PHOTOCHEMICAL SYNTHESIS OF 1,2,4-TRIAZINES AND THEIR CHEMICAL BEHAVIORS

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Irradiation of 7-benzyl-2,5-diphenyl-3,4,7-triaza-2,4-norcaradiene (1a) with Pyrex filter in benzene gave 4-benzyl-3,7-diphenyl-1,2,4(4H)-triazepine (2a) as the major product in addition to 4-benzylamino-3,6-diphenylpyridazine (3a), 1-benzyl-2,3-diphenylpyrrole (4a), and 1-benzyl-3-phenylimidazole (5a). Similar irradiation of 7-cyclohexyl-2,5-diphenyl-3,4,7-triaza-2,4-norcaradiene (1b) gave the corresponding products, including 4-cyclohexyl analog (2b), but not 5b.

It was confirmed that 4a arises photochemically from 2a, and that 5a arises thermally from 1a. The formation of 2a involves a novel photochemical walk rearrangement of the aziridine part in 1a followed by norcaradiene-triazepine valence isomerization. Quenching experiments showed that the singlet and the triplet excited states are responsible for the formation of 2a and 3a, respectively.

Thermolysis of 2a gave six products, 4a, 5a, 2,4-diphenylpyrimidine (6a) (major product in aprotic solvents), 3(5)-phenylpyrazole, 2-benzyl-3,7-diphenyl-1,2,4(2H)-triazepine (7a), and N-[α-(3-phenylpyrazolyl)]benzylideneamine (8a) (major product in water-containing solvents). 2b gave similar products but products corresponding to 6a and 7a were not formed. The formation of 6a is interpreted in terms of the thermal [1,3] or [1,5] benzyl shift of 2a followed by elimination of benzyl nitrene. Based on tracer experiments, in which we found the incorporation of deuterium of D_2O into position 4 of 8a, the formation of 8a is suggested to occur via the initial protonation to 2a. The mechanism differs from the previously proposed ones.

In relation to this mechanism, the acid-catalyzed reactions of 2a and 2b were investigated. In the presence of a weak acid such as acetic acid, 2a and 2b were found to give a 1 : 1 solvent adduct, water or methanol adduct, while they were extensively hydrolyzed with concentrated hydrochloric acid to give 3(5)-phenylpyrazole, 1-benzyl-2-phenyl-1,3,4-triazole, N-benzoylbenzylamine, and acetophenone.

The implications of the results in heteropine chemistry are discussed.