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Walther Reaction in the Benzazoles Series and Preparation of Their 2-Deutero Derivatives

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Abstract—Reactions of 2-hydrazino-substituted 1-methylbenzimidazole, benzothiazole, and benzoxazole with azobenzene at 160–180°C resulted in hydrazino group elimination and formation of the corresponding 2-*H*-benzazoles. Under similar conditions the 2-deuterohydrazinobenzazoles prepared from 2-hydrazinobenzazoles and heavy water were converted into 2-deuterobenzazoles.

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An elegant reaction between azobenzene and phenylhydrazone that at 125–130°C led to elimination of the hydrazino group and to formation of benzene, nitrogen, and hydrazobenzene in nearly quantitative amounts was discovered by R. Walther to the end of nineteen century [1, 2]. This reaction was used in [3] in order to remove a hydrazine group and to obtain the previously unknown 1,3-dimethylimidazo[4,5-*C*]pyridin-2-one. The reaction also occurred with a quantitative yield of the target product and hydrazobenzene.

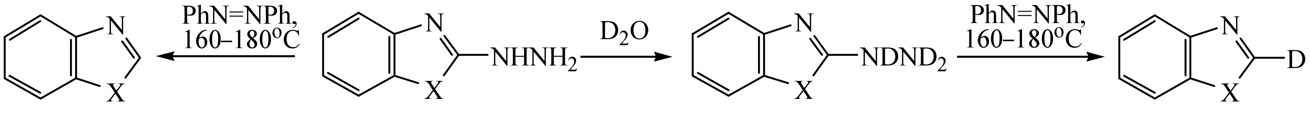
We report here on the results of oxidation with azobenzene of 2-hydrazino derivatives of benzoxazole, benzothiazole, and 1-methylbenzimidazole, and also of their N-deutero derivatives aimed at conversion of these hydrazines into the corresponding benzazoles. It turned out that the reaction on azobenzene with 2- hydrazino derivatives of 1-methylbenzimidazole (**I**), benzothiazole (**II**), and benzoxazole (**III**) occurred under more stringent conditions than with phenylhydrazine, and afforded the expected benzazoles **IV–VI** in 88–97% yields (Table 1).

In the same fashion the oxidation with azobenzene of N-deuterohydrazino derivatives of azoles **VII–IX** afforded 2-D-benzazoles **X–XII**. Deuterated hydrazines **VII–IX** were prepared by triple recrystallization from the heavy water of bases **I–III**. After thorough drying the samples of the deuterohydrazines were fused with azo-benzene at 160–180°C. Azoles **V** and **XII** were isolated from the reaction mixture by distillation, and 1-methylbenzimidazole (**X**) was eluted with benzene from sorbent (aluminum oxide).

The composition and structure of compounds obtained **IV–XII** were confirmed by elemental analysis (Table 1) and ^{1}H NMR spectra (Table 2). The chemical shift of aromatic protons signals in the spectra of compounds **IV** and **VI** are identical to the published data [4]. The signals of aromatic protons of 2-deutero derivatives **VII–XII** are observed in the stronger field with respect to those of the unsubstituited benzazoles **IV–VI** (7.31–8.17 ppm).

EXPERIMENTAL

^{1}H NMR spectra of compounds synthesized were registered on a spectrometer Gemini-200 at operating frequency 200 MHz in $CDCl_3$ for compounds **IV–VI** and **X–XII** and in DMSO-d_6 for compounds **VII–IX**. HMDS was used as internal reference. The purity and homogeneity of compounds obtained was checked by TLC on Silufol UV-254 plates (eluents ethanol or chloroform), development under UV irradiation or in iodine vapor. The syntheses of initial compounds **I–III** were described in [8–10] respectively.



IV–VI **I–III** **VII–IX** **X–XII**

X = NMe (**I, IV, VII, X**), S (**II, V, VIII, XI**), O (**III, VI, IX, XII**).

Table 1. Yields, melting (boiling) points, and elemental analyses of compounds **IV–XII**

Compd. no.	Yield, %	mp (bp), °C	Found, %			Formula	Calculated, %		
			C	H (H+D)	N		C	H (H+D)	N
IV	90	64–65	72.51	6.05	21.03	$C_8H_8N_2$	72.70	6.10	21.20
V	97	(222–224)[a]	62.04	3.67	10.19	C_7H_5NS	62.19	3.73	10.36
VI	88	(180–182)[b]	70.45	4.18	11.58	C_7H_5NO	70.58	4.23	11.76
VII	94	130–132	58.02	7.85	33.78	$C_8H_7D_3N_4$	58.18	7.93	33.92
VIII	92	193–194	49.80	5.93	24.84	$C_7H_4D_3N_3S$	49.99	5.99	24.98
IX	80	139–140	55.11	6.55	27.49	$C_7H_4D_3N_3O$	55.27	6.62	27.62
X	90	62–63	72.01	6.74	20.87	$C_8H_7DN_2$	72.16	6.81	21.04
XI	90	(219)	61.54	4.38	10.10	C_7H_4DNS	61.74	4.44	10.29
XII	94	(177–178)	69.88	4.95	11.50	C_7H_4DNO	70.00	5.03	11.66

[a] Publ.: bp 223–225°C [5]. [b] Publ.: bp 183°C [6], mp 66°C [7].

Table 2. ^1H NMR spectra of compounds **IV–XII**

Compd.no.	Chemical shift, δ, ppm
IV	3.86 s (3H, NCH_3), 7.31–7.40 m (3H, H^4, H^5, H^6), 7.83–7.88 m (1H, H^7), 7.89 s (1H, H^2)
V	7.48 d (1H, H^5, *J* 7.8 Hz), 7.53 d (1H, H^6, *J* 7.8 Hz), 7.99 d (1H, H^4, *J* 7.8 Hz), 8.17 d (1H, H^7, *J* 7.8 Hz), 9.02 s (1H, H^2)
VI	7.42 q (2H, H^5, H^6), 7.64 t (1H, H^4), 7.84 t (1H, H^7), 8.15 s (1H, H^2)
VII	3.60 s (3H, NCH_3), 6.82–6.94 m (1H, H^6), 6.96–7.05 m (1H, H^5), 7.12 d (1H, H^4, *J* 7.0 Hz), 7.22 d (1H, H^7, *J* 7.0 Hz)
VIII	7.01 q (1H, H^5), 7.22 q (1H, H^6), 7.36 d (1H, H^4, *J* 7.9 Hz), 7.61 d (1H, H^7, *J* 7.9 Hz)
IX	7.05–7.39 m (4H, H^4, H^5, H^6, H^7)
X	3.85 s (3H, NCH_3), 7.30–7.44 m (3H, H^4, H^5, H^6), 7.82–7.86 m (1H, H^7)
XI	6.70 d (1H, H^5, *J* 7.7 Hz), 6.80 d (1H, H^6, *J* 7.7 Hz), 7.18 t (2H, H^4, H^7)
XII	6.64–6.81 m (2H, H^5, H^6), 7.12–7.20 m (2H, H^4, H^7)

Benzazoles IV–VI. A mixture of 10 mmol of an appropriate 2-hydrazinobenzazole **I–III** with an equimolar amount of azobenzene was heated at 160–180°C till the end of nitrogen liberation. Compounds **V** and **VI** were isolated from the reaction mixture by simple distillation at the atmospheric pressure in a nitrogen flow. Compound **IV** was separated by column chromatography on aluminum oxide, eluent benzene.

2-Deuterohydrazinobenzazoles VII–IX. A mixture of 10 mmol of an appropriate 2-hydrazinobenzazole **I–III** and 10 ml of D_2O was heated to boiling for 2 h. On cooling the water layer was decanted, 10 ml of D_2O was added, and the mixture was boiled for 2 h. These operations were thrice repeated. Then the solution was cooled, the reaction product was filtered off, dried in a desiccator over P_2O_5, and used for further transformations without additional purification. When required, 2-deuterohydrazinobenzazoles **VII–IX** were purified by recrystallization from anhydrous benzene.

2-Deuterobenzazoles X–XII. A mixture of 10 mmol of an appropriate 2-deuterohydrazinobenzazole **VII–IX** and 10 mmol pf azobenzene was heated at 160–180°C till the nitrogen liberation ceased. Reaction products XI and **XII** were purified by vacuum distillation in a nitrogen flow, and compound **X** was subjected to column chromatography on aluminum oxide, eluent benzene.

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