pTsOH. The reaction was stirred at room temperature for 12 h. Solid $NaHCO_3$ and Na_2SO_4 were added. The mixture was filtered through a cotton plug and concentrated under reduced pressure. Purification of the crude product by chromatography (SiO_2, 1:1 hexane/Et_2O) afforded 18.3 mg (97%) of **64** as a clear oil: ^1H NMR (300 MHz, $CDCl_3$) δ 5.90 (dd, J = 3.7, 2.7 Hz, 1 H), 4.10 (m, 1 H), 3.67 (br s, 2 H), 3.11 (m, 2 H), 2.03-1.94 (m, 2 H), 1.87-1.78 (m, 2 H), 1.74-1.24 (m, 11 H), 0.99 (dq, J = 12.1, 3.5 Hz, 1 H), 0.09 (s, 9 H); IR (thin film) 3550-3050, 2940, 2860, 1600, 1450, 1365, 1245, 1050, 835 cm^{-1}; high resolution mass spectrum (EI) for $C_{16}H_{30}O_2Si$ (M^+), calcd 282.2015, found 282.2009. Anal. Calcd for $C_{16}H_{30}O_2Si$: C, 68.03; H, 10.63. Found: C, 67.89; H, 10.73.

Acknowledgment. This research was generously supported by the National Institute of General Medical Sciences (GM 26782).

Supplementary Material Available: ^1H NMR spectra of **2, 20**, acetate derivative of **24b, 25a, 36, 40, 41, 42, 44, 46c, 48c, 48d, 51, 55**, and **56** (15 pages). Ordering information is given on any current masthead page.

A New General Synthesis of Polycyclic Aromatic Compounds Based on Enamine Chemistry

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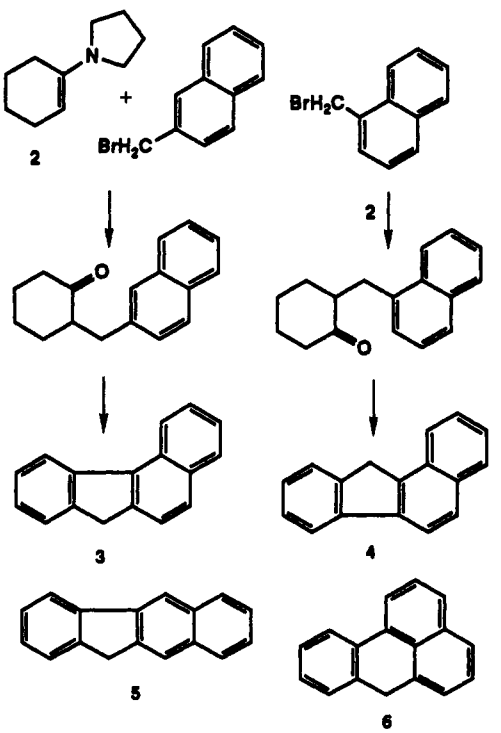
Received August 7, 1990

Alkylation of enamines and enamine salts by benzylic and (β-haloethyl)aryl halides, respectively, followed by acidic cyclodehydration and dehydrogenation provides an efficient synthetic approach to a wide range of polycyclic aromatic compounds of diverse structural types. Specific polycyclic hydrocarbons synthesized by this route include benzo[*a*]- and benzo[*c*]fluorene, 7*H*-dibenzo[*c,g*]-, 13*H*-dibenzo[*a,i*]-, and 13*H*-dibenzo[*a,g*]fluorene, 15*H*-tribenzo[*a,c,i*]fluorene, dibenzo[*b,def*]chrysene, benzo[*rst*]pentaphene, indeno[1,2-*b*]fluorene, fluoreno-[3,4-*c*]fluorene, octahydrodibenz[*a,j*]anthracene, dibenz[*a,j*]anthracene, octahydrodibenz[*a,h*]anthracene, dibenz[*a,h*]anthracene, picene, benzo[*c*]picene, 1*H*-benz[*bc*]aceanthrylene, and 4*H*-cyclopenta[*def*]chrysene. This method with appropriate modifications appears to be potentially broader in scope than established traditional methods of polycyclic hydrocarbon synthesis.

Development of methods for the synthesis of polycyclic aromatic hydrocarbons (polyarenes) has lagged behind expanding interest in their chemistry and biological properties. Polyarenes are widely distributed environmental contaminants formed by incomplete combustion of fossil fuels and other organic matter. Some polyarenes exhibit relatively potent carcinogenic activities.[1,2] The classical synthetic methods, which are still widely employed, were developed prior to the modern era of synthetic organic chemistry.[3] These methods frequently require harsh reagents and conditions, tend to furnish mixtures of isomeric products that are difficult to separate, and entail relatively large numbers of synthetic steps with relatively low overall yields.

This investigation is part of a program to devise novel, more efficient synthetic approaches to polycyclic aromatic molecules that do not suffer from these limitations. Specifically, we have investigated the alkylation of enamines and imine salts as the basis of potential synthetic routes to polycyclic aromatic compounds. The possible utility of this approach was suggested by prior studies[4] in which it was found that alkylation of the bromomagnesium salt of *N*-cyclopentenylcyclohexanimine with 2-(1-naphthyl)ethyl iodide, followed by acidic cyclization and dehydrogenation furnished 16,17-dihydro-15*H*-cyclopenta[*a*]phenanthrene (**1**), a key intermediate in the synthesis of the carcinogenic 17-keto derivatives of 1, previously available only by more complex multistep synthesis. We now report that this methodology with appropriate modifications provides convenient synthetic access to a wide range of polyarenes, nonalternant as well as alternant, including very large polycyclic ring systems and polyarenes relatively unobtainable by classical methods.

Scheme I



(1) *WHO Monograph on the Evaluation of the Carcinogenic Risks of the Chemical to Man: Polynuclear Aromatic Compounds*; Int. Agency Res. Cancer, W.H.O.: Lyon, France, 1983.
(2) Harvey, R. G. *Polycyclic Hydrocarbons and Carcinogenesis*; American Chemical Society: Washington, DC, 1985.
(3) Clar, E. *Polycyclic Hydrocarbons*; Academic Press: New York, 1964.
(4) Lee, H.; Harvey, R. G. *J. Org. Chem.* **1988**, *53*, 4253-4256.

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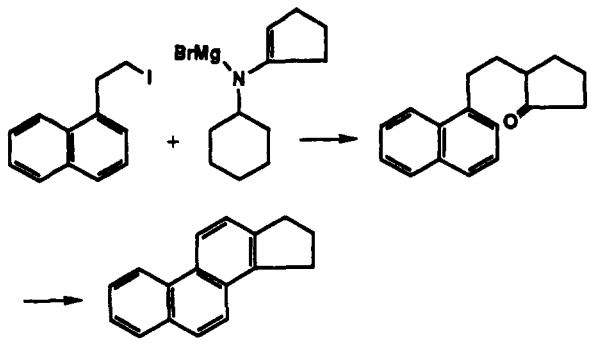

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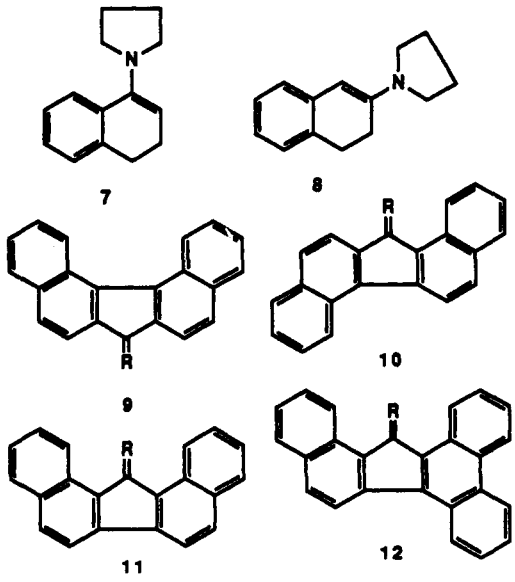
Results

Alkylation of Enamines. Initial experiments were conducted with the readily available enamine derivative of cyclohexanone, 1-pyrrolidino-1-cyclohexene (**2**) (Scheme I). Reaction of this enamine with 2-(bromomethyl)-naphthalene furnished the corresponding alkylated cyclohexanone, which underwent smooth acid-catalyzed cyclodehydration in methanesulfonic acid or liquid HF to yield tetrahydrobenzo[*c*]fluorene. Dehydrogenation with DDQ provided the fully aromatic compound 7*H*-benzo-[*c*]fluorene (**3**) in good overall yield. Analogous reaction of the same enamine with 1-(bromomethyl)naphthalene, followed by cyclization and dehydrogenation, furnished the isomeric 11*H*-benzo[*a*]fluorene (**4**). Cyclization appeared to be regiospecific in both cases, since 11*H*-benzo[*b*]-fluorene (**5**) and 7*H*-benz[*de*]anthracene (**6**), the products expected to arise from cyclization in the alternative direction, were not detected, although they may be formed in small amounts. These syntheses provide the most efficient synthetic approaches currently available to both of these hydrocarbons.[3]

This method was also utilized to synthesize several dibenzo- and tribenzofluorenes. Thus, analogous reaction sequences with 1- and 2-(bromomethyl)naphthalene and the enamine derivatives of α- and β-tetralone (**7** and **8**)

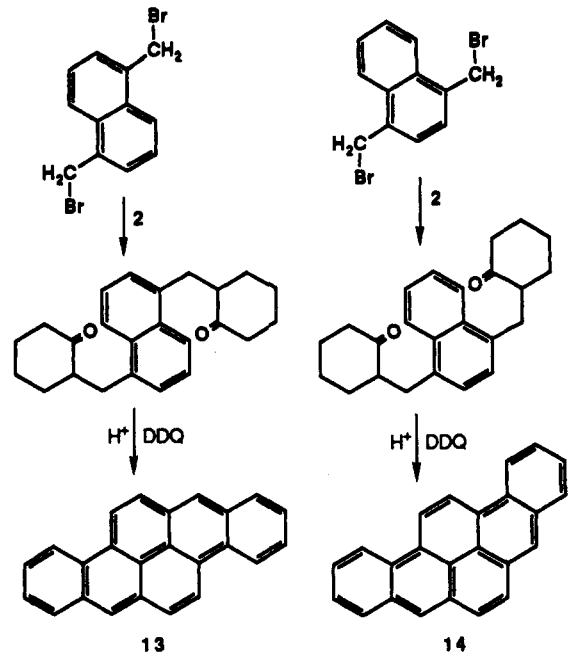


7 8 9 10 11 12

a. R = H_2; b. R = O

provided 7*H*-dibenzo[*c*,*g*]-, 13*H*-dibenzo[*a*,*i*]-, and 13*H*-dibenzo[*a*,*g*]fluorene (**9–11a**). Similar reaction of 9-(bromomethyl)phenanthrene with **8** followed by cyclodehydration and dehydrogenation furnished 15*H*-tribenzo[*a*,*c*,*i*]fluorene (**12a**). These hydrocarbons were all obtained in good overall yields. Their structures were confirmed by analysis of their high resolution 500-MHz NMR spectra, which were generally consistent with the assignments and inconsistent with alternative isomeric structures, and by conversion to the corresponding fluorenones (**9–12b**), which are known compounds. Oxidation of the fluorenes was smoothly effected by treatment with DDQ in aqueous acetic acid.[5]

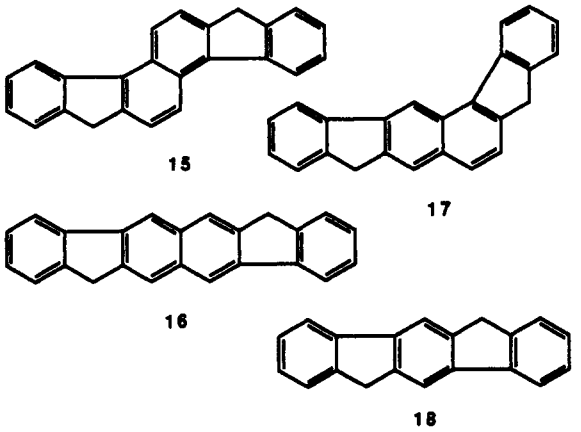
Scheme II



In the foregoing examples, the direction of cyclization of the ketone intermediates is to the substituted ring with formation of a five-membered ring, even in cases where cyclization to the adjacent ring with formation of a new six-membered ring is possible. However, this is not a rigorous rule, since in other cases the alternative mode of cyclization occurs preferentially. Thus, reaction of 2 equiv of the enamine **2** with 1,5-bis(bromomethyl)naphthalene gave the expected diketone, which underwent double cyclodehydration in both cases to the adjacent aromatic ring (Scheme II). Dehydrogenation of the product yielded dibenzo[*b*,*def*]chrysene (**13**) containing six benzenoid rings. Analogous reaction of 1,4-bis(bromomethyl)naphthalene furnished benzo[*rst*]pentaphene (**14**), also via a reaction pathway that involves double cyclization to the adjacent aromatic ring. Both of these hydrocarbons are relatively potent carcinogens, previously accessible only by more cumbersome synthetic routes.[3]

The scope of the method was also extended to the synthesis of polycyclic ring systems containing two five-membered rings. Reaction of 2 equiv of enamine **2** with 2,6-bis(bromomethyl)naphthalene furnished a diketone product, which underwent double cyclodehydration and dehydrogenation to yield 5,12-dihydrofluoreno[3,4-*c*]-fluorene (**15**). This isomer is readily distinguished from the alternative isomer structures 7,14-dihydrofluoreno-[2,3-*b*]fluorene (**16**) and 5,9-dihydrofluoreno[3,4-*b*]fluorene (**17**) by analysis of its high resolution 500-MHz proton NMR spectrum. As expected for **15**, but not for **17**, the spectrum revealed a high degree of symmetry. In particular, there was noted a lone methylene singlet at δ 4.06 (4 H), two low field doublets at δ 8.79 and 8.42 assigned to the sterically crowded pseudo bay region protons $H_{7,14}$ and $H_{1,8}$, respectively, a pair of doublets at δ 7.82 and 7.64

(5) Lee, H.; Harvey, R. G. *J. Org. Chem.* **1988**, *53*, 4587–4589.

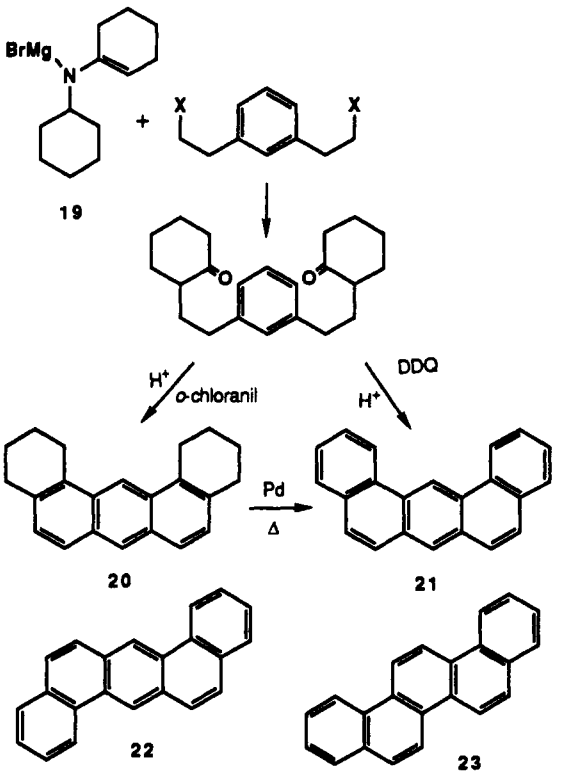


($H_{4,6,11,13}$), and a pair of triplets at δ 7.48 and 7.34 ($H_{2,3,9,10}$). This splitting pattern is entirely consistent with **15** and inconsistent with **16** or **17**. Reaction of the same enamine with 1,4-bis(bromomethyl)benzene provided the symmetrical 6,12-dihydroindeno[1,2-*b*]fluorene (**18**). The same high degree of regioselectivity was observed in this cyclization. It is interesting that these dehydrogenations failed to proceed past the stage of **15** and **18** to fully unsaturated products. This is consistent with the prior generalization that dehydrogenation of five-membered rings fused to benzenoid rings cannot generally be effected by palladium catalysts.[6]

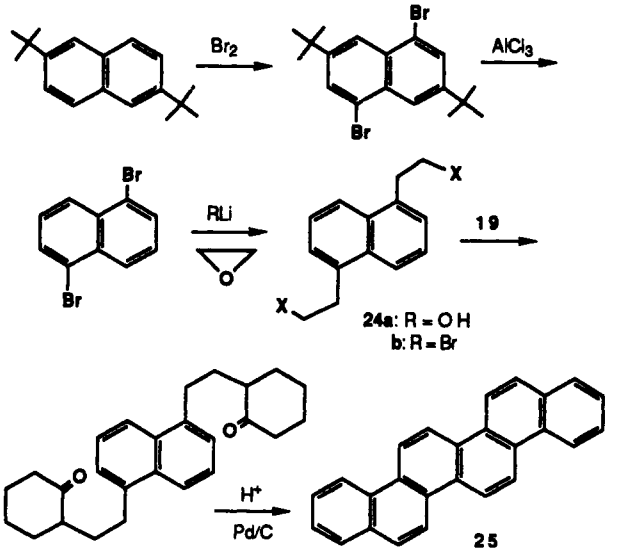
Alkylation of Imine Salts. In contrast to the benzylic halides employed in the preceding examples, primary aliphatic halides are insufficiently reactive to alkylate enamines directly. However, primary halides readily enter into reaction with the salts of imines,[7] a property that has been exploited to further extend the scope of the method. Thus, reaction of 2 equiv of the bromomagnesium salt of the imine derivative of cyclohexanone (**19**) with 1,3-bis(iodoethyl)benzene afforded a diketone intermediate that underwent smooth acid-catalyzed double cyclodehydration to dodecahydrodibenz[*a,j*]anthracene (Scheme III). The diodide afforded a better yield of the alkylated diketone intermediate than the corresponding dibromide. Mild dehydrogenation of the cyclized product with *o*-chloranil yielded 1,2,3,4,10,11,12,13-octahydrodibenz[*a,j*]anthracene (**20**), and dehydrogenation of **20** over a palladium–charcoal catalyst furnished the fully aromatic dibenz[*a,j*]anthracene (**21**). Dehydrogenation of the cyclized dodecahydrodibenz[*a,j*]anthracene with DDQ provided **21** directly and essentially quantitatively. This transformation was also effected by *o*-chloranil, but the reaction was slower, requiring 48 h for completion versus 2 h for DDQ. The isomeric polyarene that might be expected to arise from the alternative mode of cyclization was not detected. Similar reaction of 1,4-bis(iodoethyl)benzene with the same imine salt furnished a diketone intermediate that underwent double cyclization to dodecahydrodibenz[*a,h*]anthracene. Dehydrogenation of this with excess *o*-chloranil afforded dibenz[*a,h*]anthracene (**22**). A similar reaction sequence with 1,2-bis(iodoethyl)benzene as the dihalide furnished dodecahydropicene, which underwent dehydrogenation with DDQ to provide picene (**23**) as the principal product. These methods provide convenient synthetic access to these polyarenes previously available only via complex multistep syntheses.[3]

Another interesting application is in the synthesis of the rare polyarene benzo[*c*]picene (**25**) (Scheme IV). The dihalide required for this purpose, 1,5-bis(2-haloethyl)-

Scheme III



Scheme IV

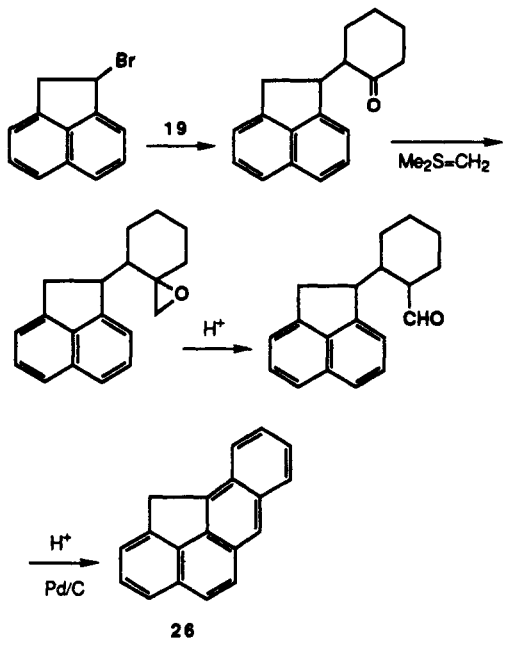


naphthalene **24b**, is not readily available by direct substitution methods. However, it was readily obtained from 2,6-di-*tert*-butylnaphthalene, the *tert*-butyl groups of which block substitution in all but the 3,7-positions. Reaction of 2,6-di-*tert*-butylnaphthalene with excess bromine afforded smoothly the 3,7-disubstituted derivative, which on deblocking with $AlCl_3$ gav 1,5-dibromonaphthalene. Treatment of this with *n*-butyllithium, followed by reaction of the dilithio salt with ethylene oxide, gave the dialcohol **24a**. Reaction of the latter with PBr_3 furnished 1,5-bis(2-bromoethyl)naphthalene (**24b**). Reaction of **24b** with the bromomagnesium imine salt **19** provided the expected diketone product, which underwent acid-catalyzed cyclodehydration and dehydrogenation to yield benzo[*c*]picene (**25**).

This synthetic methodology may also be modified for the preparation of linear acene-type polyarenes and

(6) Fu, P. P.; Harvey, R. G. *Chem. Rev.* **1978**, *78*, 317–361.
(7) Stork, G.; Dowd, S. R. *J. Am. Chem. Soc.* **1963**, *85*, 2178–2180.

Scheme V



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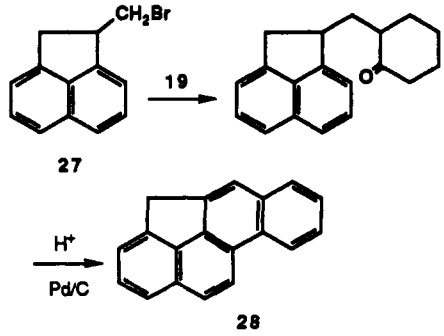
Scheme VI



27

28

methylene-bridged hydrocarbons. This is illustrated by the syntheses of 11*H*-benzo[*bc*]aceanthrylene (**26**) (Scheme V) and 4*H*-cyclopenta[*def*]chrysene (**28**) (Scheme VI). Reaction of 1-bromoacenaphthene with the imine salt **19** furnished the corresponding alkylated cyclohexanone. Reaction of this ketone with dimethylsulfonium methylide,[8] gave the corresponding epoxide which underwent acid-catalyzed rearrangement to an aldehyde with one additional carbon atom. Acid-catalyzed cyclodehydration followed by catalytic dehydrogenation furnished **26**. The reaction of 1-(bromomethyl)acenaphthene (**27**) with the imine salt **19** required longer time for completion of the alkylation reaction than usual (2 days) but furnished smoothly the alkylated ketone product. Acid-catalyzed cyclodehydration and catalytic dehydrogenation provided **28**. These synthetic routes to **26** and **28** appear to offer some advantage in comparison with alternative methods.[9,10]

Discussion

The foregoing results demonstrate that alkylation of enamines and enamine salts followed by acidic cyclodehydration and dehydrogenation provides an efficient approach to the synthesis of polycyclic aromatic compounds of diverse structural types. The types of polycyclic hydrocarbons synthesized include benzo-, dibenzo-, and tribenzofluorenes (**3**, **4**, **9–12a**), hexacyclic dibenzopyrenes (**13** and **14**), bis-fluorenes (**15** and **18**), angular pentacyclic dibenzanthracenes (**21** and **22**) and picene (**23**), angular hexacyclic phenes (**25**), methylene-bridged polyarenes (**26** and **28**), and linear acenes (**26**). This synthetic approach was successful in all the cases examined, and good overall yields were generally realized. The majority of these polyarenes are less conveniently available by established conventional synthetic methods, and there is no single alternative synthetic approach that could provide all of them.

In the cyclodehydration step a remarkable degree of regioselectivity was observed in the direction of cyclization. In all the cases examined, although two or more isomers were usually possible, only a single major isomeric cyclization product was isolated. For previously unknown polyarenes, the isomeric structural assignments were readily made by analysis of their high resolution 500-MHz proton NMR spectra, which generally revealed distinctive splitting patterns in comparison with those of alternative isomer structures. No attempt was made in these initial exploratory studies to examine product residues to isolate and characterize minor isomeric products that may be present. However, it is likely that minor amounts of other isomers are also formed.

Steric interaction appears to be one of the principal factors controlling regioselectivity. Thus, in the synthesis of the pentacyclic dibenzanthracenes **21** and **22** the diketone intermediates cyclize exclusively in the direction in which steric interaction is minimized in the intermediate. This factor may also be operative in the regioselective syntheses of **14** and **18**. Another factor that contributes significantly to determining the preferred direction of cyclization is the relative susceptibilities of the adjacent ring positions to electrophilic substitution. This is evident in the synthesis of benz[*c*]fluorene in which cyclization of the ketone precursor takes place preferentially to the more reactive α-naphthalene position to furnish **3** rather than to the less reactive β-naphthalene position to generate **5**. This factor appears to also play an important role in the syntheses of **9a**, **10a**, and **15**. On the other hand, the ketone precursors of **4**, **11a**, and **12a** cyclize preferentially to the β-positions of the same ring rather than to the α-positions of the adjacent rings, although the latter leads to formation of six- rather than five-membered rings. The reason again appears to be steric, since in these cases the alternative products all contain sterically crowded "bay" or "fjord" (in the case of **10a**) regions. Less obvious are the cases of **13** and **14** for which double cyclizations of the ketone intermediates take place exclusively to the α-positions in the adjacent rings. This mode of cyclization of the ketone precursor of **13** may be favored by activation of the adjacent ring by alkyl substitution. However, this explanation cannot hold for preferential formation of **14** from its precursor. Further investigations will be required to elucidate all the factors involved in determining the preferred directions of cyclization of these ketone intermediates.

Disproportionation of the primary olefinic products of cyclodehydration to mixtures of more saturated and less saturated polyarene products was observed in some cases. Disproportionation is commonly observed in acid-catalyzed cyclizations[11,12] and generally presents no problem since dehydrogenation of the mixtures affords the same fully aromatic polyarene products as would be otherwide obtained.

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(9) Ray, J.; Harvey, R. G. *J. Org. Chem.* **1983**, *48*, 1352–1354.
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Conclusion

Alkylation of enamines and enamine salts followed by acidic cyclodehydration and dehydrogenation provides an efficient synthetic approach to a wide range of polycyclic aromatic compounds. This method appears to be potentially broader in scope than well-established traditional methods of polycyclic hydrocarbon synthesis. It utilizes readily available reagents and mild conditions, entails relatively few synthetic steps, is readily adaptable to synthesis on any scale, and provides generally good overall yields. It is also, in principle, readily adaptable to the synthesis of the substituted derivatives of polyarenes, including their oxidized carcinogenic metabolites.

Experimental Section

Materials and Methods. 1-Pyrrolidino-1-cyclohexene (**2**), 1- and 2-(bromomethyl)naphthalene, 1,4-bis(bromomethyl)benzene, 1,2-, 1,3-, and 1,4-phenylenediacetic acid, and α- and β-tetralone were purchased from the Aldrich Chemical Co. *N*-Cyclohexenylcyclohexanimine and its bromomagnesium salt (**19**) were synthesized by procedures already described.[7] 1-Bromoacenaphthene and 1-acenaphthylacetic acid were prepared by the method of Bachmann.[13] 9-(Bromomethyl)phenanthrene (mp 115–117 °C, lit.[14] mp 112–115 °C) was synthesized from 9-methylphenanthrene by bromination with *N*-bromosuccinimide in CCl_4 in the presence of benzoyl proxide. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was purified by recrystallization from benzene. *N*-Bromosuccinimide (NBS) was crystallized from water. Triglyme, tetrahydrofuran (THF), and dioxane were freshly distilled from $LiAlH_4$.

The proton NMR spectra were obtained on a Varian EM360 spectrometer or the University of Chicago 300- or 500-MHz NMR spectrometers in $CDCl_3$ with tetramethylsilane as internal standard unless stated otherwise. Integration was consistent with all structural assignments. Ultraviolet spectra were taken on a Perkin-Elmer Lambda 5 spectrometer.

Synthesis of Alkyl Halides. 1,4-Bis(bromomethyl)naphthalene. A mixture of 1,4-dimethylnaphthalene (12.5 g, 0.080 mol), NBS (30.6 g, 0.17 mol), and benzoyl peroxide (0.4 g) in 70 mL of CCl_4 was heated at reflux for 1 h. The solution was cooled and the copious precipitate was filtered off and washed with CCl_4. A suspension of this solid in 500 mL of water was stirred for 45 min; then the insoluble material was filtered, washed with water, and dried to yield the crude product (20.09 g), mp 187–190 °C. Recrystallization from ethyl acetate furnished the pure dihalide, mp 192–193 °C. Anal. Calcd for $C_{12}H_{10}Br_2$: C, 45.90; H, 3.21; Br, 50.89. Found: C, 46.09; H, 3.17; Br, 50.94.

1,5-Bis(bromomethyl)naphthalene. Analogous NBS bromination of 1,5-dimethylnaphthalene gave the pure dihalide (84%), mp 214.5–215.5 °C. Anal. Calcd for $C_{12}H_{10}Br_2$: C, 45.90; H, 3.21; Br, 50.89. Found: C, 46.16; H, 3.25; Br, 51.10.

2,6-Bis(bromomethyl)naphthalene. Analogous NBS bromination of 2,6-dimethylnaphthalene provided the pure dihalide (58%), mp 182–184 °C. Anal. Calcd for $C_{12}H_{10}Br_2$: C, 45.90; H, 3.21; Br, 50.89. Found: C, 45.81; H, 3.23; Br, 50.84.

1,3-Bis(2′-iodoethyl)benzene. 1,3-Phenylenediacetic acid (10.0 g, 51 mmol) was added to a suspension of $LiAlH_4$ (7.6 g) in freshly distilled THF. The solution was stirred at ambient temperature under argon for 24 h. The reaction was quenched with water and acidified with HCl, the aqueous layer was saturated with NaCl, and the product was extracted with ether and washed with brine to provide 1,3-bis(2′-hydroxyethyl)benzene (8.0 g, 96%) as a colorless oil. This dialcohol was converted to the corresponding dimesylate (98%) by reaction with mesyl chloride and triethylamine by the procedure of Crossland and Servis.[15] A solution of the dimesylate (15 g, 45 mmol) and NaI (19.2 g, 135 mmol) in 500 mL of dry acetone was stirred at reflux under argon for 5 h. The solution was cooled and poured into ice water, and the product was extracted with CH_2Cl_2, evaporated to dryness, and chromatographed on a column of Florisil. Elution with hexane furnished the pure diiodide as a colorless oil (16 g, 92%): NMR δ 3.52 (t, 4, CH_2), 3.27 (t, 4, CH_2), 6.98–7.32 (m 4, Ar). Anal. Calcd for $C_{10}H_{12}I_2$: C, 31.12; H, 3.13; I, 65.75. Found: C, 31.10; H, 3.24; I, 65.69.

1,4-Bis(2′-iodoethyl)benzene. Similar reduction of 1,4-phenylenediacetic acid (25 g) with $LiAlH_4$ furnished 1,4-bis(2′-hydroxyethyl)benzene (8.0 g, 92%), mp 75–76 °C, which was converted to 1,4-bis(2′-(mesyloxy)ethyl)benzene (88%), mp 115–118 °C, by the above procedure. Reaction of the dimesylate with NaI afforded the corresponding diiodide (94%) as a white solid, mp 111–112 °C: NMR δ 3.32 (t, 4, CH_2), 3.14 (t, 4, CH_2), 7.11 (s, 4, Ar). Anal. Calcd for $C_{10}H_{12}I_2$: C, 31.12; H, 3.13; I, 65,75. Found: C, 31.15; H, 3.15; I, 65.67.

1,2-Bis(2′-iodoethyl)benzene. Reduction of 1,2-phenylenediacetic acid (25 g) with $LiAlH_4$ by the same procedure furnished 1,2-bis(2′-hydroxyethyl)benzene (8.0 g, 96%) as a colorless oil. This was converted by the usual procedure to 1,2-bis(2′-(mesyloxy)ethyl)benzene (97%), a pale yellow oil. Reaction of the dimesylate with NaI gave the corresponding diiodide (86%) as a colorless oil: NMR δ 3.30 (t, 4, CH_2), 3.18 (t, 4, CH_2), 7.16–7.22 (m, 4, Ar). Anal. Calcd for $C_{10}H_{12}I_2$: C, 31.12; H, 3.13; I, 65.75. Found: C, 31.11; H, 3.11; I, 65.72.

1,5-Dibromo-3,7-di-*tert*-butylnaphthalene. To a stirred solution of di-*tert*-butylnaphthalene (24.04 g, 0.10 mol) in 240 mL of CH_2Cl_2 containing 50 mg of anhydrous $AlCl_3$ was added a solution of Br_2 in 100 mL of CH_2Cl_2 dropwise over 110 min. This solution was stirred for 18 h at room temperature, washed with water and saturated $NaCO_3$ solution, and dried, and the solvent was removed under vacuum. The semicrystalline residue was recrystallized from benzene–ethanol to provide the title compound (21.39 g), mp 206.5 °C; from the mother liquors an additional 1.74 g of product, mp 203–207 °C, was recovered for an overall yield of 58%: NMR δ 1.41 (s, 18, CH_3), 7.84 (s, 2, Ar), 8.07 (s, 2, Ar). Anal. Calcd for $C_{18}H_{22}Br_2$: C, 54.29; H, 5.57; Br, 40.14. Found: C, 54.52; H, 5.76; Br, 40.23.

1,5-Dibromonaphthalene. To a stirred solution of the 2,6-di-*tert*-butyl derivative of the title compound (19.0 g, 47.2 mmol) in 380 mL of dry benzene at room temperature was added anhydrous $AlCl_3$ (6.29 g, 47.2 mmol). The mixture was stirred for 1 h and then poured into icewater. This mixture was stirred for 5 min; then the organic layer was washed with water and dried, and the solvent was removed. The residue was crystallized from ethanol to give 7.60 g (56%) of 1,5-dibromonaphthalene, mp 129–130 °C (lit.[16] mp 130–131 °C).

1,5-Bis(2′-bromoethyl)naphthalene (24b). To a solution of *n*-butyllithium (16 mL of a 2.5 M solution in anhydrous THF, 40 mmol) cooled in an ice bath was added a solution of 1,5-dibromonaphthalene (4.29 g, 15 mmol) in 50 mL of THF dropwise over 20 min with stirring under N_2. The solution was stirred for 1 h; then a stream of ethylene oxide was introduced for 10 min. The mixture was stirred for an additional 25 min and then decomposed by dropwise addition of 25 mL of 15% HCl. The product mixture was extracted with 100 mL of EtOAc, the extracts were washed with water and dried, and the solvent was removed under vacuum. Chromatography of the residue on a column of Florisil eluted with benzene–ether (4:1) gave the crude dialcohol (2.57 g), which was recrystallized from benzene to yield pure 1,5-bis(2′-hydroxyethyl)naphthalene (**24a**) (1.87 g, 58%), mp 116–117 °C. Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.84; H, 7.34.

A solution of PBr_3 (4.33 g, 16 mmol) in 6 mL of anhydrous benzene was added dropwise with stirring to a suspension of **24a** (2.60 g, 12 mmol) in 20 mL of benzene. The mixture was maintained at 75 °C for 2.5 h; then it was poured on ice and filtered, and the organic layer was washed with $NaHCO_3$ solution and dried, and the solvent was evaporated to yield the dibromide (1.49 g, 36%), mp 141–143 °C. Anal. Calcd for $C_{14}H_{14}Br_2$: C, 49.16; H, 4.12; Br, 46.72. Found: C, 49.32; H, 4.37; Br, 46.44.

1-(Bromomethyl)acenaphthene. This compound was prepared from 1-acenaphthenylacetic acid by Barton's alternative

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to the Hunsdiecker reaction.[17] To a stirred solution of the acid (1.0 g, 4.7 mmol) in 10 mL of dry CH_2Cl_2 at room temperature was added 3 mL of 2 N oxalyl chloride (6.0 mmol), and the solution was stirred at room temperature for 2 h. After removal of the solvent under vacuum, the product was dissolved in Cl_3CBr and added dropwise to a refluxing solution of the sodium salt of 2-mercaptopyridine *N*-oxide (681 mg, 5.2 mmol) dissolved in 10 mL of Cl_3CBr. The mixture was heated at reflux for an 1.5 h; then allowed to cool to room temperature. Ether (130 mL) was added, and the organic layer was washed with saturated $NaHCO_3$ solution and then with water and dried. After removal of the solvent, the crude mixture was separated by chromatography on silical gel. Elution with hexane–CH_2Cl_2 (4:1) furnished the product (1.12 g, 95%) as an oil: NMR δ 7.62 (d, 1, Ar), 7.57 (d, 1 Ar), 7.43 (m, 2, Ar), 7.31 (d, 1, Ar), 7.25 (d, 1, Ar), 4.08 (m, 1, methine), 3.82 (q, 1, CH_2), 3.64 (q, 1, CH_2), 3.49 (t, 1, CH_2), 3.28 (q, 1 CH_2); IR (film) 3040, 2920, 1610, 1423, 1367, 1230, 800, 780, 615 cm^{-1}. Anal. Calcd for $C_{13}H_{11}Br$: C, 63.18; H, 4.49. Found: C, 63.27; H, 4.52.

7*H*-Benzo[*c*]fluorene (3). To a solution of 2-(bromomethyl)naphthalene (5.00 g, 22.6 mmol) in 25 mL of dry dioxane was added the enamine **2** (22.6 mmol), and the solution was heated at reflux for 18 h under N_2. Water was added, and heating was continued for an additional hour. Then the solvent was evaporated under vacuum, and the residue was extracted with ether. The ether phase was washed consecutively with 5% HCl, 5% $NaHCO_3$ solution, and water, then dried, and evaporated. The residue was chromatographed on silica gel eluted with benzene–hexane (1:1) to provide an alkylated ketone product (4.5 g, 84%) as a white solid, mp 58–60 °C: NMR δ 7.25–7.76 (m, 6, Ar), 7.56 (s, 1, H_1), 3.36–3.39 (m, 2, benzylic CH_2), 1.37–2.65 (m, 9, aliphatic); MS m/e = 238 (M^+, 100). A solution of this ketone (1.2 g, 5.04 mmol) in 30 mL of 10% (v/v) methanesulfonic acid in $CHCl_3$ was stirred for 2 h at room temperature. At the end of this time, TLC indicated the absence of the ketone and formation of a nonpolar product. The reaction was quenched by careful addition of aqueous bicarbonate solution, and the organic phase was diluted with CH_2CL_2 and washed with $NaHCO_3$ solution and water, then dried, and evaporated. Chromatography of the residue on Florisil gave on elution with hexane an oil (865 mg), shown by HPLC analysis to be a mixture of three components assumed to be a mixture of isomeric olefins and/or their disproportionated products. A portion (200 mg, 0.91 mmol) was dehydrogenated directly by heating with 90 mg of 10% Pd/C in 10 mL of triglyme at reflux for 16 h. Conventional workup followed by chromatography on Florisil (hexane) gave **3** (153 mg, 64% from the ketone), mp 119–120 °C (EtOH) (lit.[18] mp 123–124 °C): NMR δ 8.73 (d, 1, H_1, $J_{1,2}$ = 8.98 Hz), 8.36 (d, 1, H_{11}, $J_{10,11}$ = 7.80 Hz), 7.93 (d, 1, J = 8.20 Hz), 7.79 (d, 1, J = 8.21 Hz), 7.65 (d, 1, J = 8.29 Hz), 7.60 (d, 1, J = 7.93 Hz), 7.31–7.49 (m, 4, Ar), 4.00 (s, 2, CH_2).

11*H*-Benzo[*a*]fluorene (4). Analogous reaction of 1-(bromomethyl)naphthalene with **2** provided the corresponding alkylated ketone (86%) as a colorless oil: NMR δ 7.90 (d, 1, J = 7.49 Hz), 7.82 (d, 1, J = 6.51 Hz), 7.68 (d, 1, J = 7.99 Hz), 7.27–7.47 (m, 4, Ar), 3.81–3.85 (m, 2, CH_2), 3.45 (m, 1, methine), 1.42–2.77 (m, 8); MS m/e = 238 (M^+, 100). Acid-catalyzed cyclization of this ketone followed by dehydrogenation in the same manner furnished **4** (82%), mp 186–187 °C (EtOH) (lit.[19] mp 183–184 °C); the isomeric 7*H*-benz[*de*]anthracene (**6**) melts at 81–82 °C[3]: NMR δ 7.98 (d, 1, J = 8.21 Hz), 7.50–7.89 (m, 5, Ar), 7.27–7.49 (m, 4, Ar), 4.17 (s, 2, CH_2).

1-(1-Pyrrolidino)-3,4-dihydronaphthalene (7). To a solution of α-tetralone (25 g, 171 mmol) in 250 mL of benzene were added 18.2 g (256 mmol) of pyrrolidine and 600 mg of *p*-toluenesulfonic acid. The solution was heated at reflux for 24 h on a Dean–Stark separator. After cooling, the solution was washed quickly with 200 mL of water and dried, and the solvent was removed. The residue was distilled at 0.05 mm pressure to give **7** (25.81 g, 76%), bp 93–98 °C, employed directly in the next step. Anal. Calcd for $C_{14}H_{17}N$: C, 84.37; H, 8.60; N, 7.03. Found: C, 83.92; H, 8.39; N, 6.73.

2-(1-Pyrrolidino)-3,4-dihydronaphthalene (8). This enamine was prepared from β-tetralone by a similar procedure in 92% yield. It melted at 78–79 °C. Anal. Calcd for $C_{14}H_{17}N$: C, 84.37; H, 8.60; N, 7.03. Found: C, 84.19; H, 8.44; N, 6.84.

7*H*-Dibenzo[*c*,*g*]fluorene (9a). Reaction of **7** with 2-(bromomethyl)naphthalene by the usual method (24-h reaction time) furnished the corresponding alkylated ketone (79%), mp 56.5–58.0 °C: NMR δ 7.00–8.25 (m, 11, Ar), 3.55 (m, 1, methine), 2.52–3.00 (m, 4, benzylic), 1.45–2.25 (m, 2, aliphatic). Cyclodehydration of this ketone (8 g) in anhydrous HF for 72 h at room temperature afforded 8,9-dihydro-**9a** (92% based on 5.0 g of unrecovered starting material), mp 133–134 °C. A solution of the dihydro compound (4.03 g, 15 mmol) and DDQ (3.75 g, 16.5 mmol) in 190 mL of dry benzene was heated at reflux for 5 min under N_2. The hydroquinone that separated on cooling was removed by filtration, and the solution was evaporated to dryness. The residue was dissolved in hexane–benzene (2:1) and filtered through a short column of Florisil. Evaporation of the solvent left 3.40 g (85%) of **9a**, mp 142.5–143 °C (hexane–benzene) (lit.[20] mp 152–152.5 °C): NMR δ 8.71 (d, 2, $H_{1,12}$, J = 8.33 Hz), 7.94 (d, 2, $H_{4,10}$, J = 7.98 Hz), 7.83 (d, 2, $H_{5,8}$, J = 8.12 Hz), 7.69 (d, 2, $H_{6,8}$, J = 8.08 Hz), 7.50 (m, 4, $H_{2,3,11,12}$), 4.08 (s, 2, CH_2); UV λ_{max} (EtOH) 360 (ϵ 26 576), 345 (25 045), 239 (36 306), 215 (120 990), 197 (37 207).

7*H*-Dibenzo[*c*,*g*]fluorenone (9b). DDQ (1.36 g, 6 mmol) was added to a hot solution of **7** (533 mg, 2 mmol) in 100 mL of acetic acid and 20 mL of water, and the solution was heated at reflux for 30 min under N_2. After cooling, the solution was diluted with 100 mL of benzene, washed twice with water and twice with $NaHCO_3$ solution, and dried, and the solvent was removed. The residue was chromatographed on Florisil. Elution with benzene furnished **9b** (319 mg, 57%), mp 222–225 °C (lit.[20] mp 222–222.5 °C).

13*H*-Dibenzo[*a*,*g*]fluorene (10a). This hydrocarbon was synthesized via a sequence analogous to that employed for the the preparation of **9a**. Reaction of 2-(bromomethyl)naphthalene with the enamine **8** furnished the corresponding alkylated ketone (76%), mp 67–68 °C. Cyclodehydration of this ketone (9 g) with methanesulfonic acid for 1 h at room temperature by the procedure employed for the preparation of **3** gave a mixture of cyclized products (72%), which failed to crystallize. Dehydrogenation of this product mixture with DDQ in refluxing benzene furnished **10a** (54%), mp 175–175.5 °C (benzene) (lit.[21] mp 174–175 °C): NMR δ 8.79 (d, 1 H_7, J = 8.47 Hz), 8.50 (d, 1, H_6, J = 8.61 Hz), 8.03 (d, 1, H_1, J = 8.13 Hz), 7.91 (m, 3, Ar), 7.78 (d, 1, Ar, J = 8.23 Hz), 7.72 (d, 1, Ar, J = 8.16 Hz), 7.20–7.63 (m, 4, Ar), 4.25 (s, 2, CH_2); UV λ_{max} (EtOH) 349 (ϵ 24 037), 333 (23 664), 276 (17 390), 254 (65 400), 248 (55 960), 212 (65 466).

13*H*-Dibenzo[*a*,*g*]fluorenone (10b). Oxiation of **10a** with DDQ in moist acetic acid by the usual procedure provided **10b** (59%), mp 164–165 °C (acetone) (lit.[21] mp 164–165 °C).

13*H*-Dibenzo[*a*,*i*]fluorene (11a). This hydrocarbon was synthesized from the reaction of 1-(bromomethyl)naphthalene with **8** via a similar sequence. The alkylated ketone obtained in 76% yield did not crystallize. Cyclodehydration of this ketone (9 g) with methanesulfonic acid by the usual procedure gave dihydro-**11a** (71%), mp 118–119.5 °C. Dehydrogenation with 10% Pd/C in refluxing triglyme furnished **11a** (50%), mp 218–220 °C. Recrystallization from ethyl acetate raised the melting point to 231–233 °C (lit.[21] mp 230–231 °C): NMR δ 8.06 (d, 2, $H_{6,7}$, J = 8.43 Hz), 7.92 (d, 2, $H_{1,12}$, J = 8.39 Hz), 7.96 (m, 4, $H_{4,5,7,8}$), 7.52 (t, 2, $H_{3,10}$), 7.42 (t, 2, $H_{2,11}$), 4.43 (s, 2, CH_2); UV λ_{max} (EtOH) 331 (ϵ 14 925), 287 (16 985), 278 (39 045), 264 (110 650), 213 (43 770), 198 (25 176).

13*H*-Dibenzo[*a*,*i*]fluorenone (11b). Oxidation of **11a** with DDQ in moist acetic acid by the usual procedure gave **11b** (64%), mp 269–270 °C (lit.[22] mp 270 °C).

15*H*-Tribenzo[*a*,*c*,*i*]fluorene (12a). This hydrocarbon was synthesized from the reaction of 9-(bromomethyl)phenanthrene with **8** via a similar sequence. The alkylated ketone obtained in

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83% yield melted at 133–134.5 °C (ether). Cyclodehydration of this ketone (8.5 g) with methanesulfonic acid by the usual procedure gave a crystalline residue, which was stirred with 125 mL of benzene for 20 min. The insoluble solid was filtered off to yield **12a** (2.90 g, 36%), mp 237–238 °C; the mother liquors were evaporated to dryness and stirred with 25 mL of acetone for 20 min. The insoluble residue of 8c,9,10,14b-tetrahydro-**12a** was filtered off (4.06 g, 50%); it melted at 167.5–168.5 °C. Dehydrogenation of 8c,9,10,14b-tetrahydro-**12a** with 10% Pd/C in refluxing triglyme furnished **12a** (35%, overall yield 71%), mp 239–240 °C (lit.[23] mp 238–239 °C): NMR δ 8.91 (d, 1 $H_{4\text{ or }5}$, J = 8.42 Hz), 8.79 (d, 1, $H_{4\text{ or }5}$, J = 8.46 Hz), 8.71 (d, 1, H_8, J = 8.10 Hz), 8.52 (d, 1, H_9, J = 8.65 Hz), 8.14 (m, 2, $H_{1,14}$), 7.92 (dd, 2, $H_{10,11}$), 7.22–7.74 (m, 6, Ar), 4.52 (s, 2, CH_2); UV λ_{max} (EtOH) 345 (ϵ 17 320), 289 (33 184), 278 (43 660), 261 (60 030), 253 (65 390), 247 (63 690), 212 (34 105), 203 (39 190).

15*H*-Tribenzo[*a*,*c*,*j*]fluorenone (12b). Oxidation of **12a** with DDQ in moist acetic acid by the usual procedure gave **12b** (86%), mp 244–245 °C (benzene) (lit.[23] mp 230–231 °C).

Dibenzo[*b*,*def*]chrysene (13). Reaction of 1,5-bis(bromomethyl)naphthalene with a 10% excess of the enamine **2** by the usual procedure furnished the expected diketone (90%), mp 208–212 °C. Cyclodehydration of this ketone in liquid HF by the usual procedure gave decahydro-**13** (77%), mp 237–238 °C. Dehydrogenation with 10% Pd/C in refluxing triglyme furnished **13** (49%), mp >290 °C (lit.[3] mp 308 °C): NMR δ 8.98 (d, 2, $H_{5,12}$), 8.94 (d, 2, $H_{4,11}$), 8.84 (s, 2, $H_{7,14}$), 8.33 (d, 2, $H_{1,8}$), 8.28 (d, 2, $H_{6,13}$), 7.76 (m, 4, $H_{2,3,9,10}$); UV λ_{max} (EtOH) 446 (ϵ 30 610), 420 (24 240), 396 (14 395), 310 (135 910), 297 (72 120), 268 (30 760), 254 (31 210), 203 (36 210).

Benzo[*rst*]pentaphene (14). Reaction of 1,4-bis(bromomethyl)naphthalene with a 10% excess of **2** by the usual procedure gave the expected diketone (69%), mp 129–31 °C (Et_2O). Cyclodehydration in liquid HF afforded decahydro-**14** (59%). Dehydrogenation of this with 10% Pd/C in refluxing triglyme furnished **14** (49%), mp 280–282 °C (lit.[3] mp 280 °C): NMR δ 9.18 (s, 2, $H_{13,14}$), 9.00 (d, 2, $H_{1,12}$, J = 8.26 Hz), 8.28 (s, 2, $H_{5,8}$), 8.18 (d, 2, $H_{4,9}$, J = 8.06 (Hz), 7.77 (s, 2, $H_{6,7}$), 7.73–7.80 (m, 4, $H_{2,3,10,11}$): UV λ_{max} (EtOH) 392 (ϵ 64 650), 370 (43 140), 352 (17 910), 329 (16 860), 314 (19 535), 294 (65 350), 282 (43 490), 271 (29 650), 241 (67 093), 233 (34 070), 222 (28 605), 211 (28 605).

5,12-Dihydrofluoreno[3,4-*c*]fluorene (15). Reaction of 2,6-bis(bromomethyl)naphthalene with a 10% excess of **2** by the usual procedure gave the expected diketone (78%), mp 186–188 °C (benzene). Cyclodehydration in methanesulfonic acid by the usual procedure provided octahydro-**15** (31%), mp 208–210 °C. Dehydrogenation of this with 10% Pd/C in refluxing triglyme furnished **15** (91%), mp 282–283 °C: NMR δ 8.78 (d, 2, $H_{7,14}$, J = 8.44 Hz), 8.42 (d, 2, $H_{1,8}$, J = 7.87 Hz), 7.82 (d, 2, $H_{6,13}$, J = 8.51 Hz), 7.64 (d, 2, $H_{4,11}$, J = 8.01 Hz), 7.48 (t, 2, $H_{3,10}$), 7.34 (t, 2, $H_{2,9}$), 4.06 (s, 4, $H_{5,12}$); UV λ_{max} (EtOH) 363 (ϵ 36 670), 345 (25 985), 333 (18 940), 252 (37 200), 238 (55 330), 204 (47 270). Anal. Calcd for $C_{24}H_{16}$: C, 94.70; H, 5.30. Found: C, 94.74; H, 5.33.

6,12-Dihydroindeno[1,2-*b*]fluorene (18). Reaction of 1,4-bis(bromomethyl)benzene with a 10% excess of **2** by the usual procedure gave the expected diketone (70%), mp 137–139 °C. Cyclodehydration in liquid HF furnished octahydro-**18** (40%), mp 195–198 °C. Dehydrogenation of this with 10% Pd/C in refluxing triglyme furnished **18** (73%), mp >290 °C: NMR δ 8.09 (s, 2, $H_{5,11}$), 7.92 (d, 2, $H_{4,10}$), 7.58 (d, 2, $H_{1,7}$), 7.38 (t, 2, $H_{3,9}$ or $H_{2,8}$), 7.29 (t, 2, $H_{3,9}$ or $H_{2,8}$); UV λ_{max} (EtOH) 332 (ϵ 48 300), 325 (29 760), 318 (27 090), 301 (32 000), 288 (25 820), 213 (46 730). Anal. Calcd for $C_{20}H_{14}$: C, 94.45; H, 5.55. Found: C, 94.35; H, 5.58.

1,2,3,4,10,11,12,13-Octahydrodibenz[*a*,*j*]anthracene (20). A solution of *N*-cyclohexenylcyclohexanimine (7 g, 39 mmol) and ethylmagnesium bromide (13 mL of a 3 M solution in ether, 39 mmol) in THF (80 mL) was heated at reflux for 3 h. The solution of **19** was cooled to room temperature; then 1,3-bis(2′-iodoethyl)benzene (5 g, 13 mmol) in 20 mL of THF was added and the solution was refluxed for 24 h. The reaction was again cooled and 100 mL of 10% HCl was added cautiously, and refluxing was continued for another 3 h and followed by the usual workup. The product was purified by passage through a short column of Florisil eluted with benzene to yield the expected diketone (95%) as a pale yellow oil. Anal. Calcd for $C_{22}H_{30}O_2$: C, 80.94; H, 9.26. Found: C, 80.85; H, 9.28.

Cyclodehydration of this diketone in methanesulfonic acid by the usual procedure provided dodecahydro-**20** (97%) shown by NMR to be a mixture of partially disproportionated products. Treatment of this with 2 equiv of DDQ (2 h in refluxing benzene) gave a mixture of dehydrogenated products (2.4 g) consisting predominately of **20**. Careful chromatography of this on a column of Florisil gave on elution with hexane pure **20** (30%), mp 192–193 °C: NMR δ 8.49 (s, 1, H_{14}), 8.24 (s, 1, H_7), 7.71 (d, 2, $H_{6,8}$), 7.12 (d, 2, $H_{5,9}$), 3.23 (t, 4, $H_{1,13}$), 2.92 (t, 4, $H_{4,10}$), 1.91 (m, 8, $H_{2,3,11,12}$). Anal. Calcd for $C_{22}H_{22}$: C, 92.26; H, 7.74. Found: C, 92.11; H, 7.77. Similar reaction with *o*-chloranil (48 h required for completion) furnished pure **20** virtually quantitatively.

Dibenz[*a*,*j*]anthracene (21). Dehydrogenation of **20** with 10% Pd/C in refluxing triglyme by the usual procedure furnished **21** (93%), mp 199–200 °C (benzene–hexane) (lit.[3] mp 196 °C): the 500-MHz NMR spectrum of **21** matched closely that of an authentic sample.[24] Dehydrogenation of dodecahydro-**20** with excess DDQ gave directly pure **21** (88%), mp 199–200 °C.

Dibenz[*a*,*h*]anthracene (22). This hydrocarbon was synthesized from the reaction of 1,4-bis(2′-iodoethyl)benzene with **19** by a similar procedure. The alkylated diketone (95%) melted at 90–91 °C. Anal. Calcd for $C_{22}H_{30}O_2$: C, 80.94; H, 9.26. Found: C, 80.84; H, 9.29. Cyclodehydration of this ketone with methanesulfonic acid by the usual procedure gave dodecahydro-**22** (98%) shown by NMR to be a mixture of partially disproportionated products. Treatment of this mixture with 10 equiv of *o*-chloranil (48 h) furnished **22** (94%), mp 265–266 °C (benzene–hexane) (lit.[3] mp 262 °C): the 500-MHz NMR spectrum of **22** matched closely that of an authentic sample.[24]

Picene (23). This hydrocarbon was synthesized from the reaction of 1,2-bis(2′-iodoethyl)benzene with **19** by a similar procedure. The alkylated diketone (94%) was obtained as a pale yellow oil. Anal. Calcd for $C_{22}H_{30}O_2$: C, 80.94; H, 9.26. Found: C, 80.86; H, 9.30. Cyclodehydration of this ketone with methanesulfonic acid by the usual procedure gave dodecahydro-**23** (92%) shown by NMR to be a mixture of partially disproportionated products. Treatment of this mixture with excess DDQ (16 h) furnished **23** (94%) as a very insoluble off-white solid, mp >280 °C (lit.[3] mp 364 °C): NMR δ 8.93 (s, 2, $H_{13,14}$), 8.82 (d, 2, $H_{6,7}$), 8.75 (d, 2, $H_{1,12}$), 7.99 (m, 4, $H_{4,5,8,9}$), 7.71 (t, 2, $H_{2,11}$ or $H_{3,10}$), 7.63 (t, 2, $H_{2,11}$ or $H_{3,10}$). Dehydrogenation of dodecahydro-**23** with *o*-chloranil (48 h required for completion) furnished pure **23** essentially quantitatively.

Benzo[*c*]picene (25). Reaction of 1,5-bis(2′-bromoethyl)-naphthalene (**24b**) with **19** by the usual procedure afforded the expected diketone (80%), mp 136–138 °C. Cyclodehydration of this diketone with methanesulfonic acid by the usual procedure gave dodecahydro-**25** (64%) shown by NMR to be a mixture of partially disproportionated products. Dehydrogenation of this mixture with 10% Pd/C in refluxing triglyme furnished **25** (63%), mp >300 °C (lit.[25] mp 444–446 °C): the NMR spectrum could not be obtained due to the extreme insolubility of **25**; the UV spectrum of **25** was in good agreement with the published spectrum.[25] Anal. Calcd for $C_{26}H_{16}$: C, 95.09; H, 4.91. Found: C, 95.18; H, 4.92.

11*H*-Benz[*bc*]aceanthrylene (26). Reaction of 1-bromoacenaphthene with 10% excess **2** by the usual procedure gave the expected alkylated ketone (83%) as an oil. To a stirred solution of 91 mL (119 mmol) of 1.3 M *sec*-butyllithium (in cyclohexane) in 140 mL of dry THF cooled to −78 °C were added 15.1 mL (13.26 g, 108 mmol) of Me_3SiCH_2Cl and 17.2 mL (13.20 g, 114 mmol) of tetramethylethylenediamine under N_2. The solution was stirred for 40 min; then the temperature was allowed to rise to −60 °C and a solution of 25 g (100 mmol) of the alkylated ketone in 50 mL of dry THF was added. After the addition was complete, the temperature was allowed to rise to −40 °C over 40 min and then maintained at this level for 30 min additional. The cooling bath was removed and the reaction mixture was allowed to come to

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room temperature over 75 min. The solution was poured into saturated NH_4Cl solution, stirred for 10 min, and then extracted with EtOAc. The extract was dried and the solvents were removed. The residue (30.16 g) was chromatographed on Florisil. Elution with hexane–benzene (4:1) provided the epoxide product (13.81 g), while further elution with benzene gave recovered starting ketone (10.20 g). The product was dissolved in THF (130 mL) and 15 mL of water; then the solution was cooled in ice and 8 mL of 70% $HClO_4$ was added dropwise. Stirring was continued at 0 °C for 5 min, and the solution was allowed to warm to room temperature for 6 h. It was then poured on ice and worked up conventionally to afford the crude product (11.56 g), which was purified by chromatography on Florisil. Elution with hexane–benzene (2:1) gave the pure aldehyde (5.76 g), which failed to crystallize.

A solution of this aldehyde (5 g) in 200 mL of methanesulfonic acid was stirred at 70 °C for 5 h under N_2. The solution was poured on ice and worked up in the usual manner followed by chromatography on Florisil to provide hexahydro-**26** (75%). Dehydrogenation of this mixture over a 10% Pd/C catalyst in refluxing triglyme furnished **26** (36%), mp 120.5–121 °C (acetone–hexane) (lit.[9] mp 123 °C); the NMR spectrum of **26** was in good agreement with that of an authentic sample; UV λ_{max} (EtOH) 306 (ϵ 7730), 289 (48100), 282 (44900), 271 (36220), 258 (37320), 221 (32310), 205 (27670). Anal. Calcd for $C_{19}H_{12}$: C, 94.96; H, 5.04. Found: C, 94.72; H, 5.00.

4*H*-Cyclopenta[*def*]chrysene (28). Reaction of 7-(bromomethyl)acenaphthene (620 mg, 2.51 mmol) with 40% excess **19** was carried out by the standard procedure (50 h). The usual workup followed by chromatography on silica gel furnished the alkylated ketone (300 mg, 68% based on conversion of the starting compound) as an oil along with 210 mg of the unreacted alkyl bromide. To a solution of 300 mg of the ketone in 12 mL of CH_2Cl_2 in an ice bath was added 4.5 mL of methanesulfonic acid. This solution was maintained at 0 °C for 30 min; then the reaction was worked up in the usual way to afford hexahydro-**28** (270 mg, 94%). Dehydrogenation of this mixture over a 10% Pd/C catalyst in refluxing triglyme (30 min) furnished **28** (58% based on the ketone), mp 172.5–173.5 °C (hexane) (lit.[26] mp 172.4–172.9 °C): IR (KBr) 1400, 765, 751 cm^{-1}; NMR δ 8.66 (d, 1, H_{10}, J = 8.06 Hz), 8.49 (d, 1, H_9, J = 8.83 Hz), 8.04 (d, 1, Ar, J = 7.52 Hz), 8.01 (d, 1, Ar, J = 8.48 Hz), 7.97 (s, 1 H_5), 7.92 (t, 1, Ar), 7.2–7.8 (m, 4, Ar), 4.40 (s, 2, CH_2); UV λ_{max} (EtOH) 326 (ϵ 12600), 312 (10900), 300 (11800), 269 (87300), 217 (28000).

Acknowledgment. This research was supported by grants from the National Institute of Environmental Health Sciences (ES 04266) and the National Cancer Institute (CA 36097 and CA 14599).

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Methylenomycin B: New Syntheses Based on β- and γ-Keto Phosphonates and γ-Keto Phosphine Oxides†

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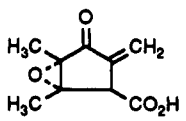
Received April 17, 1990

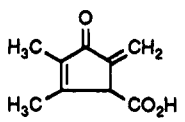
Methylenomycin B has been synthesized from diethyl 2-oxobutanephosphonate (**4**) in three steps in 39% overall yield. Starting from diethyl 3-oxobutanephosphonate (**10**) and diphenyl(3-oxobutyl)phosphine oxide (**13**), methylenomycin B has been obtained in 34% and 27% overall yield, respectively. A characteristic feature of these syntheses of methylenomycin B is that the *exo*-methylene function is introduced via the Horner–Wittig reaction of formaldehyde (36% aqueous solution) with the corresponding α-phosphorylcyclopentenones **6** and **20**. The latter were obtained from phosphorylated 1,4-diketones by intramolecular base-catalyzed cyclization. A brief discussion of some mechanistic aspects of the Conant reaction is also given.

Introduction

Methylenomycin A (**1**), desepoxy-4,5-didehydromethylenomycin A (**2**), and methylenomycin B (**3**) have recently been isolated[1] from the culture broth of *Streptomyces* species and belong to a family of cyclopentanoid antibiotics.[2]



1



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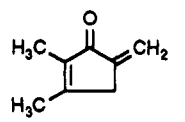

3

Although the structure of methylenomycin B is deceptively simple, its synthesis is not trivial. Due to the presence of the two α,β-unsaturated ketone moieties, methylenomycin B is an unstable compound that undergoes easy decomposition under acidic or basic conditions. Since the first total synthesis,[3] which led to the revision of the original structure proposed by Haneishi et al.,[1] methylenomycin B has attracted considerable attention of many research groups as a synthetic target.[4]

In the course of our studies on the application of organic phosphorus and sulfur compounds for the synthesis of 1,4-dicarbonyl compounds and functionalized cyclo-

† Dedicated to the memory of the late David Ginsburg.

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0022-3263/91/1956-1217$02.50/0 © 1991 American Chemical Society