ONE-ELECTRON OXIDATION AND TRIPHENYL-METHYLATION OF BENZIMIDAZOLINES BY THE TRIPHENYLMETHYL CATION

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With triphenylmethyl perchlorate (tetrafluoroborate) 1,2,2,3-tetrasubstituted benzimidazolines undergo electrophilic triphenylmethylation at position 5. In further reaction with the electrophilic agent the obtained 5-triphenylmethylbenzimidazolines are converted into radical-cations. They undergo a similar transformation during the action of silver perchlorate and molecular oxygen. The results from investigation of the radical-cations by ESR and PMR are given.

Electrophilic substitution in benzimidazolines (2,3-dihydrobenzimidazoles) is hindered by their tendency to form dehydrogenation or oxidation products during reaction with electrophiles. For instance, no case has so far been known of such substitution in benzimidazolines with a $C_{(2)}$ -H bond, since these compounds are easily dehydrogenated to benzimidazolium salts by various electrophiles, including trichloromethane [1-4]. In some cases benzimidazolines not containing a hydrogen atom at position 2 can be nitrated quite smoothly and formylated to 5-nitro- and 5-formyl derivatives [4, 5]. Both the benzimidazolium salts and electrophilic substitution products can be formed from one and the same initial intermediate (the radical-cation substrate) formed during electron transfer from the heterocycle to the electrophile [1-6]. Experimental data in favor of the one-electron path during the nitration of benzimidazolines were presented in [4, 5].

In the present work we found that benzimidazolines with a blocked position 2 react with the triphenylmethyl cation by an electrophilic substitution path. This reaction probably also has radical-ion character and also leads to entry of the substituent at position 5, which has the highest density of the unpaired electron in the radical-cation form [4, 5]. The structure of the obtained 5-triphenylmethylbenzimidazolines was established by analysis of their PMR spectra and also by an alternative synthesis from derivatives of o-phenylenediamine and ketones.



1--111 a R¹, R² = Mc, R³ = Ph; b R¹ = Mc, R² = Et, R³ = Ph; c R¹ = Mc, R², R³ = -(CH₂)₄-; d R¹ = Mc, R², R³ = -(CH₂)₅-; e R¹ = Et, R² = Ph, X = ClO₄, BF₄

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Fig. 1. The ESR spectra of the radical-cations (Va) (top left) and (Vc) (top right). A computer reconstruction of the spectra is given below.



Fig. 2. The ESR spectra of the radical-cations (Ve) (top left) and (VI) (top right). The spectra obtained by reconstruction are given below.

The ability of benzimidazolines to transfer one electron to the triphenylmethyl cation is confirmed by the formation of the triphenylmethyl radical during the dehydroaromatization of benzimidazolines by triphenylchloromethane [7, 8]. According to the data from semiempirical calculation [8], the second-sphere transfer of an electron from simple benzimidazolines to triphenylmethyl cation must take place at a high rate. Nevertheless, we were unable to detect the radical-cations (IIa-e) by ESR in the (Ia-e)-Ph₃C⁺ system. This can be explained by their short lifetime under the reaction conditions.

5-Triphenylmethylbenzimidazolines are incapable of further triphenylmethylation for steric reasons. The reaction of compounds (IIIa-e) with the triphenylmethyl cation therefore stops at the stage of the formation of the radical-cations, which are easily detected by ESR. 1,2,3,5-Tetramethyl-2-phenylbenzimidazoline (IV) reacts in a similar way. Compounds (IIIa-e, IV) are also transformed into radical-cations by the action of silver perchlorate, which acts as a mild one-electron oxidizing agent. In this respect they behave like other benzimidazolines [3-6].



III a-e, $Va-e R = Ph_3C$; IV, VI R, R^1 , $R^2 = Me$, $R^3 = Ph$

The ESR spectrum of the radical-cation (Va) represents a group of eleven (undecet) of doublets (1:1) with the intensities of the individual components of the doublets in ratios close to 1:8:30:70:113:132:113:70:30:8:1 (Fig. 1). Such a spectrum results from the coupling of the unpaired electron with the proton at position 6 (doublet splitting) and the system of two nitrogen nuclei and six protons of the N-methyl groups at

$$a_{\rm N(1)} = a_{\rm N(3)} = a_{\rm H}^{1-{\rm Me}} = a_{\rm H}^{3-{\rm Me}}.$$

The radical-cations (Vb, d) have similar spectra.

In the ESR spectrum of the spirobenzimidazoline radical-cation (Vc) only undecet splitting is observed (Fig. 1). This indicates a significant redistribution of the density of the unpaired electron in this radical-cation and, in particular, a marked decrease in the hyperfine coupling with the proton at position 6. This effect is probably due to changes in the geometry of the imidazoline fragment, due to the effects of the adjacent spirocycle.

The ESR spectrum of the radical (Ve) (Fig. 2) consists of 14 equally distant lines with splitting of 3.2 Oe and is due to the coupling of the unpaired electron with the nitrogen nuclei and with the protons of the N-methylene groups and position 6 with the hfs constants in the ratios:

$$a_{N(1)} = a_{N(3)} = 2a_{H1}^{1-CH2} = 2a_{H}^{3-CH2} = 2a_{H(6)}$$

The radical-cation (VI) has an odd ESR spectrum (Fig. 2) of 15 lines. The multiplicity is due to hyperfine coupling of the unpaired electron with the nitrogen nuclei, the proton at position 6, and the nine protons of the methyl groups at positions 1, 3, and 5 with the respective hfs constants equal.

The hfs constants of the benzimidazoline radical-cations are given in Table 1.

The observed twofold decrease in the ratio of the a_N constant to the hfs constant of the α -protons of the N-alkyl groups in the transition from the radical-cations (Va-d) to the radical-cation (Ve) indicates restricted rotation of the N-ethyl groups of the radical (Ve) about the C-N bond with fairly free rotation of the N-methyl groups in the other radicals. Analogous characteristics are shown by the radical-cations of 1,2,2,3-tetrasubstituted benzimidazolines [4] and also the radical-cations of the phenothiazine series [9].

The accuracy of the interpretation of the ESR spectra of the radical-cations is confirmed by investigation of the PMR spectra of the corresponding benzimidazolines, having undergone one-electron autooxidation when their solutions in a mixture of deuterated chloroform and benzene were held briefly in air (see [10]). The process leads to the accumulation of the radical-cation impurity in the solutions at concentrations sufficient for detection by ESR. Both components of the binary systems formed in this way are in a state of rapid electron exchange, which shows up in the PMR spectrum as broadening of the signals of diamagnetic form [11]:

HetH + H_{ctH^+} + H_{ctH^+} + H_{ctH^+} + HetH (1)

The broadening of the various signals is not identical and is more clearly defined the larger the hfs constant of the respective proton (protons) in the paramagnetic form [12, 13]. This makes it possible to determine the sequence of decrease of the proton hfs constants in the radical-cation. The PMR spectrum of compound (IIIa) recorded in air is presented in Fig. 3 as an example. From its analysis it follows that the hfs constants in the radical-cation of benzimidazoline (Va) decrease in the following order:

$$N_{(1)}$$
-Me ~N₃-Me > 6-H > 7-H > 4-H > Ph.

The ratio of the broadening of the signal of each of the N-methyl groups (in Hz) to the broadening of the signal for the $H_{(6)}$ proton in the spectra of the benzimidazoline (IIIa) is not equal to the square of the ratio of the respective proton hfs constants. For instance, for the spectrum presented in Fig. 3 the first value is 1.5, whereas the second value is 3.6. This means that the condition of a weak paramagnetic pulse is not fulfilled for the indicated protons [12, 13]. The condition of a strong pulse is also not fulfilled for them, otherwise the broadening of the signals would hardly depend at all on the values of the proton hfs constants [13]. Thus, the two above-mentioned types of protons are subject to the influence of paramagnetic pulses of medium strength under the experimental conditions. This makes it possible to estimate the rate constant of reaction (1) for the benzimidazoline (IIIa) starting only from the ratio of the broadenings of the two PMR signals (R), the corresponding hfs

constants of the radical-cation (Va), and the concentration of the diamagnetic form (c_d) with unknown concentration of the paramagnetic form [13]:

$$k = 0.5a_1a_2c_d^{-1} [(R-1)(a_1^2 - a_2^2R)^{-1}]^{0.5} \approx 3 \cdot 10^7 \text{ liter/mole \cdot sec}$$

$$a_1 = a_H^{\text{NMe}} = 1.8 \cdot 10^7 \text{ Hz}, a_2 = a_H(6) = 9.8 \cdot 10^6 \text{ Hz},$$

$$R = \Delta \Delta \nu_1 / 2^{\text{NMe}} / \Delta \Delta \nu_1 / 2^{6-\text{H}}.$$

Reaction (1) has approximately the same k value in the case of benzimidazoline (Ia), which is an analog of compound (IIIa) not containing a triphenylmethyl group [14]. Consequently, the introduction of the bulky triphenylmethyl group into the benzimidazoline system has an insignificant effect on the rate of electron exchange with the radical-cation. The process is characterized by comparatively small energy barriers, due to the internal reorganization of the benzimidazoline system during its transition from the diamagnetic state to the paramagnetic state.

The introduction of the triphenylmethyl substituent at position 5 of the benzimidazolines significantly increases the stability of the radical-cations. Thus, the radicals (Va, b, e) decompose at room temperature in acetonitrile only after several months. It was possible to isolate the perchlorate of the radical-cation (Va) in the form of a dark-green paramagnetic powder, which gradually decomposes during storage. During reduction with zinc dust the salt captures one electron and changes into the benzimidazoline (IIIa). At the same time the presence of the spirocycle at position 2 of the 5-triphenylmethylbenzimidazolines leads to destabilization of the radical-cations — in solution the radical-cation (Vd) decomposes after several days. The stability of the radical (Vc) is even lower, and its lifetime is measured in a few minutes. The described dependence of the stability of the radical-cations on the presence or absence of the spirocycle is similar to the relation observed in the series of benzimidazolines not containing the triphenylmethyl group [3, 6].

The radical-cations (Va-e) have a green color in solution, and this distinguishes them from the pale-blue radical-cations of compound (IV) and 1,2,2,3-tetrasubstituted benzimidazolines. The electronic spectra of both groups of radical-cations differ considerably in the position of the two most long-wave absorption bands. Thus, the spectra of the radical-cation (IIa) and its triphenylmethyl-containing analog (Va) are characterized by λ_{max} values (in acetonitrile) of 322, 374 (sh), 760 nm [3] and 334, 440, and 715 nm. Consequently, the triphenylmethyl group at position 5 has a significant effect on the energetics of the MO in the benzimidazoline radical-cations, and this appears in spite of the absence of conjugation.

EXPERIMENTAL

The ESR, PMR, and electronic spectra were recorded on Radiopan SE-2543, Tesla BS-487C (80 MHz), and Specord M-40 spectrometers at room temperature. The elemental analyses of the synthesized compounds for C, H, and N agree with the calculated data. The initial benzimidazolines (Ia-d) were obtained by the procedures described in [2, 6, 10, 15].

N,N'-Diethyl-o-phenylenediamine. To 200 ml of a saturated alcohol solution of potassium hydroxide we added 50 g (0.2 mole) of 1,1-diethylbenzimidazolium bromide. The reaction mixture was kept without access to air for 24 h. It was then poured into 500 ml of water, and the diamine was extracted with ether. The ether extract was dried over potassium carbonate, the solvent was distilled, and the residue was distilled under vacuum. The yield of the diamine was 22 g (69%). The product was a colorless oil boiling at 225-230°C (10 mm Hg).

1,3-Diethyl-2-methyl-2-phenylbenzimidazoline (Ie). A mixture of 9 g (55 mmole) of N,N'-diethyl-o-phenylenediamine, 17 g (141 mmole) of acetophenone, and 0.2 ml of trifluoroacetic acid was heated while the water that formed and the excess of acetophenone were distilled. An oily residue was obtained and crystallized after prolonged holding in air. It was rubbed with a small amount of methanol, and the product was filtered off and dried. The yield was 4.5 g (30%); mp 52.0- 53.5° C (from aqueous methanol).

1,2,3,5-Tetramethyl-2-phenylbenzimidazoline (IV). The compound was obtained similarly from N,N',4-trimethyl-ophenylenediamine and acetophenone. The residue obtained after distillation of the excess ketone was dissolved in hexane and passed through a column of aluminum oxide. The product after distillation of the solvent from the eluate was kept under vacuum until it crystallized and rubbed with a small amount of methanol. The benzimidazoline was filtered off. The yield was 36%; mp 55-56°C (from aqueous methanol).

Radical- cation	hfs Constants, Oe				
	a _N	a _H N-Me	aHN-CH5	^a H(6)	a _H C-Me
IIe	6,6		3,3	3,3	
Va	6,6	6,6		3,5	
V b	6,3	6,3		3,3	
Vc	5,7	5,7			
Vd	6,3	6,3		3,5	
v,e	6,4		3,2	3,2	
VI	5,8	5,8		5,8	5,8[C(5)-Me]

TABLE 1. hfs Constants of Benzimidazoline Radical-Cations



Fig. 3. PMR spectrum of compound (IIIa), having undergone slight oneelectron autooxidation during the preparation of its solution in a mixture of perdeuterobenzene and deuterochloroform (6:1) in air ($c_d = 0.15$ M).

1,2,3-Trimethyl-2-phenyl-5-triphenylmethylbenzimidazoline (IIIa). A. To a solution of 6.0 g (25 mmole) of 1,2,3trimethyl-2-phenylbenzimidazoline (Ia) in 30 ml of acetonitrile we added with cooling in water and stirring 8.8 g (26 mmole) of triphenylmethyl perchlorate. After 5 min the mixture was poured into 200 ml of a dilute solution of ammonia (1:3). The oily product was separated and dissolved in 150 ml of hot benzene. The solution was dried with potassium carbonate and passed through a column of aluminum oxide. The fraction with the largest R_f value was collected. The residue after evaporation of the eluate was boiled with 50 ml of alcohol, and the undissolved part [compound (IIIa)] was filtered off. The yield was 8.3 g (69%); mp 213-214°C (from benzene). PMR spectrum (C_6D_6): 1.10 (3H, s, C-Me), 1.83 (3H, s, N-Me), 2.03 (3H, s, N-Me), 5.88 (1H, d, 7-H), 6.08 (1H, d, 4-H), 6.58 (1H, dd, 6-H), 6.87-7.63 ppm (20H, m, phenyl groups).

B. To a mixture of 0.3 g (0.8 mmole) of N,N'-dimethyl-4-triphenylmethyl-o-phenylenediamine [8] and 1.0 g (8.3 mmole) of acetophenone we added 0.05 ml of trifluoroacetic acid. The mixture was boiled for 5 min, and the excess of acetophenone and the water were distilled. The residue was boiled with 5 ml of alcohol, and the undissolved part was filtered off and purified as described above. The yield of compound (IIIa) was 0.15 g (41%); mp 210-211°C (from benzene). A mixed melting test with a sample obtained by method A did not give a melting point depression.

1,3-Dimethyl-2-ethyl-2-phenyl-5-triphenylmethylbenzimidazoline (IIIb). The compound was obtained similarly to compound (IIIa) from benzimidazoline (Ib) and triphenylmethyl tetrafluoroborate. The yield was 32%; mp 188-191°C (from acetonitrile).

1,3-Dimethyl-2,2-tetramethylene-5-triphenylmethylbenzimidazoline (IIIc). The compound was obtained in the reaction of benzimidazoline (Ic) with triphenylmethyl perchlorate and also by the condensation of N,N'-dimethyl-4-triphenylmethyl-o-phenylenediamine with cyclopentanone. Acetic acid was used as acidic catalyst. The yield of (IIIc) was 26% in the first method and 32% in the second; mp 210-211°C (from benzene). PMR spectrum (C_6D_6): 1.3-1.7 [8H, m (CH_2)₄], 1.96 (3H, s, N-Me), 2.15 (3H, s, N-Me), 5.83 (1H, d, 7-H), 5.98 (1H, d, 4-H), 6.53 (1H, dd, 6-H), 6.7-7.4 ppm (15H, m, 3PhH).

1,3-Dimethyl-2,2-pentamethylene-5-triphenylmethylbenzimidazoline (IIId). The compound was synthesized by the triphenylmethylation of compound (Id) with triphenylmethyl perchlorate. The yield was 24%; mp 197-198°C (from acetonitrile).

1,3-Diethyl-2-methyl-2-phenyl-5-triphenylmethylbenzimidazoline (IIIe). The compound was obtained by the triphenylmethylation of the benzimidazoline (Ie) with triphenylmethyl perchlorate. The oil that separated after addition of the reaction mixture to ammonia solution was separated and boiled with ethanol. The precipitated triphenylmethyl derivative was filtered off, washed with ethanol, and dried in air. The yield was 52%; mp 172-173°C (from ethyl acetate).

Perchlorate of the Radical-Cation of Benzimidazoline (IIIa). To a suspension of 0.6 g (1 mmole) of compound (IIIa) in 4 ml of acetonitrile we added 0.46 g (1.2 mmole) of the salt $AgClO_4 \cdot 4MeCN$ [16]. The reaction mixture was stirred for 15 min. The initial benzimidazoline passed into solution, and the solution acquired a strong dark-green color. The precipitated metallic silver was filtered off, and the salt of the radical-cation was precipitated from the filtrate with dry ether. The yield was 0.54 g (75%).

Reduction of the Perchlorate of the Radical-Cation (Va). A solution of 0.4 g of the salt of the radical-cation obtained by the previous method in 15 ml of acetonitrile was stirred with 3 g of zinc dust until the green color of the radical-cation had disappeared. The excess of the metal was filtered off, the solvent and the reduction products [benzimidazoline (IIIa)] were distilled from the filtrate, and the mixture was extracted with hot benzene. The yield of (IIIa) was 0.3 g (90%); mp 211-213°C (from benzene). A mixed melting test with an authentic sample melted without depression.

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