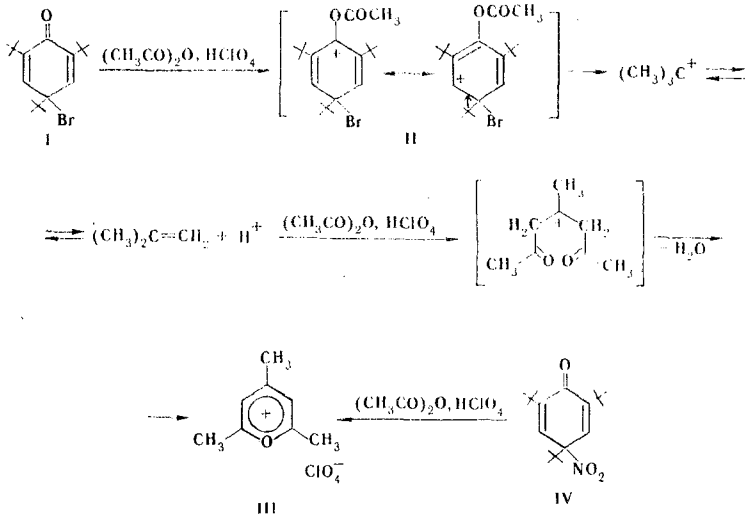
# FORMATION OF PYRYLIUM CATIONS IN THE ACYLATION OF QUINOLIDE COMPOUNDS

L. Yu. Ukhin, Z. S. Morkovnik, and V. N. Komissarov

UDC 547.567'812.5:542.951.1

It is known that aromatization of the ring may occur in the action of acids on quino bromide compounds (I, for example) as a consequence of splitting out of a bromine cation, as well as a geminal tert-butyl grouping in the form of a carbonium cation [1].

We have found that a tert-butyl grouping is split out from I by the action of a solution of 70% perchloric acid in acetic anhydride; trimethylpyrylium perchlorate (III) is formed in ~90% yield (based on one detached tert-butyl group) as a consequence of diacylation of the isobutylene that exists in equilibrium with the tert-butyl cation [2,3]. It may be supposed that debutylation is the result of O-acylation of I and subsequent intramolecular oxidation of the C—C bond in carbonium ion II:



The reaction takes place in 10-15 min, and the pyrylium salt is precipitated quantitatively by means of ether. Uncrystallizable [even after chromatography ($Al_2O_3$, chloroform)] syrupy reaction products remain after separation of the pyrylium salt and removal of the solvent. However, the absence of νOH bands in their IR spectra and the presence of a very strong νCO band (1760 $cm^{-1}$) constitute evidence for O-acylation of the starting quinolide compound.

Replacement of perchloric acid by boron trifluoride etherate or $SbCl_5$ leads to the formation of pyrylium salts with $BF_4^-$ and $SbCl_6^-$ gegenions, respectively. 2,6-Diethyl-4-methylpyrylium cations are formed in propionic anhydride.

The corresponding quinonitrol IV reacts in the same way as quinobromide I (salt III is obtained in 74% yield).

The formation of pyrylium salts is a convenient test reaction for splitting out of tert-butyl groupings. By means of this test reaction we observed that 2,6-di-tert-butyl-4-nitrophenol (V) is also debutylated in a mixture of acetic anhydride with $HClO_4$. It might be assumed that in this case phenol V is initially oxidized to 2,6-di-tert-butyl-p-quinone (as described in [4] for 2,6-diphenyl-4-nitrophenol); the formation of pyrylium salts from the latter will be the subject of a separate publication.

Scientific-Research Institute of Physical and Organic Chemistry at Rostov State University, Rostov-on-Don 244006. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 420-421, March, 1983. Original article submitted July 5, 1982.

0009-3122/83/1903-0345$07.50  

LITERATURE CITED

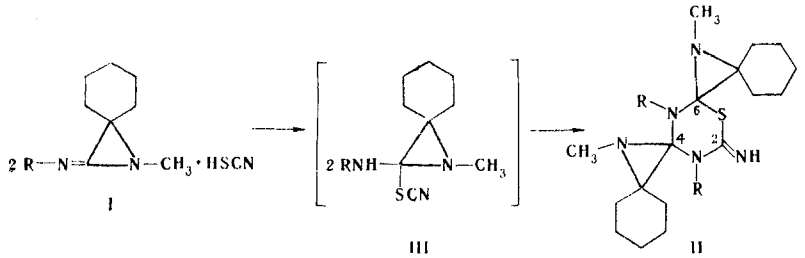
1. V. V. Ershov, G. A. Nikiforov, and A. A. Volod'kin, Sterically Hindered Phenols [in Russian], Khimiya, Moscow (1972), p. 208.
2. A. T. Balaban and C. D. Nenitzescu, Ann. Chem., 625, 74 (1959).
3. P. F. G. Praill and A. L. Whitear, Proc. Chem. Soc., No. 10, 312 (1959).
4. E. E. Jones and J. Kenner, J. Chem. Soc., No. 6, 1842 (1931).

# ACTION OF BASES ON AZIRIDINEIMMONIUM THIOCYANATES

A. I. Polyakov, L. A. Medvedeva, and Yu. A. Baskakov

UDC 547.8+547.87

In an attempt to obtain aziridineimines in the free state by decomposition of their thiocyanates I with organic or inorganic bases we observed the condensation of two molecules of the aziridineimine and thiocyanic acid. The thiadiazine structure of the condensation products is in agreement with the results of elementary analysis and data from the IR, PMR, $^{13}C$ NMR, and mass spectra.



Compounds of the II type are formed in quantitative yields even during chromatography of salts I on $Al_2O_3$ (activity II). The unusual ease of the cyclization is evidently a consequence of the increased reactivity of the exocyclic C=N bond of the aziridineimine, which facilitates the possibility of the base-catalyzed formation of hypothetical aziridine III.

IR spectra (KBr) of thiadiazines II: 3370-3470 (NH) and 1610-1625 $cm^{-1}$ (C=N). PMR spectrum of thiadiazine II (R = $C_6H_5CH_2$) ($d_6$-DMSO, 60°C): 1.61 (m, 10H, cyclohexylidene fragments): 1.88, 2.06 (two s, 3H, $CH_3$—N); 4.21, 4.27 (two s, 2H, $CH_2C_6H_5$); 7.12, 7.17 (two s, 5H, $C_6H_5$); 8.53 ppm (broad s, NH). The shift of the signals of the protons of the N—$CH_3$ group to stronger field as compared with aziridineimine is presumably due to shielding of the benzene rings that are drawn close to them in space. $^{13}C$ NMR spectrum of this compound: 170.2 [$C_{(2)}$], 127.9 [$C_{(6)}$], 117.3 [$C_{(4)}$], 68.3 and 63.6 (spiro-C of the cyclohexylidene groups); 140.1, 136.9, 127.3, 127.1, 126.4, and 125.9 ($C_6H_5$); 45.5 and 45.1 ($CH_2$—$C_6H_5$); 35.6, 35.3, 31.4, 31.0, 27.7, 26.9, 24.8, 23.9, 22.3, 22.0, and 21.8 ppm (cyclo-$C_6H_{10}$). Mass spectrum, m/z (relative intensities, %): $M^+$ 516 (17.8), 405 (7.3), 365 (9.4), 286 (100.0), 232 (5.2), 117 (15.7), 111 (13.6), 68 (5.2), 34 (6.3).

The results of thin-layer chromatography and data from the PMR and $^{13}C$ NMR spectra constitute evidence that only one isomeric form of thiadiazine II is obtained in the condensation.

Thiadiazines II are stable under normal conditions and react with difficulty with carboxylic acid chlorides; the reaction with excess $CH_3I$ leads to the formation of a monosubstituted compound.

All-Union Scientific-Research Institute of Chemical Agents for the Protection of Plants, Moscow 109088. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, p. 421, March, 1983. Original article submitted August 16, 1982.

 0009-3122/83/1903-0346$07.50 