

Review

Synthesis and Reactions of Acenaphthenequinones-Part-2. The Reactions of Acenaphthenequinones

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Abstract: The reactions of acenaphthenequinone and its derivatives with different nucleophiles, organic and inorganic reagents are reviewed. This survey also covers their oxidation and reduction reactions, in addition to many known reactions such as Friedel Crafts, Diels-Alder, bromination and thiolation.

Keywords: Acenaphthenequinones; Reduction products; Ring cleavage and enlargement Thiolation; Reactions with Phosphite and Phospholanes; Decarbonylation; Reactions with nitrogen nucleophiles; Condensations of acenaphthenequinone.

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1. Introduction

The broad spectrum of applications of acenaphthenequinone and its derivatives as biologically active compounds, dyes, etc has prompted us to review their chemistry and uses. The syntheses of acenaphthenequinone (**1**) and its derivatives, which are based mainly on the use of starting materials having the carbon skeleton of **1** and their reactivity towards nitrogen nucleophiles have been discussed in the first part of this series [1]. In this part, the reactions of acenaphthenequinones are reviewed.

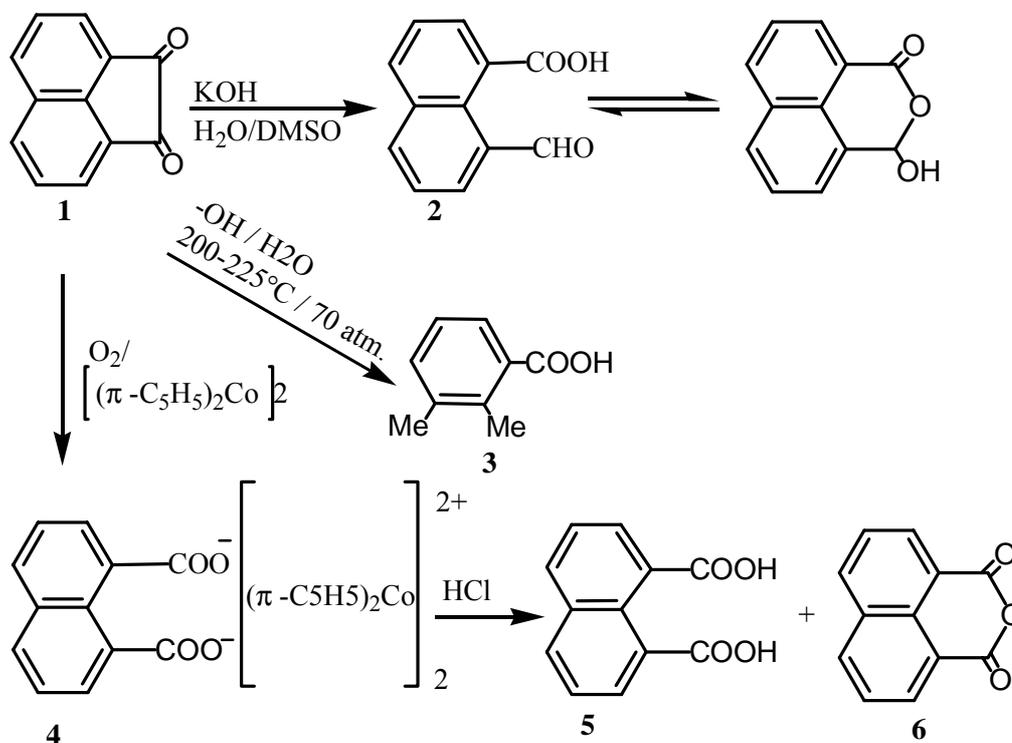
2. Reactions of Acenaphthenequinones

2.1 Ring opening and enlargement

Ring cleavage of acenaphthenequinone (**1**) with an aqueous potassium hydroxide solution in dimethylsulphoxide at room temperature led to formation of 1, 8-naphthaldehydic acid (**2**) which exists in equilibrium with the corresponding cyclic structure [2-4]. The reaction of **1** in aqueous alkali gave 2,3-dimethylbenzoic acid (**3**) [5]. The alkaline permanganate oxidation of **1** gave 2,6-dicarboxyphenylglyoxylic acid [6]. On the other hand, oxidation of **1** with molecular oxygen in propionic acid containing a homogeneous catalyst such as cobalt (II) acetate or manganese (II) acetate gave 1,8-naphthalic anhydride (**6**) [7]. Addition of potassium bromide to this reaction mixture increased the rate of reaction. A similar transformation was effected by oxygen in the presence of copper (I) chloride and pyridine [8]. On the other hand, the oxidative cleavage of **1** by the oxygen adduct of cobaltocene gave cobaltocenium carboxylate (**4**) that upon reaction with hydrogen chloride in ether, acid halides or dialkyl sulphates gave naphthalene-1,8-dicarboxylic acid (**5**), or its anhydride or ester, respectively [9].

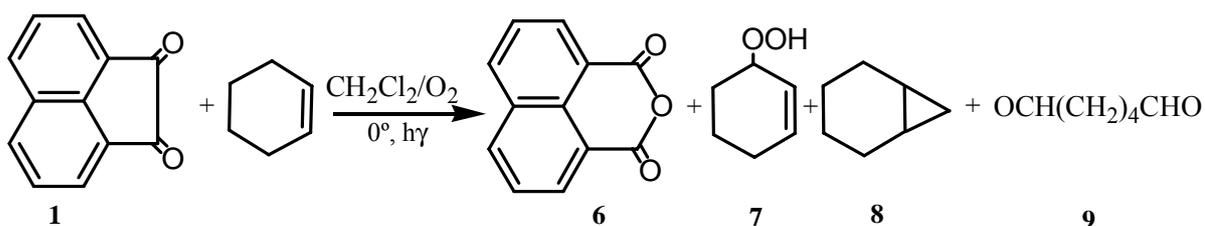
When ozonolyses of vinyl ethers were conducted in presence of **1**, it afforded **6** in addition to unreacted **1** [10]. This was attributed to the transfer of an oxygen atom from the carbonyl oxides, generated from the vinyl ethers, to **1** to give a Baeyer-Villiger type product. Heating of **1** with sodamide and treating with water gave naphthalene and oxalamide [11].

Scheme 1



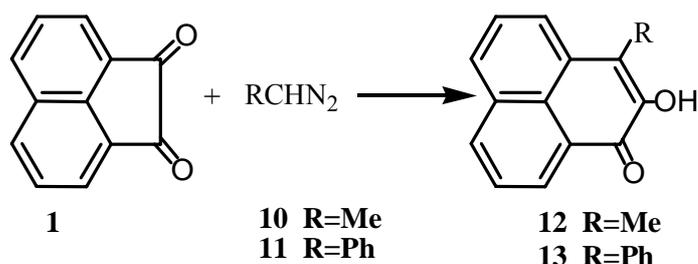
Photolysis of acenaphthenequinone in methylene chloride saturated with oxygen [12,13] gave 1,8-naphthalic anhydride (**6**). When an olefin such as cyclohexene was included in the reaction, it was converted to a mixture of oxidized products consisting, mainly the allylic hydroperoxide (**7**), epoxide (**8**), and adipaldehyde (**9**) in addition to **6**. The quantum efficiency for quinone oxidation was independent of quinone and olefin concentrations. A mechanism was suggested in which an initial reaction between excited quinone and oxygen resulted in covalent bond formation whose subsequent rearrangement accounted for the formation of the products.

Scheme 2



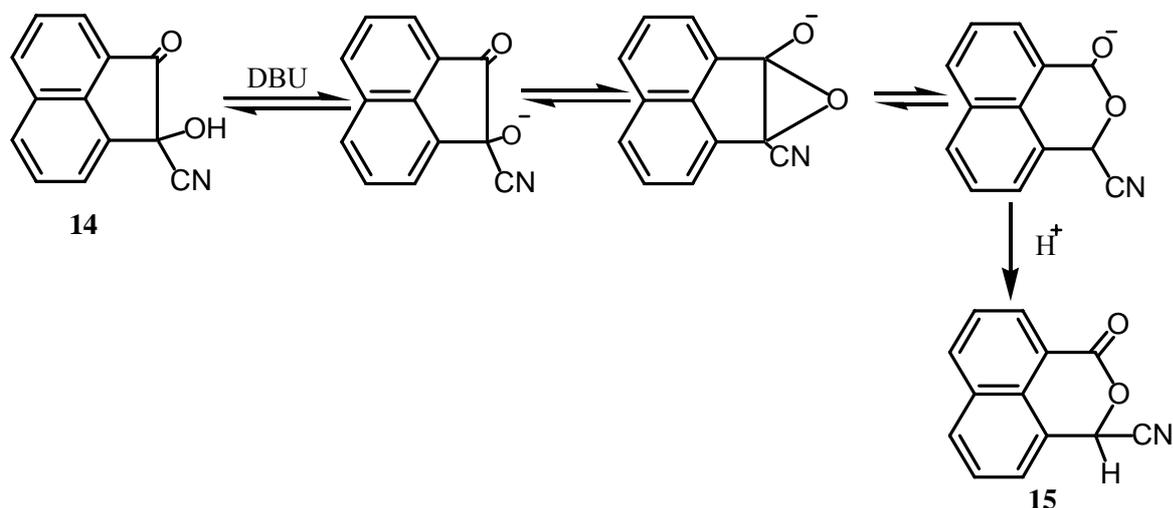
The acenaphthenequinone was cleaved electrochemically in presence of oxygen to give, after methylation, the corresponding ester of 1,8-naphthalene dicarboxylic acid [14]. Schmidt rearrangement of **1** with sodium azide gave naphthalic anhydride [15]. Reaction of **1** with the diazoalkanes **10** or **11** yielded 3-substituted-2-perinaphthen-2-ol-1-one **12** or **13**, respectively (Scheme 3)[16]. The products could be extracted from the reaction mixture with dilute aqueous alkali in order to prevent undesirable side reactions [17] which led to difficulties in isolating the products.

Scheme 3



The cyanohydrin **14** undergoes facile base-catalyzed carbon-to-oxygen acyl rearrangement to peri ring-expanded naphthalides **15** [18]. The proposed mechanism (Scheme 4) involved base-catalyzed formation of an intermediate α -oxanol followed by bridgehead carbon-carbon bond cleavage to an aromatic carbanion isoelectronic with the 14 π -electron phenalenyl carbanion. The reaction could also be extended to other analogues of **14** where the CN is replaced by other substituents.

Scheme 4

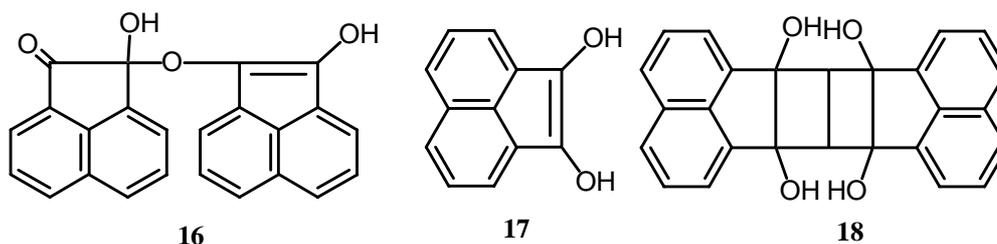


2.2 Reduction

Acenaphthenequinone is easily reduced as a consequence of the involvement of its carbonyl groups in the conjugated system [19]. Treatment of **1** with iron in acetic acid, until a water soluble colorless compound is formed, yields easily soluble alkali salts, which are of a violet-blue color, in the presence

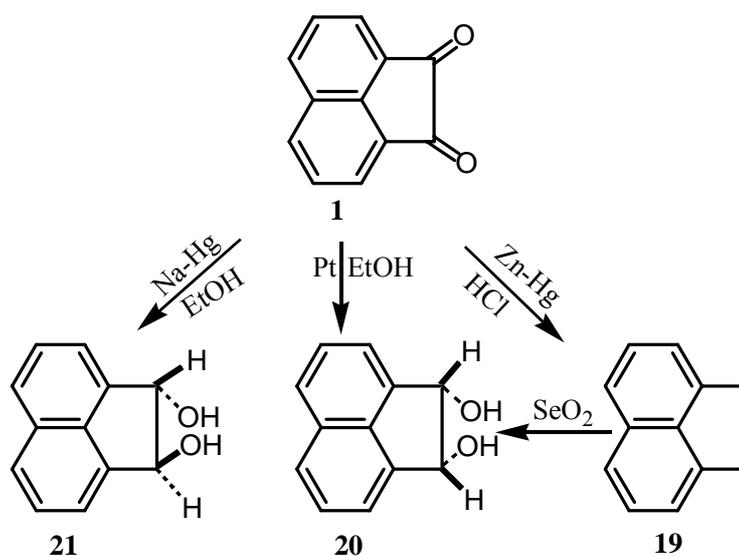
of an excess of caustic alkali. Condensing the reduced products with 3-hydroxy-1-thionaphthene or indoxyl derivatives gave vat-dyeing materials [20]. Reduction products of acenaphthenequinone were obtained by confining the reduction to the formation of compound **16** which is poorly soluble in water and yields with alkalis deep blue salts which are also poorly soluble in water (Scheme 5). On the other hand reduction of **1** could be carried until the formation of **17**, which is soluble in water. It forms with excess of alkalis readily soluble violet-blue salts [21,22]. When acenaphthenequinone absorbed five moles of hydrogen, in the presence of platinum in aqueous ammonium hydroxide or dilute alkali [23], it yielded exclusively the bimolecular substance **18**. Its catalytic hydrogenation in presence of nickel salts was also studied [24].

Scheme 5



Clemmensen reduction of **1** with amalgamated zinc in hydrochloric acid gave acenaphthene **19** (Scheme 6) [25]. When the reduction was carried out with amalgamated sodium in ethanol, in an atmosphere of nitrogen, it gave 38% of the transglycol **21** [26]. The product did not give a condensation product with acetone and it did not decolorize bromine in warm chloroform. Catalytic reduction of **1** in presence of platinum in ethanol gave a mixture of *cis*- and *trans*-acenaphthylene glycols (**20** and **21**). Reduction with LiAlH_4 gave also the *trans* diol accompanied by the *cis* diol whose derivatives were prepared [27]. The *cis*-diol could be prepared by selenium dioxide oxidation of acenaphthene [25].

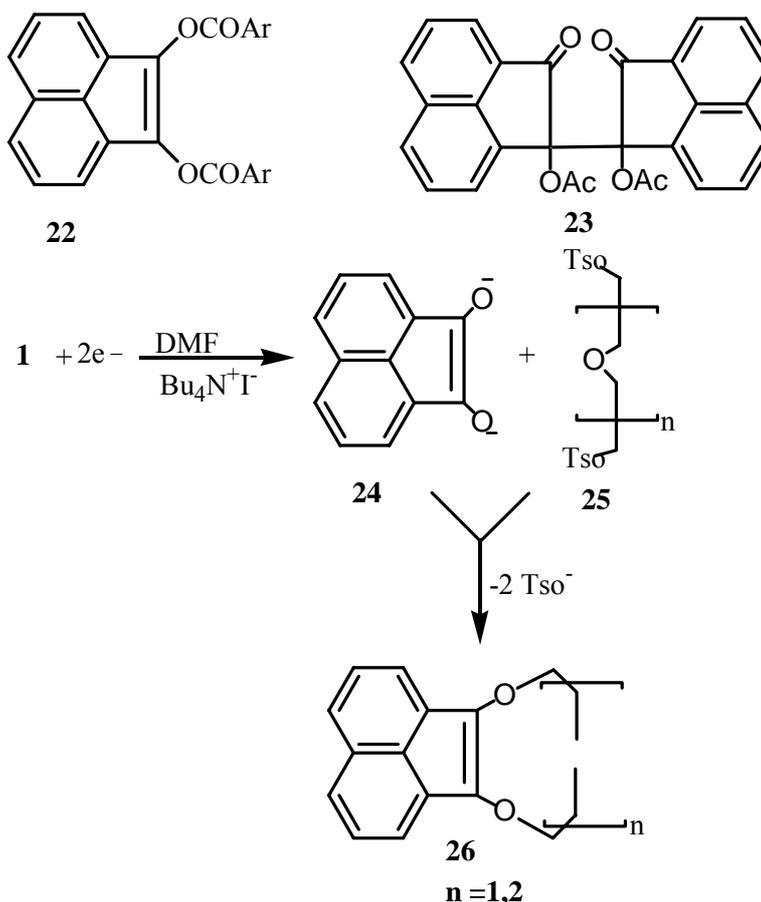
Scheme 6



Treatment of **1** with alkali metals e.g. sodium and potassium in tetrahydrofuran gave three reduced forms [28], which behave like a monovalent, a divalent, and a trivalent base, respectively. It was found that tris(triphenylphosphine)chlororhodium is an effective catalyst for the homogeneous reductive hydrosilylation of quinones [29] which offer an easy procedure for protecting the highly reactive quinonic moiety. Thus, reductive silylation of **1** with Et_3SiH over tris(triphenylphosphine)-chlororhodium as a catalyst gave the bis(silyl) ethers of the hydroquinone which could be oxidatively desilylated with $\text{PhI}(\text{OAc})_2$ [30]. The respective 1,2-bis(trimethylsiloxy)ethene analogue was prepared from reaction of **1** with hexamethyldisilane in presence of Pd or Pt catalyst [31].

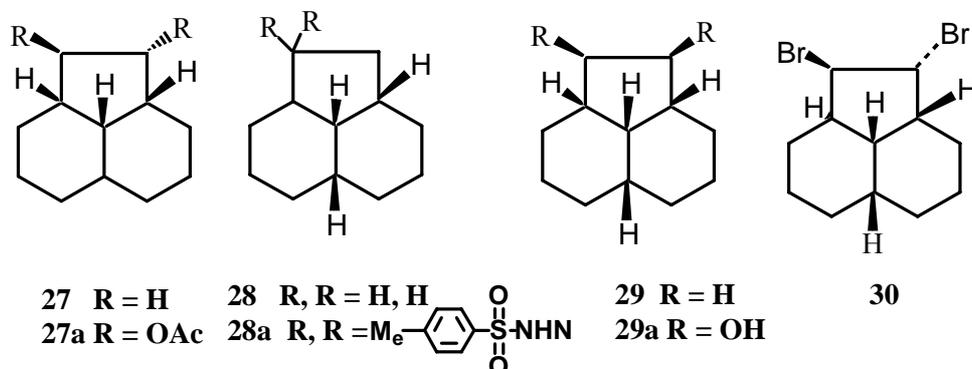
Electrochemical reductions of **1** at a mercury cathode were carried out under a constant potential, in presence of nonelectroactive aryl chlorides to give the 1,2-diaroyloxyacenaphthylene derivatives **22**, in good yields (Scheme 7) [31,33]. Their formation corresponds to the transfer of an overall two-electron process. However, when acetic anhydride was used, a one-electron transfer process had taken place to give meso-bis (1-acetoxy-2-oxoacenaphthen-1-yl) (**23**). The structure of the last compound was determined by x-ray crystallography [32]. The effect of metal ions and solvents on the polarographic reduction of **1** was studied [34]. The dependence of limiting currents and half-wave potentials were determined [35]. The mechanism and kinetics of the polarographic reduction of **1** in DMF and in the presence of phenol as proton donor was found to involve 4-electrons in successive 1-electron steps [36]. Reductive methylation of **1** had taken place electrochemically in presence of methylhalides via coupling of the radical anion of **1** with the methyl radical [37]. Electrochemical reduction in DMF- Bu_4NI gave a binucleophile **24**, which underwent cyclization with **25** to give heterocyclic macrocycles **26** [38].

Scheme 7



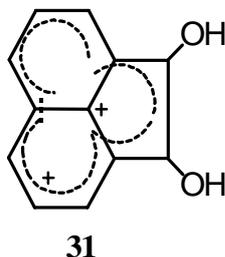
The three stereoisomers **27-29** of the six possible dodecahydroacenaphthylene were prepared (Scheme 8)[39]. The configurations were confirmed *inter alia* by X-ray analysis of the precursors.

Scheme 8



2.3 Protonation

Protonation of acenaphthenequinone (**1**) gave a diprotonated species [40], the structure of which was determined as **31** by ¹H- and ¹³C-NMR. The relative photochemical reactivity of acenaphthenequinone as an α -diketone was investigated in hydrogen donating solvents [41].

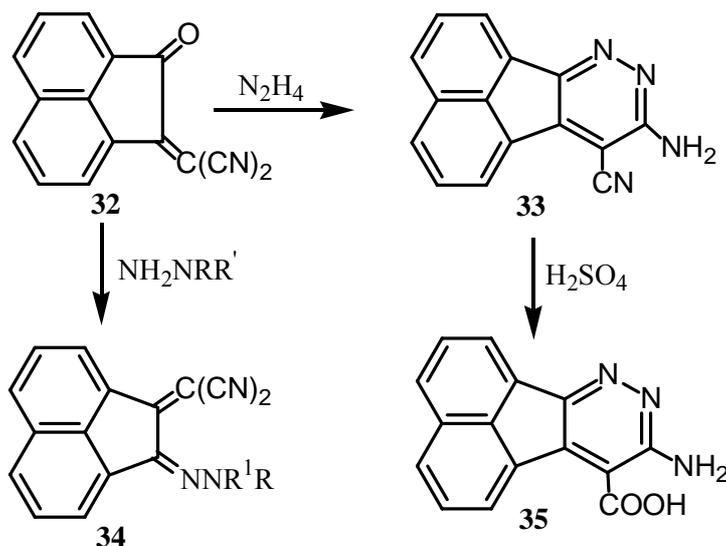


2.4 Reaction with active methylene compounds

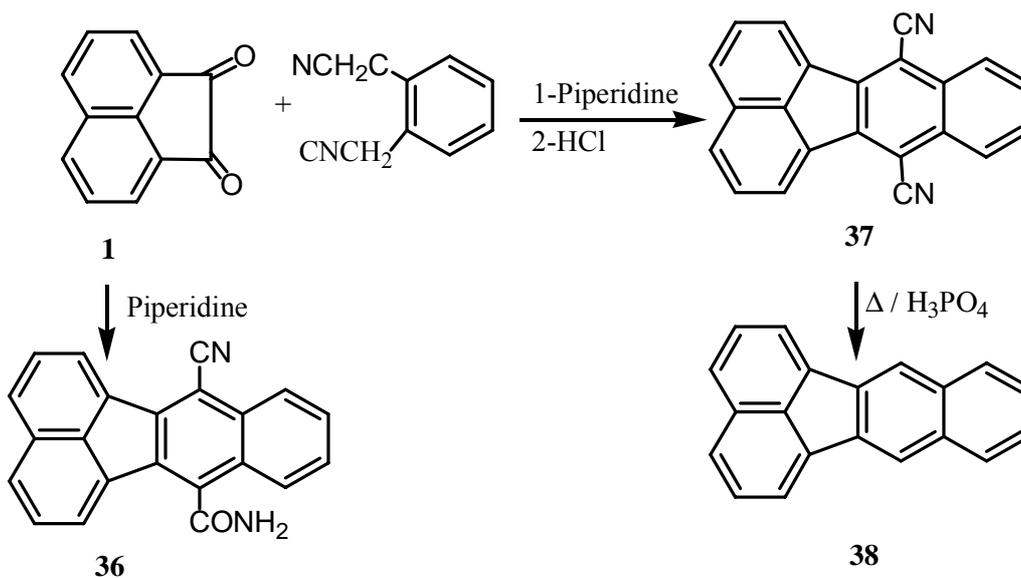
Reaction of **1** with malononitrile gave 1-(dicyanomethylene) acenaphthen-2-one (**32**) whose reaction with hydrazine gave **33** that hydrolyzed with sulfuric acid to give **35** (Scheme 9) [42]. Reaction of **32** with substituted hydrazines gave deeply colored hydrazones **34**, which are classified as azacyanine types polymethine dyes [43]. Reaction of **1** with malononitrile in presence of bases yielded a blue compound namely 6 β -hydroxy-8-imino-7, 8-dihydro-6 β -H-cyclopenta[a] acenaphthylene-7,7,9-tricarbonitrile [44].

Reaction of **1** with o-phenylene diacetonitrile in presence of piperidine at room temperature [45, 46] gave the dinaphthylenenitrile amide (**36**) and not the expected dinitrile **37** (Scheme 10). The product could not be hydrolyzed to the dicarboxylic acid; hydrolysis ceases at the diamide stage [47]. However, the cyclocondensation of o-phenylene diacetonitrile with **1** was reported in a more recent publication to give **37** that followed by decyanation to give benzo[k]fluoranthene (**38**) [48].

Scheme 9



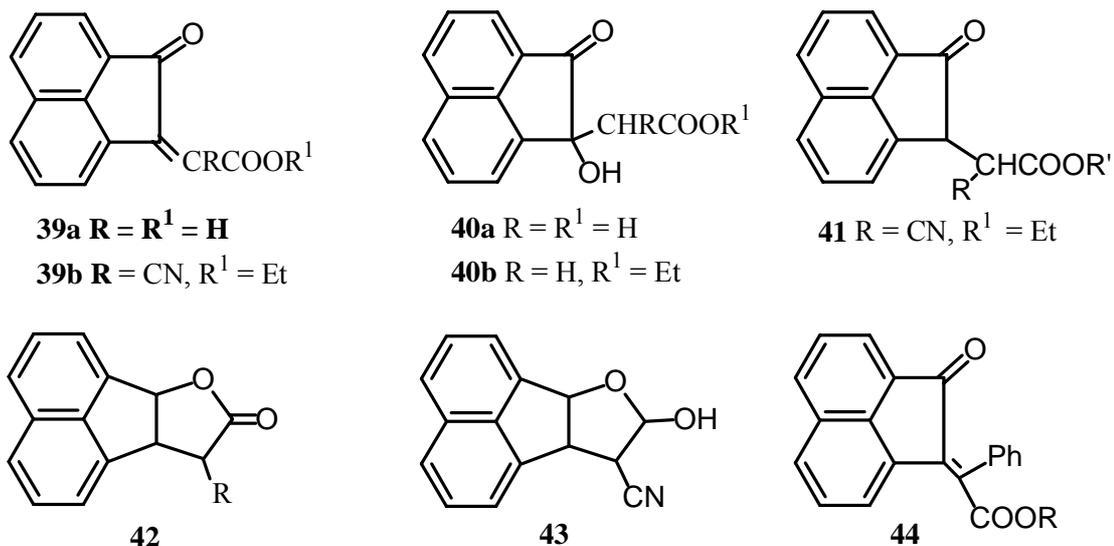
Scheme 10



Condensation of ethyl cyanoacetate and malonic acid with **1** gave the acid **39a** and the ester **39b**, respectively (Scheme 11) [49]. Esterification of **40a** gave the corresponding ester **40b**. Dehydration of **40a** gave **39a**.

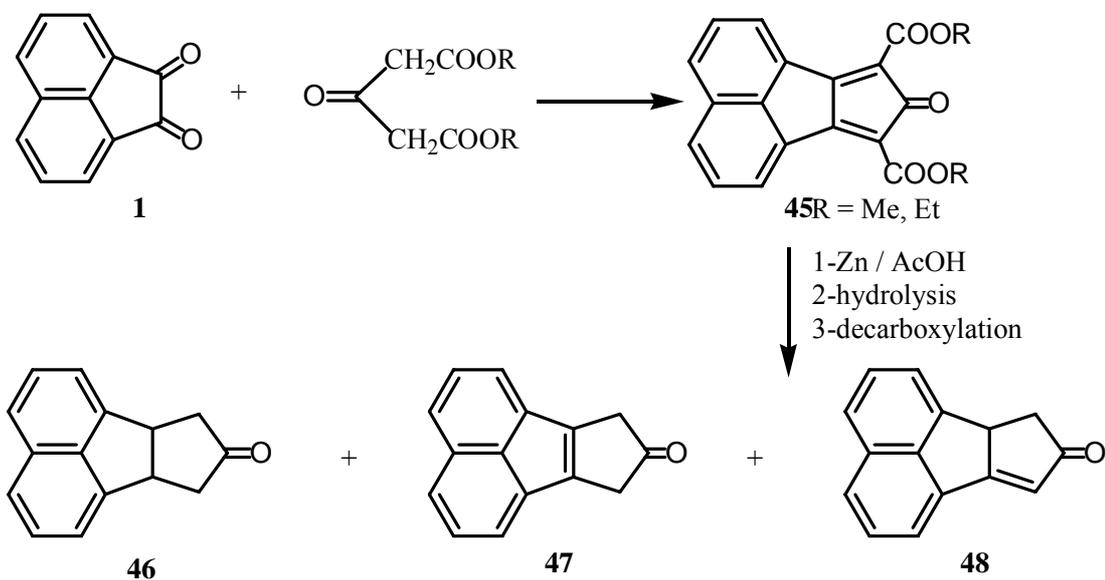
Hydrogenation of **39b** in presence of Adams' catalyst gave **41**. Reduction of **41** gave either the lactone **42** ($R=CN$) or the hemiacetal **43** depending upon the conditions employed. The lactone (**42**, $R=H$) was prepared by reaction of hemiacetal **43** with hot alkali followed by acidification. Claisen-Stobbe condensation of **1** with phenylacetic esters afforded the benzylidene derivatives **44** [50].

Scheme 11



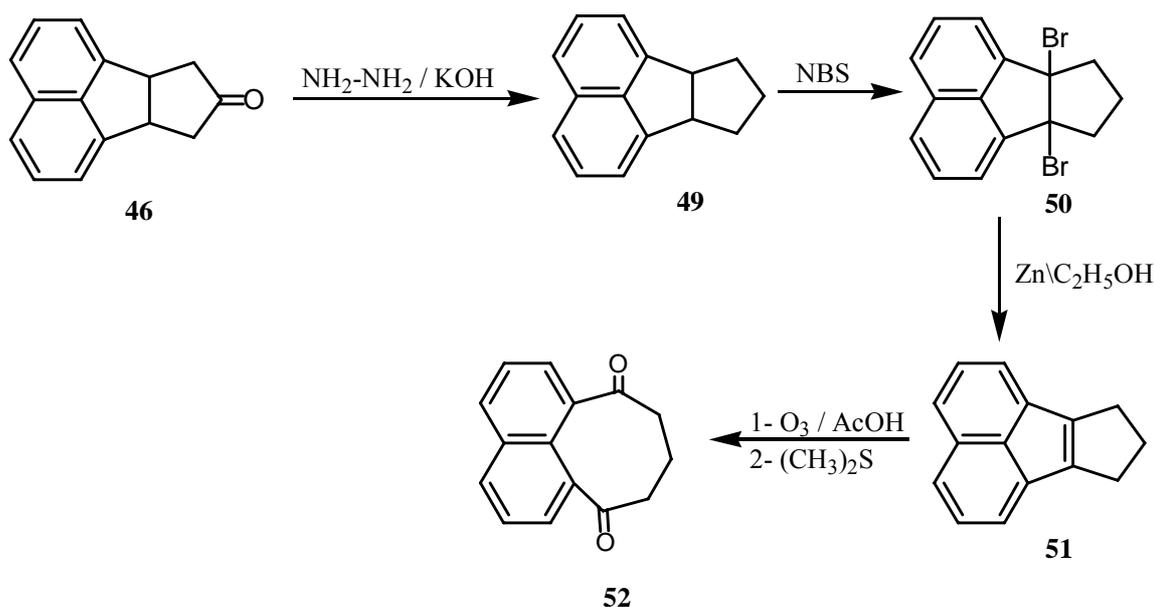
Reaction of **1** with diethylacetone dicarboxylate gave the substituted cyclopentadienone (**45**) (Scheme 12) [51]. Reduction of **45** by zinc and acetic acid followed by hydrolysis and decarboxylation afforded the ketones **46**, **47** and **48**.

Scheme 12



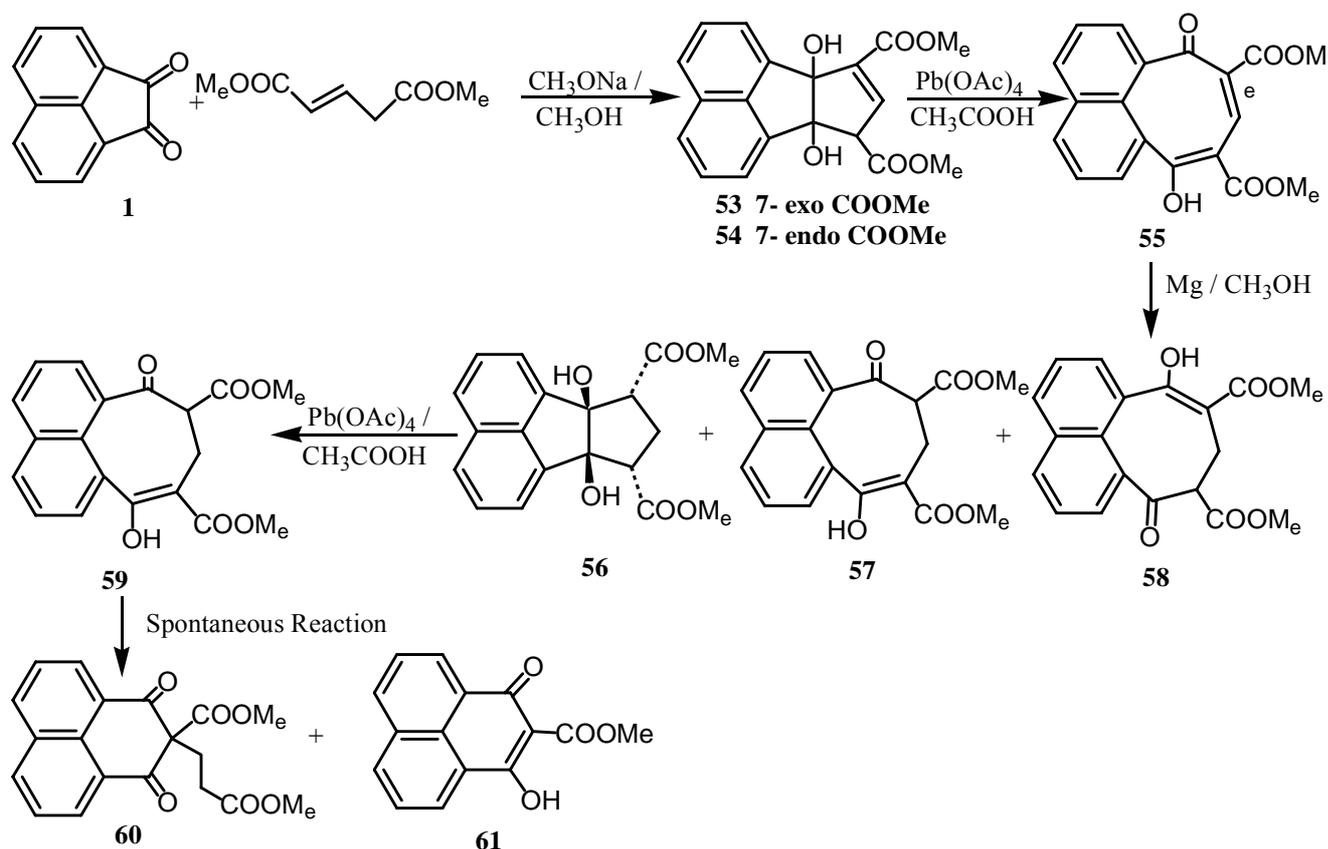
The ketone **46** is a valuable precursor for the synthesis of peri-diketone **52** via the conversions to **49-52** (Scheme 13).

Scheme 13

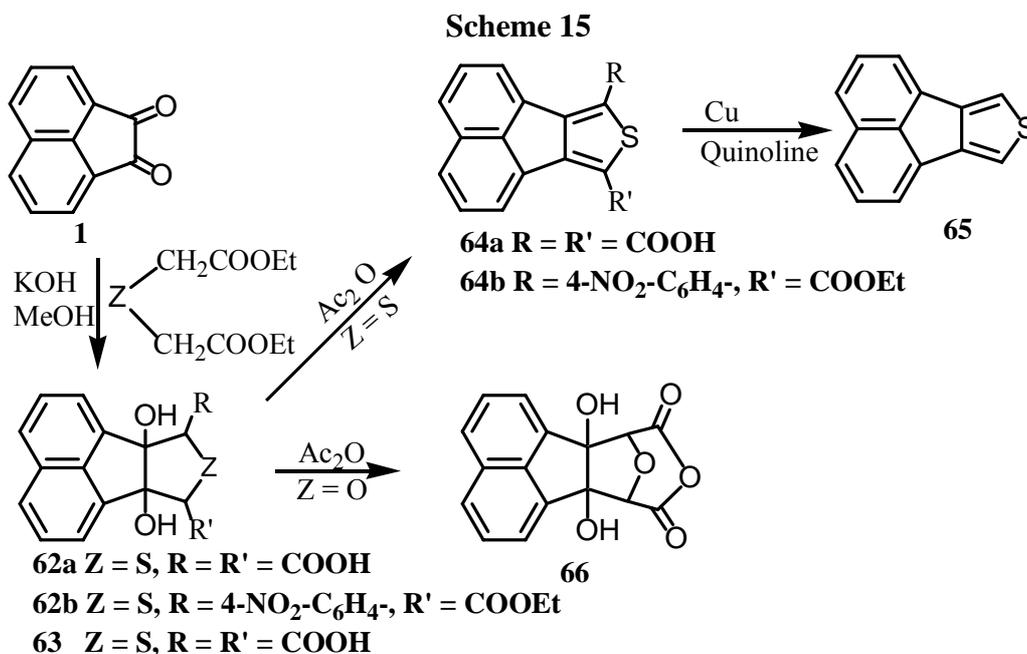


Condensation of acenaphthenequinone (1) with dimethyl pentenedioate (dimethyl glucatonate) [52] gave the epimeric diesters **53** and **54** (Scheme 14). The diester **53** was oxidized by lead tetraacetate to **55** whose reduction was effected by magnesium in methanol in order to reduce the conjugated 8,9-double bond while preserving the keto-ester groups, whereby compounds **56**, **57**, and **58** were obtained.

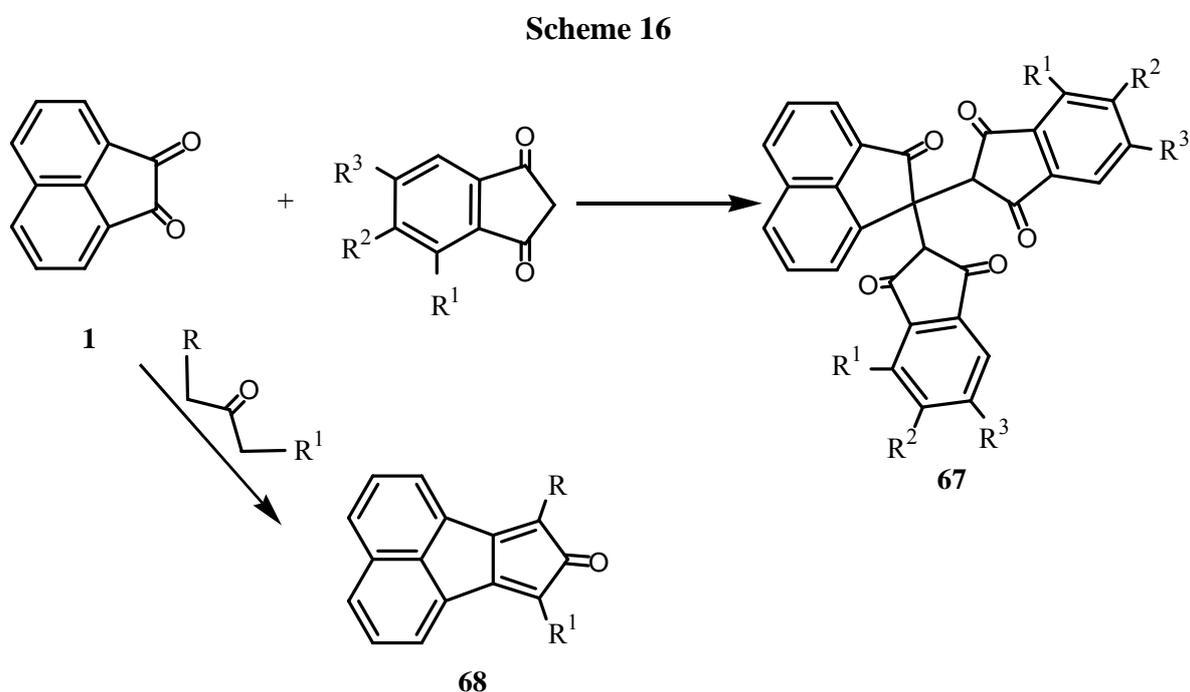
Scheme 14



Reaction of **56** with lead tetraacetate gave **59**, which could be a precursor for the peri-diketone **52**, however, **59** was spontaneously transformed to **60** and **61** and consequently this approach for **52** was precluded. Acenaphthenequinone (**1**) was condensed with $S(CH_2CO_2Et)_2$ or $p\text{-NO}_2\text{BnSCH}_2CO_2Et$ in the presence of base to give tetrahydroacenaphthothiophenes **62a** and **62b** (Scheme 15). Dehydration of **62a** in sulfuric acid or acetic anhydride gave acenaphtho[1,2-c]thiophene (**64a**) [53]. Heating of **64a** with copper and quinoline gave **65** [54]. On the other hand, when **1** was treated with $O(CH_2CO_2Et)_2$, it gave **63**, which upon reaction with acetic anhydride gave **66** [55].

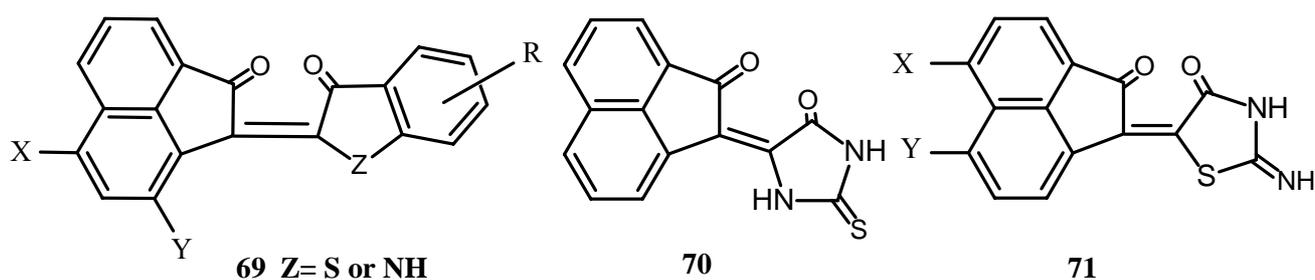


Condensation of **1** with 1,3-indandione (Scheme 16) gave 2,2-bis(1,3-indandion-2-yl) acenaphthene-1-one (**67**) [56-58]. The reaction of **1** and 2,2-dihydroxy-1,3-phenylenedione gave 1,8-naphthalic anhydride in high yield [59]. Condensation of **1** with the appropriate 2-propanones gave **68** [60,61].



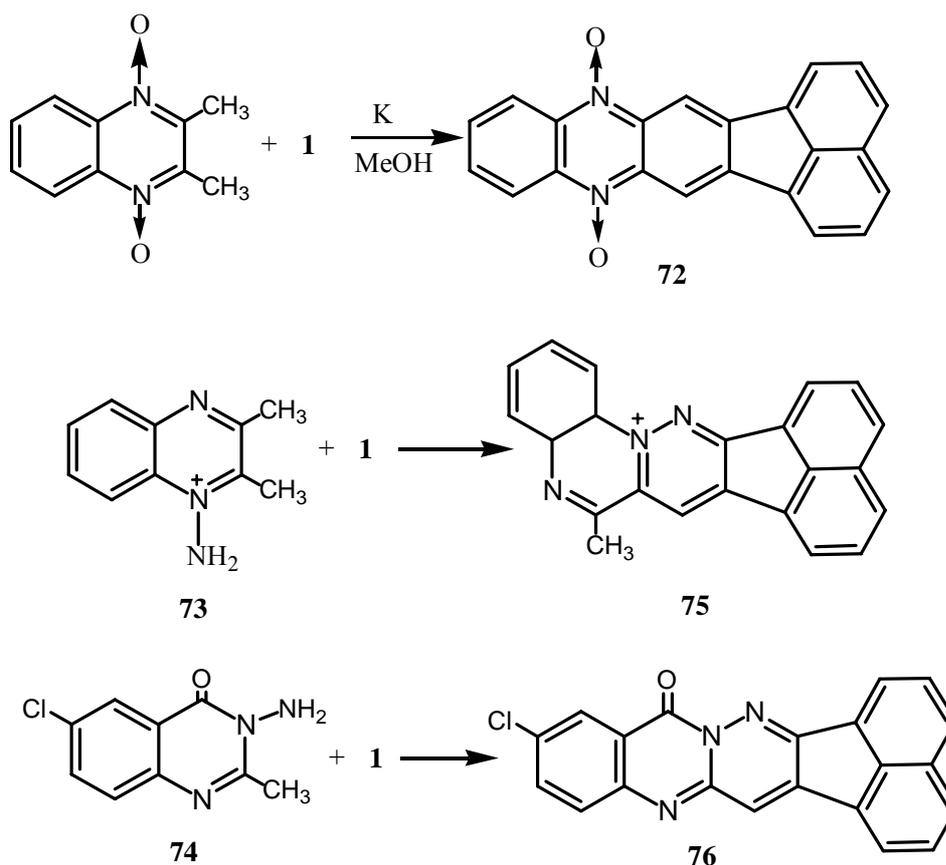
Reaction of acenaphthenequinone and 6-chloro-3-hydroxy-thionaphthene gave 2-(6-chloro-thionaphthene)acenaphthylene indigo [6-chloro-2-(2-oxo-1-acenaphthylidene)-3(2H) thionaphthenone] which was used as a dye [62]. Similarly, condensation of substituted acenaphthenequinone with 3-hydroxythionaphthenes or indoxyl in the presence of a catalytic amount of hydrochloric acid gave **69** or its isomer which was not specifically identified (Scheme 17) [63-66]. Reaction of **1** or its halogen derivatives with thiohydantion [67], pseudothiohydantion [68] or rhodanine gave products of the type **70** or **71** [69].

Scheme 17



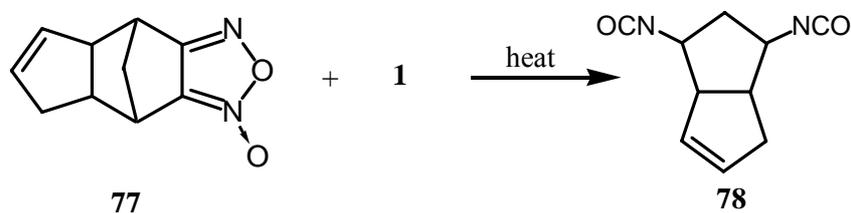
Reaction of **1** with 3,4-dehydro-DL-proline gave a product in which the pyrroline ring is converted into an N-substituted pyrrole [70]. Cyclocondensation of 2,3-dimethylquinoxaline-1,4-dioxide with **1** gave phenazine dioxide **72** (Scheme 18) [71]. When dialkyl-N-aminoazinium salts **73** or the quinazoline derivative **74** have been condensed with **1**, they gave the new heterocycles **75** and **76**, respectively, with a quaternary N in the bridgehead position (Scheme 19) [72,73].

Schemes 18-19



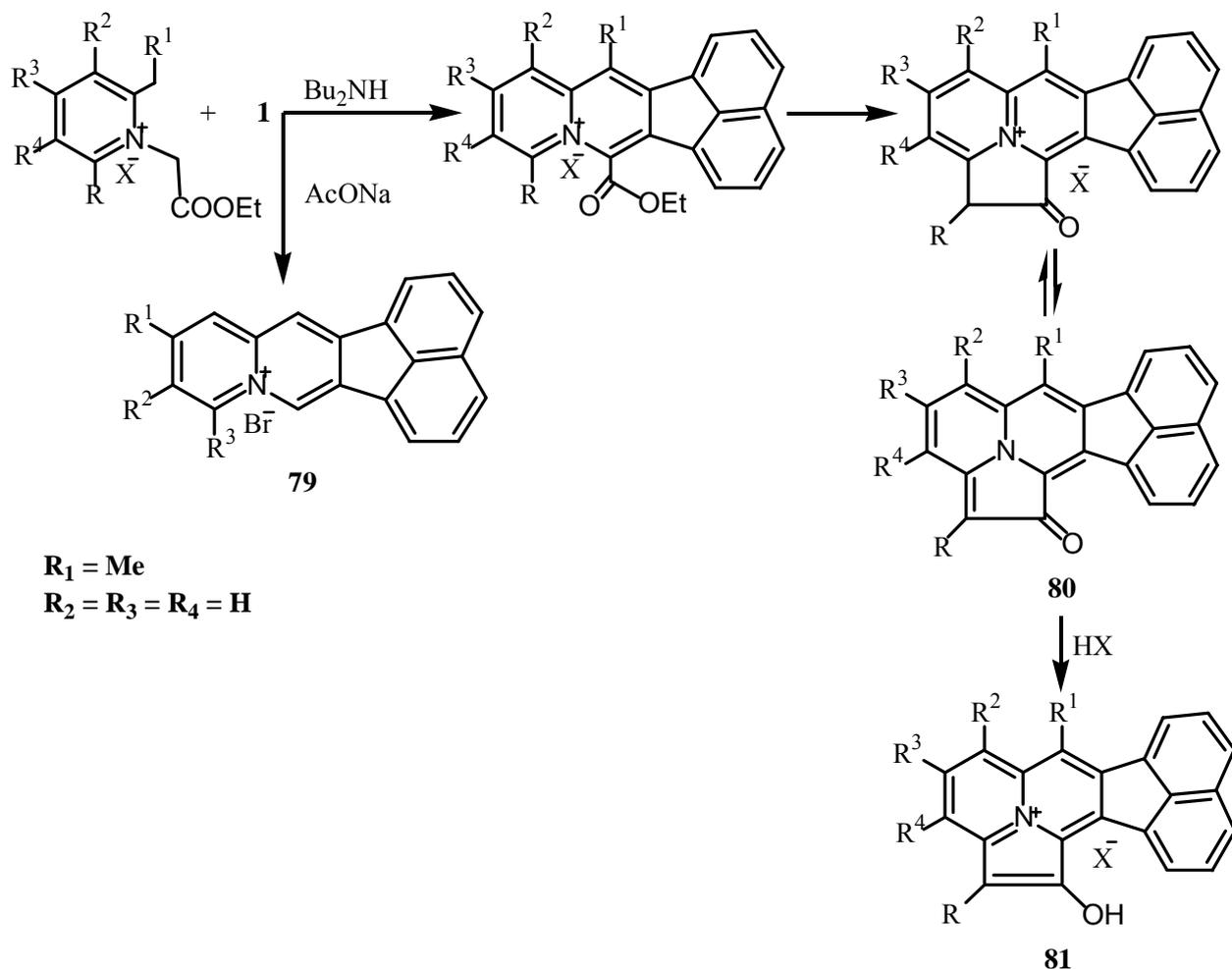
When **1** was treated with the furoxan derivative **77**, an addition product was formed whose heating gave the diisocyanate **78** (Scheme 20) [74].

Scheme 20

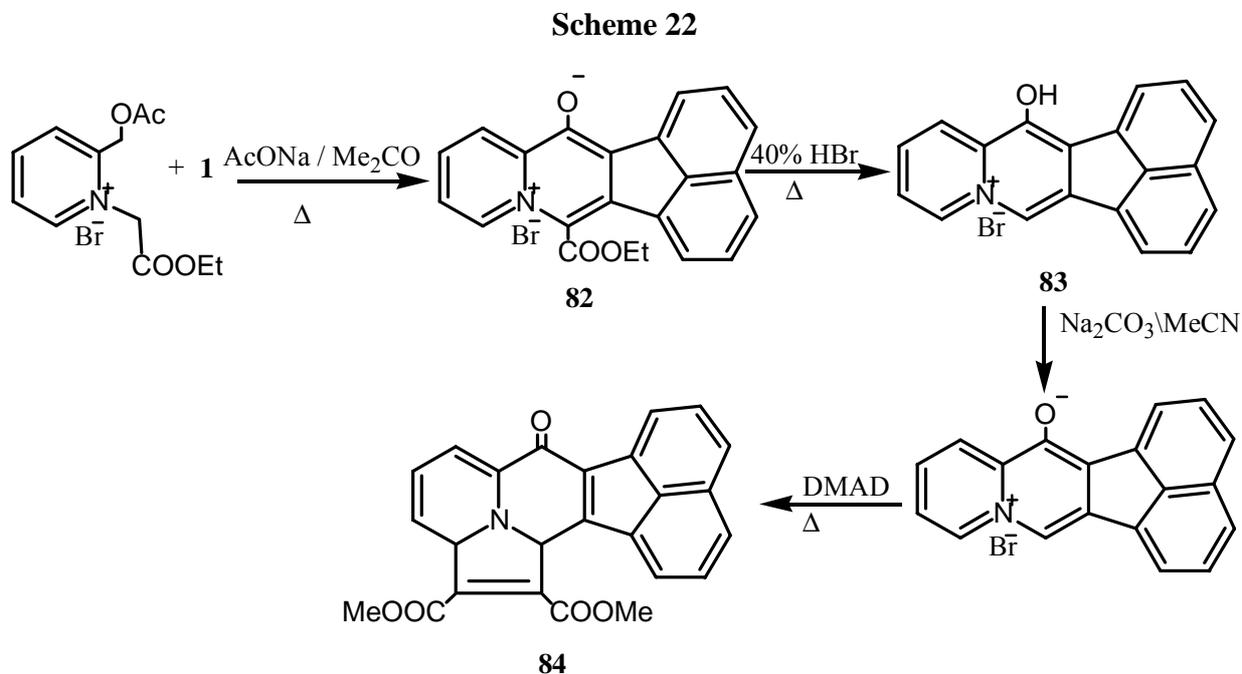


The Westphal condensation was used for the synthesis of different types of heterocycles from **1**. Thus, condensation of 2-methylpyridinium, quinolinium or isoquinolinium salts with **1** in presence of a sodium acetate yielded the quinolizium salts **79** [75,76]. When 1-ethoxycarbonylmethyl-2, 6-dimethylpyridinium salt was heated with acenaphthenequinone in the presence of di-*n*-butylamine, deep purple precipitate of [2,3,3]cyclizin –1–one derivatives **80** were formed whose formation was rationalized as presented in Scheme 21. All cyclazinone derivatives **80** were isolated as hydrobromides **81** [77].

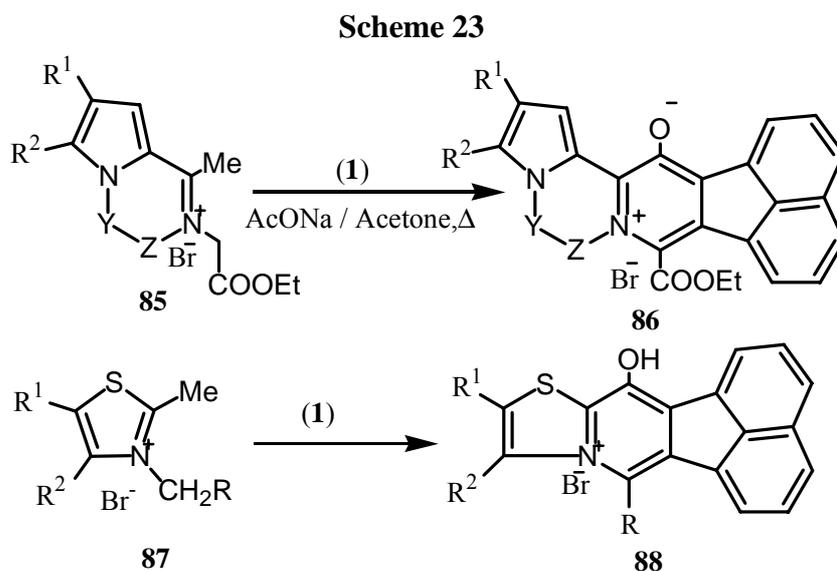
Scheme 21



The [2,3,3] cyclazin-6-one was prepared by condensation of acetoxyethylpyridinium bromide and **1** in presence of sodium acetate to yield the 4-ethoxycarbonylquinolizinium-1-olate (**82**) which upon reaction with hydrobromic acid produced **83** (Scheme 22). Treatment of the latter with sodium carbonate followed by DMAD gave [2,3,3] cyclazin-6-one derivative **84**.

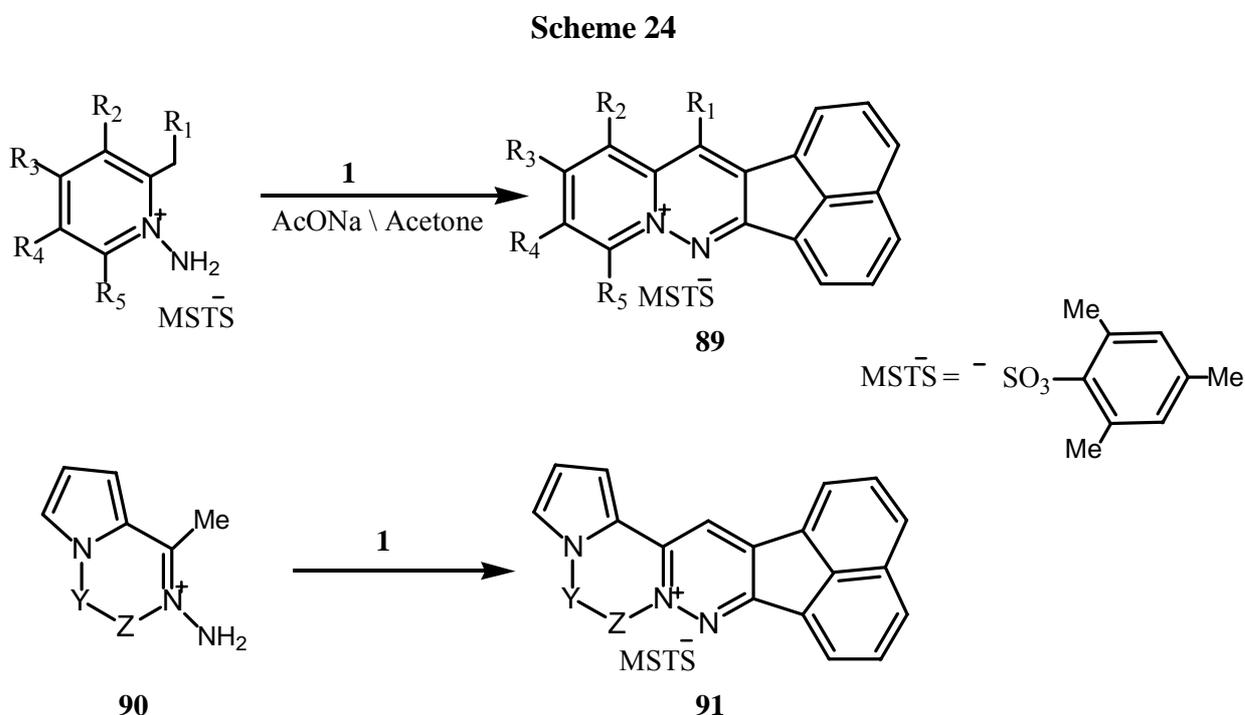


The Westphal condensation was also used for the synthesis of π -donor- π -acceptor heterocycles such as pyridopyrrolopyrazinium **86** by the condensation of **1** with pyrrolopyrazinium compounds **85** (Scheme 23) [78]. Similarly, the 2-methylthiazolium salts (**87**) were used as 1,4-dinucleophiles for the synthesis of thiazolo [3,2-a] pyridinium salts **88** [79].



Y-Z	R ₁	R ₂
-CH ₂ -CH ₂ -	H	H
-CH=CH-	H	H
-CH ₂ -CH ₂ -	-(CH=CH) ₂ .	

Condensation of **1** with 2-alkyl-1-aminopyridinium, quinolinium or 1-alkyl-2-aminoisoquinolinium salts gave in presence of base, pyrido[1,2-b] pyridazinium salts **89** in good yield [80]. Similarly, the pyridazinopyrrolopyrazinium derivatives **91** were prepared from **90** (Scheme 24) [80].



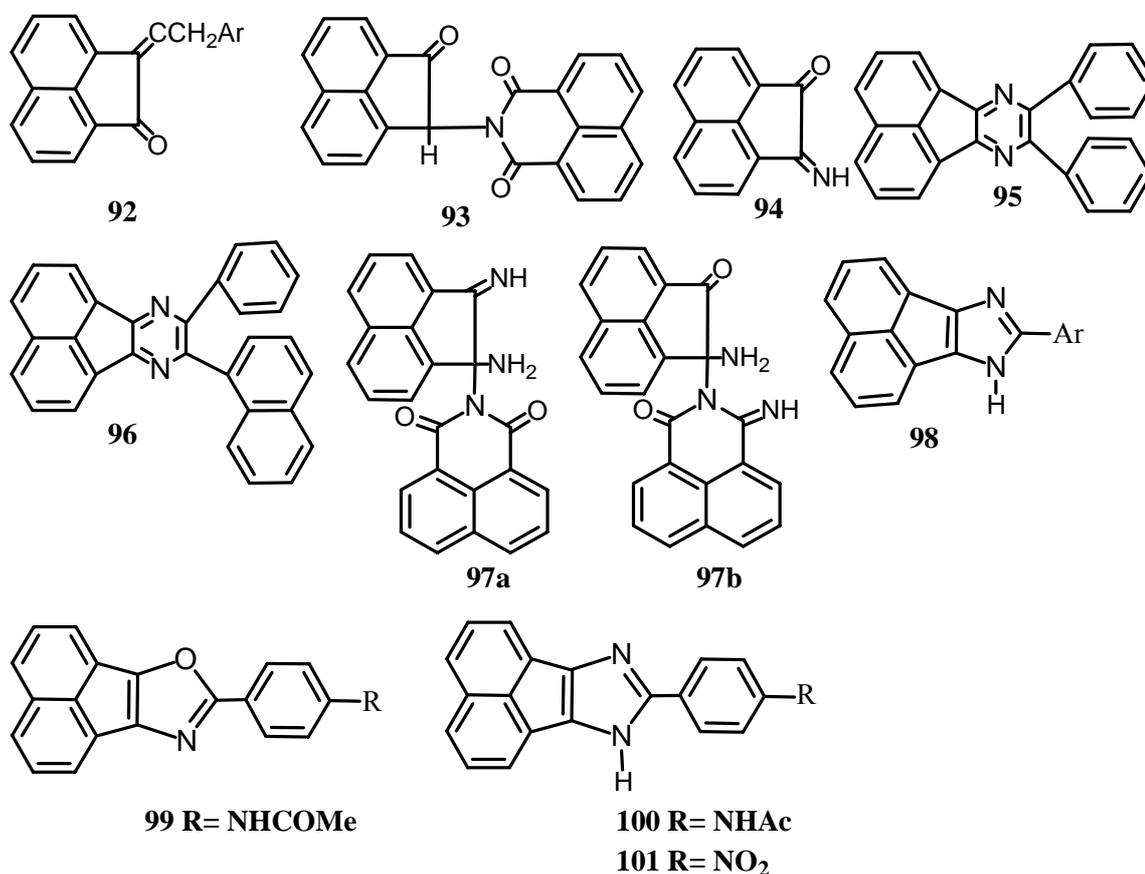
Reaction of **1** with nitromethane in alkali followed by acidification gave an adduct $\text{C}_{13}\text{H}_9\text{NO}_4$ which was formed by a 1,2-addition on one of the carbonyl groups [81].

2.5. Reaction with aldehydes and ketones

It has been shown that **1** could be condensed with aldehydes in a general manner to afford **92** that gave a violet-red color with concentrated sulfuric acid (Scheme 25) [82]. Reaction of acenaphthenequinone with acetone in presence of potassium hydroxide gave monoacetoneacenaphthenequinone [83]. Reaction of **1** with p-chlorobenzaldehyde, p-acetamidobenzaldehyde, o-nitrobenzaldehyde in presence of ammonia gave oxazoles **99** at 0 °C and imidazoles **100** at higher temperatures. On the other hand, o-chloro-benzaldehyde, o-hydroxybenzaldehyde and m-hydroxybenzaldehyde under similar condition gave a mixture of oxazoles and imidazoles, which cannot be separated [83], and at higher temperatures, only imidazoles were obtained. p-nitrobenzaldehyde, p-hydroxybenzaldehyde and p-methoxybenzaldehyde gave only imidazoles. Vanillin and p-bromosalicylaldehyde react very slightly at 0°C, but at higher temperature imidazoles **98** were formed. Heating the corresponding oxazole with ammonia in a sealed tube caused a partial conversion into the imidazole. When the reaction of **1** with o-hydroxybenzaldehyde was exposed to light for one month, it gave the monosalicylyl derivative of acenaphthenequinol [83].

When a suspension of **1** in isoamyl alcohol or anhydrous ethanol was treated with benzaldehyde in presence of ammonia, a variety of products **93-97** were obtained depending upon the condition of the reaction [84]. The structure of **97** was thought to be either **97a** or **97b**. Its hydrolysis with dilute hydrochloric acid gave **1**, naphthylimide and an unidentified compound $C_{12}H_8N_2O$. Substituted benzaldehydes were also used. Reaction of **1** with various aldehydes in boiling ammonium hydroxide and in dry ammonia gave aryl acenaphthimidazoles [83]. When dry ammonia was passed through a hot solution of **1** and p-acetamidobenzaldehyde in ammonium hydroxide, 4-acetyl-amino-2-phenyl-acenaphthoxazole (**99**), and the iminazole (**100**, R=NHAc) were obtained [85]. Treatment of **1** with ammonium acetate in presence of p-nitrobenzaldehyde gave (**101**, R=NO₂) [86]. It may be supposed that oxazoles are first formed which by subsequent replacement of the ring oxygen atom by NH forms the iminazoles.

Scheme 25

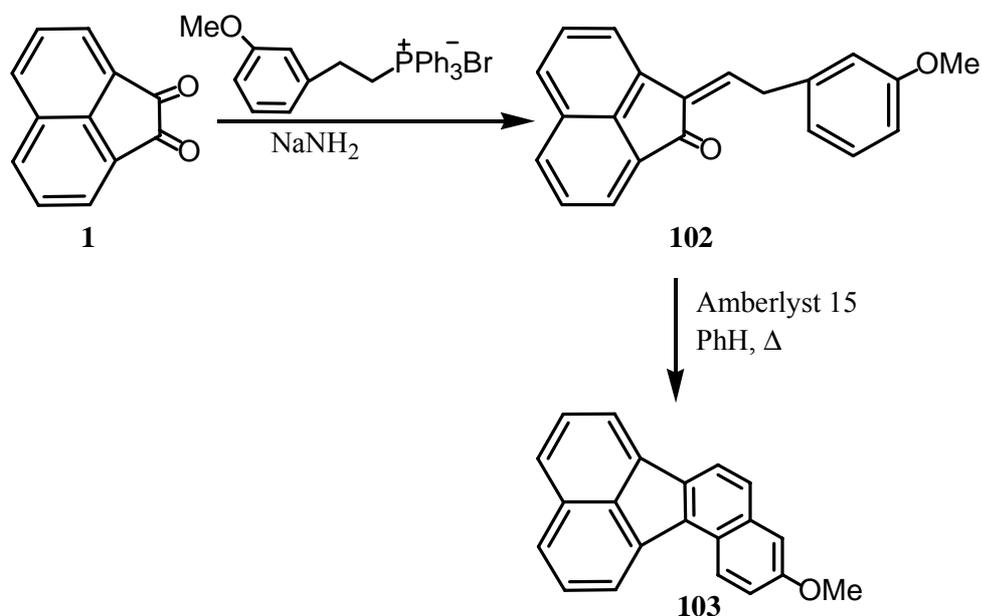


2.6. Reaction with Wittig reagents

Reaction of **1** with several Wittig reagents has been studied [87]. Thus, its reaction with equimolar amount of benzylidenetriphenylphosphorane at room temperature gave the corresponding benzylidene-acenaphthenones in fairly good yields. When the reaction of **1** was done with two molar equivalents of

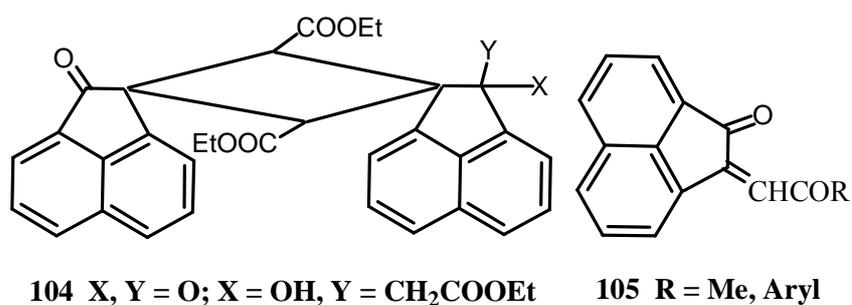
benzylidenetriphenylphosphorane under severe conditions it afforded also the benzylidene-acenaphthenone and no dibenzylidene derivative could be obtained. When **1** was reacted with 3-(methoxyphenethyl) triphenylphosphonium bromide followed by cyclization-dehydration of the intermediate **102** gave 10-methoxybenzo[*j*]fluoranthene (**103**) exclusively (Scheme 26) [88].

Scheme 26

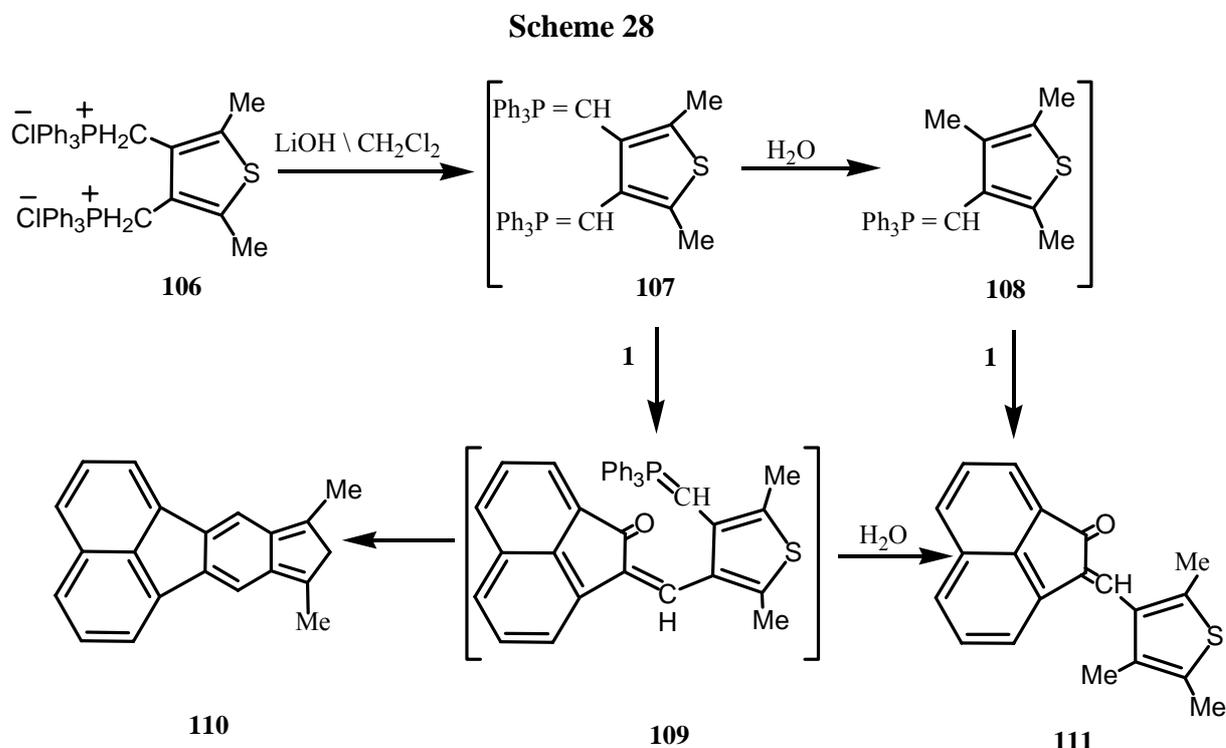


The adducts **104** were isolated from the reaction of **1** with triethyl phosphonoacetate (Scheme 27) [89]. The reaction of **1** with a resonance-stabilized phosphorane [90], such as acetonilydene-, phenacylidene- and *p*-chlorophenacylidene-phosphoranes afforded the expected α,β -unsaturated ketones **105**. The ethoxycarbonyl-methylene acenaphthenone was obtained from the reaction of **1** with diethyl ethoxycarbonyl methyl phosphonate. Methylene-phosphorane was reacted with **1** to give methyleneacenaphthenone in poor yield. On the contrary, the reaction with ethylidenephosphorane gave 2,2'-methylenebisacenaphthenone, which was also formed by the reaction of acenaphthenone with glyoxal, in good yield.

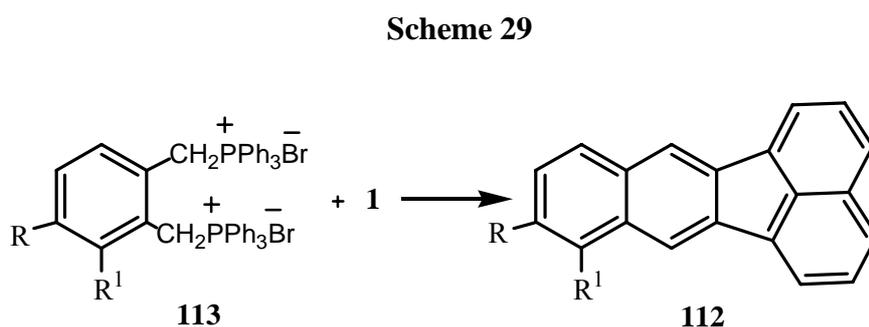
Scheme 27



When equimolar amounts of the bisphosphonium salt **106** and **1** were treated with aqueous 5 M-lithium hydroxide (Scheme 28), 8,10-dimethylfluorantheno[8,9-c]thiophene (**110**) and 2-(2,4,5-trimethyl-3-thienyl-iden)acenaphthylen-2-one (**111**) were obtained [91]. Compound **111** was isolated in only one configuration and its formation may arise either *via* the o-quinomethanelylide intermediate **109** or the monoylide **108**. Intramolecular Wittig reaction of **109** gave **110**.

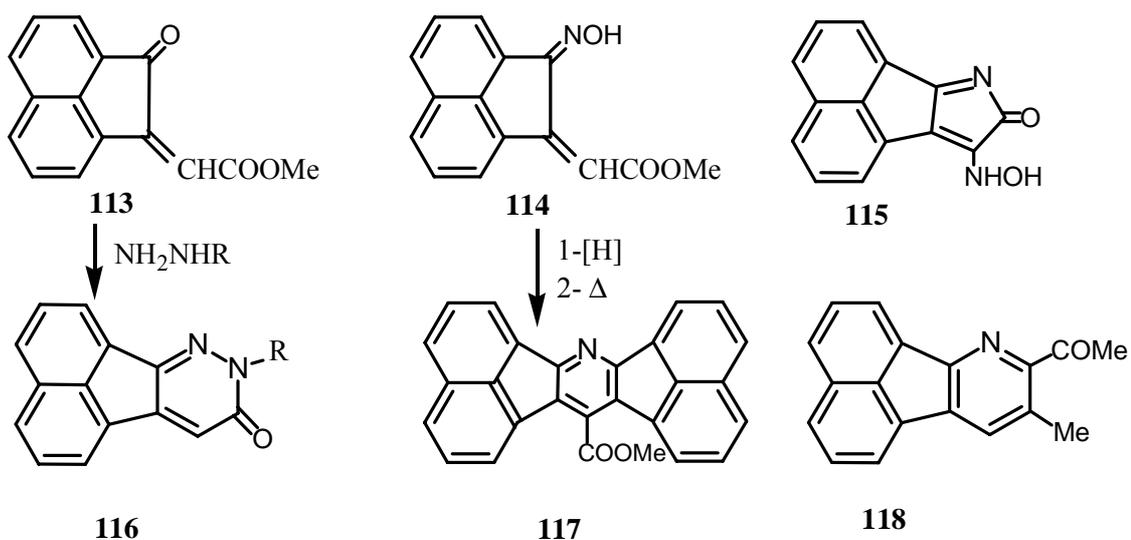


Wittig reaction of bis(triphenylphosphonium) dibromides with **1** under phase-transfer conditions gave **112** (Scheme 29) [92].



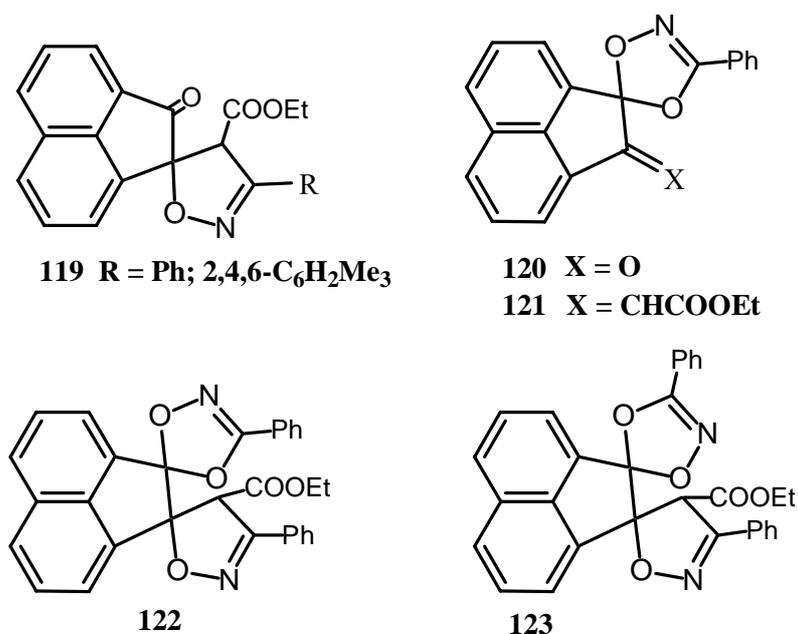
Reaction of **113** with hydroxylamine gave the oxime **114** and the pyrrole derivative **115**, whereas its reaction with hydrazines afforded the pyridazinones **116** (Scheme 30) [93]. Reaction of the monoxime of **1** with $\text{Ph}_3\text{P}=\text{CHCO}_2\text{Me}$ afforded stereoisomeric products of **114**, whereas the reaction with ylide $\text{Ph}_3\text{P}=\text{CHCOMe}$ gave the pyridine derivatives **118**. Hydrogenation of **114** and thermal cyclization gave the polycyclic compounds **117** [94].

Scheme 30



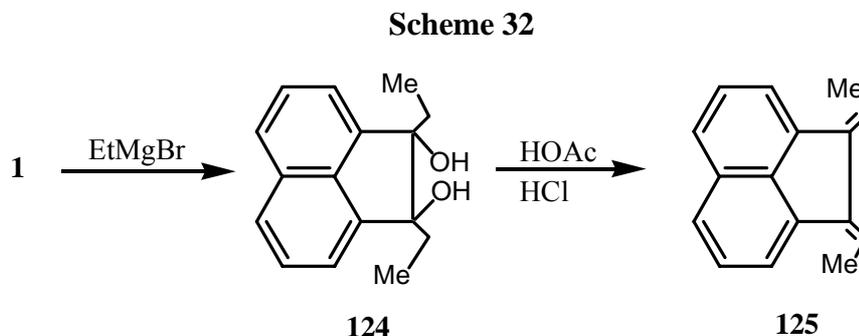
Spiro acenaphthyleneisoxazoles **119** were prepared by the regioselective 1,3-dipolar cycloaddition reaction of **113** with nitrile oxides (Scheme 31) [95]. The reaction of **1** with nitrile oxide gave acenaphthylenedioxazoles **120**, which underwent a Wittig reaction with $\text{Ph}_3\text{P}=\text{CHCO}_2\text{Et}$ to give **121**. The cycloaddition reaction of **120** with PhCNO gave a mixture of the dispiro compounds **122** and **123**. Catalytic hydrogenation of **121-123** over Pd/C cleaved the dioxazole rings, whereas the isoxazole ring of **119** was cleaved by reduction over Raney nickel or by treatment with sodium ethoxide.

Scheme 31

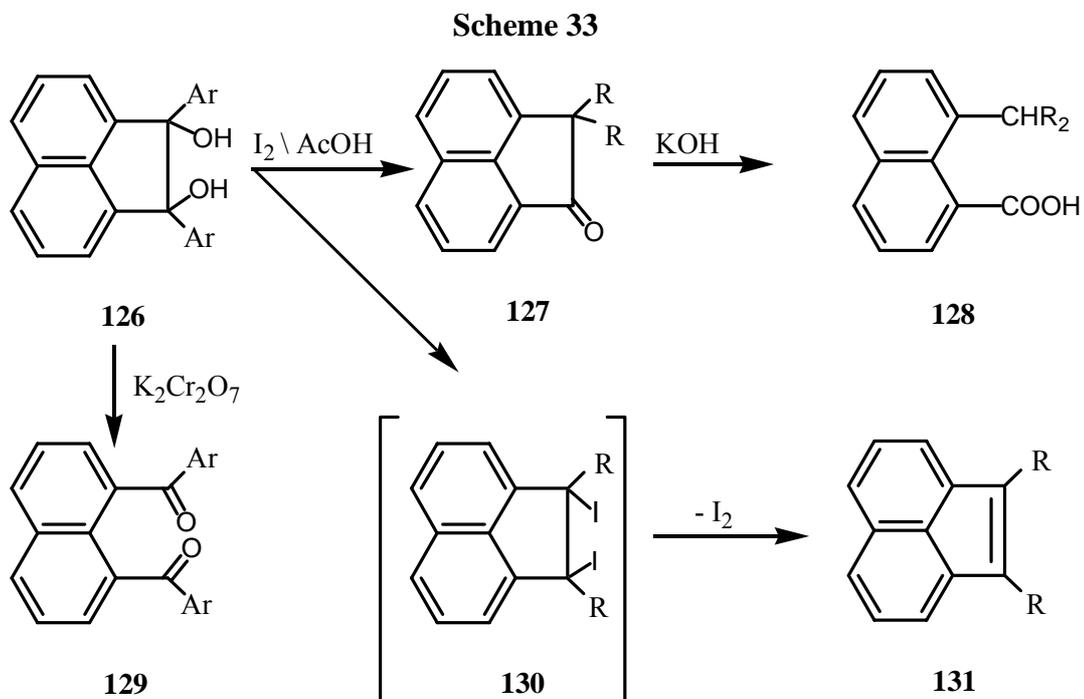


2.7. Reaction with magnesium and lithium reagents

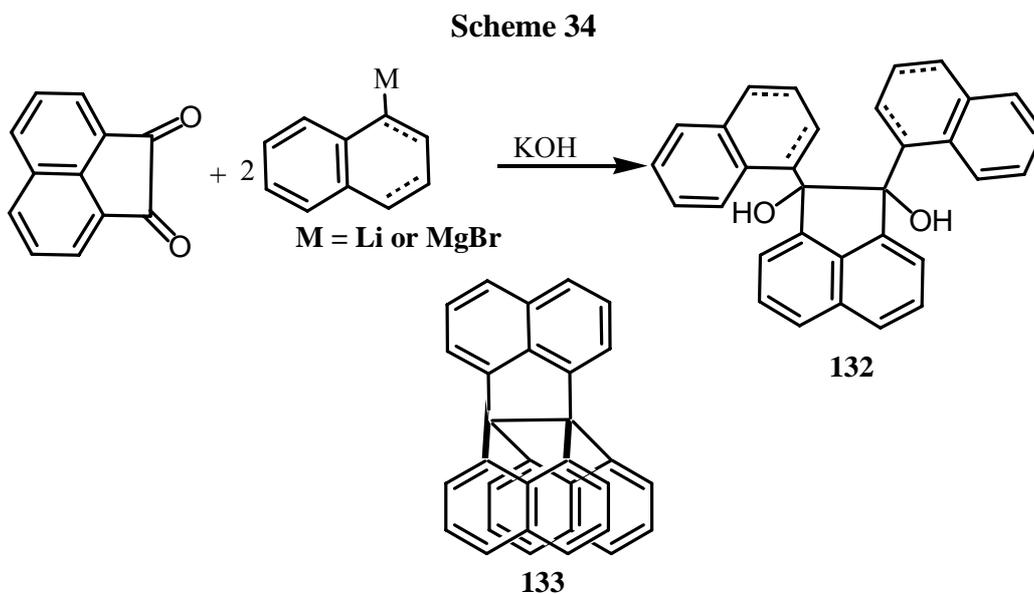
Various reports on the reaction of Grignard reagents with **1** have been published [96-102]. Thus, reaction of **1** with EtMgBr gave 1,2-diethylacenaphthoglycol **124** [96] whose dehydration with acid gave 1,2-diethylideneacenaphthene **125** (Scheme 32). The latter could be oxidized back to **1** with sodium dichromate in acetic acid.



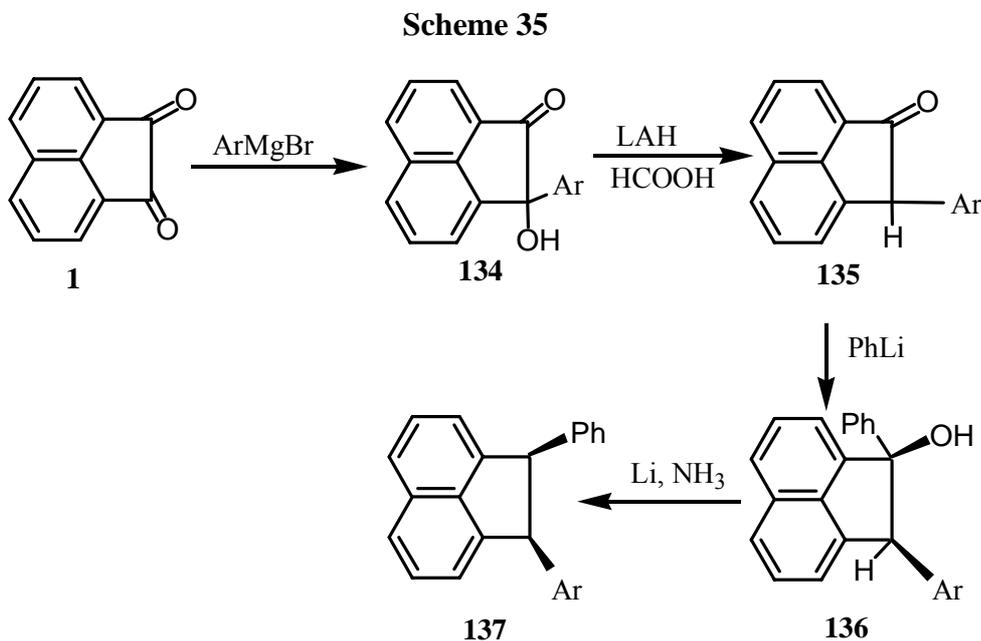
The dehydration behavior of **124** is unlike that of the diphenyl derivative, which gave a pinacolone under this treatment [96]. Reaction of **1** with arylmagnesium bromides gave 7,8-diarylnaphthenediols (**126**) (Scheme 33) [97,98] in which the simple aryl group migrates exclusively to give the 7,7-diarylnaphthenones (**127**) [99]. The latter could be cleaved into the naphthoic acid derivatives **128** by alkali. Some derivatives of **126** gave low yields of **127** due to the formation of **131**. The latter were prepared from **126** via **130**. Ring opening of **126** was achieved by chromic acid to give the aroyl naphthalene **129** [99-103].



Reaction of acenaphthenequinone with several organolithium and organomagnesium reagents gave **132** (Scheme 34) [104]. This and its derived pinacol rearrangement product failed to cyclize under a variety of the acidic conditions, perhaps due to the poor stereoelectronic alignment for cyclization. On the other hand, when a less rigid analogue such as 1-lithio-3,4-dihydronaphthalene was used the tricyclo[4.3.0.0]nonane **133** was formed by di-oxy-Cope rearrangement followed by the unprecedented criss-cross $2\pi+2\pi$ cycloaddition of the two enolate ions formed [104]. The structure was confirmed by X-ray crystallography.

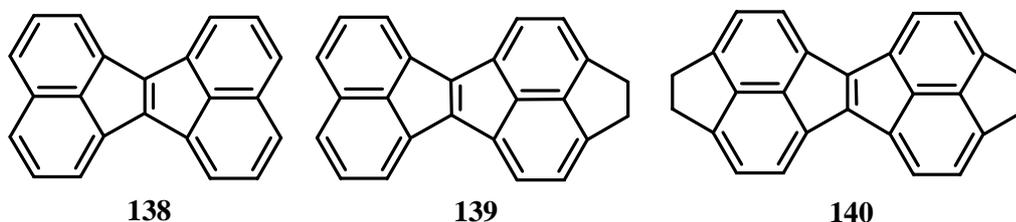


The addition of mesityl or triisopropyl magnesium bromide to **1** led (*via* a single electron transfer) to the formation of the corresponding semiquinone [105] to give **134** that upon reduction with lithium aluminum hydride gave **135** (Scheme 35). Reaction of the latter with phenyl lithium gave **136** that upon Birch reduction gave the diaryl derivative **137** [106]. Reaction of vinyl chloride with **134** gave the corresponding vinyl ethers [107].



When 1,8-diiodonaphthalene and 5, 6-dibromoacenaphthene were lithiated and treated with acenaphthenequinone, and then the diol cycloaddition products were treated with hydrofluoric acid, acenaphth[1,2-a]acenaphthylenes, **138-140** were obtained (Scheme 36) [108].

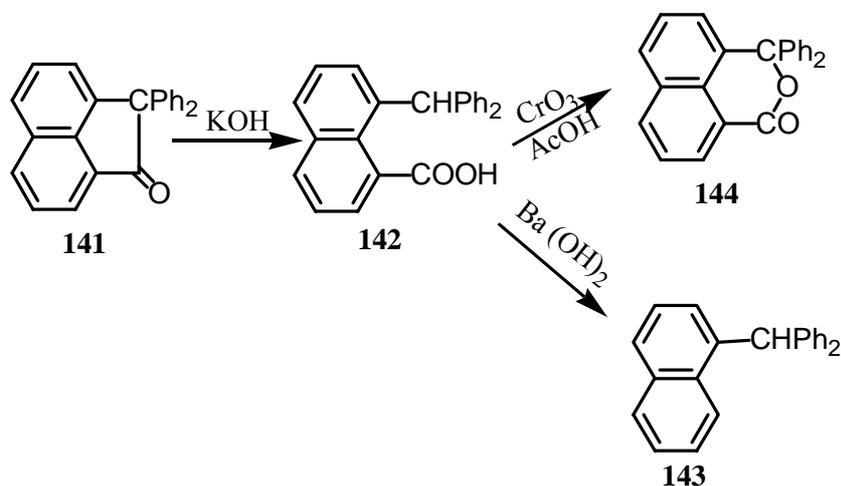
Scheme 36



2.8. Friedel Crafts reaction

Condensation of acenaphthenequinone with benzene in presence of aluminum chloride gave 1,1-diphenyl-2-acenaphthenone (**141**) (Scheme 37) [109]. Boiling alcoholic potassium hydroxide converts **141** into 8-diphenylmethyl-1-naphthoic acid (**142**). Its distillation with barium hydroxide gave diphenyl naphthylmethane (**143**) whereas its treatment with chromium trioxide in acetic acid gave the lactone derivative **144**.

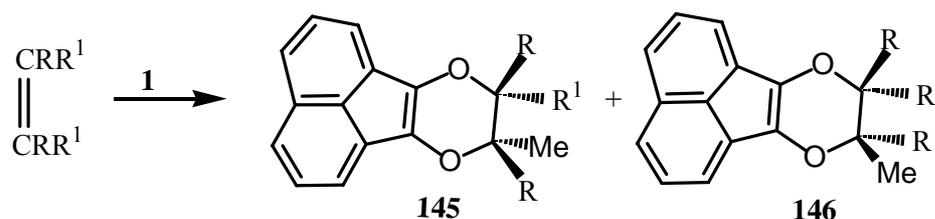
Scheme 37



2.9. Diels-Alder reaction

Photochemical Diels-Alder reaction of acenaphthenequinone with olefin led to the formation of **145** and **146** (Scheme 38) [110].

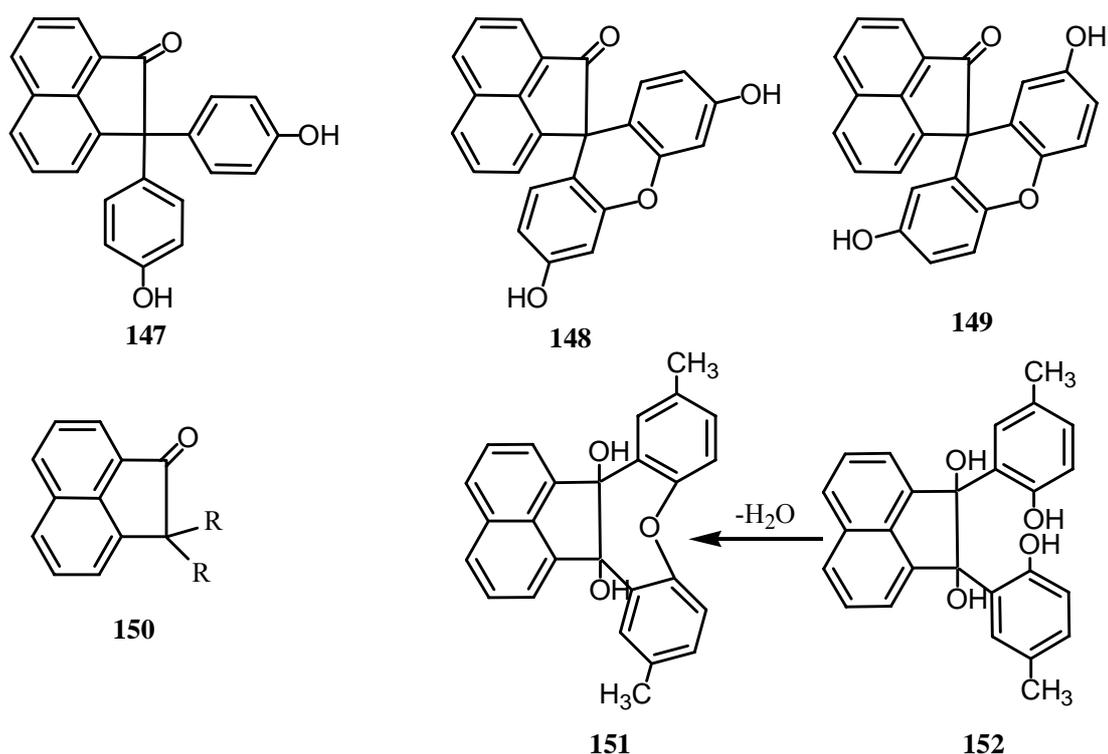
Scheme 38



2.10. Reaction with phenolic compounds

The reaction of phenol with **1** was successful in presence of concentrated sulfuric acid [111,112]. Since the para-position is the most reactive in phenol, the product may probably be given the structure 1,1-bis [4'-hydroxyphenyl]-2-acenaphthenone (**147**) (Scheme 39). Reaction of **1** with resorcinol in presence of zinc chloride gave **148** [109], and the reaction with hydroquinone gave **149** [111]. To explain the formation of such anhydro derivatives it must be assumed that the oxygen of the quinone reacts with a hydrogen atom in the o-position to one of the hydroxyl groups in the dihydroxy compound [110]. The compound from catechol formed no anhydride and as the hydrogen atom in the p-position to one of the hydroxy groups in the catechol is the most reactive, the product must be 1,1-bis[3',4'-dihydroxyphenyl]-2-acenaphthenone. Condensation of acenaphthenequinone with asymmetric o-xyleneol, or gave **150**. Thymol yields dithymol acenaphthenone. Nitrophenols reacted more sluggishly with **1** and a large excess of the phenol and the condensing agent was required [114]. This was explained on the basis of theoretical electrostatic considerations. Reaction with o-nitrophenol gave 1,1-bis(3-nitro-4-hydroxy-phenyl)-2-acenaphthenone, and with p-nitrophenol gave anhydro-1,1-bis(5-nitro-2-hydroxyphenyl)-2-acenaphthenone.

Scheme 39



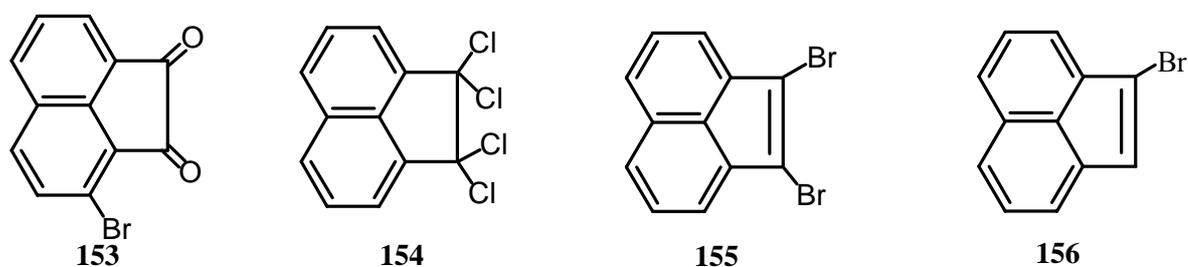
It was found that condensation of acenaphthenequinone with cresols and naphthols does not always give, like mono- and dihydric phenols, compounds of the type **150**. Thus, reaction of **1** with p-cresol, gave **151** and **152**; the relative amounts of which depend on the amount of sulfuric acid used as condensing agent [115].

2.11. Halogenation reactions

Treatment of **1** with N-bromosuccinimide in polar solvents gave 5-bromoacenaphthenequinone [116]. Reaction of **1** with bromine gave the 3-bromo derivative [114]. No further bromination could be effected with bromine alone but in presence of iron filings, acenaphthenequinone gave the 2,3,5-tribromo derivative. Prolonged bromination of **1** in presence of iron gave the 2,3,4,5-tetrabromo derivative. The position of the bromine atoms has not been definitely determined [117]. On the other hand, treatment of **1** with bromine in chlorobenzene as a solvent gave 1,8-naphthalic anhydride whereas the reaction did not take place in nitrobenzene [118].

Haloacenaphthenes or haloacenaphthylenes were successively brominated, dehydrobrominated, chlorinated and hydrolyzed with sulfuric acid to give haloacenaphthenequinones [119]. Reaction of **1** with PCl_5 gave dichloroacenaphthenone whose reduction with powdered Fe in glacial acetic acid gave acenaphthenone (Scheme 40) [120,121]. Haloacenaphthenequinones **153** were prepared from the corresponding tetrachlorides **154** by successive reaction with sulfuric acid and sodium sulfite and hydrolysis (Scheme 40). The tetrachloro derivatives **154** were prepared by chlorination [122] of dibromo derivatives **155**, which were prepared by bromination of **156**.

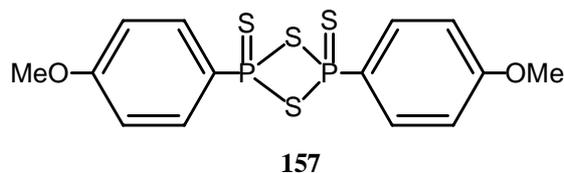
Scheme 40



3-Bromo- and 3-iodoacenaphthenequinone were obtained from the 2-bromo- and 2-iodo-acenaphthenes, respectively by oxidation with sodium dichromate [63]. Reaction of 3-iodo-acenaphthenequinone and sodium dichromate in acetic acid gave 2-iodo-1,8-naphthalic anhydride.

2.12. Thiation reactions

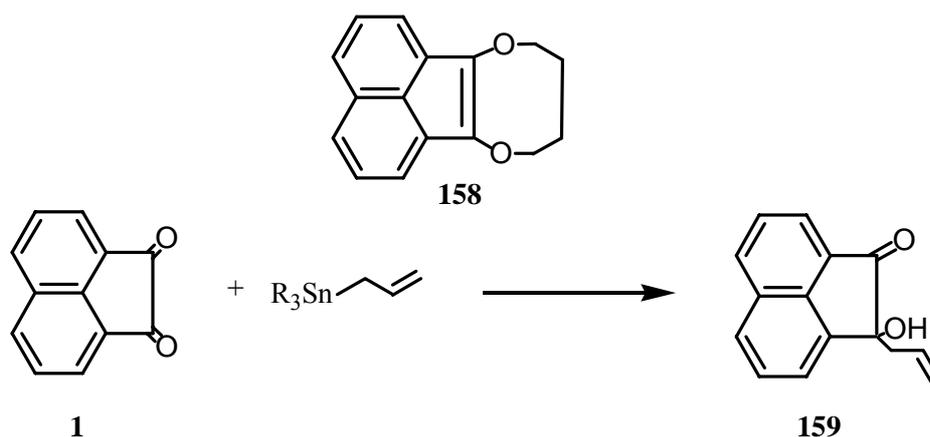
Acenaphthenequinone underwent mono thiation [123] on treatment with dithiadiphosphetane disulfide **157**.



2.13. Alkylation reactions

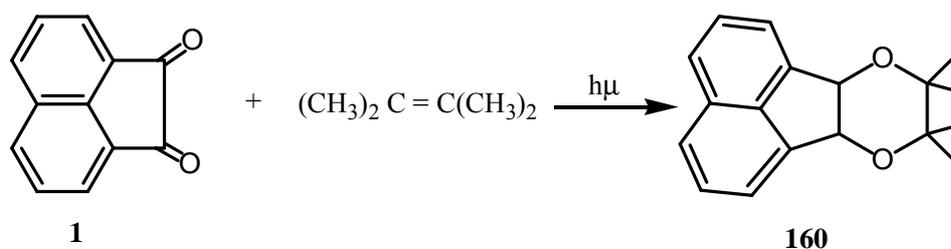
When acenaphthenequinone was treated with sodium in dry tetrahydrofuran, followed by 1,4-dichlorobutane], the product was 1,4-dioxacine derivative **158** (Scheme 41) [124]. Mercuration of acenaphthene-quinone under various conditions was failed [125]. Irradiation of a solution of **1** in acetonitrile in presence of allylic stannanes afforded homoallylic alcohols in good yields. When unsymmetrical allylstannens were used, the allylic groups were introduced predominantly at the α -positions. Complete regioselective introduction could be achieved by irradiation in presence of sodium hydroxide or cobalt chloride [126]. Reaction of **1** with trialkylallyltin gave the corresponding allylhydroquinone **159** [127] which was catalyzed by the Lewis acid [127].

Scheme 41

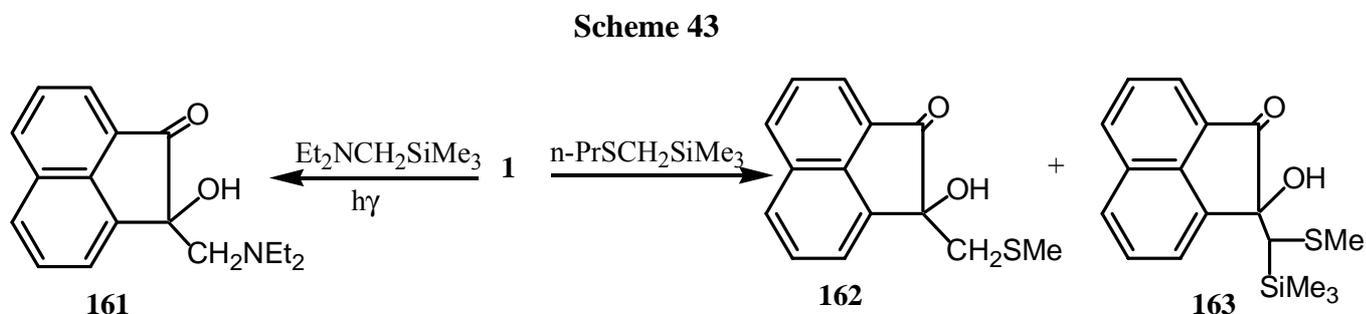


The photoaddition of **1** to cycloheptatriene gave various cycloadducts, (2+2) π -, and (2+6) π -cycloadducts together with ene product [128]. Irradiation of **1** in benzene in the presence of 2,3-dimethyl-2-butene led to a facile formation of a single photoproduct (Scheme 42) [129].

Scheme 42



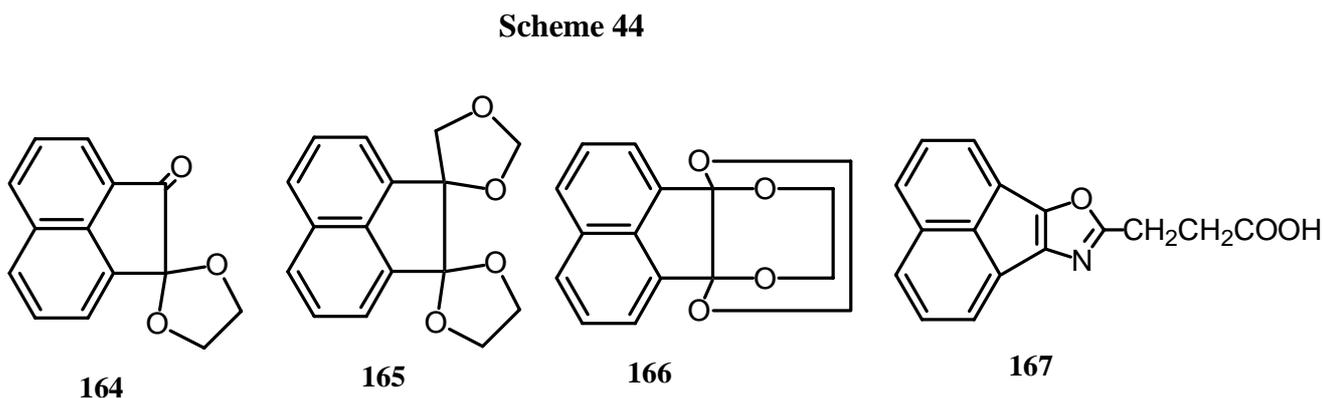
The photoaddition reaction of **1** with α -silyl n-electron donors *via* triplet single electron transfer desilylation and triplet hydrogens abstraction pathways was explored [129]. Thus, photoaddition of $\text{Et}_2\text{NCH}_2\text{SiMe}_3$ to **1** produced 2-hydroxy-2-[(diethylamino) methyl] acenaphthylen-1-one (**161**), whereas the photoaddition of $n\text{-PrSCH}_2\text{SiMe}_3$ to **1** generates two photoproducts **162** and **163** along with a photoreduction dimer of **1** (Scheme 43).



2.14. Ketal derivatives

The products of the reaction of **1** and ethylene glycol in benzene were identified by using mass spectroscopy [130,131]. The least polar compound was **164** whereas the products of the highest and intermediate polarity were **165** and **166**, respectively. Reaction of simple mercaptans with **1** gave monomercaptols (Scheme 44) [132].

The antiphlogistic compound acenaphth[1,2-b]oxazole-8-propionic acid (**167**) was prepared from **1** *via* its monoethylene ketal and 1-hydroxy-2-acenaphthenone and subsequent esterification with succinic anhydride and reaction with ammonium acetate [133].



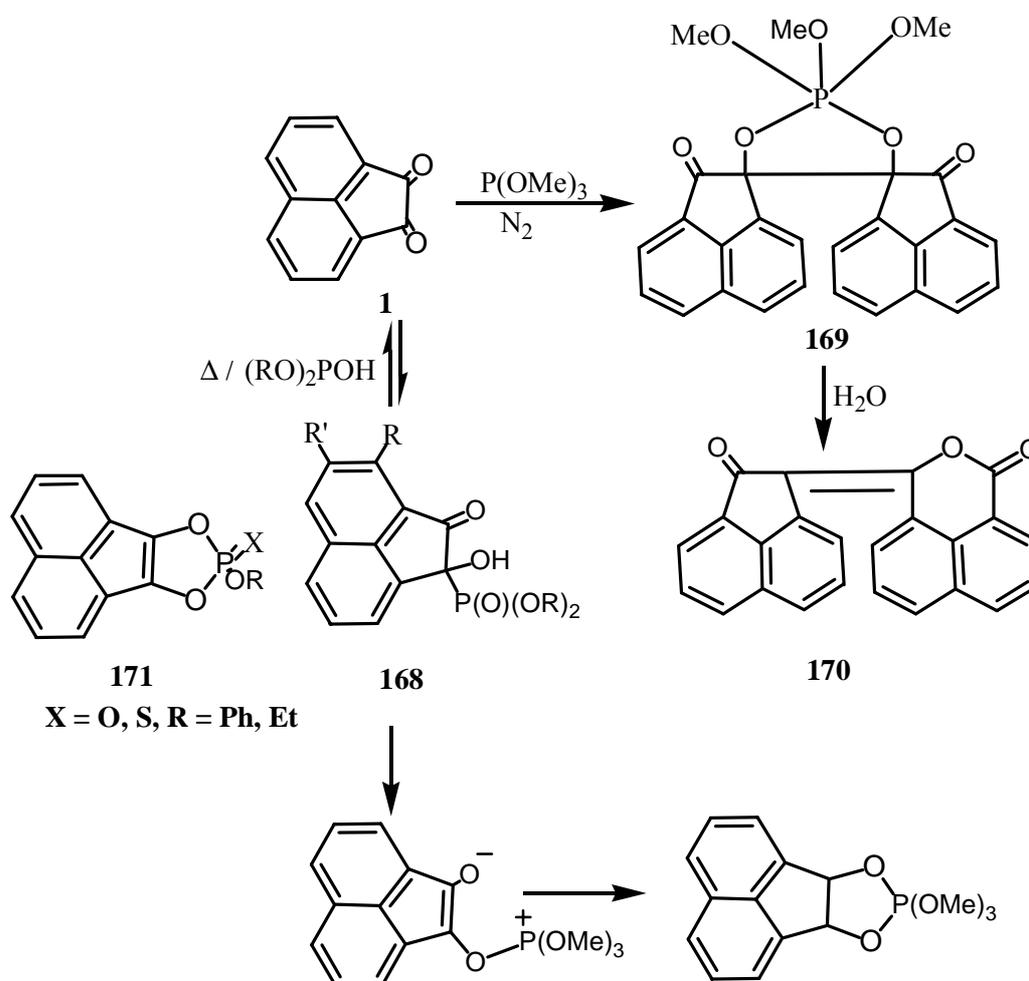
Condensation of **1** with N-(hydroxymethyl) trichloroacetamide gave 1,2-dioxo-4-trichloroacetylaminomethyl acenaphthene that was oxidized by dilute nitric acid in a sealed tube to give a $\text{C}_6\text{H}_2(\text{CO}_2\text{H})_4$ (prehnitic acid) [2].

2.15. Reaction with phosphites and phospholanes

Reaction of **1** with dialkyl phosphites yielded the phosphonates **168** [134] whose heating gave the starting quinone. Treatment of **168** with hydrogen peroxide-sodium hydroxide gave naphthalene-1, 8-dicarboxylic acid (Scheme 45).

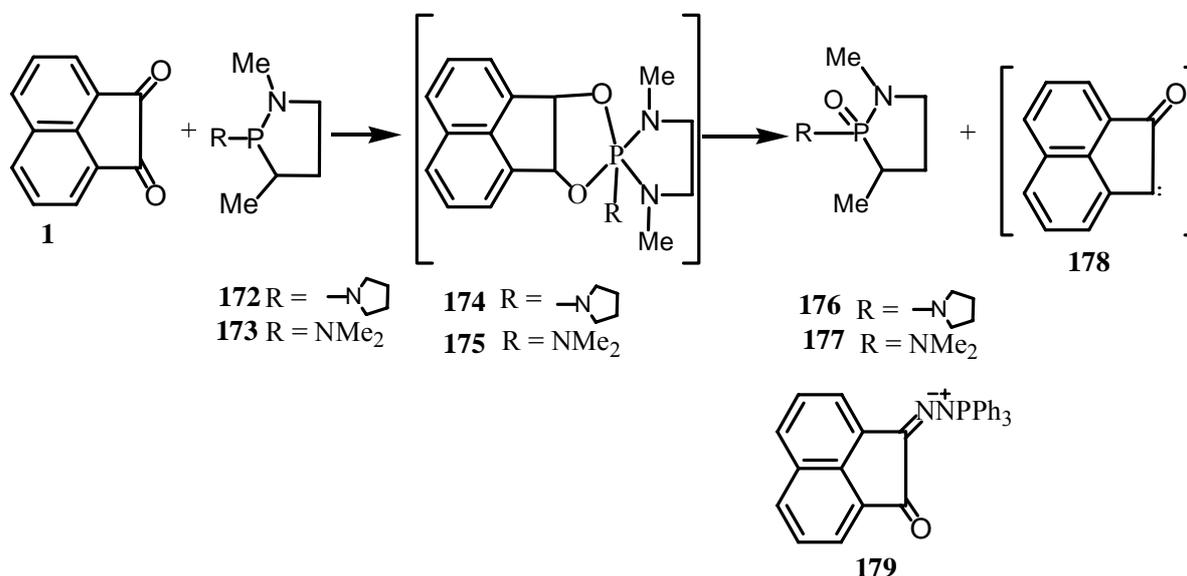
The reaction of $\text{P}(\text{OMe})_3$ with **1** under air afforded $\text{P}(\text{O})(\text{OMe})_3$ and a 1:2 adduct **169** which was rearranged into the δ -lactone **170** by addition of water, while **169** was only obtained quantitatively under nitrogen atmosphere [135,136]. E.S.R and U.V spectra, decolorization of 1,1-diphenyl-2-picrylhydrazyl, and initiation of styrene polymerization suggest the transient formation of radical ions. A mechanism, which involves one-electron transfer from phosphite to **1** followed by autoxidation, was proposed for the reaction under air [135]. The kinetic of the reaction to form a 1:1 adduct that cyclized was studied in anhydrous dioxan [137]. Treatment of **1** with sodium in tetrahydrofuran followed by $\text{Cl}_2\text{P}(\text{X})\text{OR}$ gave a fused di-oxophospholes **171** [138].

Scheme 45



The reaction of **1** with 2-N-pyrrolidino-1,3-dimethyl-1,3,2-diazaphospholane (**172**) was quite vigorous in methylene chloride solution even at -70°C (Scheme 46) [139]. When the solution was allowed to reach 20°C , a deep brown mixture was produced from which the only isolable product was 2-N-pyrrolidino-2-oxo-1,3-dimethyl-1,3,2-diazaphospholane (**176**). A similar behavior was noted when **1** was treated with 2-dimethylamino-1,3-dimethyl-1,3,2-diazaphospholane (**173**). The only isolable product was 2-dimethylamino-2-oxo-1,3-dimethyl-1,3,2-diazaphospholane (**177**). No intermediate could be detected in these reactions, but it was assumed by analogy with previous reactions that the phosphorus of the cyclic aminophosphines attacked the oxygen of **1** to give a 1:1 dipolar adduct **174** or **175**. The dipolar adduct apparently was too unstable to form the cyclic phospholene analogous to those of benzil. Instead, the 1:1 dipolar adduct lost phosphoramidate to yield a carbenoid fragment **178** which underwent further transformations. Reaction of the diazides of **1** with triphenylphosphine gave the phosphazine (**179**) [140].

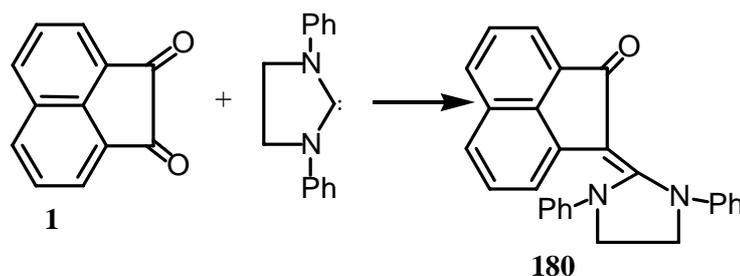
Scheme 46



2.16. Reaction with carbenes

Addition of 1,3-diphenylimidazolidin-2-ylidene to **1** gave **180** (Scheme 47) [141].

Scheme 47



2.17. Decarbonylation

Stepwise elimination of carbonyl groups occurs when a vapor of **1** was passed through glow discharge plasmas to give 1,8-dehydronaphthalene, part of which dimerizes to give perylene [142].

2.18. Reaction with nitrogen nucleophiles

The reactions of **1** with nitrogen nucleophiles namely ammonia, amines, urea, hydroxylamines, aminoacids, o-diamines and hydrazines are included in the previous review [1]. These reactions produce heterocyclic compounds or products that are precursors for the synthesis of heterocyclic compounds. Various types of heterocyclic compounds could be prepared via the use of such nitrogen nucleophiles.

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