Rearrangement of 1,2,4-Triazin-3-ones to Imidazolin-2-ones and of Cinnolin-3-one to Oxindole

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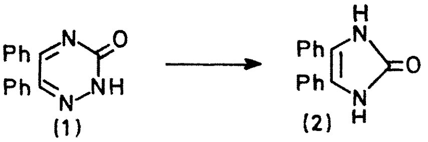
Summary Amination of cinnolin-3-one with hydroxylamine-*O*-sulphonic acid gives 2-aminocinnolin-3-one which undergoes a novel rearrangement to oxindole; similar treatment of 1,2,4-triazin-3-ones gives high yields of the analogous ring-contracted products, imidazolin-2-ones, directly.



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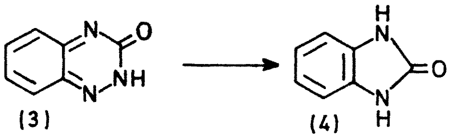

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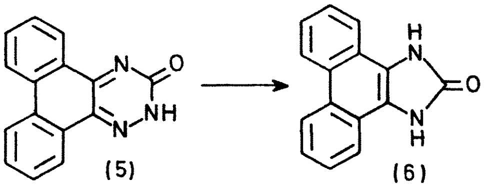

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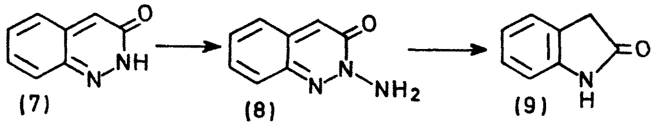

(7) (8) (9)

ATTEMPTED *N*-amination of 5,6-diphenyl-1,2,4-triazin-3(2*H*)-one (**1**) with hydroxylamine-*O*-sulphonic acid in aqueous alkali at about 70° gave 4,5-diphenylimidazolin-2-one (**2**) (68%) in a new ring contraction reaction; similarly, benzo-1,2,4-triazin-3-one (**3**) gave benzimidazolin-2-one (**4**) (87%) and phenanthro[9,10-*e*][1,2,4]triazin-3(2*H*)-one (**5**), in aqueous ethanolic alkali, gave phenanthro[9,10-*d*]-imidazolin-2-one (**6**), m.p. >350°, (74%). *N*-Amino-compounds could not be obtained, even under milder conditions, only starting material or imidazolinone being isolated. Nor could they be obtained by treatment of the sodium salts of triazinones (**1**), (**3**), and (**5**) with *O*-(2,4-dinitrophenyl)-hydroxylamine[1] in methylene chloride or dimethylformamide at room temperature; again the imidazolinones, (**2**), (**4**), and (**6**), were formed in up to 80% yield.

However, the *N*-amino-compounds are presumed to be intermediates in a sequence involving ring contraction and loss of nitrogen, possibly as shown in the Scheme. Such a mechanism does not require the presence of the 4-aza-nitrogen and hence cinnolin-3-one (**7**) was treated with hydroxylamine-*O*-sulphonic acid in aqueous alkali at 60°. The analogous ring-contracted product, oxindole (**9**) (32%), was indeed formed, but now the *N*-amino-compound (**8**), m.p. 130°, could be isolated in low yield (7%); this yield increased, to 22%, at lower temperatures. The 2-amino-structure of (**8**) was proved by its quantitative deamination to (**7**) with nitrous acid and by its formation[2] (with methanolic cupric chloride) of a green copper chelate, m.p. 184—186°, in which the carbonyl absorption had shifted characteristically from 1665 to 1620 cm.$^{-1}$

Under the amination conditions the *N*-amino-compound (**8**) gave oxindole (**9**), lending support to the above mechan-

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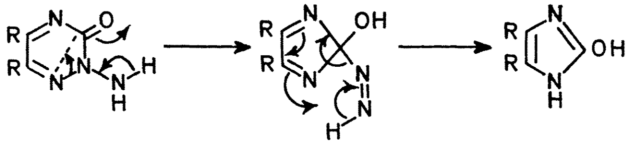
ism. Furthermore, (8) decomposed vigorously at its melting point to give oxindole (64%), and more smoothly in boiling toluene (90%), presumably by a mechanism similar to that for formation of the imidazolinones above. Cinnolin-3-one and 2-methylcinnolin-3-one gave no such ring contraction, even in boiling 1,2,4-trichlorobenzene (210°). A mechanism involving initial Cope-type opening of the heterocyclic ring to a keten is thus less likely.



SCHEME

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[1] T. Sheradsky, *Tetrahedron Letters*, 1968, 1909.

[2] *Cf.* I. E. El-Kholy and F. K. Rafla, *J. Chem. Soc.* (*C*), 1969, 974.