

1,4(2H,5H)-DIOXOIMIDAZO[1,5,4-h,i]INDAZOLINE:

A NEW HETEROCYCLIC RING SYSTEM

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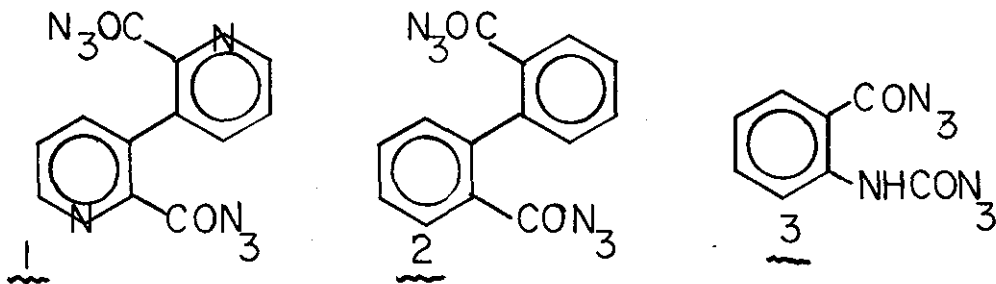
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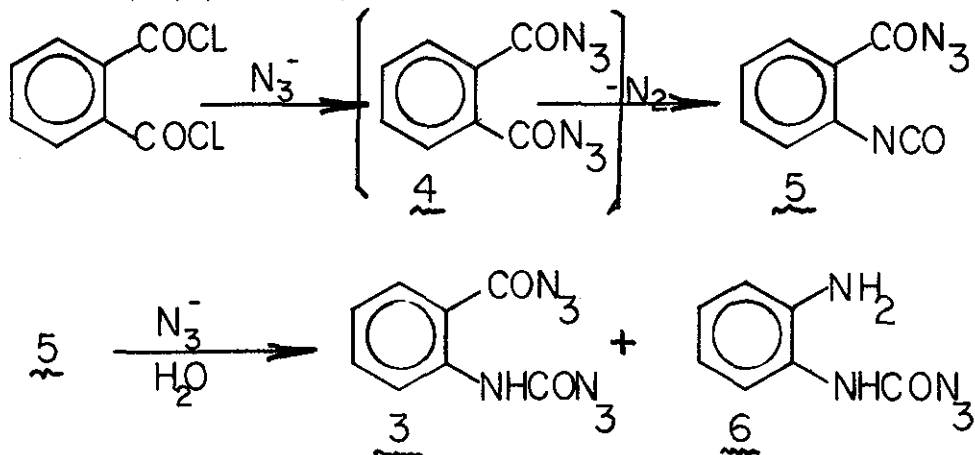
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Thermolysis or photolysis of isatoic acid azide (3) in non-nucleophilic solvents gives rise to a novel rearrangement product which has been described as the 1,4(2H,5H)-dioxoimidazo[1,5,4-h,i]indazoline (8).

For the past several years this laboratory has been interested in the chemistry of various aromatic and heteroaromatic bisacylazides such as (1) and (2). These systems have been synthesized and examined with regard to their unique thermal and photolytic reactivity.^{1,2} The following discussion describes the results of a similar study with isatoic acid diazide (3).³

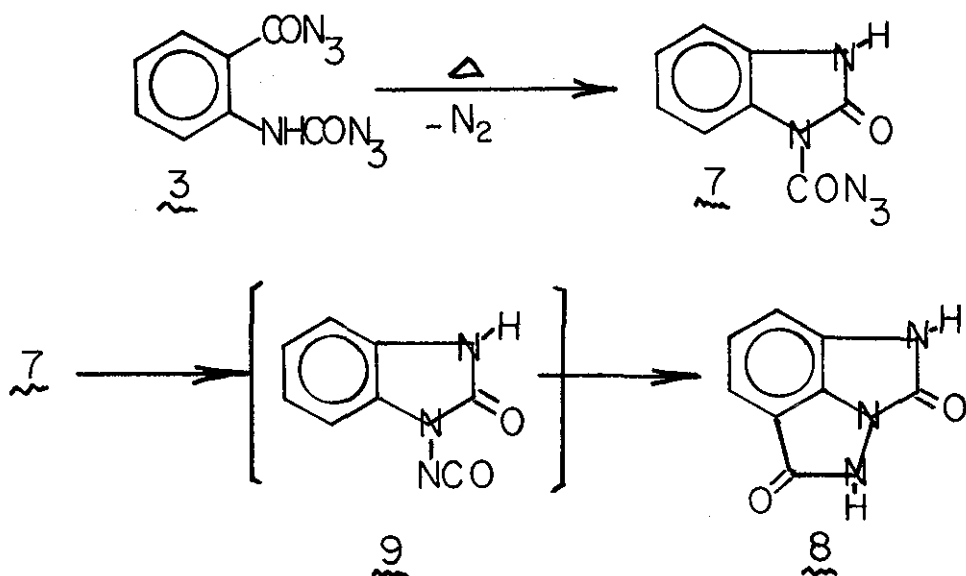


Isatoic acid diazide (3), first reported by Darapsky and Gaudian,⁴ can be prepared from the reaction of phthaloyl chloride with excess sodium azide in acetone/water. Although no intermediates were isolated in the original work, we have reexamined this synthesis and find that one can isolate both the phthaloyl azide (4)^{5,6} and the 2-azidocarbonylphenyl isocyanate (5). The latter compound, m.p. 48°; elemental analysis; calcd. for C₈H₄N₄O₂: C, 51.07, H, 2.4; N, 29.78, found: C, 50.60; H, 2.37; N, 29.44; ir(KBr): 2300, 2150 and 1690 cm⁻¹; ¹H-nmr δ (CD₃COCD₃), 6.8-7.8(4H, m, Ar), could be isolated within minutes from the reaction mixture. Nucleophilic attack by azide ion on (5) gives rise to (3), m.p. 101° (Lit.⁴, m.p. 101°) which has been found to undergo a subsequent degradation in some instances to give a mixture of (3) and the new carbamoyl azide (6), m.p. 144°; ir(KBr) 3500, 3300 and 2150 cm⁻¹; ¹H-nmr δ (CD₃COCD₃), 4.7(2H, s, -NH₂), 7.3(1H, t, Ar, J=4Hz), 7.6-8.2(2H, m, Ar), 8.9(1H, d, Ar, J=4Hz) and 11.3(1H, s, amide NH).

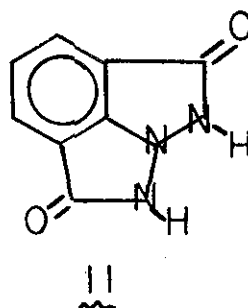
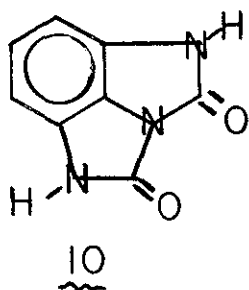


Thermolysis of (3) in various non-nucleophilic solvents such as chloroform, benzene and tetrahydrofuran (THF) gave rise to the 1-acylazido-2(3H)-benzimidazolone (7), (62%), m.p. 160°; elemental analysis; calcd. for $C_8H_5N_5O_2$: C,47.29; H,2.48; N,34.48; found: C,47.50; H,2.97; N,34.04; ir(KBr) 3210,2150,1735 and 1690 cm^{-1} ; 1H -nmr δ (D_6MSO), 7.0(3H,m,Ar), 7.8(1H,m,Ar) and 11.5 (1H, s,amide NH). The structural nature of this product was supported by hydrolysis of (7) to the known 2(3H)-benzimidazolone m.p. 312° (Lit.,^{4,5} m.p. 312°).

In higher boiling solvents such as DMF or chlorobenzene the benzimidazolone (7) was observed to undergo a further rearrangement to give the 1,4-(2H,5H)-dioxoimidazo[1,5,4-h,i]-indazoline (8), m.p. 260°; elemental analysis; calcd. for $C_8H_5N_3O_2$: C,54.86; H,2.88; N,23.99, found: C,54.38; H,2.88; N,23.34; ir(KBr) 3210 and 1740 cm^{-1} ; 1H -nmr δ (D_6MSO), 7.1(3H,s, Ar), 9.8(1H,s,amide NH) and 11.0(1H,s,amide NH). Similarly, photolysis of either (3) or (7) in THF at 2537A° gave rise to (8) in 36% and 78% yield respectively. This product presumably arises via the intermediate N-isocyanato-amine (9)⁷ as a result of the thermal Curtius rearrangement of (7) and the photolytic Curtius rearrangement of (3) and subsequently (7).



A number of similar cyclizations have been observed with a variety of aromatic systems.^{1,2,8,9,10} Alternate mechanisms involving "thermal nitrenes"¹¹ or nitrene species^{12,13} would presumably give rise to symmetrical products such as (10) or (11) which are not consistent with our preliminary spectral data.



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