)_3C$	$(CH_3)_3C$
X	Cl	Br	I	Cl	Br	Br	I	I	Cl	Br	I	Cl	Br
Y	H	H	H	Cl	Br	H	I	H	Cl	Br	I	H	H

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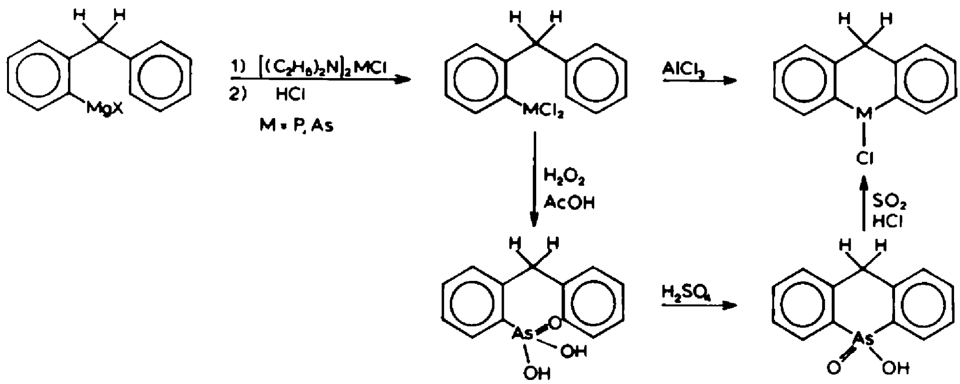


Friedel Crafts reaction of the dichloroarsine gave lower yields than the alternative, namely oxidation to the corresponding arsonic acid, ring closure with sulphuric acid followed by reduction with sulphur dioxide and hydrogen chloride.[8] Silicon[9,10] and tin[10,11] have only been introduced via the bisorgano-metallic compounds, because ring closure of 2-siladiphenylmethane derivatives failed[9] and antimony[10,11] was incorporated by reaction of antimony trichloride with the corresponding tin derivative.

The 9-heteroanthracenes obtainable from the dihydro precursors were not stable for phosphorus[2,3] and arsenic;[12] there was no observable formation of such tricyclic aromatic compounds at all in the case of silicon[9] and antimony.[13] It was therefore of interest to investigate the possibility of stabilizing unsubstituted 9-heteroanthracenes by introduction of a substituent in the 10-position. The most promising substituents are the phenyl group[2,14–16] and the t-butyl group. As introduction of these substituents via the 9,10 - dihydro - 9 - heteroanthracenes was not possible, we had to synthesize precursors of the triphenylmethane type **4f**, **4h**, **4i**, **4j** and **4k**, respectively and of the t-butyldiphenylmethane type **4l** and **4m**. We therefore investigated the synthesis of 2-halo- and 2,2′-dihalodiphenylmethanes and methine substituted derivatives and the formation of the corresponding organometallic derivatives.

RESULTS AND DISCUSSION

In the following, the synthesis of the different types of compounds is described together with illustrations of their application in the preparation of 9,10 - dihydro - 9 - hetero - anthracenes (Experimental).

I. *Derivatives of diphenylmethane*

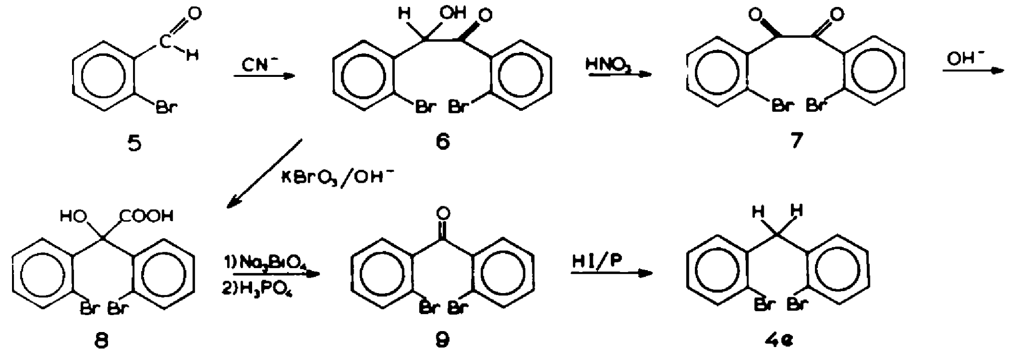
2,2′-Dibromodiphenylmethane (**4e**). This compound was first synthesized from benzophenone by the method of Thorp and Wildman,[17] which involved many steps and gave a very low overall yield. Therefore, we hoped to prepare **4e** in a better yield along the route analogous to the synthesis of 2,2′ - dichlorodiphenylmethane (**4d**).[18,19]

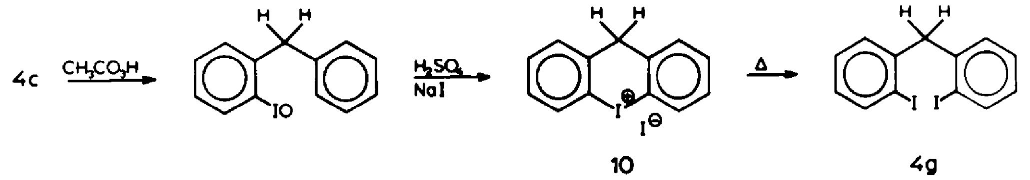
The benzoin condensation of 2 - bromobenzaldehyde (**5**) yielded **6**, which was oxidized with nitric acid to 2,2′ - dibromobenzil (**7**), followed by rearrangement with base to **8**. However, **6** could be directly converted to **8** by oxidation with potassium bromate in sodium hydroxide solution analogous to the procedure described for the unsubstituted benzoin.[20] Reduction of 2,2′ - dibromobenzophenone (**9**) with hydroiodic acid and red phosphorus[21,22] yielded 2,2′ - dibromodiphenylmethane (**4e**) (9% yield, based on **5**). Because of the relatively long route and the low yield, **4e** was normally not used for the synthesis of heteroanthracenes (see below). For the preparation of 2,2′ - dibromotriphenylmethane (**4j**), however, the intermediate 2,2′ - dibromobenzophenone (**9**) was of value.

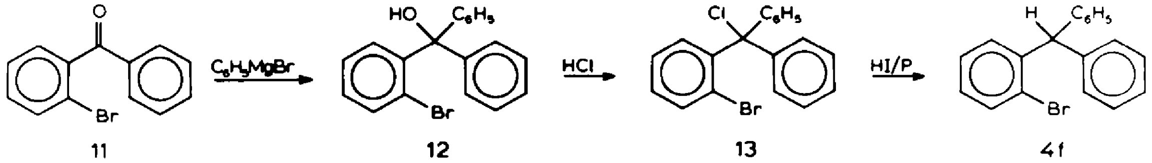
2,2′ - Diiododiphenylmethane (**4g**). 2,2′ - Diiododiphenylmethane (**4g**) was obtained in three steps in high yield from 2 - iododiphenylmethane (**4c**)[23] via oxidation with peracetic acid, ring closure with sulphuric acid, followed by pyrolysis of the iodininium iodide **10**.[24]

2,2′ - Diiododiphenylmethane (**4g**) reacted with lithium metal or n-butyllithium to form the dilithio derivative in 71% yield (double titration). Reaction with dimethyldichlorosilane yielded **1a** ($R_1=H$, $R_2=R_3=CH_3$); with dimethyltin dichloride **1b** ($R_1=H$, $R_2=R_3=CH_3$) was obtained (66% yield based on dimethyltin dichloride). When a two fold excess of 2,2′ - dilithiodiphenylmethane was added to tetrachlorosilane or germanium tetrachloride, the spiro compounds **3a** and **3b** were obtained in 13 and 25% yield, respectively.

As shown by Jutzi,[10] 2,2′ - dichlorodiphenylmethane (**4d**) reacts with magnesium to yield the di-Grignard reagent; addition of dimethyltin dichloride afforded **1b** ($R_1=H$, $R_2=R_3=CH_3$) in 60% yield. It is the starting







material of choice for 9,10 - dihydro - 9 - hetero-anthracenes rather than the dibromo- or diiodo derivatives **4e** and **4g**.

II. *Derivatives of triphenylmethane*

2 - *Bromotriphenylmethane* (**4f**). 2 - Bromotriphenylmethane (**4f**), first prepared by Tschitschibabin,[25] was obtained by a new route in comparable yield.

2 - Bromobenzophenone (**11**)[26] reacted with phenylmagnesium bromide and yielded crude **12**, which could not be purified by crystallization (compare Gomberg[27]). Efforts to reduce crude **12** with hydroiodic acid and red phosphorus to **4f** were not successful. However, treatment of crude **12** with gaseous hydrogen chloride furnished 2 - bromotriphenylmethyl chloride (**13**)[27] in pure state; reduction of **13** with hydroiodic acid and red phosphorus yielded 2 - bromotriphenylmethane (**4f**) in 30% yield (based on **11**). One of the reasons for this rather low yield is intramolecular nucleophilic aromatic substitution of bromine by the Grignard reagent.[28] The Grignard reagent derived from **4f** was used for the introduction of phosphorus[2,14] (45% yield), and borium[29] (72% yield).

2,2′ - *Dichlorotriphenylmethane* (**4i**). 2,2′ - Dichlorotriphenylmethane (**4i**) was synthesized in two ways. The first method started with the addition of phenyllithium to 2,2′ - dichlorobenzophenone (**14**),[18] the second method with the addition of 2 - chlorophenylmagnesium bromide to benzoylchloride. Both methods yielded the carbinol **15**, which after reduction with hydroiodic acid and red phosphorus yielded **4i**, 50% and 19% based on **14** and benzoylchloride, respectively. Although the second method gave a lower yield, it has the advantage of readily available starting material.

Compound **4i** did not react with magnesium and in low yield with lithium metal (±1%). The dilithio derivative was formed in better yield with naphthyllithium[30] and reacted with dimethyldichlorosilane to form **1a** ($R_1=C_6H_5$, $R_2=R_3=CH_3$; 10% yield based on **4i**).

2,2′ - *Dibromotriphenylmethane* (**4j**). 2,2′ - Dibromotriphenylmethane (**4j**) was obtained according to the first method for the preparation of **4i**. However, the yield of **4j**, based on 2,2′ - dibromobenzophenone (**9**) was low (28%), probably for the same reason as given for **4f**.[28] The Grignard reagent of **4j** gave after reaction with dimethyldichlorosilane only 8% of **1a** ($R_1=C_6H_5$, $R_2=R_3=CH_3$); the dilithio derivative formed from **4j** with n-butyllithium gave the same compound in 75% yield. Reaction of phenyltrichlorosilane with the Grignard derivative gave no isolable product at all; however, with the dilithio derivative **1a** ($R_1=R_2=C_6H_5$, $R_3=Cl$) was formed for 34%.

Shorter routes for the synthesis of **4j** were investigated but proved unsuccesful; e.g. low temperature reaction of 1,2 - dibromobenzene with n-butyllithium or magnesium followed by addition of benzoylchloride or of 2 - bromobenzophenone had no result.

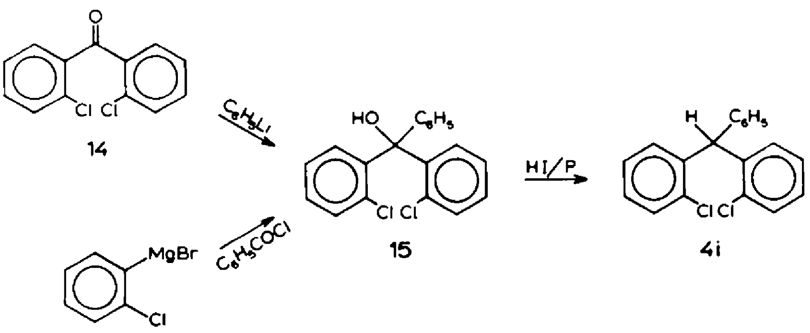
2,2′ - *Diiodotriphenylmethane* (**4k**). Two routes towards the synthesis of 2,2′ - diiodotriphenylmethane (**4k**) were explored.

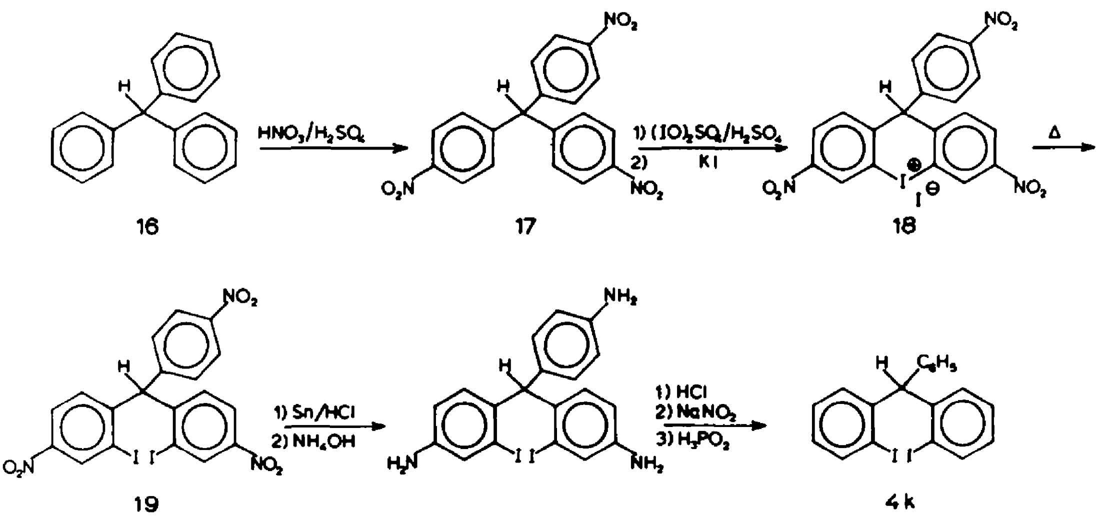
Triphenylmethane (**16**) was nitrated to **17**,[31] which was converted to **18**;[32] pyrolysis of **18** yielded **19**. Reduction of **19** with tin and hydrochloric acid and deamination of the resulting hydrochloride yielded **4k** (11% yield based on **16**).

Alternatively, 2 - nitrobenzaldehyde (**20**) was reacted with benzene in the presence of aluminium chloride and yielded 2 - nitrotriphenylmethane (**21**),[33,34] which was reduced catalytically with hydrogen to 2 - aminotriphenylmethane (**22**).[35] A Sandmeyer reaction converted **22** to 2 - iodotriphenylmethane (**4h**). 2,2′ - Diiodotriphenylmethane (**4k**) was synthesized from **4h** as described for 2,2′ - diiododiphenylmethane (**4g**) (yield 18% based on **20**).

Attempted synthesis of **4k** from **4g** as shown did not yield any **24** and was abandoned.

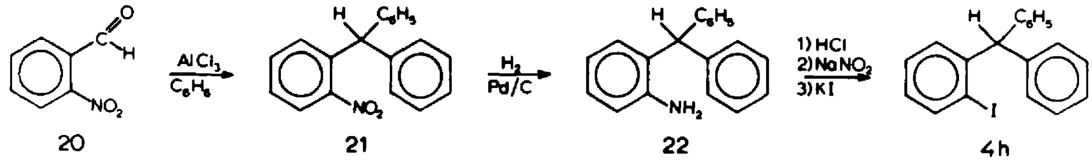
The reaction of **4k** and lithium metal followed by addition of dimethyltin dichloride gave **1b** ($R_1=C_6H_5$, $R_2=R_3=CH_3$) in about 70% yield; on heating this



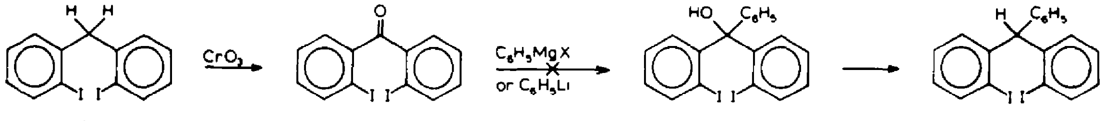


16 17 18

19 4k



20 21 22 4h



4g 23 24 4k

compound with antimony trichloride **2c** ($R_1=C_6H_5$, $R_2=Cl$) was obtained in 47% yield.

III. *Derivatives of t-butyldiphenylmethane*

1 - (2 - *Bromophenyl*) - 1 - *phenyl* - 2,2 - *dimethylpropane* (**4m**). In order to prepare 10 - t - butyl - 9 - heteroanthracenes we needed precursors with a t-butyl group at the projected 10-position. Expectedly, introduction of an alkyl group into the anion **25**, although successful with ethyl iodide, did not yield the desired product with t-butyl chloride.

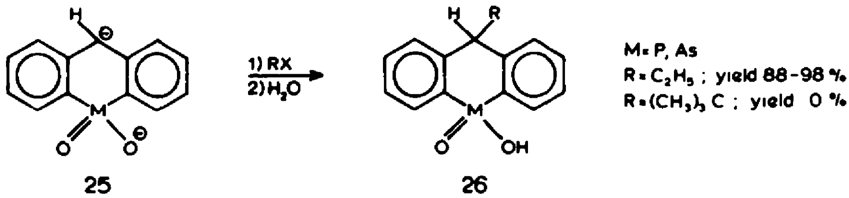
Similarly, the reaction between 2 - bromobenzophenone and t - butylmagnesium bromide or t - butyllithium yielded hardly any addition products. We therefore explored a new route to 1 - (2 - bromophenyl) - 1 - phenyl - 2,2 - dimethylpropane (**4m**).

The reaction between t - butylmagnesium chloride and 2 - bromobenzaldehyde followed by oxidation with chromic trioxide in dilute acetic acid yielded 1 - (2 - bromophenyl) - 2,2 - dimethylpropanone - 1 (**27**). The addition of phenylmagnesium bromide occured hardly in etherial solution, but was successful in refluxing benzene and yielded the carbinol **28**. Reduction of **28** with hydroiodic acid and red phosphorus gave several products; the resulting mixture was difficult to separate. The NMR spectrum showed that about half of the desired product **4m** was present; the rest consisted mainly of **29** and **30**. These side products are presumably formed by rearrangement of the intermediate carbonium ion **31**, which besides reduction to **4m**, can undergo migration of a Me group to **32** followed by migration of either of the two aryl groups and by reduction to **29** and **30**; it is noticed that the major isomer **30** is formed by 1,2 migration of the 2 - bromosubstituted aryl group. Surprisingly, **33**, the reduction product of the primary rearranged cation **32**, was not observed, probably because **32** is less stable than the other cations involved.

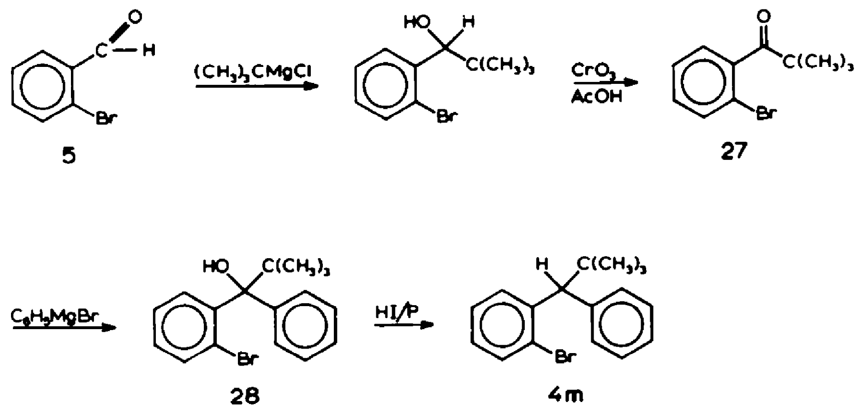
Other reducing agents, such as LAH and aluminium chloride in ethereal solution, zinc amalgam in ethanol–hydrochloric acid,[16] or hydrogen and copper chromite,[17] failed to give **4m** from **28**.

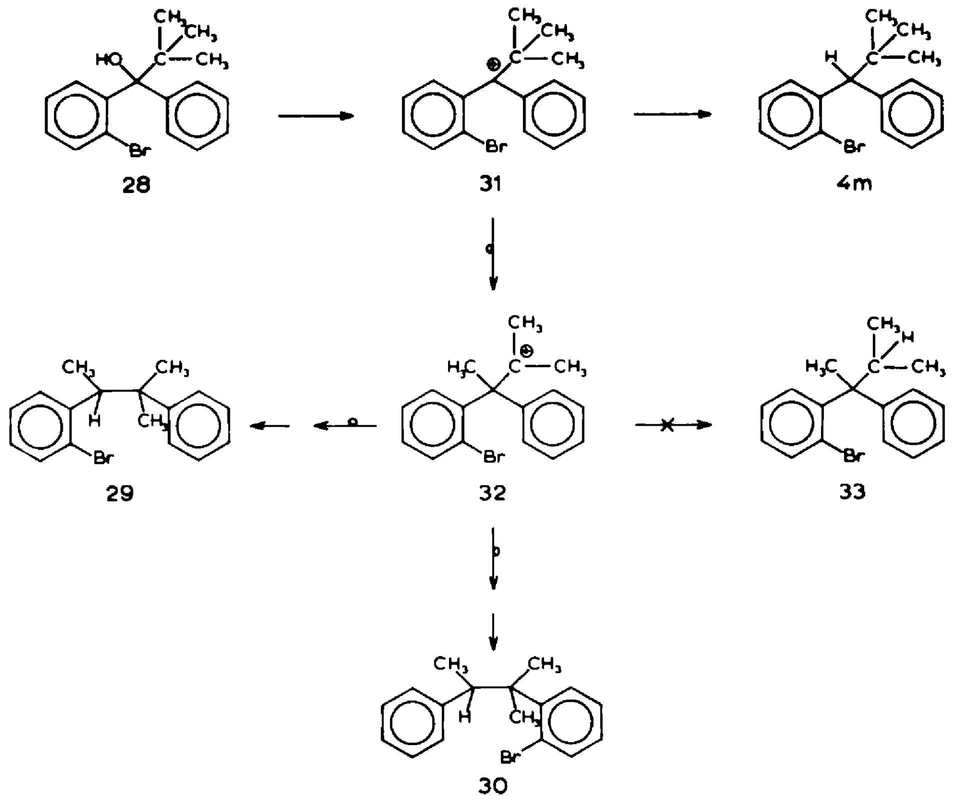
The Grignard derivative **34** reacted with bisdiethylaminochlorophosphine[2-4] or the corresponding arsine followed by treatment with gaseous hydrogen chloride to **35a** and **b** in 57% and 60% yield, respectively.

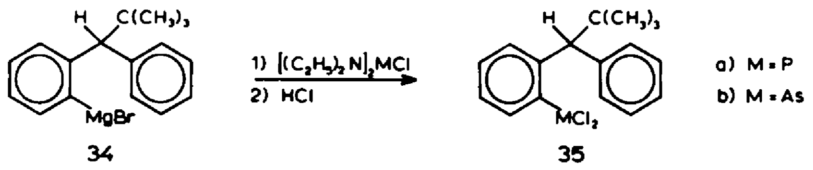
1 - (2 - *Chlorophenyl*) - 1 - *phenyl* - 2,2 - *dimethylpropane* (**4l**). 1 - (2 - Chlorophenyl) - 2,2 - dimethylpropanone - 1 (**36**) was formed in one step by the reaction

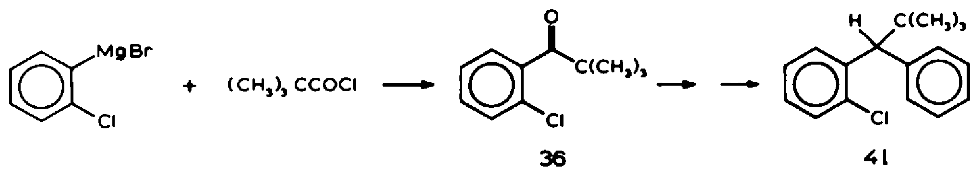


25 26


(CH3)3CMgCl
CrO3
AcOH
C6H5MgBr
HI/P
5
27
28
4m


28
31
4m
a
29
32
33
b
30


1) [(C2H5)2N]2MCl
2) HCl
a) M = P
b) M = As
34
35


(CH3)3CCOCl
36
41

of 2 - chlorophenylmagnesium bromide and pivalic acid chloride. The synthesis of **4l** is further analogous to the synthesis of **4m**. Compared to **4m**, the reaction of **4l** and magnesium followed by introduction of phosphorus or arsenic in the usual way gave low yields of **35a** and **35b**.

EXPERIMENTAL

M.ps and b.ps are uncorrected. The IR spectra were obtained on a Perkin-Elmer model 237 spectrophotometer, NMR spectra with a Varian A-60 spectrometer (chemical shifts relative to TMS as an internal standard, $\delta = 0$ ppm). Mass spectra were recorded on a Varian MAT CH5 spectrometer with electron-impact at 70 eV. A 15% SE-30 column was used for GLC analysis. Elemental analyses were performed under supervision of Mr. W. J. Buis at the Microanalytical Department of the Institute for Organic Chemistry TNO, Utrecht, The Netherlands.

I. *Derivatives of diphenylmethane*

2,2′ - *Dibromodiphenylmethane* (**4e**): 2,2′ - *Dibromobenzoin* (**6**). Compound **5** (87.2 g; 0.472 mole) in 96% EtOH (65 ml) was subjected to the benzoin condensation by refluxing it during 0.5 hr with NaCN (5 g) in water (50 ml). Since the oily product could not be crystallized after working up, crude **6** was used for the next step.

2,2′ - *Dibromobenzil* (**7**). Conc HNO_3 (570 ml, $d = 1.4$ g/ml) was added slowly to crude **6** (192.2 g; 0.520 mole), while it was stirred at 100°. When the addition was complete, heating was continued during 7 hr and afterwards the mixture was poured into water. The yellow ppt was crystallized (EtOH) and yielded **7** (52.3 g, 60% based on **6**), m.p. 127–128° [Found: C, 45.8; H, 2.0; Br, 43.3. $C_{14}H_8O_2Br_2$ (M = 368.04) requires: C, 45.69; H, 2.19; Br, 43.43%].

2,2′ - *Dibromobenzilic acid* (**8**): (a) *By benzilic rearrangement of* **7**. A mixture of **7** (32.3 g; 0.168 mole), 96% EtOH (45 ml), KOH (18.3 g) and water (35 ml) was refluxed for 15 min and then diluted with water. The ppt formed on acidification with dil HCl was crystallized (C_6H_6) and yielded **8** (24.3 g, 72%), m.p. 152–154° [Found: C, 43.2; H, 2.7; Br, 40.8. $C_{14}H_{10}O_3Br_2$ (M = 386.06) requires: C, 43.54; H, 2.62; Br, 41.40%].

(b) *By oxidation of* **6** *with potassium bromate in the presence of sodium hydroxide*. Reaction of crude **6** (20 g; 0.054 mole) with NaOH (12 g) and $KBrO_4$ (3 g) in water (20 ml) analogous to the procedure described for the preparation of the unsubstituted benzilic acid form benzoin[20] yielded after crystallization **8** (4.9 g, 24%), m.p. 148–150°.

2,2′ - *Dibromobenzophenone* (**9**). Compound **8** (16.5 g; 0.043 mole) in glacial AcOH (65 ml) was stirred violently with sodium bismuthate (15.0 g; 0.054 mole) at 50–60° during 5 hr. After addition of a mixture of 85% phosphoric acid (9 ml), water (13 ml) and standing overnight at room temp, ether (250 ml) was added. The organic layer was separated, washed successively with water, dil NaOHaq and water, the solvent removed and the residue crystallized (EtOH), yielding **9** (12.3 g, 84%), m.p. 84.5–85.5° (lit.[17], 86°).

2,2′ - *Dibromodiphenylmethane* (**4e**).[17] A mixture of **9** (12.3 g; 0.0362 mole), red P (31 g) and 57% HI (33 ml) were refluxed for 48 hr, diluted with water and extracted twice with toluene (50 ml). The organic layer was washed several times with water, dried and the solvent removed. Vacuum distillation yielded **4e**, (11.1 g, 94%), b.p. 120–121°/0.01 mm [Found: C, 47.7; H, 3.0; Br, 48.9. $C_{13}H_{10}Br_2$ (M = 326.05), requires C, 47.88; H, 3.09; Br, 49.01%]. NMR (CCl_4): 8.16–7.28 (m, 8, aryl protons); 4.60 (s, 2, methylene protons).

2,2′ - *Diiododiphenylmethane* (**4g**): 2 - *Iododiphenylmethane* (**4c**). This compound was synthesized according to the method of Blackwell and Hickinbottom.[23] Distillation *in vacuo* yielded **4c**; b.p. 110–111°/0.01 mm, $n_D^{22.5°} = 1.6417$ (lit.,[23] b.p. 177°/12 mm; $n_D^{20} = 1.6406$) [Found: C, 53.34; H, 3.74; I, 43.19. $C_{13}H_{11}I$ (M = 294.14), requires: C, 53.08; H, 3.77; I, 43.15%]. NMR (CCl_4): 7.91–6.70 (m, 9, aryl protons); 4.06 (s, 2, methylene protons).

9,10 - *Dihydrodibenz*[b,e]*iodininium iodide* (**10**). This compound was synthesized according to the method of Sandin *et al.*[24] Recrystallization (H_2O) yielded **10**, m.p. 177–178° (lit.,[24] 184.5–185.5°) [Found: C, 37.33; H, 2.52; I, 60.58. $C_{13}H_{10}I_2$ (M = 420.04) requires: C, 37.17; H, 2.40; I, 60.43%].

2,2′ - *Diiododiphenylmethane* (**4g**). Compound **10** (99.9 g; 0.238 mole) was heated under N_2 at 190° for 10 min. After cooling the product was dissolved in diethylether (300 ml), shaken twice with 0.1 N $Na_2S_2O_3$ (50 ml) was washed twice with water (25 ml). Drying the organic layer, evaporation of the solvent, vacuum distillation and crystallization (Et_2O) yielded **4g** (83.9 g, 84%), m.p. 79° [Found: C, 37.31; H, 2.54; I, 60.28. $C_{13}H_{10}I_2$ (M = 420.04), requires: C, 37.17; H, 2.40; I, 60.43%]. NMR (CCl_4): 7.97–7.73 (m, 2, aryl protons); 7.38–6.67 (m, 6, aryl protons); 4.09 (s, 2, methylene protons).

Applications of **4g**: 9,9 - *Dimethyl* - 9,10 - *dihydro* - 9 - *silaanthracene* (**1a**, $R_1 = H$, $R_2 = R_3 = CH_3$). Under N_2 **4g** (8.4 g; 0.020 mole) was dissolved in dry ether (160 ml). Cut Li wire 0.30 g (0.043 mole) was added under vigorous stirring in portions at such a rate that the mixture refluxed gently. After refluxing for an additional 2 hr the mixture was cooled and filtered. To this soln of the dilithium derivative of **4g** slowly a soln of dichlorodimethylsilane (2.6 g; 0.02 mole) in dry ether (100 ml) was added. After stirring overnight, water (20 ml) was added, the organic layer washed with water, dried and after removal of the solvent *in vacuo* 5.1 g of crude **1a** was obtained. Vacuum distillation afforded pure **1a** (2.95 g, 66%), b.p. 104–106°/1 mm (lit.,[10] b.p. 102°/2 mm). NMR (CCl_4): 7.66–7.35 (m, 2, aryl protons); 7.35–7.01 (m, 6, aryl protons); 4.03 (s, 2, methylene protons); 0.42 (s, 6, methyl protons).

9,9 - *Dimethyl* - 9,10 - *dihydro* - 9 - *stannaanthracene* (**1b**, $R_1 = H$, $R_2 = R_3 = CH_3$). A filtered soln of the dilithium derivative of **4g** prepared from **4g** (10.0 g; 0.024 mole) and cut Li wire (0.33 g; 0.047 mole) in dry ether (160 ml) was added gradually to a soln of dimethyltin dichloride (3.71 g; 0.017 mole) in dry ether (100 ml). After stirring overnight, the mixture was refluxed for 1 hr. The solvent was removed and the residue extracted twice with dry cyclohexane (100 ml). After removal of the solvent the residual oil was distilled *in vacuo* yielding **1b** (3.5 g, 66%, calculated on dimethyltin dichloride), b.p. 95–96°/0.001 mm (lit.,[10] b.p. 125°/0.001 mm), m.p. 67–68° (lit.,[10] m.p. 64°). NMR (CCl_4): 7.65–6.94 (m, 8, aryl protons); 3.89 (s+d, $^4J_{^{117,119}Sn-H} = 13$ Hz, 2, methylene protons); 0.49 (s+2d, $^2J_{^{117}Sn-H} = 93$ Hz, $^2J_{^{119}Sn-H} = 97$ Hz, 6, methyl protons).

9,9 - *Spirobis* - 9,10 - *dihydro* - 9 - *silaanthracene* (**3a**). n-BuLi (0.024 mole) in dry ether (25 ml) was added slowly under N_2 at 0° to **4g** (5.0 g; 0.012 mole) dissolved in dry ether (100 ml). After stirring for 4 hr at room temp. the mixture was cooled to −70° and tetrachlorosilane (1 g; 0.006 mole) added, stirred at room temp for 36 hr and refluxed for 1 hr. After addition of water (20 ml) and working up, the residual oil was crystallized (CCl_4) yielding **3a** (278.9 mg, 13%), m.p. 254–256° (lit.,[10] m.p. 242°). NMR ($CDCl_3$): 7.60–6.99 (m, 16, aryl protons); 4.37 (s, 4, methylene protons). Mass spectrum *m/e* (%): 360 (100), 282 (33), 194 (23), 193 (28). $C_{26}H_{20}Si^+$ calc. 370.1334, found 360.1346.

9,9 - *Spirobis* - 9,10 - *dihydro* - 9 - *germaanthracene* (**3b**). The same dilithium derivative of **4g** was prepared in equimolar quantities as in the case for **3a**. The mixture was cooled to −50° and tetrachlorogermane (1.3 g; 0.006 mole) was added. After stirring for 16 hr at room temp. and 2 hr refluxing, water was added. Working up in the usual way and crystallization (CCl_4) yielded **3b** (613.6 mg, 25%), m.p. 250–254° [Found: C, 77.30; H, 4.99. $C_{26}H_{20}Ge$ (M = 405.02) requires: C, 77.10; H, 4.98%]. NMR ($CDCl_3$): 7.60–7.01 (m, 16, aryl protons); 4.30 (s, 4, methylene protons).

II. *Derivatives of triphenylmethane*

2 - *Bromotriphenylmethane* (**4f**): 1 - (2 - *Bromophenyl*) - 1,1 - *diphenylmethanol* (**12**). A soln of the Grignard compound, prepared from bromobenzene (191.5 g; 1.220 mole) and Mg (32.6 g; 1.340 mole) in dry ether (450 ml), was added gradually to an air free soln of **11** (312.2 g; 1.196 mole)[26] in dry ether (530 ml). After completion of the addition the mixture was refluxed for 1 hr and after working up 381.3 g of crude **12** was obtained.

1 - (2 - *Bromophenyl*) - 1,1 - *diphenylchloromethane* (**13**). Crude **12** (381.3 g) was dissolved in benzene (1600 ml) and saturated with gaseous HCl. After removal of the water formed, $CaCl_2$ was added and after renewed saturation with gaseous HCl the soln was filtered, evaporated to dryness and yielded 389.5 g of oily residue.

Crystallization from dry ligroin yielded **13** (128.5 g, 30%), m.p. 121.5–123°.

2 - *Bromotriphenylmethane* (**4f**). A mixture of **13** (98.3 g; 0.275 mole), red P (360 g) and 57% HI (370 ml) was boiled for 47 hr. After working up in the usual way the crude product was crystallized (MeOH) and yielded **4g** (62.9 g, 71%), m.p. 79–80.5° (lit.,[25] 81°). NMR (CCl_4): 7.75–6.80 (m, 14, aryl protons); 5.92 (s, 1, methine proton).

2,2′ - *Dichlorotriphenylmethane* (**4i**): (a) *Addition of phenyllithium to 2,2′ - dichlorobenzophenone* (**14**), *followed by reduction.* A soln of **14** (9.7 g; 0.039 mole) in dry benzene (150 ml) was added to phenyllithium (0.058 mole) in dry diethyl ether (370 ml) over a period of 15 min. After stirring for 1 hr and refluxing for 2 hr the mixture was worked up and yielded crude **15** (15.35 g), which was stirred at 150° during 48 hr with red P (54 g) and 57% HI (54 ml). After working up the residue was crystallized (EtOH) yielding **4i** (6.9 g, 50% based on **14**), m.p. 114.5–115.5° [Found: C, 72.86; H, 4.59; Cl, 22.67. $C_{19}H_{14}Cl_2$ (M=312.88) requires: C, 72.86; H, 4.51; Cl, 22.64%]. NMR (CCl_4): 7.55–6.62 (m, 13, aryl protons); 6.22 (s, 1, methine proton).

(b) *Reaction of 2 - chlorophenylmagnesium bromide with benzoylchloride, followed by reduction.* 2 - Chlorobromobenzene (100 g; 0.520 mole) in dry ether (220 ml) was added under N_2 within 1 hr to Mg (13.4 g; 0.550 mole), refluxed for 1 hr and filtered. To this mixture was added at 0° benzoylchloride (16.86 g; 0.120 mole) in dry ether (100 ml). After refluxing for 16 hr the mixture was poured into ice water. After working up it yielded 59 g of crude **15**. This was reduced with red P and 57% HI in the usual way. Distillation *in vacuo* and crystallization (EtOH) yielded **4i** (7.0 g, 18.5%, based on benzoylchloride).

Application of **4i**: *9,9 - Dimethyl - 9,10 - dihydro - 10 - phenyl - 9 - silaanthracene* (**1a**, $R_1 = C_6H_5$, $R_2 = R_3 = CH_3$). To a soln of naphthalene (5.25 g; 0.0411 mole) in THF (75 ml) cut Li wire (0.3 g; 0.0429 mole) was added. After stirring for 2 hr at room temp., the naphthylene lithium soln[30] was filtered, cooled to −65° and a soln of **4l** (3 g; 0.0095 mole) in THF (15 ml) was added. After stirring for 1 hr at 0° this mixture was added within 1 hr to a boiling soln of dimethyldichlorosilane (1.5 ml; 0.0125 mole) in dry ether (10 ml). The mixture was purified by chromatography over neutral aluminium oxide, followed by GLC and yielded **1a** (280 mg, 10%), m.p. 79.5–82.5° [Found: C, 83.95; H, 6.90. $C_{21}H_{20}Si$ (M=300.46) requires: C, 83.94; H, 6.71%].

2,2′ - *Dibromotriphenylmethane* (**4j**). Under N_2 0.846 N phenyllithium in dry ether (35 ml) was added slowly to a soln of **9** (5.0 g; 0.015 mole) in dry ether (100 ml) and refluxed for 1 hr. After working up, 5.2 g of an oily product was obtained. This was reduced with red P (17.5 g) and 57% HI (17 ml) and worked up in the usual way. Distillation followed by crystallization (EtOH) yielded **4j** (1.65 g, 27.5%), m.p. 131–133° [Found: C, 56.91; H, 3.61; Br, 39.43. $C_{19}H_{14}Br_2$ (M = 402.13) requires: C, 56.74; H, 3.51; Br, 39.75%]. NMR (CCl_4): 7.67–7.42 (m, 2, aryl protons); 7.42–6.66 (m, 11, aryl protons); 6.13 (s, 1, methine proton).

Applications of **4j**: *9 - Chloro - 9,10 - diphenyl - 9,10 - dihydro - 9 - silaanthracene* (**1a**, $R_1=R_2=C_6H_5$, $R_3=Cl$). n-BuLi (0.0184 mole) in n-hexane (8.2 ml) was added within 1 min to a soln of **4j** (3.59 g; 0.0089 mole) in dry ether (40 ml). The mixture was added within 45 min to a boiling soln of phenyltrichlorosilane (2.35 g; 0.0111 mole) in dry ether (45 ml). After removal of the solvent and extraction with cyclohexane, the crude product was purified by GLC yielding **1a** (1.14 g, 34%) as two stereoisomers in the ratio 1:1. NMR (CCl_4): 8.1–6.5 (m, 18, aryl protons); 5.49 (s, 0.5, methine proton); 5.40 (s, 0.5, methine proton). Mass spectrum $C_{25}H_{19}{}^{28}Si^{35}Cl$: calc. *m/e* 382.0961, found *m/e* 382.0944.

9,9 - Dimethyl - 9,10 - dihydro - 10 - phenyl - 9 - silaanthracene (**1a**, $R_1=C_6H_5$, $R_2=R_3=CH_3$): (a) *Reaction of* **4j** *with magnesium.* Compound **4j** (0.97 g; 0.00242 mole) in dry THF (25 ml) was added within 2 hr to Mg (0.19 g; 0.0077 mole) under reflux. After boiling for 1 hr the Grignard reagent was filtered and added at the same time with a soln of dimethyldichlorosilane (0.31 g; 0.0024 mole) in THF (15 ml) to dry THF (5 ml) at 0°. After this addition was complete (2.5 hr) the mixture was refluxed for 14 hr, the solvent removed and the residue extracted with cyclohexane. Vacuum sublimation and GLC yielded **1a** (58 mg, 8%), identical with **1a** derived from **4i**.

(b) *Reaction of* **4j** *with n-butyllithium.* n-BuLi (0.0266 mole) in hexane (1.54 ml) was added within 1 min to **4j** (0.54 g; 0.00133 mole) in dry ether (20 ml), stirred for 4 hr and added gradually to a boiling soln of dimethyldichlorosilane (0.19 g; 0.00146 mole) in dry ether (15 ml). The mixture was filtered, the solvent evaporated and the residue extracted with CCl_4. Vacuum sublimation at 110°/0.01 mm yielded **1a** (0.3 g, 75%).

2,2′ - *Diiodotriphenylmethane* (**4k**): 4,4′,4″ - *Trinitrotriphenylmethane* (**17**). This compound was synthesized according to the method of Shoesmith *et al.*, m.p. 216–217° (lit.,[31] 212.5°). NMR (D6-DMSO): 8.43−8.10 (m, 6, aryl protons); 7.70−7.33 (m, 6, aryl protons); 6.32 (s, 1, methine proton).

3,7 - *Dinitro* - 10 - (4 - *nitrophenyl*) - 9,10 - *dihydrodibenz*[b,e]*iodininium iodide* (**18**). Following a modified method of Masson and Race,[32,38] I_2 (6.0 g; 0.024 mole) and $NaIO_4$ (14.0 g; 0.071 mole) were dissolved in H_2SO_4 (d=1.84 g/ml, 300 ml). Powdered **17** (45.0 g; 0.135 mole) was then added portionwise at *ca* 0°. The mixture was stirred at room temp. for 23 hr, and then poured into ice-water (1800 ml). The ppt was filtered off, washed with warm benzene, and after drying dissolved in formic acid (360 ml). Slow addition of KI (24 g; 0.145 mole) dissolved in formic acid (150 ml) precipitated a crystalline solid which was filtered, washed with formic acid (50 ml), water (225 ml), acetone respectively, and dried to give **18** (63.7 g, 75%). m.p. 170° (lit.,[32] 151–152°) [Found: C, 35.88; H, 1.99; I, 40.00. $C_{19}H_{11}I_2N_3O_6$ (M = 631.11) requires: C, 36.16; H, 1.76; I, 40.21%].

2,2′ - *Diiodo - 4,4′,4″ - trinitrotriphenylmethane* (**19**). Under N_2 **18** (49.9 g; 0.079 mole) was heated at 175° for 10 min. After cooling the product was dissolved in chloroform and poured on a column of aluminium oxide (Woelm, basic I), using chloroform as eluent. Evaporation of the solvent and crystallization (acetone) yielded **19** (40.3 g, 80%), m.p. 205–206° [Found: C, 36.39; H, 1.91; I, 39.96; N, 6.51. $C_{19}H_{11}I_2N_3O_6$ (M=631.11) requires: C, 36.16; H, 1.76; I, 40.21; N, 6.66%]. NMR (D6-DMSO): 8.84–8.64 (m, 2, aryl protons); 8.48–8.09 (m, 4, aryl protons); 7.57–6.89 (m, 4, aryl protons); 6.15 (s, 1, methine proton).

2,2′ - *Diiodo - 4,4′,4″ - triaminotriphenylmethane.* To a suspension of **19** (14.5 g; 0.023 mole) in conc HCl (120 ml) and AcOH (6 ml), Sn granules (24.5 g; 0.206 mole) was added in portions. When the soln had become clear, the mixture was brought to pH=8 with conc. NH_4OH. A ppt formed and was collected and washed with water (25 ml). Ppt and mother liquor were extracted with ether (500 ml). After drying over Na_2SO_4 and evaporation of the ether 2,2′ - diiodo - 4,4′,4″ - triaminotriphenylmethane could not be purified by crystallization. NMR (D6-DMSO): 7.14 (s, 2, aryl protons); 6.79–6.27 (m, 8, aryl protons); 5.28 (s, 1, methine proton); 4.28 (broad s, 6, amino protons).

2,2′ - *Diiodotriphenylmethane* (**4k**). Crude 2,2′ - diiodo - 4,4′,4″ - triaminotriphenylmethane (14.0 g; 0.020 mole) was mixed with THF (50 ml), conc. HCl (250 ml), water (80 ml) and diazotized at 5–10° with a soln of $NaNO_2$ (5.4 g; 0.081 mole) in water (25 ml). After stirring for 30 min 50% hypophosphoric acid (300 ml) was added and the mixture stirred for 24 hr at room temp. and diluted with water; the ppt was collected, dried, dissolved in chloroform and poured on a column of aluminium oxide using chloroform as eluent. Crystallization ($CHCl_3$–MeOH) yielded **4k** (6.6 g, 65%), m.p. 127° [Found: C, 46.13; H, 2.80; I, 51.26. $C_{19}H_{14}I_2$ (M=496.14) requires: C, 46.00; H, 2.84; I, 51.16%]. NMR (CCl_4): 7.94–7.60 (m, 2, aryl protons); 7.34–6.42 (m, 11, aryl protons); 5.76 (s, 1, methine proton).

2 - *Iodotriphenylmethane* (**4h**): 2 - *Nitrotriphenylmethane* (**21**). This compound was prepared according to Kliegl,[33] Ungnade and Crandell,[34] m.p. 90.5–92° (lit., m.p. 93–94°,[33] 88–89°[34]).

2 - *Aminotriphenylmethane* (**22**). Compound **21** (20.5 g; 0.079 mole) was reduced with H_2 and 10% Pd–C (2 g) in abs EtOH (160 ml). After 3 hr the reduction was completed, the mixture heated to 60° and filtered. Crystallization (EtOH) yielded **22** (13.5 g, 73%), m.p. 126–128° (lit.,[35] 128–130°). NMR (CCl_4): 7.55–6.37 (m, 14, aryl protons); 5.40 (s, 1, methine proton); 3.23 (s, 2, amino protons).

2 - *Iodotriphenylmethane* (**4h**). Compound **22** (24.0 g; 0.092 mole) was dissolved in conc HCl (40 ml) and water (1 l) and diazotized at 0° with a soln of $NaNO_2$ (8.0 g; 0.120 mole) in water

(40 ml). After stirring for 30 min a soln of KI (60 g; 0.362 mole) in water (60 ml) was added within 15 min, the mixture stirred overnight and worked up. Vacuum distillation and crystallization (MeOH) yielded **4h** (26.1 g, 76%), m.p. 78–79° [Found: C, 61.99; H, 4.15; I, 34.02. $C_{19}H_{15}I$ (M = 370.21) requires: C, 61.64; H, 4.08; I, 34.28%]. NMR (CCl_4): 7.91–6.65 (m, 14, aryl protons); 5.76 (s, 1, methine proton).

2,2' - *Diiodotriphenylmethane* (**4k**): 9,10 - *Dihydro* - 10 - *phenyl* - *dibenz*[b,e]*iodininium iodide*. To **4h** (3.2 g; 0.0086 mole) dissolved in Ac_2O (80 ml), 30% H_2O_2 (16 ml) was added at such a rate that the temp. of the mixture did not exceed 50°. After stirring for 4 days conc. H_2SO_4 (8 ml) was added slowly, stirred for another 2 days, poured into water (150 ml) and extracted twice with benzene (25 ml) to remove any unchanged **4h**. To the water layer was added a soln of KI (2.5 g) in water (10 ml); the ppt was collected and dried, yielding 9,10 - dihydro - 10 - phenyl - dibenz[b,e]iodininium iodide (3.0 g, 70%), m.p. 188–189° [Found: C, 46.75; H, 3.06; I, 49.98. $C_{19}H_{14}I_2$ (M = 496.10) requires: C, 46.00; H, 2.84; I, 51.16%].

2,2' - *Diiodotriphenylmethane* (**4k**). 9,10 - Dihydro - 10 - phenyl - dibenz[b,e]iodininium iodide (26.55 g; 0.0535 mole) was heated under N_2 at 200° for 4 min, dissolved in chloroform and poured on a column of aluminium oxide (Woelm, basic I) using chloroform as eluent. Crystallization ($CHCl_3$–MeOH) yielded **4k** (19.05 g, 72%), m.p. 124–127°, identical with the product obtained from 2,2' - diiodo - 4,4',4" - triaminotriphenylmethane.

2,2' - *Diiodobenzophenone* (**23**). To a soln of **4g** (5.0 g; 0.021 mole) in AcOH (80 ml) was added CrO_3 (10 g) at such a rate that the temp. of the mixture remained at about 65°. After heating at 100° for 5 hr the mixture was poured into water (500 ml) and extracted 6 times with ether (50 ml). Working up and crystallization (EtOH) yielded **23** (2.79 g, 54%), m.p. 108–109° [Found: C, 36.11; H, 1.95; I, 58.08; O, 3.66. $C_{13}H_8I_2O$ (M = 434.03) requires: C, 35.97; H, 1.86; I. 58.48; O, 3.69%]. IR (KBr) ν_{max} in cm^{-1}: 1665 (C=O).

Applications of **4k**: 9,9 - *Dimethyl* - 9,10 - *dihydro* - 10 - *phenyl* - 9 - *stannaanthracene* (**1b**, $R_1 = C_6H_5$, $R_2 = R_3 = CH_3$). To a soln of **4k** (0.50 g; 0.0010 mole) in dry ether (10 ml) was added under violent stirring cut Li wire (0.08 g; 0.011 mole) and the mixture was refluxed for 45 min. The red–brown soln of the dilithium derivative of **4k** was filtered and dimethyltin dichloride (0.27 g; 0.012 mole) in dry ether (8 ml) added. After refluxing for 1 hr and stirring overnight at room temp. the mixture was filtered, the solvent removed and the residue extracted with CCl_4 (10 ml). After evaporation of the solvent the residue was crystallized (MeOH) yielding **1b** (0.27 g, 69%), m.p. 110–111° [Found: C, 64.71; H, 5.08. $C_{21}H_{20}Sn$ (M = 391.07) requires: C, 64.66; H, 4.91%]. NMR (CCl_4): 7.63–6.45 (m, 13, aryl protons); 5.18 (s, 1, methine proton); 0.28 (s, 3, alkyl protons); −0.53 (s, 3, alkyl protons).

9 - *Chloro* - 9,10 - *dihydro* - 10 - *phenyl* - 9 - *stibaanthracene* (**2c**, $R_1 = C_6H_5$, $R_2 = Cl$). Compound **1b** (195 mg; 0.5 mmole) ($R_1 = C_6H_5$, $R_2 = R_3 = CH_3$) and antimony trichloride (114 mg; 0.5 mmole) were heated in a Carius tube at 110° for 1 hr. After opening of the tube, the dimethyltin dichloride formed was removed by sublimation at 60°/0.01 mm. The oily residue solidified with a little dry ether and was sublimed at 130°/0.01 mm, yielding **2c** (94.3 mg, 47%), m.p. 177–178° [Found: C, 56.44; H, 3.68; Cl, 8.66; Cl, 8.66. $C_{19}H_{14}SbCl$ (M = 399.56), requires: C, 57.11; H, 3.53; Cl, 8.87%]. NMR ($CDCl_3$): 7.93–7.68 (m, 2, aryl protons); 7.62–6.93 (m, 9, aryl protons); 6.88–6.50 (m, 2, aryl protons); 5.40 (s, 1, methine proton).

III. *Derivatives of t-butyldiphenylmethane*

9 - Hydroxy - 9 - oxo - 10 - ethyl - 9,10 - dihydro - 9 - phosphaanthracene (**26**, M = P) 140 mg (0.61 mmole) of 9 - hydroxy - 9 - oxo - 9,10 - dihydro - 9 - phosphaanthracene[6] was dissolved under N_2 in dry DMSO (10 ml) and a 2.25 N n-BuLi soln in hexane (1.3 ml) was added. After stirring for 15 min EtI (0.3 ml) was added to the deep red soln of **25**. After decoularization water (2 ml) was added and the solvent was distilled off *in vacuo*. The residue was dissolved in dil NaOH aq acidification with HCl precipitated crude **26**, which yielded after crystallization (EtOH) pure **26** (154.2 mg, 98%), m.p. 227–229°. NMR (D6-DMSO): 8.07 – 7.55 (m, 2, aryl protons); 7.55 – 7.10 (m, 6, aryl protons); 6.90 (s, 1, hydroxy proton); 3.96 (t, 1, methine proton, $^3J_{H-H} = 7.4$ Hz); 1.86 (quintet, 2, alkyl protons, $^3J_{H-H} = 7.4$ Hz); 0.84 (t, 3, alkyl protons, $^3J_{H-H} = 7.4$ Hz). IR (KBr) ν_{max} in cm^{-1}: 2100 (P–OH), 1200 (P=O).

9 - *Hydroxy* - 9 - *oxo* - 10 - *ethyl* - 9,10 - *dihydro* - 9 - *arsaanthracene* (**26**, M = As). The same method was used for the corresponding arsinic acid; 9 - hydroxy - 9 - oxo - 9,10 - dihydro - 9 - arsaanthracene[8] (822.4 mg; 3.0 mole) in dry DMSO (50 ml), n-butyllithium in hexane (6.5 ml) and EtI (1.5 ml) in an N_2 atmosphere, yielded after crystallization (dil. AcOH) pure **26** (795 mg, 88%), m.p. 238–241° [Found: C, 59.59; H, 5.29; As, 24.77; O, 10.72. $C_{15}H_{15}AsO_2$ (M = 302.18) requires: C, 59.62; H, 5.00; As, 24.79; O, 10.59%]. NMR (CF_3COOH): 8.24–7.93 (m, 2, aryl protons); 7.93–7.25 (m, 6, aryl protons); 4.29 (t, 1, methine proton, $^3J_{H-H} = 7.0$ Hz); 2.00 (quintet, 2, alkyl protons, $^3J_{H-H} = 7.0$ Hz); 0.93 (t, 3, alkyl protons, $^3J_{H-H} = 7.0$ Hz). IR (KBr) ν_{max} in cm^{-1}: 2360, 1710 (As–OH), 890 (As=O).

1 - (2 - *Bromophenyl* - 1 - *phenyl* - 2,2 - *dimethylpropane* (**4m**): 1 - (2 - *Bromophenyl*) - 2,2 - *dimethylpropanol* - 1. To a filtered Grignard reagent prepared from t-BuCl (700 g; 7.6 mole) and Mg (200 g; 8.23 mole) in dry ether (2.5 l) was added at 0°, **5** (490 g; 2.65 mole). After stirring overnight at room temp., the mixture was hydrolyzed with sat NH_4Cl aq. (2 l). Working up and distillation *in vacuo* yielded 1 - (2 - bromophenyl) - 2,2 - dimethylpropanol - 1 (405 g, 63%), b.p. 100–104°/1 mm [Found: C, 54.32; H, 6.02; Br, 32.85; O, 7.00. $C_{11}H_{15}BrO$ (M = 243.15) requires: C, 54.33; H, 6.21; Br, 32.86; O, 6.58%]. NMR ($CDCl_3$): 7.63–6.84 (m, 4, aryl protons), 4.98 (s, 1, methine proton); 2.87 (s, 1, hydroxy proton); 0.95 (s, 9, alkyl protons). IR (CCl_4) ν_{max} in cm^{-1}: 3620 (C–OH). Mass spectrum *m/e* (%): 244 (0.3), 242 (0.3), 187 (63), 185 (63), 163 (20), 159 (16), 157 (19), 107 (19), 105 (20), 79 (22), 78 (31), 77 (75), 58 (81), 57 (100).

1 - (2 - *Bromophenyl*) - 2,2 - *dimethylpropanone* - 1 (**27**). To a cooled soln of 1 - (2 - bromophenyl) - 2,2 - dimethylpropanol - 1 (416 g; 1.71 mole) in AcOH (150 ml; 75%), CrO_3 (1.89 mole) in AcOH (1 l) and water (35 ml) was added at such a rate that the temp. of the mixture did not exceed 10°. After stirring overnight at room temp. the mixture was warmed at 50° for 45 min and poured into water (1.5 l). The mixture was extracted with chloroform (450 ml). The chloroform layer was separated, washed with water, dired and evaporated to dryness. The residue was vacuum distilled and yielded **27** (271.4 g, 70%), b.p. 92–95°/1 mm [Found: C, 55.11; H, 5.42; Br, 32.37; O, 6.65. $C_{11}H_{13}BrO$ (M = 241.13) requires: C, 54.79; H, 5.43; Br, 33.14; O, 6.64%]. NMR ($CDCl_3$): 7.71–6.98 (m, 4, aryl protons), 1.23 (s, 9, alkyl protons). IR (CCl_4) ν_{max} in cm^{-1}: 1690 (C=O). Mass spectrum *m/e* (%): 242 (2), 240 (2), 185 (100), 183 (100), 157 (17), 155 (17), 105 (34), 77 (20), 76 (21), 75 (21), 57 (65).

1 - (2 - *Bromophenyl*) - 1 - *phenyl* - 2,2 - *dimethylpropanol* - 1 (**28**). A filtered Grignard reagent prepared from bromobenzene (266 g; 1.694 mole) and Mg (45 g; 1.851 mole) in dry ether (1 l) was added to **27** (290.4 g; 1.204 mole) in dry benzene (1 l). The ether was distilled off and the mixture refluxed for 0.5 hr. After standing overnight the mixture was poured into 20% NH_4Cl (3 l). Extraction with chloroform, working up and distillation *in vacuo* followed by crystallization (MeOH) yielded **28** (340 g, 89%), m.p. 74–76° [Found: C, 63.99; H, 6.10; O, 4.99; Br, 24.85. $C_{17}H_{19}BrO$ (M = 319.24) requires: C, 63.95; H, 5.96; O, 5.02; Br, 25.07%]. NMR ($CDCl_3$): 8.29–8.02 (m, 1, aryl proton); 7.65–6.87 (m, 8, aryl protons); 3.98 (s, 1, hydroxy proton); 1.25 (s, 9, alkyl protons). IR (KBr) ν_{max} in cm^{-1}: 3580, 3550 (C–OH). Mass spectrum *m/e* (%): 320 (< 0.1), 318 (< 0.1), 264 (15), 263 (100), 262 (15), 261 (100), 185 (46), 183 (46), 105 (41), 77 (34), 57 (11).

1 - (2 - *Bromophenyl*) - 1 - *phenyl* - 2,2 - *dimethylpropane* (**4m**). Compound **28** (35.0 g; 0.110 mole) was reduced with red P (120 g) and 57% HI (200 ml) in the usual way. After working up 34.79 g of an oil was obtained. The NMR spectrum showed that it consisted of 4 products: **4b**, **4m**, **29** and **30** in the ratio of about 1:5:2:3, respectively. Vacuum distillation on a spinning band column yielded **4b**, b.p. 130–140°/5 mm, NMR ($CDCl_3$): 7.67–7.46 (m, 1, aryl proton), 7.46–6.74 (m, 8, aryl protons); 4.04 (s, 2, methylene protons) and **4m** (9.6 g, 29%), b.p. 164–165°/ mm [Found: C, 67.67; H, 6.41; Br, 25.99; $C_{19}H_{19}Br$ (M = 303.24), requires: C, 67.33; H, 6.32; Br, 26.35%], NMR ($CDCl_3$): 7.91–6.83 (m, 9, aryl protons); 4.59 (s, 1, methine proton), 1.07 (s, 9, alkyl protons). Mass

spectrum *m/e* (%): 304 (0.5), 302 (1.6), 300 (1.1), 248 (17), 247 (21), 246 (17), 245 (21), 167 (20), 166 (42), 165 (33), 119 (24), 105 (8), 91 (18), 57 (100). The distillation residue consisted mainly of **29** and **30**, which can in principle be identified by their mass spectra (**29** is expected to give under electron-impact fragment ions at *m/e* 183 and *m/e* 119 and **30** fragment ions at *m/e* 197 and *m/e* 105). Separation by GLC afforded **29** (NMR ($CDCl_3$): 7.84–7.76 (m, 9, aryl protons); 3.79 (q, 1, methine proton, $^3J_{H-H}=7.0$ Hz); 1.33 (s, 3, methyl protons); 1.27 (s, 3, methyl protons); 0.99 (d, 3, methyl protons, $^3J_{H-H}=7.0$ Hz). Mass spectrum *m/e* (%): 304 (0.1), 302 (0.2), 300 (0.1), 185 (1), 183 (1), 119 (100), 105 (6), 91 (50)] and **30** [NMR ($CDCl_3$): 7.84–6.82 (m, 9, aryl protons); 4.30 (q, 1, methine proton, $^3J_{H-H}=7.0$ Hz); 1.40 (s, 3, methyl protons); 1.33 (s, 3, methyl protons); 1.08 (d, 3, methyl protons, $^3J_{H-H}=7.0$ Hz). Mass spectrum *m/e* (%): 304 (1), 302 (1), 199 (40), 197 (40), 119 (27), 105 (100), 91 (65)].

Applications of **4m**: 1 - (2 - *Dichlorophosphinophenyl*) - 1 - *phenyl* - 2,2 - *dimethylpropane* (**35a**). The filtered Grignard compound **34**, prepared under N_2 from **4m** (27.0 g; 0.090 mole) and Mg (2.5 g; 0.103 mole) in dry THF (150 ml), was added to bisdiethylaminochlorophosphine[39] (18 ml; 0.090 mole) in dry ether (130 ml), which was cooled at −60°. After stirring overnight the solvent was distilled off and the residue was extracted with dry cyclohexane (300 ml). After filtration under N_2, the soln was saturated with gaseous HCl and after renewed filtration and evaporation of the filtrate, the residue was vacuum distilled and yielded **35a** (16.8 g, 57%), b.p. 141–151°/0.1 mm. NMR ($CDCl_3$): 8.57–8.24 (m, 1, aryl proton); 7.76–7.30 (m, 8, aryl protons); 3.91 (d, 1, methine proton, $^4J_{P-H}=11$ Hz); 1.10 (s, 9, methyl protons).

1 - (2 - *Dichloroarsinophenyl*) - 1 - *phenyl* - 2,2 - *dimethylpropane* (**35b**). The filtered Grignard compound **34**, prepared from **4m** (11.8 g; 0.039 mole) and Mg (1.02 g; 0.042 mole) in dry THF (95 ml) was added to bisdiethylaminochloroarsine[40] (12.1 ml; 0.060 mole) in dry ether (75 ml) at −60°. The mixture was worked up in the same way as **35a** and yielded **35b** (8.4 g, 60%), b.p. 154–158°/0.01 mm. NMR ($CDCl_3$): 8.30–8.04 (m, 1, aryl proton); 7.69–7.05 (m, 8, aryl protons); 4.35 (s, 1, methine proton); 1.08 (s, 9, methyl protons).

1 - (2 - *Chlorophenyl*) - 1 - *phenyl* - 2,2 - *dimethylpropane* (**41**): 1 - (2 - *Chlorophenyl*) - 2,2 - *dimethylpropanone* - 1 (**36**). To a soln of pivalic acid chloride (46.0 g; 0.380 mole) in dry ether (90 ml) 2 - chlorophenylmagnesium bromide (0.380 mole) in dry ether (200 ml) was added at room temp. over a period of 0.5 hr. The mixture was refluxed for 1 hr and treated with 2 N HCl (200 ml). The water layer was extracted with ether (150 ml), washed with 7% $NaHCO_3$ aq (100 ml), dried and after evaporation of the solvent the residue was vacuum distilled yielding **36** (42.8 g, 60%), b.p. 116–117°/10 mm [Found: C, 67 01; H, 6.74; Cl, 17.79; O, 8.41. $C_{11}H_{13}ClO$ (M=196.68) requires: C, 67.18; H, 6.66; Cl, 18.03; O, 8.13%]. NMR ($CDCl_3$): 7.51–6.97 (m, 4, aryl protons); 1.20 (s, 9, methyl protons). IR (CCl_4) ν_{max} in cm^{-1}: 1690 (C=O). Mass spectrum *m/e* (%): 198 (1.2), 196 (3.2), 141 (39), 139 (100), 113 (6), 111 (17), 77 (5), 76 (5), 75 (12), 57 (32).

1 - (2 - *Chlorophenyl*) - 1 - *phenyl* - 2,2 - *dimethylpropanol* - 1. Compound **36** (40.0 g; 0.203 mole) in dry benzene (500 ml) was heated under reflux and PhMgBr (0.305 mole) in dry ether (310 ml) was added gradually. The ether was distilled off, the mixture refluxed for 3 hr and hydrolyzed with 20% NH_4Cl aq (400 ml). The water layer was extracted twice with chloroform (25 ml) and the combined extracts dried. After evaporation of the solvent the residue was vacuum distilled yielding 1 - (2 - chlorophenyl) - 2,2 - dimethylpropanol - 1 (42.8 g, 77%), b.p. 122–137°/0.5 mm [Found: C, 74.06; H, 6.99; Cl, 12.61; O, 6.15. $C_{17}H_{19}ClO$ (M=274.79) requires: C, 74.31; H, 6.97; Cl, 12.90; O, 5.82%]. NMR ($CDCl_3$): 8.26–8.01 (m, 1, aryl proton); 7.50–7.00 (m, 8, aryl protons); 3.90 (s, 1, hydroxy proton); 1.22 (s, 9, methyl protons). IR (KBr) ν_{max} in cm^{-1}: 3580 (C–OH). Mass spectrum *m/e* (%): 276 (<0.1), 274 (<0.1), 220 (6), 219 (33), 218 (18), 217 (100), 141 (21), 139 (63), 105 (26), 77 (20), 57 (15).

1 - (2 - *Chlorophenyl*) - 1 - *phenyl* - 2,2 - *dimethylpropane* (**41**). 1 - (2 - Chlorophenyl) - 1 - phenyl - 2,2 - dimethylpropanol - 1 (20.0 g; 0.073 mole) was reduced with red P (80 g) and 57% HI (120 ml) in the usual way. After working up, 14.0 g of an oil was obtained and the NMR spectrum showed that it consisted of three products: **41** and the chloro compounds corresponding to **29** and **30** (Br=Cl) in the ratio of about 5:2:3, respectively. Vacuum distillation on a spinning band column yielded **41** (6.5 g, 35%), b.p. 98–100°/2 mm [Found: C, 79.28; H, 7.46; Cl, 12.96. $C_{17}H_{19}Cl$ (M=258.79) requires: C, 78.90; H, 7.40; Cl, 13.70%]. NMR ($CDCl_3$): 7.90–7.65 (m, 1, aryl proton); 7.65–7.00 (m, 8, aryl protons), 4.55 (s, 1, methine proton); 1.05 (s, 9, methyl protons). Mass spectrum *m/e* (%): 260 (1.2), 258 (3.3), 222 (6), 204 (23), 203 (40), 202 (71), 201 (93), 168 (24), 167 (62), 166 (62), 165 (7), 119 (36), 105 (15), 91 (20), 77 (7), 57 (100).

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