extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was chromatographed over silica gel with hexane-ethyl acetate (2:1) to give a cycloadduct 14 or 15. As compounds **14a**, **14c**, and **14d** were previously prepared in our laboratory, their structures were determined by the comparison of spectral data.[9]

14b: colorless liquid; IR (neat) 1655 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.16 (6 H, d, Me of *i*-Pr), 3.0–3.3 (1 H, m, CH of *i*-Pr), 3.70 (1 H, dd, J = 12.0 and 8.0 Hz, one of 4-H), 4.12 (1 H, dd, J = 12.0 and 9.0 Hz, the other of 4-H), 5.45 (1 H, dd, J = 9.0 and 8.0 Hz, 5-H), and 7.1–7.5 (5 H, m, Ph); MS, m/z 189 (M$^+$) and 77 (base peak). Anal. Calcd for $C_{12}H_{15}NO$: C, 76.15; H, 7.98; N, 7.40. Found: C, 76.07; H, 7.92; N, 7.27.

15a: colorless liquid; IR (neat) 1660 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 4.68 (2 H, s, 4-H), 7.1–7.7 (8 H, m, Ph), 7.7–7.9 (5 H, m, Ph), and 8.0–8.2 (2 H, m, Ph); MS, m/z (relative intensity) 182 (M$^+$ − 117, 41), 105 (base peak), and 77 (71). Anal. Calcd for $C_{21}H_{17}NO$: C, 84.42; H, 5.72; N, 4.67. Found: C, 84.31; H, 5.60; N, 4.70.

15b: colorless liquid; IR (neat) 1642 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.77 (3 H, s, Me), 4.07 (2 H, s, 4-H), 7.0–7.5 (8 H, m, Ph), and 7.7–8.0 (2 H, m, Ph); MS, m/z (relative intensity) 237 (M$^+$, 9), 118 (11), 117 (base peak), 105 (10), and 76 (27). Anal. Calcd for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90. Found: C, 80.87; H, 6.42; N, 5.63.

Chemistry of Azido Quinones. Cyanophenols from 4-Alkynyl-3-azido-1,2-benzoquinones

Harold W. Moore,* Ken Chow, and Nghi V. Nguyen

Department of Chemistry, University of California, Irvine, California 92717

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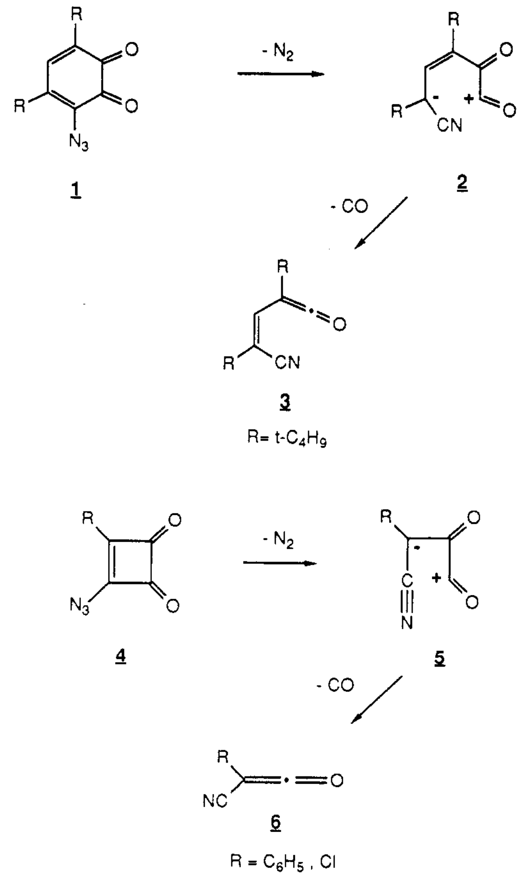
4-Alkynyl-3-azido-6-chloro-5-ethoxy-1,2-benzoquinones are shown to undergo thermolysis to (2-alkynyl-2-cyanoethenyl)ketenes. These conjugated ketenes undergo intramolecular cyclization to zwitterionic intermediates that proceed to highly subsituted 4-cyanophenols via inter- or intramolecular trapping by nucleophilic attack at the aryl cation site. The mechanism and scope of these unusual transformations are discussed.

The thermal chemistry of azido-1,4-benzoquinones has received detailed study. These compounds have been shown to function as precursors to a large variety of carbocyclic, heterocyclic, and acyclic systems.[1,2] In this context, the most useful reaction is their conversion to cyanoketenes.[3] Azido-1,2-benzoquinones, unlike the 1,4-regioisomers, have received very little attention, but here also their conversion to cyanoketenes has recently been reported. For example, 3-azido-1,2-benzoquinones have been shown to give vinylketenes upon thermolysis in refluxing benzene.[4] A specific example is the conversion of 3-azido-4,6-di-*tert*-butyl-1,2-benzoquinone (1) to the zwitterion 2, which gives the remarkably stable vinylketene 3 upon loss of carbon monoxide (Scheme I). In a related series, azidocyclobutenediones 4 fragment even at low temperature (−30 °C) to carbon monoxide, dinitrogen, and the corresponding cyanoketene 6; the zwitterionic intermediate 5 has been proposed as the ultimate intermediate (Scheme I).[5-8]

Scheme I



Reported in this manuscript are the details of a study of the in situ thermolytic conversion of 4-alkynyl-3-azido-1,2-benzoquinones 7 to (2-alkynyl-2-cyanoethenyl)ketenes 8. Conjugated ketenes of this type have not previously been reported.[9] They express unusual chemistry in undergoing cyclization to the proposed zwitterions 9 and these proceed to cyanophenols 10 upon inter- or intramolecular trapping by nucleophiles (Nu). This transformation is generally outlined in Scheme II. For the study reported here, the azidoquinones investigated are all 4-alkynyl-3-azido-6-chloro-5-ethoxy-1,2-benzoquinones. These are available from the corresponding dichloro-

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[1] Moore, H. W. *Chem. Soc. Rev.* **1973**, *2*, 415.

[2] Moore, H. W.; Goldish, D. "Vinyl, Aryl, and Acyl Azides" in *Chemistry of the Pseudohalogens*; Patai, S., Ed.; Wiley: New York, 1983.

[3] Moore, H. W.; Gheorghiu, M. D. *Chem. Soc. Rev.* **1981**, *10*, 289.

[4] Dorsey, D. A.; King, S.; Moore, H. W. *J. Org. Chem.* **1986**, *51*, 2814.

[5] Moore, H. W. *Acc. Chem. Res.* **1979**, *12*, 125.

[6] Fishbein, P. L.; Moore, H. W. *J. Org. Chem.* **1984**, *49*, 2190.

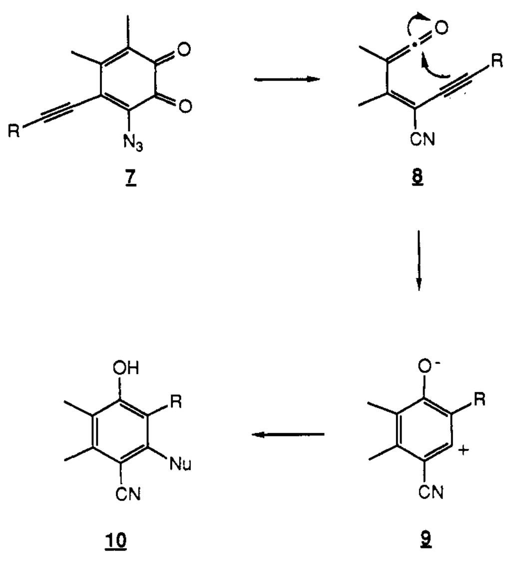
[7] DeSelms, R. C. *Tetrahedron Lett.* **1969**, 1179.

[8] Schmidt, A. H.; Ried, W. *Tetrahedron Lett.* **1969**, 2431.

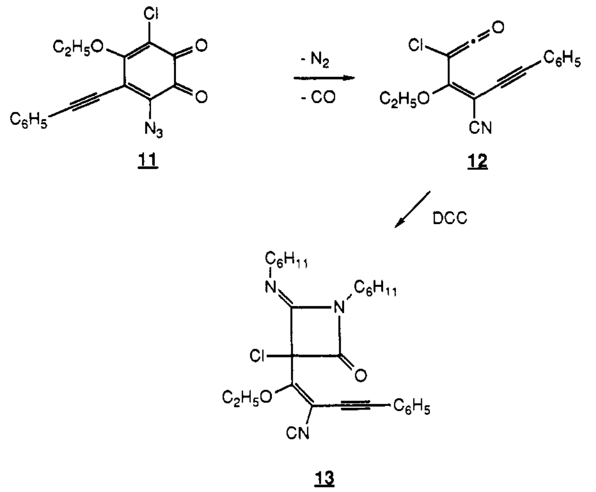
[9] A preliminary account of this work has appeared. See: Nguyen, N. V.; Chow, K.; Karlsson, J. O.; Moore, H. W. *J. Org. Chem.* **1986**, *51*, 419.

0022-3263/87/1952-2530$01.50/0

Scheme II



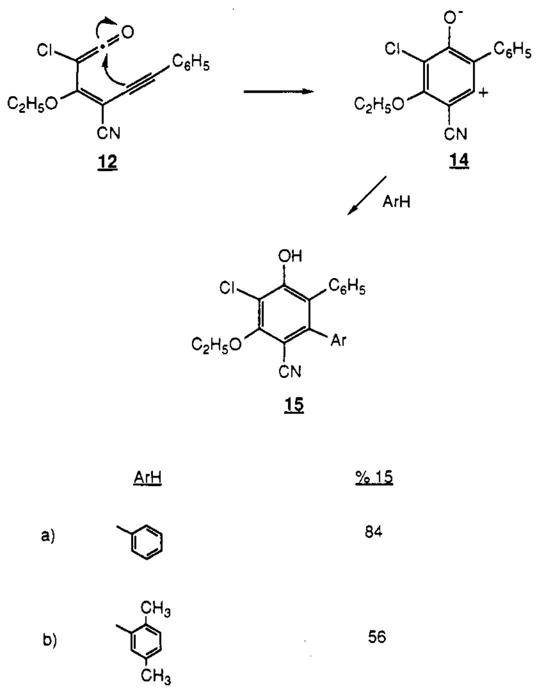
Scheme III



quinones which, in turn, are easily prepared via treatment of 2,5-dichloro-3,6-diethoxy-1,4-benzoquinone with 1 equiv of an alkynyllithium agent followed by hydrolysis of the resulting 1,2-addition products.[10] The generality of the transformations formally outlined in Scheme II remains to be established. However, the results presented in this study along with previous reports regarding the conversion of other (alkynylethenyl)ketenes to quinones suggests a generality to this reaction sequence.[11,12]

It was initially found that 3-azido-6-chloro-5-ethoxy-4-(phenylethynyl)-1,2-benzoquinone (**11**) gave the conjugated ketene **12** upon thermolysis in refluxing cyclohexane (Scheme III). Evidence for the ketene was obtained when the thermolysis was accomplished in the presence of an excess of dicyclohexylcarbodiimide (DCC); the expected β-lactam **13** was realized in 44% yield as a single diastereomer. Its stereostructure was not established but is suggested to be as indicated on the basis of the observed ring closures of ketenes such as **12** to the corresponding zwitterion **14** (Scheme IV). Thus, the *Z* configuration of **12** and **13** is assumed.

Scheme IV



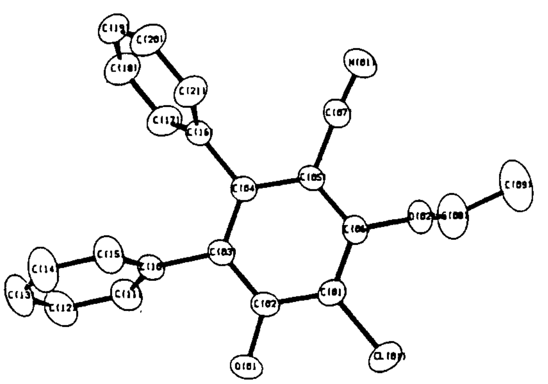


Figure 1. ORTEP view of 2-chloro-4-cyano-3-ethoxy-5,6-diphenylphenol (**15a**).

Evidence for zwitterionic intermediate **14** comes from a study of the thermolysis of **11** in aromatic solvents. Specifically, when this azido quinone was subjected to thermolysis in benzene or *p*-xylene, the respective terphenyls **15a,b** were obtained (Scheme IV). These are viewed as arising from the ketene **12**, which undergoes ring closure to the zwitterion **14** and subsequent electrophilic attack of the aryl cation on the solvent. Arylation of **14** was also observed in yields ranging from 31% to 56% when *m*-xylene, toluene, or chlorobenzene was used. However, in these cases mixtures of the regioisomers were obtained. On the other hand, **15a,b** were obtained as pure compounds and their structures are based upon characteristic spectral properties as well as upon a complete single-crystal X-ray analysis of **15a** (Figure 1).[13]

When thiophene was used as the solvent a different reaction course insued. Specifically, in addition to a small yield (12%) of an inseparable mixture of **17** and **18**, the annelated products **19** and **20** were isolated in the respective yields of 22% and 12% (Scheme V). It is assumed that the major isomer is **19** on the basis of the preference of thiophene for electrophilic attack at posi-

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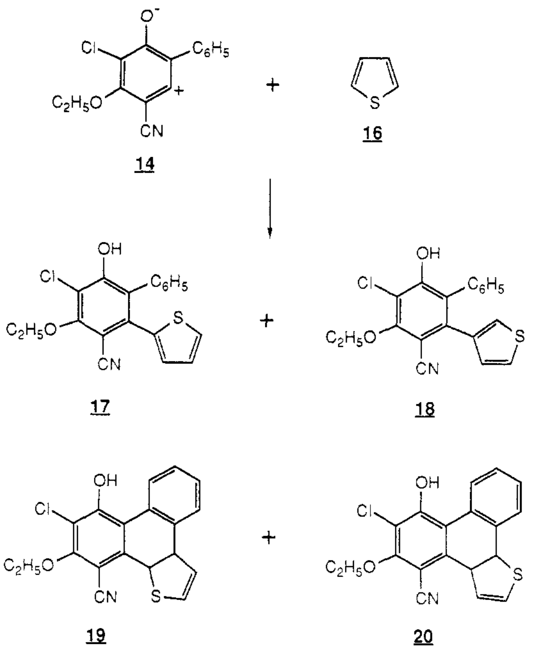
[10] Moore, H. W.; Wriede, U.; Nguyen, N. V.; Fernandez, M. *J. Org. Chem.*, submitted for publication.

[11] Karlsson, J. O.; Nguyen, N. V.; Foland, L. D.; Moore, H. W. *J. Am. Chem. Soc.* **1985**, *107*, 3392.

[12] Perri, S. T.; Foland, L. D.; Decker, O. H. W.; Moore, H. W. *J. Org. Chem.* **1986**, *51*, 3067.

[13] We thank Professor Robert J. Doedens, University of California, Irvine for the X-ray structural studies.

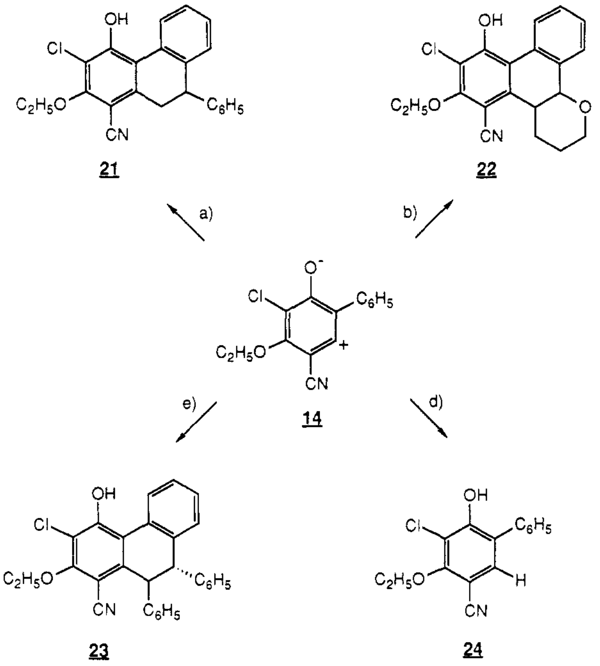
Scheme V



tion-2. The resulting carbocation could either lose a proton to give **17** or attack the adjacent phenyl ring to give **19**. Compounds **18** and **20** are viewed as arising analogously. Both **19** and **20** show a low field absorption for a single aromatic proton in their ^1H NMR spectra (δ 8.43–8.47 and 8.35–8.39). In addition, these absorptions show a positive NOE enhancement when the OH proton absorption was preirradiated. Such a result is in good agreement with the ring systems proposed. However, the assignment of the regiochemistry with respect to the position of the sulfur atom could not be established but, as noted above, is implied on the basis of mechanistic considerations.

The trapping of the zwitterion **14** with thiophene suggested the possibility of a more general annelation method using more reactive alkenes. Thus, the generation of **14** from the thermolysis of the azido quinone **11** was accomplished in the presence of styrene, *trans*-stilbene, and dihydropyran. This gave the dihydrophenanthrenes **21**, **22** and **23** in respective isolated yields of 60%, 54%, and 37% (Scheme VI). These compounds, like **19** and **20**, also showed the low field aryl proton absorption in their ^1H NMR spectra. A NOE difference experiment on **21** again showed enhancement of this absorption upon preirradiation of the phenolic hydroxyl absorption. In addition, a 2-D ^{13}C–^1H long-range coupling heteroatom correlation NMR experiment was carried out on **21**, and this confirmed its structure.[14,15] This experiment establishes a correlation between a carbon and a hydrogen when the coupling constant (J_{C-H}) is in the range of 7–10 Hz, i.e., only two- or three-bond couplings are evaluated. When this technique was applied to **21**, it was found that the methylene protons correlate to four carbon atoms and one of these is at relatively high field (95 ppm). This absorption is reasonably assigned to that carbon bearing the nitrile group. These data along with fact that the IR spectrum of **21** shows a broad OH stretch at 3328 cm^{-1} and an intense C≡N stretch at 2209 cm^{-1} provide the critical structural information for **21**. By analogy, the regiochemistry of **22** and **23** are assigned.

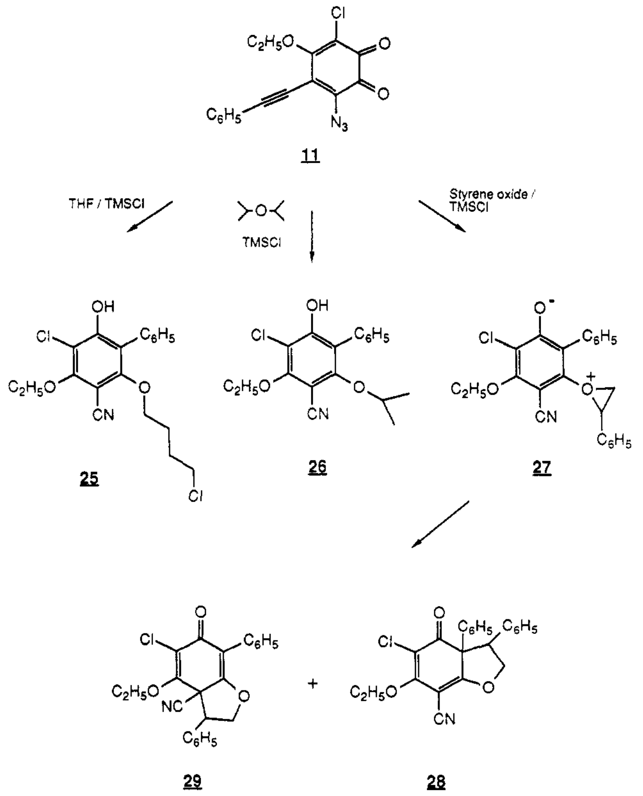
Scheme VI



a) $CH_2=CHC_6H_5$ b) DHP c) trans - $C_6H_5CH=CHC_6H_5$

d) c - C_6H_{10} or $(CH_3)_2C=C(CH_3)_2$

Scheme VII



When unactivated alkenes were employed in further attempts to accomplish the above annelation, hydride abstraction rather than cycloaddition was observed. For example, generation of **14** in cyclohexene gave a complex mixture from which 2-chloro-4-cyano-3-ethoxy-6-phenylphenol (**24**) was isolated in 26% yield. This same product

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(14) We are indebted to Dr. Shoumo Chang for conducting this experiment.

(15) Wimperisand, S.; Freeman, J. *J. Magn. Reson.* **1984**, *58*, 348; **1985**, *62*, 147.

Table I. Single-Crystal X-ray Data

interatomic distances			interatomic distances			interatomic distances		
from	to	distance, Å	from	to	distance, Å	from	to	distance, Å
C(01)	C(06)	1.380 (2)	C(05)	C(06)	1.398 (2)	C(12)	C(13)	1.384 (3)
C(01)	C(02)	1.398 (2)	C(05)	C(07)	1.435 (2)	C(13)	C(14)	1.362 (3)
C(01)	C(01)	1.723 (2)	C(06)	O(02)	1.364 (2)	C(14)	C(16)	1.384 (3)
C(02)	O(01)	1.347 (2)	C(07)	N(01)	1.137 (2)	C(16)	C(17)	1.381 (2)
C(02)	C(03)	1.404 (2)	C(08)	O(02)	1.442 (3)	C(16)	C(21)	1.382 (2)
C(03)	C(04)	1.396 (2)	C(08)	C(09)	1.480 (3)	C(17)	C(18)	1.389 (2)
C(03)	C(10)	1.493 (2)	C(10)	C(15)	1.383 (3)	C(18)	C(19)	1.380 (3)
C(04)	C(05)	1.410 (2)	C(10)	C(11)	1.387 (2)	C(19)	C(20)	1.369 (3)
C(04)	C(16)	1.491 (2)	C(11)	C(12)	1.381 (3)	C(20)	C(21)	1.387 (2)

positional parameters				positional parameters			
atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
C(01)	0.47241 (19)	0.33291 (17)	0.73112 (14)	C(14)	0.36248 (32)	0.25517 (27)	0.22956 (22)
C(02)	0.39668 (18)	0.29701 (17)	0.63526 (14)	C(15)	0.44813 (25)	0.29905 (21)	0.31912 (18)
C(03)	0.48221 (18)	0.25625 (16)	0.51118 (13)	C(16)	0.64465 (18)	0.21934 (16)	0.35166 (13)
C(04)	0.64777 (17)	0.25880 (15)	0.48271 (13)	C(17)	0.69062 (22)	0.07936 (18)	0.29687 (16)
C(05)	0.72417 (18)	0.29943 (16)	0.57992 (14)	C(18)	0.78097 (25)	0.04419 (20)	0.17427 (17)
C(06)	0.63555 (19)	0.33478 (16)	0.70419 (14)	C(19)	0.92597 (24)	0.14917 (21)	0.10716 (15)
C(07)	0.89381 (20)	0.30298 (18)	0.55511 (15)	C(20)	0.198071 (24)	0.28760 (21)	0.16097 (17)
C(08)	0.67297 (34)	0.25710 (26)	0.86328 (21)	C(21)	0.89150 (22)	0.32349 (18)	0.28352 (16)
C(09)	0.79962 (46)	0.30594 (35)	0.93344 (29)	N(01)	1.02689 (20)	0.30665 (19)	0.54135 (16)
C(10)	0.39367 (19)	0.21166 (17)	0.41251 (14)	O(01)	0.24050 (15)	0.30381 (15)	0.66826 (12)
C(11)	0.25302 (22)	0.08102 (19)	0.41485 (17)	O(02)	0.71400 (15)	0.37388 (13)	0.79559 (10)
C(12)	0.16951 (25)	0.03716 (22)	0.32431 (21)	Cl(01)	0.36285 (06)	0.37912 (05)	0.88326 (04)
C(13)	0.22593 (31)	0.12587 (27)	0.23141 (22)				

bond angles				bond angles			
from	through	to	angle, deg	from	through	to	angle, deg
C(06)	C(01)	C(02)	120.50 (13)	O(02)	C(08)	C(09)	107.88 (21)
C(06)	C(01)	Cl(01)	119.90 (12)	C(15)	C(10)	C(11)	119.11 (15)
C(02)	C(01)	Cl(01)	119.59 (12)	C(15)	C(10)	C(03)	121.21 (15)
O(01)	C(02)	C(01)	116.86 (13)	C(11)	C(10)	C(03)	119.67 (15)
O(01)	C(02)	C(03)	122.66 (13)	C(12)	C(11)	C(10)	120.74 (18)
C(01)	C(02)	C(03)	120.48 (13)	C(11)	C(12)	C(13)	119.37 (18)
C(04)	C(03)	C(02)	119.43 (13)	C(14)	C(13)	C(12)	120.19 (18)
C(04)	C(03)	C(10)	121.54 (13)	C(13)	C(14)	C(15)	120.74 (20)
C(02)	C(03)	C(10)	119.03 (13)	C(10)	C(15)	C(14)	119.83 (18)
C(03)	C(04)	C(05)	119.21 (13)	C(17)	C(16)	C(21)	119.08 (14)
C(03)	C(04)	C(16)	121.16 (12)	C(17)	C(16)	C(04)	121.01 (14)
C(05)	C(04)	C(16)	119.63 (12)	C(21)	C(16)	C(04)	119.91 (14)
C(06)	C(05)	C(04)	121.02 (13)	C(16)	C(17)	C(18)	120.47 (16)
C(06)	C(05)	C(07)	117.84 (13)	C(19)	C(18)	C(17)	120.10 (17)
C(04)	C(05)	C(07)	121.22 (13)	C(10)	C(19)	C(18)	119.41 (16)
O(02)	C(06)	C(01)	121.42 (14)	C(19)	C(20)	C(21)	120.81 (17)
O(02)	C(06)	C(05)	119.29 (13)	C(16)	C(21)	C(20)	120.09 (16)
C(01)	C(06)	C(05)	119.28 (13)	C(16)	O(02)	C(08)	114.26 (14)
N(01)	C(07)	C(05)	176.82 (17)				

was observed in yields ranging from 11% to 22% when the azido quinone **11** was subjected to thermolysis in chloroform, cyclohexane, and carbon tetrachloride containing trimethyl orthoformate.

A particularly interesting transformation was observed when **11** was decomposed in refluxing cyclohexane containing an excess of THF and Me_3SiCl. In this case, the highly functionalized phenol **25** was obtained in 72% isolated yield (Scheme VII). This product is seen as arising from the zwitterion **14**, which proceeds to an oxonium ion upon attack of THF; silylation of the phenoxide ion, opening of the oxonium ion by attack of the released chloride ion, and final hydrolytic desilylation would then result in **25**. It is noted that the presence of Me_3SiCl is essential for this transformation since in its absence a very complex reaction mixture was observed.

An NOE difference experiment performed on **25** shows a strong enhancement of aromatic proton absorptions upon preirradiation of the phenolic hydroxyl proton absorption. This is, of course, consistent with the proposed structure that places the phenyl group ortho to the phenolic hydroxyl. Further structural proof was obtained from a 2-D ^{13}C–^{1}H long-range heteroatom correlation NMR experiment. Here it was observed that the OH proton correlates with one low field carbon absorption (154.64 ppm) and two upfield absorptions (119.63 ppm and 110.82 ppm). Chemical shifts of these upfield absorptions are in accord with the calculated values (117.7 ppm and 110.6 ppm) for the carbons at positions-2 and -6.[16] Thus, the cyanophenol can be confidently assigned structure **25**.

The above experimental procedure also applies to the interception of **14** with acyclic and cyclic ethers. For example, generation of the zwitterion **14** in the presence of diisopropyl ether and Me_3SiCl resulted in a 26% isolated yield of **26** (Scheme VII). The presence of Me_3SiCl was again observed to be important since in its absence the yield of **26** dropped to 8%. When styrene oxide was used as the trap for **14**, no cyanophenol was observed. Rather, two cyclohexadienones **28** and **29** was isolated in 12% and 10% yields, respectively. An oxonium ion is again viewed as resulting from the attack of **14** on the ether oxygen. Thus, **27** is suggested as a key intermediate to **28** and **29**.

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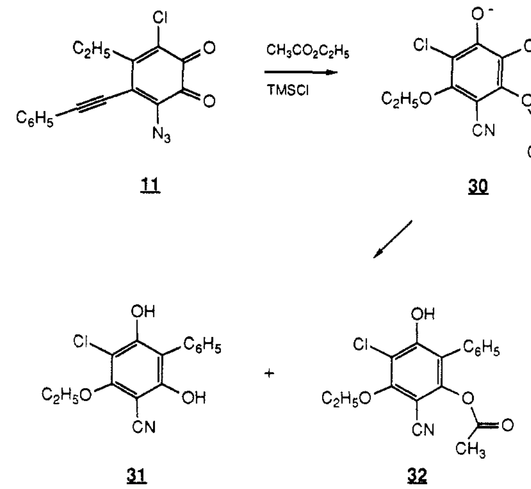
(16) Pretsch; Clerc; Seibl; Simon. *Table of Spectral Data for Structure Determination of Organic Compounds*; Springer-Verlag, Berlin, 1983.

Scheme VIII



Opening of this to the corresponding benzyl cation and attack at the positions ortho and para to the phenoxide ion would result in the observed products.

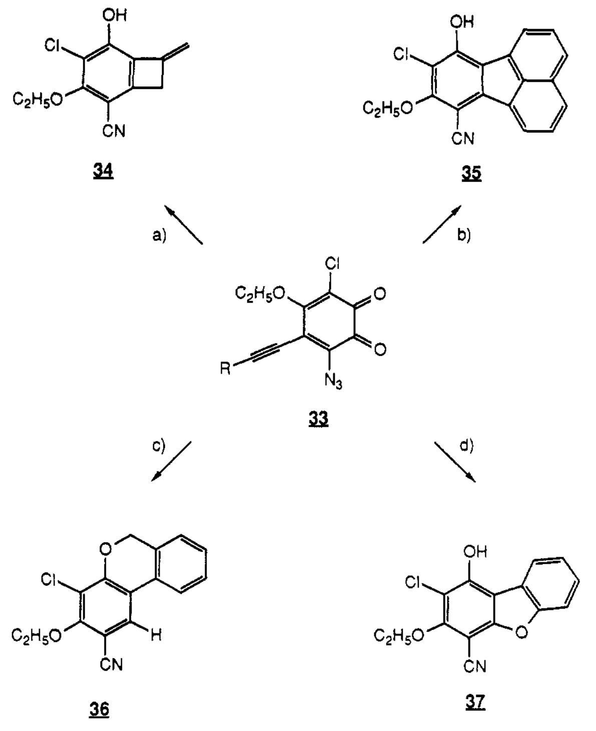
The structures of 28 and 29 are based upon their spectral properties. Particularly revealing is the fact that 28 contains a conjugated chromophore and is yellow, and 29, which has a cross-conjugated dienone moiety, is colorless. This is further documented by the UV spectrum of 28, which shows a λ_{max} at 381 nm (ϵ 3201) (calcd value λ_{max} = 383) and that of 29 is 312 nm (ϵ 738e (calcd value 307).[17] Moreover, the IR spectrum of only 28 shows an intense absorption at 2220 cm^{-1}, and this is typical of a conjugated nitrile group.

An interesting hydroxylation reaction was observed when **11** was decomposed in ethyl acetate containing an excess of Me$_3$SiCl (10 equiv). This resulted in a mixture of **31** and **32**, which were isolated in yields of 39% and 27%, respectively (Scheme VIII). These are viewed as arising from the intermediate **30**, which upon silylation would release chloride ion, and this could facilitate deethylation to give a trimethylsilyl derivative of **32**. Subsequent hydrolysis during workup would lead to the observed products. Again it is noted that if this reaction is attempted in the absence of Me$_3$SiCl, a very complex mixture of products is formed and no pure compound could be isolated.

Finally, a series of interesting intramolecular trapping experiments are reported that lead to a variety of polycyclic ring systems (Scheme IX). Specifically, the azido quinones **33a–d** were subjected to thermolysis in refluxing carbon tetrachloride, which gave respectively **34** (33%), **35** (24%), **36** (16%), and **37** (76%). Special note is made concerning the formation of the dibenzofuran **37** since once again the thermolysis must be carried out in the presence of Me$_3$SiCl. Without it a complex mixture results from which a significantly reduced amount (16%) of the methoxy derivative of **37** was isolated.

The assigned structures of **34–37** are all in strict accord with their individual spectral properties (Experimental Section). The formation of these compounds is also mechanistically reasonable in view of the results presented earlier. Thus, **33a–d** would be expected to lead to zwitterionic species analogous to **14** and these, in turn, proceed to the observed products via intramolecular trapping. Specifically, the aryl cation from **33a** would ring close to **38**, which upon proton transfer would give **34**. Direct ring closure of **39** via an electrophilic substitution pathway would give **35**. Hydride transfer from the initially formed zwitterion from **33c** would give **40**, which upon ring closure leads to **36**. Finally, intramolecular trapping of the zwitterion from **33d** would give the oxonium ion **41** after silylation of the phenoxide ion. Chloride ion initiated demethylation would then result in **37**.

Scheme IX

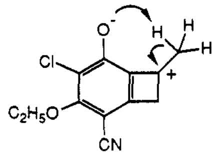


a) R = C(CH$_3$)=CH$_2$

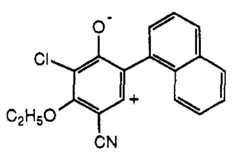
b) R = - C$_{10}$H$_7$ (1-naphthyl)

c) R = - C$_6$H$_4$-o-CH$_3$

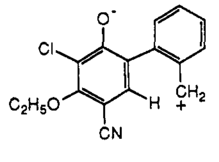
e) R = - C$_6$H$_4$-o-OCH$_3$



38



39



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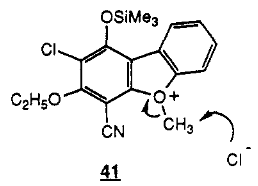

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In conclusion, we note the significant points to arise from this study: (1) for the first time (2-alkynyl-2-cyanoethenyl)ketenes have been generated in situ; (2) such cumulenes undergo intramolecular ring closure to unique zwitterionic intermediates, which proceed to a variety of highly substituted cyanophenols.

Experimental Section

3-Azido-6-chloro-5-ethoxy-4-(phenylethynyl)-3,5-cyclohexadiene-1,2-dione (11). Into a stirred solution of 0.10 g (0.31 mmol) of 3,6-dichloro-4-ethoxy-5-(phenylethynyl)-3,5-cyclohexadiene-1,2-dione[10] in 20 mL of acetone was added dropwise 0.02 (0.31 mmol) of sodium azide in 2 mL of distilled water at -5 °C. Upon addition, the solution immediately turned from red

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[17] Silverstein, R. M.; Bassler, G. C.; Morril, T. C. *Spectrometric Identification Of Organic Compounds*; Wiley: New York, 1981.

to dark purple in color. After stirring for an additional 30 min at −5 °C, 100 mL of water was added to the black solution. The resulting precipitate was collected and recrystallized from dichloromethane/hexane to afford 0.88 g (86%) of a black solid, mp decomposed >104 °C, with the evolution of gas; ^{1}H NMR 7.36–7.63 (m, 5 H), 4.64 (q, J = 7 Hz, 2 H), 1.53 (t, J = 7 Hz, 3 H); IR (KBr) 3059 (w), 2980 (w), 2098 (s), 1654 (s), 1595 (w), 1572 (m), 1513 (m), 1364 (s), 1268 (m), 1230 (m); MS, *m/e* 299 (M^+ − 28, EI), 300 (M^+ + 1 − 28, CI).

3-Chloro-1-cyclohexyl-3-(2-cyano-1-ethoxy-4-phenyl-1-buten-3-ynyl)-4-(*N*-cyclohexylimino)-2-azetidinone (13). A solution of 0.15 g (0.45 mmol) of 3-azido-6-chloro-5-ethoxy-4-(phenylethynyl)-3,5-cyclohexadiene-1,2-dione (11) in 20 mL of dry cyclohexane was added dropwise to a refluxing solution of 1.89 g (9.17 mmol) of dicyclohexylcarbodiimide in 250 mL of dry cyclohexane under an atmosphere of argon for 30 min. After being refluxed for an additional 2 h, the solution turned from dark purple to light brown and was concentrated. The dark oily residue was absorbed onto silica gel then subjected to flash column chromatography (hexane/ethyl acetate) to give 0.97 g (44%) of a yellowish oil: ^{1}H NMR 7.27–7.47 (m, 5 H), 4.67 (q, J = 7 Hz, 2 H), 3.58–3.71 (m, 1 H), 3.37–3.46 (m, 1 H), 1.13–1.99 (m, 23 H); ^{13}C NMR 166.25, 161.50, 144.36, 131.34, 129.57, 128.62, 121.61, 113.74, 97.89, 81.81, 80.29, 71.17, 72.18, 60.07, 53.15, 34.16, 33.98, 29.72, 29.57, 25.62, 25.02, 24.46, 15.54; IR (neat) 3045 (w), 2931 (s), 2857 (s), 2242 (w), 2215 (m), 1833 (s), 1710 (s), 1562 (s), 1356 (s); MS, *m/e* 477 (EI), 478 (CI); exact mass calcd for $C_{28}H_{32}ClN_3O_2$ 477.2183, found 477.2191.

2-Chloro-4-cyano-5,6-diphenyl-3-ethoxyphenol (15a). The following is a representative procedure used for the synthesis of **15a,b**. A solution of 0.10 g (0.30 mmol) of 3-azido-6-chloro-5-ethoxy-4-(phenylethynyl)-3,5-cyclohexadiene-1,2-dione (11) in 20 mL of dry benzene was added dropwise to a refluxing solution of 200 mL of dry benzene under an atmosphere of argon for 30 min. After being refluxed for an additional 3 h, the solution turned from dark red to light brown and was then concentrated. The dark oily residue was absorbed onto silica gel and then subjected to flash column chromatography (hexane/ethyl acetate) to give a yellowish solid. Recrystallization from dichloromethane/hexane gave 0.09 g (84%) of a white solid: mp 201–202 °C; ^{1}H NMR 7.06–7.31 (m, 10 H), 6.02 (s, 1 H), 4.36 (q, J = 7 Hz, 2 H), 1.55 (t, J = 7 Hz, 3 H); ^{13}C NMR 158.54, 153.95, 145.36, 136.43, 133.58, 130.90, 129.98, 128.85, 128.37, 128.18, 125.66, 115.64, 114.72, 101.93, 71.70, 15.93; IR (KBr) 3302 (b), 3041 (w), 3022 (w), 2979 (w), 2222 (s), 1544 (s), 1421 (s); MS, *m/e* 349 (EI), 350 (CI).

Anal. Calcd for $C_{21}H_{16}ClNO_2$: C, 72.11; H, 4.61. Found: C, 72.36; H, 4.58.

2-Chloro-4-cyano-5-(2,5-dimethylphenyl)-3-ethoxy-6-phenylphenol (15b): white solid (56%, 0.13 g, dichloromethane/hexane); mp 184–185 °C; ^{1}H NMR 6.75–7.25 (m, 8 H), 6.01 (s, 1 H), 4.37 (q, J = 7 Hz, 2 H), 2.18 (s, 3 H), 1.54 (t, J = 7 Hz, 3 H); ^{13}C NMR 158.10, 153.89, 145.42, 135.78, 134.81, 133.35, 132.43, 130.48, 130.23, 129.99, 129.42, 128.57, 128.33, 125.72, 115.21, 114.37, 102.08, 71.54, 20.92, 19.37, 15.81; IR (KBr) 3324 (b), 3044 (w), 3016 (w), 2971 (w), 2220 (s), 1549 (s), 1425 (s); MS, *m/e* 377 (EI), 378 (CI).

2-Chloro-4-cyano-3-ethoxy-6-phenyl-5-(thiacyclopenta-2,4-dien-2-yl)phenol (17 and 18). A solution of 0.20 g (0.61 mmol) of 3-azido-6-chloro-5-ethoxy-4-(phenylethynyl)-3,5-cyclohexadiene-1,2-dione (11) in 250 mL of dry thiophene was refluxed for 3 h, after which the solution turned from dark red to light brown and was then concentrated. The dark oily residue was absorbed onto silica gel and then subjected to flash column chromatography (dichloromethane/ethyl acetate) to give, along with 19 and 20, 0.02 g (12%) of a white solid, identified as mixture of the isomers 17 and 18: ^{1}H NMR 7.00–7.34 (m, 8 H), 5.98 (s, 1 H), 4.31–4.40 (m, 2 H), 1.50–1.58 (m, 3 H); IR (KBr) 3260 (s), 2972 (w), 2222 (s), 1539 (s), 1418 (s); MS, *m/e* 355 (EI), 356 (CI); exact mass calcd for $C_{19}H_{14}ClNO_2S$ 355.0434, found 355.0415.

9-Chloro-11-cyano-10-ethoxy-8-hydroxy-3a,11b-dihydro-1-thiacyclopenta[*l*]phenanthrene (19). From the above reaction 0.05 g (22%) of 19 was isolated as a white solid: mp 217–219 °C; ^{1}H NMR 8.43–8.47 (m, 1 H), 7.26–7.36 (m, 3 H), 6.70 (s, 1 H), 6.46 (d, J = 6.2 Hz, 1 H), 6.37 (dd, J = 6 Hz, J' = 3.7 Hz, 1 H), 5.40 (d, J = 7.7 Hz, 1 H), 4.33 (q, J = 7 Hz, 2 H), 4.06 (dd, J = 3.7 Hz, J' = 7.7 Hz, 1 H), 1.52 (t, J = 7 Hz, 3 H); ^{13}C NMR 157.47, 153.54, 137.46, 134.25, 130.14, 128.89, 127.46, 127.22, 127.15, 126.43, 119.10, 115.88, 114.63, 101.58, 71.90, 52.47, 45.71, 15.91; IR (KBr) 3300 (b), 3060 (w), 2971 (w), 2918 (w), 2219 (s), 1567 (s), 1413 (s); MS, *m/e* 355 (EI), 356 (CI); exact mass calcd for $C_{19}H_{14}ClNO_2S$ 355.0434, found 355.0454.

6-Chloro-4-cyano-5-ethoxy-7-hydroxy-3a,11b-dihydro-1-thiacyclopenta[*l*]phenanthrene (20). From the above reaction, 0.02 g (12%) of a white solid resulted: mp 176–178 °C; ^{1}H NMR 8.35–9.39 (m, 1 H), 7.70–7.74 (m, 1 H), 7.31–7.35 (m, 2 H), 6.68 (s, 1 H), 6.31 (dd, J = 5.8 Hz, J' = 3.1 Hz, 1 H), 5.75 (dd, J = 5.8 Hz, J' = 2.2 Hz, 1 H), 4.84 (d, J = 7.6 Hz, 1 H), 4.57 (ddd, J = 7.6 Hz, J' = 3.2 Hz, J'' = 2.2 Hz, 1 H), 4.34 (q, J = 7 Hz, 2 H), 1.53 (t, J = 7 Hz, 3 H); ^{13}C NMR 157.47, 153.20, 139.82, 134.28, 129.86, 128.71, 128.39, 127.84, 127.33, 124.62, 118.57, 115.15, 114.98, 100.83, 71.69, 51.19, 50.50, 15.78; IR (KBr) 3340 (s), 3060 (w), 2972 (m), 2219 (s), 1562 (s), 1410 (s); MS, *m/e* 355 (EI), 356 (CI); exact mass calcd for $C_{19}H_{14}ClNO_2S$ 355.0434, found 355.0444.

3-Chloro-1-cyano-2-ethoxy-4-hydroxy-9-phenyl-9,10-dihydrophenanthrene (21). A solution of 0.40 g (1.22 mmol) of 3-azido-6-chloro-5-ethoxy-4-(phenylethynyl)-3,5-cyclohexadiene-1,2-dione (11) in 40 mL of dry carbon tetrachloride was added dropwise to a refluxing solution of 0.63 g (6.11 mmol) of styrene in 150 mL of dry carbon tetrachloride for 1 h under an atmosphere of argon. The solution was then refluxed for an additional 3 h, after which it turned from dark purple to light brown. The solution was concentrated and the dark oily residue was absorbed onto silica gel and subjected to flash column chromatography (hexane/ethyl acetate) to give a white solid. Recrystallization from dichloromethane/hexane yielded 0.29 g (63%) of a white solid: mp 203–204 °C; ^{1}H NMR 8.32 (dd, J = 1.2 Hz, J' = 7.9 Hz, 1 H), 7.01–7.39 (m, 8 H), 4.28 (q, J = 7 Hz, 2 H), 4.16 (dd, J = 8.45 Hz, J' = 5.4 Hz, 1 H), 3.26–3.46 (dq, J = 8.5 Hz, J' = 5.4 Hz, 2 H), 1.48 (t, J = 7 Hz, 3 H); ^{13}C NMR 156.85, 152.95, 142.03, 141.33, 139.89, 130.54, 128.71, 128.25, 128.14, 128.07, 126.99, 119.39, 115.34, 114.22, 100.57, 71.46, 43.73, 35.52, 15.68; IR (KBr) 3328 (b), 3058 (w), 3010 (m), 2977 (m), 2880 (w), 2209 (s), 1561 (s), 1440 (s), 1421 (s); MS, *m/e* 375 (EI), 376 (CI); exact mass calcd for $C_{23}H_{18}ClNO_2$ 375.1026, found 375.1013.

10-Chloro-12-cyano-11-ethoxy-9-hydroxy-2,3,4a,12b-tetrahydro-4(1*H*)-oxatriphenylene (22). A solution of 0.20 g (0.61 mmol) of 3-azido-6-chloro-5-ethoxy-4-(phenylethynyl)-3,5-cyclohexadiene-1,2-dione (11) in 30 mL of dry tetrahydrofuran was added dropwise to a refluxing solution of 100 mL of dry cyclohexane for 1 h under an atmosphere of argon. The solution was then refluxed for an additional 3 h, after which it turned from dark purple to light brown. The solution was concentrated and the dark oily residue was absorbed onto silica gel and subjected to flash column chromatography (hexane/ethyl acetate) to give a white solid. Recrystallization from dichloromethane/hexane yielded 0.08 g (37%) of a white solid: mp 202–203 °C; ^{1}H NMR 8.34–8.37 (m, 1 H), 7.62–7.66 (s, 1 H), 7.35–7.44 (m, 2 H), 6.64 (s, 1 H), 5.22 (d, J = 6 Hz, 1 H), 4.32 (q, J = 7 Hz, 2 H), 3.69–3.81 (m, 2 H), 3.51 (ddd, J = 12 Hz, J' = 6 Hz, J'' = 4 Hz, 1 H), 1.35–1.60 (m, 5 H); ^{13}C NMR 157.21, 153.34, 144.46, 134.04, 129.78, 128.47, 127.27, 125.98, 117.77, 114.79, 114.61, 100.25, 72.16, 60.71, 39.74, 25.78, 24.26, 15.75; IR (KBr) 3381 (b), 3060 (w), 2942 (s), 2858 (m), 2218 (s), 1562 (s), 1440 (s), 1422 (s); MS, *m/e* 355 (EI), 356 (CI); exact mass calcd for $C_{20}H_{18}ClNO_3$ 355.0975, found 355.0962.

3-Chloro-1-cyano-2-ethoxy-4-hydroxy-9,10-diphenyl-9,10-dihydrophenanthrene (23). A solution of 0.50 g (1.53 mmol) of 3-azido-6-chloro-5-ethoxy-4-(phenylethynyl)-3,5-cyclohexadiene-1,2-dione (11) in 40 mL of dry carbon tetrachloride was added dropwise to a refluxing solution of 1.38 g (7.65 mmol) of *trans*-stilbene in 150 mL of dry carbon tetrachloride for 1 h under an atmosphere of argon. The solution was then refluxed for an additional 3 h, after which it turned from dark purple to light brown. The solution was concentrated and the dark oily residue was absorbed onto silica gel and subjected to flash column chromatography (hexane/ethyl acetate) to give a white solid. Recrystallization from dichloromethane/hexane yielded 0.38 g (54%) of a white solid: mp 184–185 °C; ^{1}H NMR 8.45–8.48 (m, 1 H), 7.00–7.36 (m, 13 H), 6.83 (s, 1 H), 4.89 (s, 1 H), 4.44 (s, 1 H), 4.14 (q, J = 7 Hz, 2 H), 1.35 (t, J = 7 Hz, 3 H); ^{13}C NMR 157.21, 153.29, 142.30, 140.41, 135.64, 130.95, 130.36, 128.74, 128.52, 127.89, 127.65, 127.60, 127.45, 126.99, 126.63, 119.95, 114.84, 114.66, 101.48, 71.33, 51.99, 51.39, 15.43; IR (KBr) 3445 (b), 3075 (m), 3041 (m), 2991 (m), 2225 (s), 1565 (s), 1449 (s), 1420 (s); MS, *m/e* 451 (EI); exact mass calcd for $C_{29}H_{22}ClNO_2$ 451.1339, found 451.1336.

2-Chloro-4-cyano-3-ethoxy-6-phenylphenol (24). A solution of 0.40 g (1.22 mmol) of 3-azido-6-chloro-5-ethoxy-4-(phenylethynyl)-3,5-cyclohexadiene-1,2-dione (**11**) in 30 mL of dry chloroform was added dropwise to refluxing solution of 150 mL of dry chloroform for 1 h under an atmosphere of argon. The solution was then refluxed for an additional 3 h, after which it turned from dark purple to light brown. The solution was concentrated and the dark oily residue was absorbed onto silica gel and subjected to flash column chromatography (hexane/ethyl acetate) to give a yellow semisolid. Recrystallization from dichloromethane/hexane yielded 0.09 g (26%) of a yellowish solid: mp 128–129 °C; ^{1}H NMR 7.40–7.48 (m, 6 H), 6.28 (s, 1 H), 4.35 (q, J = 7 Hz, 2 H), 1.52 (t, J = 7 Hz, 3 H); ^{13}C NMR 157.41, 153.72, 135.03, 132.94, 129.12, 128.57, 125.91, 116.21, 115.56, 99.70, 71.44, 15.71; IR (KBr) 3300 (b), 3015 (w), 2972 (m), 2919 (s), 2222 (s), 1591 (s), 1465 (s), 1418 (s), 1154 (s); MS, *m/e* 273 (EI), 274 (CI).

2-Chloro-5-[(4-chlorobutyl)oxy]-4-cyano-3-ethoxy-6-phenylphenol (25). A solution of 0.25 g (0.76 mmol) of 3-azido-6-chloro-5-ethoxy-4-(phenylethynyl)-3,5-cyclohexadiene-1,2-dione (**11**) in 20 mL of dry tetrahydrofuran was added dropwise to a refluxing solution of 5 mL of dry trimethylsilylchloride in 150 mL of dry cyclohexane for 1 h under an atmosphere of argon. The solution was then refluxed for an additional 3 h, during which it turned from dark purple to light brown. The solution was concentrated and the dark oily residue was absorbed onto silica gel and subjected to flash column chromatography (hexane/ethyl acetate) to give a white solid. Recrystallization from dichloromethane/hexane yielded 0.21 g (72%) of a white solid: mp 117–118 °C; ^{1}H NMR 7.23–7.53 (m, 5 H), 6.09 (s, 1 H), 4.34 (q, J = 7 Hz, 2 H), 3.65–3.70 (m, 2 H), 3.31–3.36 (m, 2 H), 1.59–1.65 (m, 4 H), 1.51 (t, J = 7 Hz, 3 H); ^{13}C NMR 159.18, 158.10, 154.64, 131.03, 130.57, 128.93, 128.80, 119.63, 113.86, 110.82, 95.77, 74.07, 71.41, 44.42, 28.82, 27.21, 15.65; IR (KBr) 3300 (b), 3080 (w), 3057 (w), 2975 (m), 2940 (s), 2224 (s), 1572 (s), 1420 (s), 1295 (s); MS, *m/e* 379 (EI), 380 (CI).

Anal. Calcd for $C_{19}H_{19}Cl_2NO_2$: C, 60.01; H, 5.04. Found: C, 59.97; H, 4.87.

2-Chloro-4-cyano-3-ethoxy-5-[(1-methylethyl)oxy]-6-phenylphenol (26). A solution of 0.20 g (0.61 mmol) of 3-azido-6-chloro-5-ethoxy-4-(phenylethynyl)-3,5-cyclohexadiene-1,2-dione (**11**) in 20 mL of dry carbon tetrachloride was added dropwise to a refluxing solution of 0.62 g (6.11 mmol) of dry diisopropyl ether in 150 mL of dry carbon tetrachloride for 30 min under an atmosphere of argon. The solution was then refluxed for an additional 3 h, during which it turned from dark purple to light brown. The solution was concentrated and the dark oily residue was absorbed onto silica gel and subjected to flash column chromatography (hexane/ethyl acetate) to give a yellow semisolid. Recrystallization from dichloromethane/hexane yielded 0.02 g (28%) of a white solid: mp 139–140 °C; ^{1}H NMR 7.37–7.52 (m, 5 H), 6.02 (s, 1 H), 4.34 (q, J = 7 Hz, 2 H), 3.92 (heptet, J = 7 Hz, 1 H), 1.51 (t, J = 7 Hz, 3 H), 1.03 (s, 3 H), 1.01 (s, 3 H); IR (KBr) 3340 (b), 3058 (w), 2991 (s), 2940 (m), 2241 (s), 1591 (s), 1429 (s), 1300 (s); MS, *m/e* 331 (EI); exact mass calcd for $C_{18}H_{18}ClNO_3$ 331.0975, found 331.0972.

Preparation of 6-Chloro-8-cyano-2,3-dihydro-3,4-diphenyl-7-ethoxy-5-benzofuranone (28) and 6-Chloro-4-cyano-2,3-dihydro-3,8-diphenyl-5-ethoxy-7-benzofuranone (29). A solution of 0.45 g (1.37 mmol) of 3-azido-6-chloro-5-ethoxy-4-(phenylethynyl)-3,5-cyclohexadiene-1,2-dione (**11**) in 40 mL of dry carbon tetrachloride was added dropwise to a refluxing solution of 0.33 g (2.75 mmol) of styrene oxide in 250 mL of dry carbon tetrachloride for 1 h under an atmosphere of argon. The solution was then refluxed for an additional 3 h, after which it turned from dark purple to brown in color. The solution was concentrated and the dark oily residue was absorbed onto silica gel and subjected to flash column chromatography (hexane/ethyl acetate) to give a crude yellow solid. Purification on HPLC (hexane/ethyl acetate) gave two products. Compound **28**: yield 10%, yellow solid; mp 211–212 °C; ^{1}H NMR 7.08–7.34 (m, 10 H), 4.91 (dd, J = 7.9 Hz, J' = 9.3 Hz, 1 H), 4.66 (dd, J = 9.3 Hz, J' = 11.9 Hz, 1 H), 4.26 (dd, J = 7.9 Hz, J' = 11.9 Hz, 1 H), 4.44 (dq, J = 7 Hz, J' = 2.11 Hz, 2 H), 1.33 (t, J = 7 Hz, 3 H); ^{13}C NMR 179.9, 163.71, 155.50, 131.14, 130.45, 129.89, 129.53, 128.86, 128.47, 128.21, 118.27, 115.13, 114.22, 75.55, 71.64, 76.84, 51.93, 50.93, 14.82; IR (KBr) 3080 (w), 3038 (w), 2980 (w), 2905 (w), 2220 (m), 1680 (s), 1641 (s), 1529 (m); UV 381 nm (ε 3201); MS, *m/e* 391 (EI), 392 (CI); exact mass calcd for $C_{23}H_{18}ClNO_3$ 391.0975, found 391.0980.

Compound 29: yield 6%, white solid; mp 181–182 °C; ^{1}H NMR 7.25–7.59 (m, 10 H), 4.89 (dd, J = 9.6 Hz, J' = 11.4 Hz, 1 H), 4.75 (dd, J = 7.5 Hz, J' = 9.6 Hz, 1 H), 4.48 (dq, J = 7 Hz, J' = 2.5 Hz, 1 H), 4.06 (dd, J = 7 Hz, J' = 2.5 Hz, 1 H), 3.85 (dd, J = 7.5 Hz, J' = 11.4 Hz, 1 H), 0.86 (t, J = 7 Hz, 3 H); ^{13}C NMR 190.35, 181.85, 161.65, 131.27, 130.92, 130.44, 129.53, 129.03, 128.89, 128.45, 127.96, 127.83, 111.90, 108.63, 76.63, 70.46, 67.90, 50.40, 15.56; IR (KBr) 3042 (s), 2969 (m), 2219 (s), 1649 (s), 1610 (s), 1495 (m); UV 312 mm (ε 738); MS, *m/e* 391 (EI), 292 (CI); exact mass calcd for $C_{23}H_{18}ClNO_3$ 391.0975, found 391.0972.

4-Chloro-6-cyano-5-ethoxy-2-phenyl-1,3-benzenediol (31). A solution of 0.40 g (1.22 mmol) of 3-azido-6-chloro-5-ethoxy-4-(phenylethynyl)-3,5-cyclohexadiene-1,2-dione (**11**) and 1 mL of trimethylsilyl chloride in 40 mL of dry ethyl acetate was added dropwise to a refluxing solution of 150 mL of dry cyclohexane for 1 h under an atmosphere of argon. The solution was then refluxed for an additional 3 h, after which it turned from dark purple to brown in color. The solution was concentrated and the dark oily residue was adsorbed onto silica gel and subjected to flash column chromatography (hexane/ethyl acetate) to give 0.11 g (27%) of **32** and 0.14 g (39%) of **31** as a yellow solid: mp 146–147 °C; ^{1}H NMR 7.33–7.50 (m, 5 H), 5.99 (b, 2 H), 4.33 (q, J = 7 Hz, 2 H), 1.50 (t, J = 7 Hz, 3 H); ^{13}C NMR 157.97, 155.50, 154.12, 130.63, 130.04, 129.65, 129.30, 113.51, 112.46, 107.31, 89.26, 71.40, 15.68; IR (KBr) 3380 (b), 3082 (w), 2981 (w), 2220 (s), 1575 (s), 1445 (s); MS, *m/e* 289 (EI), 290 (CI); exact mass calcd for $C_{15}H_{12}ClNO_3$ 289.0509, found 289.0483.

2-Chloro-4-cyano-5-(ethanoyloxy)-3-ethoxy-6-phenylphenol (32). From the above experiment 0.11 g (27%) of **32** was obtained as pinkish solid: mp 140–141 °C; ^{1}H NMR 7.43–7.46 (m, 3 H), 7.26–7.29 (m, 2 H), 6.17 (s, 1 H), 4.38 (q, J = 7 Hz, 2 H), 2.02 (s, 3 H), 1.51 (t, J = 7 Hz, 3 H); ^{13}C NMR 168.06, 157.79, 154.71, 149.88, 130.03, 129.92, 128.97, 120.33, 113.04, 112.86, 95.89, 71.64, 20.23, 15.66; IR (KBr) 3300 (b), 3078 (w), 3041 (w), 2998 (m), 2942 (w), 2241 (s), 1786 (s), 1602 (s), 1433 (s), 1309 (s); MS, *m/e* 331 (EI), 332 (CI); exact mass calcd for $C_{17}H_{14}ClNO_4$ 331.0611, found 331.0611.

3-Chloro-5-cyano-4-ethoxy-2-hydroxy-8-methylenebicyclo[4.2.0]octa-1,3,5-triene (34). A solution of 0.15 g (0.51 mmol) of **33a** in 10 mL of dry benzene was added dropwise to 50 mL of refluxing benzene. The solution was heated to reflux for 1 h and then concentrated. The residue was absorbed on to silica gel and subjected to flash chromatography (1:1 hexanes/ethyl acetate) to give 40 mg (33%) of a yellow solid (**34**): mp >140 °C dec; ^{1}H NMR 5.36 (br s, 1 H), 5.06 (br s, 1 H), 4.30 (q, J = 7 Hz, 2 H), 3.64 (t, J = 1.3 Hz, 2 H), 1.48 (t, J = 7 Hz, 3 H); IR 3350 (br), 2940 (m), 2200 (m), 1600 (s), 1450 (s), 1380 (s), 1330 (s), 1250 (m), 1080 (s), 950 (m); MS, *m/e* 235 (EI); exact mass calcd for $C_{12}H_{10}ClNO_2$ 235.03999, found 235.04044.

8-Chloro-10-cyano-9-ethoxy-7-hydroxyfluoranthene (35). A solution of 0.25 g (0.66 mmol) of **33b** in 30 mL of dry CCl_4 was added dropwise to 250 mL of refluxing CCl_4. The solution was heated at reflux for 2 h and then concentrated. The residue was absorbed on to silica gel and subjected to flash chromatography (7:3 hexanes/ethyl acetate) to give 50 mg (24%) of yellow crystals (**35**): mp 239–240.5 °C; ^{1}H NMR 8.53 (d, J = 7 Hz, 1 H), 8.18 (d, J = 7 Hz, 1 H), 8.00 (d, J = 8.4 Hz, 1 H), 7.90 (d, J = 8.4 Hz, 1 H), 7.68–7.76 (m, 2 H), 6.49 (s, 1 H), 4.39 (q, J = 7 Hz, 2 H), 1.58 (t, J = 7 Hz, 3 H); IR 3300 (s), 2220 (s), 1560 (s), 1270 (s), 1200 (s), 1165 (s); MS, *m/e* 321 (EI); exact mass calcd for $C_{19}H_{12}ClNO_2$ 321.0556, found 321.0568.

1-Chloro-3-cyano-2-ethoxy-6*H*-dibenzo[*b*,*d*]pyran (36). A solution of 0.20 g (0.59 mmol) of **33c** in 75 mL of dry CCl_4 was added dropwise in 250 mL of refluxing CCl_4. The solution was heated at reflux for 1.5 h and then concentrated. The residue was absorbed on to silica gel and subjected to flash chromatography (4:1 hexanes/ethyl acetate) to give 27.4 mg (16%) of an off-white solid (**36**): mp 152.5–154 °C; ^{1}H NMR 7.85 (s, 1 H), 7.62 (d, J = 7 Hz, 1 H), 7.33–7.46 (m, 2 H), 7.18 (d, J = 7 Hz, 1 H), 5.31 (s, 2 H), 4.33 (q, $J = 7$ Hz, 2 H), 1.52 (t, $J = 7$ Hz, 3 H); IR 2220 (m), 1595 (m), 1440 (s), 1150 (s); MS, m/e 285 (EI); exact mass calcd for $C_{16}H_{11}ClNO_2$ 285.0556, found 285.0553.

2-Chloro-4-cyano-3-ethoxy-1-hydroxydibenzofuran (37). A solution of 0.25 g (0.70 mmol) of **33d** and 0.10 mL (0.77 mmol) of trimethylsilyl chloride in 75 mL of dry CCl_4 was added dropwise to 300 mL of refluxing CCl_4. The solution was heated at reflux for 1.5 h and then concentrated. The residue was absorbed on to silica gel and subjected to flash chromatography (1:1 hexanes/ethyl acetate) to give 0.15 g (76%) of off-white crystals (37): mp 214–215 °C; ^1H NMR 8.06 (d, $J = 6$ Hz, 1 H), 7.62 (d, $J = 6$ Hz, 1 H), 7.38–7.51 (m, 2 H), 6.63 (br s, 1 H), 4.43 (q, $J = 6$ Hz, 2 H), 1.54 (t, $J = 6$ Hz, 3 H); IR 3340 (br), 2240 (m), 1600 (s), 1450 (m), 1200 (m), 1165 (s); MS, m/e 287 (EI); exact mass calcd for $C_{15}H_{10}ClNO_3$ 287.03491, found 287.0340.

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Synthesis of Alkynyl Quinones and Related Compounds

Harold W. Moore,* Kevin F. West, Ulrich Wriede, Ken Chow, Mario Fernandez, and Nghi V. Nguyen

Department of Chemistry, University of California, Irvine, Irvine, California 92717

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A general synthetic route to alkynyl-substituted 1,4- and 1,2-benzoquinones is presented. This involves the 1,2-addition of lithium acetylides to a variety of alkoxy quinones followed by hydrolysis of the 3-hydroxy enol ether moiety of the resulting quinols. The use of these quinols and alkynyl quinones in the synthesis of various aromatic phenols and potential bioreductive alkylating agents is also presented.

Previously we reported a new method for the synthesis of 2,5-dialkylated-1,4-benzoquinones.[1] This involves treating a 2,5-dialkoxy-1,4-benzoquinone with 1 equiv of a lithium acetylide followed by a second equivalent of the same or a different lithium reagent and subsequent hydrolysis of the resulting adduct. At this time we report an expansion of this work that further illustrates the general synthetic scope.[2] Specifically, this methodology is shown to provide a simple and efficient procedure for the construction of a variety of alkynylated benzoquinones from readily available haloalkoxy quinones.[3] Such products are of interest since, as a class of compounds, alkynyl quinones have received very little attention[4] and its members represent useful precursors to a variety of other quinones and aromatic systems by taking advantage of the synthetically versatile alkyne moiety.[5] Our specific interest in developing synthetic routes to these quinones stems from their potential utility as precursors to bioreductive alkylating agents,[6] to 3-azido-4-alkynyl-1,2-benzoquinones, which are easily converted to cyanophenols,[7] to 2,5-dialkynyl-3,6-diazido-1,4-benzoquinones, which give (alkynylcyano)ketenes upon thermolysis,[8] and to polyalkynyl quinones, which might show unusual electronic properties. Outlined below are the details of this study.

Table I. Atomic Parameters for 1,2-Bis(phenylethynyl)-4,5-dimethoxy-3,5-cyclohexadiene-1,2-diol (2a) with Standard Deviations in Parentheses

atom	x	y	z
C(01)	0.1766 (1)	0.1638 (1)	0.0187 (2)
C(02)	0.2011 (1)	0.1260 (1)	0.1689 (2)
C(03)	0.2158 (1)	0.0476 (1)	0.1543 (2)
C(04)	0.1854 (1)	0.0115 (1)	0.0350 (2)
C(05)	0.1369 (1)	0.0469 (1)	−0.0878 (2)
C(06)	0.1300 (1)	0.1177 (1)	−0.0933 (2)
C(07)	0.1509 (1)	0.2351 (1)	0.0351 (2)
C(08)	0.1361 (1)	0.2949 (1)	0.0506 (2)
C(09)	0.1197 (1)	0.3679 (1)	0.0689 (2)
C(10)	0.0812 (2)	0.3827 (2)	0.1461 (4)
C(11)	0.0677 (2)	0.4557 (3)	0.1639 (5)
C(12)	0.0930 (2)	0.5099 (2)	0.1076 (5)
C(13)	0.1306 (2)	0.4948 (2)	0.0359 (4)
C(14)	0.1441 (1)	0.4241 (1)	0.0149 (3)
C(15)	0.2587 (1)	0.1628 (1)	0.2608 (3)
C(16)	0.3072 (1)	0.1910 (1)	0.3268 (3)
C(17)	0.3665 (1)	0.2253 (1)	0.3995 (3)
C(18)	0.3763 (1)	0.2681 (2)	0.5197 (3)
C(19)	0.4328 (1)	0.3030 (2)	0.5822 (4)
C(20)	0.4779 (1)	0.2949 (2)	0.5288 (3)
C(21)	0.4713 (1)	0.2517 (2)	0.4106 (3)
C(22)	0.4147 (1)	0.2172 (1)	0.3455 (3)
C(23)	0.2402 (1)	−0.0971 (1)	0.1235 (3)
C(24)	0.0651 (1)	0.0267 (2)	−0.3259 (3)
O(01)	0.2277 (1)	0.1744 (1)	−0.0316 (2)
O(02)	0.1519 (1)	0.1336 (1)	0.2256 (2)
O(03)	0.1939 (1)	−0.0590 (1)	0.0089 (2)
O(04)	0.1028 (1)	−0.0016 (1)	−0.1881 (2)

Synthesis of Alkynyl Quinones. In general, the methodology described here rests on a well-known carbonyl transposition sequence involving initial 1,2-addition of an organometallic reagent to the carbonyl group of 3-alkoxy enones. Subsequent acid hydrolyses of the resulting adducts results in 3-substituted enones. A particularly useful example of this reaction sequence as it applies to synthetic routes to substitued quinones is given in Scheme I. Here, 4,5-dimethoxy-1,2-benzoquinone (1)[9] was treated with a variety of lithium acetylides to give excellent yields (70–95%) of the corresponding 6-alkynyl-6-hydroxy-3,4-

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