and one-half molar excess of the alkylamine (in the case of isopropylamine we used a five-fold excess of it) was added a few drops of concentrated hydrochloric acid, and the mixture was allowed to stand for a day at room temperature. The organic layer was salted out and dried with solid alkali; then it was distilled.

LITERATURE CITED

1. S. L. Zhdanov and A. A. Potekhin, Khim. Geterotsikl. Soedin., No. 3, 417 (1977).
2. A. A. Potekhin, S. L. Zhdanov, V. A. Gindin, and K. A. Ogloblin, Zh. Org. Khim., 12, 2090 (1976).
3. C. Glacet and D. Veron, Bull. Soc. Chim. Fr., No. 5, 1789 (1965).
4. J. Tesse, C. Glacet, and J. Couturier, C. R., C, 280, 1525 (1975).
5. E. Eliel, N. Allinger, S. Engial, and G. Morrison (eds.,) Conformational Analysis. Wiley (1965).
6. V. G. Dashevskii, Conformations of Organic Molecules [in Russian], Khimiya, Moscow (1974).
7. G. J. Karabatsos and S. S. Lande, Tetrahedron, 21, 3907 (1968).
8. J. Stoddart, Stereochemistry of Carbohydrates, Wiley (1971).
9. J. V. Paukstelis and R. M. Hammaker, Tetrahedron Lett., No. 32, 3557 (1968).
10. Organic Syntheses [Russian translation], Izd. Inos. Lit., Moscow, Vol. 4, 399 (1953).
11. R. Paul and S. Tchelitcheff, Bull. Soc. Chim. Fr., No. 1, 197 (1948).
12. I. S. Trubnikov and Yu. A. Pentin, Zh. Obshch. Khim., 32, 3590 (1962).
13. C. Glacet and J. C. Couturier, Bull. Soc. Chim. Fr., No. 6, 2097 (1962).
14. C. Glacet and F. Blanchard-Bielli, C.R., 247, 1467 (1958).

REACTION OF 2-METHYL-4-TERT-BUTYLOXAZOLE WITH 2-VINYLPYRIDINE

P. B. Terent'ev M. I. Rakhimi, and A. N. Kost

UDC 547.787'82:543.51

We previously established [1, 2] that the reaction of 2-vinylpyridine hydrochloride (I) with 2,4-disubstituted oxazoles proceeds by G. Ya. Kondrat'eva's reaction scheme [3, 4] forming 4-pyridyl-3-hydroxypyridines. This reaction course was characteristic for oxazoles containing both a methyl and phenyl group in position 4.

In order to clarify the effect of the bulk of the substituent in position 4 of the oxazoles on the direction and nature of the cycloaddition reaction, we introduced 2-methyl-4-tert-butyloxazole (II) into the reaction. After boiling the components in n-butanol for 20 h, neutralizing with sodium bicarbonate, extracting the reaction products, then vacuum distilling them, 2-(2-butoxyethyl)-pyridine (III) was isolated. Besides the intense molecular ion, the ions $(M - C_3H_7)^+$ (m/e 136) and $(M - C_4H_9O)^+$ (m/e 106) are observed in its mass spectrum. In addition to the characteristic signals of the four protons in the pyridine ring in the strong field there are three triplets of the methylene protons ($R-CH_2-CH_2-O-CH_2-$) and a multiplet of seven aliphatic protons in the PMR spectrum. It is known [5] that the pyridylethylation of alcohols proceeds easily in the presence of basic catalysts. The case we found is the first example of the pyridylethylation of alcohols in an acid medium.

Using preparative chromatography we succeeded in isolating another two compounds from the reaction mixture in pure form. One of them, 3-hydroxy-4-(2-pyridyl)-6-methyl-2-tert-butylpyridine (VI), is the normal reaction product from the cycloaddition of oxazoles II to vinylpyridine I. A singlet of the nine protons in the tert-butyl group is observed in its

M. V. Lomonosov Moscow State University, Moscow 117234. Kabul Polytechnic Institute (Afghanistan).

Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1323-1326, October, 1979. Original article submitted December 5, 1978.

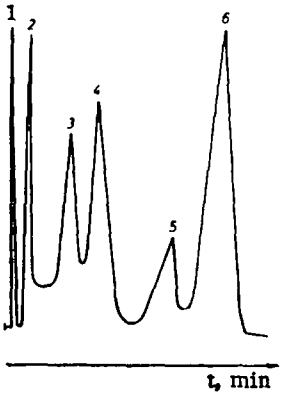


Fig. 1. Chromatographic mass spectrometric investigation of the reaction mixture: 1) 2-vinylpyridine; 2) compound III; 3) compound V; 4) compound VII; 5) compound VI; and 6) compound IV.

PMR spectrum along with a singlet of the three protons in the methyl group, a singlet of the single proton in position 5 of the hydroxypyridine ring, and signals of the four protons in the 2-pyridine moiety with characteristic spin–spin splitting. The mass spectral decomposition of its molecular ion is characterized by the successive loss from the molecular ion of a CH_3 group (m/e 227) and C_2H_4 group (m/e 199), which is characteristic for tert-butylarenes [6] and tert-butylhetarenes [7], and also by the elimination of the CO and CHO (m/e 171 and 170) from the latter ion. Such a course is typical for the fragmentation processes of 3-hydroxypyridines [6, 8].

The second compound isolated is 3-butoxy-4-(2-pyridyl)-2-tert-butyl-6-methylpyridine (IV). Its PMR spectrum in the weak field is close to the PMR spectrum of compound VI, and in the strong field a multiplet of the seven aliphatic protons in the butoxyl group (δ 1.0-1.4) and a triplet of the protons in the CH_2–O group are observed in the 4.0 ppm region in addition to the singlet signals of the tert-butyl and methyl groups. In addition to the successive elimination of the CH_3 and C_2H_4 groups the mass spectral decomposition is also characterized by the $(M - CH_3 - C_4H_8)^+$ and $(M - CH_3 - C_2H_4 - C_4H_9)^+$ ions. The loss of an olefin molecule is characteristic for the fragmentation of alkoxyarenes [6]. When hydroxydipyridyl (VI) is butylated according to Williamson, an ether is formed whose spectral properties are identical to the properties of compound IV.

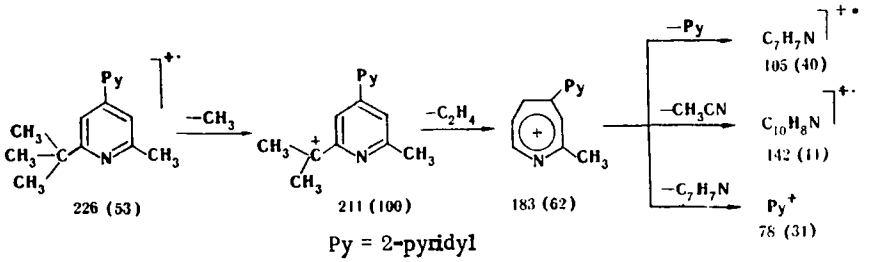
Having assumed that other reaction products are possible, we carried out a chromatographic mass spectral investigation of the reaction mixture obtained during the reaction of oxazole II with vinylpyridine I, and established the presence of six compounds in it (Fig. 1). Peak 1 corresponds to 2-vinylpyridine from the retention time, molecular mass, and nature of its fragmentation.

The compounds corresponding to peaks 2, 5, and 6 correspond respectively to compounds III, VI, and IV from their retention times, molecular masses, and nature of their decomposition. The compound corresponding to peak 3 has a molecular mass of 226, which corresponds to 4-(2-pyridyl)-2-tert-butyl-6-methylpyridine (V). The nature of its mass spectral decomposition (see scheme 1) confirms this proposal.

The molecular mass of compound VII (peak 4) is 2 a.m.u. greater than for compound VI. The molecular ion of compound VII is poorly stable (see scheme 2), and the processes involving losses of the CH_3 and C_2H_4 groups by them do not have a dominating effect. The peak of the ion with m/e 160 is the maximum one in the mass spectrum. The peaks of the $M^+ - 17$ (OH) or $M^+ - 18$ ions (H_2O) are absent; this does not allow us to ascribe the structure 3-hydroxy-4-(2-pyridyl)-2-tert-butyl-2-methyl-3,4-dihydropyridine (VIII) to this compound. On the other hand the ease by which 84 a.m.u. is eliminated agrees well with the structure of the initial adduct, i.e., compound VII. Unfortunately all attempts to isolate it from the reaction mixture using preparative chromatography proved fruitless.

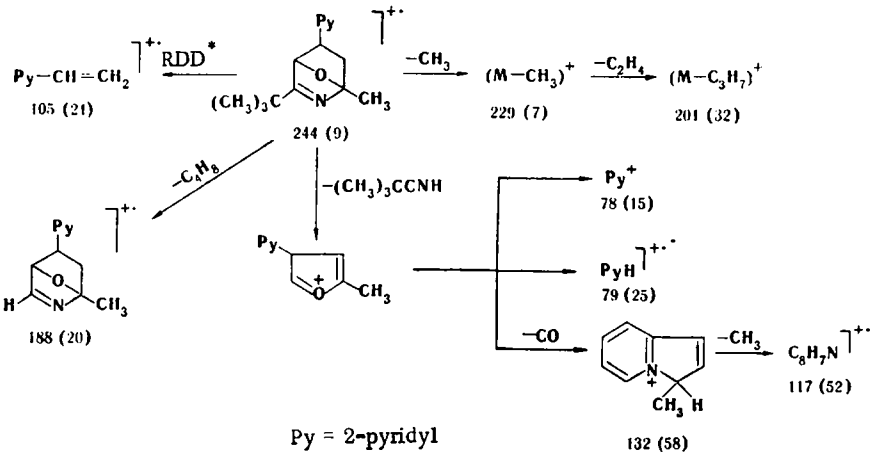
The compounds identified in the reaction mixture permit one to propose a general scheme for the reaction between 2-vinylpyridine and 2-methyl-4-tert-butyloxazole (scheme

Scheme 1



Py = 2-pyridyl

Scheme 2

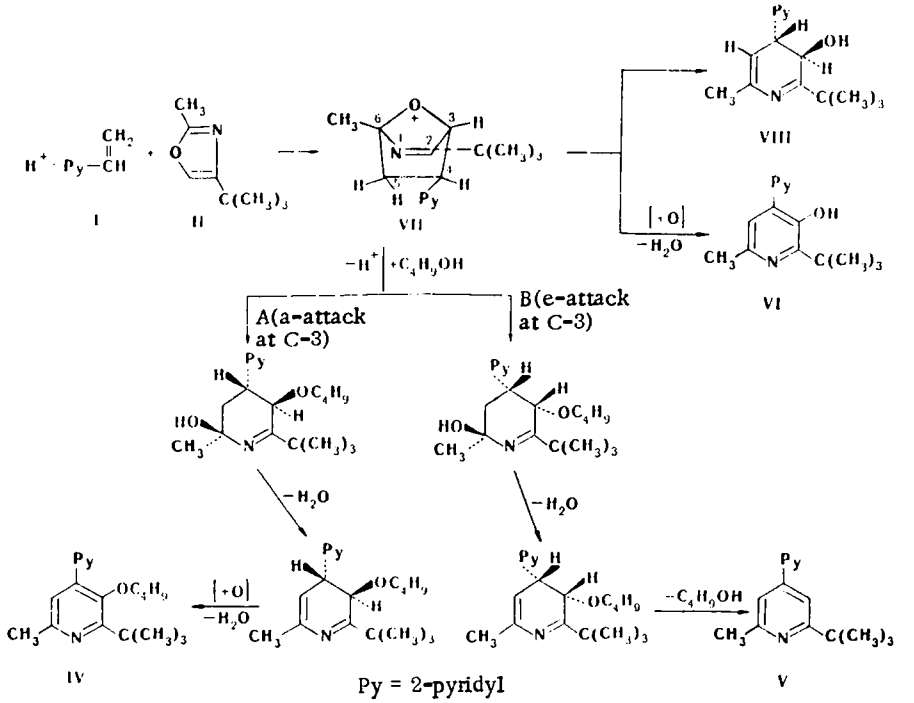


Py = 2-pyridyl

*RDD is retro-diene decomposition.

3). The adduct initially formed (compound VII) on the one hand undergoes acid splitting leading to the formation of the 3-hydroxy derivative VI. On the other hand, nucleophilic attack of the adduct by the solvent in position 3 is more probable. During the axial attack (route A) the ring scission leads to the formation of compound IV, and during the equatorial attack compound V is formed.

Scheme 3



Py = 2-pyridyl

Thus the reaction of 2-vinylpyridine with an oxazole containing a bulky substituent in position 4 leads to an adduct whose further conversion can proceed in part with the participation of the solvent molecules; this makes it possible to refine the previously [9] proposed decomposion scheme of the initial adduct of the Kondrat'eva reaction.

EXPERIMENTAL

The chromatographic mass spectra were obtained on a Varian MAT-111 instrument on a 1.5 m column containing 5% OV-1 on Polysorb, using an oven temperature of 230°C. The mass spectra were run at an ionization energy of 80 eV. The PMR spectra were obtained on a Varian T-60 and XL-100 instrument; the external standard was HMDS. The preparative separation was accomplished on (18 × 24) Al_2O_3 (III degree of activity) plates, 1 mm thick, benzene–methanol, 9:1. The UV spectrum was run on a Cary-15 instrument in methanol.

The synthesis of oxazole II was accomplished by a known method [10] and its purity (>99%) was checked chromatographic mass spectrometrically.

Reaction of 2-Vinylpyridine with 2-Methyl-4-tert-butyloxazole. Forty grams (0.28 mole) of 2-vinylpyridine hydrochloride and 13.0 g (0.09 mole) of 2-methyl-4-tert-butyloxazole was boiled in 150 ml of n-butanol for 20 h. The mixture was evaporated to dryness in a vacuum created by a waterjet pump, neutralized with a 20% sodium bicarbonate solution, and extracted with ether. The extract was concentrated to 50 ml and subjected to a chromatographic mass spectral investigation (there was 14.0 g of the substance in the extract). After vacuum distilling 7.0 g of the extract 1.2 g of 2-(2-butoxyethyl)pyridine (III) was obtained, b.p. 130-134°C (8 mm), n_D^{20} 1.4718. PMR spectrum (CCl_4) (here and subsequently δ, the number of H, the multiplicity, J, Hz are given): 0.9-1.5; 7H, m, — ; 2.90, 2H, t, 7; 3.27, 2H, t, 7; 3.53, 2H, t, 7; 6.9-7.1, 2H, m, — ; 7.40, 1H, sextet, $J_{3,4} = J_{4,5} = 8.0$, $J_{4,6} = 1.5$; 8.40, 1H, quad., $J_{6,5} = 5$, $J_{6,4} = 1.5$. Mass spectrum [here and subsequently the m/e (relative intensity, %) are given]: M 179 (3.0), 162 (5.1), 136 (5.8), 122 (34.5), 107 (61.0), 106 (97.6), 105 (15.1), 104 (1.6), 94 (43.6), 93 (100), 92 (5.3), 87 (10.1), 80 (6.7), 79 (30.2), 78 (57.0), 66 (20.7), 65 (14.0), 57 (38.1), 56 (3.0), 52 (12.7), 51 (13.5), $C_{11}H_{17}NO$. Calculated: M 179. Found: C 73.5; H 9.4%. $C_{11}H_{17}NO$. Calculated: C 73.7; H 9.56%.

After separating 0.5 g of the extract on a thin layer of aluminum oxide 100 mg of oily compound IV was isolated from the band with R_f 0.7-0.8. Mass spectrum: M 298 (44.4), 297 (33.3), 283 (100), 270 (36.0), 269 (36.0), 255 (97.0), 242 (70.8), 241 (22.7), 228 (19.4), 227 (77.7), 226 (16.0), 225 (22.5), 214 (14.3), 213 (60.0), 211 (28.0), 201 (14.0), 200 (91.6), 199 (30.5), 185 (28.1), 184 (40.2), 183 (11.8), 163 (25.0), 159 (12.1), 122 (36.5), 106 (75.1), 92 (48.6), 79 (75.1), 78 (88.6), 65 (10.8), 57 (42.3), 56 (14.8), 51 (10.8). $C_{19}H_{26}N_2O$. Calculated: M 298.

PMR spectrum [$(CD_3)_2SO$]: 1.0-1.4, 7H, m,— ; 1.45, 9H, s,— ; 2.40, 1H, s,— ; 4.00, 2H, t, 7; 7.4, 1H, quad., $J_{4,5} = 7.0$, $J_{4,6} = 1.5$, 7.26, 1H, s, —; 7.50, 1H, d, $J_{5,4} = 7.0$; 7.90, 1H, t, $J_{5,4} = 7.0$, $J_{5,6} = 5.0$; 8.65, 1H, quad., $J_{6,5} = 5.0$, $J_{6,4} = 1.5$.

Forty milligrams of compound VI was isolated from the band with R_f = 0.15-0.25, mp 176-178°C; UV spectrum, λ_{max} (log ε); 214 (4.49), 297 (3.86), Mass spectrum: M 242 (41.7), 241 (18.7), 227 (75.4), 200 (4.0), 199 (48.1), 186 (24.1), 185 (100), 171 (12.1), 170 (11.7), 160 (6.5), 157 (9.5), 132 (5.4), 118 (5.4), 117 (7.1), 106 (8.1), 105 (7.6), 105 (8.3), 93 (9.8), 79 (10.1), 78 (11.4), 57 (14.8), 51 (6.8). $C_{15}H_{18}N_2O$. Calculated: M 242. PMR spectrum [$(CD_3)_2SO$]: 1.45, 9H, s, —; 2.40, 3H, s,—; 7.3, s, —; 7.4-8.0, 3H, m, —; 8.60, 1H, d, $J_{6,5} = 5$.

Thirty milligrams of compound VI was added to a solution of 120 mg of potassium hydroxide in 1 ml of methanol, 250 mg of n-butyl bromide was added, the mixture was boiled for 2 h, the residue filtered off, the filtrate was neutralized with a 30% sodium bicarbonate solution, and extracted with ether. After evaporating the extract 25 mg of an oil was obtained. Its retention time, mass spectrum, and PMR spectrum coincided with the retention time and with the spectra of compound IV.

LITERATURE CITED

1. P. B. Terent'ev, M. I. Rakhimi, A. A. Zaitsev, and A. N. Kost, Vestn. Moskovsk. Univ., Ser. Khim., No. 2, 123 (1969).

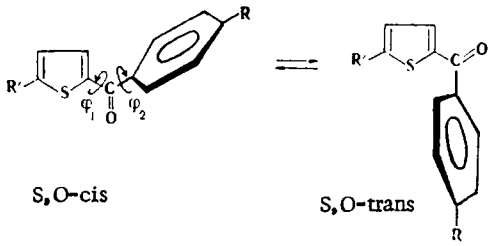
2. P. B. Terent'ev, A. N. Kost, A. A. Zaitsev, and M. I. Rakhimi, Inventor's Certificate 250,142 (1968), Byull. Izobr., No. 26, (1969).
3. G. Ya. Kondrat'eva, Khim. Nauka Promst., 2, 666 (1957).
4. G. Ya. Kondrat'eva, Doctoral Dissertation in Chemical Sciences, Moscow (1974).
5. A. A. Artamonov, A. K. Sheinkman, and B. A. Rozenberg, The Pyridylethylation Reaction, in: Reactions and Methods of Investigating Organic Compounds [in Russian], Vol. 14, Khimiya, Leningrad (1964), p. 173.
6. H. Budzikiewicz, C. Djerassi, and D. H. Williams, Mass Spectrometry of Organic Compounds, Holden Day, San Francisco (1967).
7. P. B. Terent'ev and N. P. Lomakina, Khim. Geterotsikl. Soedin., No. 11, 1472 (1974).
8. N. D. Filyugina, K. M. Dyumaev, A. A. Dubrovin, and I. A. Rotérmel', Zh. Org. Khim., 6, 2131 (1970).
9. M. Ya. Karpeiskii and V. L. Florent'ev, Usp. Khim., 38, 1244 (1969).
10. P. B. Terent'ev (Terentiev), V. G. Kartzew, N. P. Lomakina, and A. N. Kost, Org. Prep. Proced., 6, 145 (1974).

ELECTROOPTICAL PROPERTIES AND STRUCTURE OF CERTAIN 2-BENZOYLTHIOPHENES

V. N. Sheinker, A. S. Kuzharov, V. F. Lavrushin, N. F. Pedchenko, and O. A. Osipov

UDC 541.67.634:543.52:547.734

In 2-benzoylthiophenes, the maximal conjugation between the two aromatic fragments and the carbonyl group in a completely planar structure ($\varphi_1 = \varphi_2 = 0$) is hindered by repulsive interactions, leading to a rotation of one or both fragments to a certain angle φ with respect to the trigonal plane of the carbonyl group:



In several papers it was shown by methods of IR [1, 2], UV [2, 3] and NMR spectroscopy [4], and also from the values of dipole moments [5] that the carbonyl group is more conjugated with the thiophene radical than with the phenyl. This should result in the latter leaving the plane at a greater angle than the heteroaryl ($\varphi_1 < \varphi_2$). In the electron spectra, the nonequivalence of the two radicals with respect to the carbonyl group is mainly observed as a change in the position of the absorption bands when substituents are introduced into the thiophene ring, and as the insensitivity of the spectrum to changes in the phenyl fragment [2, 3].

The authors of [5] assumed the possible rotation of not only the phenyl, but also the heteroaryl fragment with respect to the C=O plane. However, they were unable to evaluate this value quantitatively. Meanwhile, by the combined application of the dipole moments method and the Kerr effect over a wide range of 2-substituted 2-furyl phenyl ketones, it was possible [6] to determine the position of the conformational equilibrium and the acoplanarity angle of the phenyl group.

Rostov State University, Rostov-on-Don 344006. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1327-1330. October, 1977. Original article submitted November 23, 1978.

