LETTERS TO THE EDITOR

REACTION OF 3-AMINO-2-PHENYLCARBAMOYL-2H-AZIRINE WITH DIMETHYL ACETYLENEDICARBOXYLATE

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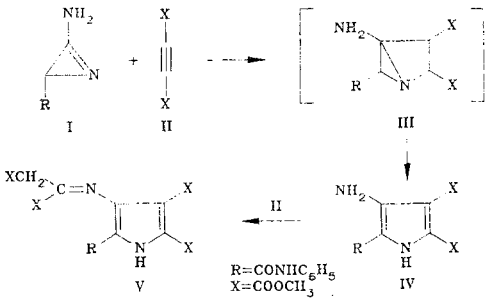
It is known [1] that in reactions with electrophilic reagents (isocyanates, isothiocyanates, carbon disulfide, and carboxylic acid chlorides) 3-amino-2-phenylcarbamoyl-2H-azirine (I) usually undergoes isomerization to a 2-substituted α-amino nitrile, which then reacts with the electrophile to give the final product.

We have established that the reaction of azirine I with dimethyl acetylenedicarboxylate (II) proceeds via a mechanism of the [2 + 2]-cycloaddition type through intermediate bicyclic system III, cleavage of the endocyclic C—N bond in which leads to 3-amino-substituted pyrrole IV; the latter, in turn, adds a second molecule of II at the amino group to give aminopyrrole V:



The reaction of azirine I was carried out with a threefold excess of dimethyl acetylenedicarboxylate in THF at room temperature. Compounds IV and V were isolated by preparative HPLC with a Du Pont 830 Prep LC chromatograph with a UV spectrometer as the detector (λ 254 nm), a Zorbax SIL column (22.7 by 250 mm), and hexane—2-propanol (3:2) as the mobile phase.

3-Amino-4,5-dimethoxycarbonyl-2-phenylcarbamoylpyrrole (IV, $C_{15}H_{15}N_3O_5$). This compound was obtained as a colorless oily liquid. IR spectrum: 1685, 1740 (C=O); 3310 cm^{-1} (NH). PMR spectrum ($CDCl_3$): 3.60 and 3.67 (3H each, s, $COOCH_3$), 6.9-7.6 (5H, m, C_6H_5), 9.86 ppm (1H, broad s, NHCO). The signals of the NH protons are located under the multiplet of the phenyl group. M^+ 317. The yield was 15%.

3-N-(1,2-Dimethoxycarbonylethylidene)amino-4,5-dimethoxycarbonyl-2-phenylcarbamoylpyrrole (V, $C_{21}H_{21}N_3O_9$). This compound was obtained as a light-yellow crystalline substance with mp 70-72°C. IR spectrum: 1610 (C=N); 1672, 1715, 1740 (C=O); 3300 cm^{-1} (NH). PMR spectrum ($CDCl_3$): 3.73; 3.80; 3.82 and 3.87 (3H each, s, $COOCH_3$); 4.53 (1H, s, NH); 7.0-7.6 (5H, m, C_6H_5); 9.8 ppm (1H, broad s, NHCO). M 459. The yield was 56%.

The results of elementary analysis of the compounds obtained were in agreement with the calculated values.

LITERATURE CITED

1. I. P. Piskunova, "Synthesis and properties of 3-amino-2H-azirines," Author's Abstract, Master's Dissertation, Riga (1987), p. 12.

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