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SCIENTIFIC PAPER

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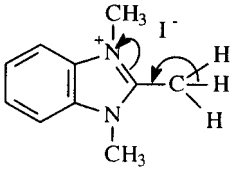
BENZAZOLE DERIVATIVES. V. THE REACTIVITY OF SOME 2–P–TOLYL– AND 2–P–METHYLSTYRYL– BENZIMIDAZOLIUM SALTS

The reactivity of the p–substituted methyl group in 1–methyl–2–p–tolyl–benzimidazolium and 1–methyl–2–p–methylstyrylbenzimidazolium iodides with p–nitroso–dimethylaniline (p–NDMA) and aromatic aldehydes was studied. According to literature data on the steric effects produced by the bulky N–I methyl group, the 2–p–tolyl substituted salt does not react with p–NDMA. On the other hand, 2–p–methylstyryl substituted salts give condensation reactions, similarly to 1,2,3–trimethylbenzimidazolium iodides. The compounds obtained from the reaction with aromatic aldehydes can be used as dyeing substances, photosensitizers or as dienic monomers, due to the conjugated chain from C–2.



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1,2,3–Trimethylbenzimidazolium iodide (1) and its derivatives mono– and di–substituted in the benzene ring are known to have a reactive 2–methyl group. The electron withdrawing effect (–I, hyperconjugation) of the immonium nitrogen atom with a positive charge causes labilization of the hydrogen atoms from the C–H bonds of the 2–methyl group.

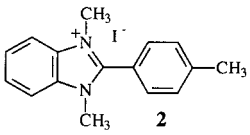
Electron transfer is partial because of the compensation of the positive charge through the internal mesomery between the two nitrogen atoms [1,2].

In previous papers [3–5] we showed that the benzimidazolium salts, like other heterocycles with quaternized nitrogen, give condensation reactions at the 2–methyl group with p–NDMA and aromatic aldehydes. Azomethynic and ethylenic compunds, having structures of azahemicyanine and hemicyanine dyes respectively have been obtained from these reactions.

We were interested to what extent the analogous quaternary salts having the methyl group more distant from the positive charge of the nitrogen atom (such as in 2–p–tolyl– and 2–p–methylstyryl benzimidazolium iodides) could give condensation reactions with p–NDMA and aromatic aldehydes.

RESULTS AND DISCUSSION

Examination of the 1–methyl–2–p–tolylbenzimidazolium– and 1–methyl–2– (p–methylstyryl) benzimidazolium iodides (2 and 3) shows that a styryl moiety consisting of a system of alternating simple and double bonds has been interposed between the methyl group and C–2 a phenyl ring.



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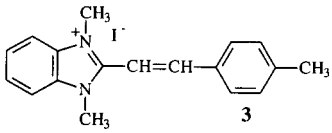

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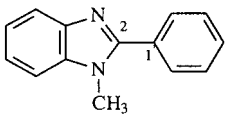
The system of conjugated bonds must be coplanar in order to transmit the influence of the positive charge to the methyl group.

Reactivity of 1–methyl–2–p–tolylbenzimidazole iodomethylate



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The literature confirms that the quaternized 2–phenyl–benzimidazole (2) or its N–1 methylated derivative (4) exhibit a steric hindrance at the sigma bond C^2–$C^{1'}$ that turns the phenyl ring away from coplanarity.

Catálan et al., made an extensive study on 2–phenyl benzimidazole and other benzazole conformations in the fundamental and excited state using UV–Vis and fluorescence spectral data and theoretical calculations [6]. According to those studies, the bulky methyl group increases the non–planarity of the fundamental state, generating some loss in π system conjugation. ^{1}H–NMR spectra also confirm that the phenyl ring is turned away from planarity [7].

Counting on a partial deviation from coplanarity of the phenyl ring with respect to the benzimidazole system, we thought that the reaction at the methyl group could occur using more severe reaction conditions.

In order to verify the above supposition, compound (2) was obtained according to reaction scheme 1.

o–Phenylenediamine reacted with p–tolylaldehyde leading to the Schiff base 5, which, then suffered an oxidative cyclization in nitrobenzene, giving the benzimidazole 6. In the literature, this compound has been synthetized by the Weidenhagen reaction [8]. Finally, the 2–p–tolyl–^{1}H–benzimidazole was quaternized with methyl iodide, under pressure, the iodomethylate 2 being thus obtained.

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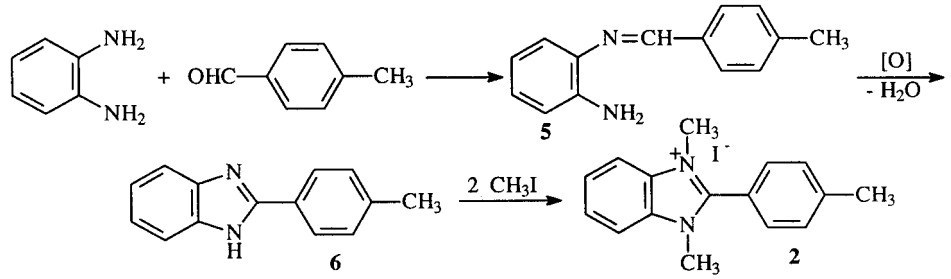


Scheme 1. Synthesis of 1-methyl-2-p-tolylbenzimidazole iodomethylate

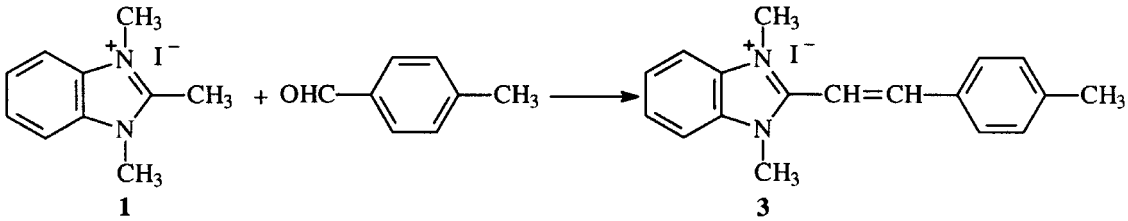
The reactivity of the salt 2 with p-nitrosodimethylaniline was then investigated.

Proceeding as for the quaternary 1,2,3-trimethylbenzimidazolium salts, equimolar amounts of 1-methyl-2-p-tolylbenzimidazole iodomethylate and p-NDMA, both dissolved in ethanol, vere refluxed for 2 hours, using pyperidine as a catalyst. During the heating, the solution colour darkened, thus concealing the green shade due to NDMA. After cooling and standing, a crystalline product separated that proved to be the unreacted quaternary salt, the initial amount being recovered almost completely.

The reactivity of the methyl group in 1-methyl-2-p-tolylbenzimidazole iodomethylate was thus confirmed to be considerably reduced, even canceled because of the steric effects.

Reactivity of 1-methyl-2-p-methyl-styrylbenyimidayole iodomethylate

The quaternary 2-p-methylstyryl substituted salt 3 was synthetised from 1,2,3-trimethyl- benzimidazolium iodide 1 and p-tolylaldehyde, by refluxing in ethanol, using pyperidine as a catalyst [3-5], according to the following reaction:



We reckoned on the fact that by interposing a double bond between the benzimidazole moiety and phenyl ring the whole system would become coplanar. Thus, the influence of the positive charge delocated on the two nitrogen atoms from the imidazole ring could be transmited all the way to the methyl group, which became as reactive as the methyl group bonded at the C-2 of the benzimidazole ring.

In order to practically verify the lability of the hydrogen atoms in the methyl p-substituted group, the salt 3 was condensed with p-NDMA and some aromatic aldehydes. Scheme 2 was applied.

Reaction with p-NDMA

It was carried out in ethanol, with pyperidine as a catalyst. At the beginning of the refluxing, the solution colour changed from green (due to p-NDMA) to dark brown. The mixture was refluxed for 1.5 hours, then cooled, but the azomethine 7 did not separate from solution. The residue obtained by ethanol vaporization, a red-brown solid with a glassy aspect, could not be purified by recrystallization.

Condensation with aromatic aldehydes

The reaction was carried out similarly to 1,2,3-trimethyl-benzimidazolium iodides. The reactants, dissolved in ethanol, containing 2-3 drops of pyperidine, were refluxed for 2-4 hours. After cooling, the salts 8 a-d were separated from solution as crystals. The synthetised benzimidazolium salts 8 are listed in Table 1.

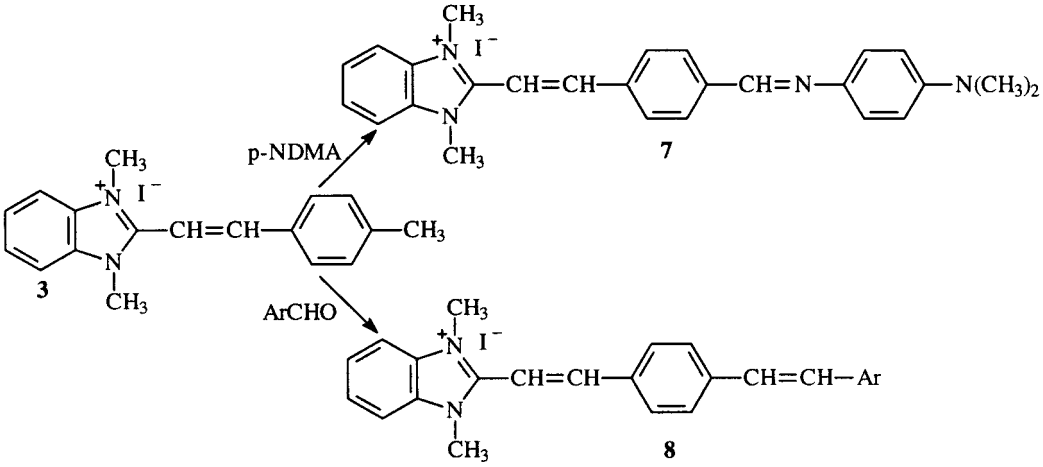
The reaction is interesting because it leads to extensively conjugated molecules, with highly delocated electrons. Because of the p-phenylene system attached to the benzimidazole ring, the compounds could have colouring properties and some original applications in the polymer field.

The structures of compounds 8 were confirmed by elemental analysis and IR spectra (Table 2).

The investigated substances, even if they have two double bonds separated by a phenyl ring, behave like a unitary system, that could adopt various configurations, as any conjugated diene. The different moieties at the end of the molecule, make it asymmetrical.

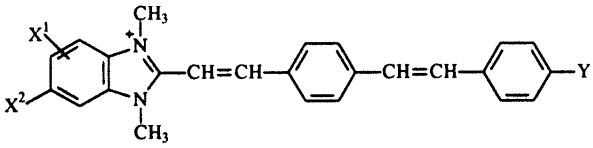
The compound 8a was two different absorptions at 1647 and 1679 cm^{-1}, corresponding to double bonds (C=N and C=C), whereas 8b-d are characterized by a single band at 1622 and 1651 cm^{-1}, respectively. It is possible in this case that the absorption at the lower frequency is concealed by the strong band at 1598 cm^{-1}.

The benzene rings are identified by the stretching vibration bands n=CH, between 3000-3100 cm^{-1} (3022, 3076, 3099 etc), that could also be assigned to =C-H bonds from the vinyl moiety. The band around 1595 cm^{-1}, generated by νC-C aromatic stretching vibrations, is also important. The methyl groups gave the bands at 2852, 2926 and 2978 cm^{-1}, corresponding to νC-H



Scheme 2. Reaction of the 2–p–methylstyryl substituted salt with p–NDMA and aromatic aldehydes

Table 1. 1–Methyl–2[arylvinyl–(styryl)]benzim idazole iodomethylates



Comp.	X^1	X^2	Y	M.p.	Colour	Molecular formula	Analysis N, %	
							calc.	exp.
8a	Br	–	NO_2	268–270	brown	$C_{25}H_{21}BrN_3O_2I$	6.976	7.04
8b	NO_2	–	NO_2	243–245	brown	$C_{25}H_{21}N_4O_4I$	9.859	9.98
8c	NO_2	–	CH_3O	218–220	yellow–orange	$C_{26}H_{24}N_3O_3I$	7.595	7.72
8 d	NO_2	NO_2	NO_2	210–212	rusty–brown	$C_{25}H_{20}N_5O_6I$	11.42	11.56

Table 2. IR absorptions for the compounds 8

Comp.	**Characteristic bands (cm^{-1}) and their intensity** (VS=very strong, S=strong; M=medium; W=weak; VW=very weak)
8 a	513.06 VW, 592.15 VW, 669.30 W, 700.16 W, 748.38 W, 854.46 M, 1012.63 W, 1056.99 W, 1107.14 M, 1163.07 M, 1219.01 W, 1342.45 VS, 1404.17 M, 1419.61 M, 1471.68 M, 1514.12 VS, 1593.20 S, 1647.21 M, 1679.99 M, 1772.58 VW, 2850.78 VW, 2926.01 VW, 3022.45 VW, 3088.03 VW.
8 b	505.35 VW, 640.37 VW, 698.23 W, 746.45 W, 815.89 W, 854.46 M, 1010.70 W, 1109.07 M, 1170.79 M, 1197.79 M, 1303.88 S, 1344.38 VS, 1382.96 M, 1421.53 W, 1456.25 M, 1516.05 VS, 1597.06 S, 1652.99 M, 2850.78 W, 2926.01 W, 3074.53 VW, 3105.39 VW.
8 c	522.71 W, 638.44 VW, 667.37 VW, 732.95 W, 750.31 W, 810.10 M, 831.32 M, 883.40 W, 966.33 W, 1016.48 M, 1078.21 W, 1114.85 M, 1172.72 M, 1213.22 M, 1259.51 S, 1294.23 M, 1319.31 S, 1350.17 S, 1381.03 W, 1456.25 M, 1492.90 M, 1525.69 VS, 1571.98 M, 1598.98 VS, 1622.13 M, 1685.78 W, 2839.21 VW, 2926.01 W, 2978.08 W, 3026.31 W.
8 d	640.37 VW, 669.30 VW, 700.16 W, 750.31 W, 821.67 W, 856.39 W, 906.54 VW, 1012.63 W, 1112.92 M, 1170.79 W, 1303.88 S, 1344.38 VS, 1384.89 M, 1454.32 M, 1516.05 S, 1595.13 S, 1651.06 M, 2852.71 VW, 2926.01 W, 3076.45 VW.

stretching vibrations and at about 1380 and 1454 cm^{-1}, due to deformation vibrations dCH_3 sym. and asym. The substituents in the benzene ring (NO_2, Br, OCH_3) produce characteristic absorptions.

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.

The following synthetic methods were applied:

2–p–Tolylbenzimidazole by the modified Weidenhagen method

o–Phenylendiamine (4.75 g, 0.04 mol) and p–tolylaldehyde (5 g, 5 ml, 0.04 mol) in 5 ml ethanol were added to 20 g Cu acetate in 250 ml of water. The obtained suspension was heated for 0.5 hours in a water bath. The Cu complex salt of 2–p–tolylbenzimidazole was separated by filtration and washed with water. The precipitate was dissolved in 3% aqueous HCl, boiling it in order to decompose the complex salt. After the filtrate cooled, the 2–p–tolylbenzimidazole hydrochloride separated, which was transformed into the corresponding benzimidazole by refluxing with ethanolic K_2CO_3. Finally, colourless needles were obtained. M.p.

= 271°C. The cyclization of the Schiff base in nitrobenzene occurred by a previously described reaction [5].

1,3–Dimethyl–2–p–tolylbenzimidazolium iodide

2–p–Tolylbenzimidazole (0.7 g; 0.034 mols) in 5 ml of methanol was treated with methyl iodide (1.19 g; 0.52 ml; 0.084 mol) and the mixture heated in an autoclave at 140°C for 4 hours. The obtained crystalline mass was purified by recrystallization from water adding charcoal. η = 76%. M.p.= 307–308°C.

1,2,3–Trimethylbenzimidazolium iodide

The product was obtained from 1,2–dimethylbenzimidazole and methyl iodide, in methanol [5].

1,3–Dimethyl–2–(p–methylstyryl)–benzimidazolium iodide

1,3–Dimethyl–2–p–tolylbenz–imidazolium iodide (0.87 g, 3 mmol) in 10 ml of ethanol, was treated with 0.36 g (0.32 ml, 3 mmol) of p–tolylaldehyde in 5 ml of ethanol. After adding 5 drops of pyperidine the reaction mixture was refluxed for 2 hours. After cooling and standing for a couple of days, light yellow crystals separated that were filtered and washed with methyl acetate. A product (0.9 g, η = 76%) melting at 307–308°C was obtained.

Synthesis of 1–methyl–2–[arylvinyl–(styryl)]benzimidazole iodomethylates

Condensation of 4–bromo–1–methyl–2–(4'–methylstyryl)benzimidazole iodomethylate with p–nitrobenzaldehyde 8a: The styryl derivative (0.47 g, 1 mmol) dissolved in 25 ml of ethanol was treated with p–nitrobenzaldehyde (0.157 g; 1 mmol) in 10 ml of ethanol and 2–3 drops of pyperidine added. After heating a dark solution was obtained, which was refluxed for 2 h. After cooling and filtering a brown product was separated, having the m.p. = 268–270°C.

Reaction of 1–methyl–2–(4'–methylstyryl)–5– nitrobenzimidazole iodomethylate with p–nitrobenzaldehyde 8b: The styryl derivative (0.43 g, 1 mmol) in 20 ml of etahnol, p–nitro–benzaldehyde (0.15 g, 1 mmol) dissolved in 5 ml ethanol and 2–3 drops of pyperidine were refluxed for 2 h. A rusty–brown solution was obtained at the very beginning. Finally, a dark brown product separated. A small amount of product melting at 243–245°C was separated from the evaporated filtrate that was dissolved in ethyl acetate and precipitated with ethylic ether.

Reaction of 1–methyl–2–(4'–methylstyryl)–5–nitrobenzimidazole iodomethylate with p–anysaldehyde 8c: The styryl derivative (0.435 g, 1 mmol) in 15 ml of ethanol, anysaldehyde (0.13 g; 0.11 ml; 1 mmol) and 5 drops of pyperidine were refluxed for 2 hours. A yellow–orange product (0.2 g) was separated after cooling. From the vaporised filtrate another 0.15 g of product were obtained by dispersing with methyl acetate. M.p.= 218–220°C.

Reaction of 1–methyl–2–(4'–methylstyryl)–5,6– dinitrobenzimidazole iodomethylate with p– nitrobenzaldehyde 8d: The styryl derivative (0.48 g, 1 mmol) in ethanol (15 ml), p–nitrobenzaldehyde (0.15 g, 1 mmol) in 3 ml of ethanol and 5 drops of pyperidine were refluxed for 2 h. After cooling, a rusty–brown product (0.2 g) was separated. From the evaporated filtrate an additional small amount of product was recovered, which was dispersed with ethyl acetate. M.p.= 210–212°C.

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IZVOD

DERIVATI BENZAZOLA.
V. Reaktivnost nekih 2–p–Toluil– i 2–p–Metilstirilbenzimidazolijumskih soli

(Naučni rad)

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U radu je proučavana reaktivnost p–supstituisanih metil grupa u 1–metil–2–p–toluil– benzimidazolijum jodida i 1–metil–2–p–metilstiril–benzimidazolijum jodida sa p–nitrozo–dimetilanilinom (p–NDMA) i aromatskim aldehidima. Na osnovu literaturnih podataka o sternim smetnjama koje su prouzrokovane prostorno velikom N–I metil grupom, pokazano je da 2–p–toluil supstituisane soli ne reaguju sa p–NDMA. Nasuprot tome, 2–p–metilstiril supstituisane soli učestvuju u reakcijama kondenzacije, slično kao i 1,2,3–trimetilbenzimidazolijum jodid. Jedinjenja dobijena u reakciji sa aromatičnim aldehidima mogu se koristiti kao boje, kao fotosenzitivna jedinjenja ili kao dienski monomeri, s obzirom na konjugovane veze u C–2 fenilnom prstenu.

Ključne reči: Derivati benzazola • Reaktivnost • 1–Metil–2–p–toluil–benzimidazolijum jodid • 1–Metil–2–p–Metilstiril–benzimidazolijum jodid • p–Nitrozo–dimetilanilinom • Aromatski aldehidi •

Key words: Benzazole Derivatives • Reactivity • 2–p–Tolyl–benzimidazolium iodide • 2–p–Methylstyryl–benzimidazolium iodide • p–Nitroso–dimethylaniline • Aromatic aldehydes •