ANOMALOUS PMR SPECTRA OF 1,2,3-TRIMETHYL-2-PHENYLBENZIMIDAZOLINE IN APROTIC SOLVENTS

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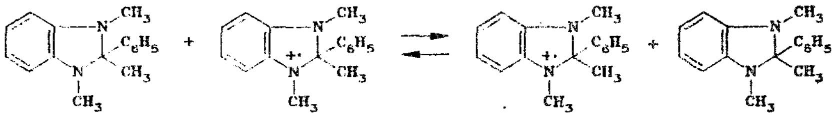
UDC 547.785.5+541.515+541.128.24

We have found that in contrast to other imidazoles [1], 1,2,3-trimethyl-2-phenylbenzimidazoline (I)[*] has unusual PMR spectra in deuterochloroform and deuteroacetonitrile. Within 5 min after dissolution of the benzimidazoline in $CDCl_3$ the N-methyl and the 5-H and 6-H proton signals are strongly broadened, and the broadening increases rapidly with time and quickly leads to their complete disappearance. (PMR spectrum of compound I in $CDCl_3$ within 5 min after preparation of solution: 1.55 (s, 3,[†] 3H, $C-CH_3$), 2.36 (s, 48,[†] 6H, $N-CH_3$), 5.93-6.29 (m, 2H, 4.7-H), 6.51 (broad singlet, 2H, 5.6-H), 7.1-7.7 ppm (m, 5H, C_6H_5)). The signals of the remaining protons undergo insignificant broadening. The width of the C-methyl signal is 5 Hz one day after dissolution of I. In the same time the incompletely resolved multiplet of the 4,7-H protons is converted to a broad singlet by loss of resolution.

Analogous results were obtained when the solvent was deuteroacetonitrile.

The reason for this phenomenon is the rapid electron exchange between compound I and its radical cation that forms in very low concentration by autooxidation of benzimidazoline:



I   I$^{+\cdot}$

Such an effect has apparently not previously been observed in the PMR spectra of heterocyclic compounds, but for aromatic compounds the possibility has been demonstrated for N,N,N',N'-tetramethyl-p-phenylenediamine [2]. It was shown that the more strongly the PMR singal broadens, the faster is the electron exchange, the higher is the concentration of paramagnetic form, and the stronger is the interaction of the respective protons with the unpaired electron in the radical cation.

The weak broadening of the C-methyl and phenyl group signals and of the 4-H, 7-H proton signals of compound I in the presence of the radical cation is attributable to the fact that the unpaired electron density at these protons in the paramagnetic form is insignificant (cf. [3]).

When a solution of I in $CDCl_3$ is treated with pyridine one day after preparation (the radical cation is decomposed [4]), the PMR spectrum shows N-methyl and 5-H, 6-H proton signals whose width is close to normal. (The widths of the N- and C-methyl signals are respectively 6 and 3 Hz.) The broadening of the PMR signals of compound I is completely absent in deuterobenzene, in which solvent the radical cation evidently does not form.

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[*] Obtained by the reaction of N,N'-dimethyl-o-phenylenediamine and acetophenone.
[†] Line width at half height for singlet signals.

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FORMATION OF DISPROPORTIONATION PRODUCTS FROM BENZIMIDAZOLE PSEUDOBASES.

THE FIRST INSTANCE OF PSEUDOBASE DISPROPORTIONATION IN THE ABSENCE OF ALKALI

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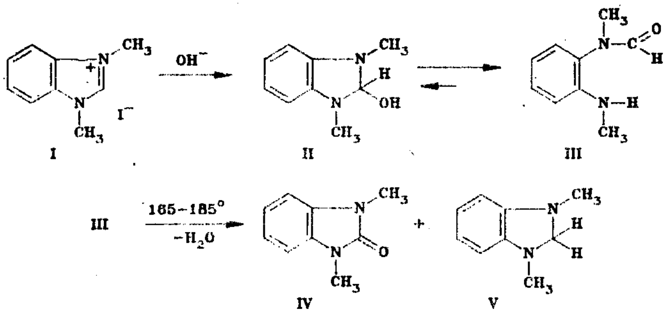
It is known that the pseudobases that form by the action of alkali on heteroaromatic cations undergo disporportionation in a number of cases to form the respective oxo- or dihydro derivatives. Such conversion are encountered most frequently among electron-deficient azines (acridines, phenanthridines, 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].

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