Rearrangements of Azidoquinones. XV. Thermal Rearrangement of 2,3-Diazido-1,4-quinones to 2-Aza-3-cyano-1,4-quinones[1]

Dan S. Pearce, Michael J. Locke, and Harold W. Moore[2]*

Contribution from the Department of Chemistry, University of California, Irvine, California 92664. *Received November 2, 1974*

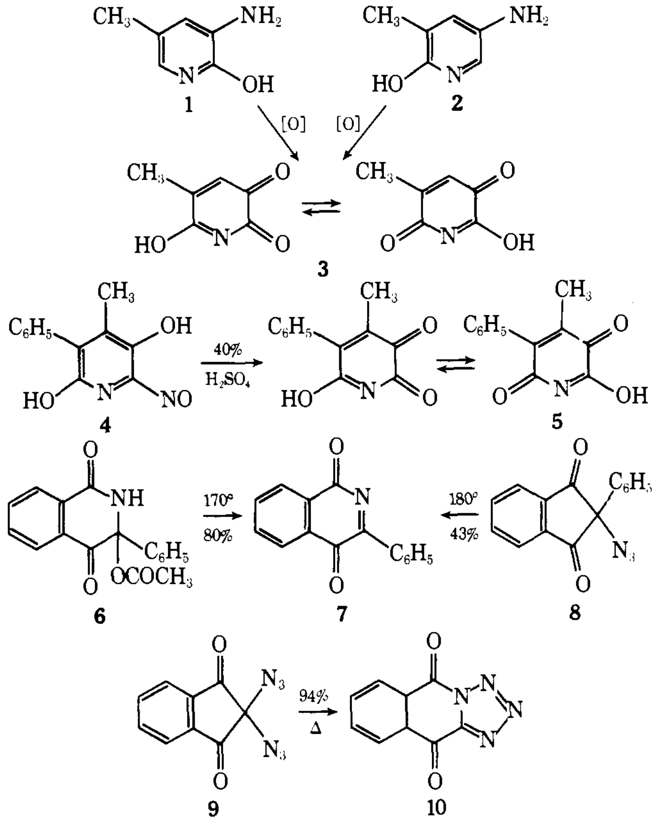
Abstract: 2,3-Diazidoquinones undergo a thermal rearrangement to 2-aza-3-cyano-1,4-benzoquinones. This transformation proceeds in two distinct stages. Below 100°, the diazides give diacyl cyanides and 2-azido-2-cyano-1,3-cyclopentene (or indan) -diones. The latter ring expands at temperatures above 100° to the corresponding azaquinones. Analogous ring expansions were also observed for 2-azido-2-phenyl- and 2,2-diazido-1,3-indandione. The monoazide gave 2-aza-3-phenyl-1,4-naphthoquinone, and the diazide gave a tetrazoloquinolinedione. The azaquinones are powerful dienophiles and can thus function as useful precursors to a variety of highly substituted heterocyclic compounds.

Examples of the nitrogen heterocyclic analogs of quinones, azaquinones, are now available from the thermal rearrangement of 2-azido-1,3-cyclopentene (or indan) -diones. These interesting heterocyclic compounds have received only limited attention in the past. In fact, 2-aza-3-phenyl-1,4-naphthoquinone (**7**) is the only bona fide example to previously appear in the literature.[3,4] All other reported examples are hydroxylated derivatives which can exist in several tautomeric forms, and no evidence has been presented which unambiguously establishes which isomer or isomers predominate.[5-9]

To some extent, the paucity of chemical information relating to azaquinones is undoubtedly due to a lack of viable synthetic routes to such compounds. Boyer and Kruger[7] have reported that oxidation of the aminopyridones **1** and **2** or 3-hydroxy-2-pyridone with manganese dioxide, chromium trioxide, or potassium bromate results in hydroxylation of the unsubstituted α-position and formation of the corresponding tautomeric hydroxyazaquinones **3** which were isolated as quinhydrones. Hydrolysis of 2-nitroso-3,6-dihydroxy-4-methyl-3-phenypyridine (**4**) to the azaquinone **5** was reported by Moore and Marascia.[6] Felner and Schenker[3] realized a good yield (80%) of 2-aza-3-phenyl-1,4-naphthoquinone (**7**) when the isoquinoline derivative **6** was subjected to thermolysis at 170°. Finally, this same azaquinone was described by us, in a preliminary communication,[4] as the major product (43%) obtained upon thermal decomposition of 2-azido-2-phenyl-1,3-indandione (**8**) in refluxing decalin. In addition, we observed[4] that 2,2-diazido-1,3-indandione (**9**) thermally rearranged in refluxing toluene to the tetrazole (**10**) in 94% isolated yield and proposed 2-aza-3-azido-1,4-naphthoquinone as its precursor. The experimental details of these ring expansion reactions as well as a related new fascinating rearrangement of 2,3-diazido-1,4-quinones to 2-aza-3-cyano-1,4-quinones are reported here (Scheme I).

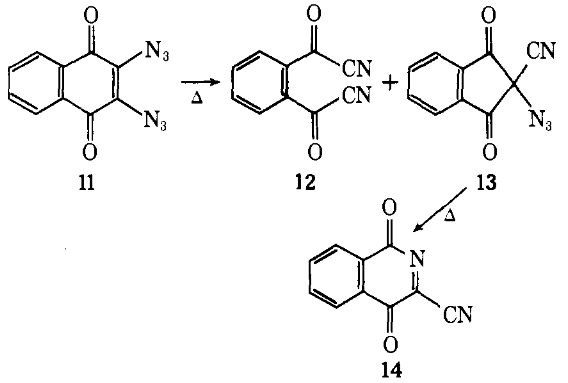
The observed[4] ring expansions of 2-azido-2-phenyl- (**8**) and 2,2-diazido-1,3-indandione (**9**), along with the established propensity of 2,6-diazido- and 2,5-diazido-1,4-quinones to undergo facile, thermally induced ring contractions to 2-cyano-4-azido-1,3-cyclopentene (or indan) -diones,[10] suggested a unique synthetic route to 2-aza-3-cyano-1,4-quinones. Specifically, it was anticipated that 2,3-diazido-1,4-quinones would also thermally rearrange to give initially the ring contracted 2-azido-2-cyano-1,3-cyclopentene (or indan) -diones which would subsequently ring expand to the heterocyclic quinones. It was further anticipated that the yields of azacyanoquinones produced by this route might not be particularly high since Van Allan, Priest, Marshall, and Reynolds[11] had previously reported that 2,3-diazido-1,4-naphthoquinone (**11**) suffers thermal cleavage[12] to give o-phthaloyl cyanide (**12**) in 52% yield. Nevertheless, a study of the thermal chemistry of a series of 2,3-diazido-1,4-quinones was initiated and, to our gratification, 2-aza-3-cyano-1,4-quinones were indeed formed.

Scheme I



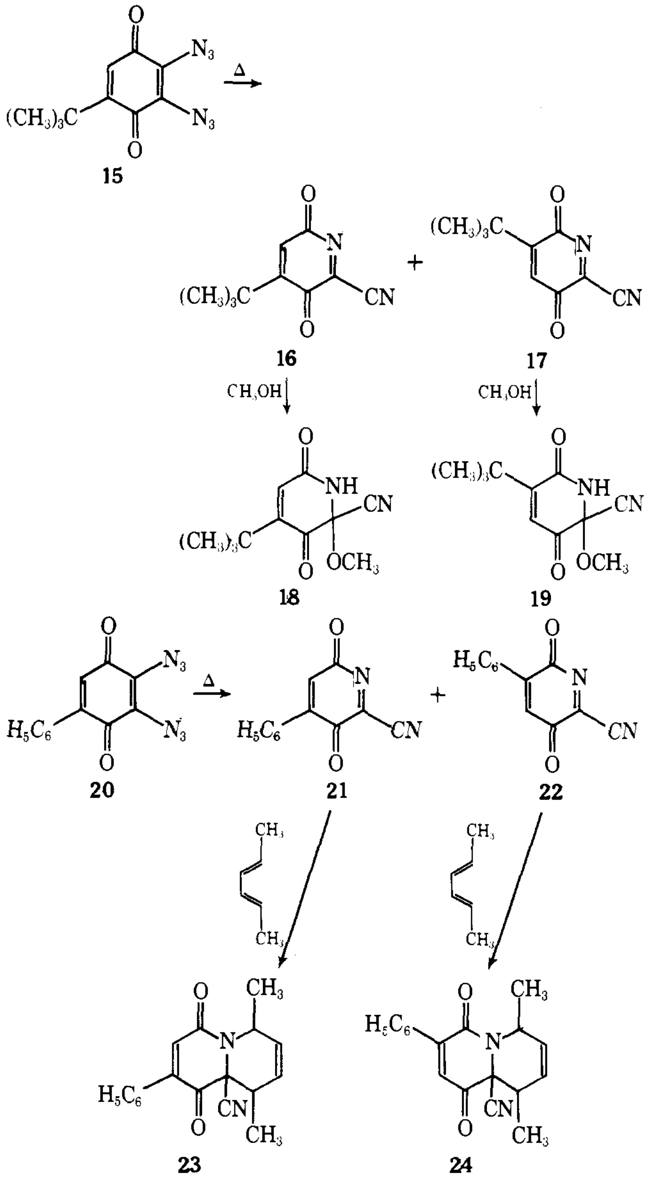
Thermolysis of 2,3-diazido-1,4-naphthoquinone in refluxing o-dichlorobenzene was initially investigated, and o-phthaloyl cyanide[11] (**12**) (40%) and 2-aza-3-cyano-1,4-naphthoquinone (**14**) (20%) were isolated. The above yields are lower limits as evidenced by the fact that these compounds could be trapped in situ to give adducts in higher yields based upon the starting diazide. For example, addition of *trans,trans*-2,4-hexadiene followed by anhydrous methanol to the reaction solution after it was cooled to ambient temperature gave the Diels–Alder adduct (**37a**) (38%) and 3-cyano-3-methoxyphthalide (48%). In separate experiments, the cycloaddition of the azaquinone to the diene was found to give **37a**, in nearly quantitative yield, and the reaction of *o*-phthaloyl cyanide with methanol gave an 80% yield of the phthalide.

The penultimate precursor to the azaquinone **14**, 2-azido-2-cyano-1,3-indandione (**13**), was isolated in 18% yield when 2,3-diazido-1,4-naphthoquinone was decomposed in chlorobenzene at 95–100°. Under these conditions, a 61% yield of *o*-phthaloyl cyanide was also realized, and no azaquinone was detected. Subsequent thermolysis of **13** in refluxing *o*-dichlorobenzene gave the azaquinone **14** in 75% isolated yield.

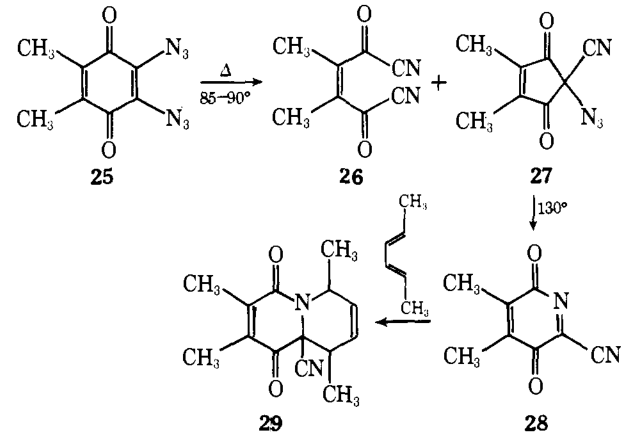


In an analogous fashion, the thermal chemistry of 2,3-diazido-5-*tert*-butyl- (**15**) and 2,3-diazido-5-phenyl-1,4-benzoquinone (**20**) was investigated. When the thermolyses of these compounds were carried out in refluxing *o*-dichlorobenzene, the *tert*-butyl analog gave nearly equal amounts of the isomeric azaquinones **16** and **17** in overall 55% isolated yield (Scheme II). The orientation of the *tert*-butyl substituents in these isomeric azaquinones is based upon the ^{1}H NMR spectra of their methanol adducts **18** and **19**. The vinyl proton of the 6-*tert*-butyl isomer **19** appears as a sharp singlet, while that in the 5-*tert*-butyl isomer **18** is broadened due to long range coupling with the amide proton, a process well documented in analogous systems.[13] 2,3-Diazido-5-phenyl-1,4-benzoquinone (**20**) also gave a mixture of isomeric azaquinones **21** and **22** which were isolated as their Diels–Alder adducts to *trans,trans*-2,4-hexadiene, respectively, 6-cyano-7,10-dimethyl-4-phenyl- (**23**) (11%) and 6-cyano-7,10-dimethyl-3-phenyl-1-azabicyclo[4.4.0]deca-3,7-diene-2,5-dione (**24**) (9%). The assignment of the position of the phenyl substituent in these isomeric adducts is somewhat tenuous. It is based upon a comparison of the chemical shifts of the 3- and 4-vinyl protons of these adducts with those in the analogous adducts of the *tert*-butyl analogs **37b** and **37c**. The 3-vinyl proton of the 4-*tert*-butyl isomer **37c** appears 0.3 ppm upfield from that of the 4-vinyl proton in the 3-*tert*-butyl isomer. Similarly, the chemical shift of the vinyl proton in the product assigned as the 4-phenyl isomer **23** appears 0.23 ppm upfield from that of its isomer **24**.

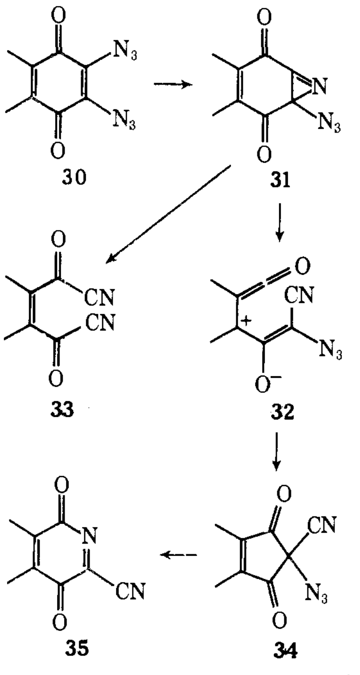
Scheme II



Thermolysis of 2,3-diazido-5,6-dimethyl-1,4-benzoquinone (**25**) in refluxing *o*-dichlorobenzene gave a very complex reaction mixture. However, lowering the reaction temperature to 85–90° gave a pale amber solution which displayed only two methyl absorptions in its ^{1}H NMR spectrum in a ratio of 1:5 coming respectively at δ 1.5 and 1.9. The ir spectrum of this solution showed characteristic absorptions at 2200 (CN), 2100 (N$_3$), 1760, 1700 cm^{-1} (C=O). Addition of anhydrous methanol to an aliquot of this solution caused a shift in the major methyl resonance in the ^{1}H NMR spectrum and the appearance of a new carbonyl absorption in the ir at 1800 cm^{-1}. It is thus assumed that the major product is 2,3-dimethylmaleoyl cyanide (**26**) which reacts with methanol to give the corresponding phthalide, and the minor product is 2-azido-2-cyano-4,5-dimethyl-1,3-cyclopentenedione (**27**). In agreement with this assignment, particularly with respect to the latter compound, is the observation that subsequent thermolysis of this reaction solution at 130° for 4 hr in the presence of excess *trans,trans*-2,4-hexadiene gave a 14% isolated yield of 6-cyano-3,4,7,10-tetramethyl-1-azabicyclo[4.4.0]deca-3,8-diene-2,5-dione (**29**), the Diels–Alder adduct of the diene to the azaquinone **28**.



It is thus clear that thermal rearrangements of 2,3-diazido-1,4-quinones proceed in two discrete stages. The first involves the formation of diacyl cyanides and 2-azido-2-cyano-1,3-cyclopentene (or indan) -diones; the second entails the subsequent ring expansion of these cyclic azides to 2-aza-3-cyano-1,4-quinones. The formation of the 2-azido-2-cyano-1,3-cyclic diones in the initial stage is, in essence, a further example of the thermal rearrangement of 2-azido-2-substituted 1,4-quinones to 2-cyano-2-substituted 1,3-cyclopentene (or indan) -diones, and the mechanism of this transformation has been reported.[14] Briefly, this rearrangement proceeds by collapse of the azidoquinone **30** to the azirine **31** followed by ring opening to the zwitterion **32** which undergoes C-acylation to the cyclic dione **34**. The mode of formation of diacyl cyanides is not as readily apparent. A nitrene mechanism is not attractive since the 2,3-diazido-1,4-quinones decompose at 80–90°, whereas organic azides which lead to nitrenes in the rate-determining step require temperatures in the range of 140–170°.[15] A mechanism involving the formation of a diazene intermediate[16] in the rate-limiting step is also untenable on the bases of existing kinetic data. For example, the relative rates of nitrogen evolution observed for the thermal decomposition (*m*-xylene, 110°) of 2,3-diazido-1,4-naphthoquinone, 2-azido-1,4-naphthoquinone, and 2-azido-3-chloro-1,4-naphthoquinone are respectively 1.0:0.9:0.3.[11,17] Thus, the absence of any significant rate enhancement suggests that the 2,3-diazidoquinones may follow a pathway in their thermal decomposition which is analogous to that observed for the monoazidoquinones. Therefore, the azidoazirines **31** are suggested as common intermediates to both the diacyl cyanides **33** and the 2-azido-2-cyano-1,3-cyclopentenediones **34**.

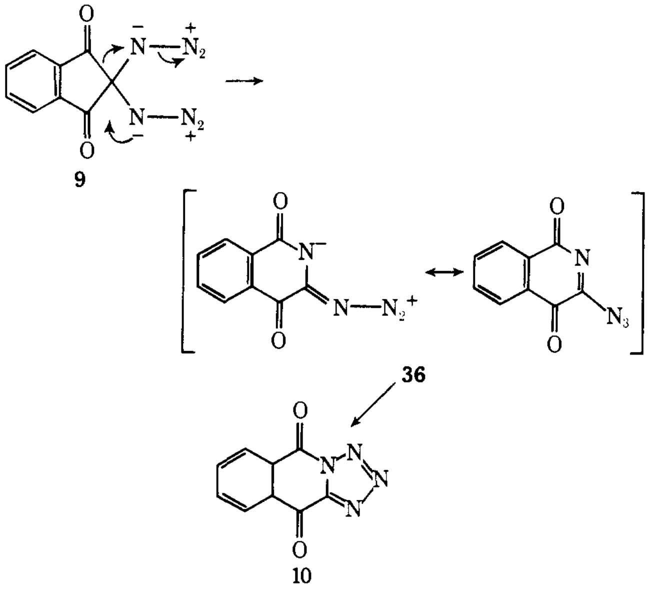


The higher temperature (>130°) required for convenient conversion of 2-azido-2-phenyl- (**8**), 2-azido-2-cyano-1,3-indandione (**13**), and 2-azido-2-cyano-4,5-dimethyl-1,3-cyclopentenedione (**27**) to the respective azaquinones is suggestive of a nitrene mechanism. 2,2-Diazido-1,3-indandione (**9**) is anomalous since this compound smoothly rearranges to the tetrazole at temperatures well below 100°. The rate of this transformation was found to be accurately first order in terms of nitrogen evolution over the entire range and showed activation parameters which are inconsistent with a nitrene intermediate; i.e., $\Delta H^{\ddagger} = 27.3$ kcal/mol and $\Delta S^{\ddagger} = +1.4$ eu.[18] Rate data for this reaction are listed in Table I.

Table I. Rates of Nitrogen Evolution for 2,2-Diazido-1,3-Indandione

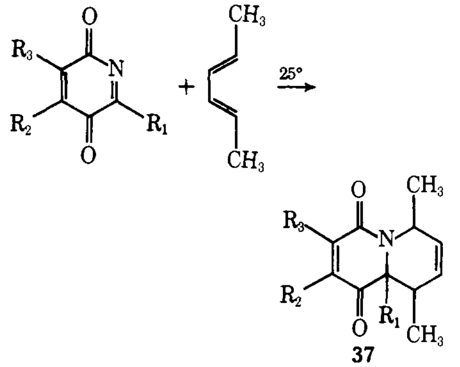
Solvent	T, °C	$\frac{1}{2}k \times 10^4$, sec^{-1}
Chlorobenzene	81.40	1.14
Chlorobenzene	81.40	1.17
o-Dichlorobenzene	81.40	1.12
m-Xylene	81.40	1.13
Chlorobenzene	72.17	0.39
Chlorobenzene	72.17	0.38
Chlorobenzene	64.35	0.16
Chlorobenzene	64.35	0.15

For comparison, the rate of rearrangement of 2-azido-2-phenyl-1,3-indandione (**8**) in *o*-dichlorobenzene was measured at two different temperatures and found to be 2.63×10^{-4} (148.58°) and 1.11×10^{-4} sec^{-1} (138.48°). The calculated rates for the decomposition of the diazide analog **9** at these temperatures are 0.065 (148.58°) and 0.028 sec^{-1} (138.38) which correspond to a rate enhancement by a factor of 250. Such an acceleration may be a reflection of ground state energy differences between **8** and **9** or of an anchimeric assistance of the adjacent azide in **9**, as formally outlined below, to give 2-aza-3-azido-1,4-naphthoquinone (**36**) as an intermediate to the tetrazoloquinolinedione **10**. Analogous transformations of the geminal diazides, dimethyl diazidomalonate[19] and benzophenone diazide,[20] to 1,5-disubstituted tetrazoles have been observed to occur under photolytic conditions, but mechanistic details are lacking.



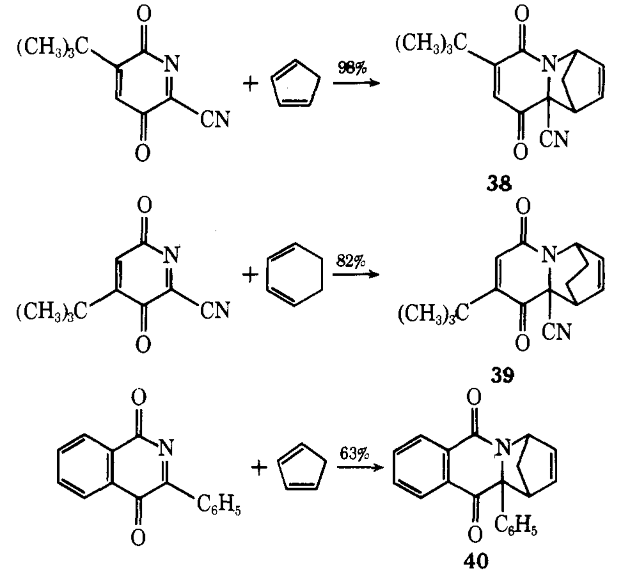
The chemistry of azaquinones centers around the electron deficient imine double bond. For example, Felner and Schenker[3] showed that water, methanol, ammonia, methylamine, nitromethane, *m*-xylene, and enamines all add readily to the imine double bond in 2-aza-3-phenyl-1,4-naphthoquinone. As mentioned in the preceding discussion, azaquinones are also potent dienophiles and thus can function as starting materials for a large variety of highly substituted new heterocyclic compounds. The 2-aza-3-cyano-1,4-quinones react within seconds at 25° ($k > 0.1$ l. mol^{-1} sec^{-1}) with a variety of dienes giving high yields of the corresponding cycloadducts. For comparison, dehydrohydantoins, which are also diacylimines and among the most reactive dienophiles known, cycloadd to dienes with an estimated second-order rate constant >0.01 l. mol^{-1} sec^{-1}.[21] The cycloaddition of selected azaquinones with *trans,trans*-2,4-hexadiene, cyclopentadiene, and cyclohexadiene are outlined in Scheme III.

Scheme III



37

37a, R_1 = CN; R_2 = -CH=CH—CH=CH- = R_3 (>95%)
37b, R_1 = CN; R_2 = $C(CH_3)_3$; R_3 = H (98%)
37c, R_1 = CN; R_2 = H; R_3 = $C(CH_3)_3$ (97%)



38

39

40

In conclusion, the work described here illustrates further the unique synthetic versatility of azidoquinones.[22] Depending upon their substitution pattern and oxidation state, this readily available class of compounds can be employed as precursors to α-cyanoalkylidene-$\Delta^{\alpha,\beta}$-butenolides, 2-cyano-4-cyclopentene-1,3-diones, cyanoketenes, azepine-2,5-diones, aminoquinones, indolequinones, 2-alkenyl-2,3-dihydroindole-4,7-diones, 4-acetoxy-1,2-quinone-2-(*N*-acetyl)imines, *trans,trans*-1,4-diacetoxy-*cis,cis*-1,3-butadienes, aryl azides, and as shown here, diacyl cyanides and 2-aza-3-cyano-1,4-quinones.

Experimental Section

2-Aza-3-phenyl-1,4-naphthoquinone (7). A suspension of 0.52 g (2.0 mmol) of 2-azido-2-phenyl-1,3-indandione[23] (**8**) in 7 ml of anhydrous decalin was refluxed for 15 min, cooled to ambient temperature, and filtered to give a deep red semisolid. The crude product was triturated with 1 ml of cyclohexane and then recrystallized from a mixture of carbon tetrachloride-cyclohexane to give 0.2 g (43%) of 2-aza-3-phenyl-1,4-naphthoquinone (**7**) as a deep maroon solid which was identical with the known compound reported by Felner and Schenker.[3]

Phthaloyl-1,5-1*H*-tetrazole (10). A solution of 1.87 g (8.2 mmol) of 2,2-diazido-1,3-indandione (**9**)[24] in 25 ml of anhydrous toluene was refluxed for 20 min. At the end of this time, a yellow precipitate had formed which was collected after cooling the reaction mixture to give 1.38 g of phthaloyl-1,5-1*H*-tetrazole (**10**), mp 216° (detonates). Addition of petroleum ether to the mother liquor gave an additional 0.16 g of **10** to bring the total yield to 94%. The combined yellow crystalline solid was recrystallized from ethylene dichloride, but this had no apparent effect upon the purity of the product. Characteristic spectral properties of **10** follow: ir (Nujol) 1750, 1680, 1560 cm^{-1}; uv (acetonitrile) 2.41 (4.37), 3.23 nm (3.63); mass spectrum (relative abundance) 200 (M$\cdot^+$, 16), 172 (10), 144 (11), 104 (53), 88 (100), 76 (60), 66 (55), 62 (25), 50 (41); ^{1}H NMR (CDCl$_3$) δ 8.3 (unsymmetrical multiplet).

Anal. Calcd for $C_9H_4N_4O_2$: C, 54.01; H, 2.01; N, 27.99. Found: C, 53.85; H, 2.11; N, 28.05.

Thermolysis of 2,3-Diazido-1,4-naphthoquinone (11). A. A solution of 1.0 g (4.2 mmol) of 2,3-diazido-1,4-naphthoquinone[11] (**11**) in 5 ml of warm *o*-dichlorobenzene was added slowly to 10 ml of refluxing *o*-dichlorobenzene. Nitrogen was vigorously evolved and the solution initially lightened to yellow and then darkened to red-orange. After 10 min, the solution was cooled to 10°, and the resulting orange precipitate was collected and recrystallized from ethylene dichloride-carbon tetrachloride to give 0.15 g (20%) of 2-aza-3-cyano-1,4-naphthoquinone (**14**) as fluffy orange crystals which showed the following characteristic properties: ir (Nujol) 2270, 1690, 1580 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.0 (unsymmetrical multiplet); mass spectrum (relative abundance) 184 (M$\cdot^+$, 1.5), 132 (25), 104 (100), 76 (43), 50 (33). Further recrystallization of **14** from ethylene dichloride gave an analytical sample, mp 155-160° dec.

Anal. Calcd for $C_{10}H_4N_2O_2$: C, 65.22; H, 2.19; N, 15.22. Found: C, 65.07; H, 2.18; N, 14.95.

Carbon tetrachloride was added to the mother liquor of the above reaction solution to give 0.3 g (40%) of *o*-phthaloyl cyanide (**12**), mp 100-106°. Repeated recrystallization of **12** from ethylene dichloride-carbon tetrachloride raised the melting point to 109-111° (lit.[11] mp 103°).

B. The thermolysis of 0.5 g (2.1 mmol) of 2,3-diazido-1,4-naphthoquinone was accomplished as described above except that 0.2 g of *trans,trans*-2,4-hexadiene was added to the cooled reaction solution. The characteristic orange color of the azaquinone faded after a few minutes. Methanol (0.2 ml) was then added and, after 5 min, the solvent was removed in vacuo and the resulting oil was chromatographed over 30 g of silica gel. Elution with 15% dichloromethane in pentane gave 0.19 g (48%) of 3-cyano-3-methoxyphthalide, mp 73-74°, which showed the following characteristic spectral properties: ir (Nujol) 2230, 1800, 1600 cm^{-1}; mass spectrum (relative abundance) 189 (M$^+$, 8), 158 (100), 130 (35), 115 (25), 102 (82), 76 (53), 75 (53), 51 (36), 50 (55); ^{1}H NMR (CDCl$_3$) δ 3.73 (s, 3), 7.75 (m, 4).

Anal. Calcd for $C_{10}H_7NO_3$: C, 63.49; H, 3.73; N, 7.41. Found: C, 63.58; H, 3.64; N, 7.20.

Continued elution with 30% dichloromethane in pentane gave 0.21 g (38%) of the diene adduct to the azaquinone **37a**, mp 120-123°, which showed the following characteristic spectral properties: ir (Nujol) 2230, 1710, 1670, 1660, 1600 cm^{-1}; mass spectrum (relative abundance) 266 (M$^+$, 45), 251 (43), 224 (13), 132 (16), 119 (25), 105 (17), 104 (100), 102 (11), 82 (45), 76 (62), 67 (26); ^{1}H NMR (CDCl$_3$) δ 1.06 (d, 3, J = 6.6 Hz), 1.55 (d, 3, J = 6.1 Hz), 3.4 (m, 1), 6.0 (m, 2), 8.0 (m, 4).

Anal. Calcd for $C_{16}H_{14}N_2O_2$: C, 72.16; H, 5.30; N, 10.52. Found: C, 72.17; H, 5.26; N, 10.56.

2-Azido-2-cyano-1,3-indandione (13). A solution of 1.8 g (7.5 mmol) of 2,3-diazido-1,4-naphthoquinone (**11**) in 10 ml of anhydrous chlorobenzene was heated at 95-100° for 3.5 hr, resulting in a pale yellow solution. The solvent was removed in vacuo, and the resulting orange solid was recrystallized from carbon tetrachloride to give 0.84 g (61%) of *o*-phthaloyl cyanide (**12**), mp 108-111°. The solvent was then removed in vacuo from the mother liquor, and the resulting residue was dissolved in 3 ml of anhydrous cyclohexane which, upon cooling, yielded 0.29 g (18%) of 2-azido-2-cyano-1,3-indandione. This solid was sublimed [40° (0.02 Torr)] to give the pure compound which is extremely sensitive to moisture: mp 57-59°; ir (Nujol) 2280, 2160, 1780, 1740 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 8.15 (symmetrical multiplet); mass spectrum (relative abundance) 184 (28.3), 158 (51.7), 132 (14.5), 104 (100), 76 (37.5).

Anal. Calcd for $C_{10}H_4N_4O_2$: C, 56.61; H, 1.90. Found: C, 56.79; H, 2.23.

Thermolysis of 2-Azido-2-cyano-1,3-indandione. A solution of 0.23 g of 2-azido-2-cyano-1,3-indandione (**13**) in 3 ml of *o*-dichlorobenzene was refluxed for 10 min and then cooled to ambient temperature. The resultant precipitate was collected to give 0.15 g (75%) of 2-aza-3-cyano-1,4-naphthoquinone (**14**), mp 148-154°. Recrystallization from ethylene dichloride gave the pure product (mp 155-160°) which was identical in all respect with the compound previously isolated from the thermolysis of 2,3-diazido-1,4-naphthoquinone.

Thermolysis of 2,3-Diazido-5-*tert*-butyl-1,4-benzoquinone. A solution of 4.0 g (16.3 mmol) of 2,3-diazido-5-*tert*-butyl-1,4-benzoquinone[25] (**15**) in 15 ml of warm *o*-dichlorobenzene was slowly added to 10 ml of refluxing *o*-dichlorobenzene. The solution was allowed to reflux for an additional 5 min, and then the reaction solution was concentrated to 5 ml in vacuo. Carbon tetrachloride (5 ml) was then added and, after cooling, 0.77 g (26%) of 2-aza-3-cyano-6-*tert*-butyl-1,4-quinone (**17**) was collected as light orange plates, mp 159-165° dec. Characteristic spectral properties for **17** follow: ir (Nujol) 2250, 1705, 1608, 1615, 1580 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.34 (s, 9), 6.78 (s, 1).

Anal. Calcd for $C_{10}H_{10}N_2O_2$: C, 63.14; H, 5.30; N, 14.73. Found: C, 63.32; H, 5.23; N, 14.79.

Further cooling of the above mother liquor gave 0.87 g (29%) of 2-aza-3-cyano-5-*tert*-butyl-1,4-benzoquinone (**16**) as purple plates, mp 107-113° dec, which showed the following spectral properties: ir (Nujol) 2250, 1690, 1640, 1580 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.30 (s, 9), 7.02 (s, 1). Satisfactory combustion analysis was obtained on the methanol adduct to this azaquinone (vide infra).

2-Aza-5-*tert*-butyl-3-cyano-3-methoxycyclohex-5-ene-1,4-dione (18) and 2-Aza-6-*tert*-butyl-3-cyano-9-methoxycyclohex-5-ene-1,4-dione (19). A sample of 1 g (4.1 mmol) of 2,3-diazido-5-*tert*-butyl-1,4-benzoquinone was decomposed as described above except that 1 ml of methanol was added to the cooled solution. After a few minutes, the solvent was removed in vacuo and the residue was recrystallized from carbon tetrachloride to give 0.24 g (27%) of 2-aza-5-*tert*-butyl-3-cyano-3-methoxycyclohex-5-ene-1,4-dione (**18**), mp 150-152°. This compound showed the following characteristic spectral properties: ir (Nujol) 3200, 3100, 1720, 1680, 1670, 1600 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.33 (s, 9), 3.51 (s, 3), 6.53 (s, 1), 7.8 (b s, 1). Recrystallization from carbon tetrachloride gave the analytical sample, mp 153° dec.

Anal. Calcd for $C_{11}H_{14}N_2O_3$: C, 59.44; H, 6.35; N, 12.60. Found: C, 59.54, H, 6.38; N, 12.63.

Addition of hexane to the above mother liquor followed by recrystallization of the resulting precipitate from benzene-hexane gave 0.22 g (25%) of 2-aza-6-*tert*-butyl-3-cyano-9-methoxycyclohex-5-ene-1,4-dione (**19**) which showed the following spectral properties: ir (Nujol) 3190, 3100, 1725, 1680, 1610 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.27 (s, 9), 3.51 (s, 3), 6.54 (b s, 1), 8.4 (b s, 1). The analytical sample was obtained after an additional recrystallization from carbon tetrachloride-hexane and showed a melting point at 127-128° dec.

Anal. Calcd for $C_{11}H_{14}N_2O_3$: C, 59.44; H, 6.35; N, 12.60. Found: C, 59.29; H, 6.26; N, 12.66.

In an alternate experiment, anhydrous methanol was added to solutions of ca. 20 mg of the azaquinones **16** and **17** in deuteriochloroform. The ^{1}H NMR spectra of these reaction solutions showed only absorptions corresponding to respectively the methanol adducts **18** and **19**.

Thermolysis of 2,3-Diazido-5-phenyl-1,4-benzoquinone. A solution of 1.5 g (3.8 mmol) of 2,3-diazido-5-phenyl-1,4-benzoquinone (**20**) in 10 ml of *o*-dichlorobenzene was refluxed for 5 min. It was then cooled to ambient temperature, and 0.4 ml of *trans,trans*-hexadiene was added. After 5 min, 0.5 ml of anhydrous methanol was added and, after an additional 5 min, the solvent was removed in vacuo and the resulting residue was chromatographed over 100 g of silica gel. Elution with dichloromethane-pentane (1:1) gave 0.5 g (40%) of γ-cyano-γ-methoxy-α-phenyl-$\Delta^{\alpha,\beta}$-butenolide which showed the following characteristic spectral properties: ir (Nujol) 2280, 1790, 1640 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.71 (s, 3), 7.28 (s, 1), 7.45 (m, 3), 7.84 (m, 2). Sublimation gave an analytical sample, mp 74-75°.

Anal. Calcd for $C_{12}H_9NO_3$: C, 66.97; H, 4.22; N, 6.51. Found: C, 66.96; H, 4.24; N, 6.87.

Continued elution gave 0.146 g (9%) of 6-cyano-7,10-dimethyl-3-phenyl-1-azabicyclo[4.4.0]deca-3,8-diene-2,5-dione (**24**) which was essentially pure by ^{1}H NMR analysis. Recrystallization from aqueous ethanol gave 0.08 g of the analytically pure compound, mp 90-91°, which showed the following characteristic spectral properties: ir (Nujol) 1670, 1660, 1650, 1620 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.08 (d, 3, J = 6.7 Hz), 1.52 (d, 3, J = 6.2 Hz), 3.2 (m, 1), 4.5 (m, 1), 5.9 (m, 2), 6.77 (s, 1), 7.45 (m, 5).

Anal. Calcd for $C_{18}H_{16}N_2O_2$: C, 73.95; H, 5.52; N, 9.59. Found: C, 73.89; H, 5.57; N, 9.47.

Continued elution gave 0.182 g (11%) of 6-cyano-7,10-dimethyl-4-phenylazabicyclo[4.4.0]deca-3,8-diene-2,5-dione (**23**) as a yellow crystalline solid. Recrystallization from aqueous ethanol gave 0.14 g of the analytical sample, mp 121-126°, which showed the following spectral properties: ir (Nujol) 1690, 1670, 1650 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.05 (d, 3, J = 7.0 Hz), 1.44 (d, 3, J = 6.5 Hz), 3.3 (m, 1), 4.5 (m, 1), 5.9 (m, 2), 7.02 (s, 1), 7.43 (s, 5).

Anal. Calcd for $C_{18}H_{16}N_2O_2$: C, 73.95; H, 5.52; N, 9.59. Found: C, 74.16; H, 5.51; N, 9.51.

Thermolysis of 2,3-Diazido-5,6-dimethyl-1,4-benzoquinone. A solution of 0.40 g (1.8 mmol) of 2,3-diazido-5,6-dimethyl-1,4-benzoquinone[11] (**25**) in 5 ml of anhydrous chlorobenzene was heated at 95-100° for 2 hr, resulting in a pale pink solution. A ^{1}H NMR spectrum of a small aliquot of this solution showed two singlets in a ratio of 1 to 5 at respectively δ 1.5 and 1.9; the ir spectrum showed absorptions for nitrile (2200 cm^{-1}), azide (2100 cm^{-1}), and carbonyl (1760 and 1700 cm^{-1}). Addition of anhydrous methanol to this aliquot resulted in a shift in the major methyl resonance in the ^{1}H NMR spectrum and the disappearance of the nitrile absorption in the ir spectrum with the concurrent formation of a moderately weak carbonyl absorption at 1800 cm^{-1}. *trans,trans*-2,4-Hexadiene (0.5 ml) was added to the reaction solution which was then heated at 130° for 4 hr. The solvent was then removed in vacuo, and the residue was chromatographed over 50 g of silica gel using dichloromethane-pentane (1:1) as the eluent. 6-Cyano-3,4,7,10-tetramethyl-1-azabicyclo[4.4.0]deca-3,8-diene-2,5-dione (**29**) (65 mg, 14% yield) was collected as a yellow semisolid which was essentially pure by ^{1}H NMR analyses. Recrystallization from aqueous ethanol gave the analytical sample, mp 100-102°, which showed the following spectral properties: ir (Nujol) 1670, 1625 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.98 (d, 3, J = 6.8 Hz), 1.47 (d, 3, J = 6.4 Hz), 2.04 (q, 3, J = 1.2 Hz), 2.20 (q, 3, J = 1.2 Hz), 3.2 (m, 1), 4.5 (m, 1), 5.9 (m, 2).

Anal. Calcd for $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.56; N, 11.47. Found: C, 68.83; H, 6.52; N, 11.44.

2,3-Diazido-5-phenyl-1,4-benzoquinone (20). A solution of 5 g of sodium azide in 25 ml of water was added to a well stirred solution of 5.0 g (20 mmol) of 2,3-dichloro-5-phenyl-1,4-benzoquinone[26] in 200 ml of ethanol-dichloromethane (1:1). The two-phase mixture was stirred at ambient temperature for 2 hr after which time the organic layer had become a deep purple. Water was then added and the mixture extracted with dichloromethane. After drying, the solvent was removed in vacuo and the residue recrystallized from dichloromethane-ethanol to give 4.2 g of the diazide as lustrous purple crystals, mp 115-117° dec. Characteristic spectral properties for **23** follow: ir (Nujol) 2100, 1640, 1575 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 6.65 (s, 1), 7.31 (s, 5).

Anal. Calcd for $C_{12}H_6N_6O_2$: C, 54.13; H, 2.26; N, 31.58. Found: C, 54.28; H, 2.34; N, 31.51.

3-*tert*-Butyl-6-cyano-7,10-dimethyl-1-azabicyclo[4.4.0]deca-8,9-diene-2,5-dione (37c). A solution of 0.146 g (1.76 mmol) of *trans,trans*-2,4-hexadiene in 1 ml of anhydrous benzene was added to a stirred suspension of 0.146 g (0.77 mmol) of 2-aza-6-*tert*-butyl-3-cyano-1,4-benzoquinone (**17**) in 5 ml of anhydrous benzene. In less than 10 sec, the pink color of the azaquinone faded to a pale yellow. The solvent was removed in vacuo, and the crude product was chromatographed on 15 g of silica gel using dichloromethane-pentane (1:1) as the eluent. This gave 0.203 g (97%) of the white Diels-Alder adduct **37c**, mp 96-98°, which showed the following spectral properties: ir (Nujol) 1695, 1675, 1650, 1580 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.98 (d, 3, J = 6.2 Hz), 1.4 (d with overlapping s, 12, J = 6.2 Hz), 3.1 (m, 1), 4.5 (m, 1), 5.85 (m, 2), 6.51 (s, 1); mass spectrum (relative abundance) 272 ($M\cdot^+$, 23), 257 (26), 138 (100), 110 (22), 95 (36), 82 (30), 67 (44), 41 (40).

Anal. Calcd for $C_{16}H_{20}N_2O_2$: C, 70.56; H, 7.40; N, 10.29. Found: C, 70.83; H, 7.27; N, 10.17.

4-*tert*-Butyl-6-cyano-7,10-dimethyl-1-azabicyclo[4.4.0]deca-3,8-diene-2,5-dione (37b). Using the procedure described above, 0.10 g (1.2 mmol) of *trans,trans*-2,4-hexadiene and 0.16 g (0.84 mmol) of 2-aza-5-*tert*-butyl-1,4-benzoquinone (**16**) were converted to

0.234 g (98%) of the Diels-Alder adduct **37b**, mp 120-121°, which showed the following spectral properties: ir (Nujol) 1690, 1670, 1610 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.00 (d, 3, J = 7 Hz), 1.28 (s, 9), 1.52 (d, 3, J = 6.5 Hz), 3.5 (m, 1), 4.5 (m, 1), 5.95 (m, 2), 6.83 (s, 1).

Anal. Calcd for $C_{16}H_{20}N_2O_2$: C, 70.56; H, 7.40; N, 10.29. Found: C, 70.66; H, 7.37; N, 10.29.

4-*tert*-Butyl-7-cyano-2-azatricyclo[6.2.1.0^{2,7}]undeca-3,6-diene-4,9-dione (38). To a stirred suspension of 0.24 g (1.26 mmol) of 2-aza-6-*tert*-butyl-3-cyano-1,4-benzoquinone (**17**) in 10 ml of anhydrous benzene was added 0.09 g (1.4 mmol) of freshly distilled cyclopentadiene. Within 10 sec the initial pink color had faded to pale yellow. The solvent was removed, and the residue was chromatographed over 20 g of Florisil using dichloromethane-pentane (1:1) as the eluent to give 0.381 g (98%) of the cycloadduct **38**, mp 87-89°, which showed the following characteristic spectral properties: ir (Nujol) 2220, 1690, 1660, 1600 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.32 (s, 9), 2.05 (m, 2), 3.95 (m, 1), 5.18 (m, 1), 6.23 (m, 1), 6.37 (s, 1); mass spectrum (relative abundance) 256 (M$^+$, 1.5) 138 (57), 110 (32), 138 (57), 67 (89), 66 (110), 65 (59), 41 (87), 40 (39), 39 (87).

Anal. Calcd for $C_{15}H_{16}N_2O_2$: C, 70.29; H, 6.29; N, 10.93. Found: C, 70.27; H, 6.36; N, 11.02.

4-*tert*-Butyl-7-cyano-2-azatricyclo[6.2.2.0^{2,6}]dodeca-4,9-diene-3,6-dione (39). In a manner analogous to the above, 0.139 g (0.73 mmol) of 2-aza-5-*tert*-butyl-1,4-benzoquinone (**16**) and 0.2 g (2 mmol) of 1,3-cyclohexadiene were converted to 0.162 g (82%) of the cycloadduct **39**, mp 95-96°. This Diels-Alder adduct showed the following spectral properties: ir (Nujol) 1720, 1670, 1610 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.20 (s, 9), 1.5-2.4 (m, 4), 3.55 (m, 1), 5.2 (1), 6.50 (m), with overlapping s at δ 6.57 (3).

Anal. Calcd for $C_{16}H_{18}N_2O_2$: C, 71.09; H, 6.71; N, 10.37. Found: C, 71.19; H, 6.64; N, 10.47.

Reaction of 2-Aza-3-phenyl-1,4-naphthoquinone with Cyclopentadiene. Cyclopentadiene (0.3 g) was added to a solution of 0.165 g (0.10 mmol) of 2-aza-3-phenyl-1,4-naphthoquinone (**7**) in 5 ml of anhydrous chloroform, and the solution was stirred at ambient temperature for 4 days. The solvent was then removed in vacuo, and the residue was chromatographed on silica gel using dichloromethane as the eluent to give 0.132 g (63%) of the cycloadduct (40), mp 158-160°; ir (Nujol) 1680, 1640, 1590 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.6 (m, 2), 3.9 (m, 1), 5.4 (m, 2), 6.65 (m, 2), 7.5 (m, 9).

Anal. Calcd for $C_{20}H_{15}NO_2$: C, 79.71; H, 5.01; N, 4.65. Found: C, 79.27; H, 5.23; N, 4.81.

References and Notes

(1) For paper XIV in this series on the chemistry of azidoquinones and related compounds, see D. S. Pearce, M. S. Lee, and H. W. Moore, *J. Org. Chem.*, **39**, 1362 (1974).

(2) The authors are grateful to the National Science Foundation (GP 43712x) for financial support of their project.

(3) I. Felner and K. Schenker, *Helv. Chem. Acta*, **52**, 1810 (1969).

(4) H. W. Moore and D. S. Pearce, *Tetrahedron Lett.*, 1621 (1971).

(5) H. J. Knackmuss, *Angew. Chem.*, **85**, 163 (1973).

(6) J. A. Moore and F. L. Marascia, *J. Am. Chem. Soc.*, **81**, 6049 (1959).

(7) J. A. Boyer and S. Kruger, *J. Am. Chem. Soc.*, **79**, 3552 (1957).

(8) H. Ost, *J. Prakt. Chem.*, [2], **27**, 260 (1890).

(9) R. Kudernatsch, *Monatsh.*, **18**, 613 (1897).

(10) W. Weyler, W. G. Duncan, and H. W. Moore, *J. Am. Chem. Soc.*, **97**, (1975).

(11) J. A. Van Allan, W. J. Priest, A. S. Marshall, and G. A. Reynolds, *J. Org. Chem.*, **33**, 1100 (1968).

(12) A number of analogous cleavage reactions of vicinal vinyl diazides have appeared in the literature. See, for example, J. H. Hall and E. Patterson, *J. Am. Chem. Soc.*, **89**, 5856 (1967); D. S. Pearce, M. S. Lee, and H. W. Moore, *J. Org. Chem.*, **39**, 1362 (1974); H. W. Moore and M. S. Lee, *Tetrahedron Lett.*, 3645 (1971); G. Smolinsky and C. A. Pryde, *J. Org. Chem.*, **33**, 2411 (1968).

(13) R. Richards and R. Smith, *Tetrahedron Lett.*, 2361 (1966); A. Berger, A. Loewenstein, and S. Meiboom, *J. Am. Chem. Soc.*, **81**, 62 (1959).

(14) W. Weyler, D. S. Pearce, and H. W. Moore, *J. Am. Chem. Soc.*, **95**, 2603 (1973).

(15) G. L'abbé, *Chem. Rev.*, **69**, 345 (1969).

(16) Diazenes have been proposed as intermediates in the thermolysis of *o*-diazidobenzenes to mucon准onitriles: J. H. Hall, *J. Am. Chem. Soc.*, **87**, 1147 (1965).

(17) The rate of decomposition of 2,3-diazido-1,4-naphthoquinones in *m*-xylene at 110° has been reported to be 2.24×10^{-3} (ref 11). This has been corrected to 2.8×10^{-3} sec^{-1} to account for the fact that in addition to *o*-phthaloyl cyanide, 2-azido-2-cyano-1,3-indandione is also formed in this reaction. The ratio of these two products is estimated to be 3:2, respectively.

(18) Kinetic studies of azide decompositions proceeding by way of nitrene intermediates reveal activation enthalpies usually greater than 30 kcal/mol and activation entropies generally positive ranging from −4.9 to 32.2 eu. See, for example, R. A. Abramovitch and E. P. Kyba, "The Chemistry of the Azide Group", S. Patai, Ed., Interscience, New York, N.Y., 1971, p 254 and 259.

(19) R. M. Moriarty, J. M. Kliegman, and C. Shovlin, *J. Am. Chem. Soc.*, **89**, 5958 (1967).

(20) R. M. Moriarty and J. M. Kliegman, *J. Am. Chem. Soc.*, **89**, 5959 (1967).

(21) A. B. Evnin, A. Lam, and J. Blyskal, *J. Org. Chem.*, **35**, 3097 (1970).

(22) A detailed review of the synthesis and chemistry of azidoquinones has appeared: H. W. Moore, *Chem. Soc. Rev.*, **2**, 415 (1973).

(23) E. Gudriniece and N. R. Bruvele, *Latv. PSR Zinat. Akad. Vestis, Kim. Ser.*, 379 (1970).

(24) E. Grudriniece, N. R. Bruvele, and A. Levins, *Dokl. Akad. Nauk. SSSR*, **171**, 809 (1966); *Chem. Abstr.*, **67**, 53900 h.

(25) H. W. Moore, D. L. Maurer, D. S. Pearce, and M. S. Lee, *J. Org. Chem.*, **37**, 1984 (1972).

(26) L. Ecuyer, *Can. J. Chem.*, **36**, 814 (1958); **39**, 1037 (1961).