

A SIMPLE METHOD FOR THE SYNTHESIS OF SOME 1,2-DIAZOCINES

Makhluf J. Haddadin*, Bushra J. Agha, and M. Samer Salka
Department of Chemistry, American University of Beirut, Beirut,
Lebanon.

Summary - Cyclobutanone reacts with diphenyl-1,2,4,5-tetrazine, in alcoholic base and in diethylamine, to give 3,8-diphenyl-6,7-dihydro-1,2-diazocin-4(5H)-one (5) and 4-diethylamino-3,8-diphenyl-6,7-dihydro-1,2-diazocine (8) respectively. With diethylamine the tetrazine yields 3,6-diphenylpyridazine.

The reaction of diphenyl-1,2,4,5-tetrazine (1) with some acyclic and cyclic (2) enolate anions has been shown to give pyridazine derivatives 4¹. We find that this reaction takes a different course in the case of cyclobutanone (2, n = 2) in methanolic base, at the reflux temperature. The reaction proceeded smoothly, as evidenced by the evolution of nitrogen and the gradual discharge of the purple color of tetrazine 1, to yield 3,8-diphenyl-6,7-dihydro-1,2-diazocin-4(5H)-one (5) and not the expected pyridazine 4 (n = 2). The structural evidence for 5 (mp 156-158°C, 40%) is based on its spectroscopic properties: a strong i.r. carbonyl band at 1695 cm⁻¹, and a broad detailed multiplet extending from 1-3.1 δ (6H) and two multiplets centered at 7.3 δ (6H) and 7.7 δ (4H) in the pmr. It is known that enamines react with tetrazine 1 to give pyridazine derivatives², so the above reaction was repeated in refluxing diethylamine as solvent. 4-Diethylamino-3,8-diphenyl-6,7-dihydro-1,2-diazocine (8) was isolated (mp 121°C, 50%; ir: strong enamine band at 1620 cm⁻¹; pmr: 1 δ (t, 6H), 2.7 δ (m, 8H), 4.6 δ (m, 1H), 7.4, 7.9 δ (m, 6H, 4H each)). The reaction involved the formation of enamine 6 which in turn reacted with 1. Reaction of 5 with diethylamine, under similar conditions, failed to give 8 and starting material 5 was recovered. The formation of diazocines 5 and 8, through an electrocyclic ring-opening reaction of intermediates 3 (n = 2) and 7 respectively, seems to be preferred to an elimination reaction which would have resulted in angular strain in the expected

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5. Diazocines 5 and 8 gave satisfactory elemental analyses.

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