

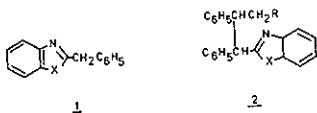
PO 1

MICHAEL ADDITION OF 2-BENZYLBENZAZOLES IN THE PRESENCE OF AQUEOUS SODIUM HYDROXIDE

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The reaction of 2-benzylbenzazoles (1, X = O or S) and α,β -unsaturated compounds, carried out in DMSO in the presence of aqueous sodium hydroxide, resulted in the formation of the corresponding Michael adducts of the type 2 in good to high yields.



X = O or S; R = COC₆H₅, COOH₃, COOC₂H₅, CN, (COOC₂H₅)₂

The reaction is highly stereoselective when benzylideneacetophenone or cinnamnitrite are used as acceptors. With methyl or ethyl cinnamate, ethyl benzylidenemalonate, benzylidene-fluorene, cyclohexene-2-one and 2-benzylidenecyclohexanone the corresponding mixtures of diastereoisomers are obtained. Configurational and conformational assignments are discussed on the basis of ¹H-NMR spectral data.

PO 2

SYNTHESIS OF 3-PHENYLBUTYL SULFONAMIDO-, NITRO-, AND 9-AMINO- DERIVATIVES OF TRYPTAMINE

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PO 3

THE SYNTHESIS AND PHOTOCHEMISTRY OF ETHYL N-(2-METHYL-4-METHYLENE-6,7-METHYLENEDIOXY-3,4-DIHYDRO-3-QUINAZOLINYL)-N-PHENYLCARBAMATE

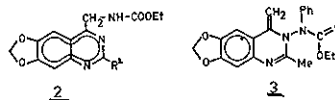
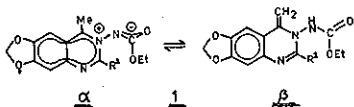
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Irradiation of the potentially tautomeric N-(4-methyl-6,7-methylenedioxy-3-quinazolinio)ethoxyformamidates 1a and 1b has been shown to yield, among other products, the novel photoisomers 2a and 2b, respectively.¹ In order to ascertain whether the possibility of tautomerization of the starting quinazolinio-amidates 1a_x and 1b_x into the isomeric methylene bases 1a_β and 1b_β, respectively, has any bearing on the photoisomerizations 1 → 2, the non-tautomeric N-phenyl derivative 3 of 1b_β was synthesised and subjected to irradiation.



1, 2: a: R²=H; b: R²=Me

The synthesis of 3 and the structures of the photoproducts obtained from 3 will be described, and the mechanism of the photoisomerizations of 3 and of compounds 1a and 1b will be discussed.

REFERENCES

- 1) J. Fetter, K. Lempert, G. Barta-Szalai and J. Möller: Acta Chim. Budapest 94, 233 (1977).

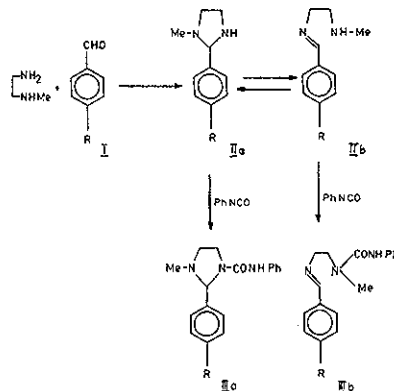
PO 4

RING-CHAIN TAUTOMERISM OF IMIDAZOLIDINE SYSTEMS

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The reaction of aldehydes (I) with N-methylethylenediamine has been studied. The products are shown by H NMR to be the cyclic imidazolidine (IIa) and the corresponding Schiff base (IIb). The composition of the products depends largely on the substituent R (-NO₂ = 100% IIa, -NMe₂ = 50% IIa). Mobil tautomeric equilibrium at a constant temperature has not been observed in solvents with different polarity.



The reaction of the mixture IIa/IIb with aromatic isocyanates (particularly with PhNCO) in different solvents and at different temperature has been investigated.

Examination of the PMR spectra demonstrates the products to be the urea derivatives IIIa and IIIb. The percent composition depends on substituent R, with open-chain compound predominating and was completely different than in the starting material. The ratio of the ingredients IIIa/IIIb depends on the temperature and the solvent in which the reaction was carried out. Interconversion of IIIa and IIIb has not been observed. All these facts can be explained by the greater reactivity toward an isocyanate of the open isomer IIb, and indicate that compounds IIa and IIb are in tautomeric equilibrium.