THE 1,3-DIMETHYL-2-PHENYLBENZIMIDAZOLINE CATION RADICAL AND ITS DECOMPOSITION

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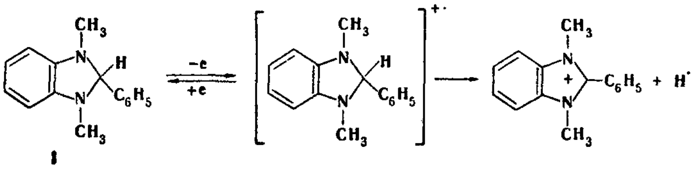
We have found that 1,3-dimethyl-2-phenylbenzimidazoline (I), which is assumed [1] to be a vigrous hydride-ion donor, undergoes oxidation to give a stable cation radical with a well-resolved EPR spectrum ($a_{N1} = a_{N2} = a_H^{CH_3} = 6.8$ Oe, $a_H^{5,6} = 3.4$ Oe, and $a_H^2 = 40$ Oe). It is convenient to use $AlCl_3$ in methylene chloride as the oxidizing agent, in this case the cation radical can be observed at room temperature. The electrochemical oxidation of I on a rotating platinum disk with a ring (with dimethylformamide as the medium and sodium perchlorate as the base electrolyte) proceeds at $E_{1/2} = 0.285$ V relative to a standard calomel electrode; the cation radical is easily recorded on a ring with a constant potential corresponding to the foot of the oxidation wave (0.150 V), which indicates the existence of a reversible one-electron step. It is characteristic that, in contrast to pyrans [2], decomposition of the cation radical with splitting out of a proton could not be detected in this case. This undoubtedly associated with the very high spin density on the "hydride-labile" proton in the 2 position. As a consequence of this, the cation radical is readily dehydrogenated by acetonitrile and stilbene; hydrogen is evolved in the free state when the cation radical is heated and also in the presence of palladium black. This is evidently the first instance of the decomposition of a cation radical with splitting out of a hydrogen atom in solution ($RH^{+\cdot} \rightarrow H^{\cdot} + R^{+}$). Triphenylpyranyl and triphenylmethyl free radicals are detected by EPR spectroscopy in the case of oxidation of I with 2,4,6-triphenylpyrylium perchlorate and trityl chloride, respectively, in acetonitrile.

Thus the dehydrogenation of I actually commences with one-electron transfer and proceeds via a scheme involving the removal of an electron and an H˙ radical, i.e.,



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