2. J. Emsley, J. Feeney, and L. Sutcliffe, High-Resolution NMR Spectroscopy, Vol. 1, Pergamon Press (1965).
3. N. T. Berberova, E. P. Ivakhnenko, A. S. Morkovnik, and O. Yu. Okhlobystin, Khim. Geterotsikl. Soedin., No. 12, 1696 (1979).
4. A. S. Morkovnik and O. Yu. Okhlobystin, Khim. Geterotsikl. Soedin., No. 8, 1011 (1980).

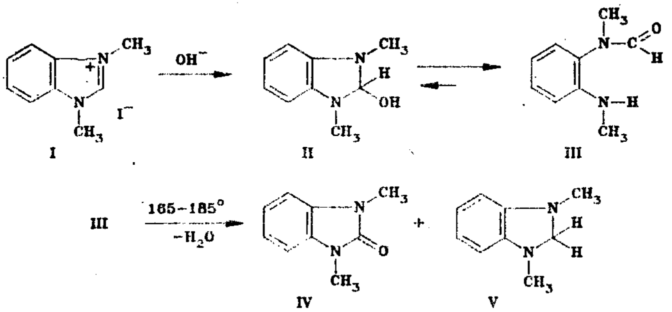
FORMATION OF DISPROPORTIONATION PRODUCTS FROM BENZIMIDAZOLE PSEUDOBASES.

THE FIRST INSTANCE OF PSEUDOBASE DISPROPORTIONATION IN THE ABSENCE OF ALKALI

A. A. Konstantinchenko,
A. S. Morkovnik, A. F. Pozharskii,
and B. A. Tertov

UDC 547.785.5+547.781.3+547.783

It is known that the pseudobases that form by the action of alkali on heteroaromatic cations undergo disporportionation in a number of cases to form the respective oxo- or dihydro derivatives. Such conversion are encountered most frequently among electron-deficient azines (acridines, phenanthridines, etc.) and extremely rarely among azoles [1]. Thus it has hitherto been known that 1,3-dialkylbenzimidazolium salts by reaction with alkali form pseudobases that exist in the solid state and in solution in acyclic form II [2, 3]:



We discovered unexpectedly that when compound III (mp 69-70°) is heated without solvent in an inert atmosphere at 165-185° it is converted to a mixture of 1,3-dimethylbenzimidazolone (IV) and 1,3-dimethylbenzimidazoline (V), the yields of which after 5 h are 49% respectively. Although the mechanism of this conversion requires special investigation, it undoubtedly proceeds via equilibrium amounts of the carbinol form of pseudobase II, which disproportionates. This observation prompted us to study more carefully the reaction of salt I with alkali. We have established that III forms in 85% yield by the action of 30-50% alkali on I for 20 min at 45-50°. But if compound I is boiled in 40% KOH solution for 5h, then the main product is N,N'-dimethyl-o-phenylenediamine which forms by deformylation of III. Moreover, under these conditions 1,3-dimethylbenzimidazolone and 1,3-dimethylbenzimidazoline form in yields of 7 and 6%. The yield of disporportionation products can be increased if the reaction is carried out under more severe conditions. Thus if I is heated in a bomb with 40% alkali at 165-170° for 1.5 h, the yields of IV and V become 39 and 38% respectively. Thus our experiments show that heteroaromatic cations for which disproportionation by the action of alkali traditionally is hardly considered typical, can react by this route under appropriate changes in reaction conditions. It should also be noted that the conversion of III in a melt to IV and V is apparently the first case of disproportionation of a pure pseudobase in the absence of alkali [1].

Scientific-Research Institute of Physical and Organic Chemistry, M. A. Suslov State University, Rostov-on-Don 344090. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1694-1695, December, 1985. Original article submitted June 4, 1985.

LITERATURE CITED

1. I. W. Bunting, Adv. Heterocycl. Chem., 25, 1 (1979).
2. C. W. Smith, R. S. Rasmussen, and S. A. Ballard, J. Am. Chem. Soc., 71, 1082 (1949).
3. P. N. Preston (editor), Benzimidazoles and Congeneric Tricyclic Compounds, Part I, (1981), p. 337.

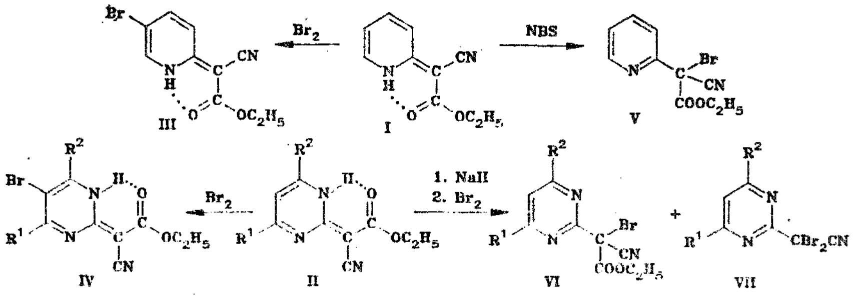
EASY BROMINATION OF DIHYDROPYRIDYLIDENE- AND DIHYDROPYRIMIDINYLIDENECYANOACETIC ESTERS

O. A. Zagulyaeva, I. V. Semushkina,
and V. P. Mamaev

UDC 547.821+547.853:542.944.2

We have shown that 1,2-dihydro-2-pyridylidene- (I) and 1,2-dihydro-2-pyrimidinylidenecyanoacetic esters (IIa, b) react with bromine in acetic acid at room temperature to form the 5-bromo derivatives III and IVa, b respectively in 70-80% yield. Judging from the PMR spectra (absence of heteroaromatic proton signals in the 5.5-9.0 ppm region) at the start of the reaction (within 1-2 h) substituted hexahydropyridines and -pyrimidines form that are probably analogous to the addition products of halogens and substituted uracils in acetic acid [1, 2]. These products are detected by TLC on Silufol in chloroform (colorless material, $R_f \sim 0.6$, detection in UV light). After 30-40 h in the reaction mixture they are converted to the ylidene derivatives III and IVa, b (yellow compounds, $R_f \sim 0.3$). When the reaction is carried out at 80°, substances III and IVa, b form in 3-4 h. When bromine reacts with the sodium salts of I and II in dimethoxyethane at room temperature, bromination takes place only in the side chain, to form a mixture of mono- and dibromoderivatives V-VII (colorless compounds, $R_f \sim 0.5$). N-Bromosuccinimide (NBS) reacts with dihydropyridine I and dihydropyrimidines II in acetic acid to give monobromoderivatives of pyridine V and pyrimidines VI, respectively. In this case TLC of the reaction mixtures did not show any ring-brominated products. With the 4,6-diphenyl-substituted dihydrophyrimidine IIc bromination takes place only in the side chain (VIc; VIIc).

The elemental compositions of III-VII agree with the calculated values. The ylidene structure of the 5-bromo derivatives III, IVa, b is confirmed by IR data (intense ν_{CN} band at 2210, ν_{CO} at 1650 cm^{-1}) UV data ($\lambda_{max} > 350$ nm), and PMR data ($\delta_{NH\cdots O}$ 13-14 ppm) [3]. The products of side-chain bromination V-VII typically show no absorption bands of conjugated nitrile, but the UV spectrum has a long wave maximum at $\lambda > 300$ nm. The entrance of bromine into position 5 of dihydropyridine III and dihydropyrimidines IVa, b or into the side chain of pyridine V and pyrimidines VI and VII is evident from PMR spectral data in the region of heteroaromatic proton signals. Compound IVa was also identified by comparison with an authentic sample.



II,IV,VI,VII a $R^1=R^2=H$; b $R^1=H$, $R^2=C_6H_5$; c $R^1=R^2=C_6H_5$

Novosibirsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Novosibirsk 630090. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1695-1696, December, 1985. Original article submitted July 2, 1985.

0009-3122/85/2112-1399$09.50