gave analytical results for C and H which agreed with a structure of a bis(*p*-chlorophenyl)-1,2-naphthalide, which had the carbonyl in the 1-naphthyl or 2-naphthyl position. Acidification of the alkaline filtrate yielded 70.0 g (58%) of a mixture of **3** and **4**.

A solution of the above mixed acid in 700 mL of concentrated H_2SO_4 was heated at 120–125 °C for 15 min and poured over ice. Crystallization from acetic acid yielded 63.0 g (84% of the 75 g) of **3**, mp 188–191 °C ((lit.[4] mp 190.0–191.6 °C).

2-[(4-Chlorophenyl)hydroxymethyl]-1-naphthoic Acid Lactone, 5. To a magnetically stirred solution of 18.6 g of **3** in 120 mL of 4% aqueous NaOH was added 2.3 g of sodium borohydride in small amounts over a period of 15 min. The reacton mixture was stirred at room temperature for 24 h and then neutralized to pH 7 by adding NH_4Cl. An additional 2.3 g of sodium borohydride was now added in small amounts (frothing) and the reaction mixture was held at 60 °C for 2 h. The neutral fraction was crystallized from benzene–hexane to yield 10.0 g (91%) of **5** as colorless prisms, mp 147–148 °C.

2-(4-Chlorobenzyl)-1-naphthoic Acid, 6. A well-stirred mixture of 60.0 g of **5**, 1.2 L of ethylene glycol, 850 mL of 30% KOH, and 250 g of zinc dust, activated by standing for 20 min with 15% HCl and then 2 g of $CuSO_4$, was held at reflux for 24 h. After the usual workup 60.0 g (97%) of colorless prisms of **6**, mp 166–167 °C, was obtained.

10-Chloro-7,12-benz[*a*]anthracenedione, 7. A mixture of 37.0 g of **6** and 1 L of concentrated H_2SO_4 was stirred at room temperature for 75 min and then poured over ice. The precipitated anthrone was added to a solution of 74 g of $Na_2Cr_2O_7{\cdot}2H_2O$ in 1.5 L of acetic acid. The mixture was refluxed for 2 h and poured on ice. The yellow solid was crystallized from benzene (or acetic acid) to yield 27.5 g (75%) of **7**, mp 229–230 °C (lit.[4] mp 232.2–232.8 °C).

10-Chloro-7,12-dihydro-7,12-dihydroxy-7,12-dimethylbenz[*a*]anthracene, 8. To a mechanically stirred suspension of 2.40 g of sublimed magnesium in 100 mL of dry ether was added 1 mL of dibromoethane and then methyl bromide as a gas until the magnesium completely dissolved. To this reagent at reflux was added a solution of 5.84 g of **7** in 600 mL of benzene during 2.5 h. The reaction mixture was held at reflux for 24 h and cooled, and 600 mL of 5% aqueous NH_4Cl was slowly added. After the usual workup the crude product was crystallized from benzene to yield 3.5 g (54%) of **8** as a colorless solid, mp 200–201 °C.

10-Chloro-7-(chloromethyl)-12-methylbenz[*a*]anthracene, 9. Dry HCl was passed into a solution of 2.5 g of **8** in 50 mL of ethyl acetate at 0 °C. After 18 h at room temperature, 2.3 g (92%) of yellow **9**, mp 148–149 °C, was obtained from ethyl acetate.[6]

10-Chloro-7,12-dimethylbenz[*a*]anthracene, 10. A mixture of 2.2 g of **9**, 60 mL of dioxane, 9 g of $SnCl_2$, and 9 mL of concentrated HCl was heated on a steam bath for 45 min and then poured into 500 mL of water. The crude product was crystallized from benzene–methanol to give 1.8 g (92%) of **10**, mp 86–87 °C, as pale yellow needles.

10-Cyano-7,12-dimethylbenz[*a*]anthracene, 11. A mixture of 1.00 g of **10**, 3.0 g of CuCN, and 10 mL of freshly distilled hexamethylphosphoramide was refluxed for 3.5 h. The reaction mixture was cooled and poured over a mixture of 100 mL of ethylenediamine and 100 mL of water. This was extracted several times with methylene chloride and the extract was worked up to give 0.8 g of a crude product which was chromatographed on a column of neutral alumina (50 g) with benzene–petroleum ether (1:3) as eluant. Crystallization from benzene–methanol gave 620 mg (64%) of **11** as yellow prisms, mp 158.5–159.5 °C.

10-Carboxy-7,12-dimethylbenz[*a*]anthracene, 12. A mixture of 0.7 g of **11**, 3 mL of 50% aqueous KOH, and 14 mL of ethylene glycol was refluxed for 24 h. After dilution with 150 mL of water and extraction with ether, the alkaline layer was acidified. The crude product was crystallized from glacial acetic acid to give 0.65 g (87%) of **12** as a pale yellow solid, mp 300 °C not sharp.

10-Carbethoxy-7,12-dimethylbenz[*a*]anthracene, 13. A mixture of 1.0 g of **12**, 20 mL of absolute ethanol, 100 mL of benzene, and 0.2 g of *p*-toluenesulfonic acid was refluxed for 72 h using a Dean-Stark separator. The reaction mixture was worked up as usual and the crude product was crystallized from ethanol to give 0.80 g (73%) of **13** as yellow prisms, mp 139–140 °C. Some **12** could be recovered.

10-(Hydroxymethyl)-7,12-dimethylbenz[*a*]anthracene, 2. To a suspension of 158 mg of lithium aluminum hydride in 60 mL of dry ether was added 1.00 g of **13** in 60 mL of dry ether and 40 mL of benzene. After being refluxed for 5 h, the reaction mixture was cooled, treated with dilute HCl, and worked up as usual to yield 800 mg (92%) of **2** as a pale yellow solid, mp 133.5–134.5 °C, from benzene–hexane.

Communications

Synthesis of *gem*-9,9-Dilithiofluorene by Thermal Rearrangement

Summary: The synthesis of an aromatic *gem*-dilithium-substituted fluorene by thermal rearrangement is described.

Sir: *gem*-Dilithium organic compounds have recently become synthetic targets as candidate molecules for observation of planar tetracoordinate carbon[1-5] and because they are of interest as reagents.

We report the first synthesis of an aromatic *gem*-dilithium-substituted compound, 9,9-dilithiofluorene, by a thermal rearrangement of 9-lithiofluorene.

The organolithium compound, 9-lithiofluorene, prepared by the reaction of fluorene with *n*-butyllithium in hexane was found to have a remarkable volatility and was purified by sublimation at 160 °C under high vacuum (10^{-4} torr). While heating at 180 °C under an inert atmosphere the compound was observed to decompose into fluorene as a volatile fraction and a dark brown nonvolatile powder which was characterized as a mixture of 9,9-dilithiofluorene, 9,9′-dilithio-9,9′-bifluorenyl, and 9,9″-dilithio-9,9′:9′,9″-terfluorenyl.

A 1.54-g sample of pure 9-lithiofluorene was placed in a small sublimation apparatus under argon. It was heated to 180 °C for a period of 22 h. The temperature was then allowed to cool to 120 °C and the system was evacuated to 10^{-4} torr. Generated fluorene was sublimed from the reaction mixture to a cold finger. This procedure was repeated two more times, giving a dark brown solid as a nonvolatile portion. Fluorene (540 mg) and the dark brown solid (910 mg) were isolated in a drybox. Hydrolysis of the dark brown powder with EtOH gave a mixture of

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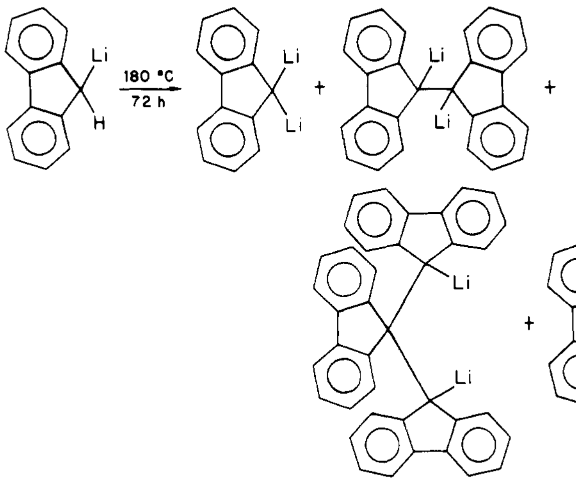

fluorene (15%), 9,9′-bifluorenyl (70%), and 9,9′:9,9″-terfluorenyl (15%) which were separated by thermal-gradient sublimation and identified by mass spectra. Hydrolysis with EtOD gave the same mixture but each compound was found to contain two deuteriums by mass spectral analysis:[6] 9,9-dideuteriofluorene [parent peak and base peak at *m*/*e* 168]; 9,9′-dideuterio-9,9′-bifluorenyl [parent peak at *m*/*e* 332 (12%), base peak at *m*/*e* 166]; 9,9″-dideuterio-9,9′:9,9″-terfluorenyl [parent peak at *m*/*e* 496 (27%), base peak at *m*/*e* 330]. Only signals due to phenyl protons appeared in their ^{1}H NMR spectra indicating that 9, 9′, and 9″ positions were all occupied by deuterium atoms.

The reaction of the dark brown powder with chlorotrimethylsilane in diethyl ether gave 9-(trimethylsilyl)fluorene, 9,9′-bis(trimethylsilyl)-9,9′-bifluorenyl, and 9,9″-bis(trimethylsilyl)-9,9′:9′,9″-terfluorenyl which were identified by mass and ^{1}H NMR spectral analyses: 9-(trimethylsilyl)fluorene [mass spectrum, parent peak at *m*/*e* 238 (90%), base peak at *m*/*e* 165; ^{1}H NMR δ −0.26 (9 H), 3.68 (1 H), 7.03–7.77 (8 H)]; 9,9′-bis(trimethylsilyl)-9,9′-bifluorenyl [mass spectrum, parent peak at *m*/*e* 474 (7%), base peak at *m*/*e* 193; ^{1}H NMR δ–0.18 (18 H), 6.668–7.90 (16 H)]; 9,9″-bis(trimethylsilyl)-9,9″-terfluorenyl [mass spectrum, parent peak at *m*/*e* 638 (3%), base peak at *m*/*e* 165; ^{1}H NMR δ 0.07 (18 H), 6.90–7.90 (24 H)]. Like other *gem*-dilithium compounds,[7] 9,9-dilithiofluorene did not give 9,9-bis(trimethylsilyl)fluorene but a hydrogen is abstracted (probably from the solvent) and monotrimethylsilylation to produce 9-(trimethylsilyl)fluorene was observed.

Presently very little is known about the mechanism of the Kawa–Lagow-modified Ziegler thermal rearrangement. An unpublished study on ^{13}C-labeled methyllithium pyrolysis has indicated only that the rearrangement is intermolecular or possibly a combination of intramolecular and intermolecular with respect to methyllithium tetramers. The range of reaction products in the present study are very interesting in this regard and a labeling study which is underway may shed more light on the mechanism of this reaction.

A feature of the Schleyer–Pople[8] proposal for planar carbon is stabilization by two lithium atoms via π acceptor and α donor character. For example, in the planar cis form of dilithiomethane, the two π-electrons are delocated in a cylic arrangement, isoconjugate with the cyclopropenium ion. Currently, we are attempting to add an additional conjugated system such as phenyl or vinyl groups into *gem*-dilithium compounds so that the "homoaromatic" π system in the planar form should be more stable.

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Registry No. Fluorene, 86-73-7; *n*-butyllithium, 109-72-8; 9-lithiofluorene, 881-04-9; 9,9-dilithiofluorene, 101248-45-7; 9,9′-dilithio-9,9′-bifluorenyl, 56833-94-4; 9,9″-dilithio-9,9′:9′,9″-terfluorenyl, 101315-86-0; 9,9′-bifluorenyl, 1530-12-7; 9,9′:9,9″-terfluorenyl, 1064-37-5; 9-(trimethylsilyl)fluorene, 7385-10-6; 9,9′-bis(trimethylsilyl)-9,9′-bifluorenyl, 76241-26-4; 9,9″-bis(trimethylsilyl)-9,9′:9′,9″-terfluorenyl, 101315-87-1.

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A Stereoselective Synthesis of the Hydronaphthalene Substructure of Kijanolide

Summary: The synthesis of a hydronaphthalene substructure of the antitumor antibiotic kijanimicin is described in which four of the seven chiral centers are introduced via a diastereoselective intramolecular Diels–Alder cyclization of an *all*-(*E*)-2,8,10,12-tetradecatetraenal.

Sir: We recently found that enals display exceptional dienophilic reactivity in Lewis acid-promoted intramolecular Diels–Alder cyclizations leading to hydronaphthalenes.[1] Such cyclizations proceed at −78 to −20 °C in a few hours with high endo selectivity. The remarkable rate enhancement and high stereoselectivity engendered by the aldehyde–Lewis acid combination suggest possible applications to the hydronaphthalene substructure of kijanolide and tetronolide, aglycones of the antitumor antibiotics kijanimicin[2a] and tetrocarin A.[2b] Accordingly, disconnection of C-2/C-3 and C-16/C-17 or C-18/C-19 of, e.g. kijanolide leads to a hydronaphthalene such as A whose assemblage could be formulated via cyclization of enal B (Figure 1).

While our preliminary work along these lines with simple 2,8,10-undecatrienals showed great promise,[1] we were concerned that the additional substituents on a more complex system such as B would raise the Diels–Alder activation energy to a point where the Lewis acid catalyst would cause decomposition of the sensitive trienyl ether moiety.[3] We were also uncertain as to the effect of the

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