Tetrahedron Letters,Vol.28,No.42,pp 5013-5016,1987 0040-4039/87 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

# (2-Aryl-2-cyanoethenyl)ketenes---Annulated Cyanophenols from Azidoquinones

Ken Chow and Harold W. Moore

Department of Chemistry, University of California

Irvine, California 92717

Abstract: Annulated cyanophenols are the products derived from the thermolysis of 3,6-diaryl-2,5-diazido-1,4-benzoquinones in the presence of an alkyne. The transformation is envisaged to involve the following steps: 1) thermal fragmentation of the azidoquinones to arylcyanoketenes, 2) cycloaddition of the ketenes to an alkyne to give 4-aryl-4-cyanocyclobutenones, 3) electrocyclic ring opening of the cyclobutenone to generate (2-aryl-2-cyanoethenyl)ketenes, and 4) ring closure of the conjugated ketenes to give the annulated cyanophenol products. Similarly, analogous products are obtained from the thermolysis of 4-aryl-3-azido-6-chloro-5-ethoxy-1,2-benzoquinones.

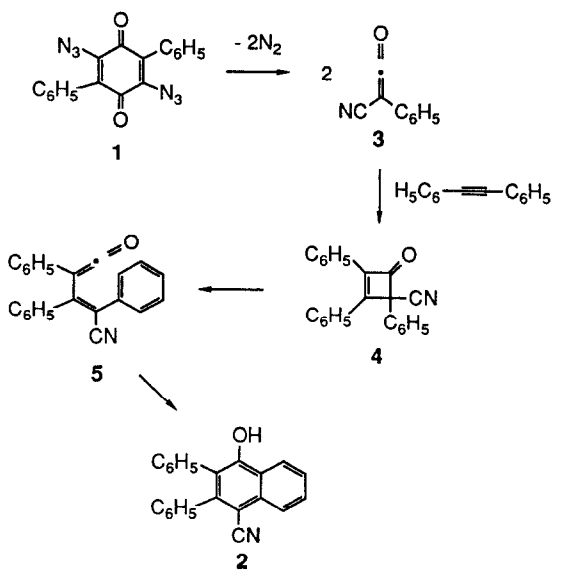
Reported here are two new synthetically useful routes to annulated cyanophenols. These both involve the generation of (2-aryl-2-cyanoethenyl)ketenes which undergo a 6 electron electrocyclic ring closure followed by proton transfer to the observed products. The two routes described in this Letter differ in their approach to the key conjugated ketene intermediates. One involves the electrocyclic ring opening of 4-aryl-4-cyanocyclobutenones and the other a fragmentation reaction of 4-aryl-3-azido-1,2-benzoquinones. The former has direct analogies in recent reports that 4-aryl-4-hydroxycyclobutenones give high yields of annulated hydroquinones when thermolyzed at 138°.[1,2] The latter is more unusual but also finds precedent in the recent report that 3-azido-1,2-benzoquinones give the corresponding ethenylketenes upon thermolysis.[3] Specific illustrative examples are provided here.

Thermolysis of 3,6-diphenyl-2,5-diazido-1,4-benzoquinone **1** in refluxing carbontetrachloride in the presence of 2.1 equivalents of diphenylacetylene gives **2** in 41% yield.[4] The product is seen to come from an initial fragmentation of **1** to generate 2 equivalents of cyanophenylketene

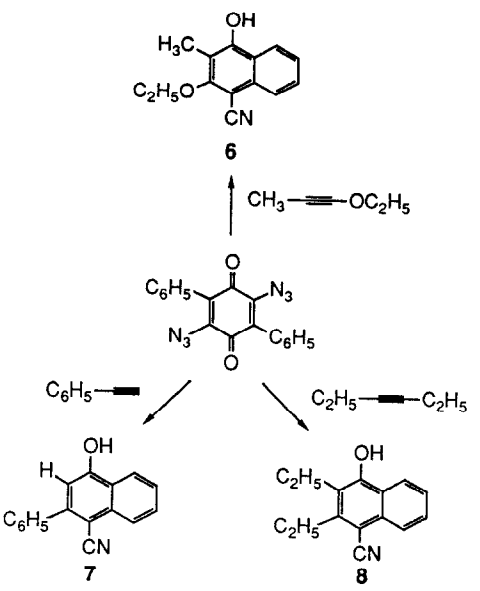
3.[5] Cycloaddition of 3 to diphenylacetylene gives 4-phenyl-4-cyanocyclobutenone 4 which undergoes an electrocyclic ring opening to (2-phenyl-2-cyanoethenyl)ketene 5. Subsequent electrocyclic ring closure of 5 followed by tautomerization finally affords 2 (Scheme 1).

Changing the alkynes in the above reaction results in variation of the substituents at the 2- and 3-positions of the cyanophenols, the regioselectivity of which is dictated by the initial ketene/alkyne cycloaddition.[6] For example, when 1-ethoxypropyne was utilized only the regioisomer 6 (30%) was isolated.[7] Similarly, when phenylacetylene and 3-hexyne were used 7 and 8 were obtained in respectively 67% and 33% yields (Scheme 2).

**Scheme 1**




**Scheme 2**

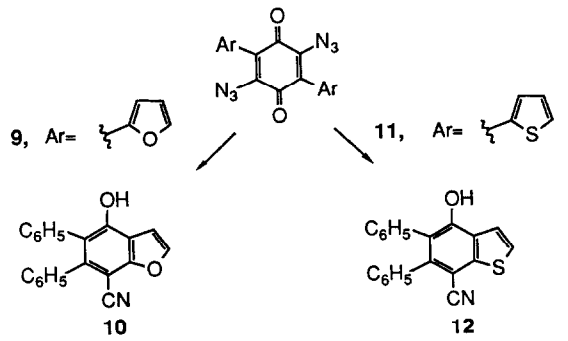



Variation of the ketene allows further flexibility in the annulation sequence. This is particularly useful for the synthesis of heterocyclic examples. As an illustration, thermolysis of 3,6-bis(2-furyl)-2,5-diazido-1,4-benzoquinone 9 in the presence of 2.1 equivalents of diphenylacetylene afforded 10 in 25% yield. In the same manner, thermolysis of the thiophene

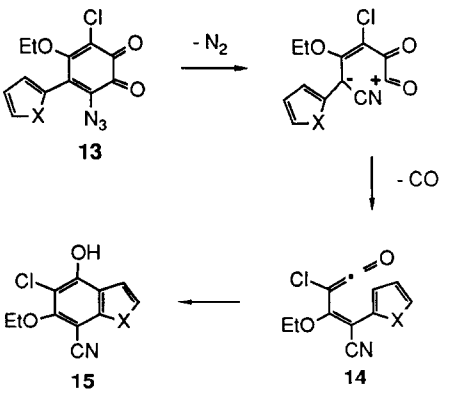
analog, 3,6-bis(2-thienyl)-2,5-diazido-1,4-benzoquinone **11**, in the presence of diphenylacetylene yielded **12** (34%) (Scheme 3).

Analogous products were also observed in the thermolysis of 4-aryl-3-azido-6-chloro-5-ethoxy-1,2-benzoquinones **13**. Under the condition of refluxing carbontetrachloride, **13** undergoes thermal fragmentation to give nitrogen, carbon monoxide, and the conjugated ketene **14**.[8,9] Electrocyclic ring closure of **14** followed by tautomerization affords the annulated cyanophenol **15** (Scheme 4).

**Scheme 3**




**Scheme 4**




| | X | % Yield 15 |
|---|---|---|
| a) | CH=CH | 28 |
| b) | S | 57 |
| c) | N-Ts | 30 |

In conclusion, we note the following significant points outlined in this Letter: 1) two routes to (2-aryl-2-cyanoethenyl)ketenes are reported; 2) these ketenes readily undergo electrocyclic ring closure to annulated cyanophenols; 3) the annulation methodology is applicable to both carbocyclic and heterocyclic example.

**Acknowledgement** The authors wish to thank the Public Health Service (GM-36312) for financial support of this work.

## References and Notes


1. Liebeskind, L. S.; Iyer, S.; Jewell, C. F., *J. Org. Chem.*, **1985**, *51*, 3065; Perri, S. T.; Foland, L. D.; Decker, O. H. W.; Moore, H. W. *ibid*, **1986**, *51*, 3067.

2. For related analogies see: Smith, L.I.; Hoehn, H.H. *J. Am. Chem. Soc.* **1939**, *61*, 2619. Smith,L.I.; Hoehn, H.H. *ibid.* **1941**, *63*, 1181. Nieuwenhuis, J.;Arens, J.F. *Rec. Trav. Chim. Pays-Bas* **1958**, *77*, 1153. Wittmann, H.; Illi, V.; Sterk, H.; Ziegler, E. *Monatsh. Chem.* **1968**, *99*, 1982. Zubovics, Z.; Wittman, H. *Liebigs Ann. Chem.* **1972**, *765*,15. Kipping, C; Schiefer, H.; Schonfelder, K. *J. Prakt. Chem.* **1973**, *315*, 887. Neuse, E.W.; Green, B.R. *Liebigs Ann. Chem.* **1974**, *9*, 1534. Mayr, H. *Angew. Chem. Int. Ed. Engl.*, **1975**, *14*, 500. Huisgen, R.; Mayr, H. *J. Chem. Soc. Chem. Commun.*, **1976**, 55. Huisgen, R.; Mayr, H. *ibid.* **1976**, 57. Danheiser, R. L.; Gee, S. K. *J. Org. Chem.*, **1984**, *49*, 1674.

3. Nguyen, N. V.; Chow, K.; Karlsson, J. O.; Doedens, R.; Moore, H. W. *J. Org. Chem.*, **1986**, *51*, 419.

4. Yields for the annulated cyanophenols are based upon ketene formation , *i.e.*, one assumes two equivalents of ketene are formed in the azidoquinone thermolyses.

5. Moore, H.W. *Acc. Chem. Res.* **1979**, *12*, 125. Ward, R.S.; " The Preparation of Ketenes ", in *The Chemistry of Ketenes, Allenes, and Related Compounds*\ Patai, S.; ed., J. Wiley and Sons, New York, 1980.

6. For regioselectivity in ketene cycloadditions see : Fleming, I. *Frontier Orbitals and Organic Chemical Reactions* J. Wiley and Sons, New York, 1976.

7. Regiochemistry was determined by difference NOE experiments.

8. Moore, H.W. *Acc. Chem. Res.* **1979**, *12*, 125.

9. Nguyen, N.V.; Chow, K.; Moore, H.W. *J. Org. Chem.* **1987**, *52*, 1315.


(Received in USA 23 June 1987)