homosarkomycin (2): IR (CCl_4) 3540–2400 (br s), 1710 (br s), 1640 (s), 910 (s) cm^{-1}; NMR (60 mHz) δ 1.27–1.97 (m, 1 H), 2.02–2.68 (m, 5 H), 2.82–3.48 (m, 1 H), 5.29 (d, J = 2.5 Hz, 1 H), 6.07 (d, J = 2.5 Hz, 1 H), 10.37 (br s, 1 H: mass spectrum, m/e 154.0628 (M^+; calcd for $C_8H_{10}O_3$, 154.063).

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Registry No. 2, 82134-78-9; 6, 68882-71-3; 7, 80963-19-5; 8, 82093-34-3; *cis*-9, 82134-76-7; *trans*-9, 82134-79-0; 10 (isomer 1), 82134-77-8; 10 (isomer 2), 82188-46-3; 11, 82149-57-3; phenyllithium, 591-51-5; triphenylvinyltin, 2117-48-8; vinyllithium, 917-57-7; triethyl orthoacetate, 78-39-7.

Synthesis of Benzo[*a*]fluoranthene and Naphtho[2,1-*a*]fluoranthene

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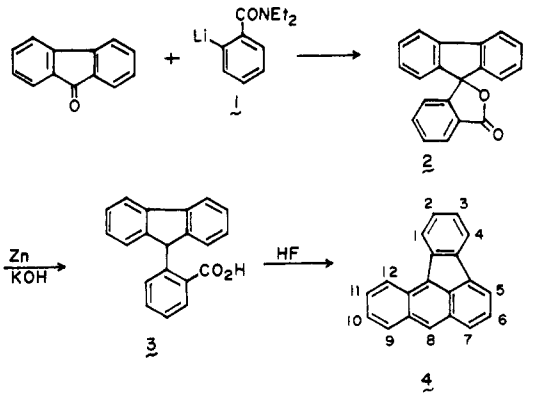
A novel synthetic approach to polycyclic hydrocarbons involving in the key step condensation of *o*-lithioaryl amides with aryl ketones has recently been described.[1-3] The carcinogenic hydrocarbons 3-methylcholanthrene, benz[*a*]anthracene, dibenz[*a*,*h*]anthracene, dibenz[*a*,*j*]anthracene, benzo[*a*]pyrene, and their methyl derivatives have been synthesized via this method in good overall yields.

We now report convenient syntheses of the nonalternant polycyclic hydrocarbons benzo[*a*]fluoranthene and naptho[2,1-*a*]fluoranthene[4] based on the same general method and involving a novel reductive cyclization.

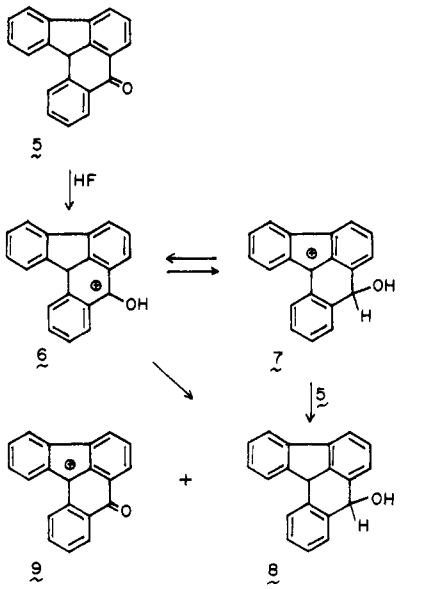
Synthesis of benzo[*a*]fluoranthene (4) is outlined in Scheme I. 2-Lithio-*N*,*N*-diethylbenzamide (1) was generated in situ by directed metalation of *N*,*N*-diethylbenzamide with *sec*-butyllithium by the method of Beak.[5] Reaction of 1 with 9-fluorenone afforded smoothly the lactone 2. Reduction of this intermediate with zinc and alkali yielded the free acid 3. Attempted cyclization of 3 with $ZnCl_2$ in acetic acid–acetic anhydride, the reagent previously employed in analogous cyclizations,[1-3] gave no reaction. However, 3 underwent reductive cyclization in liquid HF to yield benzo[*a*]fluoranthene directly in a single step! The keto intermediate 5, anticipated as the conventional product of this reaction, could not be detected among the residual products.

The mechanism of this reductive cyclization is unknown. The simplest hypothesis (Scheme II) is that the carbonium ion intermediate 6, formed by protonation of 5 in the acidic

Scheme I

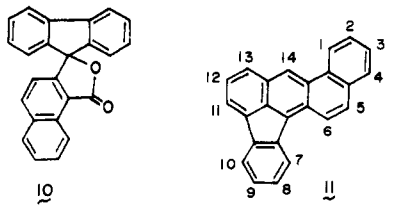


Scheme II



medium, is in equilibrium with the highly stabilized ionic intermediate 7. Hydride transfer from 5 to 6 or 7 furnishes the alcohol 8 which dehydrates to 4 along with simultaneous formation of a new ionic intermediate 9. The latter apparently yields only tarry products which could not be characterized. Since this mechanism implies that addition of an appropriate hydride donor to the medium might enhance the yield,[6] a similar experiment was conducted in the presence of triphenylmethane. Under these conditions the yield of benzo[*a*]fluoranthene virtually doubled from 36% to 71%!

Synthesis of naphtho[2,1-*a*]fluoranthene (11) was accomplished via an analogous sequence. Reaction of 2-lithio-*N*,*N*-diethyl-1-naphthamide with 9-fluorenone furnished the lactone 10 which underwent reduction with zinc



and alkali followed by reductive cyclization in liquid HF to afford 11. As in the preceding example, reductive cyclization in the presence of triphenylmethane doubled the

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(6) We are grateful to a referee for suggesting the use of a hydride donor to increase the yield.

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yield of the hydrocarbon product.

The foregoing syntheses of benzo[a]fluoranthene and naphtho[2,1-a]fluoranthene provide more convenient synthetic access to these hydrocarbons than previous methods.[7,8]

Naphtho[2,1-a]fluoranthene is reported to be weakly carcinogenic;[9] the biological activity, if any, of benzo[a]-fluoranthene is apparently unknown.

Experimental Section

General Methods. *N,N*-Diethyl-1-naphthamide was prepared as previously described.[3] *N,N,N',N'*-tetramethylethylenediamine (TMEDA) was distilled from KOH prior to use. *sec*-Butyllithium in cyclohexane (1.25 M) and 9-fluorenone were purchased from the Aldrich Chemical Co. The NMR spectra were recorded on a Varian EM360 and/or the University of Chicago 500-MHz spectrometer with tetramethylsilane as an internal standard. Melting points are uncorrected. All new compounds gave satisfactory analyses for C and H within ±0.3%.

Synthesis of Benzo[a]fluoranthene. (1) Condensation of 9-Fluorenone with 1. A solution of *N,N*-diethylbenzamide (1.4 g, 8 mmol), TMEDA (1.2 mL), and triphenylmethyl chloride (a few milligrams to serve as an indicator) in anhydrous ether (80 mL) under a nitrogen atmosphere was cooled to −75 °C and allowed to stand for 10 min. *sec*-Butyllithium (8 mL, 1.25 M) was added, and the resulting solution was stirred at −75 °C for 1 h. 9-Fluorenone (1.4 g, 8 mmol) was added, the cooling bath was removed, and the solution was stirred overnight. A conventional workup furnished the crude product (3 g) which was refluxed in benzene (300 mL) with *p*-toluenesulfonic acid (300 mg) with a Dean–Stark trap for 4 h. The usual workup afforded **2**: 1.6 g (70%); mp 224 °C (EtOAc) (lit.[7] mp 226 °C); NMR (60 MHz) δ 8.0–8.1 (d, 1, *J* = 7 Hz), 6.9–7.8 (m, 11, aromatic).

(2) Reduction of the Lactone. A solution of **2** (300 mg) in pyridine (5 mL) was heated with zinc dust (5 g, activated as described)[3] in a solution of KOH (50 mL of 10% solution) at reflux for 21 h. The usual workup gave the acid **3**: 260 mg (86%); mp 245 °C (EtOAc) (lit.[8] mp 241–242 °C); NMR (60 MHz) δ 6.59–8.11 (m, 12, aromatic), 6.39 (s, 1, benzylic).

(3) Benzo[a]fluoranthene. The acid **3** (200 mg) was stirred in liquid HF (~50 mL) for 12 h. The HF was evaporated under a stream of N_2 to yield crude **4** (170 mg). TLC of the crude product on Florisil showed on elution with benzene–hexane only a single spot corresponding to **4**; other product components remained adsorbed at the origin. Passage through a short column of silica gel eluted with hexane furnished pure **4**: 36%; mp 147 °C (ether–hexane) (lit.[7,8] mp 145–146 °C); UV max (EtOH) 257 and 225 nm, in agreement with the reported spectrum;[10] NMR (500 MHz) δ 8.76 (d, 1, H_{12}), 8.48 (s, 1, H_8), 8.39 (d, 1, H_1), 8.15 (d, 1, H_5), 8.02 (br s, 2, $H_{4,7,9}$), 7.67 (t, 1, H_{10} or H_{11}), 7.66 (t, 1, H_{10} or H_{11}), 7.53 (t, 1, H_6), 7.48 (d, 1, H_2 or H_3), 7.40 (d, 1, H_2 or H_3); $J_{1,2}$ = 7.5 Hz, $J_{2,3}$ = 7.2 Hz, $J_{5,6}$ = 8.6 Hz, $J_{11,12}$ = 8.8 Hz; MS (70 eV), *m/e* 252 (M^+). The hydrocarbon was dissolved in concentrated H_2SO_4, giving a yellow solution which changed to violet on standing, as reported by Stubbs and Tucker.[7] A similar experiment conducted in the presence of triphenylmethane (2 molar equiv) gave **4** (71%; mp 144–145 °C); a mixture melting point with authentic **4** did not depress. TLC on Florisil (benzene–hexane) showed a single spot.

Synthesis of Naphtho[2,1-a]fluoranthene. Condensation of 9-fluorenone (1.8 g, 10 mmol) with 2-lithio-*N,N*-diethyl-1-naphthamide was carried out essentially as in the preparation of **2**, except that 1 h was allowed for the metalation reaction. A similar workup gave **10**; (2.53 g (76%); mp 192 °C (ether–benzene); NMR δ 9.10–9.25 (d, 1, *J* = 7 Hz, aromatic), 6.75–8.05 (m, 13, aromatic); IR (Nujol) 1755 cm^{-1} (C=O). Reduction of **10** (300 mg) with zinc and alkali provided the free acid: 270 mg (90%); mp 237 °C (EtOAc); NMR δ 6.3–8.3 (m, 14, aromatic), 5.5 (s, 1, benzylic). Reductive cyclization of this acid (200 mg) in liquid HF in the usual manner and purification of the product by chromatography on silica gel gave pure **11**: 30%; mp 180 °C (benzene–ether) (lit.[10] mp 181–181.3 °C cor); NMR (500 MHz) δ 9.25 (s, 1, H_{14}), 8.88 (d, 1, H_1), 8.62 (d, 1, H_6), 8.40 (d, 1, H_7), 8.08 (d, 1, H_{11}), 8.04 (d, 1, H_{13}), 8.02 (d, 1, H_{10}), 7.89 (d, 1, H_4), 7.84 (d, 1, H_5), 7.71 (dd, 1, H_2 or H_{12}), 7.64 (t, 1, H_3), 7.48 (d, 1, H_8), 7.42 (t, 1, H_9); $J_{1,2}$ = 8.2 Hz, $J_{2,3}$ = 7.3 Hz, $J_{3,4}$ 7.5 Hz, $J_{5,6}$ = 9.3 Hz, $J_{7,8}$ = 7.5 Hz, $J_{8,9}$ = 7.2 Hz, $J_{9,10}$ = 7.8 Hz, $J_{11,12}$ = 8.2 Hz, $J_{12,13}$ = 8.2 Hz, $J_{12,13}$ = 6.7 Hz; MS (70 eV), *m/e* 302 (M^+).

A similar experiment with triphenylmethane present (2 molar equiv) provided **11**: 60%; mp and mmp 177–179 °C. TLC on Florisil (benzene–hexane) gave a single spot.

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Registry No. **2**, 82111-99-7; **3**, 64611-30-9; **4**, 199-54-2; **10**, 82112-00-3; **10** free acid, 82112-01-4; **11**, 203-07-6; *N,N*-diethylbenzamide, 1696-17-9; 9-fluorenone, 486-25-9; *N,N*-diethyl-1-naphthamide, 5454-10-4.

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N-Methyl-*N*-(*tert*-butyldimethylsilyl)trifluoroacetamide and Related *N*-*tert*-Butyldimethylsilyl Amides as Protective Silyl Donors[1]

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Within recent years silylation as a protective method in the synthesis of organic compounds has been increasing in use.[2] Foremost in growing utility among the many trialkylsilyl derivatives used to protect hydroxylic groups is the *tert*-butyldimethylsilyl (TBDMS) derivative.[3] Reasons for this include ease in transforming alcohols to their corresponding TBDMS ethers, selective removal of the TBDMS function under mildly acidic or nonacidic conditions,[4] and the stability of the TBDMS ethers to acetate saponification conditions, Wittig reagent, Jones (CrO_3) reagent, Grignard reagent, and hydrogenation. In addition, the TBDMS ether is approximately 10^4 times more stable to solvolysis than the corresponding trimethylsilyl (Me_3Si) ether. Because of these characteristics the TBDMS function has been employed to protect hydroxyl groups during the synthesis of many diversified compounds including ribonucleosides,[5] deoxyribonucleosides,[6,7] carbohydrates,[8-11] and analogues of throm-

(1) Acknowledge is made of the financial support under Grant HL 19160 of the National Institutes of Health, Heart, Lung, and Blood Institutes.
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