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### Title

Pyrolysis of 2-azido-1, 3-indanediones. Azanaphthoquinone synthesis

### Permalink

<https://escholarship.org/uc/item/7dd2w66x>

### Journal

Tetrahedron Letters, 12(20)

### ISSN

0040-4039

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### Publication Date

1971

### DOI

10.1016/s0040-4039(01)87417-7

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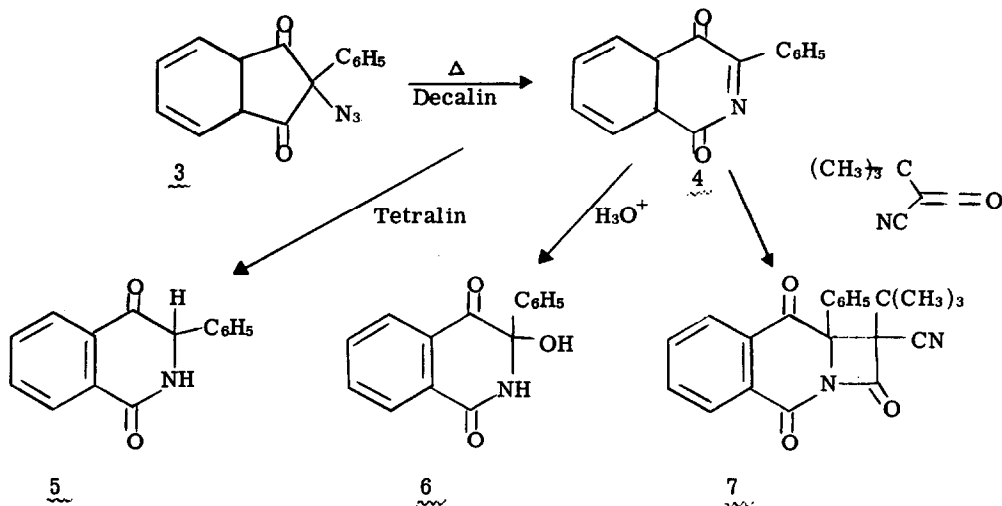
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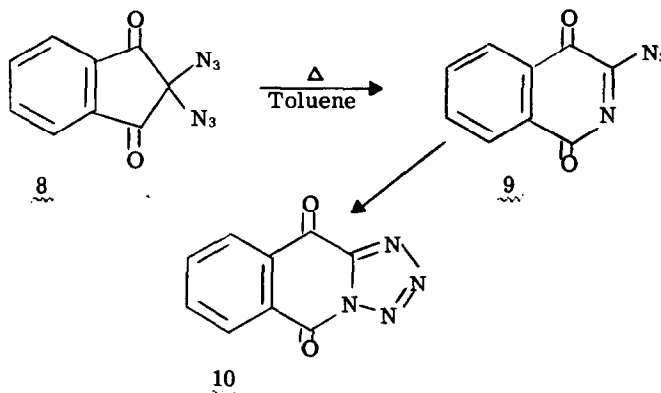


2-Azido-2-phenyl-1,3-indanedione (3) decomposes in refluxing decalin to give 3-phenyl-2-aza-1,4-naphthoquinone (4), a bright red crystalline azaquinone, identical in all respects to the compound recently reported by Felner and Schenker.<sup>7</sup> The azaquinone is rapidly reduced in refluxing tetralin to give the isoquinoline (5), which can be obtained directly by decomposing the azide (3) in tetralin. This latter decomposition results initially in ring expansion to the red azaquinone which then is reduced by reaction with the solvent. Mechanistically this transformation is in contrast to a recent report by Gudriniece and co-workers<sup>10</sup> who claimed the azide (3) decomposed in tetralin by a free radical pathway involving hydrogen atom abstraction to give (5), a mechanism not involving the intermediacy of the azaquinone (4).

The imine double bond in the azaquinone is very reactive towards the addition of protic reagents and to cycloadditions. For example, it reacts with aqueous acid and with *t*-butylcyano-ketene<sup>3</sup> to give, respectively, 1,4-dioxo-3-phenyl-3-hydroxy-1,2,3,4-tetrahydroisoquinoline<sup>6,7</sup> (6) and the  $\beta$ -lactam (7). The  $\beta$ -lactam (7) is a product characteristic of cycloaddition of ketenes to imine double bonds and shows the following characteristic structural properties: mp 212-214; ir (nujol) 2238  $\text{cm}^{-1}$  (CN), 1820, 1721, 1711  $\text{cm}^{-1}$  (C=O); nmr ( $\text{CDCl}_3$ )  $\delta$ , 1.03 s 9 C(CH<sub>3</sub>)<sub>3</sub>, 7.2-8.2 m 9 Ar-H; Anal. found for  $\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}_3$ : C, 73.77; H, 5.17; N, 7.85; uv ( $\text{CHCl}_3$ )  $\lambda_{\text{max}}$  238 nm ( $2.9 \times 10^4$ ), 273 ( $6.9 \times 10^3$ ), 303 ( $2.6 \times 10^3$ ).



Pyrolytic decomposition of 2, 2-diazo-1, 3-indanedione (8) in refluxing toluene gives the tetrazole (10) in 95% yield. A reasonable mechanism for this transformation would involve the intermediacy of 2-azido-3-aza-1, 4-naphthoquinone (9) which is converted to (10) via intramolecular cycloaddition of the azide group to the imine double bond. This mechanistic proposal is consistent with the above described formation of the azaquinone (4) as well as with other observed transformations of geminal diazides to 1, 5-disubstituted tetrazoles.<sup>11</sup> The 1, 5-substitution pattern of the tetrazole (10) is established from its nmr spectrum which shows a multiplet corresponding to four nonequivalent aromatic protons centered at  $\delta$ , 8.3.<sup>12</sup> Other pertinent structural data on the tetrazole follows: mp, 216 with violent decomposition; ir (nujol) 1750, 1680  $\text{cm}^{-1}$  (C=O), 1560  $\text{cm}^{-1}$  (C=N); uv ( $\text{CH}_3\text{CN}$ ) 241 nm ( $2.3 \times 10^4$ ), 323 nm ( $4.3 \times 10^3$ ); wt (mass spec), 200; Anal. Found for  $\text{C}_9\text{H}_4\text{N}_4\text{O}_2$ : C, 53.85; H, 2.11; N, 28.05.



#### ACKNOWLEDGEMENT

The authors are grateful to the National Science Foundation for partial financial support of the project from grant G. P. 8709.

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11. See ref. 9, p. 75.
12. E. Gudriniece and N. R. Bruvele (USSR Patent 229, 529, CA. 70: 57858 k) have recently described the pyrolytic decomposition of 2,2-diazido-1,3-indanedione. However, they claimed the product to be the symmetrical 5-phthaloyl-tetrazole which is not consistent with the observed spectral data.