und Sodafabrik, West Germany. Triiron dodecacarbonyl was prepared according to literature.[19]

Photochemical Reaction of (+)-α-Thujene (I) with $Fe(CO)_5$. Irradiation was carried out for 1 h under nitrogen in petroleum ether (40–60 °C) solution using a Philips HPK-125 lamp in a water-cooled quartz immersion vessel. Reaction solutions of 1 g of I and 2.7 g of $Fe(CO)_5$ in ~300 mL of solvent were employed. The product mixture was filtered through Celite and the solution evaporated on a rotary evaporator. The residue (1.0 g) was washed with cold ether and recrystallized from tetrahydrofuran. The light yellow crystals of III melted at 106–107 °C, yield 62%.

Anal. Calcd for $C_{14}H_{16}O_4Fe$: C, 55.2; H, 5.2. Found: C, 55.0; H, 5.0.

Thermal Reaction of I with $Fe_3(CO)_{12}$. Solutions of I (1 g, ~0.007 M) and $Fe_3(CO)_{12}$ (7.56 g, 0.014 M) were heated at reflux in benzene or tetrahydrofuran for 3 h under nitrogen. Workup of the product mixture was as described above for the photochemical reaction, yield of III 55%.

Photochemical Reaction of (−)-Umbellulone (V) with $Fe(CO)_5$. A solution of V (0.007 mol) was irradiated with $Fe(CO)_5$ (2.6 g) in petroleum ether (40–60 °C) for 6 h and the resulting green solution was chromatographed on a florisil column. The first eluted fraction contained a very labile organometallic species which could not be analyzed. The second eluted fraction contained the main product which comprised a mixture of VI and VII which could not be separated. On repeated TLC chromatographies the organometallic mixture decomposed to form (±)-umbellulone (85%).

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Registry No.—I, 563-34-8; III, 68024-48-6; V, 546-78-1; VI, 68024-49-7; VII, 68024-50-0; $Fe(CO)_5$, 13463-40-6; $Fe_3(CO)_{12}$, 17685-52-8.

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Acetyldiarylamines by Arylation of Acetanilides. Some Applications and Limitations[1]

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The Goldberg reaction (the interaction of an aryl bromide and an acetanilide) is a convenient general method for preparing *N*-acetyldiarylamines, which can usually be readily hydrolyzed to the corresponding diarylamines. Aryl bromides containing two ortho substituents, however, give only low yields of *N*-acetyldiarylamines. These amides, furthermore, are relatively resistant to hydrolysis when they contain two or more ortho substituents. It has also been found that aryl chlorides (as well as bromides) may react under the conditions of the Goldberg reaction and, therefore, mixtures may be obtained when a chloro-substituted aryl bromide is allowed to react with an acetanilide.

Over seventy years ago Goldberg[2] noted that the condensation of an aryl bromide and an acetanilide in the presence of potassium carbonate and copper iodide yields an *N*-acetyldiarylamine and that hydrolysis of the amide thus obtained yields a diarylamine. Although the Goldberg procedure has been employed in a number of laboratories,[3] it has probably been overshadowed by other methods of preparing diarylamines, especially via the Chapman rearrangement and the Ullmann condensation.[4] The Ullmann condensation, however, is useful primarily for the preparation of diarylamines containing nitro or carboxy groups, while moisture-sensitive imidoyl chlorides are necessary precursors to the use of the Chapman rearrangement. In contrast, the Goldberg reaction usually gives high yields of stable, easily handled *N*-acetyldiarylamines from readily available substances. It should be emphasized, however, that the success of the Goldberg reaction does depend on the use of rigorously dried starting materials.

The yields of *N*-acetyldiarylamines obtained by the Goldberg reaction are not adversely affected by the presence of one *o*-methyl substituent in the aryl halide or of one or two *o*-methyl substituents in the acetanilide (cf. Scheme I). Thus, the usual reaction conditions gave the amides **1**–**4** in yields that ranged from 70–90%. Low yields of *N*-acetyldiarylamines were obtained, however, when the aryl halide possessed two *o*-methyl groups. Thus, the amides **5**, **6**, and **7** were obtained in yields of only 46, 18, and 14%, respectively, when 2-bromomesitylene was allowed to react with the appropriate acetanilides.

N-Acetyldiarylamines containing no ortho substituents (or only a single *o*-methyl group) are readily hydrolyzed by refluxing with 2 equiv of potassium hydroxide in ethanol for 2–3

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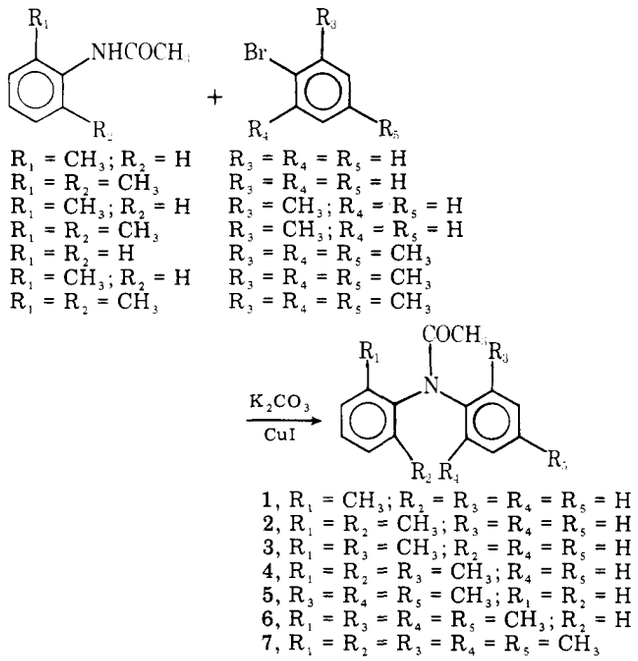
Scheme I



$R_1 = CH_3; R_2 = H$ — $R_3 = R_4 = R_5 = H$
$R_1 = R_2 = CH_3$ — $R_3 = R_4 = R_5 = H$
$R_1 = CH_3; R_2 = H$ — $R_3 = CH_3; R_4 = R_5 = H$
$R_1 = R_2 = CH_3$ — $R_3 = CH_3; R_4 = R_5 = H$
$R_1 = R_2 = H$ — $R_3 = R_4 = R_5 = CH_3$
$R_1 = CH_3; R_2 = H$ — $R_3 = R_4 = R_5 = CH_3$
$R_1 = R_2 = CH_3$ — $R_3 = R_4 = R_5 = CH_3$

1, $R_1 = CH_3; R_2 = R_3 = R_4 = R_5 = H$
2, $R_1 = R_2 = CH_3; R_3 = R_4 = R_5 = H$
3, $R_1 = R_3 = CH_3; R_2 = R_4 = R_5 = H$
4, $R_1 = R_2 = R_3 = CH_3; R_4 = R_5 = H$
5, $R_3 = R_4 = R_5 = CH_3; R_1 = R_2 = H$
6, $R_1 = R_3 = R_4 = R_5 = CH_3; R_2 = H$
7, $R_1 = R_2 = R_3 = R_4 = R_5 = CH_3$

h. In contrast, the sterically hindered amides **3–7** required much more vigorous conditions. Amide **3** could be hydrolyzed by refluxing with 4 equiv of potassium hydroxide in ethanol for 8 h, but amides **4–7** were unaffected even when the reflux period was extended to 24 h. The use of acid hydrolysis (6 N HCl, 12 N H_2SO_4, or 48% HBr at reflux for 16–18 h) was also unsuccessful in converting amides **4–7** to the corresponding amines. Relatively good yields of amines were obtained, however, when amides **4, 5,** and **6** were refluxed with 10–12 equiv of sodium hydroxide in ethylene glycol for 17–20 h. But even these very drastic conditions converted only 25% of amide **7** to the corresponding amine.

A surprising limitation of the Goldberg procedure was noted when we attempted to prepare 4,4′-dichlorodiphenylamine (**10**) via the interaction of 1-bromo-4-chlorobenzene and 4′-chloroacetanilide and found that a mixture of compounds was invariably obtained. Mass spectra of the reaction product (after hydrolysis) showed that the desired diarylamine had indeed been formed, but peaks corresponding to 4-bromo-4′-chlorodiphenylamine (**8**) and *N,N′*-bis(4-chlorophenyl)-1,4-benzenediamine (**9**) were also present. Analysis of the hydrolyzed reaction product for carbon, hydrogen, chlorine, and bromine indicated that it consisted of 62.5% **10**, 28.6% **8**, and 8.5% **9**. The formation of these compounds is rationalized by the sequence in Scheme II. In short, the chlorine (as well as the bromine) in 1-bromo-4-chlorobenzene can be displaced by 4′-chloroacetanilide. To the best of our knowledge the displacement of aromatic chlorine has not previously been observed in the Goldberg reaction. In fact, it has been reported that 1-bromo-2-chlorobenzene[3e,h] and 1-bromo-3-chlorobenzene[3f] react with acetanilides to give (after hydrolysis) good yields of chloro-substituted diarylamines. We are unable to explain these results in view of our failure to obtain pure 4,4′-dichlorodiphenylamine via the Goldberg reaction with 1-bromo-4-chlorobenzene.

We have found that the aromatic chlorine in compounds other than 1-bromo-4-chlorobenzene can also be displaced by acetanilides. Thus, diphenylamine can be obtained (albeit in only 2.4% yield) by the reaction of chlorobenzene with acetanilide and subsequent hydrolysis of the reaction product. Similarly, 4,4′-dichlorodiphenylamine was prepared in 8.5% yield by hydrolysis of the amide formed by interaction of 1,4-dichlorobenzene and 4′-chloroacetanilide.

Experimental Section

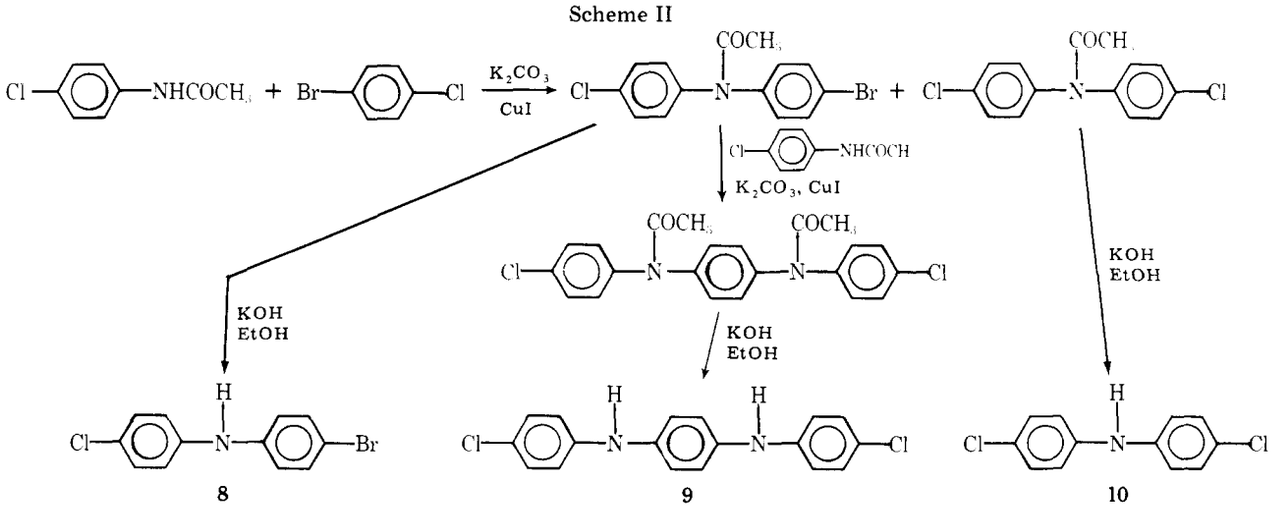
General. Melting points were determined with a Mel-Temp capillary melting point apparatus and are uncorrected. IR spectra were obtained on a Beckman IR8 spectrophotometer, UV spectra on a Unicam SP800 spectrophotometer, NMR spectra on a Perkin-Elmer R-24A spectrometer, and mass spectra on either a Varian MAT or a Varian MAT 731 mass spectrometer at 70 eV with a solid injection probe. The elemental analyses were performed by Integral Microanalytical Laboratories, Raleigh, N.C.

The reactions between the aryl halides and acetanilides were carried out in conventional three-neck round-bottom flasks equipped with a thermometer, magnetic stirrer, and reflux condenser protected by a drying tube ($CaCl_2$). The K_2CO_3 used was first dried in a vacuum oven for at least 6 h at 140–160 °C. The aryl halides were dried over molecular sieves for 24 h before use.

The general procedure used for preparing the diarylamines discussed in this paper was similar to that described below for 4-chlorodiphenylamine.

4-Chlorodiphenylamine. 4′-Chloroacetanilide (102 g, 0.600 mol) and bromobenzene (133 g, 1.50 mol) were refluxed together for 17 h in the presence of 82.8 g of K_2CO_3 and 12.0 g of CuI. The resulting mixture was cooled and then extracted with 600 mL of benzene. The benzene was stripped off at the water pump, and excess bromobenzene was then removed by distillation at 0.15 mm. The oil that remained was refluxed for 2 h with KOH (70.8 g, 1.20 mol) in 400 mL of absolute EtOH. TLC (silica gel with 9:1 benzene–EtOAc) showed that no amide remained. The EtOH was evaporated off, and the viscous residue was shaken with 800 mL of benzene and 500 mL of saturated aqueous NaCl. The benzene solution was dried ($MgSO_4$) and evaporated to dryness, and the residue was extracted with 750 mL of hot petroleum ether (bp 30–60 °C). The resulting solution was treated with charcoal and then chilled overnight at −5 °C to give 97.5 g (80%) of pure 4-chlorodiphenylamine, tan needles: mp 65–67 °C (lit.[5] mp 70.6 °C); ^1H NMR ($CDCl_3$) δ 5.50 (broad s, 1, NH), 6.80–7.40 (m, 9, ArH); IR (Nujol) 3410 cm^{-1} (NH); mass spectrum, *m/e* (relative intensity) 205 (33), 204 (15), 203 (100), 168 (16), 167 (54), 83 (25), 51 (19). Anal. Calcd

Scheme II



for $C_{12}H_{10}ClN$: C, 70.70; H, 4.95; N, 6.88. Found: C, 70.70; H, 4.98; N, 6.73.

N-Phenyl-o-toluidine. o-Acetotoluidide (89.4 g, 0.600 mol) and bromobenzene (120 g, 0.750 mol) were converted to N-phenyl-o-toluidine by the procedure described above for 4-chlorodiphenylamine. Distillation of the crude product gave 76.2 g (69%) of pure amine: $bp_{0.8}$ 112–115 °C (lit.[6] bp_{4-5} 143–146 °C); ^1H NMR ($CDCl_3$) δ 2.30 (s, 3, $ArCH_3$), 5.50 (broad s, 1, NH), 6.50–7.50 (m, 9, ArH); IR (neat) 3400 (NH), 2800 ($ArCH_3$) cm^{-1}; mass spectrum, m/e (relative intensity) 183 (100), 182 (52), 180 (21), 168 (18), 167 (30), 106 (28), 77 (23), 65 (17), 51 (26), 39 (22).

N-Phenyl-2′,6′-acetoxylidide (2) and N-Phenyl-2,6-xylidine. 2′,6′-Acetoxylidide (32.6 g, 0.200 mol) and bromobenzene (47.0 g, 0.300 mol) were refluxed together for 17 h in the presence of 27.6 g of K_2CO_3 and 4.0 g of CuI. The crude amide was obtained by the procedure used for N-acetyl-4-chlorodiphenylamine and was then recrystallized twice from petroleum ether to give pure **2**, tan prisms: mp 95–98 °C; ^1H NMR ($CDCl_3$) δ 1.90 (s, 3, $COCH_3$), 2.20 (s, 6, $ArCH_3$), 6.80–7.20 (m, 8, ArH); IR (Nujol) 1670 cm^{-1} (C=O); mass spectrum, m/e (relative intensity) 239 (34), 197 (72), 196 (41), 194 (16), 181 (18), 180 (31), 120 (19), 118 (100), 77 (28), 51 (15), 43 (38), 28 (17), 18 (30). Anal. Calcd for $C_{16}H_{17}NO$: C, 80.30; H, 7.16; N, 5.85. Found: C, 80.50; H. 7.40; N, 5.88.

The amide **2** was hydrolyzed in EtOH by refluxing for 3 h with 4 equiv of KOH. The crude amine was extracted into petroleum ether and then treated with charcoal. The resulting solution was chilled overnight at −10 °C to give pure N-phenyl-2,6-xylidine in 88% overall yield: mp 53–56 °C (lit.[7] mp 55–56 °C); ^1H NMR ($CDCl_3$) δ 2.20 (s, 6, $ArCH_3$), 5.1 (broad s, 1, NH), 6.40–7.20 (m, 8, ArH); IR (Nujol) 3420 (NH), 2950 and 2875 ($ArCH_3$) cm^{-1}; mass spectrum, m/e (relative intensity) 197 (100), 196 (49), 182 (38), 181 (21), 180 (25), 120 (23), 77 (18); UV (MeOH) λ (ε) 271 nm (9400), 243 (12 100), 211 (17 600). Anal. Calcd for $C_{14}H_{15}N$: C, 85.23; H, 7.66; N, 7.10. Found: C, 85.15; H, 7.60; N, 7.05.

Di-o-tolylamine. o-Acetotoluidide (59.6 g, 0.400 mol) and o-bromotoluene (85.5 g, 0.500 mol) were condensed, and the resulting amide **3** was hydrolyzed by refluxing for 8 h with 89.6 g (1.60 mol) of KOH in 450 mL of EtOH. The crude amine was purified by distillation (102–106 °C, 0.15 mm) to give 70.9 g (90%) of di-o-tolylamine. The oil was made crystalline by dissolving it in petroleum ether and then cooling at 5 °C. This treatment afforded colorless prisms: mp 47–49 °C (lit.[8] mp 46–48 °C); ^1H NMR ($CDCl_3$) δ 2.20 (s, 6, $ArCH_3$), 5.10 (broad s, 1, NH), 6.60–7.30 (m, 8, ArH); IR (neat) 3400 (NH), 2950 ($ArCH_3$) cm^{-1}; mass spectrum, m/e (relative intensity) 198 (17), 197 (100), 196 (54), 194 (17), 182 (62), 181 (37), 180 (45), 167 (37), 165 (19), 77 (19), 17 (59); UV (MeOH) λ (ε) 282 nm (12 800), 237 (8100), 212 (19 000). Anal. Calcd for $C_{14}H_{15}N$: C, 85.23; H, 7.66; N, 7.10. Found: C, 85.53; H, 7.67; N, 7.05.

N-(o-Tolyl)-2′,6′-acetoxylidide (4) and N-(o-Tolyl)-2,6-xylidine. 2′,6′-Acetoxylidide (20.0 g, 0.123 mol) and o-bromotoluene (31.5 g, 0.184 mol) were heated together in the presence of 2.5 g of CuI until a stirrable mixture was obtained (ca. 130 °C). Then 17.0 g of K_2CO_3 was added, and the condensation was allowed to proceed in the usual way. The reaction was worked up to give the crude amide. Two recrystallizations from Et_2O gave 26.2 g (84%) of pure **4** as colorless prisms: mp 147–150 °C; ^1H NMR ($CDCl_3$) δ 1.96 (s, 3, $COCH_3$), 2.24 (s, 6, $ArCH_3$), 2.35 (s, 3, $ArCH_3$), 6.60–7.40 (m, 7, ArH); IR (Nujol) 1670 cm^{-1} (C=O); mass spectrum, m/e (relative intensity) 253 (51), 238 (16), 211 (88), 210 (25), 196 (41), 195 (27), 194 (66), 180 (16), 132 (100), 107 (33), 104 (17), 91 (18), 77 (19), 65 (17), 43 (39). Anal. Calcd for $C_{17}H_{19}NO$: C, 80.59; H, 7.56; N, 5.53. Found: C, 80.45; H, 7.62; N, 5.47.

The amide **4** (2.1 g, 0.008 mol) was refluxed with NaOH (2.4 g, 0.060 mol) in 50 mL of $HOCH_2CH_2OH$ for 17 h. The reaction mixture was cooled and then poured into 500 mL of H_2O. The precipitate was extracted into 250 mL of benzene. The benzene solution was dried ($MgSO_4$) and then evaporated to dryness. The oil obtained (1.6 g) solidified on standing at room temperature. The solid was eluted through a short column of 60 g of silica gel (particle size 0.063–0.200 mm) with benzene to yield 1.4 g (80%) of pure amine: mp 64–66 °C; ^1H NMR ($CDCl_3$) δ 2.15 (s, 6, $ArCH_3$), 2.30 (s, 3, $ArCH_3$), 4.90 (broad s, 1, NH), 6.10–7.15 (m, 7, ArH); IR (Nujol) 3450 cm^{-1} (NH); mass spectrum, m/e (relative intensity) 212 (17), 211 (100), 196 (39), 195 (16), 194 (34), 181 (26), 180 (19), 120 (16), 107 (38), 96 (15), 17 (16). Anal. Calcd for $C_{15}H_{17}N$: C, 85.26; H, 8.11; N, 6.63. Found: C, 85.25; H, 8.05; N, 6.56.

N-Phenyl-2,4,6-trimethylacetanilide (5) and N-Phenyl-2,4,6-trimethylaniline. The reaction of acetanilide (16.9 g, 0.125 mol) and 2-bromomesitylene (36.6 g, 0.168 mol) was carried out according to the procedure described above. The cooled condensation product was extracted into 200 mL of $CHCl_3$. The solvent was removed to give crude **5**. Excess 2-bromomesitylene was removed by distillation at 16 mm. The remaining oil was eluted through a column containing 400 g of silica gel with 9:1 hexane–benzene until 3.1 g of N-phenyl-2,4,6-trimethylaniline was obtained (12%) and then with 9:1 benzene–EtOAc to give 10.7 g (34%) of **5**. Recrystallization of the latter from petroleum ether gave 8.56 g of pure **5**: mp 106–108 °C; ^1H NMR ($CDCl_3$) δ 1.90 (s, 3, $COCH_3$), 2.15 (s, 6, $ArCH_3$), 2.30 (s, 3, $ArCH_3$), 7.00 (s, 2, ArH), 7.10–7.40 (m, 5, ArH); IR (Nujol) 1670 cm^{-1} (C=O); mass spectrum, m/e (relative intensity) 253 (19), 211 (29), 210 (18), 196 (17), 194 (20), 118 (100). Anal. Calcd for $C_{17}H_{19}NO$: C, 80.59; H, 7.56; N, 5.53. Found: C, 80.36; H, 7.60; N, 5.36.

The amide **5** (2.3 g, 0.009 mol) was hydrolyzed by the procedure described for **4**. The crude amine was eluted with 18:1 hexane–benzene through a column of 60 g of silica gel to give 1.6 g of a colorless oil. The oil was dissolved in 5 mL of petroleum ether and then chilled in a dry ice bath to give an 84% yield of crystalline amine: mp 56–58 °C (lit.[9] mp 54 °C); ^1H NMR ($CDCl_3$) δ 2.12 (s, 6, $ArCH_3$), 2.27 (s, 3, $ArCH_3$), 5.00 (broad s, 1, NH), 6.38–7.25 (m, 7, ArH); IR (neat) 3450 cm^{-1} (NH); mass spectrum, m/e (relative intensity) 212 (18), 211 (100), 210 (41), 196 (42), 195 (16), 194 (23), 181 (21), 134 (16). Anal. Calcd for $C_{15}H_{17}N$: C, 85.26; H, 8.11; N, 6.63. Found: C, 84.89; H, 8.13; N, 6.64.

N-(o-Tolyl)-2,4,6-trimethylacetanilide (6) and N-(o-Tolyl)-2,4,6-trimethylaniline. The reaction of o-acetotoluidide (18.6 g, 0.125 mol) with 2-bromomesitylene (36.6 g, 0.168 mol) was carried out by the procedure described above for the preparation of **5**. Chromatography on 322 g of silica gel afforded 6.2 g of **6**. The solid was dissolved in petroleum ether, and the resulting solution was treated with charcoal. The solution obtained was concentrated to precipitate 6.0 g (18%) of pure **6** (white leaves): mp 110–112 °C; ^1H NMR ($CDCl_3$) δ 1.97 (s, 3, $COCH_3$), 2.20 (s, 6, $ArCH_3$), 3.32 (s, 6, $ArCH_3$), 6.65–7.40 (m, 6, ArH); IR (Nujol) 1670 cm^{-1} (C=O); mass spectrum, m/e (relative intensity) 267 (23), 225 (30), 210 (16), 208 (30), 132 (100), 121 (21), 16 (47). Anal. Calcd for $C_{18}H_{21}NO$: C, 80.86; H, 7.92; N, 5.24. Found: C, 81.15; H, 8.07; N, 5.18.

A solution of **6** (2.3 g, 0.009 mol) in 40 mL of $HOCH_2CH_2OH$ was refluxed for 18 h with NaOH (5.0 g, 0.125 mol). The crude amine was obtained by the procedure used for N-(o-tolyl)-2,6-xylidine. It was eluted through 60 g of silica gel with 9:1 hexane–benzene to give 1.0 g of pure amine (52%), colorless prisms: mp 79–81 °C (lit.[10] mp 78.5–79.5 °C); ^1H NMR ($CDCl_3$) δ 2.12 (s, 6, $ArCH_3$), 2.28 (s, 6, $ArCH_3$), 4.82 (broad, s, 1, NH), 6.10 (s, 1, ArH), 6.20 (s, 1, ArH), 6.55–7.20 (m, 4, ArH); IR (Nujol) 3450 cm^{-1} (NH); mass spectrum, m/e (relative intensity) 226 (16), 225 (100), 210 (31), 208 (25), 195 (23), 194 (18), 121 (39). Anal. Calcd for $C_{16}H_{19}N$: C, 85.28; H, 8.50; N, 6.22. Found: C, 85.16; H, 8.72; N, 6.13.

N-(2,6-Dimethylphenyl)-2,4,6-trimethylacetanilide (7) and N-(2,6-Dimethylphenyl)-2,4,6-trimethylaniline. 2′,6′-Dimethylacetoxylidide (20.4 g, 0.124 mol) and 2-bromomesitylene (36.6 g, 0.168 mol) were converted to **7** by the procedure described for **5** and **6**. Chromatography of the crude amide gave 5.0 g of pure **7** (14%) as a colorless viscous oil. This material could not be induced to crystallize: ^1H NMR ($CDCl_3$) δ 2.05 (s, 12, $ArCH_3$), 2.25 (s, 6, $COCH_3$ and $ArCH_3$), 6.80–7.10 (m, 5, ArH); IR (neat) 1740 cm^{-1} (C=O); mass spectrum, m/e (relative intensity), 281 (62), 267 (18), 266 (91), 240 (16), 239 (100), 238 (16), 224 (33), 223 (43), 222 (99), 208 (25), 207 (19), 160 (22), 146 (68), 132 (21), 121 (19), 120 (18), 119 (17), 105 (15), 91 (32), 77 (26), 43 (62), 18 (15).

7 (2.0 g, 0.007 mol) was refluxed with NaOH (5.0 g, 0.125 mol) in 40 mL of $HOCH_2CH_2OH$ for 20 h. The reaction was worked up, and the crude amine was purified as described for N-(o-tolyl)-2,6-xylidine. Thus was obtained 0.4 g (25%) of pure amine as off-white prisms: mp 97–99 °C; ^1H NMR ($CDCl_3$) δ 1.95 (s, 12, $ArCH_3$), 2.20 (s, 3, $ArCH_3$), 4.65 (broad s, 1, NH), 6.60–7.00 (m, 5, ArH); IR (Nujol) 3440 cm^{-1} (NH); mass spectrum, m/e (relative intensity) 240 (19), 239 (100), 224 (29), 222 (26), 209 (24), 208 (23), 132 (21), 121 (23), 120 (24), 119 (15), 91 (21), 77 (16). Anal. Calcd for $C_{17}H_{21}N$: C, 85.36; H, 8.79; N, 5.86. Found: C, 85.40; H, 8.98; N, 5.81.

Interaction of 1-Bromo-4-chlorobenzene and 4′-Chloroacetanilide. 4′-Chloroacetanilide (170 g, 1.00 mol) and 1-bromo-4-chlorobenzene (219 g, 1.14 mol) were allowed to react according to the procedure described for 4′-chloroacetanilide and bromobenzene. The reaction mixture was cooled and then extracted with Et_2O. Evaporation of the resulting solution gave a thick dark oil. It was refluxed with basic EtOH in the usual way to remove the acetyl group. The EtOH was then removed, and the material obtained was extracted with Et_2O. The Et_2O was removed at reduced pressure, and the residue was distilled (130–155 °C, 0.1–0.3 mm) to give 96.9 g of crude amine. The amine was further purified by recrystallization from li-

groine (bp 60–100 °C) to give 88.4 g of amine: mp 75.5–79.5 °C. Mass spectrum, *m/e* (relative intensity): 328 (<1), which corresponds to the molecular ion for **9**; 283 (7) and 281 (5), which correspond to the molecular ion for **8**; 241 (12), 239 (67), and 237 (100), which correspond to the molecular ion for **10**. Anal. Calcd for 62.9% **10**, 28.6% **8**, and 8.5% **9**: C, 58.24; H, 3.69; Br, 8.09; Cl, 24.15. Found: C, 57.83; H, 3.49; Br, 8.08; Cl, 24.15.

Registry No.—**2**, 68014-50-6; **3**, 19020-41-8; **4**, 68014-51-7; **5**, 68014-52-8; **6**, 68014-53-9; **7**, 68014-54-0; **8**, 13676-98-7; **9**, 68014-55-1; **10**, 6962-04-5; *N*-phenyl-4′-chloroacetanilide, 68014-56-2; 4-chlorodiphenylamine, 1205-71-6; *N*-phenyl-*o*-toluidine, 1205-39-6; *N*-phenyl-2,6-xylidine, 4058-04-2; di-*o*-tolylamine, 617-00-5; *N*-(*o*-tolyl)-2,6-xylidine, 68014-57-3; *N*-phenyl-2,4,6-trimethylaniline, 23592-67-8; *N*-(*o*-tolyl)-2,4,6-trimethylaniline, 39267-45-3; 4′-chloroacetanilide, 539-03-7; bromobenzene, 108-86-1; *o*-acetotoluidide, 120-66-1; 2′,6′-acetoxylidide, 2198-53-0; *o*-bromotoluene, 95-46-5; acetanilide, 103-84-4; 2-bromomesitylene, 576-83-0; *N*-(2,6-dimethylphenyl)-2,4,6-trimethylaniline, 68014-58-4; 1-bromo-4-chlorobenzene, 106-39-8.

References and Notes

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Synthesis of Perfluoroalkyladamantanes[1]

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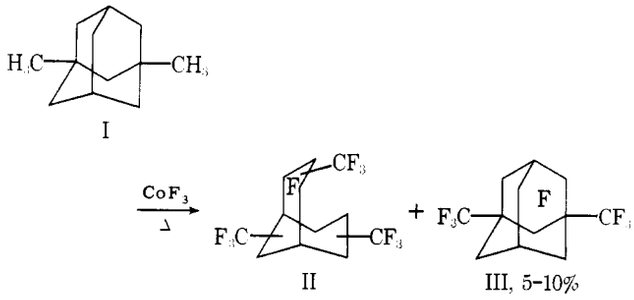
Fluorination of alkyladamantanes over CoF_3 leads to complex products with only a small amount (5–10%) of the desired perfluoroadamantane. Partial fluorination of the individual alkyladamantane substrate, however, prior to exhaustive fluorination over CoF_3 stabilizes the adamantane ring structure and allows the synthesis of perfluoroalkyladamantanes in good yield. The physical and spectral properties of three perfluoroalkyladamantanes are reported.

Because of the current interest in fluorocarbons as synthetic blood candidates[2a-d] and because of our previous work in adamantane chemistry[3a-d] we sought to synthesize perfluoroalkyladamantanes. This paper reports on the synthesis of perfluoro-1-methyl-, 1,3-dimethyl-, and 1,3,5,7-tetramethyladamantane.

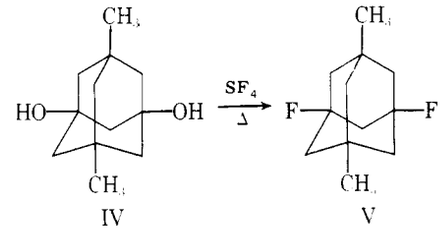
Results and Discussion

Fluorination of 1,3-dimethyladamantane over CoF_3 gives products containing two more fluorines than expected (*m/e* 562 vs. 524) had the starting adamantane structure remained intact. Subsequent isolation and analytical tests identified these as ring-opened products. Repeated preparative chromatography separations did finally result in the isolation of a small quantity of perfluoro-1,3-dimethyladamantane (III) (perfluorinated ring systems are indicated by an F).



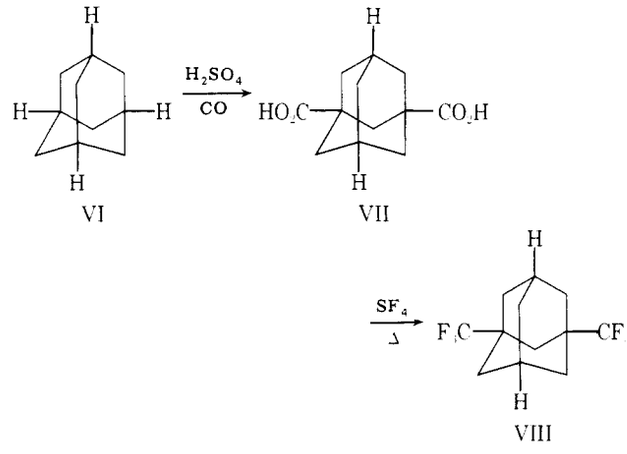
In view of the above, attempts were then made to improve the yield by incorporating fluorine into the molecule prior to exhaustive fluorination over CoF_3. Reaction of SF_4 with 1,3-dihydroxy-5,7-dimethyladamantane[4a,b] gave 1,3-difluoro-5,7-dimethyladamantane in 95% yield.

Subsequent fluorination of V over CoF_3 gave the same



products (II and III) in the same proportion as obtained from fluorination of 1,3-dimethyladamantane. This contrasts sharply with the successful results obtained by Lagow[1] from the direct fluorination of 1,3-difluoro-5,7-dimethyladamantane with fluorine.

Adamantanes containing trifluoromethyl groups were prepared in a manner analogous to earlier work done with benzene-containing trifluoromethyl groups.[5] The following



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