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BENZAZOLE DERIVATIVES

VI. Synthesis of some 2-Styrylbenzimidazoles and their quaternization

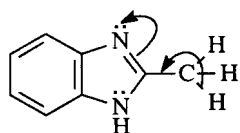
In this paper an alternative method for obtaining styrylbenzimidazolium iodides was described. Thus, some 1-methyl-2-styrylbenzimidazoles were synthesized by the condensation of 1,2-dimethylbenzimidazoles containing a mono- or di-substituted benzene ring ($X = \text{NO}_2, \text{Br}$), at their reactive 2-methyl group with aromatic aldehydes by heating at high temperature. Some of the 2-styrylbenzimidazoles were proved to be able to convert into benzimidazolium quaternary iodides by treating them with methyl iodide in an autoclave. The structures of the 2-styrylbenzimidazoles and corresponding iodomethyl derivatives were investigated by IR and ¹H-NMR spectral measurements. The obtained compounds are valuable due to their structures of polyenic dyes, with a photoexcitable ethylene bond.

Key words: Labile methyl group, Thermal condensation, Quaternization, 2-styrylbenzimidazoles, 2-styrylbenzimidazole iodomethylates.

In the literature there are numerous examples of reactions involving mobile H atoms from the methyl and methylene groups of some heterocyclic compounds. The most common ones are reactions with aromatic aldehydes and other carbonylic compounds, p-NDMA, the azoic coupling reaction and the synthesis of methylene bases or cyanine dyes.

Our interest was directed to benzimidazoles containing a reactive 2-methyl group, some of them substituted in the benzene ring and their reaction with aromatic aldehydes that are para-substituted with electron-withdrawing or donating groups.

Previously, Porai-Koshitz and Murawitch [1] studied the reactivity of 2-methyl-1H-benzimidazole and its condensing reactions with aldehyde, isatin, phenyl-antraquinone and phthalic anhydride. They estimated that the mobility of H atoms in 2-methylbenzimidazole is low, thus requiring energetic reaction parameters.

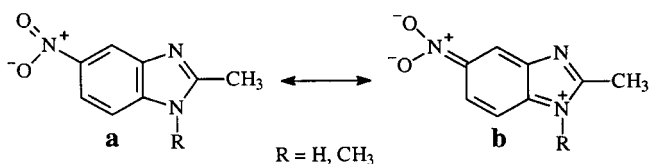


The weak reactivity of the methyl group was explained by the scant polarization due to the free electron pair of the nitrogen atom. The electronic shift was

also reduced due to the +M effect of the imino (NH) group that partially compensated the positive charge on C-2.

Kym and Jurkowski [2] found for the first time that 2-methyl-5-nitro-benzimidazole could condense with p-nitrobenzaldehyde by heating the mixture at 180–210°C, thus being obtaining a styryl intermediate which, converted into a diamine, was useful for the preparation of some azo dyes.

Similar condensations were performed with 1,2-dimethyl-5-nitrobenzimidazole [2,3]. These reactions were carried out due to the increased reactivity of the 2-methyl group of the 5-nitro derivatives which is caused by the shifting of the unshared electrons on the N-1 atom to the nitro group. In the absence of internal mesomerism in the imidazole ring, hyperconjugation between the C-H bonds and the C=N double bond is completed entirely.



Puskina et al. [4] performed condensations with 2-methyl and 1,2-dimethyl-1H-benzimidazoles even without activation due to the electrophilic nitro group. The reaction was performed at high temperatures in the presence of boric acid.

It was noticed that the yields of the condensation reaction of 2-methyl-1H-benzimidazole were 30–40% higher than those for the corresponding 2-methyl-benzoxazoles, which suggests an increased reactivity of the benzimidazoles.

Recently, a series of 2-styrylbenzimidazoles were obtained using a microwave assisted solvent-free method [5,6], using Ac₂O as the catalyst. A new efficient and convenient phase-transfer catalysed methylation procedure for 2-styryl-benzimidazoles has also been developed [7].

The aim of the investigations carried out in the present study was to synthesise some new 2-styrylbenzimidazoles in order to study their properties, especially their ability to form iodomethylates.

RESULTS AND DISCUSSION

In a previous paper [8], the synthesis of some 1-methyl-2-styryl-benzimidazole iodomethylates, starting

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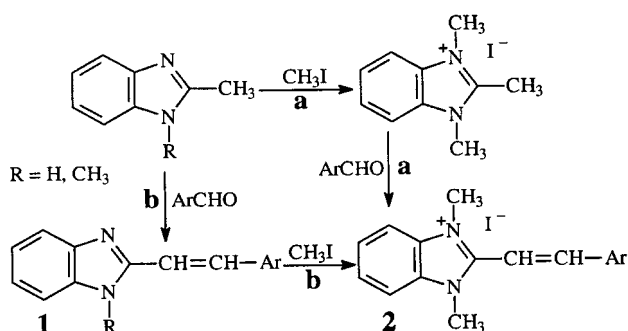
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from 1,2,3-trimethylbenzimidazolium iodide and its derivatives substituted in the benzene ring ($X = \text{NO}_2, \text{Br}, \text{Cl}, \text{CH}_3$), by the condensation with aromatic aldehydes was reported.

It is also of interest to prepare 2-styryl substituted benzimidazolium salts by applying another reaction scheme. The first stage was thought to be the condensation of the reactive 2-methyl group in the substituted and unsubstituted benzimidazoles with aromatic aldehydes. The resulting styrylbenzimidazoles would then be submitted to quaternization with methyl iodide to give the quaternary salts **2**.

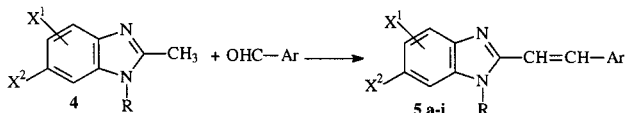
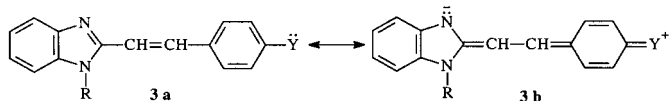
The reaction scheme 1 describes the previous procedure (path **a**) [8] and the new procedure (path **b**), in which 2-styrylbenzimidazoles are formed as intermediates convertible into quaternary salts.



Scheme 1. Reaction pathways for the synthesis of quaternary 2-styrylbenzimidazolium salts

Practically, the stages of the path **a** are to be found in path **b**, but in a reversed order. The details for path **a**, such as reactant and the substituent effects, reaction parameters, characteristic and spectral measurements of the final products were presented in a previous paper [8].

These two synthesis paths were applied in order to choose the most convenient one with regards to the reaction conditions, yields and product purity. At the same time, it was also taken into account that path **b** offers an alternative synthetic route for the synthesis of new 2-styrylbenzimidazolium salts, which would not be accessible by direct condensation. The study of 2-arylvinylbenzimidazoles as intermediates in the above mentioned reaction scheme was also of interest. They are, in fact, polyenic dyes of the structure **3a** which under the influence of the internal polar groups can adopt the amphionic limit form **3b**, which is similar to non-ionic dyes known as merocyanines.



Comp.	R	X ¹	X ²	Ar
5a	H	H	H	O ₂ NC ₆ H ₄
5b	H	4-Br	H	O ₂ NC ₆ H ₄
5c	H	4-Br	6-Br	O ₂ NC ₆ H ₄
5d	H	5-NO ₂	H	O ₂ NC ₆ H ₄
5e	CH ₃	5-NO ₂	H	(O ₂ N) ₂ C ₆ H ₃
5f	CH ₃	5-NO ₂	H	H ₃ CC ₆ H ₄
5g	CH ₃	5-NO ₂	6-NO ₂	O ₂ NC ₆ H ₄
5h	CH ₃	5-NO ₂	6-NO ₂	H ₃ CC ₆ H ₄
5i	CH ₃	5-NO ₂	6-NO ₂	H ₃ COC ₆ H ₄

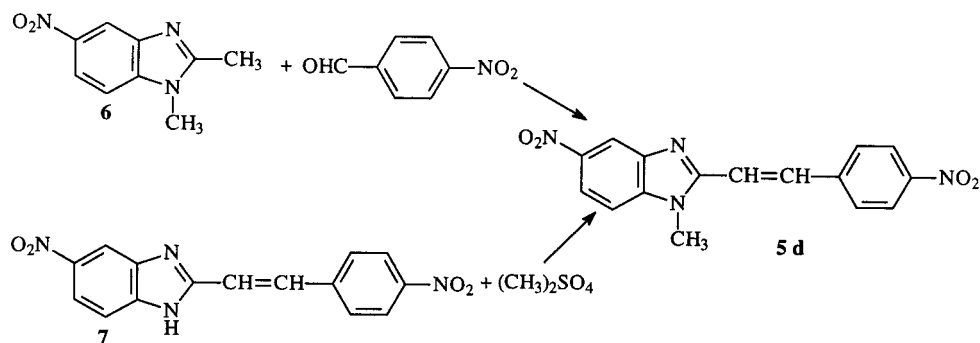
Scheme 2. Reaction scheme for obtaining 2-styrylbenzimidazoles

p-Nitrobenzaldehyde was taken for most of the reactions since it is reactive and behaves well under heating, which is also valid for 2,4-dinitrobenzaldehyde. The p-tolyl and p-anisic aldehydes are more volatile, so they were heated carefully at high temperatures. The synthesis was carried out with an equimolar ratio of the reagents at 170–180°C for a reaction time of 1–1.5 h. In some syntheses, the temperature was raised to 200–210°C. That dehydration occurred could be observed by the drops on the flask neck. Some of the condensations were performed both thermally and by refluxing in acetic anhydride. Acetic anhydride was applied with 2-methyl-1H-benzimidazole and 5,6-nitro-1,2-dimethyl-1H-benzimidazole, in reaction with p-nitro-, p-tolyl- and p-methoxybenzaldehydes. After heating for 5–6 h, the initial benzimidazoles contaminated with small amounts of the styryl derivatives separated on cooling. The melt obtained by thermal condensation was processed by dissolving in pyridine, acetonitrile or acetone (a preference for dipolar aprotic solvents was noticeable). o-Xylene is also a suitable solvent. The solid was often dispersed in methanol or in diethyl ether.

Compound **5d** was prepared by two methods: the condensation of 5-nitro-1,2-dimethyl-1H-benzimidazole **6** with p-nitrobenzaldehyde at high temperature and the methylation of 2-styrylbenzimidazole **7** with dimethylsulphate, as given in Scheme 3.

The styrylic compounds **5** are coloured in different shades from yellow-orange to brick-red. The vinylic group inserted between the benzimidazole ring and the aryl moiety produces an extended conjugated system

Preparation of 2-methylbenzimidazoles. In the first condensation stage, the reaction between 2-methyl-



Scheme 3. The preparation of 1-methyl-5-nitro-2-(p-nitrostyryl)benzimidazole

Table 1. 2-Styrylbenzimidazoles obtained by termical condensation

Comp.	M.p.	Colour	Purification Solvent	Molecular Formula	%N	
					calc.	exp.
5a	235–237	mustard	ethanol	C ₁₅ H ₁₁ N ₃ O ₂	15.85	15.92
5b	236–238	brick-red	methanol	C ₁₅ H ₁₀ N ₃ O ₂ Br	12.21	12.35
5c	252–254	orange	methanol	C ₁₅ H ₉ N ₃ O ₂ Br ₂	9.93	10.04
5d	258–260	yellow-orange	ethanol	C ₁₆ H ₁₂ N ₄ O ₄	17.28	17.40
5e	280–282	yellow-brown	acetonitrile	C ₁₆ H ₁₁ N ₅ O ₆	18.97	19.11
5f	238–240	yellow-brown	acetonitrile	C ₁₇ H ₁₅ N ₃ O ₂	14.33	14.45
5g	280–282	vivid yellow	acetone	C ₁₆ H ₁₁ N ₅ O ₆	18.97	19.11
5h	240–242	yellow-green	methanol	C ₁₇ H ₁₄ N ₄ O ₄	16.57	16.69
5i	261–263	lemon yellow	pyridine	C ₁₇ H ₁₄ N ₄ O ₅	15.82	15.93

which shifts the absorption to longer wavelengths, in the visible range. The nitro groups are chromophores and contribute to the appearance of colour. The presence of bromine in the styryl derivatives **5b** and **5c** does not produce visible colouring effects, which are given especially by the nitro group. Table 1 present some characteristics of the synthesized compounds.

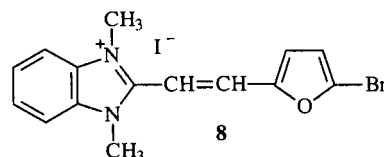
Theoretically, the 5-nitro- and 5,6-dinitrobenzimidazoles should be more reactive at the 2-methyl group, resulting in easier giving the formation of styryl derivatives.

Practically, the condensation was found to proceed also in the absence of the nitro group. Compound **5a** (X¹, X² = H), as well as **5b** and **5c** (X = Br, effect +M) are also reactive with aromatic aldehydes. The yields show some variation which seems to depend more on the solubility factor and less on the reactivity of the methyl group in the substrate.

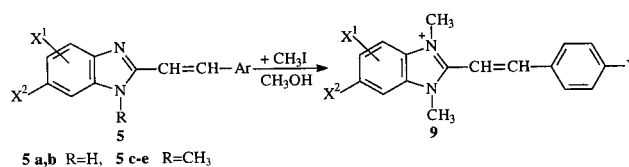
The structure of the styryl derivatives was investigated by means of elemental analysis (N, %) and spectral measurements (IR and NMR).

Transformation of 2-styrylbenzimidazoles into quaternary salts. The transformation of 2-styrylbenzimidazoles into quaternary salts has never been discussed before. Pojarski et al. [9] performed such a reaction by heating a furylbenzimidazole with methyl benzenesulphonate at 130°C for 0.5 h and then treating

the reaction mixture with a solution of KI whereby the iodide **8** resulted.



In the present study some of the thermally prepared 2-styrylbenzimidazoles **5** were selected and submitted to reaction with methyl iodide at 120°C in an autoclave, according to Scheme 4, whereby the 2-styryl substituted salts **9** were obtained.

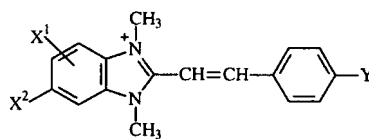


5 a,b R=H, **5 c-e** R=CH₃

Compd.	X ¹	X ²	Y
9a	H	H	NO ₂
9b	NO ₂	H	NO ₂
9c	NO ₂	H	CH ₃
9d	NO ₂	NO ₂	NO ₂
9e	NO ₂	NO ₂	CH ₃

Scheme 4. Transformation of arylvinylbenzimidazoles into quaternary salts

Table 2. Quaternized 2-styrylbenzimidazoles



Comp.	Colour	M.p., °C	Molecular Formula	% N	
				calc.	exp.
9a	rusty-brown	255-257	C ₁₇ H ₁₆ N ₃ O ₁ I	10.37	10.49
9b	yellow-red	280-281	C ₁₇ H ₁₅ N ₃ O ₄ I	12.02	12.15
9c	kaki	272-274	C ₁₈ H ₁₈ N ₃ O ₂ I	9.66	9.77
9d	rusty-brown	275-277	C ₁₇ H ₁₄ N ₃ O ₆ I	13.69	13.81
9e	yellow-orange	228-230	C ₁₈ H ₁₇ N ₄ O ₄ I	11.67	11.79

Since the solubility of some of the styryl derivatives **5** in methanol is rather low, other solvents (dioxan, benzene) were also tested for the quaternization stage. However, methanol was finally chosen because it also participates in the alkylation reaction. A styrylbenzimidazole:methanol:CH₃I ratio of 1:10:1.5, was employed, the amounts of solvent and iodide being higher than in the reaction previously performed with 2-methyl-1H-benzimidazoles [8].

According to Fischer et al. [10] the higher are the temperature and the excess of methyl iodide, the higher are the amounts of periodide formed in the alkylation reactions carried out under pressure. For this reason, the temperature was not raised above 120-130°C and the amount of methyl iodide was restricted to 1.5 mols.

When the autoclave was opened, it was noticed that the yellow iodide crystals were mixed with brown crystals of periodides as impurities. They were purified from water or from aqueous ethanol.

The quaternary salts synthesized by the path b, as well as some of their characteristic properties, are given in Table 2.

The quaternary salts **9** had melting points and spectral characteristics identical with these of the corresponding substituted derivatives prepared by path a.

A comparison between the IR spectra of the 1-methyl-2-(p-styryl)-benzimidazole iodomethylate prepared by paths **a** and **b** revealed a good coincidence of the corresponding absorptions in the two spectra, which proves that both the **a** and **b** paths led to the same compound. The conclusion can be drawn that the two procedures are applicable with comparable efficiencies. The thermal condensations are somehow advantageous, the yields being higher, due to the finally product separating in the solid state which can be facily purified. Although the procedure involving the 1,2,3-trimethylbenzimidazolium salts proceeds easy by refluxing in ethanol, the separation is rather difficult due to the solubility of both the quaternary styryl derivatives and some by-products in the reaction medium. On the other hand, the purification of iodide from its mixture with periodide is facilitated in this way.

The quaternization yields are convenient by both paths and, hence, the selection of which procedure should be employed must be analysed in each case individually.

One essential observation deserves to be mentioned, i.e. the 5-nitro- and 5,6-dinitro- substituted quaternary salts suffer under the action of p-nitrobenzaldehyde not only the condensation but also some side reactions occur which bring difficulties in the synthesis. This is why some of the trials preparations of styryl derivatives starting from nitro-substituted salts, regarded as the most reactive, and p-nitrobenzaldehyde failed. The corresponding p-nitrostyryl derivatives were obtained by path b, which proved to be suitable for these syntheses.

EXPERIMENTAL

The melting points were determined using a Boetius microscope and are uncorrected. Microanalyses were performed at the "Petru Poni" Macromolecular Chemistry Institute, Iasi. IR spectra were recorded on a Digilab Scimitar Series spectrometer, in KBr pellets, while the NMR spectra were registered on a Brücker WM 400 spectrometer, in DMSO-d₆ solution.

Synthesis of 2-styrylbenzimidazoles

2-(p-Nitrostyryl)-1H-benzimidazole (5a): 2-Methylbenzimidazole (2.64 g; 0.02 mols) and p-nitrobenzaldehyde (3.02 g; 0.02 mols) were thorough a mixed and heated on a silicone bath. When a temperature of 140°C was reached, the mixture melted, and at 150-160°C, water elimination was observed by water drops appearing on the flask neck. After 1 hour, the reaction mixture became viscous and water elimination ceased. Finally, the temperature increased to 200-210°C and held for 0.5 hours.

The reaction product was purified by dissolving in pyridine or acetonitrile, precipitation with water and resolving by heating. The substances were treated with warm methanol in order to remove the soluble impurities. A mustard product (4.7 g) was obtained (η = 88%). M. p. = 235-237°C.

The following compounds were obtained through the same procedure.

4-Bromo-2-(p-nitrostyryl)-1(3)H-benzimidazole (5b):

The red coloured solid was boiled in methanol. A brown substance remained on the filter and a brick-red product separated from the yellow-red filtrate. ($\eta = 87\%$). M.p. = 236–238°C.

4,6-Dibromo-2-(p-nitrostyryl)-1(3)H-benzimidazole (5c):

The brown solid was boiled in methanol. The insoluble fraction was dissolved in acetone and precipitated with water. ($\eta = 89\%$). M.p. = 252–254°C.

1-Methyl-2-(p-nitrostyryl)-5-nitro-1H-benzimidazole (5d):

The product was prepared from 1,2-dimethyl-5-nitrobenzimidazole and p-nitrobenzaldehyde (method a). A yellow-orange solid was obtained, which was purified from ethanol. ($\eta = 80\%$). M.p. = 258–260°C.

The method (b) was applied in which 2-(p-nitrostyryl)-5-nitro-benzimidazole, obtained according to Kym and Jurkowski [2], was N-1 methylated with dimethyl sulfate.

1-Methyl-2-(2,4'-dinitrostyryl)-5-nitro-1H-benzimidazole (5e):

The styryl derivate was obtained from 1,2-dimethyl-5-nitrobenzimidazole and 2,4-dinitrobenzaldehyde. The dark brown substance was redissolved in hot acetonitrile, in order to remove the insoluble impurities. The product could also be purified by dissolving in pyridine and precipitation with water or by boiling with acetone. In the last case an insoluble yellow-brown fraction was separated ($\eta = 90\%$), having M.p. = 283–285°C.

1-Methyl-2-(p-methylstyryl)-5-nitro-1H-benzimidazole (5f):

The condensation took place between 1,2-dimethyl-5-nitrobenzimidazole and toluic aldehyde.

The obtained solid, after washing with petroleum ether, was dissolved in warm acetonitrile. On cooling, yellow crystals separated which were filtrated and retreated with warm acetonitrile. The insoluble fraction was retained. The substance can also be purified from ethanol, toluene or o-xylene. ($\eta = 86\%$). M.p. = 238–240°C.

1-Methyl-2-(p-nitrostyryl)-1H-5,6-dinitrobenzimidazole (5g): The yellow solid was treated with warm methanol or acetone and a vivid yellow insoluble fraction separated. ($\eta = 89\%$). M.p. = 280–282°C.

1-Methyl-2-(p-methylstyryl)-1H-5,6-dinitrobenzimidazole (5h): The yellow solid was washed with petroleum ether, ground and treated with hot diethyl ether. The product was well dispersed, filtered and dissolved in boiling methanol. One part dissolved in the methanol and crystallised on cooling. ($\eta = 85\%$). M.p. = 240–242°C. The insoluble fraction was more impure.

1-Methyl-2-(p-methoxystyryl)-5,6-dinitro-1H-benzimidazole (5i): The yellow solid mass, after grounding and washing with petroleum ether, was dissolved in hot pyridine. On cooling a lemon-yellow product separated, which was filtered and washed with diethyl ether. ($\eta = 90\%$). M.p. = 261–263°C.

The NMR spectra confirm the structure of the benzimidazoles, as presented in Table 3.

Of great importance is the deshielding of the 3',5' and 4,6 protons by the nitro group, which shifts the signals downfields. The ethylenic protons are situated among the aromatic ones at variable d values depending on the structure. Their coupling constant is high.

Table 3. ¹H-NMR special data of the styryl derivatives obtained by thermal method

Comp.	Characteristic bands DMSO, δ (ppm), J(Hz)
5a	7,21–7,22 (d, 2H, H-5, H-6, $J_o=2,001$); 7,44–7,48 (d, 1H, =CH-Ar, $J_o=16,405$); 7,58 (s, 2H, H-4, H-7); 7,74–7,78 (d, 1H, Het-CH=, $J_o=16,405$); 7,90–7,92 (d, 2H, H-2', H-6', $J_o=8,403$); 8,23–8,25 (d, 2H, H-3', H-5', $J_o=8,403$); 12,79 (s, 1H, NH).
5b	7,34–7,36 (d, 1H, H-6, $J_o=8,403$); 7,43–7,47 (d, 1H, =CH-Ar, $J_o=16,405$); 7,53–7,55 (d, 1H, H-5, $J_o=8,403$); 7,77–7,81 (d, 1H, Het-CH=, $J_o=16,405$); 7,81–7,83 (d, 1H, H-7, $J_o=8,403$); 7,93–7,95 (d, 2H, H-2', H-6', $J_o=8,403$); 8,25–8,27 (d, 2H, H-3', H-5', $J_o=8,803$); 12,98 (s, 1H, NH).
5c	7,35–7,37 (d, 1H, H-5, $J_o=8,003$); 7,49 (s, 1H, NH); 7,54–7,56 (d, 1H, H-7, $J_o=8,803$); 7,83–7,85 (d, 1H, =CH-Ar, $J_o=10,8$); 7,95–7,99 (m, 3H, Het-CH=, H-2', H-6', $J_o=8,403$, $J_o=10,8$); 8,27–8,29 (d, 2H, H-3', H-5', $J_o=8,403$).
5d	4,07 (s, 3H, N-CH ₃); 7,84–7,81 (s, 2H, Het-CH=, H-6'); 8,18 (s, 2H, =CH-Ar, H-4, H-7); 8,50 (s, 1H, H-6); 8,57 (s, 2H, H-4, H-5');
5f	2,35 (s, 3H, 4'-CH ₃); 4,02–3,98 (d, 3H, N-CH ₃); 7,26–7,25 (d, 2H, H-3', H-5'); 7,47–7,40 (m, 1H, =CH-Ar, $J_o=11,6$); 7,72–7,70 (d, 3H, H-7, H-2', H-6'); 7,94–7,87 (m, 1H, Het-CH=, $J_o=11,2$); 8,12–7,01 (m, 1H, H-6, $J_o=8,802$); 8,43–8,42 (d, 1H, H-4).
5g	4,04–4,08 (d, 3H, N-CH ₃ , $J_o=14,4$); 7,73–7,77 (dd, 2H, H-2', H-6', $J_o=6,4$); 7,95–8,16 (m, 3H, =CH-Ar, H-3', H-5', $J_o=15,6$, $J_o=6,4$); 8,25 (s, 2H, H-4, H-7); 8,43–8,47 (d, 1H, Het-CH=, $J_o=15,6$).
5h	2,61 (s, 3H, CH ₃); 3,85 (s, 3H, N-CH ₃); 7,69–7,72 (d, 2H, H-3', H-5', $J_o=9,203$, $J_m=1,6$); 8,05–8,08 (dd, 1H, =CH-Ar); 8,11–8,14 (m, 2H, H-2', H-6', $J_o=9,203$); 8,39–8,43 (d, 2H, H-4, H-7, $J_o=2,006$); 8,51–8,56 (dd, 1H, Het-CH=, $J_o=12,8$).
5i	3,83 (s, 3H, N-CH ₃); 4,04 (s, 3H, O-CH ₃); 7,00–7,05 (s, 2H, H-3', H-5'); 7,39–7,42 (d, 1H, =CH-Ar, $J_o=12,8$); 7,72–7,76 (s, 1H, Het-CH=); 7,81 (s, 2H, H-2', H-6'); 7,93–7,96 (d, 1H, H-4); 8,12–8,13 (s, 1H, H-7).

Quaternization of 2-styrylbenzimidazoles

1-Methyl-2-(4'-nitrostyryl)-benzimidazole iodomethylate (9a): 2-(4'-Nitrostyryl)-benzimidazole (1.14 g; 4.33 mmols), methyl iodide (1.13 g; 0.5 ml; 8 mmols) and 10 ml methanol were heated in autoclave for 4 hours at 130°C. The obtained dark coloured solid was purified from water, whereby a rusty brown product separated. ($\eta = 78.28\%$). M.p. = 255–257°C.

The following products were obtained in a similar manner.

1-Methyl-2-(4'-nitrostyryl)-5-nitro-1H-benzimidazole iodomethylate (9b): A yellow-green product was obtained, which was been purified from water or aqueous ethanol. ($\eta = 67.66\%$). M.p. = 280–281°C.

1-Methyl-2-(4'-methylstyryl)-5-nitrobenzimidazole iodomethylate (9c): A rusty-brown product was obtained, which was purified from water and charcoal. A kaki substance separated. ($\eta = 56.45\%$). M.p. = 272–274°C.

1-Methyl-2-(4'-nitrostyryl)-5,6-dinitro-1H-benzimidazol iodomethylate (9d): A rusty-brown product was obtained, which was purified from ethanol. ($\eta = 79.48\%$). M.p. = 275–277°C.

1-Methyl-2-(4'-methylstyryl)-5,6-dinitro-1H-benzimidazole iodomethylate (9e): A rusty-yellow product was obtained, which purification from aqueous ethanol, became yellow-orange. ($\eta = 72\%$). M.p. = 228–230°C.

CONCLUSIONS

In this study an attempt was made to find a new, alternative method for preparing quaternary salts of

2-styrylbenzimidazoles. Thus, even though numerous papers exist in the literature on reactions between 2-methylbenzimidazole and aromatic aldehydes, the second step (the quaternization of 2-styrylbenzimidazoles) is completely new.

The obtained products have been compared with their analogues obtained by the "classical" method (condensation of benzimidazolium salts with aromatic aldehydes) and perfect agreements were achieved. The yields are comparable, but the described method has the advantage of enabling a larger range of styrylbenzimidazolium iodides to be synthesized.

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IZVOD

DERIVATI BENZAZOLA. VI. SINTEZA NEKIH 2-STIRILBENZIMIDAZOLA I NJIHOVA KVATERNIZACIJA

(Naučni rad)

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U ovom radu su analizirane alternativne mogućnosti sinteze i u potpunosti opisane u slučaju dobijanja stirilbenzimidazolijum jodida. Tako je pokazano da se, zagrevanjem na visokoj temperaturi, neki 1-metil-2-stirilbenzimidazoli mogu sintetizovati kondenzacijom sa aromatskim aldehidom na reaktivnoj 2-metil grupi 1,2-dimetilbenzimidazola, koji imaju mono- ili di-supstituisan prsten benzena (X=NO₂, Br). Dokazano je da je moguće neke 2-stirilbenzimidazole prevesti u benzimidazolijum kvaternerne jodide zagrevanjem u autoklavu u prisustvu metiljodida. Analizirane su, pomoću IR spektroskopije i ¹H-NMR, strukture 2-stirilbenzimidazola kao i odgovarajućih derivata dobijenih sa metiljodidom. Sintetizovana jedinjenja su vredna zbog svoje specifične strukture koja je karakteristična za polienske boje sa fotoeksitabilnom etilenskom vezom.

Ključne reči: Labilna metil grupa, Termijska kondenzacija, Kvaternizacija, 2-stirilbenzimidazoli, 2-stirilbenzimidazol jodometilati.