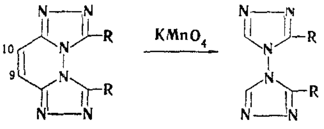
CHARACTER OF THE C_9-C_{10} BOND IN BIS-sym-TRIAZOLO[4,3-b,3',4'-*f*]PYRIDAZINES

I. B. Lundina, L. E. Deev,
E. G. Kovalev, and I. Ya. Postovskii

UDC 547.85.29'792.7

The presence of a phenanthrenoid structure in bis-sym-triazolo[4,3,b,3',4'-*f*]pyridazines (I), which are isomers of the compounds that we synthesized previously in [1], made it possible to expect that the C_9-C_{10} bond in such compounds is localized to a considerable degree and that the reactions peculiar to the C_9-C_{10} bond of phenanthrene may be realized at it.

Quantum-mechanical calculations by the Hückel MO method with the Pullman parameters demonstrated that, depending on the electronic nature of substituents R and R' (CH_2^+ and CH_2^- models), the order of the C_9-C_{10} bond in I is characterized by the values 0.710-0.807 (for phenanthrene, $p_{9,10}$ 0.775 [2]). The experimental data are in agreement with the conclusions drawn on the basis of the calculation. In the oxidation of Ia,b with potassium permanganate in aqueous pyridine, the three-ring system is cleaved even at room temperature to give 4,4'-di-1,2,4-triazolyls (II).



I a,b II a,b

I, II a $R=C_6H_5$; b $R=CH_3$

The structure of IIa,b was confirmed by the results of elementary analysis and the similarity between the UV spectra of IIa,b and the spectrum of model compound II (R = H), which was obtained by the method in [3].

The oxidation of I probably proceeds through a step involving the formation of the corresponding 5,5'-dicarboxylic acids of II, which are readily decarboxylated during the oxidation or during isolation of the products. The ease of decarboxylation, which is known in the 1,2,4-triazole series [4], is explained by the strong electron-acceptor effect of the heteroring.

EXPERIMENTAL

3,3'-Diphenyl-4,4'-di-1,2,4-triazolyl (IIa). A 0.4-g (2.5 mmole) sample of potassium permanganate was added at room temperature with stirring to a solution of 0.5 g (1.6 mmole) of Ia [5] in 30 ml of aqueous pyridine (3 : 1). After 30 min, the manganese dioxide was removed by filtration, and the filtrate was evaporated and acidified with 2 N hydrochloric acid. The precipitated IIa was removed by filtration to give 0.35 g (76%) of a product with mp 209-210° (from isoamyl alcohol). Found,%: C 66.3; H 4.4; N 29.3. $C_{16}H_{12}N_6$. Calculated,%: C 66.6; H 4.9; N 29.2.

3,3'-Dimethyl-4,4'-di-1,2,4-triazolyl (IIb). This compound was obtained in 50% yield and had mp 265-267° (from water). Found,%: C 43.8; H 5.3; N 51.1. $C_6H_8N_6$. Calculated,%: C 43.9; H 4.9; N 51.2.

S. M. Kirov Ural Polytechnic Institute, Sverdlovsk. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, p. 285, February, 1973. Original article submitted July 19, 1972.

LITERATURE CITED

1. L. E. Deev, I. B. Lundina, and I. Ya. Postovskii, Khim. Geterotsikl. Soedin., 1292 (1972).
2. K. Higasi, H. Baba, and A. Rembaum, Quantum Organic Chemistry, Wiley (1965).
3. R. K. Bartlett and J. R. Humphrey, J. Chem. Soc., C., 17, 1664 (1967).
4. T. N. Vereshchagina and V. A. Lopyrev, Khim. Geterotsikl. Soedin., 1965 (1970).
5. A. Pollak and M. Tišler, Tetrahedron, 22, 2073 (1966).