PHOTOCHEMISTRY OF 1-AMINO-2,4,6-TRIPHENYLPYRIDINIUM PERCHLORATE

V. M. Faigel'man, Ya. R. Tymyanskii,
N. I. Makarova, M. I. Knyazhanskii,
M. P. Zhdanova, and É. A. Zvezdina

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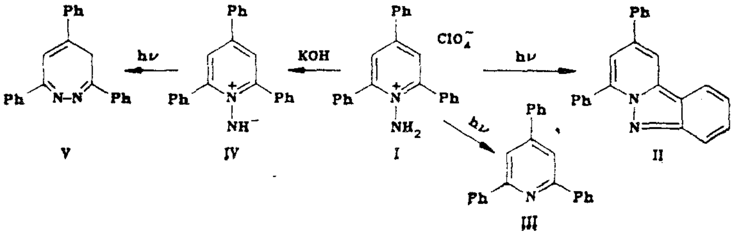
Unlike photochemically stable 1-alkyl-2,4,6-triarylpyridinium salts, under irradiation 1-amino-2,4,6-triphenylpyridinium perchlorate (I) is converted to polycyclic photochemical product II. A side photochemical process is the formation of 2,4,6-triphenylpyridine (III).



We observed an unexpected relation of the relative yields of photochemical products II and III to the concentration of the starting compound I. According to spectrophotometric data, with a concentration change from 0.00002 to 0.002 M, the yield of photochemical product II decreased practically from 100 to 42%, and the yield of triphenylpyridine increased correspondingly to 58%. The quantum efficiency of the photochemical reaction I → II for c = 0.00002 M was 0.03. Unlike starting salt I, base II is soluble in hydrocarbons. The mass spectrum contained an intense peak of a molecular ion with m/z 320, which confirmed the preservation of two nitrogen atoms in the molecule. Unlike that of salt I, the IR spectrum of photochemical product II contained no characteristic absorption bands of the amino group and the perchlorate anion, but a band of the conjugated C=N bond in the five-membered ring appeared at 1650 cm^{-1}. The proton PMR spectrum contained only signals of aromatic protons in the region of 7.23-8.64 ppm. The easily identifiable signal of pyridine protons (8.64 ppm) was a doublet (J = 2 Hz), unlike the singlet signal in symmetrical starting compound I.

When alkali was added to the solution, perchlorate I was converted to betaine IV, stable in solution, but rapidly converted to triphenylpyridine when we attempted to recover it in the crystalline state. Under photoexcitation, betaine IV was converted quantitatively to diazepine V, obtained previously in the usual way [1]. Thus, the route of the photochemical reaction depended significantly on the concentration and the pH of the medium.

Perchlorate I did not fluoresce at 293 or 77 K. The luminescence quenching was apparently due to electron transfer from the amino group to the pyridine ring, i.e., to the formation of an unusual "intramolecular exciplex." This same process was also responsible for the high reactivity of the amino group drawn into the photocyclization process. According to our data, the photochemical reaction I → II is the first example of a photocyclization reaction involving an amino group in charged systems.

1,3-Diphenyl-4a,10-dihydropyrido[1,2-b]-2H-indazole (II). This compound was prepared by irradiating 20 mg of perchlorate I in 500 ml of ethanol in a quartz photochemical reactor with a DRT-230 mercury lamp for 5 min. The yield was practically quantitative, with mp 127°C (with decomposition, from hexane). The elemental-analysis data corresponded to the calculated ones. Ultraviolet spectra (in ethanol): λ_{max}^{abs} 357 nm ($\log \varepsilon$ 4.26); λ_{max}^{fluor} 480 nm (quantum efficiency 0.25).

LITERATURE CITED

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Scientific-Research Institute of Physical and Organic Chemistry, M. A. Suslov Rustov State University, Rostov-on-Don 344,104. Translated from Khimiya Geterotsiklicheskikh Soedinenii, Vol. 24, No. 3, pp. 424-425, March, 1988. Original letter submitted May 12, 1987.