

1.23 (s, 3 H, CH₃), 1.02 (s, 3 H, CH₃), 0.80 (d, 3 H, *J* = 7 Hz, C(4) methyl). An analytical sample was prepared by recrystallization from ether; mp 161-163 °C. Anal. Calcd for C₂₂H₃₄O₅: C, 69.81; H, 9.05. Found: C, 69.78; H, 8.98.

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Registry No. 1, 75935-29-4; 2, 75924-48-0; 4, 76156-58-6; 5, 76156-59-7; 6, 76156-60-0; 7, 76156-61-1; 8, 76156-62-2; 9, 76156-63-3; 10, 76189-75-8; 12, 76156-64-4; 13 (R = H), 76156-65-5; 13 (R = Me), 76156-66-6.

Dichlorocarbene-Induced Deamination of Naphthalen-1,4-imines and Anthracen-9,10-imines

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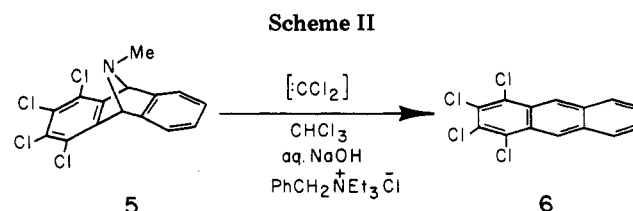
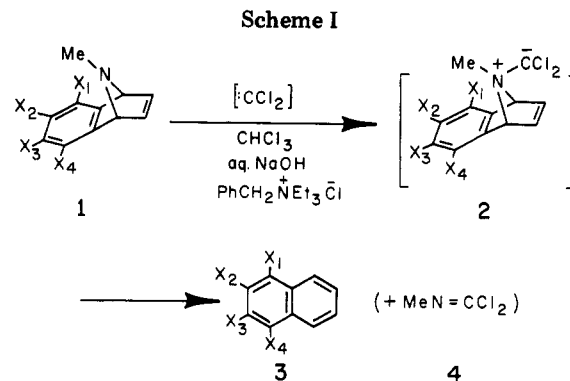
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Arenimines are useful polycyclic aromatic hydrocarbon synthetic equivalents.¹⁻³ Previously, we¹ and others^{2,3} have transformed *N*-alkyl-1,4-dihydroaren-1,4-imines into the corresponding aromatic hydrocarbons using mild oxidizing conditions (usually *m*-chloroperbenzoic acid), a reaction that may involve cheletropic extrusion⁴ of a nitrosoalkane from the derived arenimine oxide.

We now report that dichlorocarbene, generated under phase-transfer conditions by using the Makosza method,⁵ efficiently converts 9-methyl-1,4-dihydronaphthalen-1,4-imines (1) and 11-methyl-1,2,3,4-tetrachloro-9,10-dihydroanthracen-9,10-imine (5) to the corresponding naphthalenes (3, Scheme I) and 1,2,3,4-tetrachloroanthracene (6, Scheme II), respectively. Our results are summarized in Table I. By comparison, the peracid oxidation of naphthalenimines^{1,3} proceeds in 66-94% yield, and the peracid or hydrogen peroxide oxidation of anthracenimines¹ proceeds in 26-92% yield.

As suggested by the stereospecific fragmentation of aziridinium ylides (generated also from carbenes and aziridines),⁶ the present reaction pathway may involve ammonium ylide 2 which suffers rapid cheletropic loss⁴ of methyl isocyanide dichloride (4,⁷ not isolated)⁸ to furnish the arene.⁹

The requisite arenimines 1 and 5 were prepared by a Diels-Alder reaction between the appropriate benzyne and either *N*-methylpyrrole or *N*-methylisoindole, respectively.



The benzynes were generated by treating a polyhalobenzene with *n*-butyllithium and effecting either halogen-lithium exchange (e.g., chloropentafluorobenzene, hexachlorobenzene, and trichlorotrifluorobenzene) or lithiation (e.g., 1,2,4,5-tetrachlorobenzene). The syntheses of 1b-d and 5 have not been previously described and are presented in the Experimental Section.

In summary, the dichlorocarbene-induced deamination of arenimines is a convenient alternative method to the oxidative deamination procedure¹⁻³ and avoids use of the moderately expensive *m*-chloroperbenzoic acid.

Experimental Section

Melting points were obtained with a Mel-Temp Laboratory Devices apparatus in open capillary tubes and are uncorrected. Microanalyses were determined by PCR, Inc., or by Atlantic Microlab, Inc. Infrared spectra were measured with a Perkin-Elmer 137 or 599 instrument, and NMR spectra were obtained with a Perkin-Elmer R-24 spectrometer. Woelm alumina was used for column chromatography and silica gel G (Merck) was used for TLC. Mass spectra were determined at 70 eV on a Finnigan 4023 GC/MS system by C. R. Hill and R. M. Soll.

9-Methyl-5,6,7,8-tetrafluoro-1,4-dihydronaphthalen-1,4-imine (1a). To a magnetically stirred solution of chloropentafluorobenzene (15 g, 0.074 mol) in dry Et₂O (250 mL) under N₂ at -78 °C was added dropwise by syringe *n*-butyllithium (1.6 M in hexane; 50 mL, 0.080 mol). The solution was stirred for 30 min at -78 °C and then was treated with freshly distilled *N*-methylpyrrole (8 g, 0.1 mol) dropwise at -78 °C. The resulting golden yellow solution was allowed to warm slowly to room temperature overnight. The mixture was treated with H₂O (50 mL) and then extracted with 6 N HCl. The acidic extract was cooled in an ice bath, basified with 50% aqueous NaOH, and extracted with CH₂Cl₂. Rotary evaporation of the water-washed and dried (Na₂SO₄) extract gave 10.3 g of crude 1a as a brown solid which was sublimed at 80 °C (0.5 torr) to give 7.7 g (46%) of 1a as colorless crystals: mp 77-78 °C (lit.¹¹ mp 75-76 °C); ¹H NMR (CDCl₃) δ 2.2 (s, 3 H), 4.9 (m, 2 H), 6.9 (m, 2 H); IR (CHCl₃) 2950 (s), 1490 (s), 1480 (s), 1295 (m), 1270 (m), 1110 (m), 1080 (m), 1040 (s), 930 cm⁻¹ (m); mass spectrum, *m/e* (relative intensity) 229 (26), 214 (10), 203 (100), 188 (46), 174 (14), 169 (19), 161 (33), 151 (29), 123 (16), 105 (12), 99 (18), 42 (96).

9-Methyl-5,6,7,8-tetrachloro-1,4-dihydronaphthalen-1,4-imine (1b). To a magnetically stirred slurry of hexachlorobenzene (38 g, 0.13 mol) (recrystallized from EtOH) in dry Et₂O (1500 mL)

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(8) We have made no attempt to ascertain the fate of 4, but, presumably, it is hydrolyzed to methylamine and carbonate under the reaction conditions.

(9) We and others¹⁰ have found that the methiodides of arenimines fragment to aromatic hydrocarbons upon treatment with base (KOH, MeMgI) or simply on standing for extended periods. These reactions may also involve ammonium ylide intermediates.

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(11) D. D. Callander, P. L. Coe, J. C. Tatlow, and A. J. Uff, *Tetrahedron*, 25, 25 (1969), prepared 1a from pentafluorobenzene in a similar manner to that described herein.

Table I. Deamination of Arenimines to Arenes with Dichlorocarbene

arenimine	arene	mp, °C	yield, %
1a (X ₁₋₄ = F)	3a	108-110	85
1b (X ₁₋₄ = Cl)	3b	199-200	84
1c (X _{1,3} = F; X _{2,4} = Cl)	3c	104-106	90
1d (X _{1,2,4} = Cl; X ₃ = H)	3d	91-92	85
5	6	209-210	73

under N₂ at -50 °C was added dropwise over 30 min *n*-butyllithium (2.25 M in hexane; 59 mL, 0.13 mol). The light yellow solution was allowed to warm to -35 °C and was then stirred at -35 to -25 °C for 1 h. Then freshly distilled *N*-methylpyrrole (22 g, 0.27 mol) was added in one portion, and the mixture was allowed to warm slowly to room temperature overnight. The reaction mixture was cooled to 0-5 °C and extracted with cold 4 N HCl. The acidic extract was cooled, basified with NaOH (pellets), and extracted with CHCl₃. The CHCl₃ extract was washed with H₂O, dried (K₂CO₃), and evaporated in vacuo to give crude 1b as a white solid. Crystallization from MeOH-Et₂O gave 11 g (29%) of 1b as colorless flakes in two crops, mp 155-156 °C. A second crystallization gave the analytical sample: mp 156-157 °C; ¹H NMR (CDCl₃) δ 2.2 (s, 3 H), 4.8 (m, 2 H), 7.0 (m, 2 H); IR (CHCl₃) 2955 (s), 1350 (s), 1300 (s), 1270 (m), 1160 (m), 1115 (s), 915 (m), 850 (m), 690 cm⁻¹ (s); mass spectrum, *m/e* (relative intensity) 295 (22), 269 (73), 254 (12), 217 (10), 194 (11), 181 (6), 160 (3), 147 (3), 120 (6), 98 (8), 42 (100).

Anal. Calcd for C₁₁H₇NCl₄: C, 44.78; H, 2.40; N, 4.75; Cl, 48.07. Found: C, 44.69; H, 2.38; N, 4.81; Cl, 48.35.

9-Methyl-5,7-dichloro-6,8-difluoro-1,4-dihydro-naphthalen-1,4-imine (1c). To a magnetically stirred solution of 1,3,5-trichloro-2,4,6-trifluorobenzene (16.8 g, 0.071 mol) in dry Et₂O (250 mL) under N₂ at -78 °C was added dropwise *n*-butyllithium (1.6 M in hexane; 45 mL, 0.072 mol). The solution was stirred for 1 h at -78 °C, treated at -78 °C over 30 min with freshly distilled *N*-methylpyrrole (15 g, 0.19 mol), and then stirred at -78 °C for 1 h. The mixture was then allowed to warm slowly to room temperature overnight. The usual workup gave 10.9 g (59%) of crude product which was distilled to afford 1c as a colorless, low-melting solid: mp 41-42 °C; bp 95-96 °C (0.35 torr). Redistillation gave the analytical sample: bp 109 °C (0.25 torr); ¹H NMR (CDCl₃) δ 2.2 (s, 3 H), 4.8 (m, 2 H), 6.9 (s, 2 H); IR (CHCl₃) 2955 (s), 1460 (s), 1435 (s), 1410 (s), 1295 (m), 1150 (m), 1110 (m), 1060 (s), 870 (m), 840 (m), 810 cm⁻¹ (s); mass spectrum, *m/e* (relative intensity) 261 (6), 235 (19), 219 (5), 185 (4), 162 (7), 149 (5), 123 (4), 99 (4), 80 (8), 42 (100).

Anal. Calcd for C₁₁H₇NF₂Cl₃: C, 50.41; H, 2.69; N, 5.35; Cl, 27.06. Found: C, 50.41; H, 2.73; N, 5.30; Cl, 26.92.

7-Methyl-5,6,8-trichloro-1,4-dihydro-naphthalen-1,4-imine (1d). To a magnetically stirred slurry of 1,2,4,5-tetrachlorobenzene (21.6 g, 0.10 mol) in dry Et₂O (600 mL) under N₂ at -50 °C was added dropwise over 40 min *n*-butyllithium (2.28 M in hexane; 44 mL, 0.10 mol). The solution was stirred for an additional 35 min at -50 °C and then treated dropwise over 10 min with freshly distilled *N*-methylpyrrole (7.8 g, 0.096 mol). The solution was stirred at -50 to -35 °C for 5.5 h and then allowed to warm to room temperature overnight. The mixture was cooled to 0 °C and then treated slowly with cold 4 N H₂SO₄ (150 mL). The Et₂O layer was separated and discarded. The acid layer was extracted with several portions of Et₂O (discarded), cooled to 0 °C, and basified with cold 4 N NaOH. Extraction with Et₂O followed by drying (K₂CO₃) and concentration in vacuo afforded 11.6 g (46%) of crude 1d as a brown oil which crystallized in a freezer. Sublimation at 0.5 torr gave 6.85 g (27%) of pure 1d: mp 58-59.5 °C; ¹H NMR (CDCl₃) δ 2.2 (s, 3 H), 4.8 (m, 2 H), 7.0 (m, 2 H), 7.1 (s, 1 H); IR (CHCl₃) 2960 (s), 1420 (s), 1315 (m), 1300 (m), 1275 (m), 1155 (m), 1110 (s), 860 (m), 850 (m), 710 cm⁻¹ (m); mass spectrum, *m/e* (relative intensity) 259 (3), 233 (13), 217 (2), 183 (4), 160 (5), 147 (4), 123 (3), 109 (3), 98 (7), 80 (9), 42 (100).

Anal. Calcd for C₁₁H₈NCl₃: C, 50.71; H, 3.09; N, 5.38; Cl, 40.82. Found: C, 50.76; H, 3.14; N, 5.45; Cl, 40.85.

11-Methyl-1,2,3,4-tetrachloro-9,10-dihydroanthracen-9,10-imine (5). This was prepared from hexachlorobenzene and 2-methylisindole¹² by using the procedure described for 1b to

give 5 as colorless crystals: mp 163 °C, after crystallization from acetone; ¹H NMR (CDCl₃) δ 2.3 (s, 3 H), 5.2 (s, 2 H), 7.1 (m, 2 H), 7.4 (m, 2 H); IR (KBr) 2830 (m), 1355 (s), 1290 (m), 1260 (m), 1220 (m), 1090 (s), 795 (m), 730 cm⁻¹ (s); mass spectrum, *m/e* (relative intensity) 345 (29), 330 (10), 316 (14), 310 (15), 308 (15), 282 (13), 280 (15), 246 (10), 174 (8), 91 (17), 42 (100).

Anal. Calcd for C₁₅H₉NCl₄: C, 52.21; H, 2.63; N, 4.06. Found: C, 53.05; H, 3.26; N, 4.11.

General Deamination Procedure. To a magnetically stirred solution of arenimine (2 mmol) in CHCl₃ (25 mL) at room temperature under N₂ was added 50% aqueous NaOH (3 mL) and benzyltriethylammonium chloride (0.2 mmol). The resulting mildly exothermic reaction was stirred at ambient temperature overnight and then was partitioned between 3 N HCl (35 mL) and CHCl₃ (50 mL). The organic layer was water washed, dried (Na₂SO₄), and concentrated in vacuo to afford the crude product which was purified as described below. Where possible the products were compared (TLC, IR, NMR) with those compounds prepared in our earlier study¹ or with commercial samples.

1,2,3,4-Tetrafluoronaphthalene (3a). The crude product was recrystallized from hexane to give 3a: 85% yield; mp 108-110 °C (lit.¹³ mp 110-111 °C).

1,2,3,4-Tetrachloronaphthalene (3b). The crude product was recrystallized from CHCl₃ to give 3b: 84% yield; mp 199-200 °C (lit.¹⁴ mp 198 °C).

1,3-Dichloro-2,4-difluoronaphthalene (3c). The crude product was sublimed at 80 °C (0.5 torr) to give 3c: 90% yield; mp 103-104 °C (lit.¹⁵ mp 103-104 °C).

1,2,4-Trichloronaphthalene (3d). The crude product was sublimed at 80 °C (0.5 torr) to give 3d: 85% yield; mp 91-92 °C (lit.¹⁶ mp 92 °C).

1,2,3,4-Tetrachloroanthracene (6). The crude product was recrystallized from MeOH-CHCl₃ (1:1) to give 6: 73% yield; mp 209-210 °C (lit.¹⁷ mp 217-219 °C).

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Registry No. 1a, 5875-75-2; 1b, 26477-20-3; 1c, 76137-28-5; 1d, 76137-29-6; 3a, 711-55-7; 3b, 20020-02-4; 3c, 27508-76-5; 3d, 50402-51-2; 5, 76137-30-9; 6, 25283-02-7; chloropentafluorobenzene, 344-07-0; *N*-methylpyrrole, 96-54-8; hexachlorobenzene, 118-74-1; 1,3,5-trichloro-2,4,6-trifluorobenzene, 319-88-0; 1,2,4,5-tetrachlorobenzene, 95-94-3; 2-methylisindole, 33804-84-1; dichlorocarbene, 1605-72-7.

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Nucleophilic Aromatic Substitution Reaction of Some 3-Nitroimidazo[1,2-*a*]pyridines with Thioglycolate Anion in DMF

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Imidazo[1,2-*a*]pyridines 1 undergo nucleophilic¹ and electrophilic² aromatic substitution reactions. Only a few