C, 33.27; H, 2.71; N, 7.67; Cl, 38.68.

5,5,5′,5′-Tetrachloro-3,3′-hexamethylene-2,2′-spirobi[oxazolidine]-4,4′-dione (4b). A solution of 2.5 g (0.02 mol) of 1,3-diazacyclonona-1,2-diene (**1b**)[3] in 20 mL of $CHCl_3$ was added dropwise to 5.1 g (0.04 mol) of oxalyl chloride in 30 mL of $CHCl_3$ at 0 °C and brought to room temperature over a 30-min period. Removal of solvent left crude **4b** as colorless solid in virtually quantitative yield. Removal of traces of acid was best achieved by treating a chloroform solution of the product with aqueous sodium bicarbonate; further purification was by column chromatography on silica gel (Bio-Sil A, 100–200 mesh, 1,2-dichloroethane as eluent) and recrystallization from cyclohexane: mp 150–152 °C; IR ($CHCl_3$) 1750 cm^{-1} (C=O); ^{13}C NMR ($CDCl_3$) 162.2, 117.9, 100.5, 41.4, 23.4, 23.0. Anal. Calcd for $C_{11}H_{12}Cl_4N_2O_4$: C, 34.94; H, 3.20; N, 7.41; Cl, 37.52. Found: C, 34.98; H, 3.45; N, 7.39; Cl, 37.45.

1,13-Diaza-16,16-dichlorobicyclo[11.2.1]hexadecane-14,15-dione (2) and 1,13-Diazabicyclo[11.2.1]hexadecane-14,15,16-trione (3). A solution of 2.36 g (0.012 mol) of 1,3-diazacyclotetradeca-1,2-diene (**1c**) in 20 mL of chloroform was slowly added with stirring to an ice-cold solution of 1.7 g (0.013 mol) of oxalyl chloride in 30 mL of chloroform. After the mixture was allowed to warm to room temperature over a 30-min period, the solvent was removed under vacuum to give a solid reaction product **2**, which showed the following spectra: IR ($CHCl_3$) 1755 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) 4.25–3.40 (m, 4 H), 2.2–1.7 (complex m, 4 H), 1.6–1.0 (complex m, 14 H); ^{13}C NMR ($CDCl_3$) 155.6 (C-14, C-15), 103.0 (C-16), 42.6 (C-2, C-12), 28.2, 27.4, 26.3, 25.3, 25.0.

Due to the moisture sensitivity of **2**, an analytically pure sample was not obtained. Treatment of the crude reaction product with 5% aqueous acetone (60 mL) lead to its immediate and complete hydrolysis producing **3**. Filtration and drying left 3.0 g (94%) of **3**, mp 187–188 °C (toluene), colorless crystals. Anal. Calcd for $C_{14}H_{22}N_2O_3$: C, 63.13; H, 8.33; N, 10.52. Found: C, 62.94; H, 8.26; N, 10.45.

3,3′-Hexamethylene-5,5′-dimethoxy-5,5′-dichloro-2,2′-spirobi[oxazolidine]-4,4′-dione (6) and 1,3-Diaza-1,3-bis-(methyloxalyl)cyclononan-2-one (7). Solutions of 2.44 g (0.02 mol) of methyloxalyl chloride and 1.24 g (0.01 mol) of **1b** in 20 mL of dichloromethane each were combined with stirring at 0 °C. The reaction mixture was allowed to warm to room temperature (30 min.) and was concentrated in vacuum to leave a virtually quantitative yield of **6** as a colorless solid; crude mp 90–120 °C. Crude **6** shows the following spectra: IR ($CHCl_3$) 1750 cm^{-1} (C=O); ^{13}C NMR ($CDCl_3$) 162.0 (C-4, C-4′), 116.2/115.9 (C-5, C-5′), 111.6/113 (C-2), 53.6/53.3 (C[N]), 40.4/40.3, 23.5, 23.0, and 22.7 (signal splitting due to stereoisomerism). The bis cycloadduct **6** is readily hydrolyzed on stirring a dichloromethane solution with a saturated solution of potassium bicarbonate for 2 h. Drying the organic phase ($MgSO_4$), concentrating in vacuo, and recrystallization (CCl_4) gave 1.2 g (36%) of **7**: colorless crystals, mp 93–96 °C (CCl_4); IR ($CHCl_3$) 1760–1680 cm^{-1} (br m, C=O); ^{13}C NMR ($CDCl_3$) 161.5, 160.8, 159.6, 53.5, 44.5, 25.5, 21.0. Anal. Calcd for $C_{13}H_{18}N_2O_7$: C, 49.68; H, 5.77; N, 8.92. Found: C, 49.66; H, 5.61; N, 8.72.

Registry No. **1a**, 85237-12-3; **1b**, 6248-74-4; **1c**, 72995-04-1; **2**, 99798-85-3; **3**, 99798-86-4; **4a**, 99798-87-5; **4b**, 99808-62-5; **6**, 99798-88-6; **7**, 99798-89-7; $(COCl)_2$, 79-37-8; $ClCOCOOCH_3$, 5781-53-3; pentamethylenethiourea, 5269-85-2.

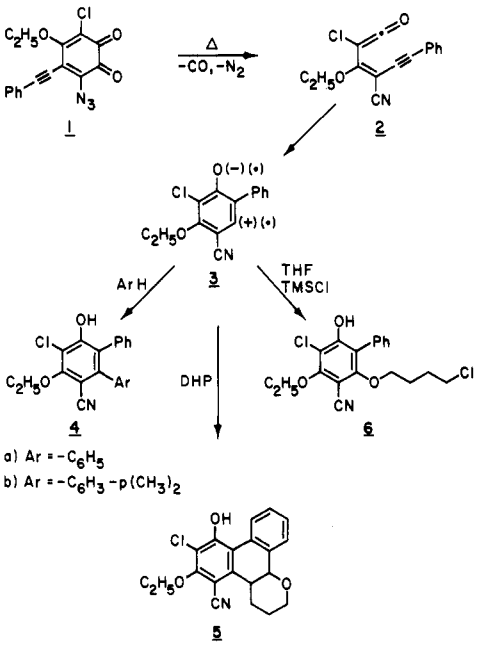
Communications

Chemistry of Azidoquinones. Conversion of 3-Azido-4-alkynyl-1,2-benzoquinones to Cyanophenols via (2-Alkynylethenyl)ketenes

Summary: Thermolysis of 4-alkynyl-3-azido-1,2-benzoquinones in refluxing benzene results in their conversion to (2-alkynylethenyl)ketenes. These, in turn, cyclize to dipolar or diradical intermediates, which proceed to products via intra- or intermolecular trapping. This provides a very unusual entry to highly substituted cyanophenols.

Sir: Reported here is a unique thermally induced rearrangement of 4-alkynyl-3-azido-1,2-benzoquinones to cyanophenols. This transformation is outlined in Scheme I and is envisaged to involve the following steps: (1) thermal fragmentation of the previously unknown azidoquinones **1** and **7** to dinitrogen, carbon monoxide, and (2-alkynylethenyl)ketenes, e.g., **2**;[1,2] (2) ring closure of the respective ketenes to the dipolar or diradical intermediates **3** and **8**; (3) intra- or intermolecular trapping of these intermediates to give the observed products.

Scheme I



Thermolysis of **1** (mp, 100 °C dec) in benzene or *p*-xylene gave respectively **4a** (84%, mp 201–202 °C) and **4b** (56%, mp 184–185 °C).[3,4] A particularly interesting

(1) For analogies to this fragmentation, see: Moore, H. W. *Acc. Chem. Res.* **1979**, *12*, 125.

(2) We have recently shown that (2-alkynylethenyl)ketenes can also be generated upon thermolysis of 4-alkynyl-4-(trimethylsiloxy)cyclobutenones. However, here the products are trimethylsilylquinones. See: Karlsson, J. O.; Nguyen, N. V.; Foland, L. D.; Moore, H. W. *J. Am. Chem. Soc.* **1985**, *107*, 3392.

(3) The structure of **4a** was established by single-crystal X-ray data. We acknowledge Professor Robert Doedens for this work.

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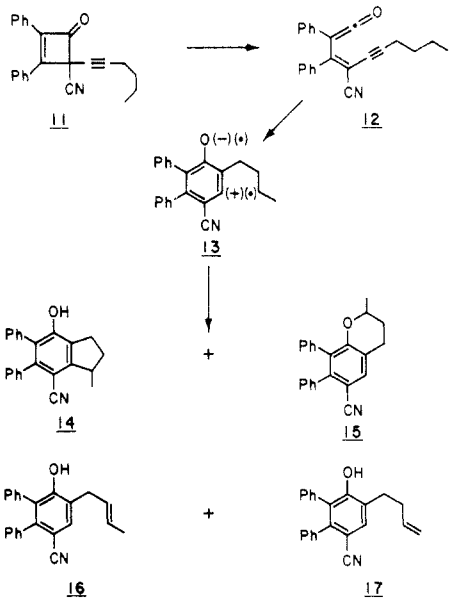
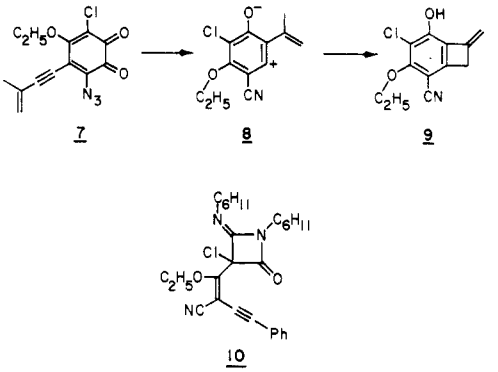
Scheme II



product was realized when **1** was decomposed in refluxing cyclohexane containing an excess (10 equiv) of dihydropyran (DHP). Here, the annulated product **5** (mp, 202–203 °C) was obtained in 37% yield. Finally, thermolysis of **1** in refluxing cyclohexane containing THF and Me_3SiCl gave the highly functionalized phenol **6** (mp 112–113 °C) in 72% isolated yield.[5] This last product can be seen to arise from **3** via silylation of the phenoxide oxygen and trapping of the aryl cation by THF. The resulting oxonium ion is then opened by attack of Cl^-, and desilylation in workup gives the observed product **6**.

In contrast to the above examples involving intermolecular condensations of the cyclized intermediate **3**, thermolysis of the azidoquinone **7** (mp 100 °C dec) in benzene resulted in an intramolecular trapping of **8** to give **9** (33%, mp, 140 °C dec).

Direct evidence for the intermediacy of (2-alkynylethenyl)ketenes in these thermolyses was obtained from an additional trapping experiment. That is, refluxing a solution of **1** in hexane containing 10 equiv of dicyclohexylcarbodiimide gave a 44% yield of **10** (oil), the anticipated product from a DCC/ketene cycloaddition.



Evidence for the electronic state of the intermediates **3** and **8** formed upon ring closure of these ketenes is less definitive. As noted above, a diradical or zwitterion can be envisaged, and the products, **4–6** and **9** are best viewed as arising from the dipolar species. However, some evidence was obtained which brings to question the possibility of a diradical intermediate for a closely related example. Specifically, hexynylcyanoketene[6] was generated in refluxing benzene in the presence of diphenylacetylene. It was anticipated that the resulting cyclobutenone **11** (Scheme II) would undergo electrocyclic ring opening to the ketene **12** and that this would proceed to products via the diradical or dipolar intermediate **13**. If this intermediate is zwitterionic, incorporation of the solvent (phenylation) would be anticipated. On the other hand, a diradical intermediate would be expected to result in products arising from hydrogen atom abstraction from the butyl side chain, and such were the only products detected. Specifically, **14** (mp 217–218 °C), **15** (mp 187–189 °C), and **16–17** (mixture) were formed in a respective ratio of 1:1:0.2:0.3 (54%).[7] Further studies are being conducted to determine the scope and mechanism of these reactions and will be presented in full.

Acknowledgment. We thank the National Institutes of Health (CA-11890, AI-15651) and the National Science Foundation (CHE-8025567) for financial support of this work.

(4) The quinones **1** and **2** were prepared by treating 2,5-dichloro-3,6-diethoxy-1,4-benzoquinone with the appropriate lithium acetylide followed by hydrolysis of the resulting adducts with TFAA/sulfuric acid. For the general procedure, see: Moore, H. W.; Sing, Y. L.; Sidhu, R. S. *J. Org. Chem.* **1980**, *45*, 5057. The resulting dichloroquinones were converted to **1** and **2** upon treatment with sodium azide.

(5) C,H analysis and/or high-resolution mass spectra were obtained on all of the new compounds reported here. Also, spectral data (NMR, IR, MS) are in agreement with their assigned structures.

(6) Nguyen, N. V.; Moore, H. W. *J. Chem. Soc., Chem. Commun.* **1984**, 1066.

(7) Hydride ion abstraction from the butyl side chain by the aryl cation site of a zwitterionic intermediate would also be consistent with these results.

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