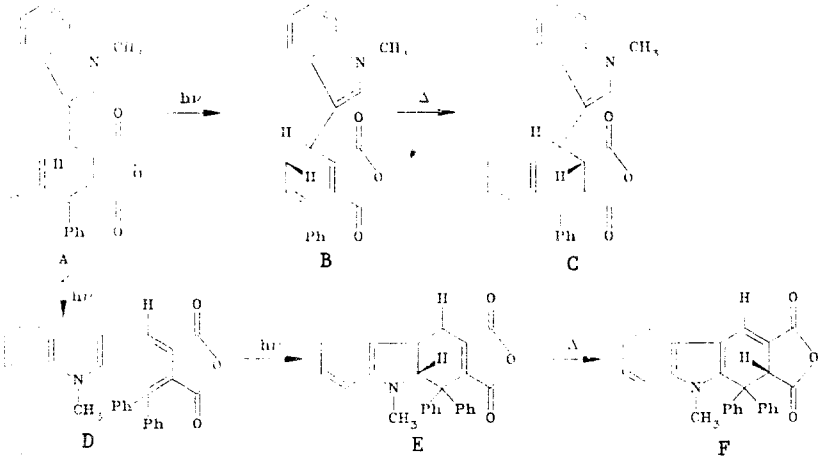
PHOTOCHEMICAL CYCLIZATION OF 1-METHYL-3-INDOLYMETHYLENE (DIPHENYLMETHYLENE) SUCCINIC ANHYDRIDE

A. V. Metelitsa, N. V. Volbushko, O. T. Lyashik, E. A. Medyantseva, A. P. Knyazev, M. I. Knyazhanskii, and V. I. Minkin

UDC 547.759'728'462.7.07:541.14

The previously prepared 1-methyl-3-indolylalkylidene (isopropylidene) succinic anhydride display photochromic properties which are determined by an electrocyclic reaction of the E-isomer form at position 2 of the indolyl fragment [1].

In the (diphenylmethylene) (1-methyl-3-indolylmethylene) succinic anhydride (A) which we have prepared the E-form is sterically hindered and the Z-isomer is formed instead. Nevertheless, on irradiation of solutions and solid phase samples (thin polydisperse films on quartz substrates) of fulgide A in a region of longwave radiation (λ_{max} 460 nm) a photoreaction is observed with the formation of a cyclization product to which, from its electronic absorption spectrum, the structure C is assigned.



The maximum of the absorption band of form C is located in hexane at 290 nm which is characteristic for compounds with a similar structure [2]. The maximum in the absorption band for form F must correspond to a longer wavelength region of the spectrum (λ_{max} 335 nm) [1].

The formation of structure B (C) under photoreaction conditons is in good agreement with the results of mass spectrometry experiments. In the mass spectrum of fulgide A after irradiation a fragment is recorded with m/z 403 (20) which is virtually absent from the spectrum of the unirradiated compound. This ion is formed by splitting of a H_2 molecule from the molecular ion which is possible only with the cyclic form B (C).

2-Diphenylmethylene-3-(1-methyl-3-indolylmethylene)succinic anhydride(fulgide A) was prepared by the method of [1]. Yield 88%, mp 240-242°C (from o-dichlorobenzene). IR spectrum (nujol mull): 1786, 1740 cm^{-1}. PMR spectrum ($CDCl_3$): 9.15 (1H, s, 4-H); 6.69-7.74 (15H, m, Ar); 3.87 ppm (3H, s, N-CH_3).

LITERATURE CITED

1. A. V. Metelitsa, O. T. Lyashik, S. M. Aldoshin, O. A. Kozina, N. V. Volbushko, E. A. Medyantseva, M. I. Knyazhanskii, V. I. Minkin, and A. O. Atovmyan, Khim. Geterotsikl. Soedin (1989) (in the press).

Scientific Research Institute for Physical and Organic Chemistry, M. A. Suslov Rostov State University, Rostov-on-Don 344104. Translated from Khimiya Geterotisiklicheskikh Soedenii, No. 5, pp. 705-706, May, 1989. Original article sumbitted October 5, 1988.

0009-3122/89/2505-0591$12.50

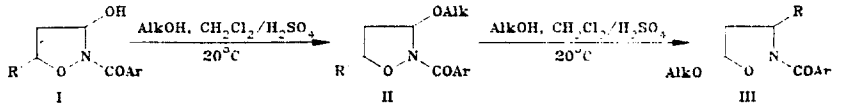
2. H. G. Heller and M. Szewcyk, J. Chem. Soc., Perkin Trans. 1, No. 8, 1498 (1974).

RECYCLIZATION OF ALKOXYISOXAZOLIDINES

I. A. Motorina, L. A. Sviridova, and G. A. Golubeva

UDC 547.786.1:543.422

The hydroxyl group of 2-acyl-3-hydroxyisoxazolidines I, which has semi-animal character, is readily substituted by the action of alcohols in the presence of an acid catalyst [1]. An increase in the reaction time leads to isomerization of the 2-acyl-3-alkoxyisoxazolidines II into the 5-alkoxyderivatives III in quantitative yield, the presence of a methyl group in position 5 of the isoxazolidine ring slowing down the isomerization from 10-30 mins in the case of compound IIa up to several hours for compound IIb.



I II III

I-III a R=H; b R=CH_3

PMR spectra show that only compound IIb with trans-arrangement of the methyl and methoxy groups undergoes recyclization, stereospecifically forming the cis-isomer IIIb.

Isomerization is accelerated in the presence of nucleophiles (water, alcohols) but occurs also in their absence at a slower rate.

Apparently isomerization can also proceed as an intermolecular process one of the stages of which is attack by a nucleophile, a role which can be played by the O atom of the ring, at the semi-aminal $C_{(3)}$ atom with exchange by hydroxamic acid fragments between the two molecules of isoxazolidine.

LITERATURE CITED

1. I. A. Motorina, L. A. Sviridova, G. A. Golubeva, K. N. Zelenin, I. P. Bezhan, A. Yu. Ershov, and Yu. G. Bundel', Khim. Geterotsikl. Soedin., No. 12, 1661 (1988).

M. V. Lomonosov Moscow State University, Moscow 119899. Translated from Khimiya Geterotsoklicheskikh Soedinenii, No. 5, pp. 706-707, May, 1989. Original article received December 21, 1988.

 0009-3122/89/2505-0592$2.50