STABLE BIRADICAL IN THE BENZIMIDAZOLINE SERIES, CONTAINING TWO CATION-RADICAL FRAGMENTS WITH STRONG EXCHANGE INTERACTIONS

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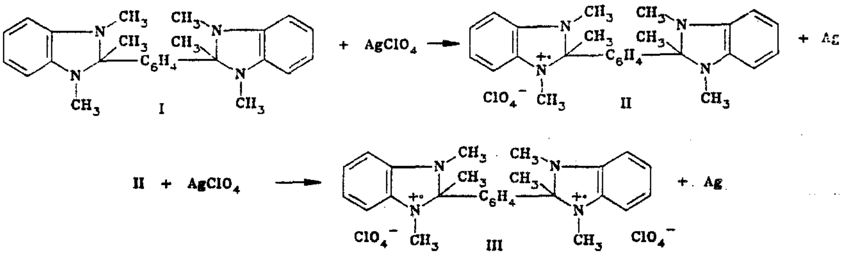
A large number of uncharged stable biradicals are known [1]; there have been practically no reports, however, of biradicals containing two cation-radical fragments [bi(cation-radicals)]. The only reported examples of radicals of this type have been polymeric viologens containing two or more unpaired electrons, in which the cation-radical functional groups are composed of nonaromatic γ,γ-dipyridylidene units [2]. The exchange interaction between the unpaired electrons in this class of radicals is negligible; thus, their EPR spectra do not differ from the spectra of the corresponding viologen monoradicals. Viologenic bi- and poly(cation-radicals) are formed upon reduction of polypyridinium salts [2]. It is assumed that two-electron oxidation of compounds of the type R—X—R, in which the R groups are more readily ionized than the bridging group X, should provide a more general method for the preparation of bi(cation-radicals). We succeeded in carrying out this type of reaction in the case of 1,4-di(1,2,3-trimethylbenzimidazolinyl-2)benzene (I),* which contains two benzimidazoline functional groups linked by a nonconjugating p-phenylene bridge.

Upon treatment with an equimolar amount of silver perchlorate in acetonitrile solution compound I loses one electron from the HOMO of one of the benzimidazoline residues to give a blue solution of cation-radical II. Its EPR spectrum is analogous to the spectrum of the 1,2,3-trimethyl-2-phenylbenzimidazoline cation-radical [3]. Thus, it is similarly composed of 23 evenly spaced lines (with a separation of 3.0 Oe), and is also analyzed in terms of interaction of the unpaired electron with two nitrogen atoms, six protons of the N-methyl groups, and two protons in positions 5 and 6 ($a_N = a_N^{N\text{-}CH_3} = 2a_H^{5,6} = 6.0$ Oe). If a solution of compound I in acetonitrile (0.01 mole/liter) is treated with a 10-15-fold excess of $AgClO_4$, both benzimidazoline functional groups undergo one-electron oxidation. The reaction product in this case consists of a blue precipitate, which is composed of the sparingly soluble bi(cation-radical) perchlorate (III) and metallic silver:



The EPR spectrum of salt III (in nitromethane at 60°C) contains, in addition to the main lines which are also found in the spectrum of the radical II (with a separation between them of 3.0 Oe also), supplementary biradical lines, which are attributed to T-transitions [1]. The biradical lines are found in the middle of the separations between the main lines, such that the spectrum of the biradical appears in the form of a multiplet of equidistant lines with a splitting constant equal to one half of $a_H^{5,6}$, i.e., 1.5 Oe. This type of spectrum is consistent with that expected in the case of a strong exchange interaction of two unpaired electrons, in which the value of the exchange integral J is significantly greater than the constant a [1]. Of the total number of lines (45) in the spectrum, only approxi-

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*This compound was prepared for N,N-dimethyl-o-phenylenediamine and p-diacetylbenzene in 41% yield; mp 157-158°C (from alcohol).

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mately half of the lines are observed, corresponding to the central, most intense portion of the spectrum. The less intense lines, located at the peripheries of the spectrum, could not be detected, since the spectrum lost resolution as the concentration of the salt III was increased. The biradical and monoradical were of comparable stability: both decomposed at room temperature in solution over a period of 1-2 days.

Electronic spectrum (in CH_3CN), λ_{max}: I, 226 and 317, nm; II, 222, 321, 370 (sh), and 762 nm; III, 218, 322, 370 (sh), and 762 nm.

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PHOTONUCLEOPHILIC SUBSTITUTION OF HALOGEN IN (5-BROMOFURYL-2)-PYRIDINIUM DERIVATIVES

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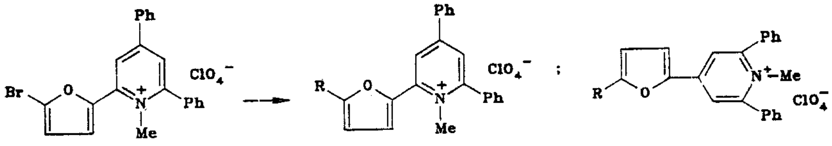
We have found that halogen atoms can be readily displaced by nucleophiles in 2-(5-bromofuryl-2)-1-methyl-4,6-diphenylpyridinium(I) and 4-(5-bromofuryl-2)-1-methyl-2,6-diphenylpyridinium (II) perchlorates upon irradiation in light.



I

III

IV

R= o- and p-tolyl, morpholino, piperidino

The reactions were carried out in acetonitrile solution in the presence of excess nucleophile in a pyrex photoreactor irradiated with a mercury DRT-220 lamp. The irradiation time was varied from 30 min to 2 h, while the extent of reaction was monitored spectrophotometrically. After removal of solvent the reaction products III and IV were isolated in near qualitative yields. Reaction with toluene resulted in the formation of a mixture of o- and p-tolyl substituted isomers in a ca. 2:3 ratio. This was established based on the integrated intensity ratio of the proton signals for the o- and p-methyl groups in the PMR spectra of compounds III [2.58 (o-CH_3) and 2.40 (p-CH_3) ppm] and IV [2.29 (o-CH_3) and 2.00 (p-CH_3) ppm].

Reactions of compound I with morpholine and piperidine, as well as of cation II with piperidine, occur at very slow rates in the dark, and are significantly accelerated upon exposure to light. Photosubstitution of halogen also takes place upon treatment of compounds I and II with benzene, p-xylene, mesitylene, furan, and sylvan (α-methylfuran). The corresponding p-bromophenyl substituted pyridinium derivatives do not participate in these types of halogen photosubstitution reactions.

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