233-234 °C (760 torr)]. Its ^{1}H NMR and IR spectra were identical with those of an authentic sample (Aldrich, benzylacetone).

(3) 1-Bromobutane Alkylation. A mixture of 80 mL of THF and 49.82 g of polymer-bound ester (10% DVB gel, 0.67 mmol of ester/g) was treated with 43.5 mmol of triphenylmethyllithium and 4.75 mL (44.2 mmol) of 1-bromobutane (Aldrich) as in the preceeding experiments. The polymer was filtered and washed twice with 10 mL of THF and with 100 mL of ethanol. The solution was acidified with concentrated HCl, rotary evaporated to an oil, and diluted with diethyl ether. Freshly prepared diazomethane (6 molar equiv in diethyl ether) was added at -10 °C under nitrogen, and the solution was allowed to stand for 3 h at room temperature. After evaporation of the solvent, methyl 2-benzylhexanoate was obtained by column chromatography over silica gel with diethyl ether as the eluant. Evaporation of the ether gave 5.87 g of material whose ^{1}H NMR and IR spectra were the same as those of the independently synthesized compound.

(4) Benzyl Bromide Alkylation. The same procedure as above was followed with 75 mL of THF, 45.73 g of polymer-bound ester (10% DVB gel, 0.67 mmol of ester/g), 40.5 mmol of triphenylmethyllithium, and 4.9 mL (41.0 mmol) of benzyl bromide. After diazomethane methylation, methyl 2-benzylhexanoate was obtained by column chromatography over silica gel with diethyl ether as the eluant. Evaporation of solvent gave 5.92 g of material whose ^{1}H NMR and IR spectra were the same as those of the independently synthesized compound.

Recycling of Polymer. The first cycle used 40.0 g of 10% cross-linked gel polymer (0.67 mmol of ester/g) for *p*-nitrobenzoylation. The yield reported in Table VIII was isolated by the large-scale procedure. The recovered polymer was filtered, washed with 100 mL of THF-water (3:1), 10 mL of THF-ethanol (3:1), and 100 mL of THF, and dried at 30 °C under vacuum overnight. The dried polymer (36.67 g) in 150 mL of THF was swollen for 6 h, and 23.1 mmol of 0.38 M triphenylmethyllithium in THF was added at -40 °C under nitrogen with mechanical stirring. The mixture warmed slowly to room temperature. After it was cooled again to -40 °C, 3-phenylpropanoyl chloride (18.43 g, 108.5 mmol) in 10 mL of THF was added with mechanical stirring. The mixture warmed to room temperature and was stirred for 24 h. The polymer was filtered, washed with 100 mL of THF-diethyl ether (3:1), 100 mL of THF-ethanol (3:1), and 100 mL of THF and dried at 30 °C under vacuum overnight.

The second and third cycles of enolate *p*-nitrobenzoylation used the same procedures. The yield in Table VIII from cycle two was isolated. The yield from cycle three was determined by GC.

Acylation of Benzyl 3-Phenylpropanoate at Room Temperature. To a solution of 0.386 g (1.65 mmol) of benzyl 3-phenylpropanoate in 15 mL of THF in a 100-mL flask was added 2.475 mmol of triphenylmethyllithium in 3 mL of THF at room temperature with mechanical stirring. After 1 min, 0.61 g (3.3 mmol) of *p*-nitrobenzoyl chloride in 5 mL of THF was added. After 4 h, 1.6 g of 50% aqueous KOH was added, and the mixture was refluxed at 75 °C for 25 h. The mixture was cooled to room temperature and acidified with concentrated HCl. The solvents were evaporated, and the yields were determined by GC as described earlier (see Results).

Acknowledgment. We thank the U. S. Army Research Office for financial support.

Registry No. 6a, 54914-77-1; **8**, 5396-91-8; **9**, 103-25-3; diethenylbenzene-(chloromethyl)ethenylbenzene copolymer, 9036-15-1.

(26) Rupe, H.; Müller, H. *Helv. Chim. Acta* **1921**, *4*, 841-860.

Applications of the Vilsmeier Reaction. 13. Vilsmeier Approach to Polycyclic Aromatic Hydrocarbons

M. Parameswara Reddy and G. S. Krishna Rao*

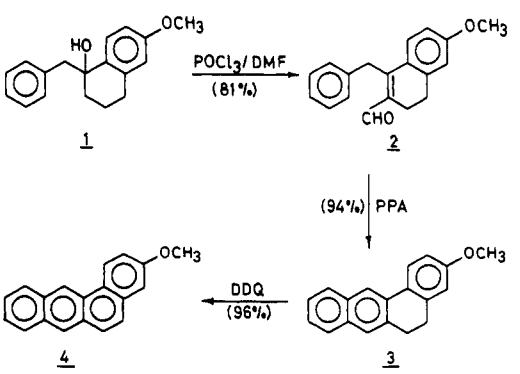
Department of Organic Chemistry, Indian Institute of Science, Bangalore 560 012, India

Received May 20, 1981

The synthesis of three typical polycyclic hydrocarbons (PAH) has been described, wherein the Vilsmeier reaction plays a major role. Vilsmeier reaction of the tetralol **1** gives the dihydronaphthaldehyde **2** which on cyclodehydration gives the dihydroarene **3**. Its dehydrogenation affords 3-methoxybenz[*a*]anthracene (**4**). Vilsmeier reaction on the dimethoxydihydronaphthalene **5** gives the versatile dimethoxydihydronaphthaldehyde **6** which has been converted to the dimethoxybenzo[*c*]fluorene **7** by direct cyclodehydration and the fulvene **10** by cyclodehydration of allylic alcohol **8** derived from **6** followed by dehydrogenation. The saturated alcohol **12** corresponding to **8** undergoes cyclodehydration to give the dimethoxyhexahydrobenzo[*c*]phenanthrene (**13**). Some of the advantages of the Vilsmeier approach to PAH have been pointed out.

Previous papers in this series deal with the application of the Vilsmeier reaction in the synthesis of diverse natural products (terpenoids,[1] chromenes,[2] and lignans[3]) and intermediates needed in the synthesis of bioactive molecules.[4] In this paper we present the synthesis of three typical polycyclic aromatics, benz[*a*]anthracene (**4**), two benzo[*c*]fluorenes (**7** and **10**), and a hexahydrobenzo[*c*]phenanthrene (**13**), wherein Vilsmeier reaction plays a key role. Because of the widespread environmental contamination of polycyclic aromatics and the high degree of hazard they pose to humans,[5] there is an ever increasing

Scheme I



(1) (a) Alexander, J.; Krishna Rao, G. S. *Tetrahedron* **1971**, *27*, 645. (b) Reddy, P. A.; Krishna Rao, G. S. *Indian J. Chem. Sect. B* **1980**, *19B*, 578. (c) Reddy, P. A.; Krishna Rao, G. S. *Ibid.* **1980**, *19B*, 753. (d) Reddy, P. A.; Krishna Rao, G. S. *Curr. Sci.* **1981**, *50*, 631. (e) Velusamy, T. P.; Krishna Rao, G. S. *Indian J. Chem., Sect. B* **1980**, *20B*, 351.

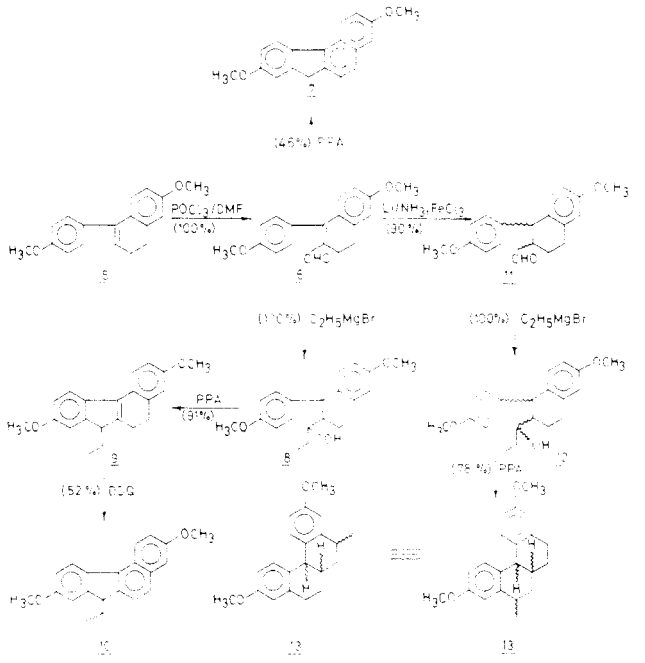
(2) (a) Naidu, M. V.; Krishna Rao, G. S. *Synthesis* **1980**, 708. (b) Naidu, M. V.; Krishna Rao, G. S. *Indian J. Chem. Sect. B* **1980**, *19B*, 313.

(3) Reddy, M. P.; Krishna Rao, G. S. *J. Chem. Soc., Perkin Trans. 1*, in press.

(4) Reddy, M. P.; Krishna Rao, G. S. *Synthesis* **1980**, 815. (b) Reddy, P. A.; Krishna Rao, G. S. *Proc. Indian Acad. Sci., Sect. A* **1980**, *89A*, 435. (c) Reddy, P. A.; Krishna Rao, G. S. *Indian J. Chem. Sect. B* **1981**, *20*, 98. (d) Reddy, M. P.; Krishna Rao, G. S. *Tetrahedron Lett.* **1981**, *22*, 3549.

0022-3263/81/1946-5371$01.25/0

Scheme II



need for the synthesis of these compounds and their metabolites in order to make them available to workers interested in studies in carcinogenesis. The Vilsmeier approach to polycyclic aromatic hydrocarbons (PAH) described in this paper may prove useful in the matters of (i) introduction of various ring substituents leading to compounds of possible carcinogenic potency,[6] (ii) easy amenability of the formyl function for further chemical manipulation, and (iii) the ease of generating perhydro arenes.[7]

Vilsmeier reaction[8] on 1-benzyl-6-methoxy-1-tetralol[9] (**1**) with dimethylformamide and phosphorus oxychloride gave 1-benzyl-6-methoxy-3,4-dihydro-2-naphthaldehyde (**2**) which on cyclodehydration with polyphosphoric acid[10] (PPA) furnished 3-methoxy-5,6-dihydrobenz[*a*]anthracene (**3**). Aromatization of **3** to the benz[*a*]anthracene[11] **4** was smoothly effected by 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in 73% overall yield by starting from **1** (Scheme I).

Vilsmeier reaction on 6-methoxy-1-(*p*-methoxyphenyl)-3,4-dihydronaphthalene[12] (**5**) gave the dihydronaphthaldehyde **6**. Its cyclodehydration with PPA afforded 3,9-dimethoxy-7*H*-benzo[*c*]fluorene (**7**, Scheme II). Treatment of the aldehyde **6** with ethylmagnesium bromide gave the allylic alcohol **8**. Its cyclodehydration with PPA gave the ethyl dihydrobenzo[*c*]fluorene **9** which exhibited in the ^{1}H NMR the two characteristic triplet patterns: [δ 0.6 (3 H, t, J = 7 Hz, CH_2CH_3), 3.33 (1 H, t, J = 5 Hz, $CHCH_2$). Dehydrogenation of **9** with DDQ gave 3,9-dimethoxy-7-ethylidenebenzo[*c*]fluorene (**10**, Scheme II; *E*/*Z* stereochemistry of **10** undetermined). The fulvene **10** clearly revealed the vinylmethyl resonance in ^{1}H NMR δ 2.41, (3 H, d, J = 8 Hz, $=CHCH_3$)]. On the other hand, cyclodehydration of the saturated alcohol **12**, corresponding to the allylic alcohol **8** obtained from the α,β-unsaturated formyl compound **6** through hydrogenation to **11** followed by Grignard reaction underwent a six-membered-ring closure, giving presumably the hexahydrobenzo[*c*]phenanthrene (**13**, Scheme II) which exhibited the characteristic secondary methyl doublet in the ^{1}H NMR [δ 0.85 (3 H, d, J = 6 Hz, $CHCH_3$)]. Its dehydrogenation by DDQ to a fully aromatic system was, however, unsuccessful.

The contrasting cyclodehydration behavior of the allylic alcohol **8** and the corresponding saturated alcohol **12** is interesting. The adjacent *p*-anisyl ring in **8** participates in a direct electrophilic attack at the allylic cation to give a benzofluorene, while in **12** the resulting olefin(s) presumably end up in a carbonium ion thermodynamically most suited for the formation of a six-membered ring.

Experimental Section

Melting points are uncorrected. Solvent extracts of reaction products were appropriately washed and dried (Na_2SO_4) before removal of the solvent. The following spectrometers were used: IR, Perkin-Elmer 397 (ν_{max} given in reciprocal centimeters); ^{1}H NMR, Varian T-60 (chemical shifts are reported in parts per million (δ) downfield from Me_4Si); UV, Beckman 26 (λ_{max} given in nanometers with log ϵ values). Bath temperature (bt) are given for short-path distillations. For TLC separations Acme silica gel was used.

1-Benzyl-6-methoxy-3,4-dihydro-2-naphthaldehyde (2). To a cooled and stirred solution of the tetralol[9] **1** (1 g) in DMF (4 mL) was added dropwise $POCl_3$ (1 mL), and the reaction mixture heated on a boiling water bath for 10 h. After the mixture cooled to room temperature, $POCl_3$ (0.5 mL) was again added and the heating continued for 5 h. The cooled reaction mixture was decomposed with aqueous NaOAc (7 g in 18 mL of water).

The product was extracted with ether (2 × 30 mL). Purification by TLC (development with benzene) of the residue left after removal of the solvent gave **2**: 0.85 g (81%); mp 116–117 °C (benzene–hexane); ^{1}H NMR ($CDCl_3$) 2.66 (4 H, br s, $2CH_2$), 3.75 (3 H, s, OCH_3), 4.33 (2 H, s, $PhCH_2$), 6.6 (1 H, dd, J = 9, 3 Hz, H_7), 6.67 (1 H, br s, H_5), 7.17 (5 H, s, C_6H_5), 7.32 (1 H, d, J = 9 Hz, H_8), 10.13 (1 H, s, CHO); IR ν_{max} (Nujol) 1680 (HC=O); UV (ethanol) λ_{max} 246 (4.0), 343 (4.18). Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.98; H, 6.52. Found: C, 82.12; H, 6.79.

3-Methoxy-5,6-dihydrobenz[*a*]anthracene (3). A mixture of **2** (400 mg) and PPA [prepared from P_2O_5 (8 g) and H_3PO_4 (5 mL)] was stirred at 85 °C for 3 h. The reaction mixture was decomposed with ice, and the ether extract (2 × 30 mL) of the product was processed to afford **3**: 352 mg (94%); mp 114–116 °C (benzene–hexane); ^{1}H NMR ($CDCl_3$) 2.93 (4 H, br s, $2CH_2$), 3.80 (3 H, s, OCH_3), 6.77 (1 H, br s, H_4), 6.87 (1 H, dd, J = 9, 3 Hz, H_2), 7.15–8.03 (7 H, m, arom H). Anal. Calcd for $C_{19}H_{16}O$: C, 87.66; H, 6.19. Found: C, 87.86; H, 6.02.

A solution of **3** (200 mg) and DDQ (200 mg) in dioxane (6 mL) was refluxed for 24 h under an N_2 blanket. The precipitated hydroquinone was filtered off and the filtrate chromatographed (neutral alumina, benzene) to yield **4**: 190 mg (96%); mp 162 °C (benzene) (lit.[11] mp 161–162 °C); ^{1}H NMR ($CDCl_3$) 3.93 (3 H, s, OCH_3), 7.16 (1 H, br s, H_4), 7.87 (1 H, dd, J = 9, 3 Hz, H_2), 7.40–8.10 (6 H, m, arom H), 8.21 (1 H, s, H_7), 8.65 (1 H, d, J = 9.5 Hz, arom H), 8.90 (1 H, s, H_{12}).

6-Methoxy-1-(*p*-methoxyphenyl)-3,4-dihydro-2-naphthaldehyde (6). To a cooled and stirred solution of **5**[12] (6 g) in DMF (10 mL) was added dropwise the Vilsmeier reagent prepared from $POCl_3$ (2.3 mL) and DMF (3 mL). The reaction mixture was stirred at room temperature for 1 h and at 60–70 °C for 30 min, when the solution became dark red. The cooled iminium complex was decomposed by the slow addition of aqueous NaOAc (15 g in 35 mL of water). The crystalline aldehyde **6** (6.6 g, quantitative) was collected by filtration: mp 105 °C (benzene–hexane); ^{1}H NMR ($CDCl_3$) 2.75 (4 H, m, $2CH_2$), 3.82 and 3.88 (6 H, 2 s, $2OCH_3$), 6.60 (1 H, dd, J = 9 and 3 Hz, H_7), 6.77 (1 H, br s, H_5), 6.87 (1

(5) Heidelberger, C. *Annu. Rev. Biochem.* **1975**, *44*, 79.
(6) (a) Sukumaran, K. B.; Harvey, R. G. *J. Org. Chem.* **1980**, *45*, 4407. (b) Newman, M. S.; Kanakarajan, K. *Ibid.* **1980**, *45*, 2301.
(7) Fu, P. P.; Lee, H. M.; Harvey, R. G. *J. Org. Chem.* **1980**, *45*, 2797.
(8) Jutz, C. In "Imminium Salts in Organic Chemistry"; Bohme, H., Viehe, H. G., Eds.; Wiley: New York, 1976, Vol. 9, p 225.
(9) Lynch, D. M.; Cole, W. *J. Med. Chem.* **1969**, *11*, 291.
(10) Popp, F. D.; McEwen, W. E. *Chem. Rev.* **1958**, *58*, 321. Uhlig, F.; Snyder, H. R. *Adv. Org. Chem.* **1960**, 1, 35–81.
(11) Smith, D. C. C. *J. Chem. Soc.* **1962**, 673. Fu, P. P.; Cortez, C.; Sukumaran, K. B.; Harvey, R. G. *J. Org. Chem.* **1979**, *44*, 4265.
(12) Bergman, F.; Smuszkowicz, J. S.; Fawaz, C. *J. Am. Chem. Soc.* **1947**, *69*, 1773.

H, d, J = 9 Hz, H_8), 6.92 (2 H, d, J = 9 Hz, $H_{3'}$ and $H_{5'}$), 7.17 (2 H, d, J = 9 Hz, $H_{2'}$ and $H_{6'}$), 9.51 (1 H, s, CHO); IR ν_{max} (Nujol) 1640 (HC=O); UV (ethanol) λ_{max} 233 (4.30), 346 (4.37). Anal. Calcd for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16. Found: C, 77.56; H, 6.49.

3,9-Dimethoxy-7*H*-benzo[*c*]fluorene (7). The aldehyde **6** (400 mg) was stirred with PPA [prepared from P_2O_5 (10 g) and H_3PO_4 (6 mL)] at 90 °C for 2 h. The reaction mixture was decomposed with ice and the product extracted with ether (2 × 30 mL). Purification by TLC (ethyl acetate/hexane, 1:4) afforded **7**: 175 mg (46%); mp 175–177 °C (methanol–hexane); ^{1}H NMR ($CDCl_3$) 3.80–3.98 (8 H, 3 s, 2 OCH_3, CH_2), 6.76–7.91 (8 H, m, arom H). Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.24; H, 5.79.

1-[6-Methoxy-1-(*p*-methoxyphenyl)-3,4-dihydro-2-naphthalenyl]propan-1-ol (8). To C_2H_5MgBr [prepared from Mg (0.4 g) and C_2H_5Br (2.25 g)] in dry ether (20 mL) was added dropwise **6** (3 g) in dry ether (30 mL) under cooling and stirring, and the reaction mixture was left overnight. After the mixture was heated to reflux for 2 h and cooled, the complex was decomposed by the slow addition of ice cold water (20 mL), followed by ice cold saturated aqueous NH_4Cl (30 mL). Processing of the ether extract afforded the allylic alcohol **8**: 3.3 g (quantitative); bt 60 °C (4 mmHg); ^{1}H NMR (CCl_4) 0.75 (3 H, t, J = 7 Hz, CH_2CH_3), 1.37 (2 H, m, CH_2CH_3), 2.0 (1 H, br, OH), 2.20, 2.80 (4 H, 2 m, $2CH_2$), 3.67, 3.73 (6 H, 2 s, $2OCH_3$), 4.03 (1 H, t, J = 7 Hz, CHOH), 6.37 (2 H, br s, H_7 and H_8), 6.53 (1 H, br s, H_5), 6.70 (2 H, d, J = 9 Hz, $H_{3'}$ and $H_{5'}$), 6.93 (2 H, d, J = 9 Hz, $H_{2'}$ and $H_{6'}$); IR ν_{max} (neat) 3420 (OH); UV (ethanol) λ_{max} 224 (4.49), 314 (4.37). Anal. Calcd for $C_{21}H_{24}O_3$: C, 77.75; H, 7.46. Found: C, 77.66; H, 7.51.

3,9-Dimethoxy-7*H*-ethyl-5,6-dihydrobenzo[*c*]fluorene (9). The allylic alcohol **8** (1 g) was stirred with PPA [prepared from P_2O_5 (20 g) and H_3PO_4 (12 mL)] at 90 °C for 2 h. The usual workup furnished **9**: 0.86 g (91%); bt 170 °C (4 mmHg); ^{1}H NMR (CCl_4) 0.60 (3 H, t, J = 7 Hz, CH_2CH_3), 1.90 (2 H, m, CH_2CH_3), 2.46, 2.73 (4 H, m, $2CH_2$), 3.33 (1 H, t, J = 5 Hz, $CHCH_2$), 3.73 (6 H, 2 s, $2OCH_3$), 6.50–6.83 (4 H, m, H_2, H_4, H_8, and H_{10}), 7.46 (2 H, dd, J = 8 Hz, H_1 and H_{11}); IR λ_{max} (neat) 1610 (C=C); UV (ethanol) λ_{max} 254 (4.56), 263 (4.55), 300 (4.11). Anal. Calcd for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24. Found: C, 82.15; H, 7.27.

3,9-Dimethoxy-7-ethylidenebenzo[*c*]fluorene (10). A mixture of **9** (300 mg) in dioxane (8 mL) and DDQ (270 mg) was refluxed for 30 h under N_2 blanket. The hydroquinone was filtered off, and the filtrate after concentration was chromatographed (neutral alumina, benzene) to yield **10**: 155 mg (52%); mp 120–121 °C (ethanol–hexane); ^{1}H NMR ($CDCl_3$) 2.41 (3 H, d, J = 8 Hz, vinyl CH_3), 3.87, 3.92 (6 H, 2 s, $2OCH_3$), 6.7–8.67 (9 H, m, vinylic H and arom H); IR ν_{max} (Nujol) 1610 (C=C); UV (methanol) λ_{max} 262 (4.71), 327 (4.27), 366 (3.91). Anal. Calcd for $C_{21}H_{18}O_2$: C, 83.42; H, 6.0. Found: C, 83.56; H, 6.17.

6-Methoxy-(*p*-methoxyphenyl)-1,2,3,4-tetrahydro-2-naphthaldehyde (11). A solution of **6** (1 g) in anhydrous THF (20 mL) was added to liquid NH_3 (100 mL) under stirring. Anhydrous $FeCl_3$ (20 mg) was then added, followed by lithium (60 mg) in small portions, and the deep blue complex was stirred for 30 min and decomposed with solid NH_4Cl. Ammonia was allowed to evaporate off, water added, and the product extracted with ether (2 × 50 mL). Removal of solvent and purification of the residue by TLC (ethyl acetate–hexane, 1:4) furnished **11**: 0.905 g (90%); bt 180 °C (5 mmHg); ^{1}H NMR (CCl_4) 1.97 (2 H, m, 3-CH_2), 2.86 (3 H, m, CHCHO and 4-CH_2), 3.72, 3.75 (6 H, 2 s, $2OCH_3$), 4.26 (1 H, d, J = 8 Hz, PhCH), 6.47–6.63 (2 H, m, H_5 and H_7), 6.67 (1 H, d, J = 9 Hz, H_8), 6.73 (2 H, d, J = 9 Hz, $H_{3'}$ and $H_{5'}$), 6.97 (2 H, d, J = 9 Hz, $H_{2'}$ and $H_{6'}$), 9.53 (1 H, d, J = 2 Hz, CHCHO); IR ν_{max} (neat) 2840 (HC=O), 1725 (HC=O). Anal. Calcd for $C_{19}H_{20}O_3$: C, 77.00; H, 6.80. Found: C, 76.81; H, 6.50.

1-[6-Methoxy-1-(*p*-methoxyphenyl)-1,2,3,4-tetrahydro-2-naphthalenyl]propan-1-ol (12). By use of the same procedure as for **8**, Grignard reaction of **11** (0.6 g) with C_2H_5MgBr afforded **12**: 0.66 g (quantitative): bt 155 °C (5 mmHg); ^{1}H NMR (CCl_4) 0.80 (3 H, t, CH_2CH_3), 1.13–1.90 (6 H, m, 2-CH, OH, CH_2CH_3, 3-CH_2), 2.80 (2 H, m, 4-CH_2), 3.26 (1 H, m, H_1), 3.67 (6 H, 2 s, $2OCH_3$), 3.92 (1 H, m, CHOH), 6.40–7.0 (7 H, m, arom H); IR ν_{max} (neat) 3400 (OH). Anal. Calcd for $C_{21}H_{26}O_3$: C, 77.27; H, 8.03. Found: C, 77.13; H, 8.35.

3,10-Dimethoxy-5-methyl-5,6,6a,7,8,12b-hexahydrobenzo[*c*]phenanthrene (13). The alcohol **12** (0.5 g) was stirred with PPA [prepared from P_2O_5 (10 g) and H_3PO_4 (6 mL)] at 90 °C for 2 h. The reaction mixture was decomposed with ice and the product extracted with ether (2 × 30 mL). Purification of the residue left after removal of solvent by TLC (silica gel; ethyl acetate–hexane, 3:7) afforded **13**: 0.37 g (78%); bt 190 °C (3 mmHg); ^{1}H NMR ($CDCl_3$) 0.85 (3 H, d, J = 6 Hz, $CHCH_3$), 1.27–1.9 (5 H, m, 6-CH_2, 6aH, 7-CH_2), 2.23–3.0 (4 H, m, $CHCH_3$, 8-CH_2, 12b-H), 3.77, 3.85 (6 H, 2 s, $2OCH_3$), 6.50–7.50 (6 H, m, arom H). Anal. Calcd for $C_{21}H_{24}O_2$: C, 81.78; H, 7.84. Found: C, 81.42; H, 7.76.

Acknowledgment. M.P.R. thanks the Council of Scientific and Industrial Research, New Delhi, for the award of a research fellowship.

Synthesis of Tertiary Phosphine Derivatives of Dihydrophenophosphazine[1]

Harold S. Freeman and Leon D. Freedman*

Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27650

Received September 2, 1981

The interaction of phosphorus trichloride and diarylamines at elevated temperatures yields chlorophosphine derivatives of the 5,10-dihydrophenophosphazine ring system. These compounds react with phenylmagnesium bromide to provide a facile synthesis of tertiary phosphine derivatives of 5,10-dihydrophenophosphazine that bear substituents on the aromatic ring. Further elaboration of the tertiary phosphines may provide compounds of therapeutic interest.

Few papers that describe the synthesis of tertiary phosphine derivatives of 5,10-dihydrophenophosphazine (**1**) can be found in the literature. Baum, Lloyd, and Tamborski[2] in 1964 reported the conversion of *o,o'*-dibromo-*N*-methyldiphenylamine to the corresponding dilithio compound and subsequent reaction of the dilithio

(1) Abstracted in part from the Ph.D. Thesis of H.S.F., North Carolina State University, 1981.

(2) G. Baum, H. A. Floyd, and C. Tamborski, *J. Org. Chem.*, **29**, 3410 (1964).

0022-3263/81/1946-5373$01.25/0