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AZO COUPLING OF 5(6)-HYDROXYBENZIMIDAZOLE AND ITS DERIVATIVES

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The azo coupling of 5(6)-hydroxybenzimidazole and its derivatives is directed toward C^4 .

In a continuation of a study of the reactivity of 5(6)-hydroxybenzimidazole (I) and its derivatives [1-3], we investigated one of the classical examples of electrophilic substitution in aromatic compounds, namely, azo coupling, in which the aryldiazonium cation $Ar - N = N \leftrightarrow Ar - N = N$. serves as the electrophile. The azo coupling of (I), 2-methyl-5(6)-hydroxybenzimidazole (II), and 1-ethyl-2-methyl-5(6)-hydroxybenzimidazole (III) was studied using diazonium salts of different reactivity prepared from aniline, p-nitroaniline, and p-sulfoaniline. The azo coupling was carried out in alkaline media using conditions similar to those described for 3-hydroxypyridine and its derivatives [4].



 $R^{1} = R^{2} = H(I), (IV), (VII); R^{1} = H, R^{2} = CH_{3}(II), (V), (VIII); R^{1} = C_{2}H_{5}, R^{2} = CH_{3}(III), (VI), (IX); R^{3} = H(a), NO_{2}(b), SO_{3}H(c).$

The azo coupling of (I) with the phenyldiazonium cation proceeds quantitatively, while (III) gives traces of several colored side products although the yield of the major product (VIa) is rather high. Under these conditions, (II) reacts with a lower yield of major product (Va).

The azo coupling with the p-nitrophenyldiazonium cation confirms an increase in reactivity in electrophilic reactions in the 5(6)-hydroxybenzimidazole series in the following order: (II) < (I) < (III) [2]. The reaction proceeds virtually without side products, especially in the case of (III).

The azo coupling of (I)-(III) with the p-sulfophenyldiazonium cation proceeds with higher yields than with the p-nitrophenyldiazonium cation and with greater selectivity than with the phenyldiazonium cation although it gives a lower yield of the final product than with the phenyldiazonium cation.

The azo coupling was directed toward C^4 of the benzimidazole system. The 4,6-bisazo product could not be obtained (Table 1).

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Com-		'Mp, °C	Chemical formula	Found, %		Calculated, %	
pound	Yield, %			С	н	C	H
(IVa) (IVb) (IVc) (Va) (Vb) (Vc) (VIa) (VIb) (VIc)	95,9 43,6 61,8 60,6 22,5 25,1 87,2 70,8 88,5	$\begin{array}{r} 147-149\\ 265-267\\ >350 (dec.)\\ 136-138\\ 214-216\\ >350 (dec.)\\ 56-57\\ 176-178\\ 330-335\end{array}$	$\begin{array}{c} C_{13}H_{10}N_4O\\ C_{13}H_9N_5O_3\\ C_{13}H_9N_5O_3\\ C_{14}H_{12}N_4O\\ C_{14}H_{12}N_4O\\ C_{14}H_{12}N_4O_4S\\ C_{16}H_{16}N_4O\\ C_{16}H_{15}N_5O_3\\ C_{16}H_{18}N_4O_4S\\ \end{array}$	65,29 55,68 49,23 66,22 56,60 50,71 67,91 58,63 53,70	4,19 3,48 3,41 4,48 3,88 3,35 5,52 4,83 4,22	65,53 55,12 49,01 66,64 56,56 50,57 68,55 59,06 53,32	4,24 3,21 3,17 4,80 3,74 3,65 5,75 4,66 4,48

TABLE 1. Physicochemical Indices of Azo Derivatives (IV)-(VI)

TABLE 2. Physicochemical Indices of Amino Derivatives (VII)-(IX)

Hydrochlor-	_	Chemical	Found, %		Calculated, %		
ide of com- pound	Mp, °C	formula	С	н	C	H	
(VII)	272-274 (dec.)	C7H7N3O·HCl	44,86	4,14	45,29	4,35	Ī
(VIII)	260-262 (dec.)	C₅H₀N₃O·HCl	47,72	5,42	48,12	5,06	
(IX)	238-240	C ₁₀ H ₁₃ N ₃ O·HCl	52,32	6,12	52,74	6,21	

TABLE 2. (Continued)

Hydrochloride	6, ppm						
of compound	2CH3	1CH₂CH₃	\mathbf{H}^{6}	H7	H²	Hz	
(VII)	-	_	7,33 d(1H)	7,77 đ(1H)	9,32·s (1H)	9,0	
(VIII)	2,87 _s (3H)	-	7,05 d (1H)	7,45d1 (1H)	-	9,0	
(IX)	2,87 s(3H)	1,52 t (3H) 4,45 qs (2H)	7,27 a (1H)	7,74 d(1H)	-	9,0	

The reductive cleavage of the azo group has great value for establishing the structure of azo coupling products. However, benzidine or semidine rearrangements may occur upon reduction of the azo compounds in acidic solution in the case of an insufficient rate of the subsequent reduction of the intermediate hydrazo derivatives [5]. Thus, we preferred the reduction by sodium hydrosulfite in alkaline medium [6].

The structures of amino derivatives (VII)-(IX) were confirmed by PMR spectroscopy. There is no downfield signal for H⁴, while the signals for H⁶ and H⁷ are doublets with SSCC $J_{6.7} = 9.0$ Hz (Table 2).

EXPERIMENTAL

The PMR spectra of the hydrochloride salts of amino derivatives (VII)-(IX) were obtained on a Varian T-60 spectrometer in D_20 with tert-butyl alcohol as the internal standard. The chemical shifts were recalculated relative to TMS.

Azo Coupling of (I)-(III). A solution of phenyldiazonium chloride prepared at $\leq 5^{\circ}$ C, consisting of 3 mmoles aniline or its derivative, 1 ml concentrated hydrochloric acid, 12 ml water, and 0.8 ml 30% NaNO₂, was added with stirring to a solution of 3 mmoles (I)-(III) in 20 ml 1 N NaOH at 3-5°C. The colored solution was stirred for an additional 20-40 min and treated with 10% sulfuric acid to pH 3-6. The suspension obtained was left overnight in a refrigerator. The precipitate was separated, washed with water, dried in the air, and recrystallized from aqueous ethanol.

The physicochemical indices of (IV)-(VI) are given in Table 1.

Reduction of Azo Compounds (IV)-(VI). A sample of sodium hydrosulfite was added gradually with stirring to a solution of 2 mmoles azo compound in 20-30 ml 2 N NaOH at 50-60°C until the solution was decolored (~4 mmoles hydrosulfite). The aniline formed was extracted with ether. The aqueous solution was neutralized and the precipitated base (VII)-(IX) was rapidly separated, dried, and converted to the hydrochloride salt by the addition of ethanolic HCl and subsequent recrystallization from absolute ethanol.

The physicochemical indices of hydrochloride salts (VII)-(IX) are given in Table 2.

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ANODIC SYNTHESIS AND MOLECULAR STRUCTURE OF

DODECAETHYLHEXAAMIDOBISPHOSPHONIUM

DIPERCHLORATE

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The electrochemical oxidation of hexaethyl triamidophosphite in the absence of nucleophiles specially introduced into the electrolyte was studied by anodic voltamperometry and preparative electrolysis. The reversible one-electron oxidation of the triamidophosphite molecule gives an unstable radical-cation, which reacts with a molecule of the starting compound to give a dimeric radical-cation, whose subsequent oxidation leads to dodecaethylhexaamidobisphosphonium diper-chlorate. This product is the first example of an acyclic, doubly charged

bisphosphonium cation with a P-P bond. The crystal structure of this compound was obtained by x-ray diffraction structural analysis.

+ +

The reactions of derivatives of phosphorus(III) radical-cations with aromatic compounds, olefins, dialkyl disulfides, and compounds with a labile hydrogen atom such as water, alcohols, and phenols, which are the basis of recently developed methods for the electrochemical synthesis of organophosphorus compounds, have been studied rather extensively [1]. All these processes presumably proceed through the following general scheme:

 $X_{3}P^{+} + HY \rightarrow [X_{3}P/YH]^{+} \xrightarrow{\sim} X_{3}P - Y + H^{+}$

However, the pathways for the annihilation of the radical-cations of organophosphorus compounds in the absence of these and similar nucleophiles, for example, under conditions of the anodic generation of X_3P^+ in an inert solvent in the presence of an indifferent base electrolyte, remain unclear. These pathways are apparently competitive relative to the desired electrosynthesis reactions and may be evident to a greater or lesser extent depending

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