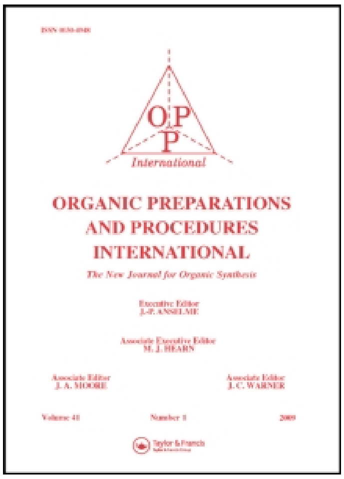

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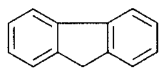
INTRODUCTION

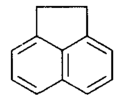
Polycyclic aromatic hydrocarbons (PAHs), more succintly termed *polyarenes*, are one of the largest classes of naturally occuring organic molecules.[1,2] They are major components of coal tars and petroleum residues and large amounts are generated from forest fires, volcanic activity and other natural sources.[3] Polyarenes have also been identified as major components of interstellar matter through their characteristic infrared emissions.[4] Indeed, it is estimated that benzenoid hydrocarbons are more abundant in interstellar space than all other known polyatomic molecules.[5] Substantial amounts of PAHs are produced in the combustion of fossil fuels and other organic matter, e.g. by coal and wood burning, internal combustion engines and heat and power generation and significant levels are present in tobacco smoke.[6,7] As a consequence, polyarenes are widespread environmental contaminants. Since some PAHs are potent carcinogens, these facts have important implications for cancer in human populations.

The patterns of polyarenes produced by pyrolysis are dependent on temperature.[8] At elevated temperatures, as in the coking of coal, the less stable alkyl bonds are cleaved affording relatively simple mixtures of unsubstituted PAHs. At intermediate temperatures, as in the smoldering of wood, complex mixtures of unsubstituted and alkylsubstituted polyarenes are formed. At lower temperatures, fragmentation of carbon-carbon bonds is less favorable and aromatization proceeds slowly. Crude petroleum formed by decay of plants over millions of years contains relatively high ratios of alkyl-substituted and bridged polyarenes.

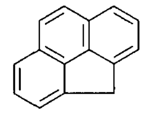
Bridged polyarenes are distinguished by the presence of a partially saturated ring with a methylene or ethylene bridge in the molecule. In most cases, the ring containing the bridge is in a five-membered ring. PAHs of this class may be regarded as higher polycyclic derivatives of fluorene, acenaphthylene and methylene-bridged polyarenes, such as 4*H*-cyclopenta[*def*]phenanthrene. Polyarenes with only six-membered rings that contain a methylene bridge are typified by 7*H*-benzanthrene and 6*H*-benzo[*cd*]pyrene which may be regarded as derivatives of phenalene. Bridged PAHs are classified as nonalternant because they contain an odd carbon atom which prevents their representation by a Kekule´ structure having only benzenoid rings. Although these molecules are generally represented by molecular formulae in which the odd carbon atom is in a saturated ring, multiple



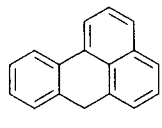
fluorene



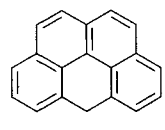
acenaphthylene



4*H*-cyclopenta[*def*]-phenanthrene



7*H*-benzanthrene



6*H*-benzo[*cd*]pyrene

isomeric structures in which the saturated position is located at alternative sites in the molecule are also conceivable.

A resurgence of interest in the chemistry of bridged PAHs has been stimulated by recent advances in several areas. These include development of flash vacuum pyrolysis as a practical synthetic route to strained nonplanar polyarenes (e.g. cyclopenta-fused PAHs[9,10] and fullerene-related PAHs),[11] identification of bridged hydrocarbons as products of incomplete combustion of fossil fuels as well as widespread environmental pollutants,[12] and the finding that some bridged PAHs, e.g. cyclopenta[*cd*]pyrene and cyclopenta[*def*]chrysene, exhibit significant activity as mutagens and carcinogens.[13-15] It has been postulated that methylene-bridged polyarenes may undergo metabolic activation by a novel pathway that involves formation of a bridge carbocation intermediate capable of directly alkylating DNA in addition to the diol epoxide pathway for other PAH carcinogens.[2,16]

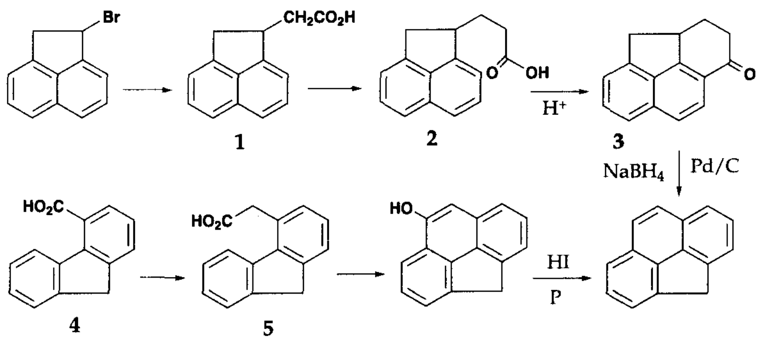
Methods for the synthesis of bridged PAHs will be reviewed with emphasis on newer methods developed since 1980. This topic has not been reviewed previously. Methods for the synthesis of bridged PAHs may be subdivided into two basic types, those based on starting compounds with a preformed bridge and those which introduce the bridge at a later stage in the synthesis. Each of these approaches has its advantages and disadvantages.

The IUPAC system of nomenclature for polycyclic aromatic hydrocarbons[17,18] is used throughout this review. The IUPAC system is employed in Chemical Abstracts and the IUPAC rules (1979) have been adopted by all major chemical societies. However, obsolete systems of naming and numbering PAHs are sometimes encountered in the literature, resulting in considerable confusion. For a relatively concise and readable introduction to the rules of PAH nomenclature, the reader is referred to the book "Polycyclic Aromatic Hydrocarbons: Chemistry and Carcinogenicity" by Harvey.[2] A more detailed version may be found in the recent book "Polycyclic Aromatic Hydrocarbons" by the same author.[1]

I. METHYLENE-BRIDGED PAHS

a) *4H-Cyclopenta[def]phenanthrene*

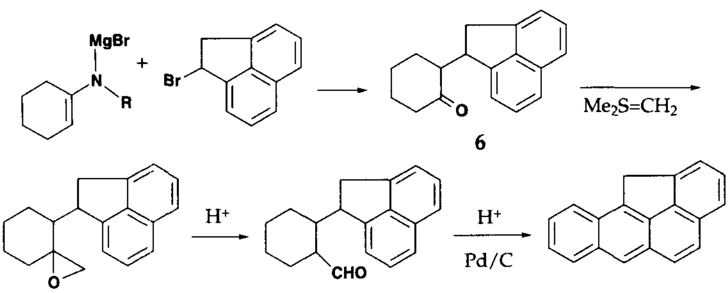
Syntheses based on the three structural components acenaphthylene, phenanthrene and fluorene have been described. For large scale preparation, the most useful method entails reaction of 1-bromoacenaphthene with the sodium salt of malonic ester followed by hydrolysis and decarboxylation to form 1-(acenaphthenyl)acetic acid (**1**).[19] This acid is converted to the corresponding propionic acid (**2**) by standard methods. Cyclo-dehydration of **2** in liquid HF furnishes the cyclized ketone **3** which is transformed to 4*H*-cyclopenta[*def*]phenanthrene by reduction with $NaBH_4$ and dehydrogenation over a palladium catalyst.



Another less practical synthesis is based on fluorene-4-carboxylic acid (**4**) which is transformed to the related acetic acid derivative (**5**) by a standard methods.[20] Cyclization of the acid chloride of **5** in the presence of $AlCl_3$ gives 8-hydroxy-4*H*-cyclopenta[*def*]phenanthrene which is reduced by HI/P to 4*H*-cyclopenta[*def*]phenanthrene. Additional syntheses which provide lower overall yields are described in the older literature.[21-23]

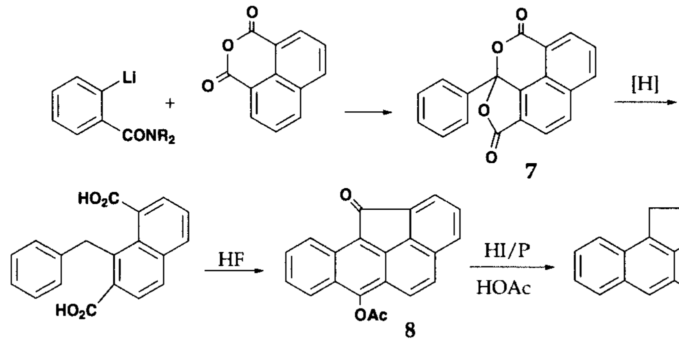
b) *11H-Benz[bc]aceanthrylene*

The most efficient synthesis involves in the key step reaction of 1-bromoacenaphthene with the bromomagnesium derivative of the imine of cyclohexanone to furnish the ketone **6**.[24] Reaction of **6** with dimethylsulfonium methylide affords an epoxide which rearranges in acid to the corresponding

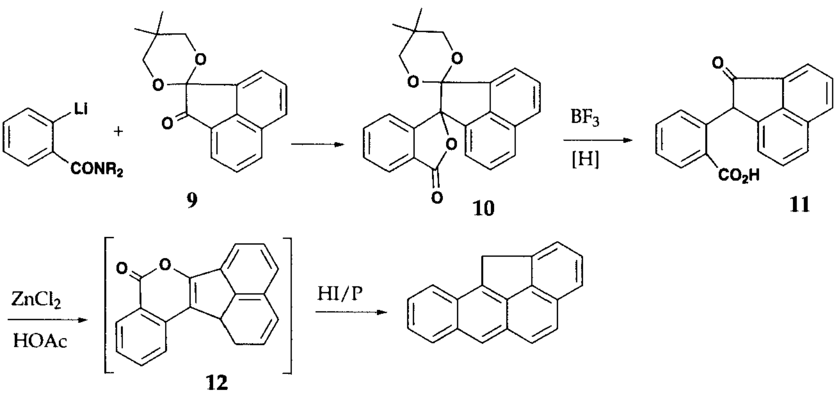


aldehyde. Acid-catalyzed cyclization followed by dehydrogenation provides 11*H*-benz[*bc*]aceanthrylene. Another new synthesis involves reaction of 1,8-naphthalic anhydride with *o*-lithio-*N,N*-diethylbenzamide to form a *bis*-lactone (**7**).[25] Reduction of **7** gives a dicarboxylic acid which undergoes double Friedel-Crafts cyclization and acetylation to provide the 11-keto-6-phenol of 11*H*-benz[*bc*]aceanthrylene (**8**). Reduction of **8** by HI/P in acetic acid gives 11*H*-benz[*bc*]aceanthrylene.

An alternative synthetic route is based on condensation of the monoketal of acenaphthylenedione (**9**) with the diethyl 2-lithio-benzamide.[26] Treatment of the lactone product (**10**) with BF_3

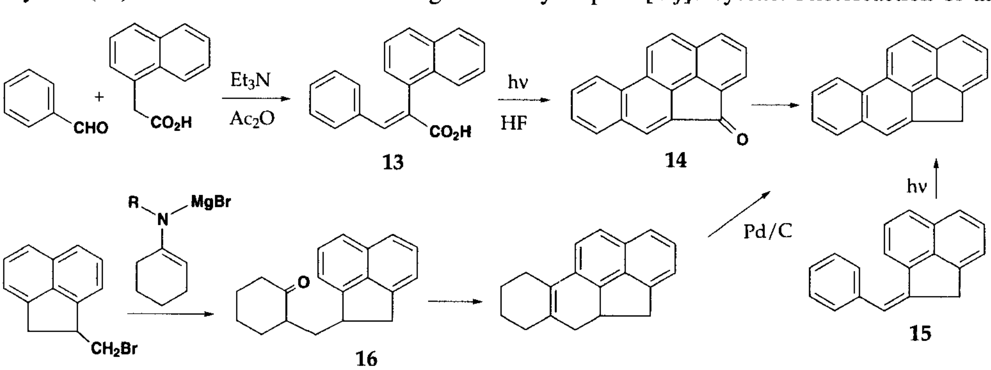


etherate followed by reduction with zinc and alkali gives the keto acid **11**. Friedel-Crafts reaction of **11** with $ZnCl_2$ in Ac_2O-AcOH affords the α-pyrone **12** rather than the expected keto-phenol **8**.[25] Reduction of **12** with HI/P gives 11*H*-benz[*bc*]aceanthrylene. A less efficient synthesis of 11*H*-benz[*bc*]aceanthrylene has also been described.[27]



c) *4H-Cyclopenta[def]chrysene*

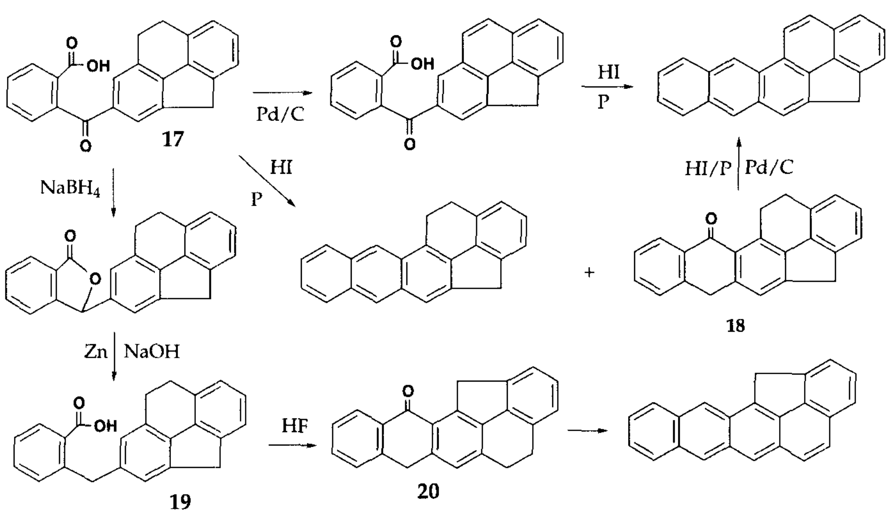
This hydrocarbon is accessible on small scale by photocyclization of a stilbene precursor (**13**) obtained from base-catalyzed condensation of benzaldehyde with 2-naphthylacetic ester.[28] The photocyclized product undergoes cyclodehydration in liquid HF to provide 4-keto-cyclopenta[*def*]-chrysene (**14**). Reduction of **14** with HI/P gives 4*H*-cyclo-penta[*def*]chrysene. Photoreaction of the



stilbene compound **15** with a preformed five-membered ring also provides 4*H*-cyclopenta[*def*]chrysene, but in lower yield.[29] Larger scale preparations are most efficiently conducted by the enamine alkylation method. Reaction of 1-bromomethylacenaphthene with the bromomagnesium salt of an enamine yields the ketone **16**.[30] Acid-catalyzed cyclization of **16** and catalytic dehydrogenation affords 4*H*-cyclopenta[*def*]chrysene. These newer methods are superior to the classic Friedel-Crafts succinoylation of 4*H*-cyclopenta[*def*]phenanthrene.[27]

d) 4H-Benzo[b]cyclopenta[mno]chrysene and 13H-indeno[2,1,7-qra]naphthacene

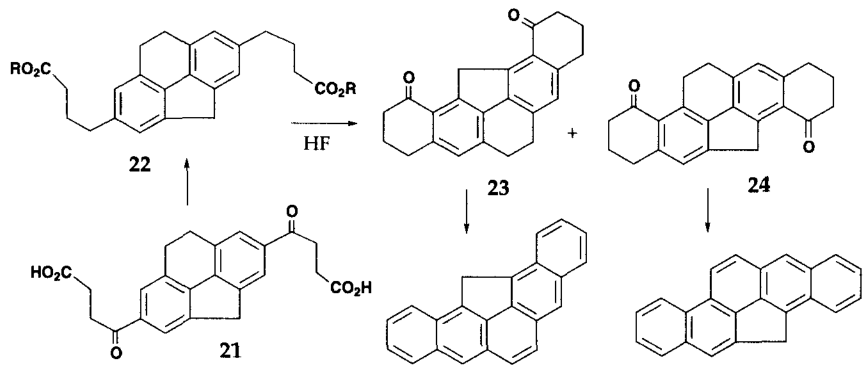
Friedel-Crafts reaction of 8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene with phthalic anhydride and $AlCl_3$ takes place selectively in the 2-position to furnish keto-acid **17**.[16] Dehydrogenation of **17** and reductive cyclization of the product with HI/P yields 4*H*-benzo[*b*]cyclopenta[*mno*]chrysene. Reduction of **17** with HI/P yields a mixture of 12,13-dihydro-4*H*-benzo[*b*]cyclopenta[*mno*]chrysene and the related ketone, 6,11,12,13-tetrahydro-4*H*-benzo[*b*]cyclopenta[*mno*]chrysen-11-one (**18**). A

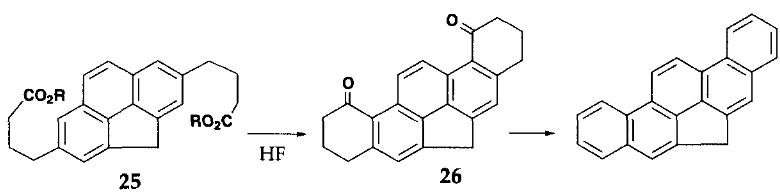


higher overall yield of 4*H*-benzo[*b*]cyclopenta[*mno*]chrysene is obtained by heating this mixture with 10% Pd/C followed by a second treatment with HI/P. 13*H*-Indeno[2,1,7-*qra*]naphthacene is obtained by a modification of this approach. Reduction of the keto-acid **17** followed by cyclization of the carboxylic acid product (**19**) in liquid HF provides ketone **20**. Reduction of **20** with zinc and alkali followed by dehydrogenation over a Pd/C catalyst affords 13*H*-indeno[2,1,7-*qra*]naphthacene.

e) 13H-Cyclopenta[rst]pentaphene, 12H-benzo[b]cyclopenta[def]chrysene and 6H-cyclopenta[ghi]picene

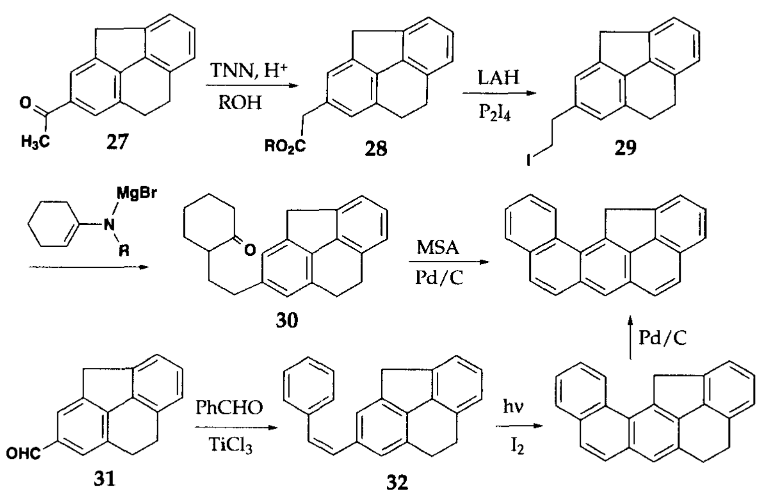
These three bridged PAHs are synthetically accessible *via* double Friedel-Crafts succinoylation of 8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene.[30] Substitution takes place regioselectively in the 2,6-positions to furnish the diketodibasic acid (**21**). Wolff-Kishner reduction of **21** provides the dicarboxylic acid **22** which cyclizes in liquid HF to yield a 3:1 mixture of diketones **23** and **24**. Reduction of **23** with $NaBH_4$ gives a diol which is converted to 13*H*-cyclopenta[*rst*]pentaphene by heating over a palladium catalyst. Similar treatment of **24** yields 12*H*-benzo[*b*]cyclopenta[*def*]chrysene. Cyclization of the aromatic diacid **25** takes place preferentially to the 1,7-positions to furnish diketone **26** which is readily transformed to 6*H*-cyclopenta[*ghi*]picene.





f) *13H-Dibenz[bc,l]aceanthrylene*

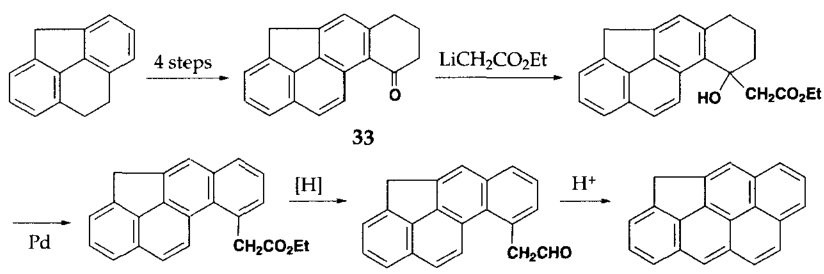
Acetylation of 8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene with Ac_2O and $AlCl_3$ at 0° C in nitrobenzene affords the 2-acetyl derivative (**27**) regiospecifically.[30] Treatment of **27** with thallium trinitrate and $HClO_4$ in MeOH provides the rearranged methyl acetate ester derivative (**28**). Reduction of **28** with $LiAlH_4$ and treatment of the alcohol product with P_2I_4 yields the 2-iodomethyl derivative (**29**). Reaction of **29** with the bromomagnesium salt of *N*-cyclohexenylcyclohexanimine furnishes the



alkylated ketone (**30**) which cyclizes regiospecifically in methanesulfonic acid to the 2-position. Dehydrogenation provides 13*H*-dibenz[*bc,l*]aceanthrylene in good overall yield. An alternative synthetic route which requires fewer steps affords a lower overall yield.[30] The 2-formyl derivative of 8,9-dihydro-4*H*-cyclopenta[*def*]phenanthrene (**31**) couples with benzaldehyde in the presence of $TiCl_3$ to provide the olefin **32**. Oxidative photocyclization of **32** gives a mixture of products which on dehydrogenation furnishes 13*H*-dibenz[*bc,l*]aceanthrylene.

g) *4H-Benzo[def]cyclopenta[mno]chrysene*

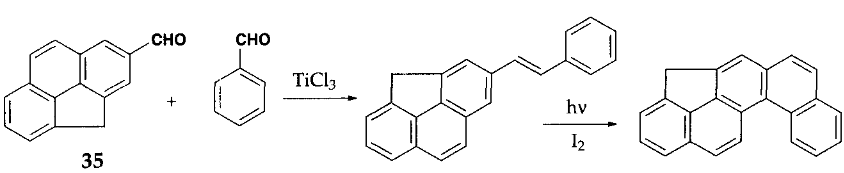
8,9-Dihydro-4*H*-cyclopenta[*def*]phenanthrene, employed in several preceding syntheses, is also the starting compound for this preparation.[31] It is transformed to a keto derivative of 6,7,8,9-tetrahydrocyclopenta[*def*]chrysene (**33**) by the standard four step sequence of Friedel-Crafts succinoylation, Wolff-Kishner reduction, dehydrogenation and HF cyclodehydration. Reaction of **33** with ethyl α-lithioacetate followed by dehydration and dehydrogenation of the adduct affords the ester **34**. This is converted to 4*H*-benzo[*def*]cyclopenta[*mno*]chrysene by reduction with *i*-Bu_2AlH and cyclization of the resulting aldehyde in $MeSO_3H$.



33
34

h) *4H-Benzo[c]cyclopenta[mno]chrysene*

Despite failure of initial attempts,[16] synthesis of this hydrocarbon was accomplished by a photochemical method similar to that used to prepare 13*H*-dibenz[*bc,l*]aceanthrylene.[32] The starting compound, 2-formyl-4*H*-cyclopenta[*def*]phenanthrene (**35**) was prepared from its 8,9-dihydro derivative (**31**) by dehydrogenation with DDQ, then coupled with benzaldehyde and $TiCl_3$. The product (**36**) was also prepared by Wittig reaction of **35** with benzyltriphenylphosphonium chloride. Oxidative photocyclization of **36** occurs regiospecifically in the 1-position to yield 4*H*-benzo[*c*]-cyclopenta[*mno*]chrysene.



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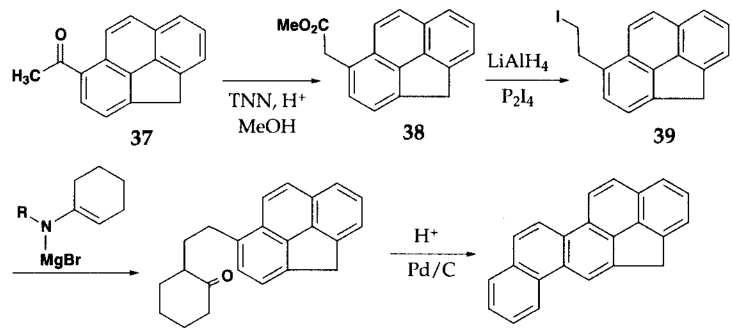
i) *4H-Cyclopenta[pqr]picene*

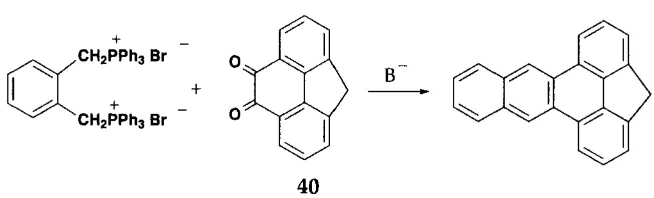
Synthesis is accomplished *via* a route analogous to that for the preparation of 13*H*-dibenz-[*bc,l*]aceanthrylene.[16] The starting compound, 1-acetyl-4*H*-cyclopenta[*def*]phenanthrene (**37**), is obtained from acetylation of 4*H*-cyclopenta[*def*]phenanthrene at -78°. A mixture of the 1-acetyl isomer (88%) and the 3-acetyl isomer (12%) are obtained. On treatment with thallium trinitrate and $HClO_4$ in methanol, **37** rearranges to the methyl acetate ester **38**. Reduction of **38** with $LiAlH_4$



followed by reaction of the resulting alcohol with P_2I_4 provides the 2-iodomethyl derivative (**39**). Reaction of **39** with the bromomagnesium salt of the enamine of cyclohexanone gives the expected alkylated ketone derivative which is transformed to 4*H*-cyclopenta[*pqr*]picene by cyclization in $MeSO_3H$ followed by catalytic dehydrogenation.

j) *4H-Benzo[b]cyclopenta[jkl]triphenylene*

bis-Wittig reaction of 4*H*-cyclopenta[*def*]phenanthrene-8,9-dione (**40**) with the *bis*(triph-enylphosphonium) salt of *o*-xylylene affords this hydrocarbon directly.[16] Sonication decreases reaction time from 72 hours to 4 hours with an increase in yield from 55% to 65%.[33] The quinone precursor is obtained from 4*H*-cyclopenta[*def*]phenanthrene by reaction with OsO_4 followed by oxidation of the dihydrodiol product with DDQ.[16]



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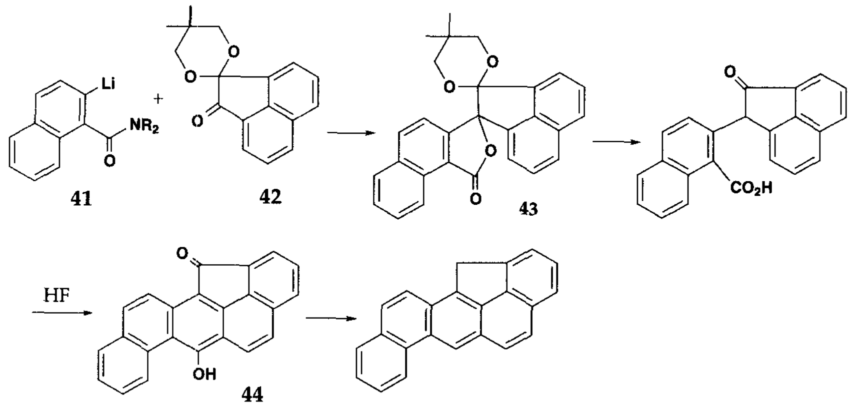
k) *13H-Dibenz[bc,j]aceanthrylene*

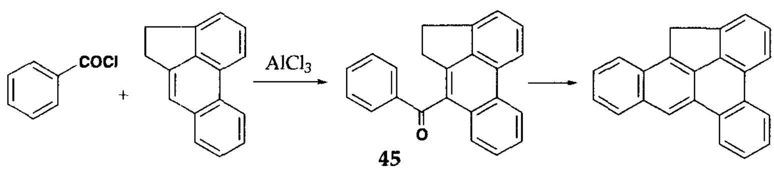
A practical synthesis is based on the monoketal of acenaphthylene (**42**).[34] Reaction of **42** with 2-lithio-*N,N*-diethyl-1-naphthamide (**41**) affords the expected keto lactone (**43**) in excellent yield. Direct reaction of **41** with 1(2*H*)-acenaphthylenone fails to provide a related lactone product due to the facility of competing enolization. Reduction of **43** with zinc and alkali gives a keto acid which



cyclizes in liquid HF to a phenolic ketone (**44**). Reduction of **44** with HI/P affords 13*H*-dibenz[*bc,j*]-aceanthrylene. Less practical multistep syntheses are described in the older literature.[35,36]

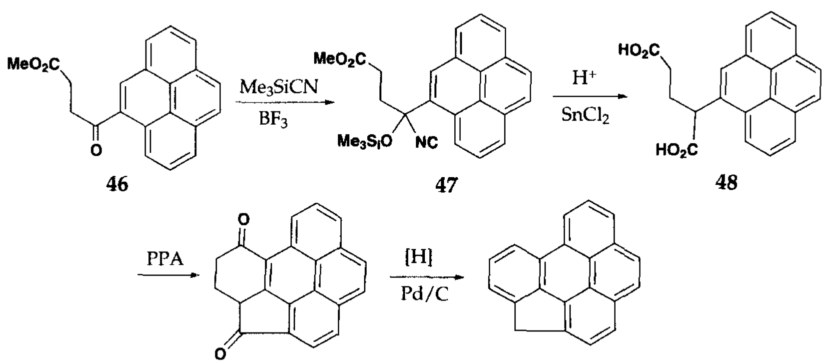
l) *13H-Benzo[b]cyclopenta[def]triphenylene*

Friedel-Crafts benzoylation of acephenanthrylene takes place regioselectively in the 6-position to furnish the ketone **45**. Elbs pyrolysis of **45** gives 13*H*-benzo[*b*]cyclopenta[*def*]triphenylene in modest yield.[37]



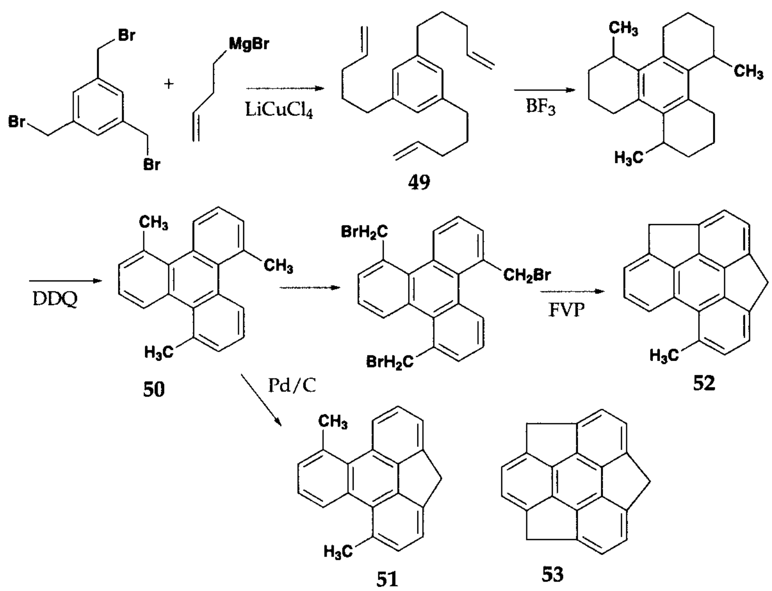
m) *3H-Indeno[2,1,7-cde]pyrene*

Synthesis is based on methyl γ-oxo-4-pyrenylbutanoate (**46**) obtained from Friedel-Crafts succinoylation of 1,2,3,6,7,8-hexahydropyrene followed by esterification and aromatization with DDQ.[31] Reaction of **46** with Me_3SiCN and BF_3 etherate gives a trimethylsilyl cyanohydrin derivative (**47**) which undergoes reductive hydrolysis by $SnCl_2$ and HCl in HOAc to furnish the diacid **48**. Treatment of **48** with PPA yields a cyclized diketone product which is converted to 3*H*-indeno[2,1,7-*cde*]pyrene by Wolff-Kishner reduction and catalytic dehydrogenation.



n) *3H,10H-Dicyclopenta[def,jkl]triphenylene*

The 6-methyl derivative (**52**) is the only derivative whose synthesis has been reported.[38] It is of special interest as a potential precursor of the nonplanar hydrocarbon, tricyclopenta[*def,jkl,pqr*]triphenylene (**53**), a structural component of buckminsterfullerene. The key intermediate in its synthesis is 1,3,5-tripentenylbenzene (**49**) obtained from cross-coupling between 1,3,5-tris(bromo-methyl)-benzene and the Grignard reagent of 4-bromobut-1-ene catalysed by dilithium tetrachlorocuprate. Compound **49** cyclizes on exposure to gaseous BF_3 to give a triphenylene derivative which is converted to 1,5,9-trimethyltriphenylene (**50**) by dehydrogenation with DDQ. Cyclodehydrogenation of **50** by heating over a Pd/C catalyst gives mainly a monobridged product (**51**). Flash vacuum pyrolysis of 1,5,9-tris(bromomethyl)triphenylene at 850° gives (**52**) (18%) and a small amount of **51**.

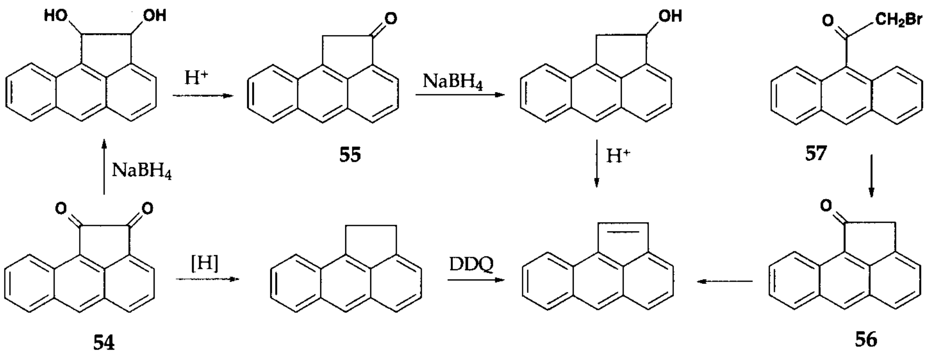


II. ACENAPHTHENES

Hydrocarbons in this series are distinguished by an ethylene bridge between adjacent aromatic rings. They may be regarded as polycyclic analogs of the prototype hydrocarbon acenapthene, the dihydro derivative of acenaphthylene. The acenaphthenes are also often referred to as cyclopenta-fused PAHs. The unique aspect of their chemistry is their potential conversion to fully unsaturated derivatives in which the bridge bond has olefin-like properties.

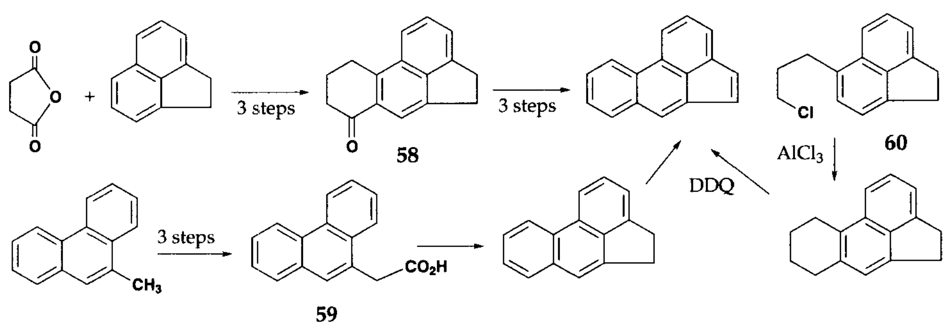
a) *Aceanthrene*

Although synthesis of aceanthrene was first reported in 1932,[39] and an improved method was described in 1958,[40] synthesis of aceanthrylene was not achieved until 1984.[41] Friedel-Crafts reaction of anthracene with oxalyl chloride and $AlCl_3$ furnishes aceanthrylene-1,2-dione (**54**). Reduction of **54** with $NaBH_4$ gives the 1,2-dihydrodiol which is converted to aceanthrylene *via* dehydration to 2-aceanthrenone (**55**), reduction with $NaBH_4$ and a second dehydration.[41,42] It was shown subsequently that **54** may be reduced to aceanthrene by the Wolff-Kishner method and converted to aceanthrylene by dehydrogenation with DDQ.[43] Another synthesis based on anthracene entails acylation with chloroacetyl chloride and $AlCl_3$ to give 1-aceanthrenone (**56**) which is converted to aceanthrylene by reduction with $NaBH_4$ and dehydration.[42] Acetylation of anthracene followed by bromination provides α-bromo-9-acetylanthracene (**57**) which cyclizes to **56** on treatment with $AlCl_3$.[44] Several additional syntheses have also been reported that are of less practical utility because of the large numbers of steps that are involved.[45-47]

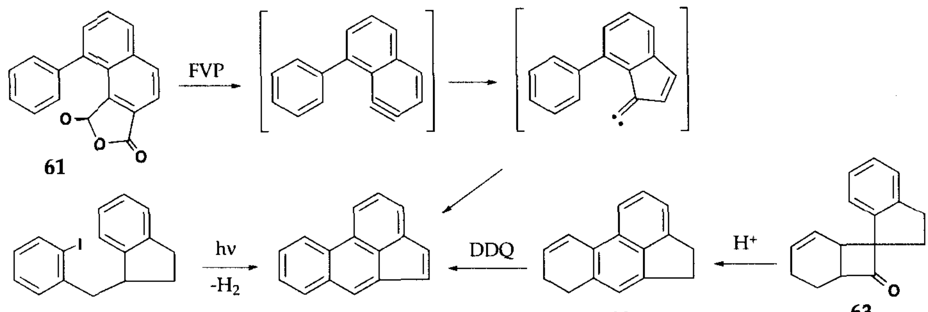


b) *Acephenanthrylene*

Annelation of acenaphthene by the standard Haworth method by reaction with succinic anhydride and $AlCl_3$ followed by reduction and acid-catalyzed cyclization affords hexahydroacephenanthrylene-7-one (**58**).[48,49] This is converted to acephenanthrylene by reduction with $NaBH_4$, acidic dehydration and DDQ dehydrogenation. This hydrocarbon is also accessible from 9-methylphenanthrene by conversion into 2-(9-phenanthryl)acetic acid (**59**) *via* bromination, reaction with KCN and hydrolysis.[50] $AlCl_3$-catalyzed cyclization of **59** followed by reduction and dehydration gives acephenanthrylene. Another route is *via* reductive alkylation of acenaphthene with lithium and 1,4-dichlorobutane in liquid ammonia which gives **60** as the major product;[51] cyclization of **60** with $AlCl_3$ and dehydrogenation with DDQ yields acephenanthrylene.



Another new synthetic approach is flash vacuum pyrolysis of 8-phenylnaphthalene-1,2-dicarboxylic anhydride (**61**) which gives a mixture of acephenanthrylene (85%) and fluoranthene (10%).[52] The mechanism involves formation of 8-phenyl-1,2-naphthyne which undergoes ring contraction to give a carbene which inserts into a C-H bond of the adjacent phenyl ring to yield acephenanthrylene.[53] This hydrocarbon is also obtained from photocyclization of 1-(*o*-iodobenzylidene)indane (**62**) followed by dehydrogenation[54] and from acidic rearrangement and dehydration of the ketone **63** to **64** followed by dehydrogenation with DDQ.[46]

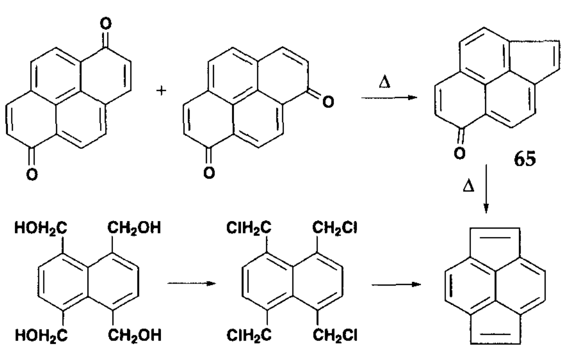


61 **62** **64** **63**

c) *Cyclopent[f,g]acenaphthylene (pyracylene)*

This hydrocarbon is of considerable theoretical interest because of its anticipated internal molecular strain. Initial attempts to synthesize it met with failure, consisent with expectation that it was an unstable "antiaromatic" molecule with a planar 12 π-electron periphery. Trost and coworkers, who reported the first synthesis, stated that its half-life was on the order of one minute,[55] consistent with its exceptionally low calculated resonance energy.[56] On the other hand, this conflicted with numerous reports that pyracylene is a major component of soot[57] and present in the harsh environment of interstellar clouds.[58] These discrepancies were resolved by Freiermuth *et al.*[59] who showed that after careful purification, pyracylene can be crystallized, stored for prolonged periods and even sublimed. The reported instability was ascribed to the presence of reactive impurities. X-ray analysis of pyracylene reveals it to be essentially planar with pronounced alternation of bond lengths.

The most direct synthesis of pyracylene is by flash vacuum pyrolysis of the mixture of quinones obtained from dichromate oxidation of pyrene (mainly the 1,6- and 3,6-diones).[59-61] The primary product is 5*H*-cyclopenta[*cd*]phenalen-5-one (**65**), formed by elimination of one molecule of



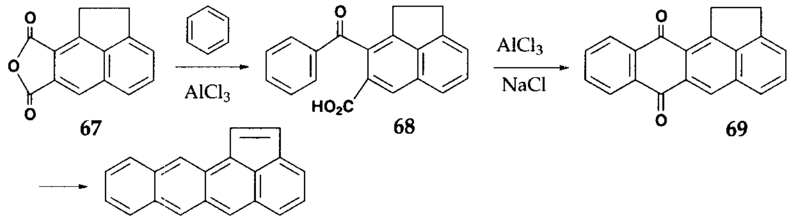
65

66

CO. Pyracylene is also obtained from reaction of PCl_3 with 1,4,7,8-tetrakis(hydroxymethyl)naphthalene to form 1,4,7,8-tetrakis(chloromethyl)naphthalene (**66**) followed by pyrolysis.[62]

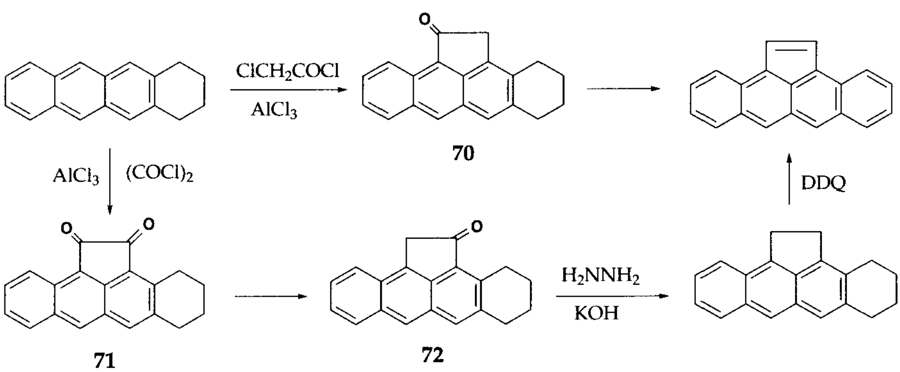
d) *Cyclopenta[de]naphthacene*

Friedel-Crafts reaction between benzene and acenaphthene-3,4-carboxylic anhydride (**67**) furnishes a mixture of isomeric keto acids including **68**.[63] Cyclization of **68** in an $AlCl_3$/NaCl melt provides quinone **69**. Reduction of **69** with zinc and alkali and dehydrogenation of the product with DDQ affords cyclopenta[*de*]naphthacene.



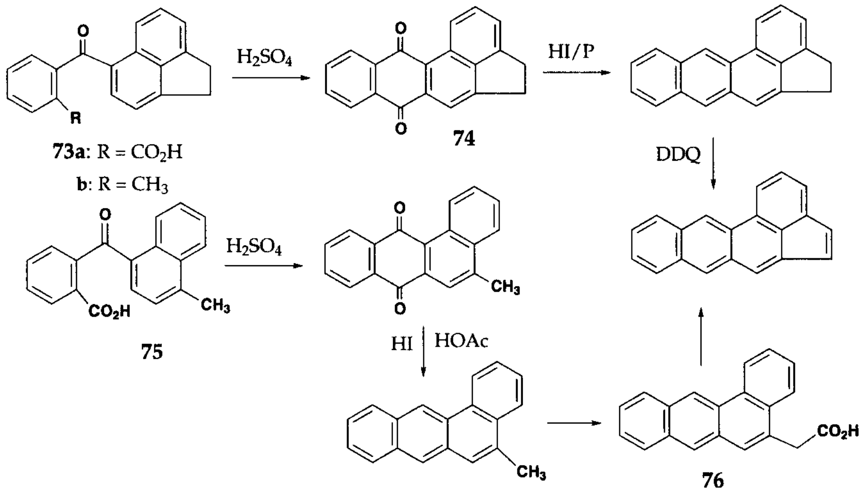
e) *Cyclopenta[fg]naphthacene*

Attempts to synthesize cyclopenta[*fg*]naphthacene by Friedel-Crafts acylation of naphthacene with chloroacetyl chloride or oxalyl chloride met with failure. However, acylation of 1,2,3,4-tetrahydronaphthacene with chloroacetyl chloride and $AlCl_3$ gave the cyclic ketone **70**.[63] Wolff-Kishner reduction of **70** and dehydrogenation of the product with DDQ gave cyclopenta[*fg*]naphthacene in low yield (10 %). Higher yield was obtained by acylation of tetrahydronaphthacene with oxalyl chloride. Reduction of the product (**71**) with $NaBH_4$ and acid-catalyzed dehydration gave ketone **72** which underwent Wolff-Kishner reduction and dehydrogenation with DDQ to furnish cyclopenta[*fg*]naphthacene.



f) *Benz[k]acephenanthrylene*

The most direct synthesis is *via* Friedel-Crafts acylation of acenaphthacene with phthalic anhydride followed by acid-catalyzed cyclization of the keto acid product (**73a**).[64,65] Reduction of the quinone product (**74**) with HI/P provides benz[*k*]acephenanthrene and dehydrogenation with DDQ yields benz[*k*]acephenanthrylene. Benz[*k*]acephenanthrylene is also obtained from Friedel-Crafts reaction of *o*-toluyl chloride with acenaphthacene followed by pyrolysis of the ketone product (**73b**).[66]

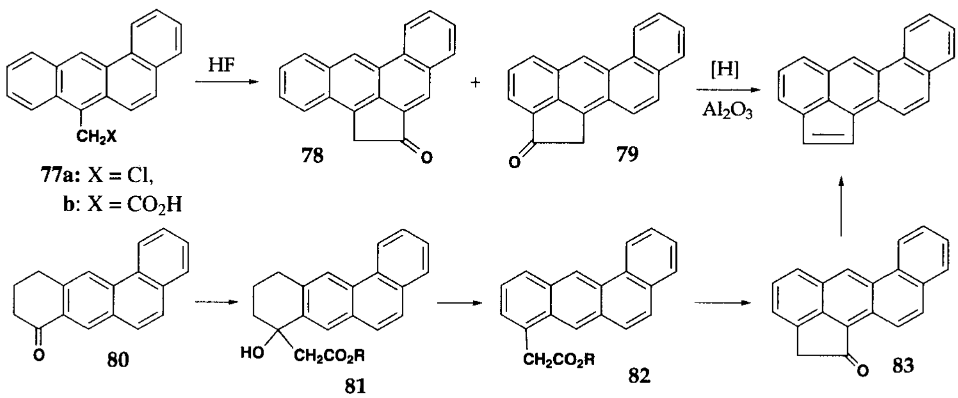


An alternative synthesis is based on 2-(4-methylnaphthoyl)acetic acid (**75**) obtained from reaction of phthalic anhydride with 1-methylnaphthalene.[64] Cyclodehydration of **75** in sulfuric acid affords the corresponding quinone which is reduced with HI and acetic acid to 5-methylbenz[*a*]anthracene.[67,68] This is converted to the acetic acid derivative **76** *via* bromination, reaction with NaCN/NaI and hydrolysis. Cyclodehydration of **76** in liquid HF followed by reduction of the ketone product with $NaBH_4$ and dehydration with alumina affords benz[*k*]acephenanthrylene.

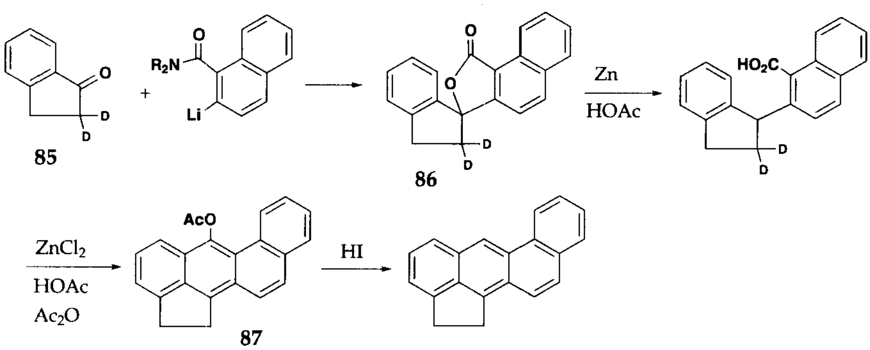
g) *Benz[j]aceanthrylene (cholanthrylene)*

This hydrocarbon is of special interest because of its relation to the potent carcinogen 3-methylbenz[j]aceanthrene, better known as 3-methylcholanthrene. The most convenient synthesis of benz[j]aceanthrylene is from benz[*a*]anthracene by chloromethylation to yield the 7-chloro derivative (**77a**) which is transformed to 7-benz[*a*]anthrylacetic acid (**77b**) by treatment with KCN and basic hydrolysis.[64] Cyclization of **77b** in liquid HF furnishes a 1:3 mixture of ketones **78** and **79**. Reduction of **79** with $NaBH_4$ followed by dehydration over alumina gives benz[*j*]aceanthrylene. An alternative synthesis is based on the ketone **80** obtained from phenanthrene by the Haworth procedure.[64] Reformatski reaction of **80** gives an adduct (**81**) which is converted to ethyl (8-benz[*a*]anthryl)acetate (**82**) by acidic dehydration and dehydrogenation with DDQ. Hydrolysis of **82** followed by cyclization in liquid HF provides the ketone **83** which is transformed to benz[*j*]aceanthrylene by reduction with $NaBH_4$ and acid-catalyzed dehydration.

Benz[*j*]aceanthrene, the saturated derivative of benz[*j*]aceanthrylene and its 3-methyl-, 6-methyl- and 3,6-dimethyl- derivatives are potent carcinogens.[1] These compounds are synthetically accessible by condensation of appropriately substituted derivatives of 2,2-dideuterioindan-1-one (**85**) and 2-lithio-*N,N*-diethyl-1-naphthamide in ether at -78°.[69] The dideuterio analogue is used to

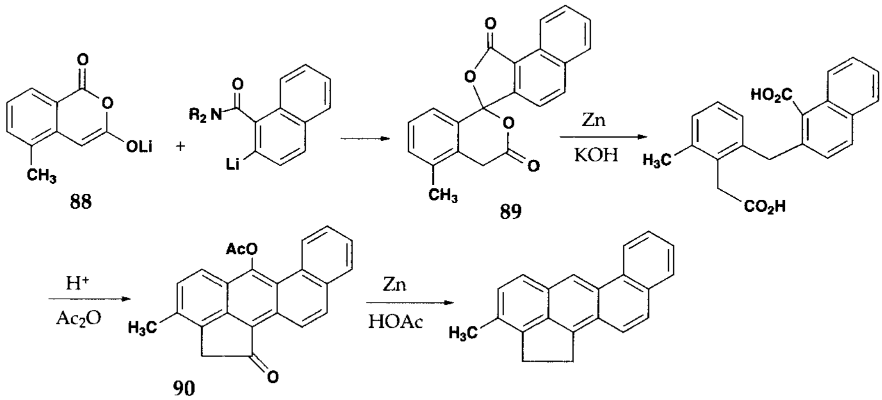


minimize enolization of the carbonyl function. Reduction of the lactone product (**86**) gives the corresponding carboxylic acid which cyclizes smoothly on treatment with $ZnCl_2$ in AcO_2)/AcOH to yield



6-acetoxybenz[*j*]aceanthrene (**87**). Reduction of **87** with HI in HOAc affords benz[*j*]aceanthrene. Short reaction time (1-2 min) is necessary to minimize overreduction. Deuterium is lost by acid-catalyzed exchange in the latter steps.

Another new synthesis of 3-methylcholanthrene entails reaction of 2-lithio-*N,N*-diethyl-1-naphthamide with the lithium enolate of 5-methylhomophthalic anhydride (**88**) followed by acidic

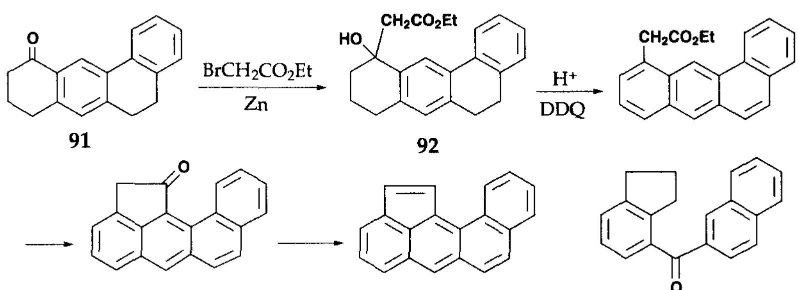


hydrolysis to furnish the spirobislactone (**89**).[70] Reduction of **89** with Zn/KOH followed by cyclization of the dicarboxylic acid product in polyphosphoric acid and acetylation provides 3-methyl-6-acetoxybenz[*j*]aceanthrene-1-one (**90**). Deoxygenation of **90** by treatment with zinc in HOAc gives 3-methylcholanthrene.

Benz[*j*]aceanthrylene-1,2-dione and benz[*e*]aceanthrylene-5,6-dione are obtained in 2:3 ratio in moderate yield from Friedel-Crafts reaction of oxalyl chloride with benz[*a*]anthracene.[71] However, attempts to separate the isomers were not successful.

h) *Benz[l]aceanthrylene*

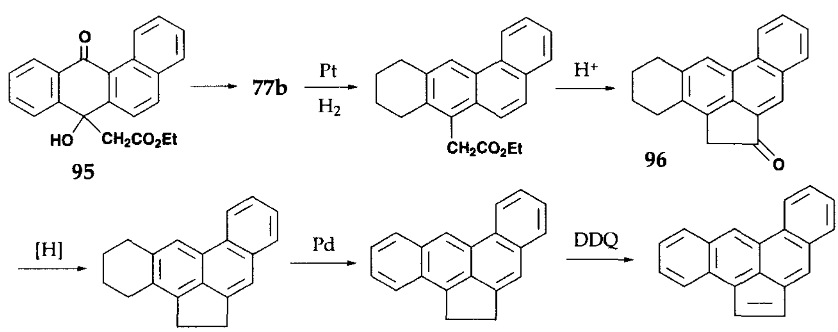
The newest synthesis is based on the ketone **91** obtained from Haworth synthesis with 9,10-dihydrophenanthrene.[64] Reformatsky reaction of **91** affords hydroxy ester **92** which is dehydrated to a mixture of exo- and endo-olefins. Aromatization of the mixture with DDQ followed by hydrolysis provides (11-benzanthryl)acetic acid which cyclizes in liquid HF to furnish ketone **93**. Reduction of **93** with $NaBH_4$ and acid-catalyzed dehydration provides benz[*l*]aceanthrylene. The overall yield is superior to Fieser's classic synthesis which entails in the key step Elbs pyrolysis of ketone **94**.[72,73]



91 92 93 94

i) *Benz[e]aceanthrylene*

The newest synthesis is based on Reformatski reaction of benz[*a*]anthracene-7,12-dione which takes place regiospecifically on the less hindered carbonyl group to afford adduct **95**.[74] Reduction with $NaBH_4$ and deoxygenation with $SnCl_2$ and HCl gives 7-benz[*a*]anthrylacetic acid (**77b**). In order to block subsequent cyclization to the terminal ring, **77b** is hydrogenated over a platinum

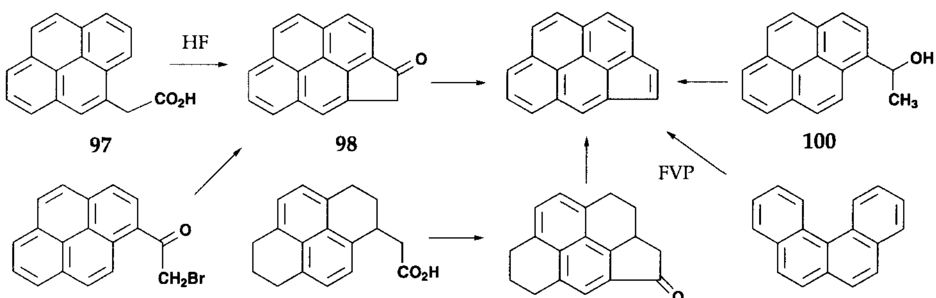


95 96

catalyst regiospecifically in this ring. Acid-catalyzed cyclodehydration of the tetrahydro acid provides ketone **96**. Wolff-Kishner reduction and catalytic dehydrogenation of **96** yields benz[*e*]aceanthrene which on treatment with DDQ affords benz[*e*]aceanthrylene. Benz[*e*]aceanthrylene is also obtained from reduction of ketone **78** with $NaBH_4$ and dehydration.[64]

j) *Cyclopenta[c,d]pyrene*

This hydrocarbon is a widespread environmental pollutant and a potent mutagen. 4-Pyrenylacetic acid (**97**) is a key intermediate in several syntheses. Cyclodehydration of **97** in liquid HF furnishes the ketone **98** which is transformed to cyclopenta[*c,d*]pyrene by reduction with $NaBH_4$ and dehydration.[75] Various modifications which differ mainly in the mode of synthesis of **97** have been



97 98 100 99

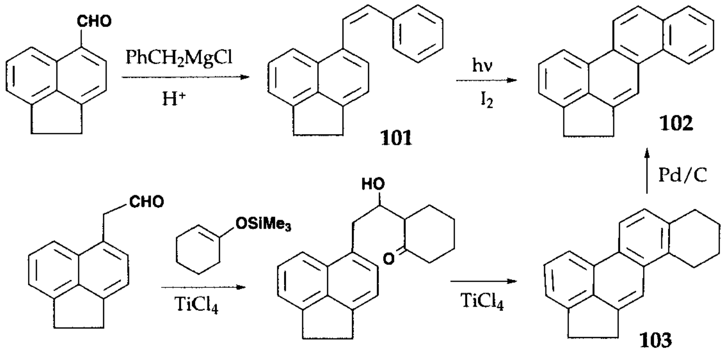
described.[75-78] One route to **97** is from 4-methylpyrene *via* bromination with NBS, conversion to the nitrile by treatment with KCN and hydrolysis.[75] Another is from 4-acetylpyrene by oxidative rearrangement with thallium trinitrate.[77] Although there was a report that this synthesis could not be duplicated,[78] no difficulty was encountered in repeating this procedure in the author's laboratory. On the other hand, the claimed synthesis of **97** by reaction of pyrene dianion in liquid ammonia with one equivalent of sodium iodoacetate and quenching with NH_4Cl and dehydrogenation of the product with DDQ[76] could not be repeated in the author's laboratory (unpublished) or by other investigators.[78]

Although 1-pyrenylacetic acid is a more conveniently accessible potential synthetic precursor of cyclopenta[*c,d*]pyrene, its attempted cyclization failed to afford the cyclized ketone.[79] This is more likely due the greater facility of self-condensation and/or polymerization than the low reactivity of the 4-position, since acid-catalyzed cyclization of the closely related 1-pyrenylcyclohexanone takes place readily in this position.[80] Cyclization of the 1,2,3,6,7,8-hexahydro analog of 1-pyrenylacetic acid (**99**) occurs quantitatively in HF to furnish the corresponding ketone which is transformed to cyclopenta[*c,d*]pyrene by Wolff-Kishner reduction and DDQ dehydrogenation.[81] The acid **99** is prepared from hexahydropyrene by oxidation with CrO_3 in HOAc followed by Wittig reaction with triethylphosphonoacetate, hydrogenation over a platinum catalyst and hydrolysis.

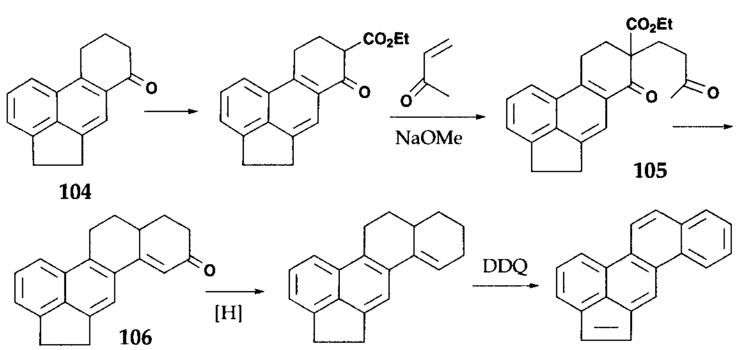
The most convenient method for small scale preparation of cyclopenta[*c,d*]pyrene is from 1-acetylpyrene *via* bromination to form 1-(bromoacetyl)pyrene followed by photocyclization, Wolff-Kishner reduction of the ketone product (**98**) and dehydrogenation with DDQ.[82] Thermolysis of benzo[*c*]phenanthrene at > 1000 C° (0.1-0.5 Torr) affords cyclopenta[*c,d*]pyrene and benzo[*ghi*]fluoranthene as principal products. At higher pressure only carbonaceous product could be recovered. Cyclopenta[*c,d*]pyrene is also obtained in low yield from 1-acetylpyrene by reduction to the alcohol (**100**) and pyrolysis at 850°.[83]

k) *Cyclopenta[hi]chrysene*

Two claimed syntheses of 4,5-dihydrocyclopenta[*hi*]chrysene (**102**) were subsequently found incorrect.[84,85] Synthesis was first successfully achieved *via* a route based on acenaphthene.[86] Formylation gives acenaphthene 5-carboxaldehyde which reacts with benzylmagnesium chloride to yield a carbinol which is dehydrated with acid to yield 5-styrylacenaphthene **101**. Photocyclization of **101** gives 4,5-dihydrocyclopenta[*hi*]chrysene. A more efficient synthesis is *via* aldol-type condensation of 2-(1-naphthyl)acetaldehyde with the cyclohexanone trimethylsilyl enol ether in the presence of 3 equivalents of $TiCl_4$ to provide 4,5,7,8,9,10-hexahydrocyclopenta[*hi*]chrysene (**103**).[87] Dehydrogenation of **103** over a Pd catalyst gives the 4,5-dihydro derivative, while treatment with DDQ in refluxing benzene provides cyclopenta[*hi*]chrysene.

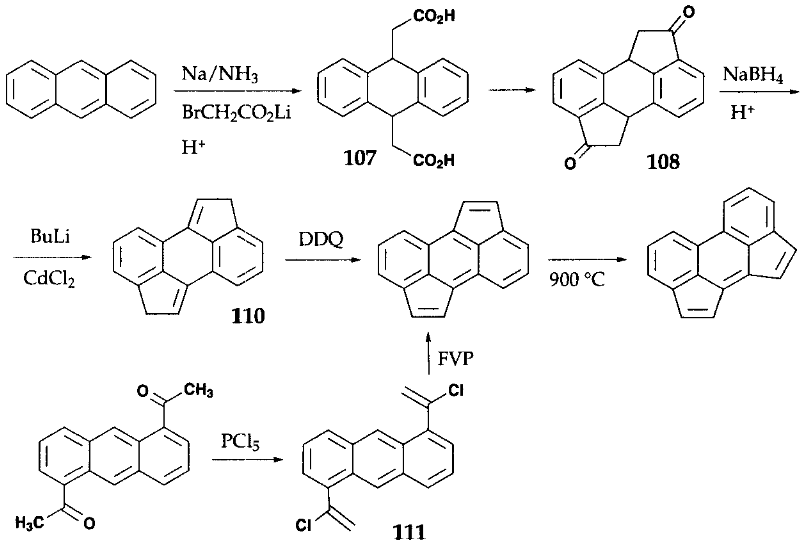


This hydrocarbon is also obtained from a synthesis based on ketone **104** obtained from acenaphthene by the standard Haworth synthesis.[63] Reaction of **104** with NaH and diethyl carbonate gives a keto ester which undergoes Robinson annelation with methyl vinyl ketone to furnish the diketo ester **105** in good yield. Ring closure takes place in boiling KOH to give **106** which undergoes Wolff-Kishner reduction and dehydrogenation to yield cyclopenta[*hi*]chrysene.



l) *Cyclopent[hi]aceanthrylene*

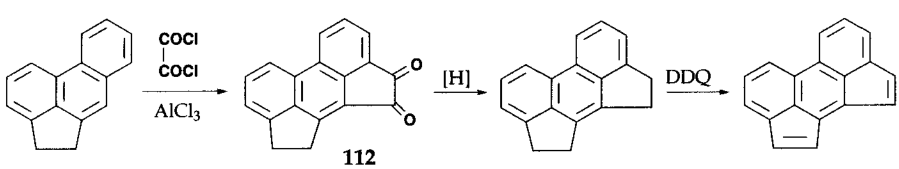
Reductive dialkylation of anthracene with Na in liquid ammonia and lithium bromoacetate affords the dicarboxylic acid adduct (**107**).[88,89] This is converted to diketone (**108**) *via* formation of the diacid dichloride and cyclization with $AlCl_3$. Reduction of **108** with $NaBH_4$ and acidic dehydration furnishes 5b,10b-dihydrocyclopent[*hi*]aceanthrylene (**109**). Treatment of **109** with BuLi and TMEDA followed by addition of $CdCl_2$[89] unexpectedly results in isomerization to 2,7-dihydrocyclopent[*hi*]-



aceanthrylene (**110**) which is aromatized with DDQ to cyclopent[*hi*]aceanthrylene. Another new synthesis is from 1,5-*bis*-acetylanthracene by reaction with PCl_5 to form 1,5-*bis*-(1-chloroethenyl)-anthracene (**111**) which is transformed to cyclopent[*hi*]aceanthrylene by flash vacuum pyrolysis.[90] At temperatures above 900° it rearranges to cyclopent[*hi*]acephenanthrylene.

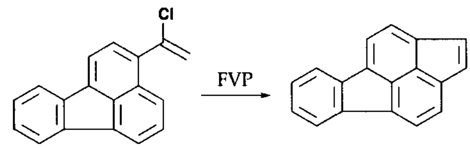
m) *Cyclopent[hi]acephenanthrylene*

As mentioned above, cyclopent[*hi*]aceanthrylene rearranges thermally to cyclopent[*hi*]-acephenanthrylene.[90] An alternative synthesis is from Friedel-Crafts reaction of acephenanthrene with oxalyl chloride and $AlCl_3$.[91] Wolff-Kishner reduction of the quinone product (**112**) and dehydrogenation with DDQ gives cyclopent[*hi*]acephenanthrylene.



n) *Cyclopenta[cd]fluoranthene*

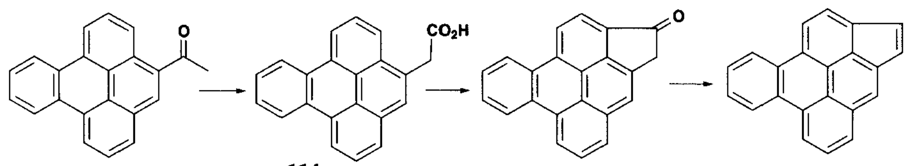
Synthesis of cyclopenta[*cd*]fluoranthene has recently been accomplished by flash vacuum pyrolysis of 3-(1-chloroethenyl)fluoranthene (**113**) obtained from reaction of 3-acetylfluoranthene with PCl_5.[92]



113

o) *Naphth[1,2,3-mno]acephenanthrylene*

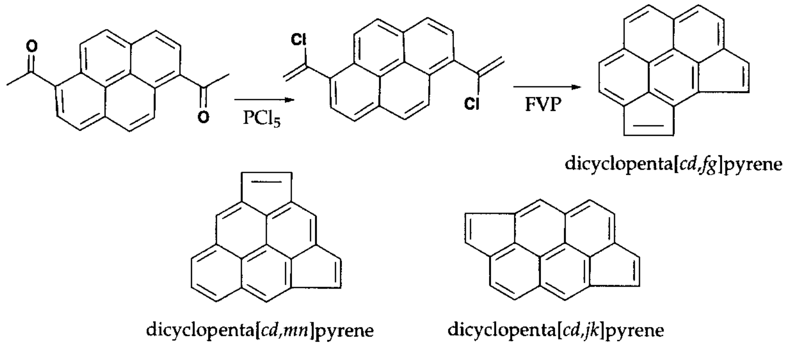
Synthesis of this hydrocarbon is based on conversion of decahydrobenzo[*e*]pyrene to 4-acetylbenzo[*e*]pyrene by acetylation with acetyl chloride and $AlCl_3$ and dehydrogenation with DDQ.[77] Oxidative rearrangement of 4-acetylbenzo[*e*]pyrene with thallium trinitrate yields (4-benzo[*e*]-pyrenyl)acetic acid (**114**) which is transformed to naphth[1,2,3-*mno*]acephenanthrylene by cyclodehydration in liquid HF, reduction of the ketone product with $NaBH_4$ and dehydration over alumina.



114

p) *Dicyclopenta[cd,mn]pyrene, dicyclopenta[cd,fg]pyrene and dicyclopenta[cd,jk]pyrene*

All three dicyclopentapyrene isomers are synthetically accessible by flash vacuum pyrolysis of the corresponding *bis*(1-chloroethenyl)pyrenes obtained from reaction of 1,3-, 1,6- and 1,8-diacetylpyrene with PCl_5.[93-95] For example, FVP of the 1,6-isomer at 1000°/~1.0 mm Hg gives dicyclopenta[*cd,fg*]pyrene. Similar reactions of the other isomers gives dicyclopenta[*cd,mn*]pyrene and dicyclopenta[*cd,jk*]pyrene. Pyrolysis at somewhat lower temperature (700-900°) gives variable amounts of intermediate products.[94]



q) *Dicyclopenta[cd,lm]perylene*

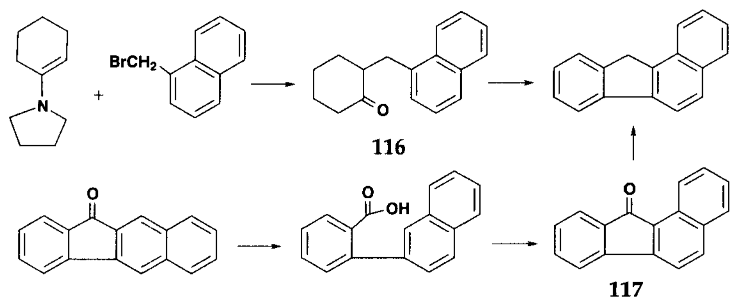
Reaction of 5,6-dibromoacenaphthene with *n*-BuLi gives 5,6-dilithioacenaphthene which couples in the presence of $Ni(acac)_2$ or $CoCl_2$ to form diaceperylene (**115**) accompanied by a small amount of dicyclopenta[*cd,lm*]perylene.[96] Dehydrogenation of **115** with DDQ provides dicyclopenta-

[*cd,lm*]perylene. This hydrocarbon is also obtained from stepwise coupling of 5-bromoacenaphthene with *n*-BuLi/$CoCl_2$ followed by bromination of the bi-acenaphthenyl with NBS and coupling of the dibromide with the same reagent, but the overall yield is no better.[97]

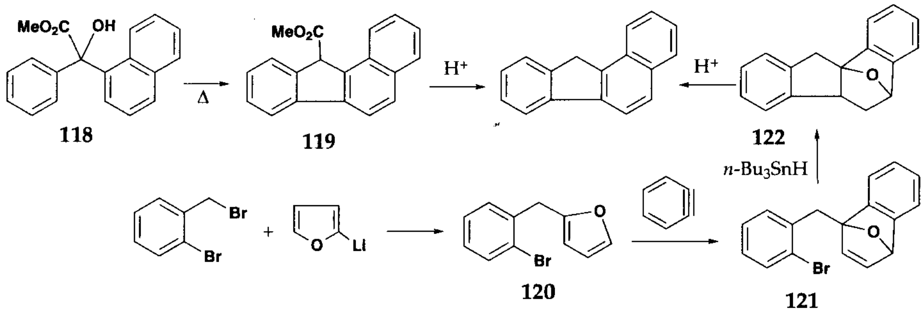
III. FLUORENES

a) *11H-Benzo[a]fluorene*

The most convenient synthesis is *via* alkylation of the enamine of cyclohexanone with 1-bromomethylnaphthalene followed by acid catalyzed cyclization of the ketone product (**116**) and dehydrogenation with DDQ.[98] An alternative synthesis is from benzo[*b*]fluorene-11-one by reaction with alkali to form the ring-open carboxylic acid which recyclizes in polyphosphoric acid to give benzo[*a*]fluorene-11-one (**117**).[99] Hydrogenolysis of **117** furnishes benzo[*a*]fluorene. Additional syntheses of **117** are found in the older literature.[100-102]



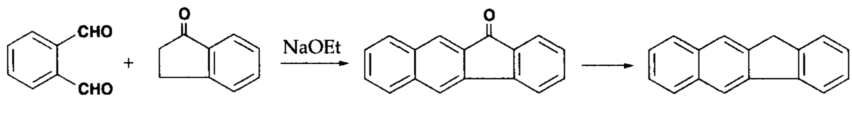
11*H*-Benzo[*a*]fluorene is also obtained from cyclodehydration of the α-hydroxyester **118** in sulfuric acid.[103] Decarboxylation of methyl benzo[*a*]fluorenecarboxylate (**119**) yields 11*H*-benzo[*a*]fluorene. This hydrocarbon is also obtained from reaction of 2-bromobenzyl bromide with 2-lithiofuran to furnish **120** which undergoes addition of benzyne to provide the cycloadduct **121**.[104]



This adduct on heating with tri-*n*-butyltin hydride cyclizes to **122** which is readily dehydrated to 11*H*-benzo[*a*]fluorene.

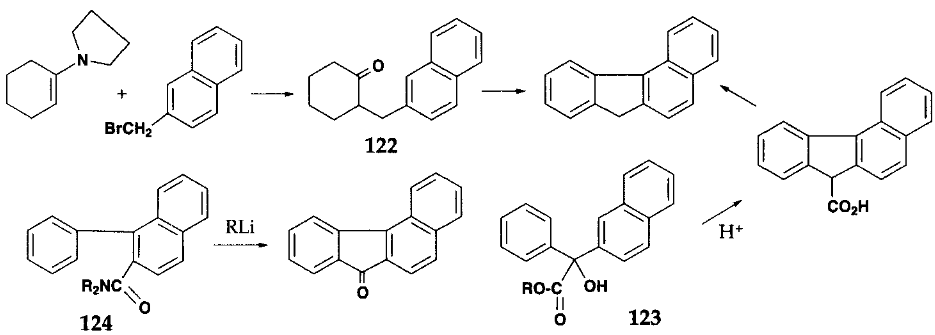
b) *11H-Benzo[b]fluorene*

Condensation of phthalic dicarboxaldehyde with indanone affords 11*H*-benzo[*b*]fluorenone which yields 11*H*-benzo[*b*]fluorene on hydrogenolysis.[99]



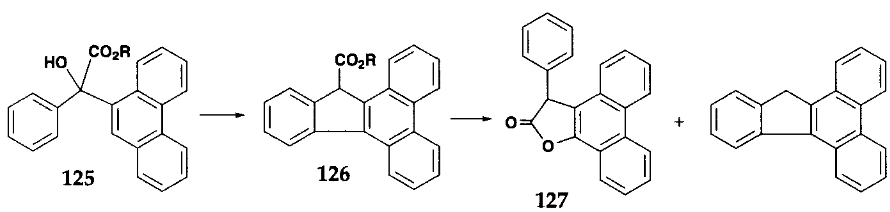
c) *7H-Benzo[c]fluorene*

This hydrocarbon is easily accessible by alkylation of the enamine of cyclohexanone with 2-bromomethylnaphthalene followed by acid-catalyzed cyclodehydration of the ketone product (**122**) and dehydrogenation with DDQ.[98] Another practical route is from acidic cyclodehydration of ester **123** and decarboxylation.[101] Benzo[*c*]fluorene-7-one is obtained by remote metalation of the biarylamide **124** with organolithium reagents and intramolecular reaction of the metalated intermediate.[105]



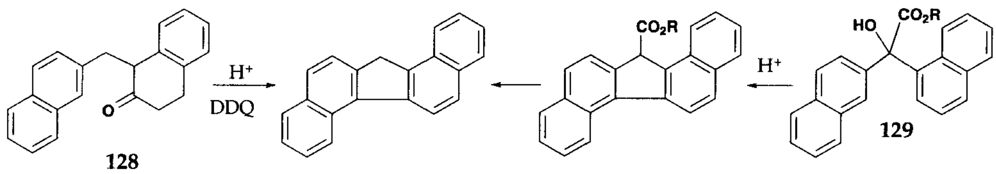
d) *13H-Indeno[1,2-l]phenanthrene*

Acid-catalyzed cyclodehydration of the α-hydroxyester **125** followed by decarboxylation of the product (**126**) yields the lactone **127** (75%) accompanied by 13*H*-indeno[1,2-*l*]phenanthrene (20%).[103] Several older syntheses of this hydrocarbon have been reported.[105,106]



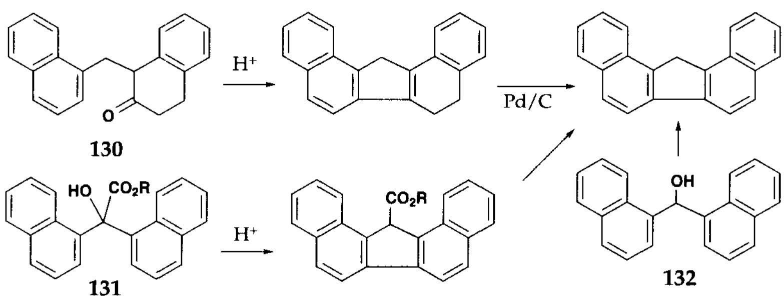
e) *13H-Dibenzo[a,g]fluorene*

The most convenient synthesis is by alkylation of the enamine derivative of ß-tetralone with 2-bromomethylnaphthalene followed by acid-catalyzed cyclodehydration of the product (**128**) and dehydrogenation.[98] Another practical route is *via* acid catalyzed cyclodehydration of the α-hydroxyester **129** followed by decarboxylation.[103] Additional syntheses are described in the older literature.[108-113]



f) *13H-Dibenzo[a,i]fluorene*

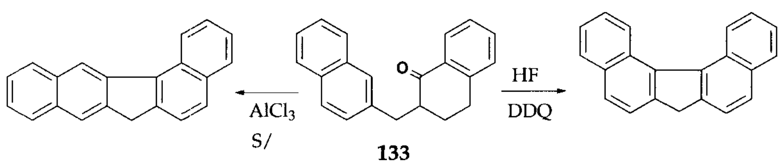
The methods employed for the preceding isomer, enamine alkylation and cyclodehydration of an α-hydroxyester, provide the most convenient synthetic access. Alkylation of the enamine of β-tetralone with 1-(bromomethyl)naphthalene affords ketone **130** which is converted to 13*H*-dibenzo-[*a,i*]fluorene by acidic cyclization and dehydrogen-ation.[98] This hydrocarbon is also accessible by



cyclodehydration of α-hydroxyester **131** followed by decarboxylation[103] and cyclization of carbinol **132** with phosphoric anhydride.[104] Additional syntheses are reported in the older literature.[110,114-116]

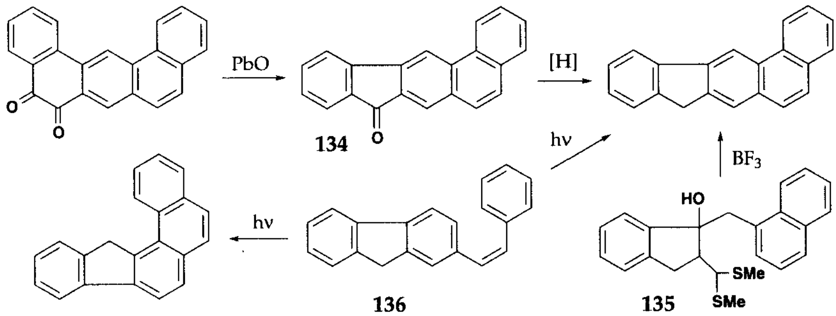
g) *7H-Dibenzo[c,g]fluorene and 7H-dibenzo[b,g]fluorene*

The former isomer is prepared from ketone **133** by cyclodehydration in HF and dehydrogen-ation with DDQ.[98] Ketone **133** is accessible by the enamine alkylation method[98] or by reaction of 2-(bromomethyl)naphthalene with α-tetralone and $NaNH_2$.[110] 7*H*-Dibenzo[*b,g*]fluorene, the product of cyclization in the alternative direction, is obtained from $AlCl_3$-catalyzed cyclization of **133** and dehydrogenation with sulfur.[109] Other syntheses of this hydrocarbon are described in the older literature.[111,117]



h) *8H-Indeno[2,1-b]phenanthrene and 13H-indeno[1,2-c]phenanthrene*

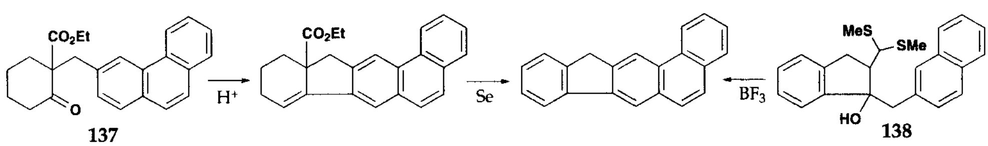
Although two syntheses of 8*H*-indeno[2,1-*b*]phenanthrene are reported, the structural assignment must be regarded as uncertain due to the wide discrepancy in the reported mps. One synthesis is *via* decomposition of dibenz[*a,j*]anthracene-5,6-dione in the presence of lead oxide to form a ketone assigned structure **134** and reduction with hydrazine hydrate in a sealed tube.[117] The second synthesis entails addition of 1-(naphthylmethyl)magnesium bromide to an α-oxoketene dithioacetal to yield carbinol **135** followed by BF_3 catalyzed cycloaromatization.[118]



8*H*-Indeno[2,1-*b*]phenanthrene is also claimed as a minor product (by NMR analysis) from photocyclization of 2-styrylfluorene (**136**).[119] The main product is 13*H*-indeno[1,2-*c*]phenanthrene formed by cyclization to the alternative position.

i) *12H-Indeno[1,2-b]phenanthrene*

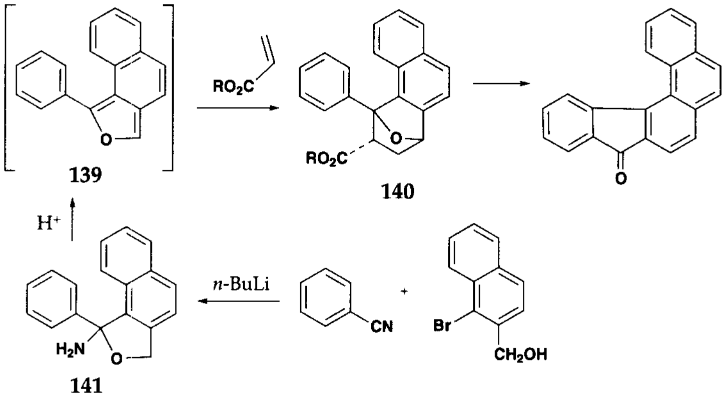
As for the preceding isomer, two syntheses are reported with wide discrepancy in the reported mps. The first reported synthesis[117] entails condensation of 3-phenanthrylmethyl bromide with the potassium salt of ethyl cyclohexanone-2-carboxylate to furnish the adduct **137**. This is



converted to 12*H*-indeno[1,2-*b*]phen-anthrene by cyclization in acidic medium followed by dehydrogenation with selenium. The second method proceeds *via* addition of 2-(naphthylmethyl)magnesium bromide to an α-oxoketene dithioacetal to yield carbinol **138** followed by treatment with BF_3 etherate.[118]

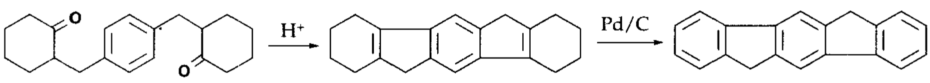
j) *9H-Indeno[2,1-c]phenanthrene*

Only the 9-keto derivative is known. Diels-Alder cycloaddition of methyl acrylate to the isonaphthofuran compound **139** affords the adduct **140** which on heating in polyphosphoric acid gives 9*H*-indeno[2,1-*c*]phenanthrene-9-one.[120] Compound **139** is generated *in situ* from reaction of 1-bromo-2-(hydroxymethyl)naphthalene with *n*-BuLi and phenylnitrile followed by acid-catalyzed reaction of the product (**141**). An alternative synthesis of this ketone has been reported.[121]



k) *6,12-Dihydroindeno[1,2-b]fluorene*

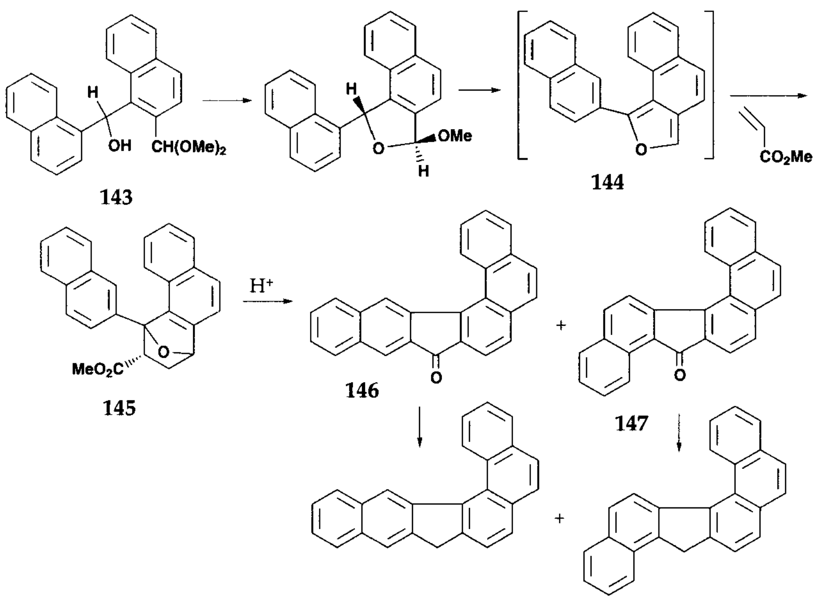
The most convenient synthesis is by enamine alkylation.[96] Reaction of 1,4-*bis*(bromomethyl)-benzene with two equivalents of 1-pyrrolidino-1-cyclohexene affords a diketone (**142**) which cyclizes regioselectively on treatment with acid to decahydroindeno[1,2-*b*]fluorene. Catalytic dehydrogenation furnishes 6,12-dihydroindeno[1,2-*b*]fluorene. Other syntheses are described in the older literature.[122,123]



142

l) *9H-Benz[5,6]indeno[2,1-c]phenanthrene and 9H-benz[4,5]indeno[2,1-c]phenanthrene*

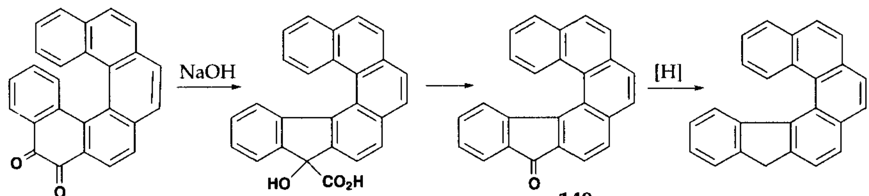
The newest synthesis entails reaction of the dimethylacetal of 1-lithio-2-naphthaldehyde with 2-naphthaldehyde to provide **143**.[120] In the presence of Dowex 50W-X8 resin **143** is converted to



a *trans* acetal which on treatment with acid affords 1-(2-naphthyl)naphtho[1,2-*c*]furan (**144**) which is trapped by reaction with methyl acrylate. The endo adduct (**145**) undergoes intramolecular acylation on heating in PPA to yield a mixture of ketones (**146** and **147**). Reduction of this mixture with hydrazine hydrate gives 9*H*-benz[5,6]indeno[2,1-*c*]phenanthrene and 9*H*-benz[4,5]indeno[2,1-*c*]phenanthrene.[121] An older synthesis based on dimerization of 3-(2-naphthyl)propiolic acid with Ac_2O has also been described.[121]

m) *7H-Benz[c]indeno[1,2-g]phenanthrene*

Benzylic acid rearrangement of hexahelicene-5,6-dione gives initially the α-hydroxy acid **148** which on further reaction is converted to benz[*c*]indeno[1,2-*g*]phenanthrene-5-one (**149**).[124]

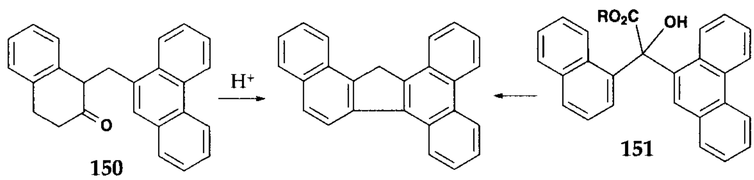


148 **149**

Wolff-Kishner reduction of **149** gives 7*H*-benz[*c*]indeno[1,2-*g*]phenanthrene.

n) *15H-Benz[4,5]indeno[1,2-l]phenanthrene*

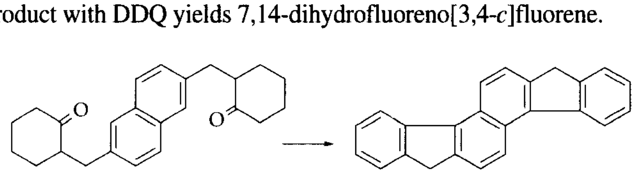
Reaction of the pyrrolidine enamine of 2-tetralone with 9-bromomethylphenanthrene provides the alkylated ketone **150** which undergoes acid-catalyzed cyclodehydration and dehydrogenation with DDQ to yield 15*H*-benz[4,5]indeno[1,2-*l*]phenanthrene.[98] This hydrocarbon is also obtained from acid-catalyzed cyclization of the α-hydroxycarboxylic ester **151** followed by decarboxylation.[103]



150 **151**

o) *7,14-Dihydrofluoreno[4,3-c]fluorene*

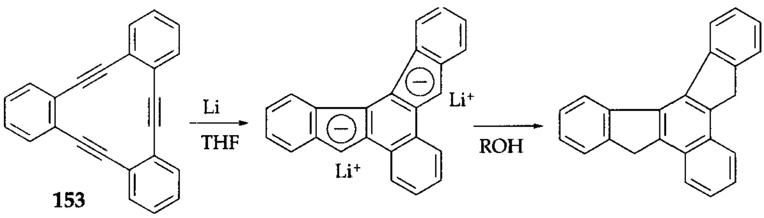
Reaction of the enamine of cyclohexanone with 2,6-*bis*-(bromomethyl)naphthalene provides the corresponding dialkylated diketone (**152**).[98] Acid-catalyzed cyclodehydration of **152** and dehydrogenation of the product with DDQ yields 7,14-dihydrofluoreno[3,4-*c*]fluorene.



152

p) *5,10-Dihydrobenz[a]indeno[2,1-c]fluorene*

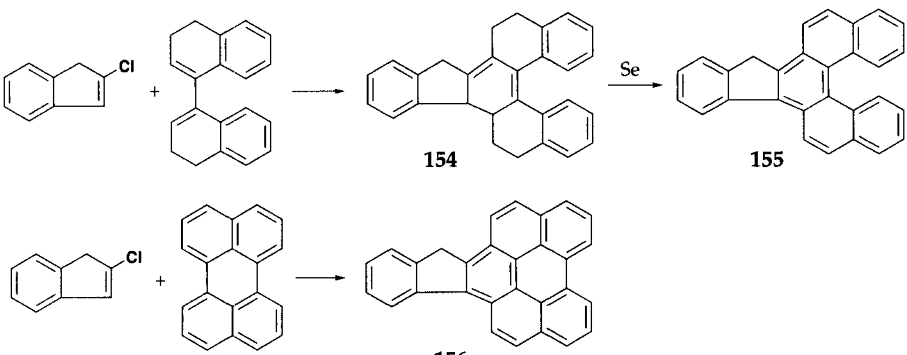
Tribenzocyclotriyne **153** cyclizes on treatment with lithium to form the dianion of benz[*a*]indeno[2,1-*c*]fluorene. Protonation by alcohol yields the neutral hydrocarbon.[123] Reaction of the dianion with Me_3SiCl affords the 5,10-*bis*-trimethylsilylated derivative which in turn reacts with *n*-BuLi to form a dimeric compound with two lithium atoms sandwiched between aromatic rings.[126]



153

q) *15H-Dibenz[c,g]indeno[1,2-l]phenanthrene and 13H-fluoreno[1,2,3,4-ghi]perylene*

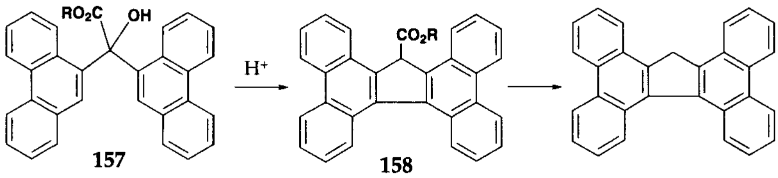
Cycloaddition of 3,3',4,4'-tetrahydrodinaphthyl to 2-chloro-3*H*-indene provides adduct **154** which aromatizes on heating with selenium to provide 15*H*-dibenz[*c,g*]indeno[1,2-*l*]phenanthrene (**155**).[127] This hydrocarbon is also obtained from condensation of 3,3',4,4'-tetrahydrodinaphthyl with indene followed by dehydrogenation of the adduct. Although attempts to further dehydrogenate **155** to 13*H*-fluoreno[1,2,3,4-*ghi*]perylene (**156**) by heating in a NaCl/$AlCl_3$ melt failed, this hydrocarbon was obtained from Diels-Alder reaction between 2-chloro-3*H*-indene and perylene.



154 155 156

r) *17H-Tetrabenzo[a,c,g,i]fluorene*

The most convenient synthetic approach is *via* acid-catalyzed cyclization of the α-hydroxyester **157** to yield the carboxylic ester derivative of 17*H*-tetrabenzo[*a,c,g,i*]fluorene (**158**).[103] Decarboxylation of the free acid yields 17*H*-tetrabenzo[*a,c,g,i*]fluorene. Reduction of the acid with $LiAlH_4$ gives the alcohol used to synthesize a series of 17-substituted derivatives.[126] An older synthesis of 17*H*-tetrabenzo[*a,c,g,i*]fluorene involving Ullmann reaction of methyl 9-bromophenanthrene-10-carboxylate has also been reported.[129]



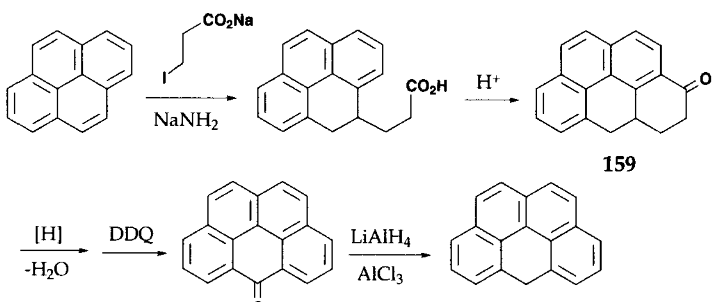
157 158

IV. PHENALENES

Although relatively few polycyclic phenalenes have been synthesized, the known examples tend to have interesting chemical properties. These hydrocarbons, which contain only six-membered rings, are distinguished by possession of a series of isomers which differ only in the site of the saturated carbon atom. Since most of these isomers are relatively close in stability, the electronic charge in their carbocation and carbanion intermediates tends to be distributed relatively equally at various sites in the molecule.

a) *6H-Benzo[cd]pyrene*

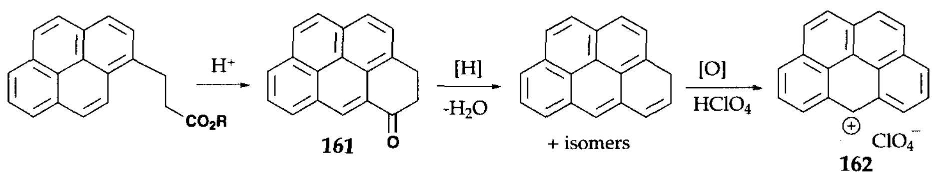
The newest synthesis is from reaction of the pyrene dianion in liquid ammonia with sodium iodopropionate followed by cyclization of the adduct in polyphosphoric acid to generate ketone **159**.[130] Reduction and dehydration of **159** and oxidation of the product with DDQ in wet toluene affords benzo[*cd*]pyrene-6-one (**160**). Reduction of **160** with $LiAlH_4$-$AlCl_3$ or Al(*i*-PrO)$_3$-*i*-PrOH provides 6*H*-benzo[*cd*]pyrene.[131]



159

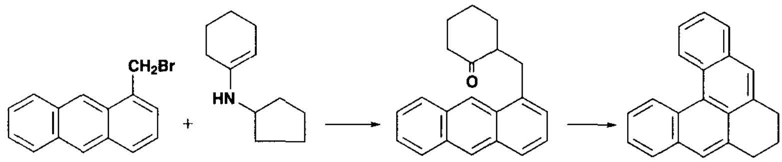
160

6*H*-Benzo[*cd*]pyrene forms stable cation, radical and anion species that possess a nonbonding molecular orbital with zero, one and two electrons, respectively. The cation is synthetically accessible by acid-catalyzed cyclization of β-1-pyrenylpropionic acid followed by reduction of the ketone product (**161**) with $LiAlH_4$ and dehydration to yield a mixture of benzo[*cd*]pyrene isomers.[130] Reaction of the mixture of benzo[*cd*]pyrene isomers with *o*-chloranil and perchloric acid gives benzo[*cd*]pyrenyl perchlorate (**162**), while air oxidation affords the stable benzo[*cd*]pyrenyl radical.[131] Reaction of benzo[*cd*]pyrene with *n*-BuLi at low temperature affords the benzo[*cd*]pyrenyl anion which reacts with electrophiles predominantly at the 6-position.[132,133]



b) *9H-Naphth[3,2,1-de]anthracene*

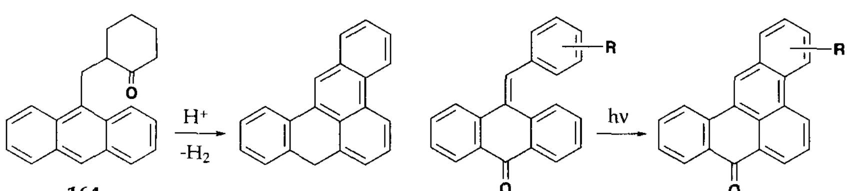
Although several syntheses of 9*H*-naphth[3,2,1-*de*]anthracene have been reported, none are entirely satisfactory.[134] A newer synthetic approach is *via* alkylation of cyclohexanone enamine with 1-(bromo-methyl)anthracene.[135] The ketone product (**163**) undergoes acid-catalyzed cyclization and catalytic dehydrogenation to furnish the 7,8-dihydro-6*H*-naphth[3,2,1-*de*]anthracene.



163

c) *8H-Dibenz[a,de]anthracene*

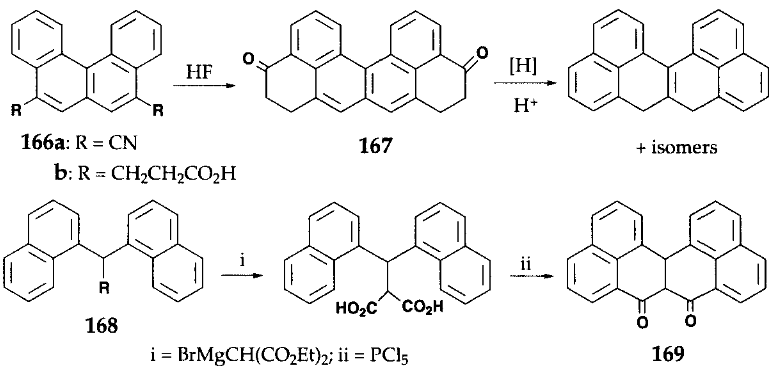
The newest and most direct synthesis is by the enamine alkylation route.[135] Reaction of 9-bromomethylanthracene with 1-pyrrolidino-1-cyclohexene affords ketone (**164**) which is converted to 8*H*-dibenz[*a,de*]anthracene by acid-catalyzed cyclization and dehydrogenation. Condensation of benzaldehyde with anthrone in pyridine furnishes benzalanthrone (**165**) which photocyclizes to 8*H*-dibenz[*a,de*]anthracene-8-one.[136] Various derivatives of this ketone (R = Cl, CH_3, OMe, Br) have been synthesized by this method.[136,137]



d) *7H,8H-Dibenzo[de,hi]naphthacene*

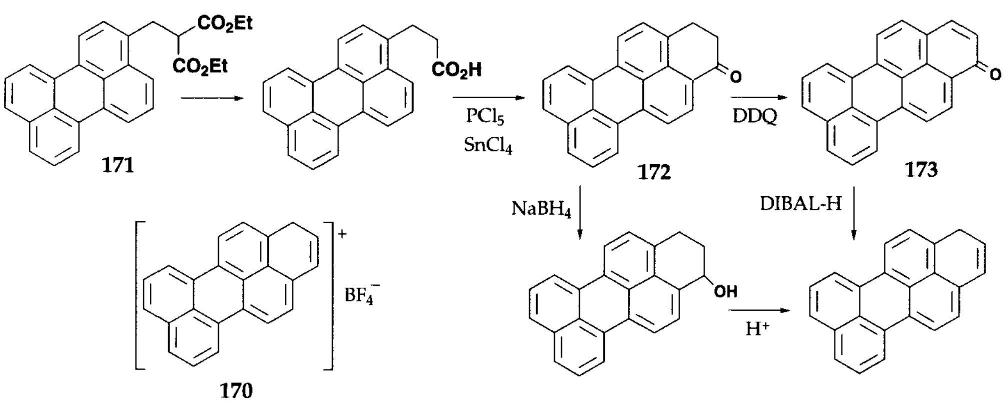
A Kekulé structure cannot be written for this hydrocarbon which has only been obtained as a mixture of dihydro isomers. Attempts to dehydrogenate the mixture led to formation of polymeric products. It is postulated that the parent fully unsaturated hydrocarbon may exist as a short-lived diradical species.[138] Stable dication and dianion species have been prepared.[139]

Synthesis of 7*H*,8*H*-dibenzo[*de,hi*]naphthacene is based on the readily available benzo[*c*]phenanthrene-5,8-dicarbonitrile (**166a**) which is converted to the dicarboxylic acid **166b** by standard methods for chain elongation.[139] Cyclization of **166b** in liquid HF gives diketone **167** which undergoes reduction with $LiAlH_4$ and dehydration to yield 7*H*,8*H*-dibenzo[*de,hi*]naphthacene shown by NMR analysis to be a mixture of isomers. This mixture reacts with *n*-BuLi at -78° to form a stable dianion, while reaction with trityl fluoroborate furnishes the dication.[139] The 7,8-diketo derivative (**169**) is obtained by an alternative method based on di-(1-naphthyl)carbinol (**168**: R = OH).[138] Transformation of **168** into the chloride followed by reaction with magnesio-malonic ester provides a diester which cyclizes with PCl_5 in nitrobenzene to give a product assumed to be the diketone **169**.



e) *1H-Benzo[cd]perylene*

Although the parent hydrocarbon could not be obtained pure due to its sensitivity toward air and heat, synthesis of a stable tetrafluoroborate salt (**170**) has been reported.[140] Base-catalyzed condensation of perylene-3-carboxaldehyde with diethylmalonate gives an unsaturated diester which is reduced with Zn/HOAc to yield the saturated diester **171**. This is converted to the cyclic ketone **172** *via* hydrolysis, decarboxylation to a propionic acid derivative, treatment with PCl_5 and $SnCl_4$-catalyzed cyclization. A small amount of the unsaturated ketone **173** is also formed. Dehydrogenation

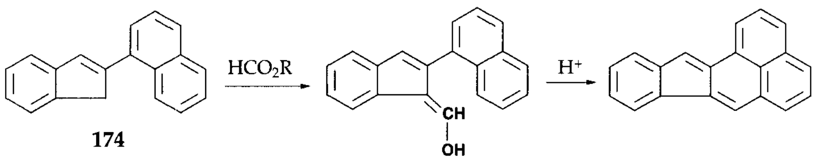


of **172** with DDQ yields **173**. Reduction of **172** with $NaBH_4$ followed by acid-catalyzed dehydration of the resulting alcohol and reduction of **173** with DIBAL-H both give 1*H*-benzo[*cd*]perylene. Treatment of this with triphenylmethyl tetrafluoroborate affords the tetrafluoroborate salt (**170**).

HYBRID RING SYSTEMS

a) *Indeno[2,1-a]phenalene*

The central double bonds of indeno[2,1-*a*]phenalene are "fixed". Its synthesis is based on reaction of 2-indanone with 1-naphthylmagnesium bromide and dehydration of the crude product to 1-(2'-indenyl)naphthalene (**174**).[141,142] Base-catalyzed condensation of **174** with ethyl formate gives an unstable hydroxymethylene intermediate which cyclodehydrates in acid to give indeno[2,1-*a*]phenalene. 7,12-Dihydroindeno[2,1-*a*]phenalene (**176**) is obtained from reaction of benzylmagnesium chloride with phenalenone to give 7-benzylphenalene (**175**) followed by reaction with $AlCl_3$.[143] Alternative syntheses of indeno[2,1-*a*]phenalene have also been reported.[144-146]



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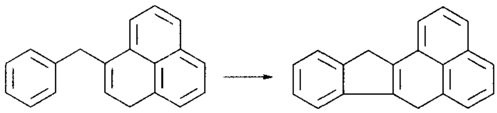
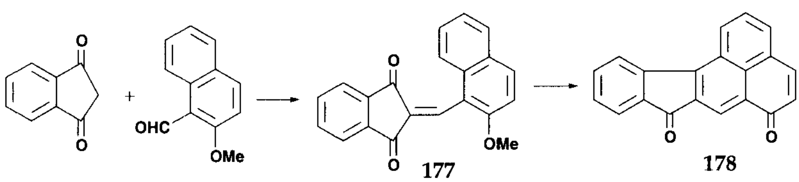


175 **176**

b) *7,8-Dihydroindeno[1,2-a]phenalene*

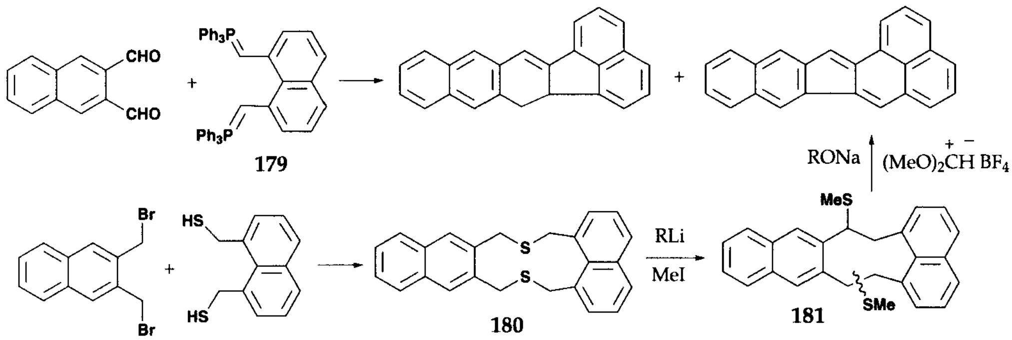
Base-catalyzed reaction of 1-formyl-2-methoxynaphthalene with 1,3-indandione gives adduct **177** which is converted to indeno[1,2-*a*]phenalene-6,8-dione (**178**) by hydrogenation over a Pt catalyst and acid-catalyzed cyclodehydration.[147] Syntheses of several derivatives of indeno[1,2-*a*]phenalene are reported in the older literature.[148-152]



177 **178**

c) *Benz[5,6]indeno[2,1-a]phenalene*

The most direct synthesis is *via* double Wittig reaction between the bisphosphonium ylide generated from the bisphosphonium salt of 1,8-bisbromomethylnaphthalene (**179**) and naphthalene-2,3-dicarboxaldehyde.[153] Benz[5,6]indeno[2,1-*a*]phenalene or 7,8-dihydronaphtho[2,3-*k*]fluoranthene is the major product, dependent upon reaction conditions. An alternative synthesis is based on extrusion of sulfur from a macrocyclic *bis*-sulfide intermediate (**180**) prepared from reaction of 2,3-*bis*(bromomethyl)naphthalene with 1,8-*bis*(mercaptomethyl)naphthalene. Treatment of **180** with *n*-BuLi followed by methylation with MeI gives a mixture of inseparable isomeric products (**181**). Further methylation of this mixture with dimethoxycarbonium tetrafluoroborate and elimination with NaOEt in EtOH affords benz[5,6]indeno[2,1-*a*]phenalene.



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