

REARRANGEMENTS OF AZIDOQUINONES VI. THERMAL

REARRANGEMENT OF AZIDO-1,4-QUINONES TO 2-CYANO-1,3-CYCLOPENTENEDIONES

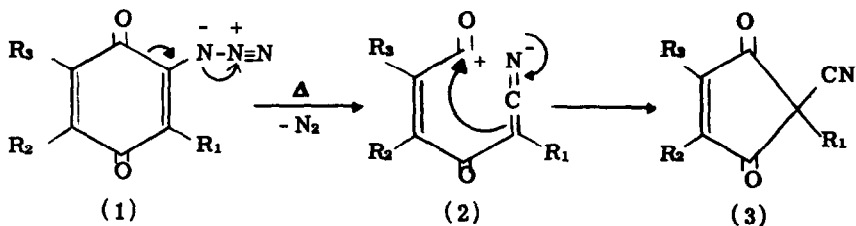
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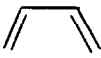
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Previously it was shown that azido-1,4-quinones undergo a highly stereoselective acid catalyzed ring contraction to γ -cyanoalkylidene- $\Delta^{\alpha, \beta}$ -butenolides.¹ Reported in the present communication is an investigation of the thermal decomposition of selected azido-1,4-quinones (1), a reaction also resulting in ring contraction giving the 2-cyano-1,3-cyclopentenedione (3) ring system. This rearrangement provides a new example of a very limited number of known methods in which thermal conversion of a six to a five membered ring can be accomplished.

The general structures (1) and (3) illustrate the overall chemical transformation as indicated by the following possible mechanistic scheme (Scheme I).



	R_1	R_2		R_3	Yield
a	CH ₃				95
b	OCH ₃				70
c	C ₆ H ₅	H		C ₆ H ₅	55
d	CH ₃	NH ₂		CH ₃	96

Scheme I

The azidoquinones (1a-c, 6) were prepared by azide displacement of halide ion from the corresponding halo-substituted quinones while compound (1d) was prepared by reduction of the corresponding diazidoquinone with dithionite as previously described.^{1,2} Decomposition of the azido-1,4-quinones (1a-d) in refluxing anhydrous chlorobenzene for a few minutes resulted in their facile rearrangement to the 2-cyano-1,3-cyclopentenediones (3a-d) in 55-96% yield. Table I lists the spectral data for these cyclopentenediones. They all show characteristic absorptions for nitrile and cyclopentenedione carbonyl groups in their ir spectra. Their nmr spectra show the correct proton count, coupling constants and chemical shifts, and the mass spectra show molecular ions and fragmentation patterns in accord with their formulations.

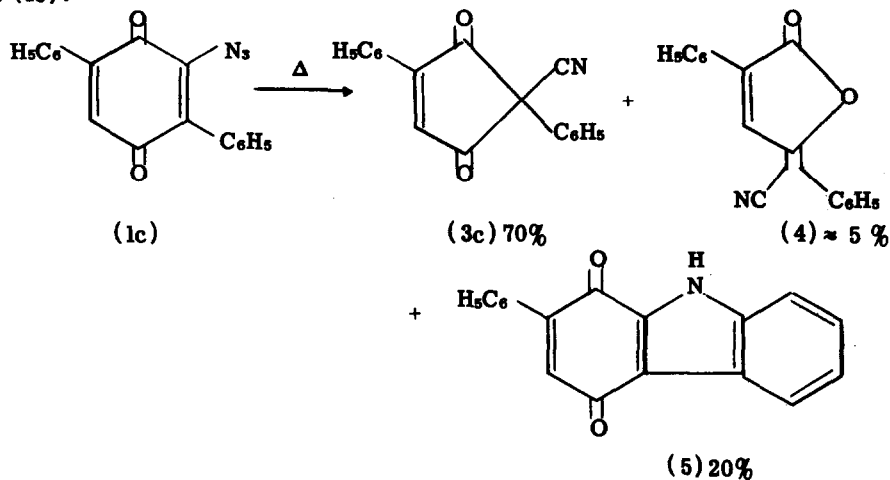
TABLE I¹⁰

Physical and Spectral Properties of 2-Cyano-1,3-Cyclopentenediones.

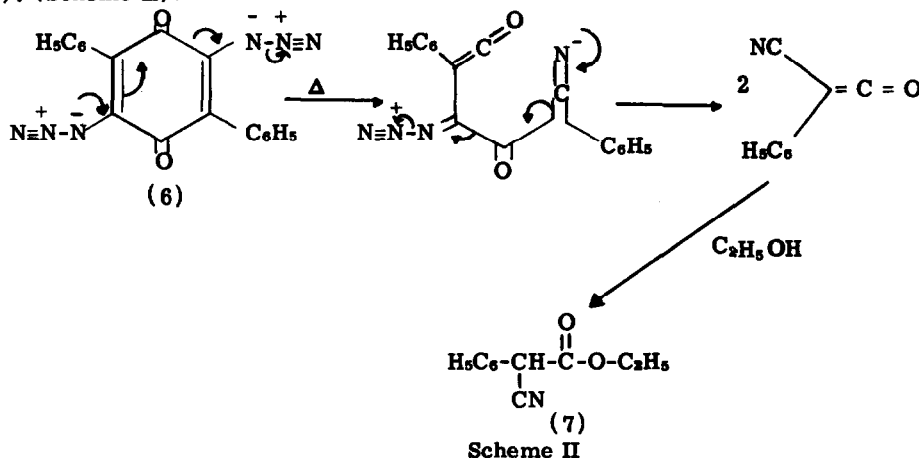
Compound	Mp °C	Ir cm ⁻¹ (nujol)	Nmr, ppm	M. W. (Mass Spec)
3a	124-127	2270, 1760 1725	8.07 s (4) 2.25 s (3)	201
3b	140.5-142	2280, 1765 1740	8.02 s (4) 4.80 s (3)	185
3c	136-138	2240, 1750 1730	7.37-7.62 m.	273
3d	148-150	3350 3200 2240 1750 1690	2.58 b (2) 1.92 s (3) 1.57 s (3)	164

The intermediacy of the zwitterionic intermediate (2) (Scheme I) is only tentatively proposed. One can also envisage this rearrangement as proceeding via a nitrene, an azirine or by a concerted process. The complexity of this mechanistic problem is further illustrated by the isolation and identification of two additional products in the decomposition of (1c). In addition to the major product (3c) the γ -lactone (4)³ and the quinone (5)¹¹ were obtained.

Compounds (3c) and (4) could reasonably come from (2) by respectively C- and O- acylation¹² while (5) appears to result from a nitrene insertion or a concerted decomposition of the azidoquinone (1c).



On the basis of the mechanism presented in Scheme I one would predict that 2,5-diazido-1,4-benzoquinones would thermally cleave to give cyanoketenes. This reaction was observed when 2,5-diazido-3,6-diphenyl-1,4-benzoquinone (6) was decomposed in refluxing tetrahydrofuran: ethanol (5:1); the major product (72%) from this reaction was the known⁴ ethyl ester (7). (Scheme II).



The thermal rearrangements of monoazidoquinones is formally analogous to the pyrolytic ring contraction of phenylazide to cyanocyclopentadiene⁵ and α -azidotropone to *o*-cyanophenol.⁶ The possibility that such ring contractions are involved mechanistically in the observed thermal bond cleavages of certain aromatic and quinoid 1,2-diazides⁷⁻⁹ is under investigation.

ACKNOWLEDGMENT

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REFERENCES

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2. H. W. Moore and H. R. Sheldon, J. Org. Chem., **33** 4019 (1968).
3. The γ -lactone (4), mp 190-191 is the major product from the acid-catalyzed decomposition of (1c). See Reference 1 and a full length paper on the acid-catalyzed decomposition of azidoquinones which will soon appear.
4. R. C. DeSelms, Tetrahedron Letters, No. 15, 1179 (1969).
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8. G. Smolinsky, J. Org. Chem., **27** 3557 (1962).
9. J. H. Hall and E. Patterson, J. Am. Chem. Soc., **87** 1147 (1965); ibid., **89** 5856 (1967).
10. C, H- analysis of all new compounds are in agreement with their formulation.
11. The quinone (5), mp 299-301; showed characteristic absorptions in its ir spectrum at 3170 (NH) and 1660, 1640 (C=O). The mass spectrum of (5) showed a molecular ion peak at *m/e* 273 (100%) in accord with the formulation C₁₈H₁₁NO₂. The nmr-spectrum (acetone-d₆) showed absorptions at δ , 7.25-8.08 m (11) and 6.76 s (1).
12. Compounds (3c) and (4) do not interconvert under the reaction conditions.