ONE-ELECTRON OXIDATION OF 1,3,5-TRIARYL-2-PYRAZOLINES BY ANTIMONY PENTACHLORIDE

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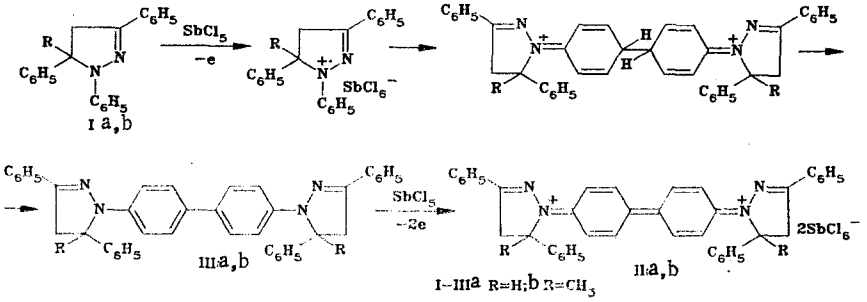
UDC 547.778:542.943:541.515

Upon reaction of 1,3,5-triphenyl- and 1,3,5-triphenyl-5-methyl-2-pyrazolines with antimony pentachloride in acetonitrile they undergo oxidation to cation radicals, which subsequently undergo rapid dimerization at the para positions of the N-phenyl groups. The final products are 4,4'-bis(3,5-diphenyl-2-pyrazolin-1-ia)- and 4,4'-bis(3,5-diphenyl-5-methyl-2-pyrazolin-1-ia)bis(cyclohexa-2,5-dienylidene) hexachloroantimonates.

Heterocyclic cation radicals are chiefly of interest as one of the active forms of heterocyclic compounds that develops in the one-electron oxidation of the latter [1]. Cation radicals are definite intermediates of many chemical, photochemical, and biochemical transformations of heterocycles; in this connection, stable cation radicals should be regarded as models of their more reactive (and, therefore, less accessible for study) analogs. Of particular interest are those cases in which the cation radical is sufficiently active to undergo further transformations and, at the same time, there is no doubt of the very fact of its formation.

In the present research we studied the one-electron oxidation of 1,3,5-triphenyl- (Ia) and 1,3,5-triphenyl-5-methyl-2-pyrazolines (Ib). Pyrazolines of this type have relatively low electrochemical-oxidation potentials [2], which indicates their relatively high reducing power and ease of conversion to cation radicals. As the one-electron oxidizing agent we selected antimony pentachloride, for which rather pronounced oxidizing properties are characteristic [3].

The action of antimony pentachloride on solutions or suspensions of pyrazolines Ia,b in acetonitrile gives dark-blue reaction solutions, from which almost black crystals of salts, which were identified as dicationic hexachloroantimonates IIa,b gradually precipitate. These salts are formed as a result of consecutive reactions, including, in particular, oxidation of the starting pyrazolines to cation radicals and their subsequent dimerization:



As previously established in [2], similar transformations also take place in the anode oxidation of 1-phenyl-2-pyrazolines. However, the salts of the dications were not isolated in the individual state in this case.

Salts IIa,b are highly reactive substances that dissolve in acetonitrile to give blue solutions and are decomposed by the action of a number of other solvents [dimethylformamide

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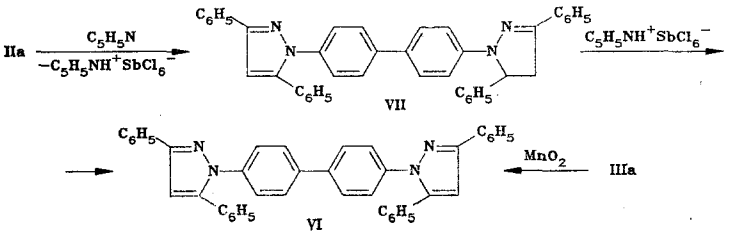
0009-3122/85/2104-0461$09.50

(DMF), dimethyl sulfoxide (DMSO), alcohol, and acetone]. In the reduction of hexachloroantimonate IIa with zinc dust it is reasily converted to the known [2] 4,4'-bis(3,5-diphenyl-2-pyrazolin-1-yl)diphenyl (IIIa). The reduction of salt IIb proceeds similarly.

It should be noted that the cation radicals of Ia,b, like the pyrazolines themselves, are racemic mixtures and, consequently, the IIIa,b formed in the dimerization of the cation radicals, as well as salts IIa,b, should exist in the form of diastereomers, viz., the meso form and the racemate. In fact, we were able to separate IIIa into two diastereomers, viz., bright-yellow IV in the crystalline state, which is only slightly soluble in benzene, and pale-yellow V, which is considerably more soluble. Both isomers have green fluorescence, have similar electronic spectra and, upon reaction with manganese dioxide, undergo dehydrogenation to the same compound, viz., 4,4'bis(3,5-diphenyl-1-pyrazolyl)diphenyl (VI). This compound was also obtained by treatment of salt IIa with pyridine. The essence of the latter reaction evidently consists in deprotonation of the starting salt by pyridine to give 4-(3,5-diphenyl-2-pyrazolin-1-yl)-4'-(3,5-diphenyl-1-pyrazolyl)diphenyl (VII) and subsequent dehydrogenation of this compound by the pyridinium hexachloroantimonate that is formed in the first step of the reaction:



This scheme is in agreement with the ability of the pyridinium hexachloroantimonate—pyridine system to dehydrogenate pyrazolines, which was established in the case of pyrazoline Ia and 1-(p-carboxyphenyl)-3,5-diphenyl-2-pyrazoline. Upon reaction with a solution of pyridinium hexachloroantimonate in pyridine these compounds are converted to the corresponding pyrazoles in good yields (also see our preliminary communication [4]).

In all likelihood, the dehydrogenation of pyrazolines by the $C_5H_5NH^+SbCl_6^-$—C_5H_5N system commences with their oxidation to cation radicals, the conversion of which to pyrazoles takes place under the influence of pyridine as the deprotonating agent and excess oxidizing agent.

As we have already noted, in media that do not contain proton acceptors the principal pathway of the transformations of the cation radicals of pyrazolines is their dimerization. Compound IIIa, rather than 1,3,5-triphenylpyrazole, was therefore obtained when the reaction of pyrazoline Ia with pyridinium hexachloroantimonate was carried out in chloroform. A similar effect of pyridine on the dehydrogenation of pyrazolines was also observed in their anode oxidation [5] and was also explained by the intermediate formation of cation radicals of the pyrazolines.

Thus the results presented in the present paper and the literature data make it possible to conclude that 1,3,5-triaryl-2-pyrazolines are quite easily converted to unstable cation radicals both by chemical oxidation and by electrochemical oxidation. In media that do not contain proton acceptors (acetonitrile, chloroform) the step involving one-electron oxidation is interlinked with the step involving dimerization of the cation radicals, which leads to the formation of 4,4'-(dipyrazolin-1-yl)diphenyls. At the same time, in a proton-acceptor medium the final products of the transformation of the cation radicals of pyrazolines are the corresponding pyrazoles.

EXPERIMENTAL

The electronic spectra were recorded with a Specord MK-40 spectrometer. The IR spectra of mineral oil suspensions of the compounds were recorded with a Specord 71-IR spectrometer. The PMR spectrum was recorded with a Tesla BS-487C spectrometer (60 MHz) in trifluoroacetic acid with hexamethyldisiloxane (HMDS) as the internal standard.

1,3,5-Triphenyl-2-pyrazoline (Ia). A mixture of 12.3 g (59 mmole) of benzalacetophenone, 6.3 g (58.8 mmole) of phenylhydrazine, 5 ml of acetic acid, and 50 ml of alcohol was refluxed for 40 min, after which 6 ml of concentrated hydrochloric acid was added, and the mixture was

heated for another 30 min. It was then cooled, and the precipitated pyrazoline Ia was removed by filtration and dried to give 13.5 g (77%) of a product with mp 136-137°C [6]. No melting point depression was observed for a mixture of this product with a genuine sample.

1,3,5-Triphenyl-5-methyl-2-pyrazoline (Ib). This compound, with mp 179-180°C (from benzene–alcohol), was obtained in 78% yield by a similar method from dypnone and phenylhydrazine. Found, %: C 84.3, H 6.6, N 9.3. $C_{22}H_{20}N_2$. Calculated, %: C 84.6, H 6.5, N 9.0.

1-(p-Carboxyphenyl)-3,5-diphenyl-2-pyrazoline. A mixture of 10.4 g (49.9 mmole) of benzylideneacetophenone, 7.6 g (50 mmole) of p-carboxyphenylhydrazine, 5 ml of acetic acid, 2 ml of concentrated HCl, and 45 ml of propanol was refluxed for 30 min, after which it was cooled to room temperature. The precipitated pyrazoline was removed by filtration, washed with 15 ml of propanol, and dried to give 13.4 g (78%) of a product with mp 226-228°C (from acetic acid). Solutions in chloroform had blue fluorescence. IR spectrum: 698 (s), 770 (s), 845 (m), 870 (m), 1110 (m), 1137 (s), 1180 (s), 1288 (s), 1410 (s), 1509 (m), 1530 (s), 1603 (vs), and 1682 cm^{-1} (vs). Found, %: C 76.8, H 5.1, N 8.3. $C_{22}H_{18}N_2O_2$. Calculated, %: C 77.2, H 5.3, N 8.2.

Pyridinium Hexachloroantimonate. A solution of 5.3 g (17.7 mmole) of antimony pentachloride in 10 ml of chloroform was added with stirring to a solution of 2 g (17.3 mmole) of pyridine hydrochloride in 30 ml of dry chloroform. After 5 min, the white precipitate of pyridinium hexachloroantimonate was removed by filtration, washed with chloroform, and dried to give 6.5 g (90%) of product. Found, %: N 3.7. $C_5H_6Cl_6NSb$. Calculated, %: N 3.4.

4,4'-Bis(3,5-diphenyl-2-pyrazolinia)bis(cyclohexa-2,5-dienylidene) Hexachloroantimonate (IIa). A suspension of 2.5 g (8.4 mmole) of pyrazoline Ia in 20 ml of acetonitrile was added with stirring in the course of 15 min to a solution of 6 g (20.1 mmole) of antimony pentachloride in 20 ml of acetonitrile. After 15 min, the precipitated salt IIa was removed by filtration and washed with acetonitrile to give 5 g (94.7%) of product. Found, %: C 40.1, H 3.0, Cl 30.0. $C_{42}H_{34}Cl_{12}N_4Sb_2$. Calculated, %: C 40.2, H 2.7, Cl 33.6.

4,4'-Bis(3,5-diphenyl-5-methyl-2-pyrazolinia)bis(cyclohexa-2,5-dienylidene) Hexachloroantimonate (IIb). This compound was similarly obtained in 54% yield from pyrazoline Ib and antimony pentachloride. Found, %: C 40.6, H 3.6, Cl 33.3. $C_{44}H_{38}Cl_{12}N_4Sb_2$. Calculated, %: C 40.9, H 3.1, Cl 32.9.

4,4'-Bis(3,5-diphenyl-2-pyrazolin-1-yl)diphenyl (IIIa). A mixture of 1.8 g (1.4 mmole) of salt IIa, 1.8 g (27.5 mmole) of zinc dust, and 20 ml of tetrahydrofuran (THF) was stirred for 10 min, after which it was treated with 40 ml of water, and the precipitate was removed by filtration, dried, and extracted with 50 ml of hot chloroform. The chloroform was removed by distillation to give 0.8 g (89%) of IIIa. This compound was separated into diastereomers by recrystallization from benzene, during which 0.35 g (39%) of virtually pure bright-yellow diastereometer IV, with mp 265-268°C (from benzene), precipitated. IR spectrum: 698 (s), 709 (s), 718 (s), 766 (s), 805 (m), 820 (s), 880 (s), 880 (s), 918 (w), 1080 (m), 1113 (m), 1128 (m), 1147 (s), 1245 (m), 1262 (m), 1282 (m), 1325 (s), 1335 (s), 1346 (s), 1500 (s), 1540 (m), 1580 (m), and 1605 cm^{-1} (s). UV spectrum ($CHCl_3$): λ_{max} 394 nm. Found, %: C 84.2, H 5.9, N 9.2. $C_{42}H_{34}N_4$. Calculated, %: C 84.5, H 6.1, N 9.4.

The residue (0.45 g) obtained by evaporation of the mother liquor contained chiefly pale-yellow diastereomer V, which was purified by repeated reprecipitation from solution in THF by means of alcohol and had mp 266-269°C. IR spectrum: 680 (s), 700 (s), 760 (s), 820 (s), 873 (m), 990 (m), 1025 (m), 1070 (m), 1090 (s), 1135 (m), 1240 (m), 1300 (m), 1320 (s), 1355 (m), 1500 (s), and 1618 cm^{-1}. UV spectrum ($CHCl_3$): λ_{max} 394 nm. Found, %: C 84.4, H 6.0, N 9.6. $C_{42}H_{34}N_4$. Calculated, %: C 84.5, H 6.1, N 9.4. Compounds IV and V were identical to the stereoisomers obtained by separation of 4,4'-bis(3,5-diphenyl-2-pyrazolin-1-yl)diphenyl [2] by the method described above.

4,4'-Bis(3,5-diphenyl-5-methyl-2-pyrazolin-1-yl)diphenyl (IIIb). The reduction of salt IIb was carried out similarly to give diphenyl IIIb, with mp 255-259°C (from DMF), in 86% yield. Found, %: C 84.9, H 6.4, N 8.8. $C_{44}H_{38}N_4$. Calculated, %: C 84.9, H 6.2, N 9.0.

4,4'-Bis(3,5-diphenyl-1-pyrazolyl)diphenyl (VI). A) A mixture of 0.6 g (1 mmole) of IV (or V), 3.5 g (40 mmole) of manganese dioxide, and 40 ml of chloroform was refluxed for 1 h, after which it was filtered, and the filtrate was evaporated to give 0.5 g (84%) of VI with mp 278-279°C (from benzene) [5]. IR spectrum: 700 (s), 770 (s), 835 (s), 868 (m), 920 (m), 965 (m), 985 (s), 1018 (m), 1036 (w), 1080 (m), 1115 (w), 1190 (m), 1312 (m), 1370 (s), 1418

(w), 1500 (s), 1545 (s), and 1600 cm^{-1} (w). PMR spectrum: 6.8-7.8 ppm (multiplet of aromatic protons). Found, %: C 85.6, H 5.6, N 9.8. $C_{42}H_{32}N_4$. Calculated, %: C 85.1, H 5.4, N 9.5.

B) A 0.5-g (0.4 mmole) sample of salt IIa was added with stirring in the course of 20 min to 10 ml of pyridine, after which the mixture was diluted with 15 ml of alcohol and 5 ml of water. The precipitate was removed by filtration, washed with water and alcohol, and dried. Compound VI was extracted by means of boiling benzene to give 0.2 g (87%) of a product with mp 277-278°C (from benzene). No melting-point depression was observed for a mixture of this product with a sample obtained by method A. Both samples were colorless crystalline substances that did not luminesce either in solutions or in the solid state.

1,3,5-Triphenylpyrazole. A solution of 0.7 g (2.3 mmole) of pyrazoline Ia in 5 ml of pyridine was added in the course of 10 min with stirring to a solution of 2.5 g (6.0 mmole) of pyridinium hexachloroantimonate in 25 ml of pyridine. The mixture was allowed to stand for 1 h and was then treated with 100 ml of water. The resulting precipitate was removed by filtration and dried, and the 1,3,5-triphenylpyrazole was extracted from it by means of hot chloroform to give 0.5 g (72%) of a product with mp 136-138°C (from alcohol). No melting-point depression was observed for a mixture of this product with a genuine sample [7].

1-(p-Carboxyphenyl)-3,5-diphenylpyrazole. This compound was similarly obtained in 86% yield by dehydrogenation of 1-(p-carboxy)-3,5-diphenyl-2-pyrazoline with pyridinium hexachloroantimonate but in the course of 2 h with refluxing of the reaction mixture. The product was obtained as colorless crystals with mp 216-218°C (from THF–dipropyl ether). Solutions of the compound in organic solvents did not luminesce. IR spectrum: 704 (s), 769 (s), 780 (m), 975 (s), 1178 (m), 1290 (s), 1315 (s), 1430 (s), 1600 (s), 1682 (s), and 2800-2950 cm^{-1}. Found, %: C 77.1, H 5.0, N 7.9. $C_{22}H_{16}N_2O_2$. Calculated, %: C 77.6, H 4.7, N 8.2.

Dehydrodimerization of Pyrazoline Ia by the Action of Pyridinium Hexachloroantimonate. A mixture of 0.60 g (1 mmole) of pyrazoline Ia, 2.20 g (5.4 mmole) of pyridinium hexachloroantimonate, and 20 ml of chloroform was stirred thoroughly for 20 min, after which 3 g (46 mmole) of zinc dust was added, and stirring was continued until a persistent yellow color developed. The precipitate was removed by filtration, washed with 20 ml of alcohol, and extracted with 30 ml of hot chloroform. The solvent was removed to give 0.36 g (37%) of IIIa. For identification, it was separated into diastereomers by the method described above to give 0.15 g of isomer IV and 0.1 g of isomer V. The IR spectra of these compounds coincided with the spectra of genuine samples obtained by reduction of salt IIa by the method described above.

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