1
Pioneers of Carbon-rich Compounds

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1.1
Introduction

This chapter provides a historical perspective on the discovery of and classical approaches to carbon-rich molecules prior to 1970. Carbon-rich is defined here as a ratio of at least one C atom per H atom. Due to the tremendous amount of research in this field, this chapter focuses on the pioneering synthetic efforts and key successes thereafter and will not attempt to serve as an inclusive document on the subject. Several excellent references have been compiled which can provide further information [1]. Additionally, the overwhelming plethora of substituted variants, while important in relation to derivatization and molecular diversity, will not be addressed unless unique in application or properties. Examples include the numerous alkyl-substituted or partially reduced derivatives of polycyclic aromatic hydrocarbons described in detail by Clar [1a]. Finally, fused benzenoid structures are described with classical numerical nomenclature instead of the alphabetical IUPAC methodology used by Harvey [1c].

1.2
19th Century Achievements

Initial research on carbon-rich systems began with the isolation of polycycles from coal-tar and other petroleum products in the mid 19th century. Separation, purification, and characterization of several different macrocycle topologies by German chemists, such as Graebe and Glaser, provided key insight into existing hydrocarbon diversity as well as potential future topologies. Such efforts normally included fractional distillation of the crude fuel, treatment with concentrated acid and base, final recrystallization or distillation, and derivatization to assist in identification. Naphthalene **1**, phenanthrene **2**, anthracene **3**, biphenyl **4**, fluorene **5**, picene **6**, pyrene **7**, and fluoranthene **8** were all isolated prior to 1900 in this fashion (Fig. 1.1) [1a].

In addition to petroleum component analyses, the late 19th century spawned the

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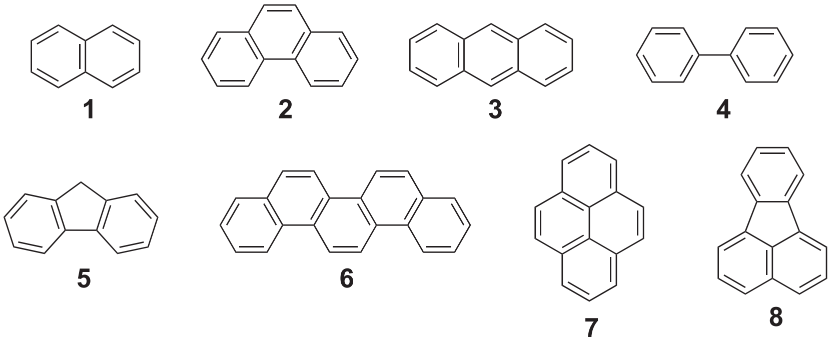
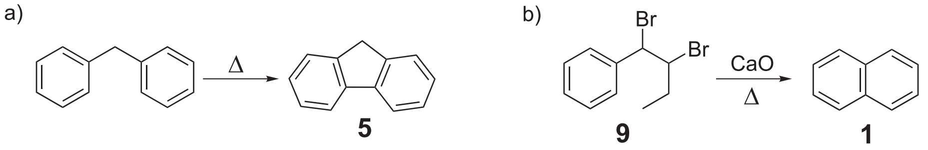


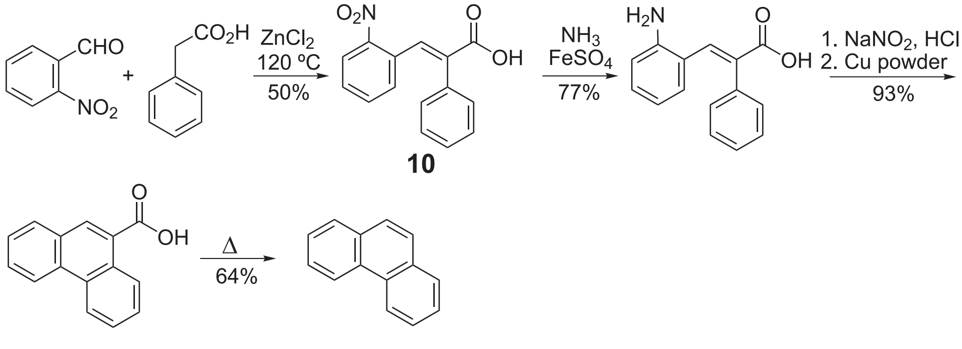
Figure 1.1. Structures **1**–**8**.

first synthetic efforts on two, three, and four linearly-annelated polycyclic systems, most of which had been previously isolated from fossil fuels, as well as *peri*-condensed benzenoid systems such as terphenyl and tetraphenyl. The majority of syntheses used pyrolysis or pyro-condensation and consisted of passing precursor molecules through red-hot tubes or distillation over broken glass at red heat [1a]. Examples include Graebe's formation of fluorene from diphenylmethane in 1874 (Scheme 1.1a) [2] and Radziszewski's production of naphthalene from (α,β-dibromobutyl)benzene **9** in 1876 (Scheme 1.1b) [3]. Pyrolysis at high temperature though, routinely resulted in poor product yield due to formation of multiple byproducts and different isomers. The reinvestigation of naphthalene pyrolysis by Lang et al. in 1957 showed the lack of specificity as three dinaphthyls, perylene, two benzofluoranthenes, ternaphthyl, and terrylene were all produced [4].



Scheme 1.1

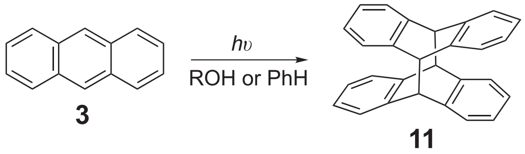
The most important early cyclization technique developed was von Baeyer's Zn-dust distillation in 1866 [5]. The procedure effectively reduced carbon-rich quinone or oxygen-containing precursors, as shown by the formation of benzene from phenol [1a]. Also of significance was the multistep production of phenanthrene by Pschorr in 1896 (Scheme 1.2) [6]. Condensation of *o*-nitrobenzaldehyde and phenylacetic acid produced the uniquely substituted intermediate **10**. Sequential nitro group reduction and diazotization followed by Cu-induced ring closure and thermal decarboxylation afforded the polycycle. Pschorr's methodology, important because of its low temperature conditions, was later used to produce several other condensed polyarenes in the coming decades, such as chrysene and picene



Scheme 1.2

[1a]. Examples of other pre-1900 ring closures include Klinger's reduction of a substituted phenanthrene to 1.2,7.8-dibenzochrysene [7] and Riese's production of *p*-terphenyl from 1,4-dibromobenzene, bromobenzene, and Na in ether [8].

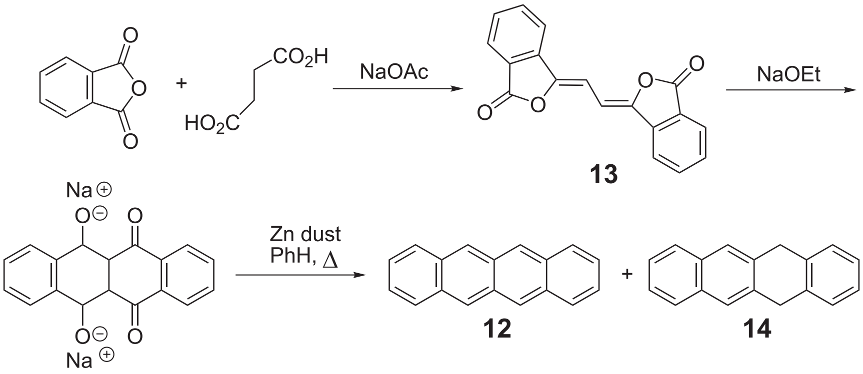
The first synthesis of a tri-annelated system occurred 30 years after its initial discovery from coal-tar in 1832 by Dumas and Laurent when Limpricht hydrolyzed benzyl chloride under heat to afford anthracene [1a]. The most significant improvement on anthracene production, however, came in 1868 when Liebermann and Graebe obtained it via Zn-dust distillation of the natural product alizarin [1a]. An interesting dimer, known as dianthracene or *p*-anthracene **11**, was obtained by several groups in the 1890s by irradiation of anthracene solutions (Scheme 1.3) [9]. Irradiation of several anthracene derivatives afforded similarly novel structures [9].



Scheme 1.3

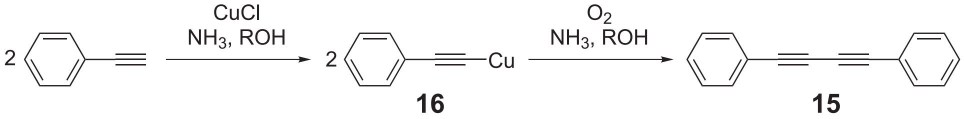
The production of tetracene **12** prior to the turn of the century marked the largest linearly-annellated polyarene at the time [10]. The synthetic pathway began with condensation of phthalic anhydride and succinic acid with NaOAc (Scheme 1.4). Rearrangement of **13** with NaOEt and subsequent Zn-dust distillation afforded a combination of **12** and dihydro-derivative **14**.

Assembly of carbon-rich molecules by means of acetylene chemistry is also of note prior to 1900. Although isolated from petroleum products in 1825 by Faraday [1a], the first total synthesis of benzene by Berthelot in 1867 via cyclotrimerization of acetylene [11] set a precedent for future thermal trimerization reactions, a key procedure to produce uniquely substituted arene rings [1e]. The first ethynyl ho-



Scheme 1.4

mocoupling occurred in 1869 when Glaser formed 1,4-diphenylbutadiyne **15** from phenylacetylene and CuCl in ammonia and alcohol (Scheme 1.5) [12]. In the process he isolated the intermediate copper complex **16**. The first cross-coupling of asymmetrical acetylides occurred in 1882 when Baeyer obtained an unsymmetrical butadiyne as well as the two symmetrical diethynyl dimers from *o*-nitrophenylacetylene and phenylacetylene [13]. Although Straus and Moreau improved alkyne coupling conditions in the early 20th century, Glaser's oxidative conditions would serve as a standard technique until the 1950s when Eglinton and Galbraith, Chodkiewicz and Cadiot, Hay, and Brockman developed alternative methods [14].

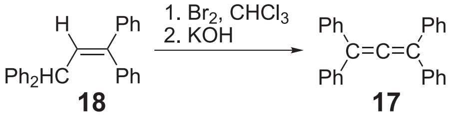


Scheme 1.5

1.3
1900–1928: Dawn of the Twentieth Century

The turn of the century and the following three decades focused mainly on the development of new, efficient routes to previously isolated structures. The replacement of pyrolysis with tailored pathways afforded increased yields and convincing proof of structure through derivatization of intermediates and products. Two examples include Mannich's production of triphenylene from an acid-catalyzed, threefold condensation of cyclohexanone followed by reduction over freshly reduced, hot Cu, [15] as well as Ullmann and Meyer's condensation of iodobenzene with Cu to afford biphenyl [16]. Of note was a significant simplification in pyrolysis for low molecular weight hydrocarbons, which consisted of inserting an electrically heated glowing wire into boiling hydrocarbon vapor [17]. Löb successfully produced biphenyl from benzene in the early 1900s via this new method.

Tetraphenylallene **17**, one of the first carbon-rich allenes, was produced in the early 1900s by Vorländer and Siebert via halogenation/dehydrohalogenation of phenyl-substituted olefin **18** (Scheme 1.6) [18]. This classical method set a standard for the preparation of arylallenes as the resultant product could not isomerize due to lack of an abstractable hydrogen [1d].



Scheme 1.6

Two important polycycles produced prior to 1920 were perylene **19** (Fig. 1.2a) and pyrene **7**, both of note as parent structures for numerous fused benzenoid analogs produced in the following decades. In 1910, Scholl, Seer, and Weitzenböck first produced perylene from an $AlCl_3$-mediated cyclization of naphthalene and/or 1,1′-binaphthyl under heat in low yield [19]. A subsequent success with improved yield occurred via treatment of 1,8-diiodonaphthalene with Cu powder. Weitzenböck was responsible for the first synthesis of pyrene in 1913 [20]. The five-step synthesis began with bromination of *o,o*′-ditolyl followed by conversion into dicarboxylic acid **20** via a dinitrile intermediate (Scheme 1.7). Cyclization and Zn-dust distillation afforded the tetra-fused structure in a well-designed synthesis, confirming its structure through intermediate analysis.

In relation to size, the most notable molecules of the early 20th century include decacyclene **21** and tetraphenyltetracene **22**, also known as rubrene (Schemes 1.8 and 1.9, respectively). Decacyclene was produced in 1903 by Dziewoński and Rehländer by heating acenaphthene **23** with sulfur (Scheme 1.8) [21]. Ten years later a new route with lead dioxide provided **21** as well as the byproduct fluorocyclene **24** [22]. Rubrene **22**, produced by Moureu, Dufraisse, and Dean in 1926, is a red hydrocarbon obtained from dimerization of phenylethynyldiphenylmethyl chloride **25** under heat (Scheme 1.9) [23]. The structure is remarkable in its acid-catalyzed

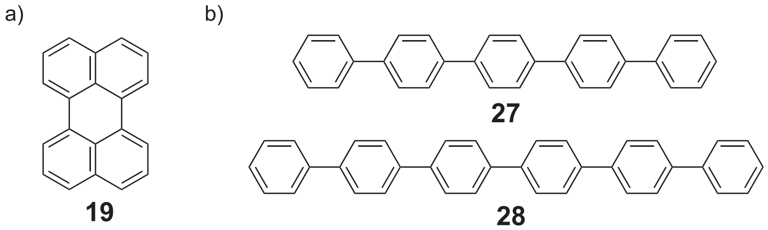
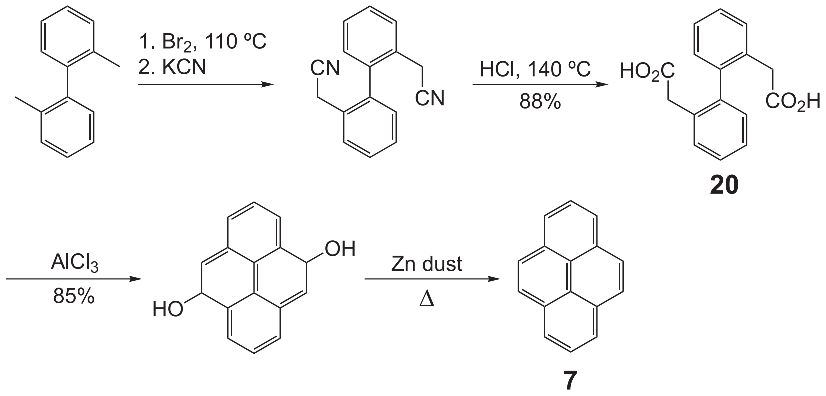
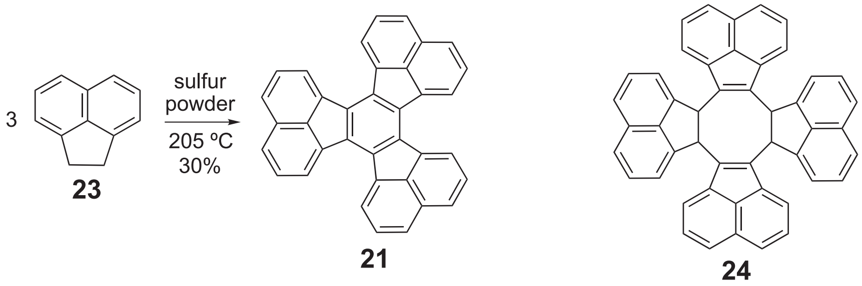


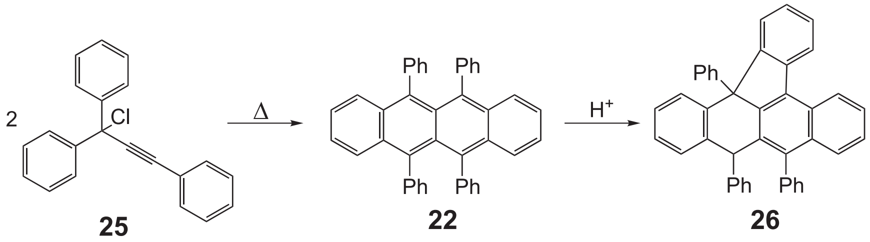
Figure 1.2. (a) Structure **19**, (b) structures **27** and **28**.



Scheme 1.7



Scheme 1.8



Scheme 1.9

isomerization to the colorless pseudorubrene **26** [24] and a photo-induced peroxide derivative that reformed rubrene upon heating [23].

Evolution to the two next largest *peri*-condensed benzenoid polyphenyls occurred in 1924 with the production of quinquephenyl **27** by Gerngross and coworkers (Fig. 1.2b) [25]. Two distinct pathways afforded the pentamer: (i) reduction of a benzenediazonium sulfate in acid with Cu powder, and (ii) Ag-mediated cross-coupling of 4-iodobiphenyl and 4-iodoterphenyl. In the same year, Pummerer and Bittner

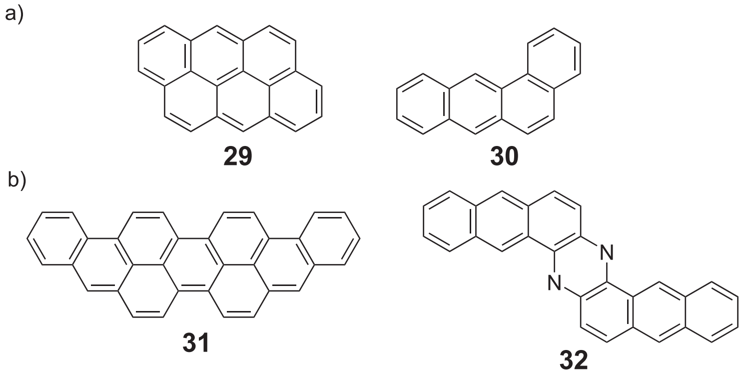


Figure 1.3. (a) Structures **29** and **30**, (b) structures **31** and **32**.

produced sexiphenyl **28** (Fig. 1.2b) via a similar Ag-mediated homocoupling of 4-iodoterphenyl [26]. Although improvements on the above two polyarenes continued in the following decades, sexiphenyl marked the largest linear, *peri*-condensed hydrocarbon prior to 1970.

1.4
1929–1949: Rise of the Polycyclic Aromatic Hydrocarbon

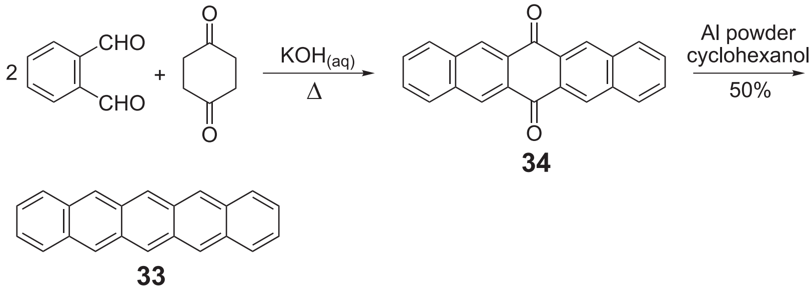
The 1930s marked a significant increase in new and larger polycyclic aromatic hydrocarbons with the first appearance of hexa-annelated systems and initial work on benzenoid isomers and derivatives of anthanthrene **29**, tetraphene **30**, pyrene, and perylene (Fig. 1.3a). In addition to continued research from distinguished chemists such as Scholl, the pioneering efforts of Erich Clar and James W. Cook were a key factor for this development. Müllen and Wu discuss recent advances in polycyclic aromatic hydrocarbons in Chapter 3.

Indisputably, the most significant contributions to polycyclic aromatic hydrocarbons originated with Clar at the beginning of this decade. His efforts were published in the journal series *Polynuclear Aromatic Hydrocarbons* and/or *Aromatic Hydrocarbons* [27] as well as in an excellent two volume series, *Polycyclic Hydrocarbons*, [1a] which provided a comprehensive look at hydrocarbon diversity. Not only did he and his coworkers produce an exceeding number of new carbon-rich structures, but his adaptation and development of new synthetic methodologies allowed confirmation of structure as well as improved yields to provide sufficient quantities for physical property studies. Clar and coworkers continued their work well into the latter parts of the 20th century. His early work focused on benzo-, naphtho-, and anthraceno-derivatives of anthracene and phenanthrene [1a].

An example of the numerous, new synthetic methods developed by Clar was the Zn-dust melt [1a]. Published in 1939, the method provided a more practical one for reduction of polycycle quinones and oxygen-containing precursors than von

Baeyer's traditional solid-state, Zn-dust distillation. The key advantage was lower decomposition rates due to incorporation of solvent. The new technique was applied to several previously known systems, such as violanthrene **31** (Fig. 1.3b) from violanthrone and tetracene from tetracenequinone [1a]. It was also shown to work on five-membered systems, such as dihydropentalene derivatives, and heterocycles, such as anthrazine **32** (Fig. 1.3b) [1a].

One of Clar's most notable early successes of the decade was pentacene **33**. Clar and John isolated **33** via dehydrogenation of a dihydropentacene isomer, several of which had been laboriously produced since 1911 when Phillipi first claimed one as **33** [28]. The combination of two groups' efforts provided a far simpler route to pentacene two decades later. The highly efficient route began with condensation of *o*-phthalaldehyde and cyclohexane-1,4-dione to afford quinone **34** (Scheme 1.10) [29]. Reduction with Al powder afforded **33** in two steps [30]. Clar and coworkers also synthesized several pentacene derivatives in the 1940s: 1.2-benzopentacene from pseduocumene and three additional dibenzopentacene derivatives from naphthalene and/or phenanthrene starting materials [1a]. The syntheses focused on condensation cyclization reactions of keto-acids to form the penultimate quinones and ultimate polycycles.



Scheme 1.10

Cook, another key personality of the decade, began delineation of his work on carbon-rich systems in two published journal series, *Polycyclic Aromatic Hydrocarbons* [31] and *Production of Cancer by Pure Hydrocarbons*, [32] in the early 1930s. The motivation for the research was the structural basis for cancer-causing compounds and his methodology consisted of administering vapor and *in vivo* doses to laboratory rats. A large part of his synthetic work focused on derivatization of parent hydrocarbons to determine the extent of activity. A typical example was increasing the alkyl chain from methyl to isopropyl on benzanthracene [33] and monitoring tumor formation in rats. His elucidation of carcinogenic activity for his own structures as well as other compounds was a major step in the acknowledgement of health issues associated with highly fused polycycles.

Cook's early research efforts focused on isolating coal-tar components [34], such as perylene and benzoperylene, as well as developing synthetic routes to previously isolated compounds. In contrast to the numerous Zn-dust distillation cyclizations,

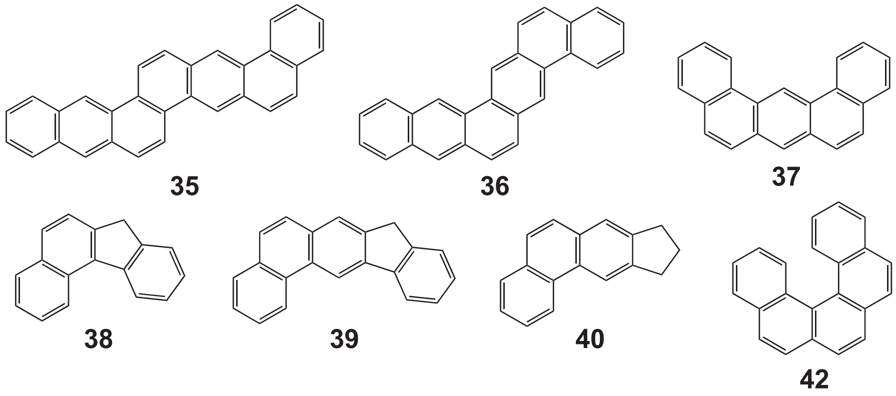
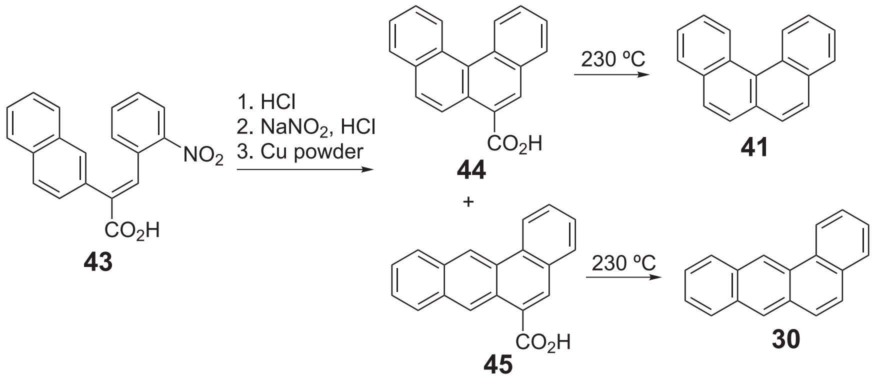


Figure 1.4. Structures **35**–**40** and **42**.

Cook utilized an atypical selenium dehydrogenation of a partially saturated keto-derivative to afford pyrene in 1934 [35]. Cook and coworkers also successfully synthesized several new polycycles and numerous derivatives through the process of their research. A few examples of novel systems produced include new isomers of benzopyrene, anthraceneotetraphene **35**, benzopentaphene **36**, dibenzanthracene **37**, as well as several condensed fluorene structures such as **38** and **39** (Fig. 1.4) [36]. Cook's formation of cyclopentenophenanthrene **40**, an important phenanthrene derivative used to produce several active natural products, was an early highlight of his career [37].

Through his synthetic research, Cook correctly elucidated the structure of several previously reported intermediates and hydrocarbons. His work on perylene and the first helicenes is of note. Although described in earlier 20th century literature by Weitzenböck and coworkers, as well as Mayer and Oppenheimer [38], confirmed isolation of the first two helicenes, tetra- **41** and pentahelicene **42**, did not occur until the early 1930s when Cook reinvestigated the work [39]. Early efforts with Pschorr methodology were shown to provide the desired product but also resulted in a mixture of polycyclic isomers when analyzed by increasingly detailed structural elucidation techniques. Cook determined that a Pschorr-like intermediate **43** of [4]helicene provided two distinct tetrabenzenoid fused carboxylic acids **44**, **45**, which lead to [4]helicene but also tetraphene (Scheme 1.11). He effectively separated **44** and **45** via their K and Na salts and characterized **30** and **41** via their picrate and quinone derivatives. For [5]helicene, Cook overcame the previous difficulties by separating the concurrently formed isomer, 1.2,5.6-dibenzanthracene, through the picrate. Although less significant in the [4]- and [5]helicenes, future helicenes would present a new facet in hydrocarbon chemistry due to their chirality resulting from steric overcrowding.

Optimization of an unsuccessful route initiated by Bentley et al. in 1907 ultimately led to the synthesis of the first hexa-annelated structure, hexacene, in 1939 by both Clar and Marschalk via two different routes [1a, 40]. In search of a hepta-



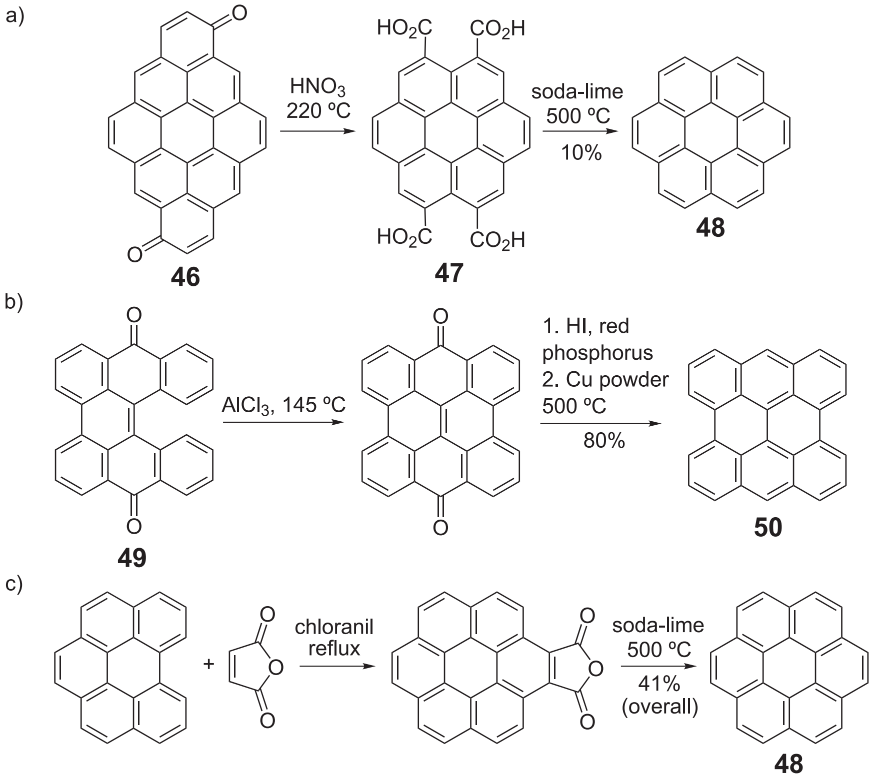
Scheme 1.11

annelated compound, Clar's initial efforts resulted in several quinone and hydroheptacene derivatives and ultimately to heptacene in 1942 in very low yield [1a]. An improved pathway confirming Clar's earlier success did not appear until a decade later when Bailey and Liao dehydrogenated a dihydroheptacene isomer with Pd/C at high temperature to afford the highly reactive heptacene in 76% yield [41]. Other early noteworthy efforts on linearly annelated structures include Marschalk's production of several hydroxyquinone and quinone derivatives of the unattainable octa-, nona-, and undecacenes in the early 1950s [42].

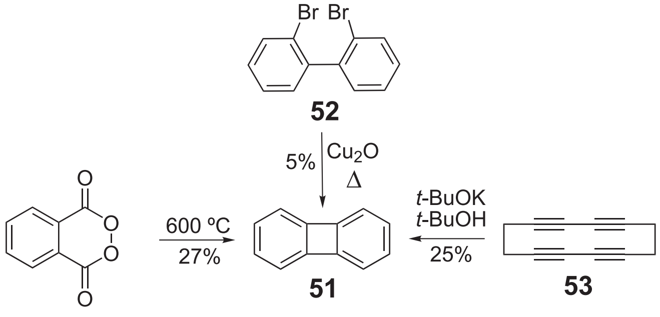
Scholl was the first to produce two fundamental polyarenes in the early 1930s that served as the basis for future benzenoid derivatives. Oxidation of dibenzoperopyrenequinone **46** with HNO_3 afforded intermediate **47** and subsequent decarboxylation with soda-lime provided coronene **48** (Scheme 1.12a) [43]. Two years later, effective reduction and dehydrogenation of his previously isolated bisanthenequinone **49** with HI and red phosphorus followed by Cu-mediated sublimation afforded bisanthene **50** (Scheme 1.12b) [44]. Clar effectively developed more efficient routes for both coronene (Scheme 1.12c) and bisanthene in the next decade [1a].

Clar further modified his Zn-dust reduction technique for quinone reduction in the late 1940s with the addition of pyridine and AcOH [1a]. The method proved much milder than previous Zn-reductions and allowed isolation of large polyarenes with decreased decomposition due to reduced reaction duration. For example, dibenzoperylenequinone was effectively reduced to dibenzoperylene [1a].

Lothrop's production of biphenylene **51** in 1941 from distillation of *o*,*o*′-dibromobiphenyl **52** with Cu_2O marked the first conclusive evidence for a stable, fused carbon-rich structure containing both four- and six-membered rings (Scheme 1.13) [45]. The history of biphenylene dates back to its first attempted manufacture in 1893 by Hosaeus, who isolated biphenyl instead [45]. All subsequent attempts prior to Lothrop utilizing Wurtz chemistry resulted in isomeric cycles or irreproducible results. Of the several routes developed after Lothrop, Wittig and Sondheimer completed the two most intriguing (Scheme 1.13). In 1961, Wittig successfully py-



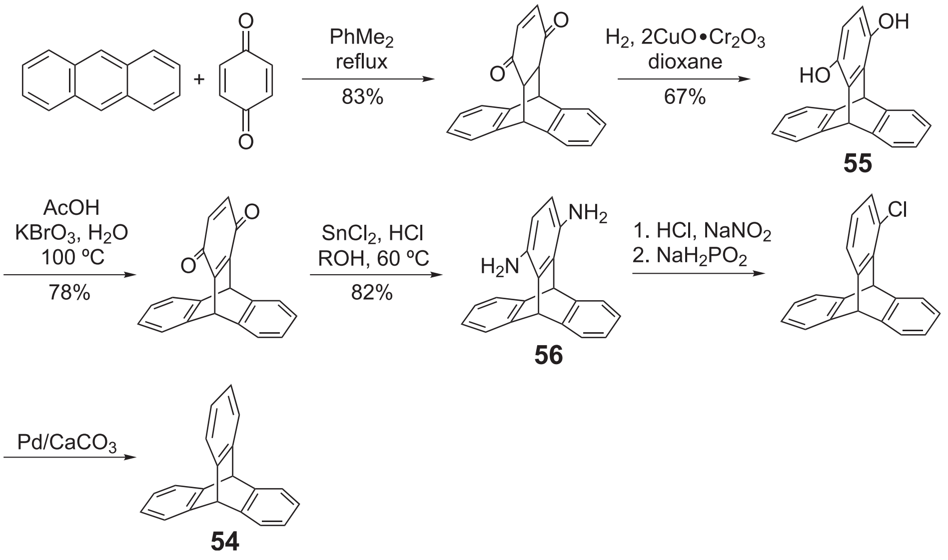
Scheme 1.12



Scheme 1.13

rolyzed phthalyl peroxide as well as subliming a mercury intermediate obtained from dilithiobiphenyl with Ag powder [46]. In 1962, Sondheimer treated cyclic tetraalkyne **53** with *tert*-BuOK [47]. The chemistry of biphenylene and larger derivatives is discussed by Miljanic and Vollhardt in Chapter 4.

One of the most remarkable molecules to originate in the 1940s was trypticene **54**, a 3-fold symmetrical structure named for the triptych of antiquity, a book with three leaves hinged on a common axis. Although Clar began initial work on the seven-step synthesis in the 1930s [1a], the hydrocarbon was finally isolated by Bartlett and coworkers in 1942 and originated from their efforts to elucidate the special properties of bridgehead substituents on bicyclic systems [48]. Diels-Alder reaction of anthracene and *p*-benzoquinone followed by reduction afforded dihydroxytriptycene **55**, which was finally reduced to triptycene after significant optimization (Scheme 1.14). Conversion of the hydroxy groups to halogen substitutents through the diamine intermediate **56** followed by Busch's heterogeneous reduction afforded **54** in low but unspecified yield.



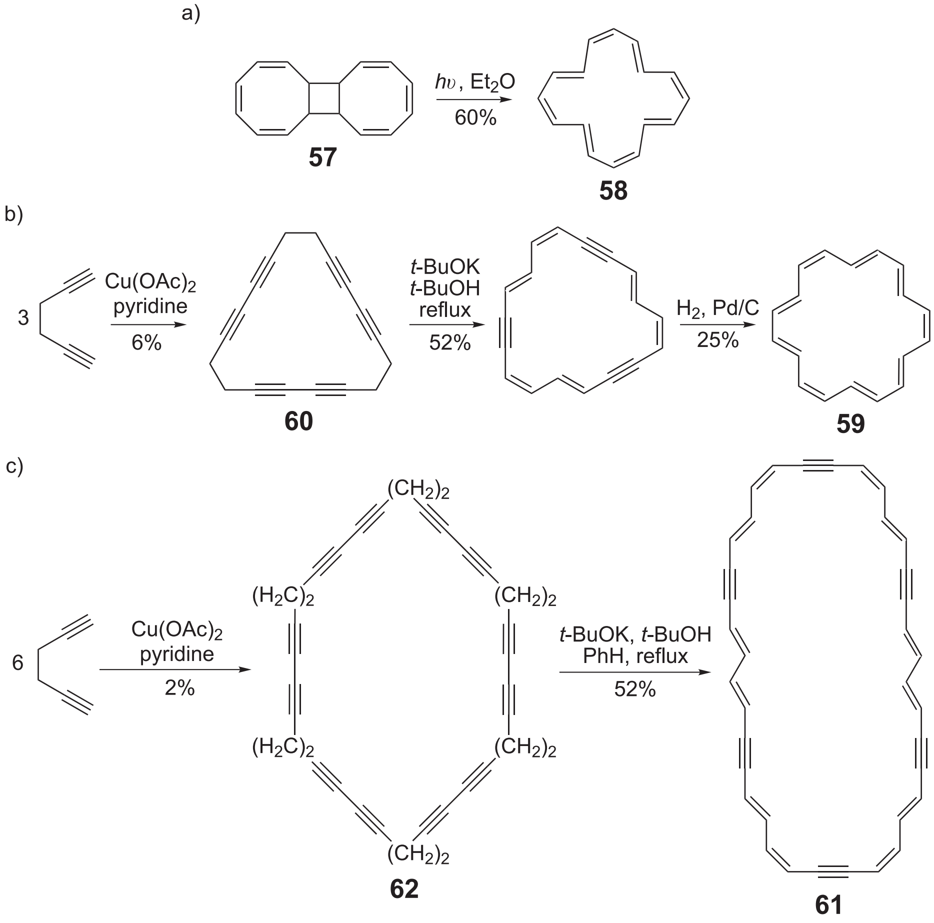
Scheme 1.14

1.5
1950–1969

After a decrease in new system development in the 1940s, the following two decades showed a sharp increase in polycyclic aromatic hydrocarbon production and diversity. The new benzenoid systems, mainly pyrene and perylene derivatives, represent the largest structures isolated prior to 1970. The introduction of the annulenes, radialenes, and fulvalenes are also of note during this time period. In addition to continued efforts by Clar, key personalities for these decades include Franz Sondheimer, Geoffrey Eglinton, Shōichi Misumi, Masazumi Nakagawa, and Georg Wittig.

1.5.1
The Annulenes, Dehydrobenzoannulenes, and Phenylacetylene Scaffolding

In the mid-1950s, Sondheimer and coworkers initiated their groundbreaking work on the annulenes and dehydroannulenes. The work was described in a publication series, *Unsaturated Macrocyclic Compounds*, [49] as well as several reviews [50]. The ensuing research probed the concept of aromaticity and set precedent for future alkyne chemistry. In addition to use of previously developed photolytic ring-opening routes by Schröder and Oth, Masamune, and van Tamelen, Sondheimer's group developed an oxidative coupling of terminal diacetylenes leading to macrocyclic polyacetylenes [50c]. An example of the previous method was photolysis of cyclooctatetraene dimer **57** to afford [16]annulene **58** (Scheme 1.15a). The synthesis of the first higher annulene, [18]annulene **59**, is an example of the latter.



Scheme 1.15

It occurred from an initial three-fold oxidative coupling of 1,5-hexadiyne to form macrocycle **60** followed by subsequent rearrangement and catalytic hydrogenation (Scheme 1.15b). With their new method, the group produced annulenes and dehydroannulenes with ring sizes ranging from 12 to 30 atoms. The configurational isomerism for Sondheimer's structures was probed through synthetic methods as well as interconversion of conformational isomerism via σ-bond rotation. One of the more spectacular systems developed by Sondheimer and coworkers was the large ring polyacetylene **61**, obtained from treatment of hexamer **62** with base (Scheme 1.15c) [51].

Concurrent with Sondheimer's annulenes, work on macrocyclic structures with ethynyl spacers between phenyl rings, known as dehydrobenzoannulenes, emerged in the chemical record. In the hope of isolating a dehydrobenzo[18]annulene, Eglinton and coworkers instead produced strained [12]annulene dimer **63** via high dilution oxidative conditions in 1960 (Fig. 1.5a) [52]. Isolation of a second dehydrobenzo[12]annulene **64** was reported in 1966 via successful trimerization of the cuprous salt of *o*-iodophenylacetylene in pyridine in 26% yield [53]. Staab et al. simultaneously reported production of **64** via an alternative, multistep pathway [54]. Several other novel phenylacetylene macrocycles appeared in the 1960s, a representative example being Akiyama and Nakagawa's successful dimerization of 1,8-diethynylanthracene with $Cu(OAc)_2$ and pyridine to afford **65** (Fig. 1.5a) [55]. Werz and Gleiter discuss current advances in diyne macrocycle chemistry in Chap-

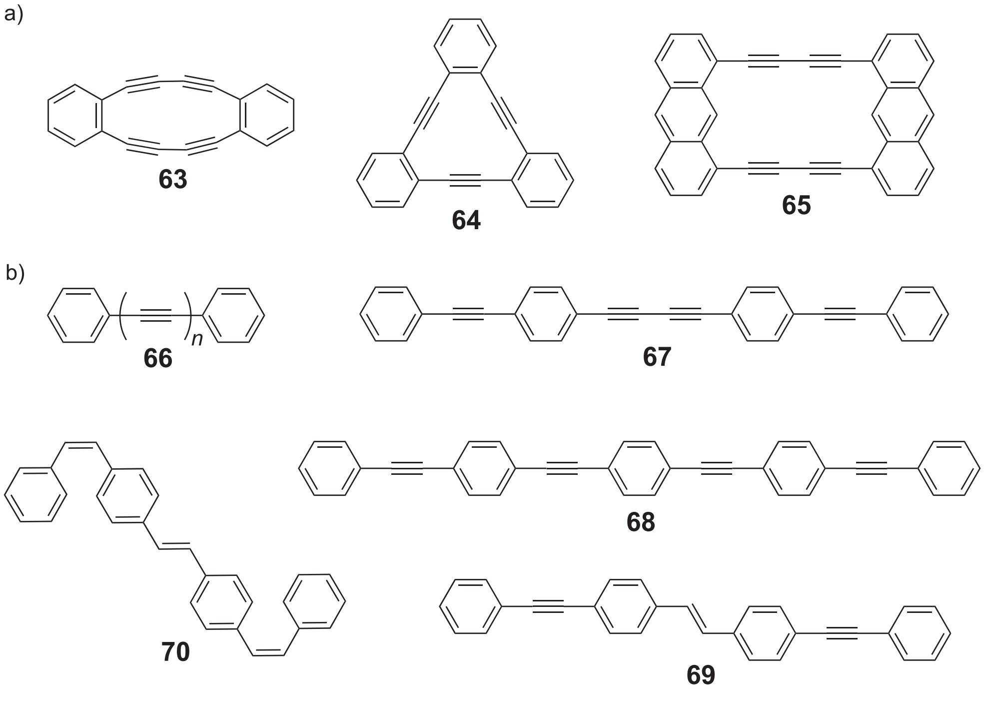


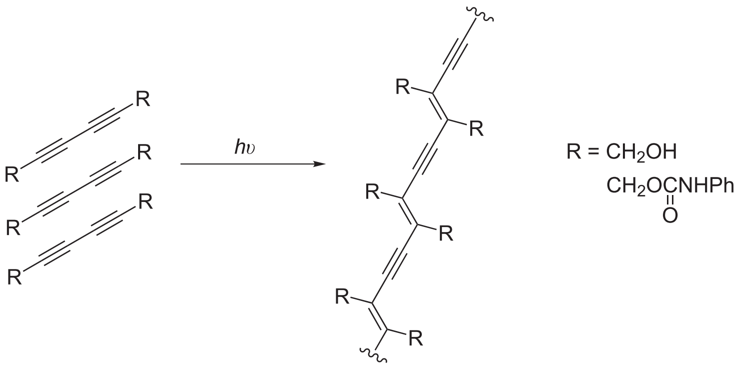
Figure 1.5. (a) Structures **63**–**65**, (b) structures **66**–**70**.

ter 7, whereas Campbell and Tykwinski outline chiral carbon-rich macrocycles in Chapter 6.

Expansion in the diphenylpolyacetylene series past Graebe's original dimer began in the early 1950s with the near simultaneous efforts of two groups. In 1951, both Schlubach and coworkers [56] and Nakagawa [57] reported isolation of diphenyltriyne **66** ($n = 3$) and diphenyltetrayne **66** ($n = 4$) (Fig. 1.5b). Schlubach used a combination of Grignard homocoupling and polyacetylenediol condensations to produce the products. In the same year, Schlubach and coworkers also reported synthesis of the pentamer **66** ($n = 5$) [58]. Three years later, Whiting and coworkers produced hexayne ($n = 6$) and octayne ($n = 8$) derivatives of **66** via either oxidative homocoupling of triyne precursors with CuCl or treatment of ene-yne-glycol intermediates with $SOCl_2$, respectively [59]. Modern polyyne chemistry is summarized by Yam and Tao in Chapter 10.

Even though the octayne derivative marked the longest linear diphenylpolyacetylene, multiple phenylacetylene scaffold topologies were developed in the following decade. Representative examples include carbon rods **67** and **68** produced by Misumi in 1961 (Fig. 1.5b) [60]. Misumi and coworkers also produced several mixed hybrid scaffolds combining ethenyl and ethynyl spacers, such as **69** (Fig. 1.5b) as well as conformational isomeric ethenyl rods, such as **70**, in 1962 [61]. Meier further discusses defined-length carbon-rich oligomers in Chapter 11, and the use of carbon-rich molecules as molecular wires is presented by Harriman and Ziessel in Chapter 2.

In 1969, Wegner reported the formation of polydiacetylene **71** via topochemical polymerization of substituted diacetylenes in the solid state (Scheme 1.16) [62]. The ene-yne polymeric structure was the result of multiple 1,4-additions between adjacent molecules. Wegner originally utilized different monomeric functional groups and determined that those capable of H-bonding, such as urethanes and diols, provided the necessary intermolecular alignment to facilitate the conjugate addition. Fowler and Lauher further elaborate on solid-state formation and chemistry of polydiacetylene and polytriacetylene in Chapter 5.



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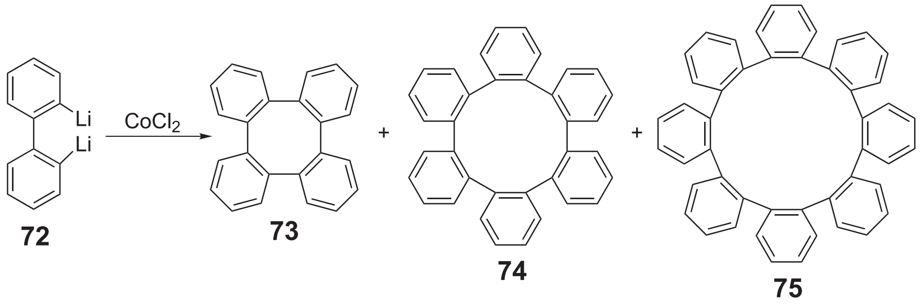
Scheme 1.16

1.5.2
Fused Polycyclic and *peri*-Condensed Benzenoid Systems

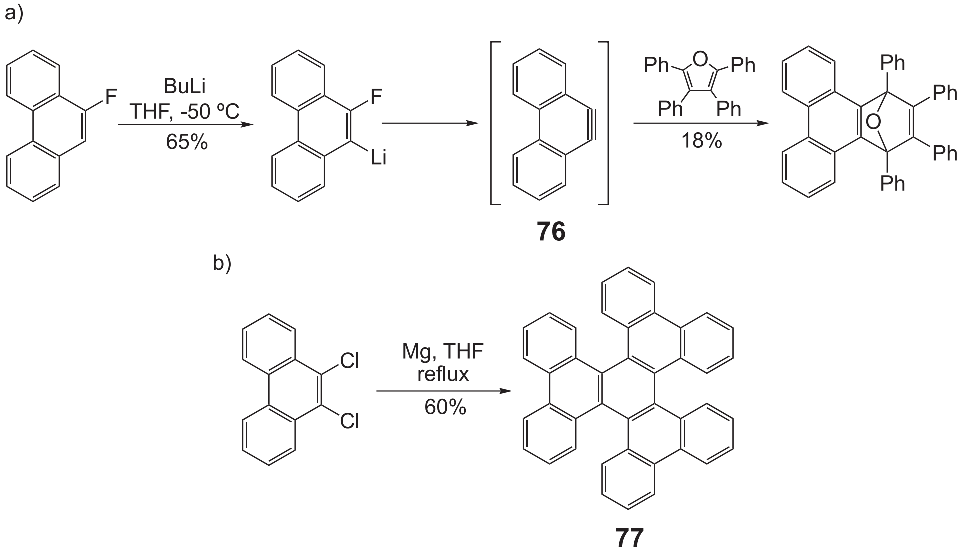
In addition to his numerous other achievements, application of benzyne chemistry to carbon-rich polyarenes in the 1950s was a signature mark of Georg Wittig. Fourteen years after the first lengthy production of triptycene, Wittig and Ludwig effectively prepared triptycene in 28% yield in one step from anthracene, *o*-bromofluorobenzene, and Mg [63]. Another excellent example was the synthesis of 1.2,6.7-dibenzopyrene from 2,2′-dilithiobiphenyl and $TiCl_4$ via a suspected tetrabenzyne intermediate in 1957 [64]. Although produced in 1943 via Grignard reaction [65], Wittig and coworkers reacted dilithiobiphenyl **72** with $CoCl_2$ to afford tetraphenylene **73** in 3% yield (Scheme 1.17) [64]. The reaction simultaneously produced hexaphenylene **74** (1%), octaphenylene **75** (17.5%), biphenyl (16%), *o*-quaterphenyl (<1%), and *o*-sexiphenyl (1%). Substitution of $NiCl_2$ for the metal complex provided only **73** and biphenyl in 46% and 12% yield, respectively. Other notable successes include phenanthryne **76** (Scheme 1.18a), obtained from BuLi and 9-fluorophenanthrene, and its subsequent reaction with anthracene and tetraphenylfuran to form interesting adducts [66]. In 1959, Carey and Millar trimerized a phenanthryne intermediate obtained from 9,10-dichlorophenanthrene to afford hexabenzotriphenylene **77** via a similar route to Wittig's triphenylene route (Scheme 18b) [67].



Scheme 1.17

The late 1950s saw several expanded biphenylene topologies. Some of the more notable include Cava's 1,2-benzobiphenylene **78** (Fig. 1.6a) obtained through a highly reactive benzocyclobutadiene [68] as well as his production of 1.2,7.8-dibenzobiphenylene **79**, a structure similar to [4]helicene [69]. One of the more spectacular biphenylene derivatives was Nenitzescu and coworkers' bulky 1,2,5,8-tetraphenyl-2.3,6.7-dibenzobiphenylene **80** produced by Diels-Alder chemistry in 1962 (Scheme 1.19) [70].

With the exception of fluoranthene, which was synthetically isolated in the 1930s by von Braun and Anton [71], and decacyclene, a key signature of 1950s chemistry was the rapid expansion of conjugated, fused systems with five-membered rings.



Scheme 1.18

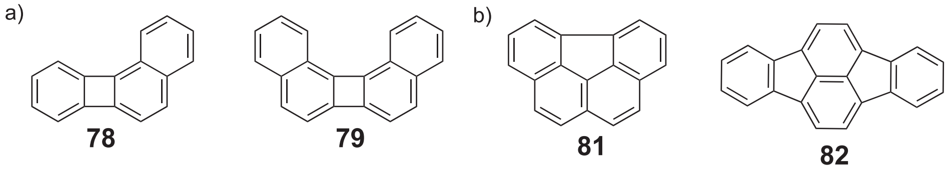
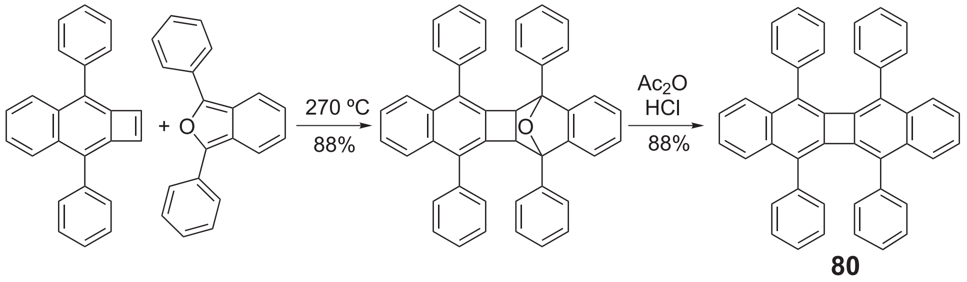
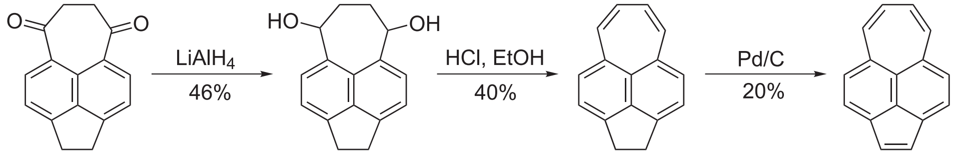


Figure 1.6. (a) Structures **78** and **79**, (b) structures **81** and **82**.



Scheme 1.19

The noteworthy investigators of these systems include Clar, Campbell, Lang, and Aitken. The majority of systems developed were benzo-derviatives of fluoranthene, benzofluoranthene **81** (Fig. 1.6b), and phenylenefluoranthene **82** [1a, 72]. Some of the more novel systems included an additional fused seven-membered ring. In 1956, Boekelheide and coworkers produced acepleiadylene **83**, unique in structure due to fusion of three ring sizes [73]. Starting from previously isolated diketone **84**,

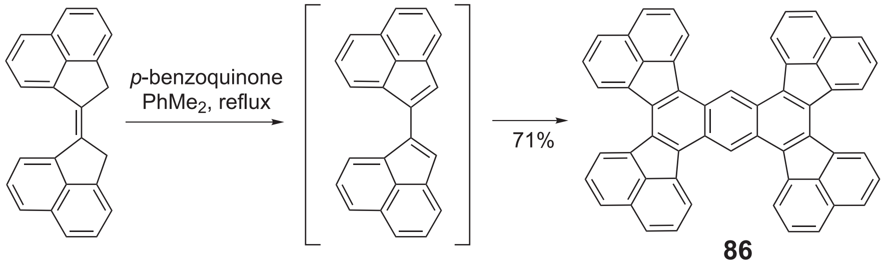


84 **85** **83**

Scheme 1.20

reduction and acid-catalyzed dehydration afforded acepleiadiene **85** (Scheme 1.20). Subsequent dehydrogenation with Pd/C produced the unsaturated **83** in 20% yield. Reid and coworkers produced a constitutional isomer of **83** one year earlier [74].

In addition to development of several novel benzofluoranthene systems, including **81**, 2.13,11.12-dibenzofluoranthene, and multiple naphthofluoranthene isomers, Campbell's key contribution was that of obtaining new routes to older fused systems, such as 10.11-benzofluoranthene and 2.3,6.7-dibenzofluoranthene [75]. The largest and most spectacular example of the fused systems, though, occurred in 1959 when Zander produced 1.2,3.4,5.6,7.8-tetra-(peri-naphthylene)-anthracene **86** via a two-fold Diels-Alder cyclization (Scheme 1.21) [76].



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Scheme 1.21

Although the majority of their work focused on saturated systems, Blood and Linstead produced dibenzopentalene **87**, one of the first stable, fully conjugated analogs containing two fused five-membered rings (Fig. 1.7a). Published in their series *Fused Carbon Rings* in 1952, the authors successfully converted a dihydropentalene intermediate into a dibromide and subsequently reduced the ultimate precursor with silver acetate [77]. The next stable carbon-rich pentalene derivative did not occur until 1962 when Le Goff produced hexaphenylpentalene **88** in excellent yield (77%) from NBS oxidation of a hexaphenyldihydropentalene precursor (Fig. 1.7a) [78]. Le Goff's structure remained the only nonbenzenoid stabilized pentalene until the early 1970s.

The 1950s and 1960s also saw work on a number of linearly-annelated benzenoid derivatives of the highly reactive hexa- and heptacene as well as the first octacene derivative. One notable structural motif present in all of the analogs is a pyr-

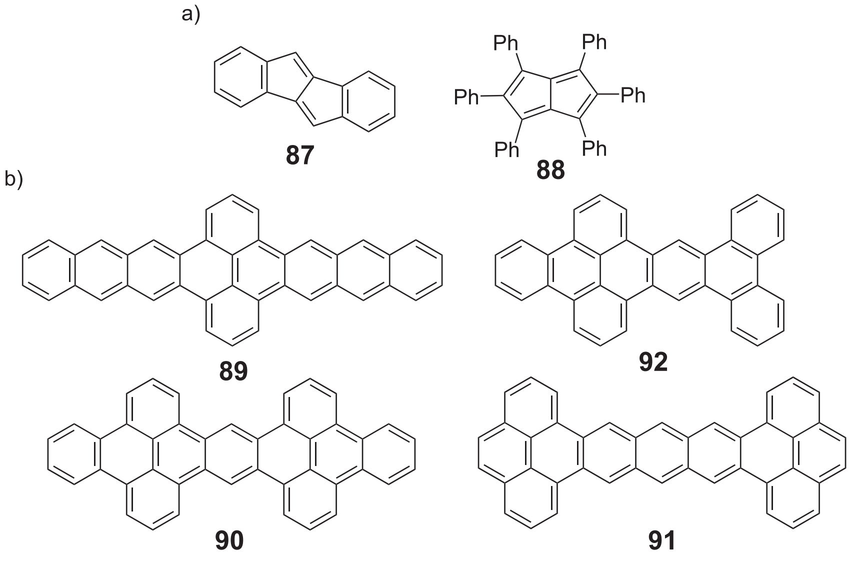


Figure 1.7. (a) Structures **87** and **88**, (b) structures **89**–**92**.

ene ring, which likely added stability over purely linear structures. Key proprietors for these molecules were Clar, Boggaino, Zander, Guye-Vuilleme, MacPherson, and McCallum. Dibenzoctacene **89** (Fig. 1.7b) was produced in 1963 by Clar and coworkers via two-fold condensation of derivatized naphthalene compounds to a central substituted-pyrene [1a]. Di- and tetrabenzoheptacene, **90** and **91**, both produced by Clar and coworkers in the 1960s, represent the two heptacene derivatives [1a]. Clar also produced the bulkiest pentacene derivative, tetrabenzopentacene **92**, in 1956 in a similar fashion to his other pentacene derivatives in the preceding decade [1a].

The largest fused benzenoid systems developed prior to 1970 were based on perylene, peropyrene **93**, terrylene **94**, coronene, and bisanthene (Fig. 1.8). Also responsible for terrylene, Clar and coworkers produced three additional benzenoid derivatives as well as circumanthrene **95**, isolated from two-fold condensation of tetracene derivatives in 1956 [1a]. Halleux and coworkers obtained tetrabenzobisanthene **96** from Zn-dust dimerization of dibenzoperinaphthone [79]. Synthesized by Clar in the same year [1a], hexabenzocoronene **97** was produced by Halleux and coworkers in 1958 from a NaCl–ZnCl melt of hexaphenylbenzene [79].

1.5.3
The Helicenes, Radialenes, Fulvalenes, and Circulenes

A resurgence in helicene chemistry occurred in 1956 when Newman and Lednicer reported production of phenanthro[3,4-*c*]phenanthrene or hexahelicene **98**, which displayed the stereotypical chirality resultant from steric overcrowding [80]. The

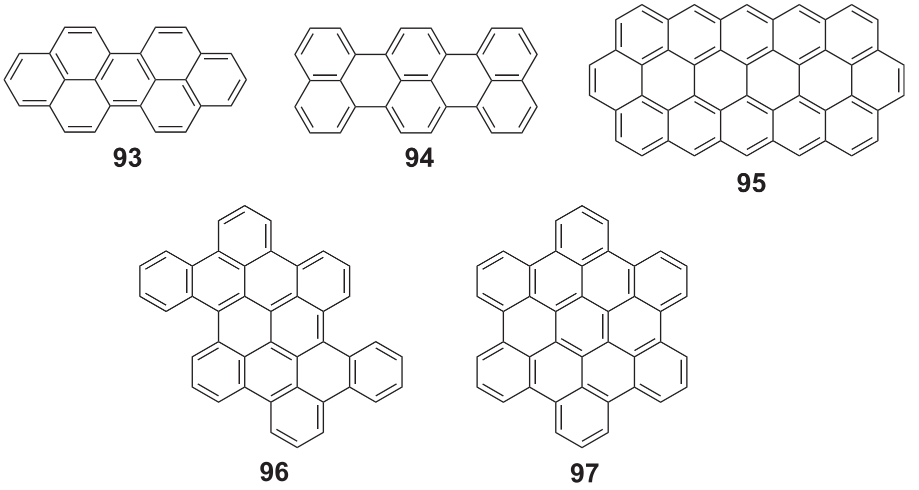


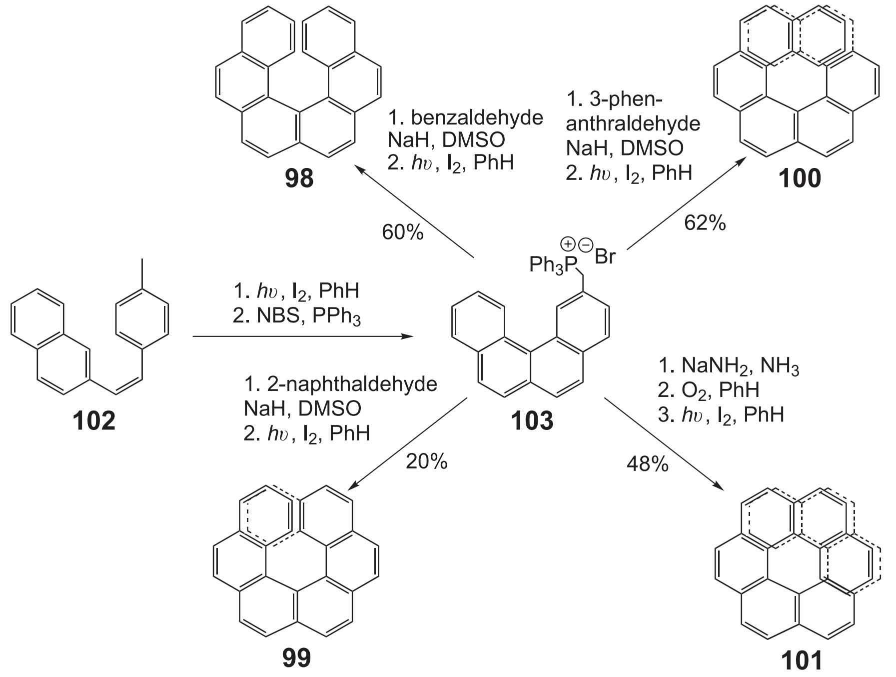
Figure 1.8. Structures **93**–**97**.

lengthy ten-step synthesis quickly introduced four of the six final benzene rings but required considerable optimization for the final steps resulting in an overall yield of less than 2%.

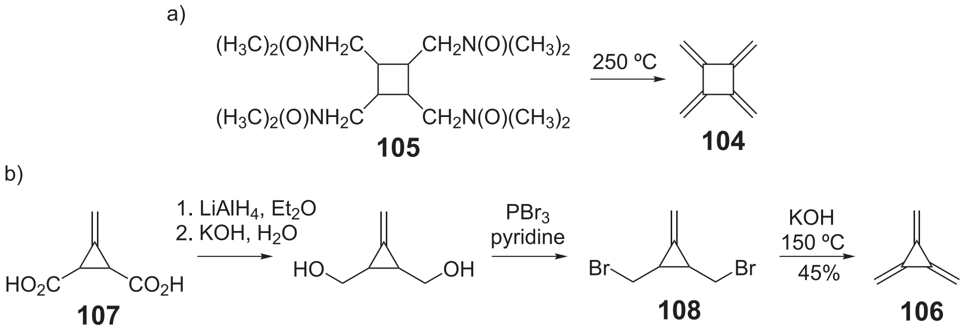
A key basis for modern helicene cyclization chemistry occurred in 1964 when Wood and Mallory effectively prepared phenanthrene via photochemical induced cyclization of stilbene [81]. The new method effectively provided efficient pathways to substituted phenanthrene derivatives, easier access to existing and new helicene structures, as well as sufficient quantities for property studies. In the mid 1960s, Martin and coworkers successfully isolated the previously made hexahelicene as well as new hepta- **99**, octa- **100**, and nonahelicenes **101** via highly efficient syntheses (Scheme 1.22) [82]. These preparations culminated in photo-induced cyclization of bisarylethylenes with an I_2 oxidant and Hg-lamp radiation source. The key improvements over previous efforts included production of a phenanthrene derivative via photo-induced cyclization of intermediate **102** and subsequent conversion to Wittig ylide **103**, a common intermediate to the four helicenes.

The 1960s also saw the appearance of the alicyclic radialenes, unique in that all ring carbons are sp^2 hybridized and double bonds are semicyclic. The production of tetramethylenecyclobutane or [4]radialene **104** from pyrolysis of a tetraamin-oxide-substituted cyclobutane **105** in 1962 by Griffin and Peterson marked the first appearance of the non-alkyl substituted **104** (Scheme 1.23a) [83]. The first parent [3]radialene or trimethylenecyclopropane **106** was produced by Dorko in 1965 [84] and Griffin and coworkers in 1966 [85]. Dorko reduced Feist's acid **107** to arrive at the dibromide **108** and then applied a base-induced β-elimination to obtain **106** (Scheme 1.23b). Griffin and coworkers obtained **106** from a triiodide as well as the trisquaternary hydroxide in lower yields.

Pentafulvalene and heptafulvalene **109**, the first symmetrical fulvalenes, were iso-

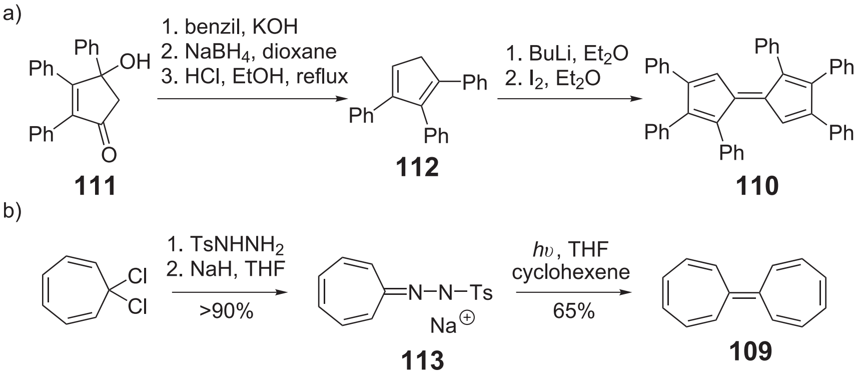


Scheme 1.22



Scheme 1.23

lated in the late 1950s by Doering [86]. A more complicated example, 1,2,3,1′,2′,3′-hexaphenylpentafulvalene **110**, was produced by Pauson and Williams in 1961 [87]. Ketone **111** was reduced and then dehydrogenated to triphenylcyclopentadiene **112** with HCl (Scheme 1.24a). Treatment of **112** with BuLi and then oxidation with iodine afforded the substituted fulvalene. Jones and Ennis developed a significant improvement for **109** in the late 1960s. Tosyl hydrazone salt **113** was obtained from 7,7-dichlorocycloheptatriene and subsequently photolyzed with cyclohexene



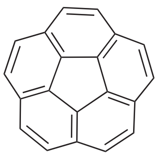
Scheme 1.24

to afford the fulvalene (Scheme 1.24b) [88]. Initial work on asymmetrical fulvalenes, such as heptapentafulvalene, began in the 1960s by Prinzbach and coworkers [89].

Barth and Lawton's production of [5]circulene or corannulene **114** (Fig. 1.9) in 1966 [90] was a significant achievement due to the fullerene-based, nonplanar structure of **114**. The 17-step synthesis began with acenaphthene and relied on alkylation, condensation, and Pd-catalyzed aromatization reactions to afford the macrocycle. The following decade would see continued efforts to isolate [7]circulene **115** (Fig. 1.9) but another decade would pass before **115** was successfully produced [1d]. Sygula and Rabideau discuss more recent work on buckybowls and fullerene fragments in Chapter 12, whereas fullerene reactivity is outlined by Kitagawa, Murata, and Komatsu in Chapter 9.

1.6
1970–Present: The Way Ahead

Chemistry research on carbon-rich molecules following that outlined here has produced and continues to produce remarkable structures in size, topology, and spatial orientation. The accomplishments of early chemists though are truly remarkable in the light of current synthetic and analytical techniques that modern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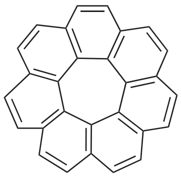
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Figure 1.9. Structures **114** and **115**.

chemists take for granted. It is unfortunate that the majority of the pioneers' efforts resulted in low yields and thus insufficient quantities for system property studies – a common theme in early synthetic chemistry. Regardless, without the groundbreaking work of early chemists such as Glaser, Scholl, and Clar, current carbon-rich molecule methodology and progress would not have achieved its present status or its future potential.

References

1 (a) E. Clar, *Polycyclic Hydrocarbons*, Vol. *I–II*, Academic Press, London, **1964**; (b) A. T. Balaban, M. Banciu, V. Ciorba, *Annulenes, Benzo-, Hetero-, Homo-, Derivatives, and their Valence Isomers, Volumes I–III*, CRC, Boca-Raton, **1987**; (c) R. G. Harvey, *Polycyclic Aromatic Hydrocarbons*, Wiley-VCH, New York, **1997**; (d) H. Hopf, *Classics in Hydrocarbon Chemistry*, Wiley-VCH, Weinheim, **2000**; (e) D. Astruc (Ed.), *Modern Arene Chemistry*, Wiley-VCH, Weinheim, **2002**.

2 C. Graebe, *Ber. Dtsch. Chem. Ges.* **1874**, *7*, 1623–1628, 1629–1630.

3 B. Radziszewski, *Ber. Dtsch. Chem. Ges.* **1876**, *9*, 260–262.

4 K. F. Lang, H. Buffleb, J. Kalowy, *Chem. Ber.* **1957**, *90*, 2888–2893.

5 A. v. Baeyer, *Ann. Chem. Pharm.* **1866**, *140*, 295–313.

6 R. Pschorr, *Ber. Dtsch. Chem. Ges.* **1896**, *29*, 496–501.

7 H. Klinger, C. Lonnes, *Ber. Dtsch. Chem. Ges.* **1896**, *29*, 2152–2156, 2157–2158, 2158–2160.

8 F. Riese, *Ann. Chem. Pharm.* **1872**, *164*, 161–176.

9 (a) C. E. Linebarger, *Am. Chem. J.* **1892**, *14*, 597–602; (b) W. R. Orndorff, F. K. Cameron, *Am. Chem. J.* **1895**, *17*, 659–681; (c) C. E. Linebarger, *J. Am. Chem. Soc.* **1895**, *17*, 354–358.

10 (a) S. Gabriel, A. Michael, *Ber. Dtsch. Chem. Ges.* **1877**, *10*, 2199–2210; (b) F. Nathanson, *Ber. Dtsch. Chem. Ges.* **1893**, *26*, 2576–2582; (c) S. Gabriel, E. Leupold, *Ber. Dtsch. Chem. Ges.* **1898**, *31*, 1159–1174.

11 Cited in Ref 1e: M. Berthelot, *Ann. Chem. Pharm.* **1867**, *141*, 173–184.

12 C. Glaser, *Ber. Dtsch. Chem. Ges.* **1869**, *2*, 422–424.

13 A. Baeyer, L. Landsberg, *Ber. Dtsch. Chem. Ges.* **1882**, *15*, 50–56, 57–61.

14 (a) T. F. Rutledge, *Acetylenic Compounds*, Reinhold Book Corp., New York, **1968**; (b) P. Siemsen, R. C. Livingston, F. Diederich, *Angew. Chem.* **2000**, *112*, 2740–2767; *Angew. Chem. Int. Ed. Engl.* **2000**, *39*, 2632–2657.

15 C. Mannich, *Ber. Dtsch. Chem. Ges.* **1907**, *40*, 159–165.

16 F. Ullmann, G. M. Meyer, O. Loewenthal, E. Gilli, *Liebigs Ann.* **1904**, *332*, 38–81.

17 Cited in Ref 1a: (a) W. Löb, *Z. Elektrochem.* **1901**, *7*, 903; (b) W. Löb, *Z. Elektrochem.* **1902**, *8*, 777.

18 D. Vorländer, C. Siebert, *Ber. Dtsch. Chem. Ges.* **1906**, *39*, 1024–1035.

19 R. Scholl, C. Seer, R. Weitzenböck, *Ber. Dtsch. Chem. Ges.* **1910**, *43*, 2202–2209.

20 R. Weitzenböck, *Monatsh. Chem.* **1913**, *34*, 193–223.

21 (a) K. Dziewoński, *Ber. Dtsch. Chem. Ges.* **1903**, *36*, 962–971; (b) P. Rehländer, *Ber. Dtsch. Chem. Ges.* **1903**, *36*, 1583–1587.

22 K. Dziewoński, S. Suknarowski, *Ber. Dtsch. Chem. Ges.* **1918**, *51*, 457–465.

23 C. Moureu, C. Dufraisse, P. M. Dean, *C. R. Acad. Sci., Paris* **1926**, *182*, 1440–1443.

24 (a) C. Moureu, C. Dufraisse, G. Berchet, *C. R. Acad. Sci., Paris* **1927**, *185*, 1085–1087; (b) C. Dufraisse, *Bull. Soc. Chim. Fr.* **1936**, *3*, 1847–1857, 1857–1872; (c) C. Dufraisse, R.

Hoclois, *Bull. Soc. Chim. Fr.* **1936**, *3*, 1873–1880, 1880–1983, 1894–1905; (d) C. Dufraisse, L. Veluz, *Bull. Soc. Chim. Fr.* **1936**, *3*, 1905–1913.

25 (a) O. Gerngross, M. Dunkel, *Ber. Dtsch. Chem. Ges.* **1924**, *57*, 739–746; (b) O. Gerngross, C. Schachnow, R. Jonas, *Ber. Dtsch. Chem. Ges.* **1924**, *57*, 747–750.

26 R. Pummerer, K. Bittner, *Ber. Dtsch. Chem. Ges.* **1924**, *57*, 84–88.

27 E. Clar, D. G. Stewart, *J. Am. Chem. Soc.* **1954**, *76*, 3504–3507 and references contained therein.

28 E. Clar, F. John, *Ber. Dtsch. Chem. Ges.* **1930**, *63*, 2967–2977.

29 W. Ried, F. Anthöfer, *Angew. Chem.* **1953**, *65*, 601.

30 V. Brückner, A. Karczag, K. Körmendy, M. Meszag, J. Tomasz, *Tetrahedron Lett.* **1960**, 5–6.

31 J. W. Cook, R. S. Ludwiczak, R. Schoental, *J. Chem. Soc.* **1950**, 1112–1121 and references contained therein.

32 G. M. Badger, J. W. Cook, C. L. Hewett, E. L. Kennaway, N. M. Kennaway, R. H. Martin, *Proc. R. Soc. London, Ser. B* **1942**, *131*, 170–182 and references contained therein.

33 (a) G. M. Badger, J. W. Cook, F. Goulden, *J. Chem. Soc.* **1940**, 16–18; (b) J. W. Cook, A. M. Robinson, *J. Chem. Soc.* **1940**, 303–304.

34 J. W. Cook, C. Hewett, I. Hieger, *Nature* **1932**, *130*, 926.

35 J. W. Cook, C. L. Hewett, *J. Chem. Soc.* **1934**, 365–377.

36 (a) J. W. Cook, *J. Chem. Soc.* **1931**, 489–499, 499–507; **1932**, 1472–1484; (b) J. W. Cook, C. L. Hewett, I. Hieger, *J. Chem. Soc.* **1933**, 395–396, 396–398; (c) J. W. Cook, C. L. Hewett, *J. Chem. Soc.* **1933**, 398–405; (d) J. W. Cook, A. Dansi, C. L. Hewett, J. Iball, W. V. Mayneord, E. Roe, *J. Chem. Soc.* **1935**, 1319–1325.

37 J. W. Cook, C. L. Hewett, *J. Chem. Soc.* **1933**, 1098–1111.

38 (a) R. Weitzenböck, H. Lieb, *Monatsh. Chem.* **1912**, *33*, 549–565; (b) R. Weitzenböck, A. Klinger, *Monatsh. Chem.* **1918**, *39*, 315–324.

39 J. W. Cook, *J. Chem. Soc.* **1931**, 2524–2528, 2529–2532; **1933**, 1592–1597.

40 (a) W. H. Bentley, A. Friedl, F. Thomas, C. Weizmann, *J. Chem. Soc.* **1907**, 411–435; (b) W. H. Bentley, A. Friedl, C. Weizmann, *J. Chem. Soc.* **1907**, 1588–1593; (c) C. Marschalk, *Bull. Soc. Chim. Fr.* **1939**, 6, 1112–1121, 1122–1125.

41 W. J. Bailey, C.-W. Liao, *J. Am. Chem. Soc.* **1955**, *77*, 992–993.

42 (a) C. Marschalk, *Bull. Soc. Chim. Fr.* **1938**, *5*, 306–308; **1941**, *8*, 354–369; **1950**, *16*, 311–317.

43 R. Scholl, K. Meyer, *Ber. Dtsch. Chem. Ges.* **1932**, *65*, 902–915.

44 (a) R. Scholl, J. Mansfeld, *Ber. Dtsch. Chem. Ges.* **1910**, *43*, 1734–1746; (b) R. Scholl, K. Meyer, *Ber. Dtsch. Chem. Ges.* **1934**, *67*, 1236–1238.

45 W. C. Lothrop, *J. Am. Chem. Soc.* **1941**, *63*, 1187–1191.

46 (a) G. Wittig, H. F. Ebel, *Liebigs Ann.* **1961**, *650*, 20–34; (b) G. Wittig, W. Herwig, *Chem. Ber.* **1954**, *87*, 1511–1512.

47 R. Wolovsky, F. Sondheimer, *J. Am. Chem. Soc.* **1962**, *84*, 2844–2845.

48 P. D. Bartlett, M. J. Ryan, S. G. Cohen, *J. Am. Chem. Soc.* **1942**, *64*, 2649–2653.

49 I. T. Storie, F. Sondheimer, *Tetrahedron Lett.* **1978**, 4567–4568 and references contained therein.

50 (a) F. Sondheimer, *Proc. R. Soc. London, Ser. A* **1967**, *297*, 173–204; (b) F. Sondheimer, *Pure Appl. Chem.* **1971**, *23*, 331–353; (c) F. Sondheimer, *Acc. Chem. Res.* **1972**, *5*, 81–91.

51 (a) F. Sondheimer, Y. Amiel, R. Wolovsky, *J. Am. Chem. Soc.* **1959**, *81*, 4600–4606; (b) F. Sondheimer, R. Wolovsky, *J. Am. Chem. Soc.* **1962**, *84*, 260–269.

52 O. M. Behr, G. Eglinton, A. R. Galbraith, R. A. Raphael, *J. Chem. Soc.* **1960**, 3614–3625.

53 I. D. Campbell, G. Eglinton, W. Henderson, R. A. Raphael, *Chem. Commun.* **1966**, 87–89.

54 H. A. Staab, F. Graf, *Tetrahedron Lett.* **1966**, 751–757.

55 S. Akiyama, M. Nakagawa, *Chem. Ind.* **1960**, 346–347.

56 H. H. Schlubach, V. Franzen, *Liebigs Ann.* **1951**, *573*, 115–120.
57 M. Nakagawa, *Chem. Abstr.* **1951**, *45*, 7081, 8486.
58 H. H. Schlubach, V. Franzen, *Liebigs Ann.* **1951**, *572*, 105–110.
59 J. B. Armitage, N. Entwistle, E. R. H. Jones, M. C. Whiting, *J. Chem. Soc.* **1954**, 147–154.
60 S. Misumi, *Bull. Chem. Soc. Jpn.* **1961**, *34*, 1827–1832.
61 S. Misumi, M. Kuwana, M. Nakagawa, *Bull. Chem. Soc. Jpn.* **1962**, *35*, 135–142.
62 G. Wegner, *Z. Naturforsch. B: Chem. Sci.* **1969**, *24*, 824–832; *Makromol. Chem.* **1970**, *134*, 219–229.
63 G. Wittig, R. Ludwig, *Angew. Chem.* **1956**, *68*, 40.
64 G. Wittig, G. Lehmann, *Chem. Ber.* **1957**, *90*, 875–892.
65 W. S. Rapson, R. G. Shuttleworth, J. N. van Niekerk, *J. Chem. Soc.* **1943**, 326–327.
66 G. Wittig, W. Uhlenbrock, P. Weinhold, *Chem. Ber.* **1962**, *95*, 1692–1702.
67 J. G. Carey, I. T. Millar, *J. Chem. Soc.* **1959**, 3144–3146.
68 M. P. Cava, D. R. Napier, *J. Am. Chem. Soc.* **1957**, *79*, 1701–1705; **1958**, *80*, 2255–2257.
69 M. P. Cava, J. F. Stucker, *J. Am. Chem. Soc.* **1955**, *77*, 6022–6026.
70 C. D. Nenitzescu, M. Avram, I. G. Dinulescu, G. Mateescu, *Liebigs Ann.* **1962**, *653*, 79–85.
71 J. v. Braun, E. Anton, *Ber. Dtsch. Chem. Ges.* **1929**, *62*, 145–151.
72 (a) N. Campbell, D. H. Reid, *J. Chem. Soc.* **1952**, 3281–3284; (b) H. W. D. Stubbs, S. H. Tucker, *J. Chem. Soc.* **1951**, 2936–2939.
73 (a) V. Boekelheide, W. E. Langeland, C.-T. Liu, *J. Am. Chem. Soc.* **1951**, *73*, 2432–2435; (b) V. Boekelheide, G. K. Vick, *J. Am Chem. Soc.* **1956**, *78*, 653–658.
74 D. H. Reid, W. H. Stafford, J. P. Ward, *J. Chem. Soc.* **1955**, 1193–1201.
75 (a) N. Campbell, H. Wang, *J. Chem. Soc.* **1949**, 1513–1515; (b) N. Campbell, N. M. Khanna, A. Marks, *J. Chem. Soc.* **1951**, 2511–2512; (c) N. Campbell, A. Marks, D. H. Reid, *J. Chem. Soc.* **1950**, 3466–3470; (d) N. Campbell, A. Marks, G. V. McHattie, *J. Chem. Soc.* **1955**, 1190–1192.
76 M. Zander, *Chem. Ber.* **1959**, *92*, 2740–2743.
77 C. T. Blood, R. P. Linstead, *J. Chem. Soc.* **1952**, 2263–2268.
78 E. Le Goff, *J. Am. Chem. Soc.* **1962**, *84*, 3975–3976.
79 A. Halleux, R. H. Martin, G. S. D. King, *Helv. Chim. Acta* **1958**, *41*, 1177–1183.
80 M. S. Newman, D. Lednicer, *J. Am. Chem. Soc.* **1956**, *78*, 4765–4770.
81 C. S. Wood, F. B. Mallory, *J. Org. Chem.* **1964**, *29*, 3373–3377.
82 (a) M. Flammang-Barbieux, J. Nasielski, R. H. Martin, *Tetrahedron Lett.* **1967**, 743–744; (b) R. H. Martin, M. Flammang-Barbieux, J. P. Cosyn, M. Gelbcke, *Tetrahedron Lett.* **1968**, 3507–3510.
83 G. W. Griffin, L. I. Peterson, *J. Am. Chem. Soc.* **1962**, *84*, 3398–3400.
84 E. A. Dorko, *J. Am. Chem. Soc.* **1965**, *87*, 5518–5520.
85 P. A. Waitkus, L. I. Peterson, G. W. Griffin, *J. Am. Chem. Soc.* **1966**, *88*, 181–183.
86 Cited in Ref 1d: (a) W. v. E. Doering, *The Kekule-Symposium*, London, **1958**, Butterworths and Co., London **1959**, 45; (b) W. v. E. Doering, *U.S. Dep. Comm. Off. Tech. Serv. Rep.* **1958**, 147, 858; (c) J. R. Mayer, Ph. D. Thesis, Yale University, **1955**.
87 P. L. Pauson, B. J. Williams, *J. Chem. Soc.* **1961**, 4153–4157.
88 W. M. Jones, C. L. Ennis, *J. Am. Chem. Soc.* **1967**, *89*, 3069–3071; **1969**, *91*, 6391–6397.
89 (a) H. Prinzbach, W. Rosswog, *Angew. Chem.* **1961**, *73*, 543; *Tetrahedron Lett.* **1963**, 1217–1221; (b) M. Neuenschwander, W. K. Schenk, *Chimia* **1972**, *26*, 194–197.
90 W. E. Barth, R. G. Lawton, *J. Am. Chem. Soc.* **1966**, *88*, 380–381; **1971**, *93*, 1730–1745.