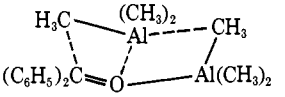
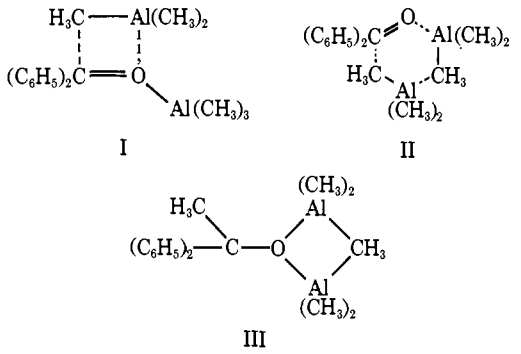
It is reasonable that attack of monomeric trimethylaluminum on the complexed ketone occurs in a way similar to the attack on uncomplexed ketone shown in the last part of Figure 3. Comparison of the enthalpies of activation is consistent with this view. The initial attack of a molecule of $(CH_3)_3Al$ on either complexed or uncomplexed ketone is at the cloud of π electrons which has its greatest density at the oxygen. In the complex, the electron density on the oxygen is decreased due to inductive withdrawal of electrons by the trimethylaluminum bond to the nonbonding electrons on the oxygen. As a result, bond formation with the attacking Al is energetically less favorable, and the activation enthalpy for attack of $(CH_3)_3Al$ on free ketone, $\Delta H^{\ddagger}_3$, is less than that for attack of $(CH_3)_3Al$ on complex, 10.5 kcal.

The transition states I and II have been suggested for this reaction in benzene[3,22] leading to the product "hemialkoxide" III. Structure I is more consistent with the description above; but examination of molecular models of both transition states I and II with reasonable bond distances and angles reveals an interesting feature. The arrangement of the atoms in what appears to be the most favorable six-membered ring II is rather like two planar four-membered rings fused at a common side with a dihedral angle of about 125°. In this structure, the four-membered ring containing the carbonyl (C=O) is not much different than the four-membered ring of transition state I. The major difference between the proposed transition states I and IV is that in structure I the trimethylaluminum molecule bound to the oxygen is free to rotate, while in structure



IV

IV rigidity is imposed by the bridging methyl group. The question is then whether or not a methyl bridge bond is formed as the free monomeric $(CH_3)_3Al$ attacks the complex. The formation of such a bond would be energetically favorable and an estimate of this effect can be made in the following way. The enthalpy change for the reaction $[Al(CH_3)_3]_2 \rightarrow 2Al(CH_3)_3$ in benzene was estimated above to be about 12.4 kcal. Since transition state IV contains one methyl bridge, it would be expected to be about 6 kcal more favorable than any transition state in which an aluminum–methyl bridge bond is not formed. The large negative entropy of activation, $\Delta S^{\ddagger} = -21.1$ eu, supports a fairly rigid cyclic transition state, such as IV.



I II III

(22) E. A. Jeffery and T. Mole, *Aust. J. Chem.*, **23**, 715 (1970).

Rearrangements of Azidoquinones. X. Thermal Rearrangements of Monoazidoquinones to 2-Cyano-4-cyclopentene-1,3-diones[1,2]

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Abstract: The thermal decomposition of monoazido-1,4-quinones (**1**) is described. This reaction results in their high yield ring contraction to 2-cyano-4-cyclopentene-1,3-diones (**2**). The synthetic scope as well as the kinetics and mechanism of this rearrangement are discussed.

Azidoquinones constitute a synthetically versatile and readily available class of compounds. Depending upon their substitution pattern and the reaction conditions, a variety of very specific and high yield transformations can be accomplished. Monoazido-1,4-quinones stereospecifically rearrange to γ-cyano-alkylidene-$\Delta^{\alpha,\beta}$-butenolides when decomposed in cold concentrated sulfuric acid.[3] On the other hand, 4-azido-1,2-naphthoquinone ring expands to 4-hydroxy-1*H*-1-benzazepine-2,5-dione under the same reaction conditions.[4] Thermal decomposition of 2,5-diazido-1,4-benzoquinones induces their cleavage to two molecules of the corresponding cyanoketene,[5,6]

(1) The authors are grateful to the National Science Foundation (GP 19263) and to the National Institutes of Health for financial support of this project.

(2) Based primarily upon the Ph.D. dissertation of Walter Weyler, Jr.

(3) H. W. Moore, H. R. Shelden, D. W. Deters, and R. J. Wikholm, *J. Amer. Chem. Soc.*, **92**, 1675 (1970).

(4) H. W. Moore, H. R. Shelden, and W. Weyler, *Tetrahedron Lett.*, 1243 (1969).

(5) H. W. Moore and W. Weyler, *J. Amer. Chem. Soc.*, **92**, 4132 (1970).

(6) H. W. Moore and W. Weyler, *ibid.*, **93**, 2812 (1971).

while the 2,3-diazido isomers give diacyl cyanides[7] and/or 3-cyano-2-azaquinones.[8] Reported here are the results of an investigation of the thermal decomposition of monoazido-1,4-quinones (**1**); this is a smooth rearrangement resulting in the ring contracted 2-cyano-4-cyclopentene-1,3-diones, (**2**).[9]

Synthetic Scope

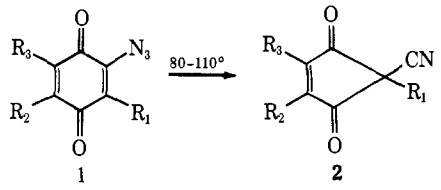
Until now, no general route has been available which would allow the synthesis of a large variety of highly substituted 4-cyclopentene-1,3-diones. Synthetic pathways to such compounds warrant detailed study since this ring system is of significant importance. A variety of natural products are 2-acyl-4-cyclopentene-1,3-diones, *e.g.*, linderone,[10] methyllinderone,[10] lucidone,[11] methyllucidone,[11] calythrone,[12] and a number of hops constituents.[13] Variously 2-substituted indan-1,3-diones show marked pharmacological activity as anticoagulants,[14] similar to that produced by the coumarin series of compounds. Pyrethrins[15] are among the most important natural insecticides and are related structurally to the cyclopentenedione ring system.[16] Indeed, even the prostoglandins,[17] which are of pivotal biological significance, can be viewed as being derivatives of the partially reduced cyclopentene-1,3-dione ring system.

The ubiquity of quinones and their ease of conversion to azidoquinones[3] provide readily available starting materials for the synthesis of 2-cyano-4 cyclopentene-1,3-diones by the method reported here. The general structures **1** and **2** illustrate the overall transformation as depicted in Scheme I.

The only synthetic limitations of this reaction thus far observed are for those azidoquinones in which the substituent adjacent to the azide group is either a proton or a vinyl moiety. The former compounds give a complex mixture of products upon pyrolytic decomposition, while the latter give a very smooth, high yield conversion to indolequinones.[18] An example of this heterocyclic ring formation reaction is illustrated below. 2-Azido-3-propenyl-1,4-naphthoquinone (**3**) is converted in 91% isolated yield to the indolequinone **4** in refluxing benzene.

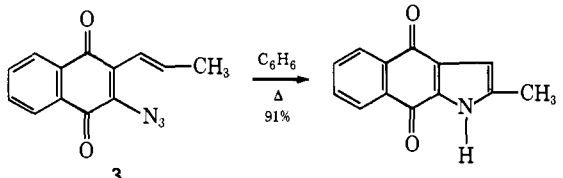
The azidoquinones **1a–o** were prepared from the respective chloro- or bromo-substituted quinones upon reaction with sodium azide in aqueous ethanolic solution as previously described.[3] All of these compounds thermally decompose at or near their melting points (sometimes violently) but are quite stable for prolonged periods of time at room temperature in the dark.

Scheme I



1 2

	R_1	R_2	R_3	Yield, %
a	CH_3	$-C{=}C-C{=}C-$		95
b	OCH_3	$-C{=}C-C{=}C-$		70
c	CH_3	H	CH_3	92
d	$CH(CH_3)_2$	$CH(CH_3)_2$	Cl	31
e	$C(CH_3)_3$	H	$C(CH_3)_3$	95
f	C_6H_5	H	C_6H_5	70
g	CH_3	NH_2	CH_3	89
h	CH_3	NH_2	$CH(CH_3)_2$	89
i	$CH(CH_3)_2$	NH_2	CH_3	92
j	NC_7H_{10}	H	$C(CH_3)_3$	78
k	Br	H	$C(CH_3)_3$	75
l	$C(CH_3)_3$	CH_3	H	80
m	CH_3	C_6H_5	CH_3	82
n	CH_3	p-$CH_3OC_6H_4$	CH_3	87
o	CH_3	p-$NO_2C_6H_4$	CH_3	65



3 4

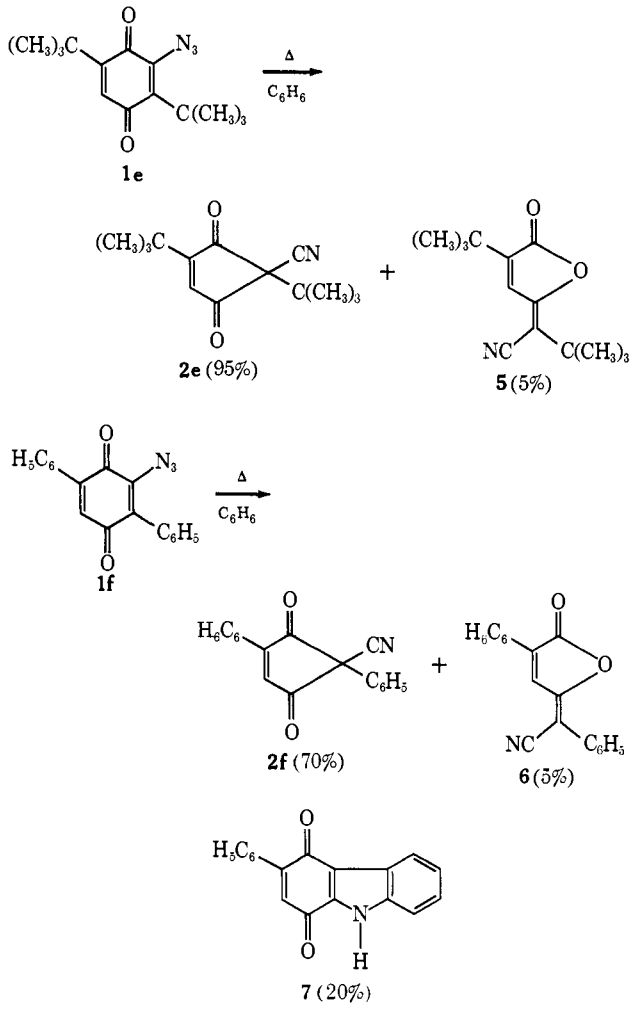
The above azidoquinones, **1a–o**, smoothly rearrange to the ring-contracted 2-cyano-4-cyclopentene-1,3-diones, **2a–o**, when decomposed in either refluxing benzene or toluene. In most cases, the reaction is easily monitored by following the evolution of nitrogen and/or the color change associated with the quinone to the nearly colorless reaction solution of the ring-contracted product.

The decomposition of 2-azido-2,6-di-*tert*-butyl-1,4-benzoquinone (**1e**) and 2-azido-3,6-diphenyl-1,4-benzoquinone (**1f**) in refluxing benzene gave minor detected products in addition to the major respective cyclopentenediones **2e** and **2f**. The former gave a small yield of the known[3] butenolide **5** (5%) and the latter gave the butenolide[3] **6** (5%) and the heterocyclic quinone **7** (20%). Only the corresponding 2-cyano-4-cyclopentene-1,3-diones (**2**) were identified as products from the other azidoquinones listed in Scheme I.

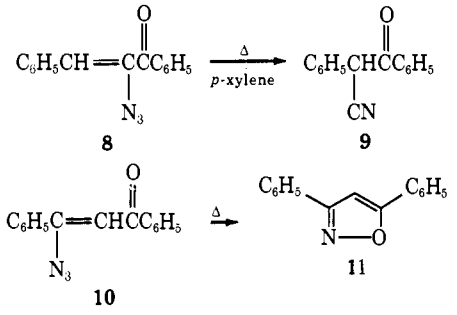
The structures of the 4-cyclopentene-1,3-diones, **2a–o**, are in complete agreement with their spectral data (see Experimental Section). They show characteristic absorptions for nitrile, carbon–carbon double bonds, and cyclopentenedione carbonyl groups in their ir spectra. Their nmr spectra show the expected proton count, coupling constants, and chemical shifts and their mass spectra show molecular ions and fragmentation patterns in accord with their formulation.

Azidoquinones are a structurally unique class of compounds. The reactive azide function could be viewed as either an α-azido- or a β-azido-α,β-unsaturated ketone. Only the latter class of compounds appear to behave analogously to the azidoquinones. Azido ketones such as **8** have recently been shown to undergo a skeletal rearrangement to α-cyano ketones

(7) J. A. Van Allen, W. J. Priest, A. S. Marshall, and G. A. Reynolds, *J. Org. Chem.*, **33**, 1100 (1968).
(8) H. W. Moore and D. S. Pearce, unpublished results.
(9) A preliminary account of this work has been presented: H. W. Moore and W. Weyler, *Tetrahedron Lett.*, 3947 (1969).
(10) A. K. Kiang, H. H. Lee, and K. Y. Sim, *J. Chem. Soc.*, 4338 (1962).
(11) H. H. Lee, *Tetrahedron Lett.*, 4243 (1968).
(12) R. O. Hellyer, *Aust. J. Chem.*, **21**, 2825 (1968).
(13) R. Stevens, *Chem. Rev.*, **67**, 19 (1967).
(14) R. Biggs and R. G. MacFarlane, "Human Blood Coagulation," 3rd ed, Oxford University Press, London, 1962.
(15) L. Crombie and M. Elliot, *Fortsch. Chem. Org. Naturst.*, **19**, 120 (1961).
(16) R. A. LeMahieu, M. Carson, and R. W. Kierstead, *J. Org. Chem.*, **33**, 3660 (1968).
(17) J. R. DiPalma, Ed., "Dill's Pharmacology in Medicine," McGraw-Hill, New York, N. Y., 1971, pp 1428–1431.
(18) H. W. Moore and P. Germeraad, unpublished results. This method, as a general synthetic route to heterocyclic quinones, will be published subsequently.



when heated in refluxing *p*-xylene.[19] On the other hand, the β-azido isomer **10** gives the isoxazole **11** upon

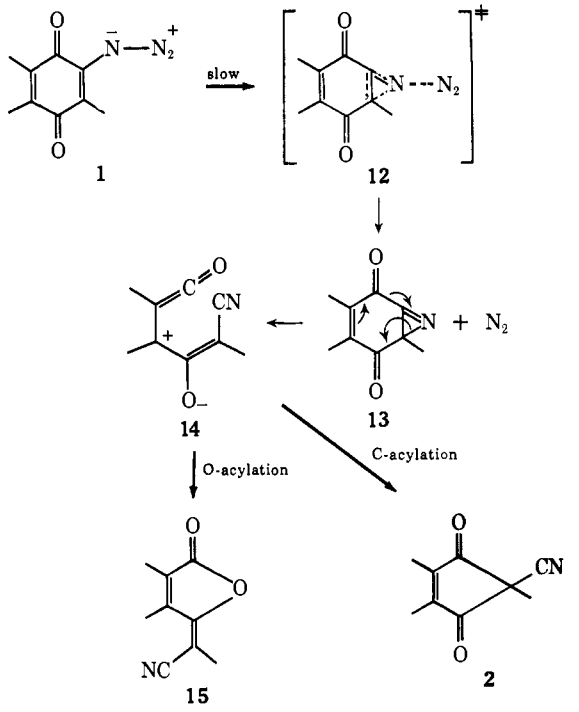


thermal decomposition,[20,21] The former reaction is believed to involve an azirine intermediate,[19] while the latter most probably is a concerted process.[22]

Mechanism

The mechanistic sequence of reactions leading from **1** to **2** is best described as depicted below in Scheme II. Formation of the proposed azirine intermediate, **13**,

Scheme II



may arise *via* a nitrene or a gradual decline to azirine from the transition state represented by structure **12**. This latter possibility is favored, since no direct evidence for nitrenes in these reactions was obtained. This is consistent, in general, with the thermal chemistry of vinyl azides. That is, no spectral evidence has been found for the formation of vinyl nitrenes during the thermal decomposition of vinyl azides;[23] also, attempts to trap such intermediates have met with failure.[24,25] Decomposition of azidoquinones in the presence of reagents known to react with nitrenes has also given no detectable nitrene products. For example, decomposition of **1c** or **1e** in cyclohexane, cyclohexene, isopropyl alcohol, and 2,4-pentadiene gave only the rearrangement products previously described.[26] It is, of course, possible that intramolecular rearrangement of a nitrene intermediate might be faster than bimolecular interactions with traps.

The kinetics of the thermal decomposition of azidoquinones are consistent with their proposed conversion to the azirine **13** (Scheme II). The thermal decomposition of the azidoquinones **1c** and **1e** takes place with conveniently measurable first-order rates in the temperature range of 75–110° (Table I). The activation parameters of thermal decomposition of representative examples of these vinylogous acyl azides compare favorably with those reported for acyl azides obtained at slightly lower temperatures (Table II). The thermal rearrangement of acyl azides to isocyanates (Curtius rearrangement) has been shown to be a concerted reaction and not one involving nitrene intermediates.[27] The $\Delta H^{\pm}$ values for these two classes of compounds are

(19) D. Knittel, H. Hemetsberger, R. Leipert, and H. Weidman, *Tetrahedron Lett.*, 1459 (1970); H. Hemetsberger, D. Knittel, and H. Weidman, *Monatsch. Chem.*, **101**, 157 (1970).

(20) F. S. Fowler, A. Hassner, and L. A. Levy, *J. Amer. Chem. Soc.*, **89**, 2077 (1967).

(21) A better model for comparison would be cyclic β-azido-α,β-unsaturated ketones. However, no example of the thermal chemistry of such compounds has appeared.

(22) B. Singh and E. F. Ullman, *J. Amer. Chem. Soc.*, **89**, 6911 (1967).

(23) G. Smolinsky, E. Wasserman, and W. A. Yager, *J. Amer. Chem. Soc.*, 84, 3220 (1962).

(24) R. E. Banks and G. J. Moore, *J. Chem. Soc. C*, 2304 (1966).

(25) G. Smolinsky and C. A. Pryde, in "The Chemistry of the Azide Group," S. Patai, Ed., Interscience, New York, N. Y., 1971.

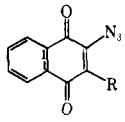
(26) Reagents such as those listed are known to react in a variety of ways with nitrenes; see, for example, W. Lwowski, Ed., "Nitrenes," Interscience, New York, N. Y., 1970, pp 199–214.

(27) A. Fry and J. C. Wright, *Chem. Eng. News.*, **46**, 28 (Jan 1, 1968).

Table I. Rates of Thermolysis of Azidoquinones in Chlorobenzene

Compd	Temp (±0.05°), °C	10^4k, sec^{-1}
1c	109.40	6.85
	109.40	6.78
	105.95	4.65
	105.95	4.77
	99.60	2.86
	88.30	0.77
1e	75.25	2.01
	75.25	2.17
	80.00	3.75
	80.00	3.75
	84.05	5.41
	84.05	5.56
	89.10	9.46
	89.10	9.74

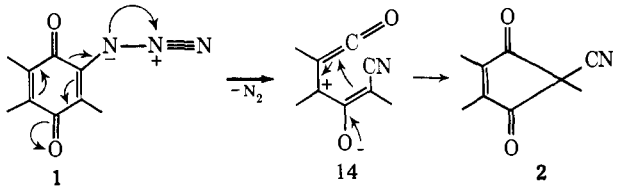
Table II. Activation Parameters for Selected Azidoquinones and Related Azides

Compd	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	Ref
1c	27.6[a]	−3.2	
1e	26.9[a]	−0.3	
	26[b]	−6.9	7
R = H			
R = N_3	27[b]	−4.6	7
$C_6H_5CON_3$	27.1[b]	+4.1	26
$C_{18}H_{37}OCON_3$	29.9[c]	+4.7	26
$C_6H_5SO_2N_3$	36.4[d]		*f*
$C_6H_5N_3$	39.0[e]	+18.7	*g*
$C_6H_{11}N_3$	47.5[e]	+32.2	*g*

[a] Chlorobenzene. [b] Toluene. [c] Diphenyl ether. [d] Naphthalene. [e] Decalin. [f] D. S. Breslow in "Nitrenes," W. Lwowski, Ed., Wiley, New York, N. Y., 1970, p 257. [g] P. Walker and W. A. Waters, *J. Chem. Soc.*, 1632 (1962).

lower than those observed for most reactions where nitrenes have been established as intermediates, *e.g.*, benzenesulfonyl azide, aryl azides, cyclohexyl azide, and azidoformates (Table II).

One can consider a mechanism in which the azidoquinone undergoes a concerted ring opening to the zwitterionic intermediate **14** which collapses to products *via* an electrocyclic ring closure, *i.e.*



1 14 2

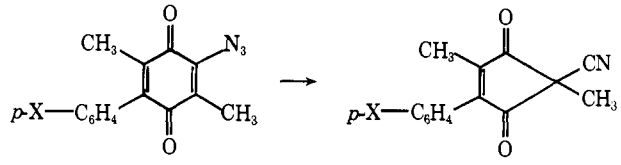
If such a transformation were operative, a solvent and substituent effect upon the rate of the reaction would be anticipated. However, such was not observed. The kinetics of decomposition of **1c** and **1e** in a variety of solvents showed very little change in rate (Table III). Also, the rates of decomposition of the azidoquinones **1c**,**m**,n,**o** are essentially the same (Table IV).

Chemical evidence for the existence of the azirine intermediate **13** comes from an investigation of the thermal decomposition of 2-azido-3,6-di-*tert*-butyl-1,4-benzoquinone (**1e**) in methanol. Here, in addition to

Table III. Rates of Decomposition of Azidoquinones **1c** and **1e** in Various Solvents

Compd	Temp (± 0.05°), °C	Solvent	10^4k, sec^{-1}
1c	105.95	Chlorobenzene	4.65
		o-Dichlorobenzene	4.27
		Benzonitrile	4.24
1e	75.25	Benzene	2.18
		Chlorobenzene	2.01
		o-Dichlorobenzene	1.98
		N,*N*-Dimethylformamide	1.85

Table IV. Substituent Effect upon the Rate of Decomposition of Azidoquinones **1c**,**m**,**n**,**o**[a]



Compd	X	10^4k, sec^{-1}
1m	H	4.32
1n	OCH_3	4.32
1o	NO_2	4.11
1c		4.71

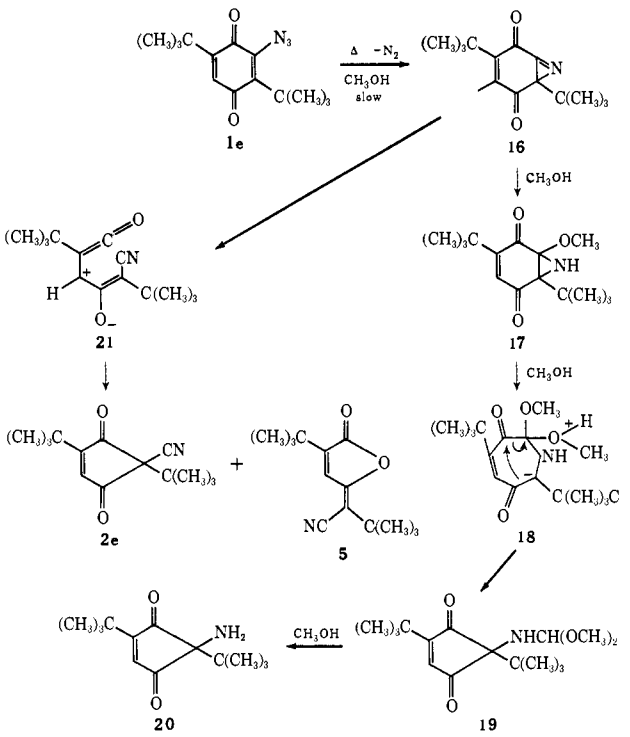
[a] 105.95 ± 0.05°, chlorobenzene.

the 4-cyclopentene-1,3-dione **2e** and the butenolide **5**, 2-amino-2,5-di-*tert*-butyl-4-cyclopentene-1,3-dione (**20**) was formed as a major product. These products were observed by glc analysis to be in a ratio of 1.0:1.9:1.7, respectively. As pointed out earlier, only **2e** and **5** are formed (1.0:0.05) when the decomposition is carried out in a nonnucleophilic solvent such as benzene. The formation of **20** is a significant result and is best explained as arising from a 1-azirine intermediate **16** as depicted in Scheme III. Addition of methanol to the double bond of the azirine would give the aziridine **17**.[28] This aziridine can be envisaged as collapsing to **20** *via* a number of possible routes. Consider, for example, nucleophilic ring opening to **18** followed by rearrangement to the acetal **19** which upon hydrolysis would give the observed product **20**. One would predict from this mechanism that the yield of **20** would decrease as the steric size of the alcohol solvent increased, *i.e.*, steric inhibition of solvent addition to the azirine would be anticipated. Indeed, this was shown to be true. Decomposition of **1e** in ethanol gave **2e**, **5**, and **20** in a ratio of 1.0:0.2:0.28. When 2-propanol was used, only **2e** and **5** were formed in the same ratio as that observed when benzene was employed as the solvent, *i.e.*, 19:1.

It should be noted from the above results that the ratio of **2e** to **5** is also dependent upon the solvent employed. In methanol, the butenolide **5** is the major product (41%), while in benzene or 2-propanol it is formed in only 5% yield. This may be a reflection of solvolytic stabilization of the zwitterionic intermediate by methanol resulting in an increase of O-acylation product, *i.e.*, **5**. Solvolytic stabilization decreases as the steric bulk of the solvent increases, thus favoring

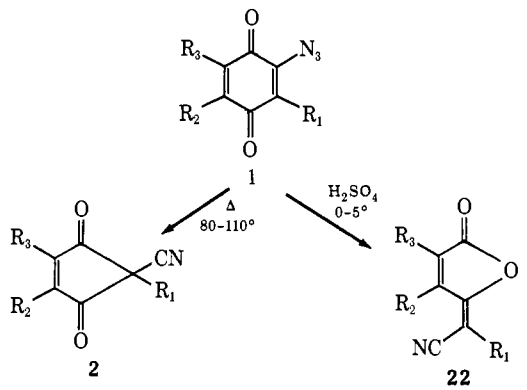
(28) Addition of methanol to 1-azirines giving amino ketals has previously been reported: H. Hassner and F. W. Fowler, *J. Amer. Chem. Soc.*, **90**, 2869 (1968).

Scheme III



electrocyclic ring closure or C-acylation. Such partitioning of an intermediate after the rate-determining step induced by changes in reaction conditions is well documented.[29]

The thermal rearrangements described here, in conjunction with the previously reported[3] complementary acid-catalyzed rearrangements of azidoquinones, **1**, provide general high yield ring contractions of quinone nuclei; the former reaction gives 2-cyano-4-cyclopentene-1,3-diones (2), the latter γ-cyanoalkylidene-$\Delta^{\alpha,\beta}$-butenolides (**22**). These ring contractions allow



the facile synthesis of highly functionalized carbocyclic or hetercyclic five-membered rings which should find importance as synthetic intermediates.

Experimental Section

General Method for Conversion of Azidoquinones to 2-Cyano-4-cyclopentene-1,3-diones. The following general method was employed for the thermal rearrangement of monoazidoquinones to 2-cyano-4-cyclopentene-1,3-diones or 2-cyano-1,3-indandiones. A solution of the azidoquinone in either benzene, toluene, or chlorobenzene was refluxed until nitrogen evolution ceased. In most cases, the color of the initial reaction solution faded as the reaction proceeded. The solvent was then removed *in vacuo* and the resulting residue recrystallized and/or sublimed to give the pure product. The spectral and analytical properties were obtained on the purified products and are given below.

2-Cyano-2-methyl-1,3-indandione (2a). 2-Azido-3-methyl-1,4-naphthoquinone[3] (**1a**) (3.4 g, 16 mmol) was converted by the general procedure to 2.9 g (95% yield) of the indandione **2a** in 75 ml of refluxing chlorobenzene after 30 min. Gas chromatographic analysis of this solid (10 ft × 1/8 in. SE-30, 145°) showed it to be almost entirely one compound. Recrystallization from hexane gave an analytical sample of **2a**, mp 124–127°.

Anal. Calcd for $C_{11}H_7NO_2$: C, 71.35; H, 3.78; N, 7.57. Found: C, 71.31; H, 3.81; N, 7.55.

Spectral data for **2a** follow: ir (Nujol, cm^{-1}) 2270 (CN), 1760, 1726 (C=O), 1590 (C=C); nmr ($CDCl_3$, δ), 1.74 (s, 3), 8.08 (s, 4).

2-Cyano-2-methoxy-1,3-indandione (2b). 2-Azido-3-methoxy-1,4-naphthoquinone[7] (2 g, 8.7 mmol) was converted by the general method to 1.2 g (70%) of the indandione **2b** in 50 ml of chlorobenzene at 120° for 1 hr. Recrystallization from carbon tetrachloride gave the analytical sample, mp 105–106°.

Anal. Calcd for $C_{11}H_7NO_3$: C, 65.66; H, 3.50; N, 6.69. Found: C, 65.44; H, 3.56; N, 6.82.

Spectral data for **2b** follow: ir (Nujol, cm^{-1}) 1755, 1720 (C=O), 1595 (C=C); nmr ($CDCl_3$, δ) 3.82 (s, 3), 8.02 (s, 4).

2-Cyano-2,4-dimethyl-4-cyclopentene-1,3-dione (2c). 2-Azido-3,6-dimethyl-1,4-benzoquinone[3] (1.0 g, 6.7 mmol) was converted by the general method to 0.81 g (92%) of the cyclopentenedione **2c** in 50 ml of refluxing toluene after 75 min. Gas chromatographic analysis (6 ft × 3/8 in. 20% SE-30 on Chrom A, 145°) and nmr analyses showed the crude reaction product to be essentially one compound. Recrystallization of **2c** from carbon tetrachloride followed by sublimation (45°, 0.025 Torr) gave the analytical sample, mp 55–57°.

Anal. Calcd for $C_8H_7NO_2$: C, 64.42; H, 4.73; N, 9.39. Found: C, 64.21; H, 4.71; N, 9.48.

Spectral properties for **2c** follow: ir (Nujol, cm^{-1}) 2245 (CN), 1750, 1710 (C=O), 1620 (C=C); nmr ($CDCl_3$, δ) 1.60 (s, 3), 2.20 (d, 3, J = 1.5 Hz), 7.09 (q, 1, J = 1.5 Hz); uv (95% ethanol, nm) λ_{max} 302 (2.71), 232 (3.97).

2,5-Diisopropyl-4-chloro-2-cyano-4-cyclopentene-1,3-dione (2d). 2-Azido-6-chloro-3,5-diisopropyl-1,4-benzoquinone[30] (**1d**) (2.2 g, 8 mmol) in 45 ml of cyclohexane was refluxed for 19 hr. Removal of the solvent and chromatography of the resulting residue gave 0.6 (31%) of pure cyclopenenedione **2e** as a pale yellow oil.

Anal. Calcd for $C_{12}H_{14}ClNO_2$: C, 60.13; H, 5.89; N, 5.84; Cl, 14.79. Found: C, 60.15; H, 5.84; N, 5.85; Cl, 14.85.

Characteristic spectral properties for **2d** follow: ir (film, cm^{-1}) 2270 (CN), 1760, 1710 (C=O); nmr (CCl_4, δ) 1.10 (doublet of doublets, 6, J = 7 Hz), 1.39 (doublet of doublets, 6, J = 7 Hz), 2.35 (h, 1, J = 7 Hz), 3.14 (h, 1, J = 7 Hz).

2,4-Di-*tert*-butyl-2-cyano-4-cyclopentene-1,3-dione (2e). 2-Azido-3,6-di-*tert*-butyl-1,4-benzoquinone[31] (1.0 g, 3.8 mmol) in 15 ml of dry benzene was refluxed for 3 hr. The solvent was removed *in vacuo* to yield a yellow oil which crystallized upon standing overnight. Analysis of this solid by both vpc (10 ft × 0.25 in. 10% Carbowax 20M on Chrom A at 185°) and nmr showed only two products in a ratio of 95:5. The major product was obtained by recrystallization of the above solid to give 0.69 g of the cyclopentenedione **2e**, mp 90–91°. The minor product was isolated in pure form by preparative vpc and shown to be identical with the known butenolide **5**.[30] Recrystallization again of the cyclopentene-1,3-dione **2e** from hexane gave the analytical sample, mp 92–93°.

Anal. Calcd for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.21; N, 6.00. Found: C, 72.00; H 8.02; N, 6.07.

The characteristic spectral properties of **2e** follow: ir (Nujol, cm^{-1}) 2238 (CN), 1745, 1730, 1695 (C=O), 1595 (C=C); nmr (CCl_4, δ) 1.10 (s, 9), 1.32 (s, 9), 6.91 (s, 1).

Decomposition of 2-Azido-3,6-di-*tert*-butyl-1,4-benzoquinone (1e) in Various Solvents. The above azidoquinone was decomposed in a variety of solvents in order to investigate the influence of the solvent on the ratio of the products **2e**:**5**:**20**.

A. Decomposition of 1e in Methanol. Formation of 2-Amino-2,4-*tert*-butyl-4-cyclopentene-1,3-dione (20). A solution of 2.0 g (7.7 mmol) of **1e** in 70 ml of anhydrous methanol was refluxed for 12

(29) W. P. Jencks, "Catalysis in Chemistry and Enzymology," McGraw-Hill, New York, N. Y., 1969, p 487.

(30) W. G. Duncan, Ph.D. Dissertation, University of California, Irvine, 1972.

(31) H. W. Moore and R. J. Wikholm, *J. Chem. Soc., Chem. Commun.* 1074 (1972).

hr. The pale yellow solution turned a maroon red during the course of the reaction period. The solvent was removed *in vacuo* and the residue was analyzed by nmr. There were three major products detected in a ratio of 1.0:1.9:1.7 which were shown to be respectively the cyclopentenedione **2e**, the buteneolide **5**, and 2-amino-2,4-di-*tert*-butyl-4-cyclopentene-1,3-dione (**20**). This mixture was separated by column chromatography on 200 g of silica gel eluting respectively with 1:4 dichloromethane–pentane (giving **5**), 4:1 dichloromethane–pentene (giving **2e**), and methanol (giving **20**). The aminocyclopenenedione **20** was isolated in 34% yield (0.59 g) by this method. Two recrystallization of this compound from hexane gave the analytical sample, mp 91–92.5°.

Anal. Calcd for $C_{13}H_{21}NO_2$: C, 69.91; H, 9.48; N, 6.27. Found: C, 70.22; H, 9.14; N, 6.28.

Characteristic spectral properties of **20** follow: ir (Nujol, cm^{-1}) 3370, 3300 (NH_2), 3085 (=CH), 1735, 1690 (C=O), 1601 (C=C); nmr (benzene-d_6, δ) 0.88 (s, 9), 1.02 (s, 9), 1.23 (b, 2), 6.45 (s, 1); uv (95% ethanol, nm) λ_{max} 390 (1.57), 335 (4.07).[31]

B. Decomposition of 1e in 95% Ethanol. Decomposition of **1e** as described above except in 95% ethanol as solvent gave **2e, 5,** and **20** in a relative ratio of 5:1:1.4, respectively, as evidenced by nmr and vpc analysis of the crude reaction mixture.

C. Decomposition of 1e in Isopropyl Alcohol. The azidoquinone **1e** was decomposed in refluxing isopropyl alcohol. Analysis of the crude reaction mixture by nmr and vpc (6 ft. × 3/8 in. column, 10% Carbowax 20M on Chrom A 40–60 mesh, 200°) showed only **2e** and **5** in a ratio of 19:1, the same ratio as that observed when benzene was employed as the solvent.

2-Cyano-2,4-diphenyl-4-cyclopentene-1,3-dione (2f). A solution of 3.61 g (12 mmol) of 2-azido-3,6-diphenyl-1,4-benzoquinone[3] (**1f**) in 90 ml of chlorobenzene was maintained at 110° for 40 min. The dark burgundy red solution became lighter in color and the dark crystalline indolequinone **7** precipitated from the reaction solution, 0.7 g (22%), mp 298–300°. Recrystallization of this compound from chloroform gave the analytical sample as a nearly black crystalline solid, mp 299–300°.

Anal. Calcd for $C_{18}H_{11}NO_2$: C, 79.12; H, 4.03; N, 5.13. Found: C, 79.36; H, 4.08; N, 4.98.

Characteristic spectral properties of **7** follow: ir (Nujol, cm^{-1}) 3170 (NH), 1660, 1640 (C=O); nmr (acetone-d_6, δ) 6.75 (s, 1), 7.25–7.42 (m, 9), 7.97–8.08 (m, 1); mass spectrum M^+ 273 (100%).

The mother liquor from above was collected and the solvent removed *in vacuo*. Chromatography of the resulting solid on silica gel using 1:1 chloroform–pentane as the eluent gave 0.16 g (5%) of the known butenolide **6**[3] and 2.5 g (70%) of 2-cyano-2,4-diphenyl-4-cyclopentene-1,3-dione (**2f**), mp 140–142°.

Anal. Calcd for $C_{18}H_{11}NO_2$: C, 79.12; H, 4.03; N, 5.13. Found: C, 79.03; H, 4.10; N, 5.11.

Characteristic spectral properties for **2f** follow: ir (Nujol, cm^{-1}) 2265 (CN), 1720 (C=O), 1600, 1580 (C=C); nmr (acetone-d_6, δ) 7.5–7.7 (m), 8.0–8.5 (m); mass spectrum, M^+ 273 (85%).

4-Amino-2-cyano-2,5-dimethyl-4-cyclopentene-1,3-dione (2g). 2-Amino-5-azido-3,6-dimethyl-1,4-benzoquinone (**1g**) (100 mg, 0.52 mmol) was converted by the general method to 75 mg (89%) of the cyclopentenedione **2g** in 15 ml of refluxing toluene for 15 min. Ir and nmr analysis of the crude product showed it to be essentially pure. Recrystallization from 95% ethanol gave the analytical sample, mp 148–150°.

Anal. Calcd for $C_8H_8N_2O_2$: C, 58.47; H, 4.87; N, 17.07. Found: C, 58.70; H, 4.92; N, 17.15.

Characteristic spectral properties for **2g** follow: ir (Nujol, cm^{-1}) 3350, 3200 (NH_2), 2240 (CN), 1750, 1690 (C=O); nmr ($CDCl_3$, δ) 1.57 (s, 3), 1.92 (s, 3), 2.58 (b, 2); mass spectrum, M^+ 164.

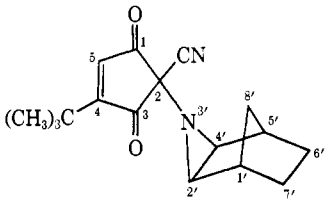
4-Amino-2-cyano-2-methyl-5-isopropyl-4-cyclopentene-1,3-dione (2h). The preparation of the title compound has previously been described.[32]

4-Amino-2-cyano-5-methyl-2-isopropyl-4-cyclopentene-1,3-dione (2i). 5-Amino-2-azido-3-isopropyl-6-methyl-1,4-benzoquinone[32] (2.2 g, 1.0 mmol) in 50 ml of refluxing toluene for 1.5 hr was converted to 1.6 g (92%) of **2i**. Recrystallization from ethanol gave the analytical sample.

Anal. Calcd for $C_{10}H_{12}N_2O_2$: C, 62.50; H, 6.25. Found: C, 62.49; H, 6.31.

Characteristic spectral properties for **2** follow: ir (Nujol, cm^{-1}) 3410, 3310 (NH_2), 2273 (CN), 1750, 1700 (C=O); nmr ($CDCl_3$, δ) 1.03 (d, 3, J = 7 Hz), 1.18 (d, 3), J = 7 Hz), 1.92 (s, 3), 2.37 (m, 1).

2-(3′-Azatricyclo[3.2.1.0$^{2',4'-exo}$]octan-3′-yl)-2-cyano-4-*tert*-butyl-4-cyclopentene-1,3-dione (2j).[33] A solution of the mixture of



2j

azidoquinone isomers **1j** (0.25 g, 0.8 mmol) in 20 ml of chlorobenzene was heated at 110–115° for 1 hr, giving a light amber solution. Removal of the solvent and recrystallization of the crude solid product from hexane gave 0.18 g (78%) of the cyclopentenedione **2j**, mp 83–85°. Characteristic spectral properties for **2j** follow: ir (Nujol, cm^{-1}) 2220 (CN), 1720 (C=O), 1200 (aziridine); nmr ($CDCl_3$, δ) 0.63 (doublet of multiplets, 1, J = 9 Hz, 8′ anti), 1.32 (m, 14), 2.4 (m, 4, 1′, 2′, 3′, 4′), 6.96 (s, 1).

Anal. Calcd for $C_{17}H_{20}N_2O_2$: C, 71.80; H, 7.09; N, 9.85. Found: C, 71.90; H, 7.09; N, 9.84.

2-Bromo-2-cyano-4-*tert*-butyl-4-cyclopentene-1,3-dione (2k). The title compound was prepared in 75% isolated yield as previously described.[34]

2-Cyano-2-methyl-4-*tert*-butyl-4-cyclopentene-1,3-dione (2l). 2-Azido-6-*tert*-butyl-3-methyl-1,4-benzoquinone (**1l**) (0.48 g, 2.16 mmol) was converted to 0.33 g (80%) of **2l**, mp 85–87°, in refluxing chlorobenzene after 1 hr.

Anal. Calcd for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.32. Found: C, 69.13; H, 6.89; N, 7.28.

Characteristic spectral properties for **2l** follow: ir (Nujol, cm^{-1}) 2255 (CN), 1710 (C=O); nmr (chlorobenzene, δ) 1.05 (s, 9), 1.32 (s, 3), 6.57 (s, 1).

2-Cyano-2,4-dimethyl-5-phenyl-4-cyclopentene-1,3-dione (2m). 2-Azido-3,6-dimethyl-5-phenyl-1,4-benzoquinone (**1m**) (0.11 g, 0.43 mmol) was converted by the general method in 10.5 ml of chlorobenzene for 4 hr at 105° to 0.080 g (82%) of the pale yellow crystalline **2m**, mp 140–102°. Recrystallization of the crude reaction product from carbon tetrachloride did not change the melting point.

Anal. Calcd for $C_{14}H_{11}NO_2$: C, 74.65; H, 4.92; N, 6.22. Found: C, 74.44; H, 4.87; N, 6.22.

Characteristic spectral properties for **2m** follow: ir (Nujol, cm^{-1}) 2220 (CN), 1750, 1700 (C=O), 1620 (C=C); nmr ($CDCl_3$, δ) 1.69 (s, 3), 2.27 (s, 3), 7.52 (s, 5).

2-Cyano-2,4-dimethyl-5-*p*-methoxyphenyl-4-cyclopentene-1,3-dione (2n). 2-Azido-3,6-dimethyl-5-*p*-methoxyphenyl-1,4-benzoquinone (**1n**) (0.10 g, 0.35 mmol) in 10.5 ml of chlorobenzene at 105° for 5 hr was converted to 0.080 g (87%) of **2n**, mp 89–90. Recrystallization from carbon tetrachloride had no effect upon the melting point.

Anal. Calcd for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49. Found: C, 70.72; H, 5.10; N, 5.47.

Characteristic spectral properties for **2n** follow: ir (Nujol, cm^{-1}) 2200 (CN), 1720, 1680 (C=O), 1580 (C=C); nmr ($CDCl_3$, δ) 1.66 (s, 3), 2.29 (s, 3), 3.98 (s, 3), 7.00–7.73 (A_2X_2, 4).

2-Cyano-2,4-dimethyl-5-*p*-nitrophenyl-4-cyclopentene-1,3-dione (2o). 2-Azido-3,6-dimethyl-5-*p*-nitrophenyl-1,4-benzoquinone (**1o**) (0.17 g, 0.57 mmol) in 5 ml of chlorobenzene was heated at 125° for 1.5 hr. After the solvent was removed *in vacuo*, the crude product was chromatographed on 20 g of silica gel (eluent, 1:1 dichloromethane–pentane) giving 100 mg (65%) of the cyclopentenedione **2o** as a pale yellow oil. Characteristic spectral properties for **2o** follow: ir (Nujol, cm^{-1}) 2250 (CN), 1750, 1710 (C=O), 1600 (C=C); nmr ($CDCl_3$, δ) 1.72 (s, 3), 2.30 (s, 3), 7.6–8.5 (m, 4).

2-Amino-5-azido-3,6-dimethyl-1,4-benzoquinone (1g). A solution of 10 g (0.0635 mol) of 2,5-diazido-3,6-dimethyl-1,4-benzoquinone[3] in 200 ml of dioxane and 200 ml of ether was cooled to 10°. To this stirred solution was added 22 g (0.126 mol) of $Na_2S_2O_4$ in 100 ml of water. After an initial darkening, the reaction solution lightened to a pale yellow. The organic layer was then washed

(32) H. W. Moore and H. R. Shelden, *J. Org. Chem.*, **33**, 4019 (1968).

(33) The spectral properties are in agreement with structure **2j**. See, for example, R. S. Daniel and A. Oehschlager, *Tetrahedron Lett.*, **25**, 1381 (1961); K. Tori, *et al.*, *ibid.*, 869 (1965); 1109 (1966).

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

three times with water and dried over anhydrous magnesium sulfate giving an etheral solution of the hydroquinone. This solution was refluxed for 72 hr under N_2 in order to accomplish the known[32] disproportionation to the aminoazidoquinone. The solution was then filtered to remove 1 g of a precipitate that was not identified. Removal of the solvent *in vacuo* (<40°) gave 7 g of a dark brown crystalline solid. Infrared and nmr analysis of this solid showed it to be essentially a single compound. Chromatography of 4 g of the above solid on silica gel gave 2.6 g of the pure 5-amino-2-azido-3,6-dimethyl-1,4-benzoquinone. This purple compound rearranges to **2g** when a melting point was attempted. The solid becomes nearly colorless upon heating and finally melts at 147–150° as the cyclopentene-1,3-dione **2g**.

Characteristic spectral properties of **1g** follow: ir (Nujol, cm^{-1}) 3410, 3300 (NH_2), 2110 (N_3), 1655, 1640, 1630, 1600 (C=O); nmr (acetone-d_6, δ) 1.78 (s, 6), 6.13 (b, 2); ($CDCl_3$, δ) 1.83 (s, 3), 1.87 (s, 3).

Anal. Calcd for $C_8H_8N_4O_2$: C, 50.00; H, 4.16; N, 29.16. Found: C, 49.83; H, 4.20; N, 29.32.

Mixture of 3- and 2-Azido-3- and 2-(3′-azatricyclo[3.2.1.0$^{2',4'-exo}$]-octan-3′-yl)-5- and -6-*tert*-butyl-1,4-benzoquinone (1j). A solution of 1.25 g (5.1 mmol) of 2,3-diazido-5-*tert*-butyl-1,4-benzoquinone[34] and 1.50 g (1.6 mmol) of bicyclo[2.2.1]heptane in 50 ml of dichloromethane was stirred at ambient temperature for 12 hr. The solvent was removed from the deep blue solution and the residue chromatographed on 50 g of silica gel. Elution with 1:1 dichloromethane–pentane gave 0.44 g (28%) of a mixture of the isomeric azido-azirideno quinones as a lavender semisolid. Repeated recrystallization from methanol gave a 2.2:1.0 (nmr) mixture of the isomers, mp 104–109°. Spectral properties of this mixture follow: ir (Nujol, cm^{-1}) 2100 (N_3), 1660, 1645 (C=O), 1575 (C=C); nmr ($CDCl_3$, δ) 6.36 and 6.30 (s, 1, two singlets in a relative ratio of 2.2 to 1.0), 2.55 (m, 4), 1.25 (m, 14), 0.81 (d, of m, 1, J = 10 Hz).

Anal. Calcd for $C_{17}H_{20}N_4O_2$: C, 65.36; H, 6.45; N, 17.94. Found: C, 65.37; H, 6.50; N, 17.90.

2-*tert*-Butyl-6-methyl-1,4-benzoquinone. To a solution of 57.1 g (0.213 mol) of Fremy's salt and 12.5 g (90 mmol) of sodium acetate in 2750 ml of water was added a solution of 15.75 g (90 mmol) of 2-*tert*-butyl-6-methylphenol in 150 ml of ethanol, while stirring. After stirring overnight, the reaction mixture was extracted with dichloromethane to give 15.8 g (99% yield) of red liquid. An analytical sample was collected by gas–liquid chromatography.

Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.15; H, 7.86.

Characteristic spectral properties for this benzoquinone follow: ir (film, cm^{-1}) 1655 (C=O); nmr (CCl_4, δ) 1.27 (s, 9), 2.01 (d, 3, J = 1 Hz), 6.48 (m, 1).

2-Chloro-3-methyl-5-*tert*-butyl-1,4-benzoquinone. Chlorine gas was passed through a solution of 15.3 g (85 mmol) of 2-*tert*-butyl-6-methyl-1,4-benzoquinone in 140 ml of acetic acid for 30 min. The solution was allowed to stand for an additional hour and then the excess chlorine was removed by passing nitrogen through the solution. To the solution was added 26 g (0.19 mol) of sodium acetate trihydrate, and the mixture was heated on the steam bath for 1 hr. The reaction mixture was poured into ice–water and extracted with dichloromethane to give 17.5 g (96% yield) of a red liquid. An analytical sample was collected by gas–liquid chromatography.

Anal. Calcd for $C_{11}H_{13}ClO_2$: C, 62.12; H, 6.16; Cl, 16.67. Found: C, 62.14; H, 6.15; Cl, 16.74.

Characteristic spectral properties for this benzoquinone follow: ir (film, cm^{-1}) 1670 (C=O); nmr (CCl_4, δ) 1.27 (s, 9), 2.17 (s, 3), 6.68 (s, 1).

2-Azido-3-methyl-5-*tert*-butyl-1,4-benzoquinone (1l). To a solution of 2.14 g (10 mmol) of 2-chloro-3-methyl-5-*tert*-butyl-1,4-benzoquinone in 40 ml of ethanol was added 0.86 g (11 mmol) of sodium azide in 4 ml of water. After standing 2 days at room temperature in the dark, the red solution was poured into water and extracted with dichloromethane. The azidoquinone was purified by column chromatography, eluting with 10% ether in pentane to give 0.89 g (40%) of the quinone as a yellow oil.

Characteristic spectral properties of **1l** follow: ir (Nujol, cm^{-1}) 2130 (N_3), 1660, 1610 (C=O); nmr (CCl_4, δ) 1.27 (s, 9), 1.90 (s, 3), 6.45 (s, 1).

2-Chloro-3,6-dimethyl-5-phenyl-1,4-benzoquinone. Diacetyl peroxide (3.5 g, 30 mmol) in 55 ml of ether was added over a 10-min period to a stirred solution of 5.0 g (27.5 mmol) of 2-chloro-5-phenyl-1,4-benzoquinone in 100 ml of acetic acid at 90–95°. After 1 hr the mixture was cooled, diluted with water, and extracted with dichloromethane. The organic layer was then washed with water and dried and the solvent removed *in vacuo*. Chromatography of the residue over 400 g of silica gel using 1:3 dichloromethane–pentane gave 2.63 g (47%) of the desired 2-chloro-3,6-dimethyl-1,4-benzoquinone which melted at 55–56° after sublimation. Characteristic spectral properties follow: ir (Nujol, cm^{-1}) 1650, 1610; nmr ($CDCl_3$, δ) 1.88 (s, 3), 2.09 (s, 3), 7.2 (m, 5).

2-Azido-3,6-dimethyl-5-phenyl-1,4-benzoquinone (1m). Sodium azide (0.6 g/3 ml of H_2O) was added to a solution of 0.78 g (3.16 mmol) of 2-chloro-3,6-dimethyl-5-phenyl-1,4-benzoquinone in 75 ml of methanol. After 10 hr at ambient temperature, an additional 1 g of aqueous NaN_3 was added. Fourteen hours later 25 ml of water was added, and the solution was cooled to 0° and filtered to give the crude azide **1m**. Recrystallization of this solid from chloroform–methanol gave 0.43 g (54%) of the azide **1m** as orange rods: mp 89–92; ir (Nujol cm^{-1}) 2100 (N_3), 1640, 1600 (C=O); nmr ($CDCl_3$, δ) 1.93 (s, 3), 1.96 (s, 3), 7.5 (m, 5).

Anal. Calcd for $C_{14}H_{11}N_3O_2$: C, 66.39; H, 4.38; N, 16.59. Found: C, 66.40; H, 4.35; N, 16.61.

2-Chloro-3,6-dimethyl-5-*p*-methoxyphenyl-1,4-benzoquinone. A solution of *p*-methoxybenzenediazonium chloride, prepared from 3.19 g (0.021 mol) of the amine, was slowly added, with stirring, to a cooled (10°) solution of 3.4 g (0.02 mol) of 2,5-dimethyl-1,4-benzoquinone and 7.7 g of sodium acetate trihydrate in 100 ml of water and 200 ml of acetone. The solution slowly turned deep orange, with some gas evolution. After standing at 10° for 2 days, then room temperature for 4 days, the solution was diluted with water and extracted with dichloromethane, the organic layer dried ($MgSO_4$), and solvent removed *in vacuo*. The resulting semisolid material was chromatographed on 150 g of silica gel. Elution with 25% dichloromethane in pentane gave, after recrystallization, 1.0 g of starting material. Further elution (30% dichloromethane in pentane) gave 1.9 g of a red-orange oil which failed to crystallize. The oil was taken up in 25 ml of acetic acid, and the solution was saturated with HCl and stirred for 1.5 hr. The crude chloroquinol was obtained by warming the solution, adding water to turbidity, and then cooling. The quinol was recrystallized (ethanol) and then oxidized with 3 g of $FeCl_3$ in 20 ml of acetic acid and 10 ml of water. The solution was diluted with water and extracted with dichloromethane. The organic layer was backwashed with water and dried ($MgSO_4$) and the solvent removed *in vacuo*. Recrystallization of the resulting red-orange oil (aqueous ethanol) gave 0.8 g (16% based on recovered 2,5-dimethylbenzoquinone) as yellow-orange crystals: mp 84–85°; ir (Nujol, cm^{-1}) 1650 (C=O), 1600 (C=C); nmr ($CDCl_3$, δ) 2.02 (s, 3), 2.20 (s, 3), 3.80 (s, 3), 7.0 (m, 4). Recrystallization from methanol gave the analytical sample, mp 84–85.5°.

Anal. Calcd for $C_{15}H_{13}ClO_3$: C, 65.13; H, 4.74; Cl, 12.82 Found: C, 65.09; H, 4.77; Cl, 12.87.

2-Azido-3,6-dimethyl-5-*p*-methoxyphenyl-1,4-benzoquinone (1n). Sodium azide (0.2 g) in 1 ml of water was added to a solution of 0.657 g (2.38 mmol) of 2-chloro-3,6-dimethyl-5-*p*-methoxyphenyl-1,4-benzoquinone in 40 ml of methanol. After the solution was allowed to stand at 10° overnight, a precipitate formed which was largely starting material. Methanol (60 ml) and 0.5 g of NaN_3 were added, and the solution was allowed to stand at 10° overnight, after which time a considerable amount of precipitate had formed. Addition of 25 ml of water and cooling to 0° gave 0.512 g (74%) of the azidoquinone **1n**, mp 127–133° dec, as beautiful orange needles: ir (Nujol, cm^{-1}) 2100 (N_3), 1700, 1640 (C=O), 1600 (C=C); nmr ($CDCl_3$, δ) 1.92 (s, 3), 1.94 (s, 3), 3.77 (s, 3), 7.0 (m, 4).

Repeated recrystallization from dichloromethane–methanol gave the analytical sample, mp 134–137° dec.

Anal. Calcd for $C_{15}H_{13}N_3O_2$: C, 63.60; H, 4.62; N, 14.83. Found: C, 63.62; H, 4.76; N, 14.71.

2,5-Dimethyl-3-*p*-nitrophenyl-1,4-benzoquinone. To a stirred solution of 3.4 g (0.025 mol) of 2,5-dimethyl-1,4-benzoquinone and 7.7 g of sodium acetate trihydrate in 150 ml of H_2O and 200 ml of acetone, cooled to 10–15°, was added an aqueous solution of *p*-nitrophenyldiazonium chloride, prepared from 3.5 g of *p*-nitroaniline. The solution darkened slightly and some gas was evolved. The solution was stirred overnight and allowed to gradually warm to room temperature. The resultant precipitate was filtered giving 3.8 g of a red brown solid. The mother liquor was diluted with water and extracted with dichloromethane. The extract and the solid material were combined and chromatographed on 150 g of silica gel. Elution with 20–30% dichloromethane in pentane gave 0.6 g of starting material. Elution with 40% dichloromethane in pentane gave, in several fractions, the crude arylquinone. Recrystallization from chloroform–ethanol gave 2.8 g, 53% (based on recovered starting material) as yellow orange plates: mp 156–159°;

ir (Nujol, cm^{-1}) 1650 (C=O), 1590 (C=C); nmr ($CDCl_3$, δ) 1.92 (s, 3), 2.08 (d, 3, J = 1.5 Hz), 6.70 (q, 1, J = 1.5 Hz), 7.3–8.3 (m, 4).

Anal. Calcd for $C_{14}H_{11}NO_4$: C, 65.36; H, 4.31; N, 5.45. Found: C, 65.41; H, 4.73; N, 5.60.

2-Chloro-3,6-dimethyl-5-*p*-nitrophenyl-1,4-benzoquinone. A suspension of 5.0 g (19.4 mmol) of 2,5-dimethyl-3-*p*-nitrophenyl-1,4-benzoquinone in 100 ml of glacial acetic acid was saturated with HCl. The quinone rapidly dissolved, and a yellow precipitate formed. After stirring for 2 hr, the suspension was heated to dissolve the precipitate, and 20 g of $FeCl_3$ in 75 ml of water was added. The solution was heated on a steam bath for 15 min and then water was added to turbidity. Cooling and filtering gave 5.4 g (95%) of the brilliant yellow chloroquinone, mp 137–138.5°. The analytical sample from ethanol melted at 138.5–140°; ir (Nujol, cm^{-1}) 1665 (C=O), 1620 (C=O), 1600 (C=C); nmr ($CDCl_3$, δ) 2.00 (s, 3), 2.22 (s, 3), 7.3–8.3 (m, 4).

Anal. Calcd for $C_{14}H_{10}ClNO_4$; C, 57.64; H, 3.46; N, 4.80; Cl, 12.16. Found: C, 57.77; H, 3.42; N, 4.86; Cl, 12.26.

2-Azido-3,6-dimethyl-5-*p*-nitrophenyl-1,4-benzoquinone (1o). 2-Chloro-3,6-dimethyl-5-*p*-nitrophenyl-1,4-benzoquinone (2.0 g, 6.9 mmol) was dissolved, with heating, in 300 ml of methanol. Sodium azide (2.7 g, 41.5 mmol) in 15 ml of water was added. Dichloromethane (100 ml) was added to dissolve the resultant precipitate, and the solution was allowed to stand at room temperature in the dark for 4 days. The deep orange solution was diluted with water and extracted with dichloromethane. After drying ($MgSO_4$), the solvent was removed *in vacuo* at room temperature. The reddish orange semisolid was recrystallized from chloroform–ethanol to give 1.2 g (59%) of the yellow-orange azidoquinone, mp 122–130° dec. The analytical sample (chloroform–ethanol) melted at 131–133° dec.

Anal. Calcd for $C_{14}H_{10}N_4O_4$: C, 56.38; H, 3.38; N, 18.79. Found: C, 56.31; H, 3.17; N, 19.20.

Characteristic spectral properties of **10** follow: ir (Nujol, cm^{-1}) 2120 (N_3), 1660, 1640 (C=O); nmr ($CDCl_3$, δ) 1.98 (s, 6); 7.30–8.25 (m, 4).

Kinetics. The rates of azidoquinone decompositions described in this manuscript were determined by measuring the rate of nitrogen evolution. The apparatus employed was similar to that described by Martin and Timberlake.[35] The reaction vessel had a 25-ml capacity and was equipped with a magnetic stirrer. The solvent (10 ml) was equilibrated in the constant-temperature bath with the system open to the atmosphere. Then 4.0–4.5 mmol of the sample dissolved in 0.5 ml of the appropriate solvent was injected and nitrogen was passed through the solution for 1.5–2.0 min. The system was then closed and the rate of increase in nitrogen pressure was automatically recorded. The reaction was allowed to go to completion to obtain P_∞. In each case, the system was not disturbed for at least 2 hr after the highest pressure was obtained in order to check for leaks; none were found. The rate constants were then obtained by plotting ln ($P_\infty - P$) against time. Plots were linear for at least 4 half-lives and in most cases for 6 or more. All azidoquinones were of analytical purity and the solvents employed were purified immediately before use.

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Differences between Excited States Produced Chemically and Photochemically. Ion Pairs of Excited States Derived from Luminol

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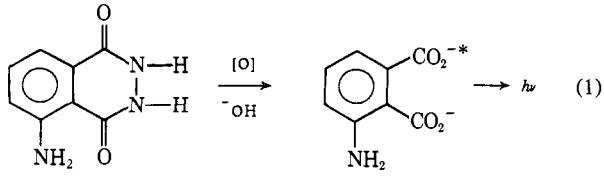
Abstract: Differences in the emission spectra of 3-aminophthalate dianion produced by absorption of light and produced chemically by the oxidation of luminol in basic aqueous dimethyl sulfoxide are attributed to specific interactions of the aminophthalate ions with alkali metal cations (*e.g.*, sodium ion). Appreciable ground-state association is indicated by changes in the absorption spectra with increasing sodium ion concentration. The fluorescence spectrum of 3-aminophthalate in the presence of sodium ion is apparently determined largely by the degree of association in the ground state prior to excitation. In the chemically produced excited aminophthalate ion, the sodium ion distribution is determined largely at the transition state stage of the reaction; a lower fraction of the ion-pair species is apparently formed by this route compared to the fluorescence route.

The chemiluminescence of luminol (I) (5-amino-2,3-dihydro-1,4-phthalazinedione) and its derivatives involves the formation of substituted phthalate ions (II) in the excited singlet state (eq 1). The reaction has



(1)

I II

been studied in both aqueous and aprotic media (*e.g.*, dimethyl sulfoxide), and aminophthalate ion has been identified as the primary product in both cases.[1-4] In either pure medium, the chemiluminescence spectrum is identical with the fluorescence of aminophthalate ion.

In mixtures of water and dimethyl sulfoxide, however, the chemiluminescence of luminol has been reported to differ from the fluorescence of aminophthalate ion in the same solvent mixture, although aminophthalate was

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