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PYROLYSIS OF 2-AZIDO-1,3-INDANEDIONES. AZANAPHTHOQUINONE SYNTHESIS

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Azidoquinones (1) have been shown to undergo a variety of interesting transformations.

γ -Cyanoalkylidene- α, β -butenolides,¹ 2-cyano-1,3-cyclopentenediones,² cyanoketenes,³ azapinediones,⁴ and acylcyanides⁵ can be prepared from azidoquinones (1) by employing the appropriate reaction conditions. Based upon these analogies, the unknown azidoazaquinones (2) represent an interesting class of compounds for investigation. However, the very rare nature of azaquinones⁶ and the fact that azidoazaquinones are unknown presents a challenging synthetic problem. Reported here is a new synthetic approach to the azanaphthoquinone, 3-phenyl-2-aza-1,4-naphthoquinone (4),⁷ and the phthaloyl-1,5-1-H-tetrazole (10), a potential precursor to the unknown azidoazanaphthoquinone ring system. These compounds are, respectively, prepared from the thermal decomposition of 2-azido-2-phenyl- (3) and 2,2-diazido-1,3-indanedione (8).

2,2-Diazido- (8) and 2-azido-2-phenyl-1,3-indanedione (3) were prepared as described by Gudriniece, Bruvele and Ievins.⁸ These compounds undergo pyrolytic decomposition in solution resulting in ring expansion. This reaction is not only of synthetic utility as a route to the little known azanaphthoquinones, but it also is of mechanistic significance being an example of acyl migration to nitrogen, a very uncommon process in the pyrolytic decomposition of azides.⁹

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.⁷ 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-workers¹⁰ 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*-butylcyanoketene³ to give, respectively, 1,4-dioxo-3-phenyl-3-hydroxy-1,2,3,4-tetrahydroisoquinoline^{6,7} (6) and the β -lactam (7). The β -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 cm^{-1} (CN), 1820 , 1721 , 1711 cm^{-1} (C=O); nmr (CDCl_3) δ , 1.03 s 9 C(CH₃)₃, 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 (CHCl_3) λ_{max} 238 nm (2.9×10^4), 273 (6.9×10^3), 303 (2.6×10^3).

Pyrolytic decomposition of 2, 2-diazido-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.¹¹ 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 δ , 8.3.¹² Other pertinent structural data on the tetrazole follows: mp, 216 with violent decomposition; ir (nujol) 1750, 1680 cm^{-1} ($\text{C}=\text{O}$), 1560 cm^{-1} ($\text{C}=\text{N}$); uv (CH_3CN) 241 nm (2.3×10^4), 323 nm (4.3×10^3); 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.

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