Synthesis of Nitrogen-heterocycles from *N*-Amino-*N,N'*-dihydrodiazinediones. Pyridazino[1,2-*a*][1,2,3]triazines and [1,2,3]Triazino[1,2-*b*]phthalazines

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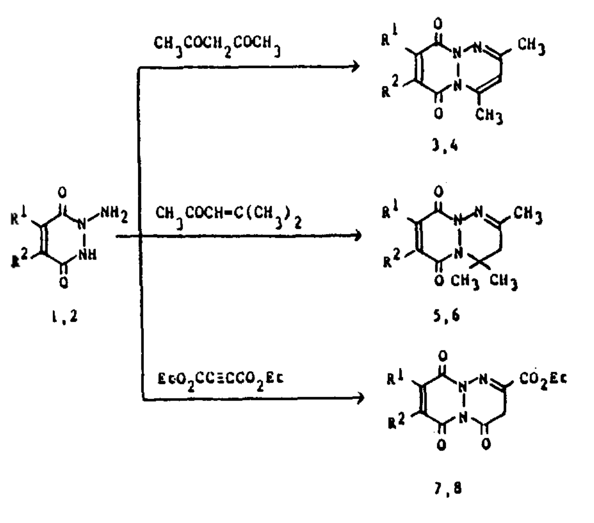
Interest in the 1,2,3-triazines has increased during the last twenty years, largely as a result of the wide range of biological activity associated with many derivatives of 1,2,3-benzotriazin-4(2*H*)-one. There have been known a variety of condensed 1,2,3-triazines.[1] However, only a limited number of condensed 1,2,3-triazines in which two nitrogen atoms are common to two adjacent rings have been reported.[2]

We have previously reported[3] that 1-amino-1,2-dihydro-3,6-pyridazinedione(1) and 2-amino-2,3-dihydro-1,4-phthalazinedione (2) were prepared from 1,2-dihydro-3,6-pyridazinedione and 2, 3-dihydro-1, 4-phthalazinedione, respectively, by *N*-amination using hydroxylamine-*O*-sulfonic acid. It was hoped that the condensation of 1 and 2 with 1,3-dicarbonyl or α,β-unsaturated carbonyl compounds afford the novel heterocyclic ring systems, pyridazino[1,2-*a*][1,2,3]triazines and [1,2,3]triazino[1,2-*b*]phthalazines.

The compound 1 and 2 were reacted with acetylacetone in the presence of polyphosphoric acid at 100°C for 1 hr to yield 6,9-dihydro-2,4-dimethyl-6,9-dioxopyridazino[1,2-*a*][1,2,3] triazine (3) and 6,11-dihydro-2,4-dimethyl-6,11-dioxo[1,2,3] triazino[1,2-*b*]phthalazine (4), respectively, in 80% yield.[4] When 1 and 2 were reacted with mesityl oxide in ethanol in the presence of acetic acid at 50°C for 2 hr, 3,4,6,9-tetrahydro-2,4,4-trimethyl-6,9-dioxopyridazino[1,2-*a*][1,2,3]triazine (5) and 3,4,6,11-tetrahydro-2,4,4-trimethyl-6,11-dioxo[1,2,3] triazino[1,2-*b*]phthalazine (6) were obtained, respectively, in 50% yield.[4] The reaction of 1 and 2 with diethyl acethylenedicarboxylate in the presence of polyphosphoric acid at 100°C for 40 min gave 2-ethoxycarbonyl-3,4,6,9-tetrahydro-4,6,9-trioxopyridazino [1,2-*a*] [1,2,3] triazine (7) and 2-ethoxycarbonyl-3,4,6,11-tetrahydro-4,6,11-trioxo[1,2,3]triazino[1,2-*b*] phthalazine (8), respectively, in 30-50% yield.[4]



1,3,5,7, $R^1 = R^2 = H$

2,4,6,8, $R^1 + R^2 = (CH=CH)_2$

The ir spectra of all products show the disappearance of amino and enolic hydroxy absorption. Their structures are supported by microanalytical and nmr spectral[5] data.

Further details of these syntheses and that of other nitrogen-heterocycles from 1 and 2 will be forthcoming.

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References

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(4) The yields herein are not optimized.

(5) The nmr spectral data for all products are summerized [$CDCl_3$/TMS, δ (ppm)].
3, 2.2 (s, 3H, N=C-CH_3), 2.4 (d, 3H, J=2Hz, N-C-CH_3), 5.6 (d, 1H, J=2Hz, N-C=CH), 7.2 (q, 2H, CH=CH); **4**, 2.2 (s, 3H, N=C-CH_3), 2.5 (d, 3H, J=2Hz, N-C-CH_3), 5.6 (d, 1H, J=2Hz, N-C=CH), 7.7-8.6 (m, 4H, C_6H_4); **5**, 1.8 (s, 6H, 2CH_3), 2.3 (s, 3H, N=C-CH_3), 2.6 (s, 2H, CH_2), 7.0 (q, 2H, CH=CH); **6**, 1.7 (s, 6H, 2CH_3), 2.3 (s, 3H, N=C-CH_3), 2.5 (s, 2H, CH_2), 7.7-8.4 (m, 4H, C_6H_4); **7**, 1.2 (t, 3H, CH_3), 3.9 (s, 2H, $COCH_2$), 4.2 (q, 2H, OCH_2), 7.1 (q, 2H, CH=CH); **8**, 1.2 (t, 3H, CH_3), 3.9 (s, 2H, $COCH_2$), 4.2 (q, 2H, OCH_2), 7.9-8.5 (m, 4H, C_6H_4).