Conjugated Ketenes: New Aspects of Their Synthesis and Selected Utility for the Synthesis of Phenols, Hydroquinones, and Quinones

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I. Introduction

This article highlights three general reactions which illustrate new syntheses and unusual chemistry of conjugated ketenes. Many of the transformations presented provide examples of intriguing mechanistic challenge and several will be of significant synthetic importance.

The first reaction emphasized is outlined in Scheme 1 and represents the ring contraction (path a) or fragmentation (path b) of appropriately substituted vinyl azides (zwittazido cleavage).[1] Particular focus is placed on the fragmentation mode since thus far this is the only synthetically useful route to cyanoketenes (**4**, Y = CO). It is a general reaction that can be employed to prepare cyanoketenes bearing a variety of substituents including alkyl, aryl, cyano, halo, alkoxy, 2-cyanoethenyl, and 2-alkynyl-2-cyanoethenyl groups. The second highlighted sequence is actually a related pair of reactions which are depicted in Schemes 10 and 14.[2,3] These interesting and useful synthetic routes to highly substituted phenols, cyclohexadienones, and cyclooctadienones are initiated by the generation of an ethenylketene from a cyclobutenone via an electrocyclic cleavage. They are unique in that they proceed by a series of pericyclic reactions (pericyclic cascade). The third general reaction is depicted in Scheme 16. Here, thermal electrocyclic ring opening of 4-aryl-4-hydroxy- and 4-alkynyl-4-hydroxy(or alkoxy or trimethylsiloxy)cyclobutenones to the corresponding conjugated ketenes is observed.[4,5,6] This conrotatory ring opening proceeds with remarkable selectivity, involving outward rotation of the electron-donating groups (OR′). Thus the resulting conjugated ketenes have the alkynyl or aryl groups and the cumulene moiety in the proximity to allow their direct interaction leading to carbocyclic ring formation. An exceptionally good synthetic route to annulated quinones and hydroquinones resulting from this reaction will be discussed.

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II. Cyanoketenes from Vinyl Azides

Scheme 1 generalizes a reaction involving the heterolysis of a C–C bond of appropriately substituted cyclic vinyl azides **1** to give the intermediate zwitterions **2**.

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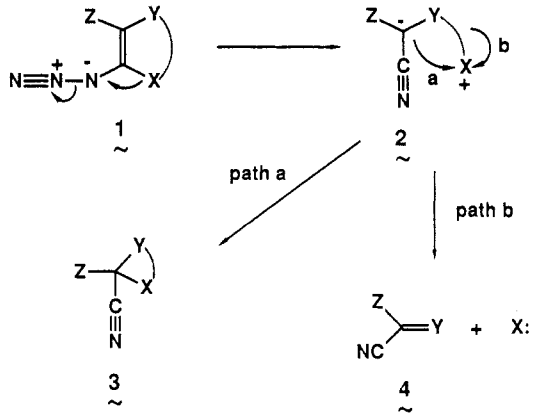
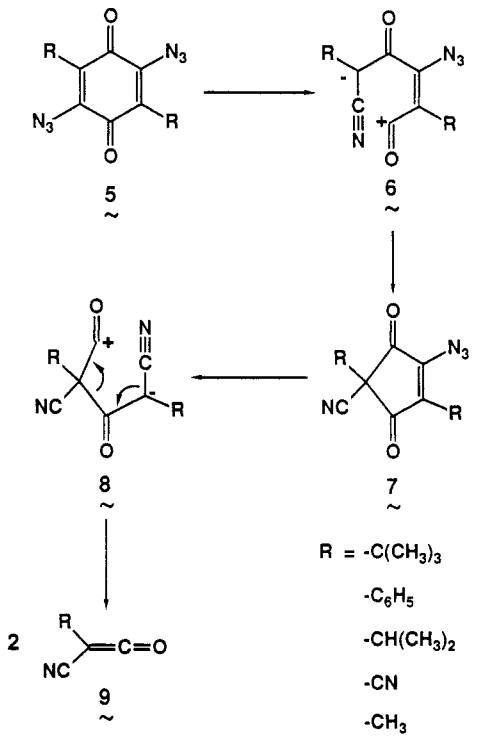
SCHEME 1



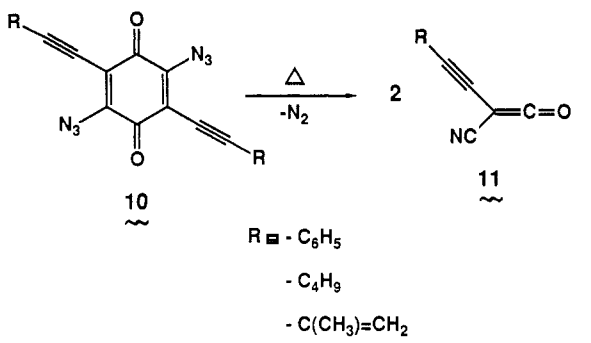
SCHEME 2



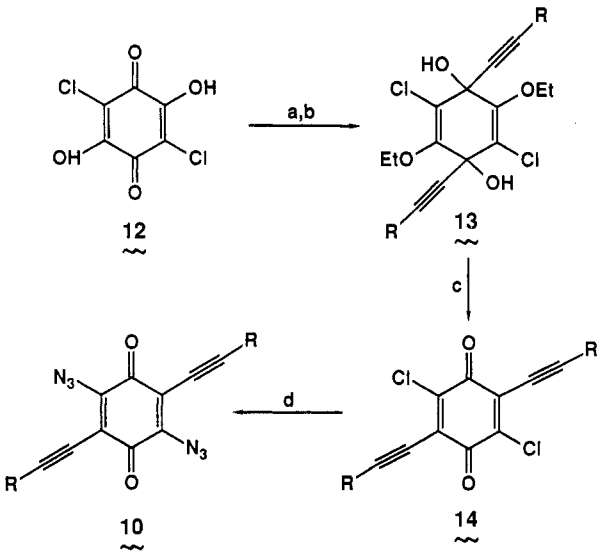
These then proceed to products **3** and **4** by the indicated pathways. Such transformations are possible when the X substituent of the starting azide can stabilize a positive charge and the Y and/or Z groups are anion stabilizing. Emphasis in this article is on the utility of vinyl azide thermolyses to cyanoketenes. However, it is noted that the appropriate vinyl azides **1** have also been shown to function as precursors to a variety of hetero- and carbocyclic ring systems. These include 2-cyanophenols,[7] 2-cyanocyclopenten-1,3-diones,[8] 4-hydroxy-5-cyanocyclopent-2-ene,[9] 2-azetidinones,[10] β-lactones,[11] mesoionic pyrimidines,[12] 2-cyano-1,3-cyclobutenediones,[13] and azaquinones.[14]

Scheme 2 illustrates a specific example of the thermolysis of 2,5-diazido-1,4-benzoquinones **5** to cyanoketenes.[15] These azidoquinone thermolyses are of particular importance for the synthesis of alkyl- and aryl-substituted cyanoketenes since they constitute the only general route to such compounds. The mechanism of the reaction has been established to involve the intermediacy of 4-azidocyclopentene-1,3-diones **7**. The zwitterions **6** and **8** are assumed to be generated during the course of the reaction.[16] One last example is provided in Scheme 3.[17] This depicts the thermolysis of 2,5-diazido-3,6-dialkynyl-1,4-benzoquinones (**10**) which results in the corresponding alkynylcyanoketenes **11**. Such compounds are noteworthy since they are the only known examples of ketenes having an alkynyl group in direct conjugation with the cumulene unsaturation. Although only a few examples of ketenes **11** have thus far been prepared, a general route is presumably now available since the azido quinones **10** are easily prepared from 2,5-dialkynyl-3,6-dichloro-1,4-benzoquinones and these result from chloranilic acid **12** as illustrated in Scheme 4.[18] Further details of this reaction will not be discussed here since the chemistry of azido quinones and their utilization as precursors to cyanoketenes have been reviewed.[19,20]

SCHEME 3



SCHEME 4[a]

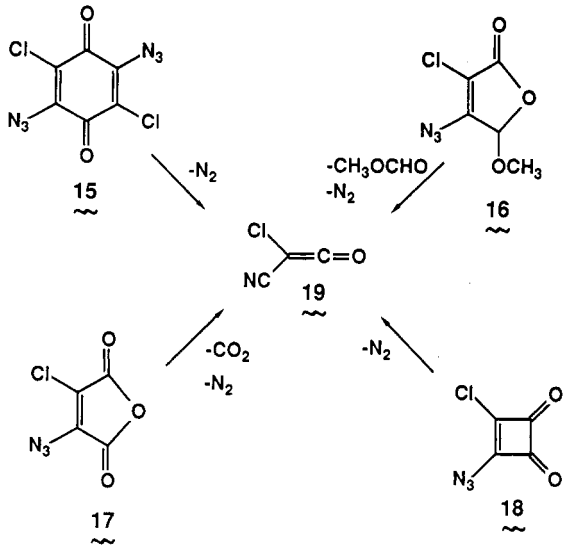


[a] (a) $CH(OC_2H_5)_3$; (b) LiC≡CR, THF, −78 °C; (c) $(CF_3CO)_2O/H^+$; (d) NaN_3.

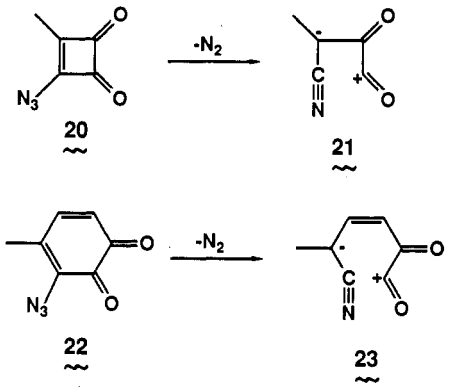
Generation of chlorocyanoketenes from the corresponding diazidoquinone (e.g., **15** → **19** Scheme 5) is not a synthetically useful reaction due to the insolubility of 2,5-diazido-3,6-dichloro-1,4-benzoquinone. However, halocyanoketenes are readily available from other vinyl azides as is predicted by the mechanistic rational outlined in Scheme 1. For example, 4-azido-3-chloro-5-methoxy-2(5*H*)-furanone (**16**) smoothly cleaves to chlorocyanoketene (**19**) and methyl formate in refluxing benzene.[21] In a related fashion the azidomaleic anhydride **17** and 3-azido-4-chlorocyclobutendione (**18**) have also been observed to give chlorocyanoketene.[22,23]

The conversion of **18** to **19** is of particular note since this takes place at temperatures as low as −30 °C when

SCHEME 5



SCHEME 6

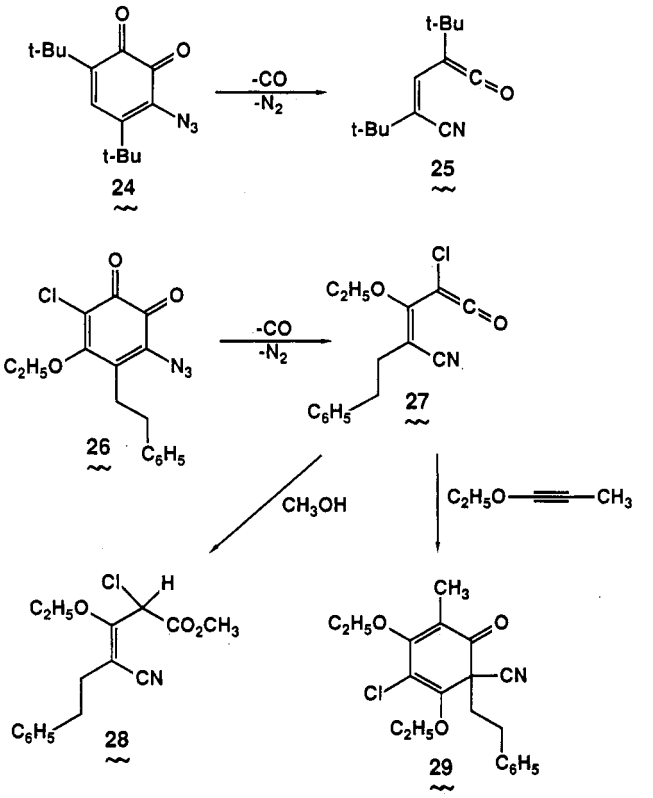


the azidocyclobutenedione is generated from 2,3-dichlorocyclobutenedione upon treatment with sodium azide in acetonitrile. The low temperature associated with the conversion of **18** to **19** and the fact that the other ketene precursors, **15**, **16**, and **17**, all require much higher temperatures (80 °C) to induce their decomposition suggests a sequence of concerted bond cleavages in the initial step of the reaction. Specifically, the decomposition of all of these azides can be mechanistically cataloged according to Scheme 1 where the first and rate-determining step is synchronous with C–C bond cleavage and loss of nitrogen. Since **15**, **16**, **17**, and **18** all possess the β-azido-α-chloro enone moiety and it is only the strained cyclobutenedione **18** which fragments at low temperature, one can conclude that the indicated conversion of **1** to **2** is concerted and involves more than the loss of nitrogen in the rate-determining step.

III. (2-Cyanoethenyl)ketenes from 3-Azido-1,2-benzoquinones

Zwitterion **21** is the intermediate proposed to arise from an azidocyclobutenedione **20** (Scheme 6). Subsequent loss of carbon monoxide would then give the corresponding cyanoketene, e.g., **19**. By analogy, it is reasoned that thermolysis of 3-azido-1,2-benzoquinones (**22**) would lead to the vinylogous zwitterion **23** and that this would provide a new entry to ethenylketenes upon loss of carbon monoxide. This was found to be the case.[24] For example, 3-azido-4,6-di-*tert*-butyl-1,2-

SCHEME 7



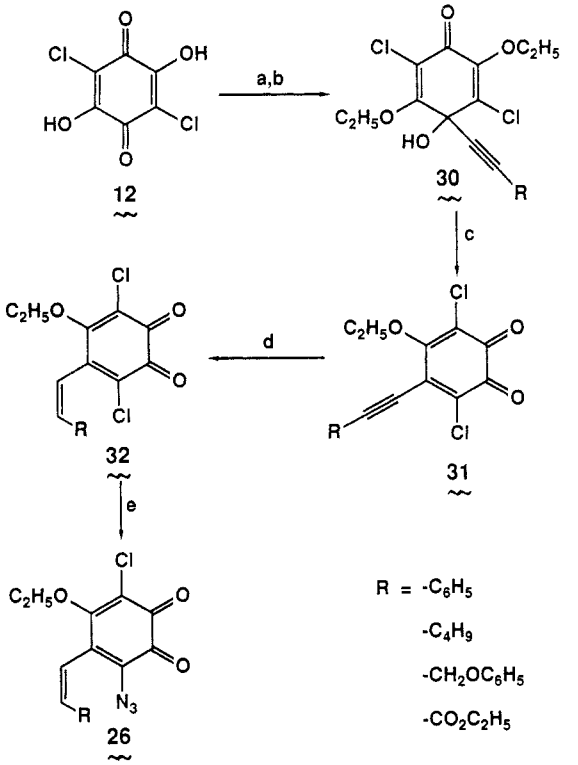
benzoquinone (**24**) was observed to give a 73% yield of the remarkably stable (2-cyanoethenyl)ketene **25** in refluxing benzene (Scheme 7). The stability of **25** is illustrated by the fact that it can be isolated as a yellow oil by distillation. Furthermore, it requires 24 h at ambient temperature to completely react with excess methanol.

In a related experiment, the azidoquinone **26** was thermolyzed in refluxing benzene in the presence of, respectively, methanol and ethoxypropyne. The former reaction gave the ester **28** and the latter the cyclohexadienone **29**. The ketene **27** could not be isolated, but the above products are consistent with its existence. For example, **28** is the product of methanol addition to a ketene, and **29** would arise via a pericyclic cascade analogous to that outlined in Scheme 12.

The azido quinone **26** is readily available from the corresponding 3,6-dichloro-4-phenethyl-5-ethoxy-1,2-benzoquinone. This, in turn, is obtained from chloranil as outlined in Scheme 8 which presents a general route to 1,2-benzoquinones **32**.[25] Generation of the monoalkynylated quinol **30** followed by hydrolysis gives good yields of the alkynyl-1,2-benzoquinones **31**. Reduction of the alkyne group then results in **32**. Treatment of **32** with azide ion provides **26**.

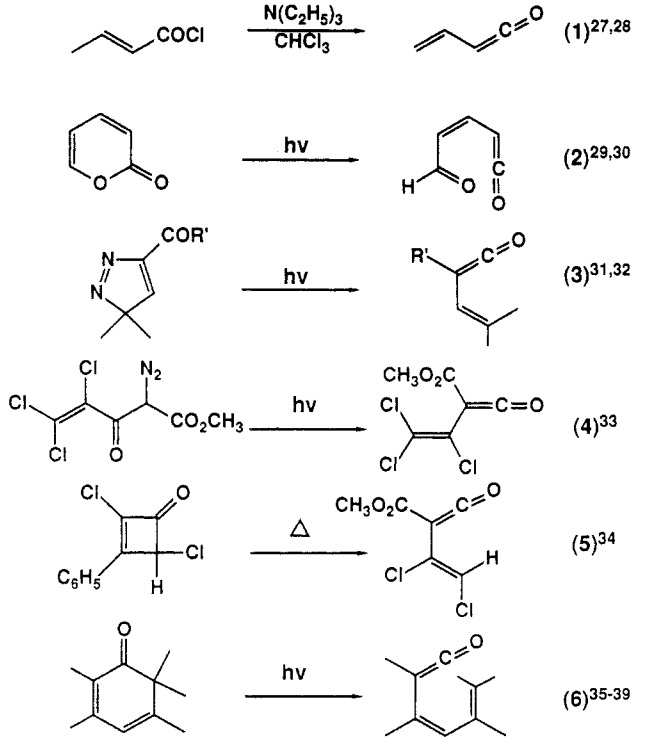
The conversion of 3-azido-1,2-benzoquinones to (2-cyanoethenyl)ketenes is noteworthy since it provides a new route to ethenylketenes, a class of cumulenes of synthetic note. To provide a detailed discussion of the synthesis of such ketenes is beyond the scope of this review. Suffice it to say that their other syntheses can be cataloged generally as dehydrohalogenation reactions, fragmentation reactions, and electrocylic ring openings. Representative examples are given in Scheme 9.[26] Particular note is made of the electrocyclic ring opening of cyclobutenones to ethenylketenes (eq 5, Scheme 9). This represents one of the most useful

SCHEME 8[a]



[a] (a) $CH(OC_2H_5)_3$; (b) LiC≡CR, -78 °C, THF; (c) $(CF_3CO)_2O$/H^+; (d) H_2; (e) NaN_3.

SCHEME 9



methods for the generation of ethenylketenes and also illustrates a key step involved in the next reaction to be highlighted—the pericyclic cascade.[2,3]

IV. Ethenylketenes from Cyclobutenones

A unique reaction sequence involving a series of pericyclic reactions has been developed for the synthesis of highly substituted aromatic compounds.[2] This is

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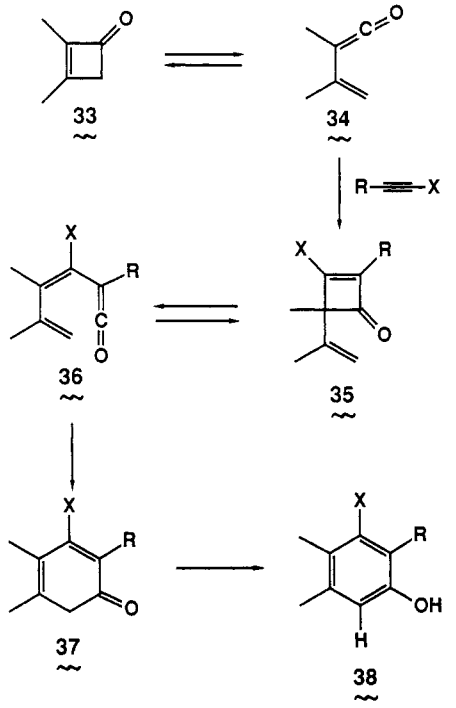
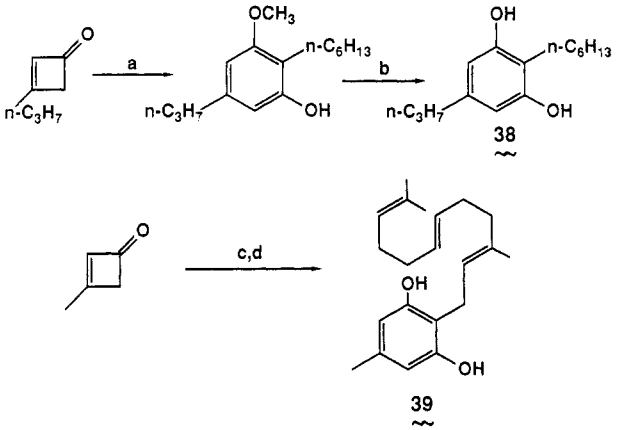


SCHEME 11[a]

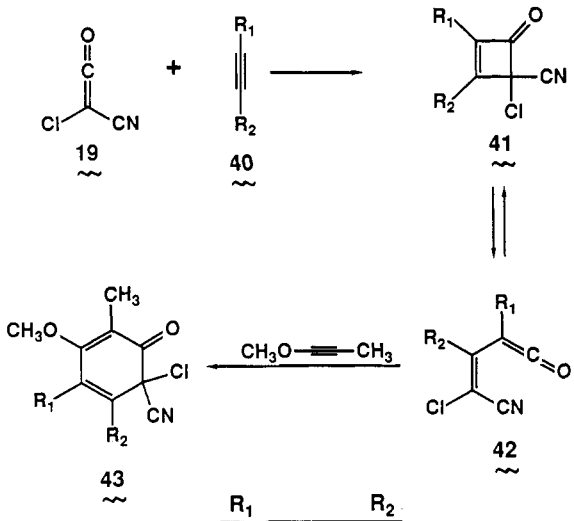


[a] (a) n-$C_6H_{13}C{\equiv}COCH_3$, 80 °C; (b) Me_3SiI, CH_3CN; (c) CH_3-$C{\equiv}C(CH_2CH{=}C(CH_3)CH_2)_2$, 80 °C; (d) MeMgI, 165 °C.

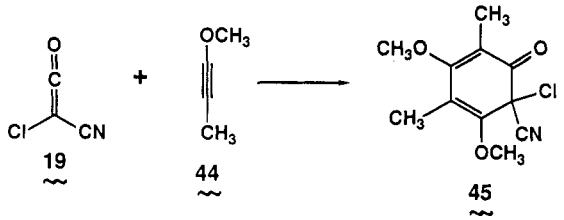
generally outlined in Scheme 10 which illustrates a cascade of four pericyclic reactions induced by treatment of a cyclobutenone with a heterosubstituted alkyne. This is envisaged to involve an initial reversible four-electron electrocyclic ring opening of the cyclobutenone **33** to the ethenylketene **34** which then combines with the ketenophilic alkyne (X = OR, SR, NR_2) in a regiospecific [2 + 2] cycloaddition to give **35**. Reversible electrocyclic cleavage of **35** furnishes the dienylketene **36** which is subject to a six-electron electrocyclization to the cyclohexadienone **37**. Final tautomerization yields the phenol **38**. This reaction sequence has been elegantly employed for the regiospecific synthesis of the antifungal antibiotic DB-2073 **38** and grifolin **39** (Scheme 11).[2]

Another example of this pericyclic cascade is given in Scheme 12.[22] Here, the cyclobutenones **41** were readily obtained from the cycloaddition of chlorocyanoketene (**19**) to a series of alkynes **40**. Treatment of a benzene solution of these cyclobutenones with methoxypropyne at ambient temperature induced an

SCHEME 12



SCHEME 13

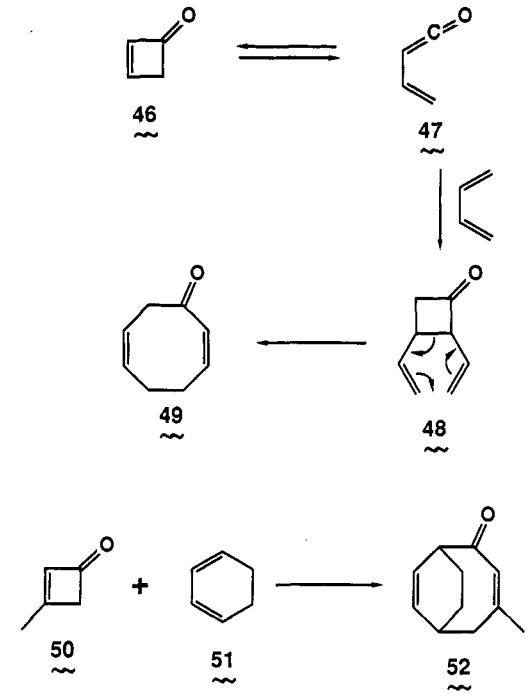


immediate reaction to give the cyclohexadienones **43** in high yield. A pericyclic cascade involving the initial formation of the ethenylketene **42** is undoubtedly inolved in this transformation. A final example is given in Scheme 13 which illustrates the formation of the cyclohexadienone **45** when chlorocyanoketene (**19**) was generated in the presence of excess methoxypropyne (**44**) at 80 °C. This transformation must involve no less than five pericyclic reactions—two [2 + 2] cycloadditions, two electrocyclic ring openings, and one electrocyclic ring closure.

Finally, a cascade involving each major class of pericyclic reactions is generally outlined in Scheme 14.[3] Electrocyclic ring opening of the cyclobutenone **46** leads to the ethenylketene **47**. When accomplished in the presence of a 1,3-diene the divinylcyclobutanone **48** is generated which upon 3,3-sigmatropic rearrangement results in 2,6-cyclooctadienones **49**. A specific example is the synthesis of the bicyclic ketone **52** which was accomplished in 49% yield when a benzene solution of the cyclobutenone **50** and 5 equiv of cyclohexadiene **51** was heated at 80 °C for 65 h.

An important but relatively unexplored stereoelectronic consequence of the electrocyclic cleavage of cyclobutenones to ethenylketenes concerns the outward vs. inward rotation of substituents at C_4. Although little has appeared on the ring opening of cyclobutenones with regard to this question, several studies have been reported on the conrotatory thermal ring opening of cyclobutenes.[52-55] This work was recently evaluated in a theoretical study which concludes that the observed outward rotation of electron-donating groups can be

SCHEME 14

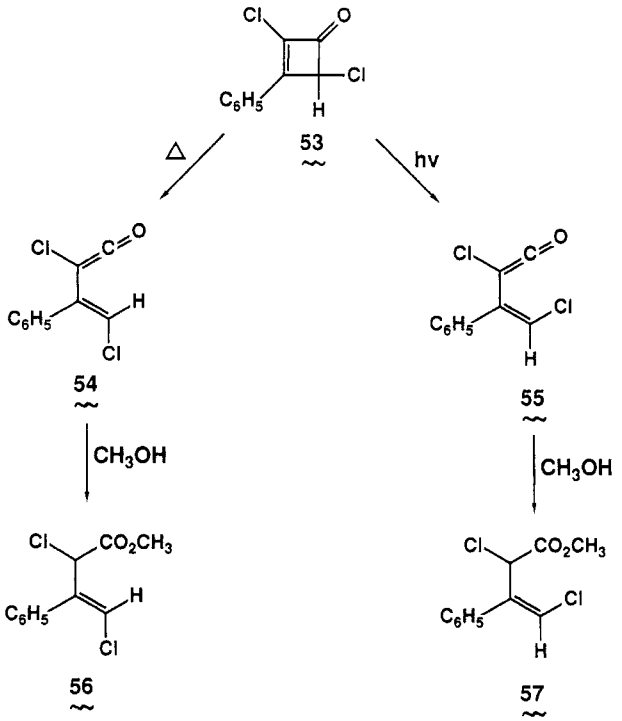


rationalized on the basis of electronic rather than steric effects.[56] It was demonstrated computationally that electron donors at C_3 and C_4 preferentially rotate outward in order to maximize the stabilizing two-electron interaction between the donor nonbonding electron pair orbitals on the substituent with the empty C_3C_4 σ^* orbital and to minimize the repulsive four-electron interaction between the same donor orbitals with the occupied C_3C_4 σ orbital. This tendency for outward rotation increases as the electron-donor ability of the substituent increases, and the selectivity can be exceptional. For example, the outward rotation of the OH group is estimated to be more favorable than inward rotation by 14 kcal/mol. Outward rotation of a Cl group is favored by 9 kcal/mol and an NH_2 by as much as 26 kcal/mol.

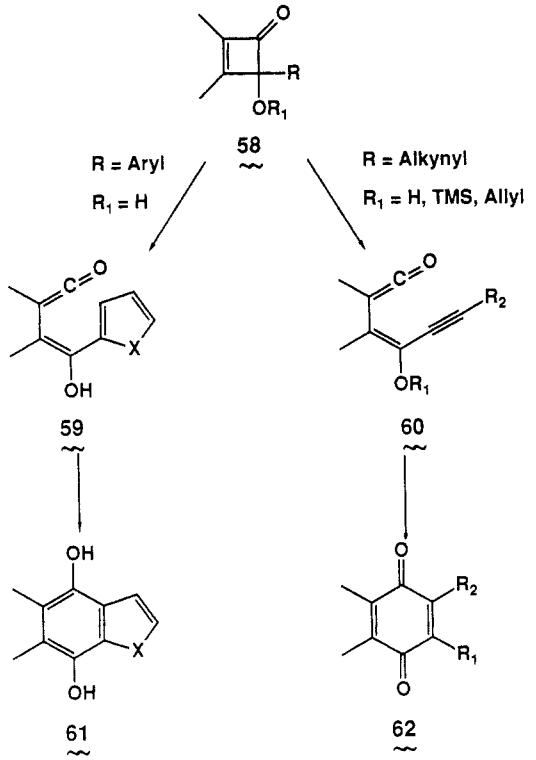
The above trends also appear to be applicable to the electrocyclic cleavage of cyclobutenones. For example, the thermolysis of **53** in methanol at 100 °C was observed to proceed stereospecifically to the (*E*)-ester **56** and presumably involves the ketene **54** which must arise via outward rotation of the chlorine substituent at C_4 (Scheme 15).[34] Interestingly, photolysis of **53** in methanol at −10 °C gives the opposite stereochemical outcome in that the (*Z*)-ester **57** was obtained. This results from addition of methanol to the ketene **55** which presumably arises from a disrotatory cleavage in which the chlorine group now rotates inward.

The above experimentally observed and theoretically explicable selectivity of the electrocyclic cleavage of cyclobutenones to ethenylketenes suggests a number of interesting mechanistic studies and synthetic applications. A particularly noteworthy example is the general and useful route to quinones and hydroquinones outlined in Scheme 16.[3,4,5] Hydroquinones **61** (X = S, O, N–Ts, CH=CH) arise from 4-aryl-4-hydroxycyclobutenones **58** (R = aryl). This is envisaged to arise via an electrocyclic cleavage to **59** (138 °C, *p*-xylene) which then gives **61** via ring closure and tautomerization. Quinones arise via an analogous ring opening of 4-alk-

SCHEME 15



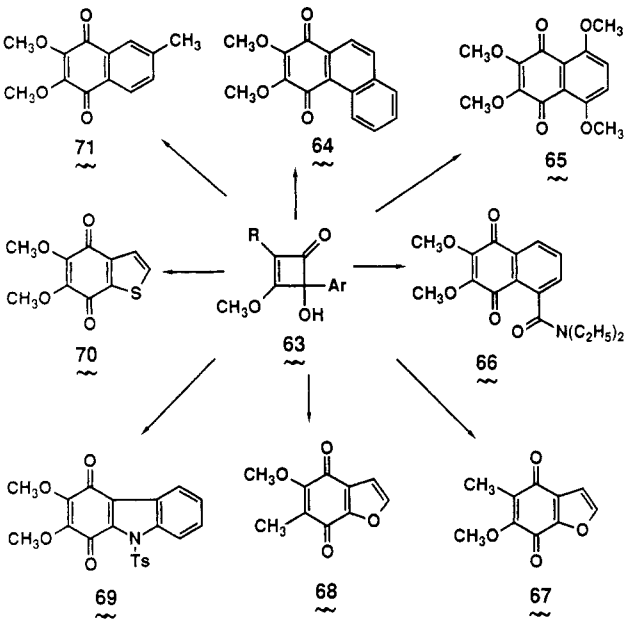
SCHEME 16



ynyl-4-hydroxy(or alkoxy or trimethylsiloxy)cyclobutenones to the ethenylketenes **60** which then undergo ring closure and a remarkable reorganization to the benzoquinones **62**. Both of these transformations are suggested to be dictated by a favored conrotatory ring opening of the cyclobutenones **58** such that the electron-donating substituents (OR′) rotate outward. Thus, the configuration of the resulting ketenes **59** and **60** is such that their electrophilic site can directly interact with the proximal alkynyl or aryl group.

Both the hydroquinone and quinone syntheses given above are likely to achieve wide applicability. They

SCHEME 17



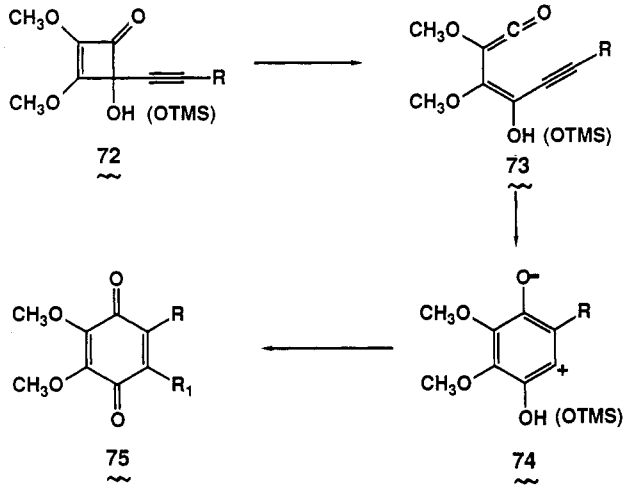
have the advantages of being convergent, and general, and of providing products in good to excellent yields. The hydroquinone synthesis is analogous to the ring expansion of 4-aryl- and 4-alkenylcyclobutenones lacking the 4-hydroxy group to naphthols and phenols.[40-50] It is also related to the reaction of metal carbonyl–carbene complexes with alkynes which constitutes still another synthesis of naphthols and most likely involves metal complexes of (2-arylethenyl)ketenes.[51] The quinone synthesis is more unusual and is without a close precedent.

Examples of the rearrangement of 4-aryl-4-hydroxycyclobutenones **63** to annulated hydroquinones are provided in Scheme 17. The products are listed as the quinones **64–71** which were isolated in 76–94% yields after oxidative workup of the initially formed hydroquinones. Particular note is made of isomers **67** and **68** since their independent syntheses demonstrate complete regiochemical control. That is, **67** arises from **63** which was obtained by treating 3-methoxy-4-methylcyclobutenedione with 2-lithiofuran and **68** stems from the same cyclobutenedione and 3-lithiofuran. In general, the starting cyclobutenones were prepared in 59–73% isolated yields by treating the cyclobutendiones (THF, −78 °C) with the appropriate aryllithium reagent and quenching the reaction with 5% NH_4Cl at −78 °C.

Surprisingly, when 4-alkynyl-4-hydroxy(or trimethylsiloxy)cyclobutenones **72** were thermolyzed in refluxing xylene as described above, they rearranged directly to the quinones **75** in yields ranging from 41–80%. This unique transformation is viewed as proceeding as outlined in Scheme 18. The initially formed (2-alkynylethenyl)ketenes **73** are proposed to ring close to the unprecedented zwitterionic or diradical intermediate **74**. Migration of the hydrogen or TMS group then gives directly the benzoquinones **75**.

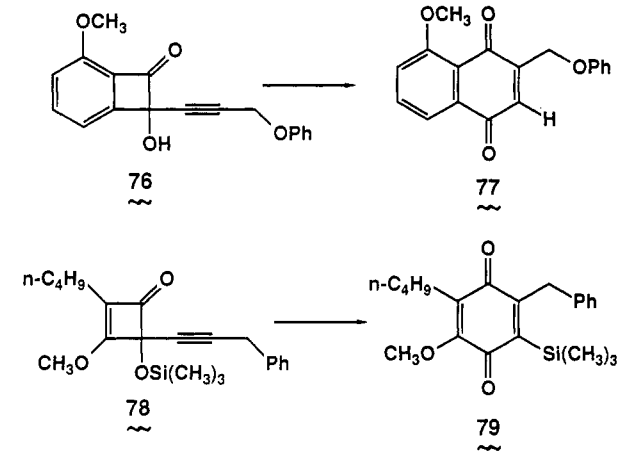
Two further examples of this rearrangement are given in Scheme 19. The first example illustrates its applicability to the regiospecific synthesis of naphthoquinone **77** from benzocyclobutenone **76**. The second documents the regiospecific synthesis of the highly functionalized benzoquinone **79** from **78**. The regiochemical control for both of these transformations takes

SCHEME 18

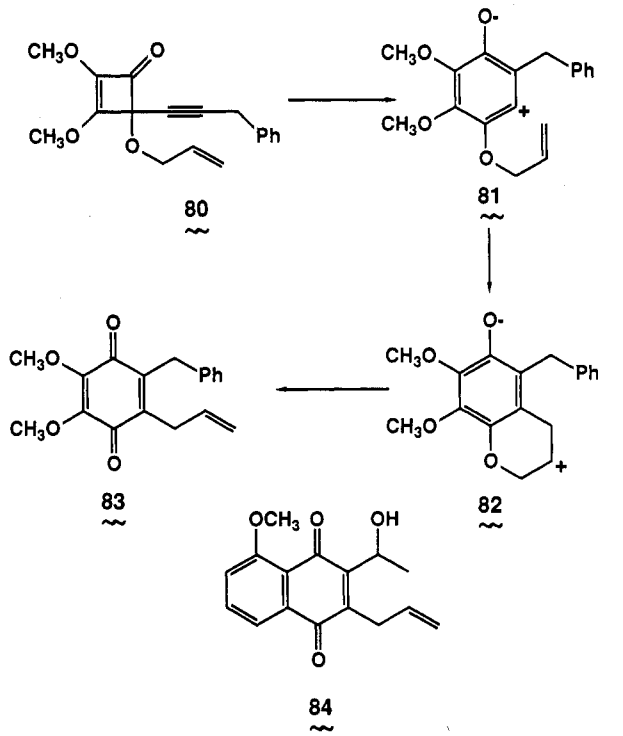


R	R_1	Yield
-n-C_4H_9	TMS	75
-n-C_4H_9	H	77
-$CH_2C_6H_5$	TMS	74
-$CH_2C_6H_5$	H	71
-CH_2OTMS	TMS	80
-CH_2OTMS	H	56
-CH_2OTHP	TMS	41
-CH_2OTHP	H	47
-$CH(CH_3)OTMS$	H	64

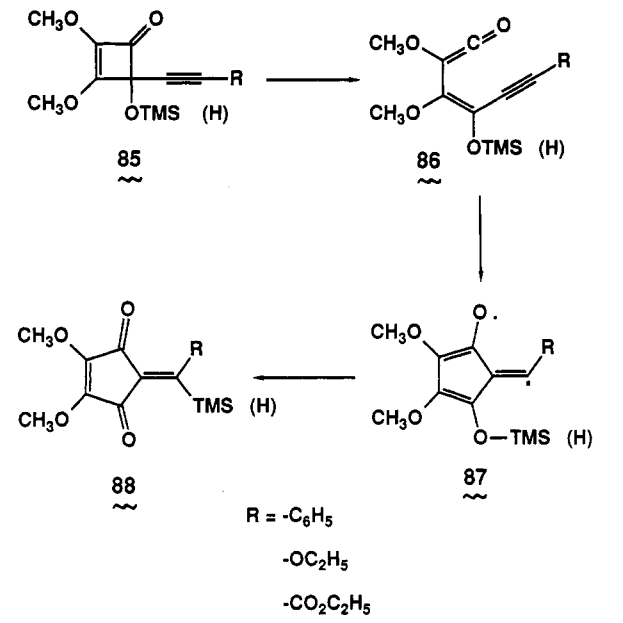
SCHEME 19



SCHEME 20



SCHEME 21

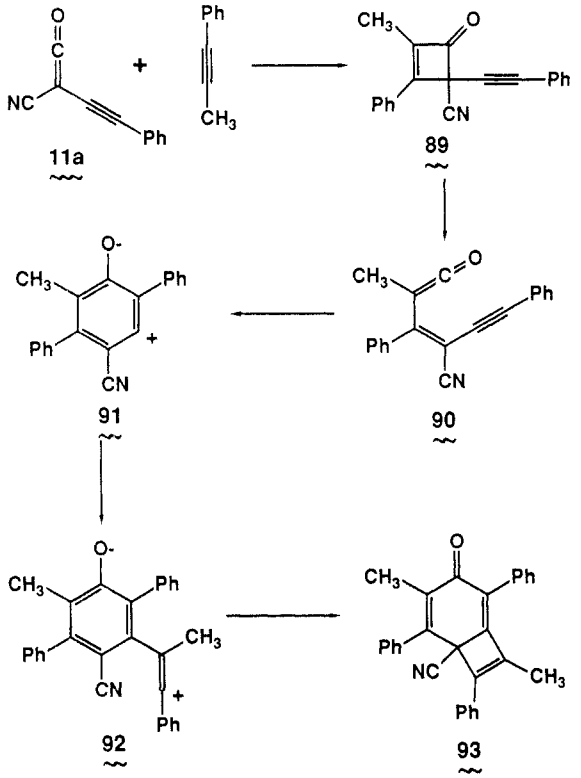


place in the initial alkynylation of the diones which proceeds with high selectivity.

A particularly interesting example of the alkynylcyclobutenone/quinone rearrangement is one involving an allyl group migration (Scheme 20). Here, the starting cyclobutenone **80** was prepared from 2,3-dimethoxycyclobutenedione via initial alkynylation followed by allylation of the resulting alcohol. Thermolysis of **80** for 1 h in refluxing *p*-xylene gave the benzoquinone **83** (76%). This rearrangement is envisaged to involve a (2-alkynylethenyl)ketene which cyclizes to the zwitterion **81**. Subsequent intramolecular attack of the cation on the allyl double bond would give **82** which proceeds to **83** upon C–O bond cleavage. By an analogous route, a regiospecific synthesis of the naphthoquinone **84** was accomplished, and this constitutes a formal total synthesis of the naturally occurring quinone, nanaomycin D.[57]

A limitation to the alkynylcyclobutenone rearrangement for the synthesis of quinones is given in Scheme 21.[4] Specifically it was observed that, at variance to the aforementioned examples having R = alkyl, the alkynylcyclobutenones **85** having R = C_6H_5, OC_2H_5, CO_2CH_3 rearrange to the 2-alkylidene-1,3-cyclopentenones **88** and gave little or none of the corresponding benzoquinones. The influence of the R-substituents in controlling five-membered ring formation suggests that the ketenes **86** ring-close to the diradical **87** which then proceeds to products. The diradical character of **87** is reasonable since the substituents are all capable of stabilizing an adjacent radical. A zwitterion structure seems less likely since only two of the substituents (C_6H_5, OC_2H_5) would provide the stabili-

SCHEME 22



zation for an adjacent cationic site. Indeed, the carbomethoxy group would be expected to destabilize the cationic center.

V. (2-Alkynylethenyl)ketenes from 4-Alkynyl-3-azido-1,2-benzoquinones and Alkynylketene/Alkyne Cycloadditions

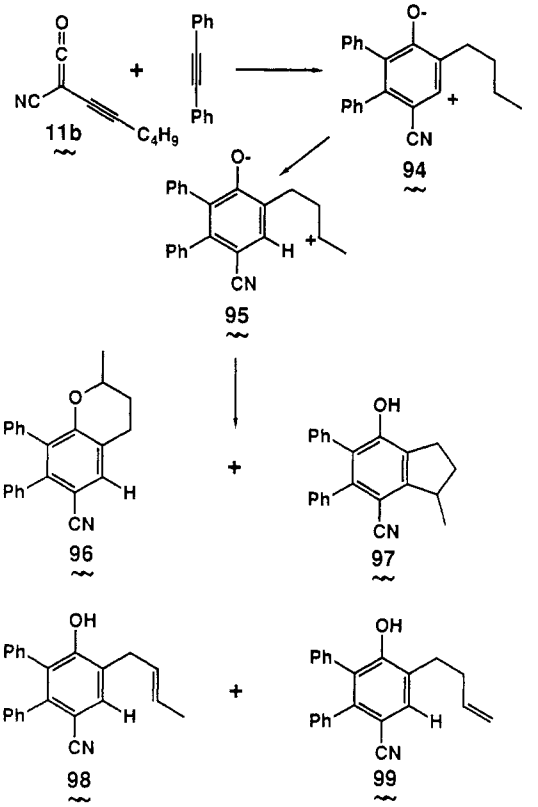
The observation that (2-alkynylethenyl)ketenes are produced by the thermal electrocyclic cleavage of 4-alkynylcyclobutenones (Scheme 16) and the fact that such cyclobutenones can be prepared by the cycloaddition of ketenes to alkynes (e.g., Scheme 12) allows the prediction that such conjugated ketenes could also be generated from the cycloaddition of alkynylketenes to alkynes. To test this postulate, phenylethynylcyanoketene was generated from the corresponding 2,5-diazidoquinone in the presence of phenylpropyne. This resulted in a most unusual transformation to give **93** in 40% isolated yield (Scheme 22). Based upon the analogies thus far presented, **93** can be envisaged to arise from the cyclobutenone **89** which results in the (2-alkynylethenyl)ketene **90** upon electrocyclic cleavage. Subsequent ring closure to the penultimate intermediate **91** and its interception with another equivalent of phenylpropyne would result in the ultimate intermediate **92** which can now collapse to **93**.

In a related study hexynylcyanoketene (**11b**) was generated in the presence of diphenylacetylene (Scheme 23).[6] The resulting cyclobutenone was not detected but is most likely formed and cleaves to the (2-alkynylethenyl)ketene which subsequently closes to the zwitterion **94**. This then undergoes intramolecular hydride abstraction to produce **95**. Subsequent ring closure and proton elimination give the products **96**, **97**, **98**, and **99** in a respective ratio of 1.0:1.0:0.2:0.3 (54%).

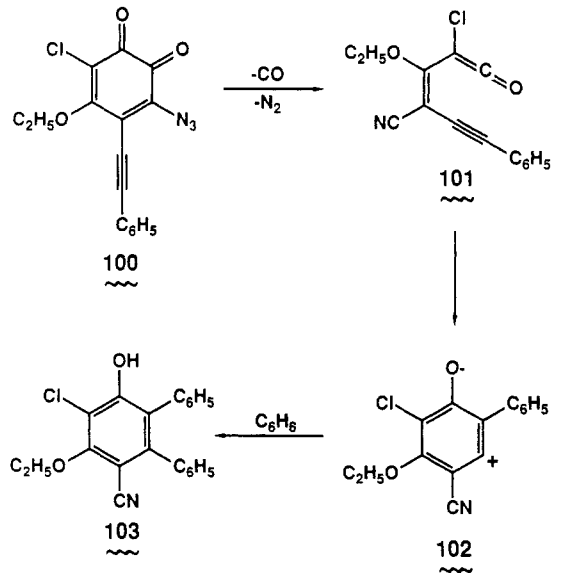
Still another route to (2-alkynyl-2-cyanoethenyl)-ketenes arises from the thermolysis of 3-azido-4-alkynyl-1,2-benzoquinones **100** (Scheme 24).[6] This is a predictable extension of the previously described conversion of 3-azido-4-alkyl-1,2-benzoquinone **26** to (2-cyanoethenyl)ketene **27** (Scheme 7). An example of an unusual transformation in the alkynylazidoquinone series is given in Scheme 24. Here **100** was subjected to thermolysis in refluxing benzene. This resulted in the formation of the cyanophenol **103** in 72% isolated yield. The ketene **101** was established to be formed during this reaction and it is suggested to give the intermediate **102** which then traps a molecule of benzene via an electrophilic aromatic substitution reaction.[6]

Further examples of the unique thermolyses of 3-azido-4-alkynyl-1,2-benzoquinones are given in Scheme 25.[21,58] Illustrated here are a number of intermolecular

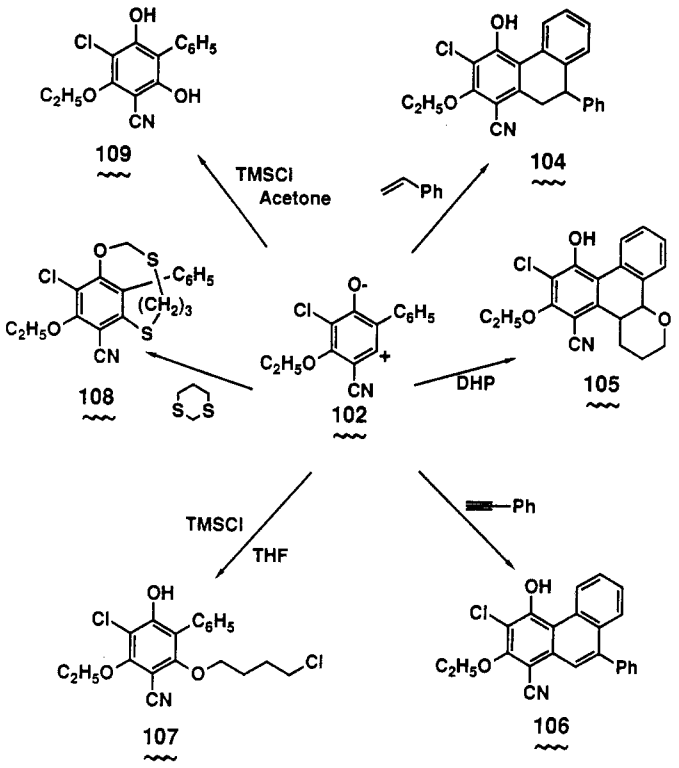
SCHEME 23



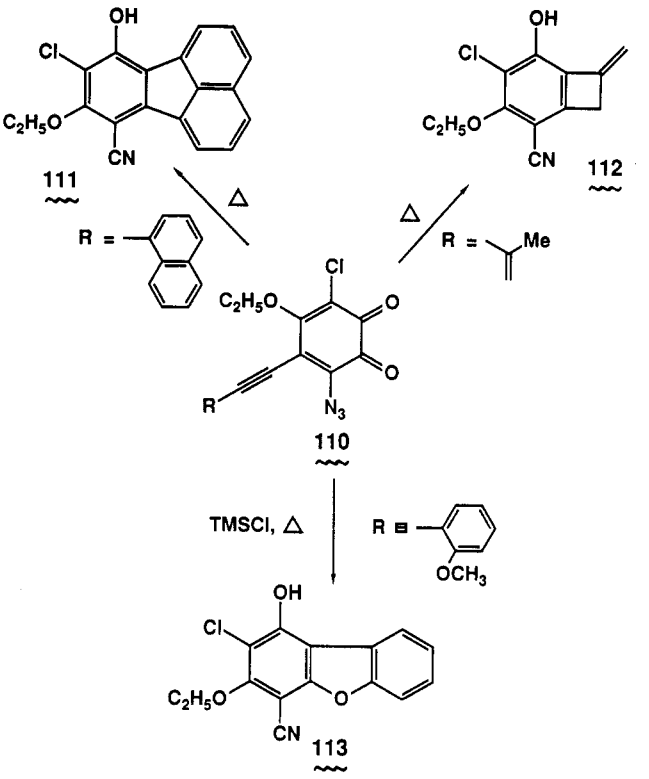
SCHEME 24



SCHEME 25



SCHEME 26



reactions between intermediates **102** and various substrates. Compounds **104**, **105**, and **106** are viewed as arising via cycloaddition reactions in which the phenyl substitutent of **102** becomes involved. The cyanophenol **107** is viewed as arising via interception of **102** by THF to give an oxonium ion. Silylation of the phenoxide ion and opening of the oxonium ion by chloride attack followed by hydrolytic workup would give **107**. The unusual metacyclophane **108** must arise via an initially formed sulfonium ion. The phenol **109** could arise via interception of **102** by acetone followed by proton loss to an enol ether. Hydrolytic workup would then give **104**.

Finally three examples involving intramolecular trapping of the presumed dipolar intermediate are given in Scheme 26.[58] The azidoquinones **110** result in the intriguing rearrangements to **111**, **112**, and **113** in refluxing benzene. A mechanism involving fragmentation of **110** to the corresponding (2-alkynylethenyl)ketene and ring closure to the zwitterionic intermediate is suggested. Subsequent intramolecular electrophilic attack at the R group would then ultimately lead to the observed products.

VI. Summary and Conclusions

The conjugated ketenes featured in this review are conveniently prepared, and their reactions exhibit high selectivity. Thus, their further utilization for practical synthetic objectives is anticipated. The zwittazido cleavage of vinyl azides provides an excellent general synthesis of cyanoketenes (Scheme 2). This reaction can be successfully extended to the preparation of (2-cyanoethenyl)ketenes from 3-azido-1,2-benzoquinones (Scheme 7) and (2-alkynyl-2-cyanoethenyl)ketenes from 4-alkynyl-3-azido-1,2-benzoquinones (Scheme 24). Various cyclobutenones undergo stereoselective electrocyclic ring openings to ethenylketenes, (2-alkenylethenyl)ketenes or (2-alkynylethenyl)ketenes (Schemes 11, 16, 20).

The conjugated ketenes described here undergo a variety of interesting reactions. Examples from many structural types show that they undergo regioselective [2 + 2] cycloadditions with alkenes and alkynes (Schemes 12, 13, 14). When the cyclobutenones produced by such cycloadditions bear alkenyl, alkynyl, or aryl groups, electrocyclic ring opening leads to ketenes with extended conjugation. These ketenes exhibit a rich chemistry of unusual synthetic promise. (2-Alkenylethenyl)ketenes undergo a six-electron ring closure to cyclohexadienones which proceed to highly substituted phenols after tautomerization (Schemes 10, 11). (2-Hydroxy-2-arylethenyl)ketenes undergo an analogous ring closure to hydroquinones (Scheme 17). (2-Hydroxy-2-alkynylethenyl)-, (2-(trimethylsiloxy)-2-alkynylethenyl)-, or (2-(allyloxy)-2-alkynylethenyl)ketenes undergo ring closure to zwitterionic intermediates which rearrange by an electrofugal migration providing quinones in excellent yield (Schemes 12, 13, 18, 19, 20). (2-Alkynyl-2-cyanoethenyl)ketenes ring-close to zwitterionic intermediates which proceed to products via intra- or intermolecular trapping of nucleophiles (Schemes 22, 23, 24, 25, 26).

The high yields and predictable selectivity of the ring forming reactions outlined in this review should prompt considerable use of conjugated ketenes for the synthesis of phenols, quinones, hydroquinones, and related compounds.

Registry No. Phenol, 108-95-2; hydroquinone, 123-31-9.

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