Communications to the Editor

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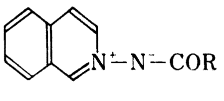
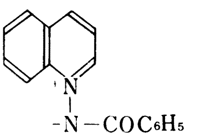
The Photorearrangement and Thermolysis of N-Benzoylimino-isoquinolinium and Quinolinium Betaines

Whereas the photochemical[1] and thermal[2,3] reactions of N-substituted iminopyridinium betaines have recently been explored to a considerable extent, the isoquinoline or quinoline cases have not been described except for the most recent study on the photolysis of N-acyliminoquinolinium betaines.[4] We now wish to report our preliminary results in this field. One of our original motivations for this study was the expectation that this would provide another example of the intramolecular 1,5-cyclization reaction of the ylides.[3]

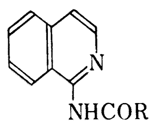
Irradiation of N-benzoyliminoisoquinolinium betaine[5] (Ia) in methanol or methylene chloride with a high-pressure mercury lamp in a Pyrex vessel, gave 1-benzamidoisoquinoline (IIIa), mp 105.5—106.5°, in 65—70% yield. The structure of IIIa was established by direct comparison with an authentic sample prepared by the known procedure.[6] Similar treatment of N-benzoyliminoquinolinium betaine[7] (II) in methanol converted to 2-benzamidoquinoline



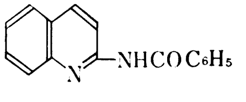
Ia : R $=C_6H_5$
Ib : R $=$ OEt
Ic : R $=$ Me



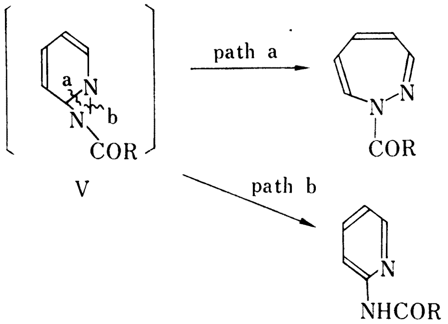
II



IIIa : R $=C_6H_5$
IIIb : R $=$ OEt
IIIc : R $=$ Me



IV



V

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[1] a) J. Streith and J.M. Cassal, *Angew. Chem.*, **80**, 117 (1968); *Tetrahedron Letters*, **1968**, 4541; J. Streith, A. Blind, J.M. Cassal, and O. Sigwalt, *Bull. Soc. Chim. France*, **1969**, 948; b) V. Snieckus, *Chem. Commun.*, **1969**, 831; V. Snieckus and G. Kan, *ibid.*, **1970**, 172; A. Balasubramanian, J. M. McIntosh, and V. Snieckus, *J. Org. Chem.*, **35**, 433 (1970); c) T. Sasaki, K. Kanematsu, and A. Kakehi, *Chem. Commun.*, **1969**, 432; T. Sasaki, K. Kanematsu, A. Kakehi, I. Ichikawa, and K. Hayakawa, *J. Org. Chem.*, **35**, 426 (1970); d) K.T. Potts and R. Dugas, *Chem. Commun.*, **1970**, 732.

[2] M. Ikeda, N. Tsujimoto, and Y. Tamura, *Org. Mass Spectrom.*, **5**, 61 (1971).

[3] Y. Tamura, N. Tsujimoto, and M. Ikeda, *Chem. Commun.*, **1971**, 310.

[4] T. Shiba, Y. Yamane, and H. Kato, *Chem. Commun.*, **1970**, 1952.

[5] a) Y. Tamura and N. Tsujimoto, *Chem. & Ind.*, **1970**, 926; b) Y. Tamura, N. Tsujimoto, and M. Uchimura, *Yakugaku Zasshi*, **91**, 72 (1971).

[6] K. Takatori and M. Ueda, *Yakugaku Zasshi*, **71**, 1373 (1951).

[7] Prepared from N-iminoquinolinium betaine[8] and benzoyl chloride; mp 193—194°.

[8] T. Okamoto, M. Hirobe, and T. Yamasaki, *Chem. Pharm. Bull.* (Tokyo), **14**, 512 (1966).

(IV) in 76% yield,[9] which was identified by direct comparison with an authentic sample.[6] The formation of IIIa and IV can be interpreted in terms of the diaziridine intermediate (V) (through path b), which was also postulated in the photoisomerization of N-acyliminopyridinium betaines to the corresponding diazepine derivatives (through path a). So far only two examples which follow the path b are known[10]; N-carbethoxyimino-3,5-dimethylpyridinium betaine[1b] and N-acetyliminoquinolinium betaine.[4]

In contrast to the photochemical transformation, thermolysis of neat Ia at 190—200° results in fragmentation to isoquinoline (80%), benzanilide (VI) (29%), diphenylurea (VII) (trace) and benzamide (VIII) (trace). Similarly the betaine (II) decomposed at 190—200° to give quinoline (60%), VI (45%), VII (trace) and VIII (trace). These results are again contrasted with the case of N-benzoyliminopyridinium betaine,[2] which, upon heating at 190—200°, gave pyridine (27%) and VII (30%) as the major fragmentation products.

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9) T. Shiba, Y. Yamane, and H. Kato,[4] reported that in the photolysis of II the fragmentation to quinoline and nitrene derivative was the main reaction path and no isomeric product could be isolated.

10) Irradiation of N-carbethoxyiminoisoquinolinium betaine (Ib, mp 129—130°) in ethanol and N-acetyliminoisoquinolinium betaine (Ic, hygroscopic crystals) in methanol gave 1-carbethoxyaminoisoquinoline (IIIb)[11] and 1-acetamidoisoquinoline (IIIc)[12] in 62 and 60% yield, respectively.

11) H. Tanida, *Yakugaku Zasshi*, **79**, 1063 (1959).

12) J.J. Craig and W.E. Cass, *J. Am. Chem. Soc.*, **64**, 783 (1942).

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The Interactions between Bisulfite and Amino Acids. The Formation of Methionine Sulfoxide from Methionine in the Presence of Oxygen

Recent investigation has shown that bisulfite reacts with a variety of nucleic acid bases: (1) By an ionic mechanism bisulfite adds to the 5,6-double bond of pyrimidine nucleosides,[1,2] and (2) by a free radical chain mechanism it reacts with 4-thiouridine[2] and with N^6-Δ^2-isopentenyladenosine.[3] Mutagenic activity of bisulfite has also been demonstrated using phage[4] and bacteria.[5] These findings have implied a possible genetic hazard of environmetal bisulfite to higher living organisms.

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