LITERATURE CITED

1. V. P. Perevalov, M. A. Andreeva, Yu. A. Manaev, Sh. G. Isaev, L. I. Baryshnenkova, and B. I. Stepanov, Zh. Org. Khim., 20, 1073 (1984).
2. M. A. Andreeva, Yu. A. Manaev, R. Ya. Mushii, V. P. Perevalov, and B. I. Stepanov, Zh. Obshch. Khim., 50, 2106 (1980).
3. B. I. Stepanov, Introduction to the Chemistry and Technology of Organic Dyes [in Russian], Moscow (1984), p. 286.
4. A. A. Kiryushkin, I. N. Kovalchuk, Kh. M. Avanesova, and A. Yu. Shibaev, Zh. Org. Khim., 20, 1052 (1984).
5. M. A. Andreeva, M. I. Bolotov, Sh. G. Isaev, R. Ya. Mushii, V. P. Perevalov, V. I. Seraya, and B. I. Stepanov, Zh. Obshch. Khim., 50, 2116 (1980).

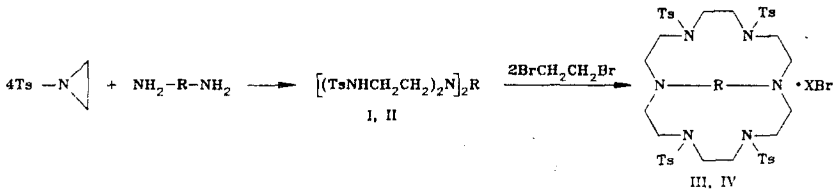
SYNTHESIS OF NITROGEN-CONTAINING CRYPTANDS UNDER INTERPHASE CATALYSIS CONDITIONS

M. G. Voronkov, V. I. Knutov, and
M. K. Butin

UDC 547.717'898.07:541.128

The cryptands, which are macrobicyclic compounds, have a greater selective ability to form complexes with metal ions than the monocyclic crown compounds. However, up to the present time, their synthesis remained multi-stage and complex [1].

We have developed a method for the synthesis of cryptands based on the reaction of tetrakis(tosylamidoethyl)alkylenediamines I and II with 1,2-dibromoethane under the interphase catalysis conditions.



$Ts = CH_3C_6H_4SO_2$; I, III $R = CH_2CH_2$; II, IV $R = -(CH_2)_6-$; III X=K; IV X=H

Diamines I and II were obtained by the reaction of tosylaziridine with ethylene- and hexamethylenediamines at 80°C in DMFA in a yield of 80...85% (the molar ratio of the corresponding reagents was equal to 4:1). The cyclization of diamines I and II with 1,2-dibromoethane was carried out in a chloroform–water two-phase system in the presence of 50% solution of KOH and an equimolar amount of triethylbenzylammonium chloride. The reaction proceeds at 55...60°C for 6 h. Under these conditions, diamine I reacts with 1,2-dibromoethane and forms a complex – 4,7,13,16-tetratosyl-1,4,7,10,13,16-hexaazabicyclo[8,8,2]-cosane potassium bromide (III) [yield 60%, mp 107...108°C. IR spectrum (KBr): 1590 (C_6H_4), 1320, 1130 cm^{-1} (SO_2). PMR spectrum ($CDCl_3$), ε: 2.39 (s, CH_3), 3.28 (m, CH_2N), 7.72 ppm (C_6H_4)] – while diamine II forms 4,7,13,16-tetratosyl-1,4,7,10,13,16-hexaazabicyclo[8.8.6]-tetracosane hydrobromide (IV) [yield 65%, mp 115°C. IR spectrum (KBr): 1590 (C_6H_4), 1310, 1130 cm^{-1} (SO_2). PMR spectrum ($CDCl_3$), δ: 2.39 (s, CH_3), 3.28 (m, CH_2N), 7.74 ppm (m, C_6H_4)].

The data of the elemental analysis of compounds I-IV correspond to the calculated values.

Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Irkutsk 664033. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, p. 1000, July, 1989. Original article submitted July 15, 1988; revision submitted November 15, 1988.

0009-3122/89/2507-0839$12.50

LITERATURE CITED

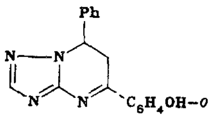
1. B. Dietrich, J. M. Lehn, and J. P. Sanvage, Tetrahedron Lett., 2885 (1969).

TAUTOMERIC FORMS OF 5-(2-HYDROXYPHENYL)-7-PHENYLDIHYDRO-1,2,4-TRIAZOLO[1,5-a]PYRIMIDINE

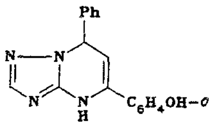
S. M. Desenko and V. D. Orlov

UDC 547.859.1

It was previously found [1] that certain aromatic substituted dihydro-1,2,4-triazolo [1,5-a]pyrimidines can form mixtures of imine and enamine tautomeric forms in solution. By exploiting the considerable influence of solvents on the tautomeric composition of 5-(2-hydroxyphenyl)-7-phenyldihydro-1,2,4-triazolo [1,5,-a]-pyrimidine, we isolated the individual 6,7- and 4,7-dihydro forms of this compound by crystallization. Thus, the crystals of tautomer I, obtained by boiling a solution of 2'-hydroxychalcone and 3-amino-1,2,4-triazole in DMFA, after dissolution in DMSO, and slow evaporation of the solution completely convert into the 4,7-dihydro form II. A reversed transition is attained by the crystallization of the latter form from methanol, ethanol, chloroform, DMFA, or mixtures of DMFA and benzene.



I



II

Tautomers I and II differ substantially in their spectral characteristics in the solid phase and also in the electronic absorption spectra of freshly prepared methanolic solutions. The UV spectrum of a solution of compound II is similar to the spectra of 5,7-diaryl-4,7-dihydro-1,2,4-triazolo[1,5-a]pyrimidines [1], the enamine structure of which has been unequivocally established. The results of their calculation by the MO LCAO SCF QI method in a PPP variant, carried out for the π-electronic fragments of these molecules [$\lambda_{\max}^{\text{calc}}$ (oscillator force): I 301 (0.32), 358 (0.60); II 243 (0.61), 280 (0.11), 290 (0.12)] also conform well with the spectra of the two tautomers. After 20 to 25 min from the dissolution of the crystals of compounds I and II in methanol, the UV spectra of the solutions obtained become completely identical, characterizing an equilibrium mixture of the two tautomers I:II 65:35.

<u>Tautomer I</u>, mp 222...224°C; $\nu_{C=N}$ (in KBr) 1615 cm^{-1}; λ_{max} nm ($\varepsilon \cdot 10^{-3}$): 305 (13.0) 365 (11.5) (in methanol).

<u>Tautomer II</u>, mp 214...216°C; $\nu_{C=C}$ 1665 cm^{-1}; λ_{max} nm ($\varepsilon \cdot 10^{-3}$): 238 (17.5), 282 (5.6).

LITERATURE CITED

1. V. D. Orlov, S. M. Desenko, K. A. Potekhin, and Yu. T. Struchkov. Khim. Geterotsikl. Soedin., No. 2, 224 (1988).

A. M. Gor'kii Khar'kov State University, Khar'kov 310077. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 1000-1001, July, 1989. Original article submitted October 3, 1988.

0009-3122/89/2507-0840$12.50