reaction took place less satisfactorily with acetaldehyde and paraformaldehyde. It was impossible to obtain products of the condensation of acetaldehyde with dimedone and benzoylacetone imine or acetylacetone imine. When paraformaldehyde was used, a large amount of bisdimedonylmethane was obtained as a by-product, this being isolated and identified by means of its melting point, behavior in paper chromatography, and UV spectra. To separate them from the bisdimedonylmethane, the condensation products **Vb** and **e** were treated with a saturated solution of $NaHCO_3$. Compounds **Va, d, f** were oxidized with chromic acid to the corresponding 3,4-disubstituted 2,7,7-trimethyl-5-oxo-5,6,7,8-tetrahydroquinolines (**VIa–c**). Attempts to oxidize compound **Vf** with H_2O_2 and chloranil were unsuccessful. After **Vf** had been boiled with chloranil in xylene for 15 hr, the starting material was recovered. Thus, the best oxidizing agent available to us was chromic acid. We have studied the IR spectra of compounds **Va, b, c, f** and **VIa**. The IR spectra were taken in paraffin oil and hexachlorobutadiene and, in the case of compound **Vb**, also in dichloroethane solution. The IR spectra of similar compounds have been considered previously [2, 3]. In the 6-μ region, compounds **Va–f** absorb in a similar manner to the 4-substituted derivatives of 3-ethoxycarbonyl-2-7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinolines that we have described previously. In the 3-μ region ν_{NH} appears. The UV absorption spectra of compounds **Va, c, f,** and **VIa, c** are similar to those of the compounds described previously [1].

EXPERIMENTAL

3-Acetyl-2,7,7-trimethyl-5-oxo-4-phenyl-1,4,5,6,7,8-hexahydroquinoline (Va). A mixture of 2 g (~0.015 mole) of dimedone, 1.42 g (~0.015 mole) of acetylacetone imine, and 1.52 g (~0.015 mole) of benzaldehyde was boiled in 30 ml of ethanol for 1 hr, assuming a dark yellow color. After the solvent had been distilled off, dilution with half a volume of water and storage at 0–4° C for 2 days gave a yellow crystalline precipitate. Yield 1.8 g (41%), mp 198–200° C (after three crystallizations from 40% ethanol). The substance dissolves in methanol, benzene, dioxane, and acetic acid. In a solution of sodium methoxide it gives a dark yellow coloration. Found, %: C 77.45; H 7.62; N 4.62. Calculated for $C_{20}H_{23}NO_2$, %: C 77.62; H 7.49; N 4.53.

3-Acetyl-2,7,7-trimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydroquinoline (VIa). An aqueous solution of 1 g of chromic anhydride was added in small portions to a solution of 2 g (~6.5 mM) of **Va** in 50 ml of acetic acid heated to 70–80° C until the color changed to dark green. After the mixture had been evaporated to half volume and had been diluted with water, a yellow crystalline substance deposited. Yield 1.01 g (51%), mp 107–108° C (from ethanol + water). Found, %: C 77.93; H 7.00; N 4.05. Calculated for $C_{20}H_{21}NO_2$, %: C 78.14; H 6.89; N 4.56.

3-Acetyl-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline (Vb). This was obtained in a similar manner to **Va** from 2 g (~0.015 mole) of dimedone, 1.4 g (~0.015 mole) of acetylacetone imine and 0.45 g (~0.015 mole) of paraformaldehyde, boiled for 3 hr in 40 ml of ethanol. After the solvent had been distilled off, to separate the desired product from the bisdimedonylmethane formed as an impurity the dry residue was treated with a saturated solution of $NaHCO_3$ and the mixture was filtered. Yellow crystalline substance, yield 0.6 g (20%), mp 209–211° C (after three crystallizations from 30% ethanol). In a solution of sodium methoxide it gave a dark yellow coloration. Found, %: C 72.48; H 8.25; N 6.11. Calculated for $C_{14}H_{19}NO_2$, %: C 72.07; H 8.21; N 6.0. The bisdimedonylmethane was identified by its mp of 189–190° C (literature 191–191.5° C), paper chromatography in the butyl acetate–methanol–0.25% ammonia solution (95:5:25) system, R_f 0.94, and its UV spectrum in ethanol (263–264nm).

The constants, yields, and spectroscopic characteristics of the substances synthesized are given in Tables 1 and 2.

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4 June 1966

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N-SUBSTITUTED 1,3-DIMETHYL-2-IMINOBENZIMIDAZOLINE

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Khimiya Geterotsiklicheskikh Soedinenii, Vol. 3, No. 6, pp. 1120–1122, 1967

UDC 547.781.5+542.95

The N-alkylation, N-arylation, and N-acylation of 1,3-dimethyl-2-iminobenzimidazoline are reported.

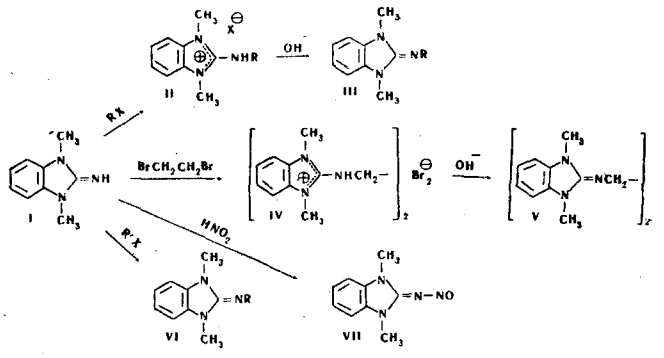
N-Substitution in the 2-iminobenzimidazoline series has not previously been studied. Our experiments have shown that the action of alkylating agents on 1,3-dimethyl-2-iminobenzimidazoline (**I**) [1] leads to the formation of benzimidazolium salts (**II**) which, on treatment with alkali, are converted into 2-alkylimino-1,3-dimethylbenzimidazolines (**III**). Similarly, 1,2-dibromoethane reacts with **I** to form **IV** and **V**.

N-Substituted 1,3-Dimethyl-2-iminobenzimidazolines

Compound	R(R′)	Conditions of the synthesis		Mp, °C (solvent for crystallization) bp, °C (pressure, mm)	Empirical formula	Found, %			Calculated, %			Yield, %
		method	temperature, °C (time, hr)			C	H	N	C	H	N	
II a	CH_3	A	135 (1.5)	164.5 (acetone)	$C_{16}H_{19}N_3O_3S$	57.87	5.65	12.61	57.65	5.74	12.60	65
II b	$CH_3(CH_2)_4$	A	125 (1.5)	195 (water)	$C_{14}H_{22}IN_3$ [a]			11.60			11.69	98
III a	CH_3	C		~60 [b], 175 (11)	$C_{10}H_{13}N_3$			23.65			23.97	87
III a, picrate				182—183 (ethanol)	$C_{10}H_{13}N_3 \cdot C_6H_3N_3O_7$	47.37	4.13	20.98	47.51	3.99	20.79	
III b	$CH_3(CH_2)_4$	C		200 (15)	$C_{14}H_{21}N_3$	72.23	9.29	18.43	72.69	9.15	18.17	70
III b, picrate				162 (ethanol)	$C_{14}H_{21}N_3 \cdot C_6H_3N_3O_7$			18.15			18.25	
IV		A	110 [c]	313—314 (50% ethanol)	$C_{20}H_{26}Br_2N_6$ [d]			16.41			16.47	71
V		C		196—197 (ethanol)	$C_{20}H_{24}N_6$	68.48	6.88	23.90	68.94	6.94	24.12	71
VI a	2,4-$(O_2N)_2C_6H_3$	A	130 [c]	232—233 (aqueous acetone)	$C_{15}H_{13}N_5O_4$	55.10	3.81		55.05	4.00		61
VI b	2,4,6-$(O_2N)_3C_6H_2$	A	120 (1.5)	226—227 (aqueous acetone)	$C_{15}H_{12}N_6O_6$	48.29	3.20		48.41	3.25		87
VI c	CH_3CO	A	110 (3)	133 (benzene and petroleum ether)	$C_{11}H_{13}N_3O$	64.73	6.54	20.41	65.00	6.45	20.67	80
VI d	C_6H_5CO	A	155 [c]	185 (50% ethanol)	$C_{16}H_{15}N_3O$	72.48	5.70	15.80	72.44	5.70	15.84	76 [e]
VI e	p-$O_2NC_6H_4CO$	A	125 (1.5)	245—246 [f] (benzene)	$C_{16}H_{14}N_4O_3$	62.15	4.55	18.24	61.93	4.55	18.08	83 [e]
VI f	$C_5H_5SO_2$	A	145 (2)	163.5 (ethanol)	$C_{15}H_{15}N_3O_2S$	59.85	5.10	13.80	59.78	5.02	13.94	81 [e]

[a] Found, %: I 35.18. Calculated, %: I 35.32. [b] Substance very hygroscopic. [c] Heated until the melt solidified. [d] Found, %: Br 31.04. Calculated, %: Br 31.31. [e] Yields by method B: VId—57, VIe—68, VIf—50%. [f] The previous figures given in [2] must be erroneous.

In the arylation and acylation of **I**, as a result of a decrease in the basicity of the system through the introduction of electrophilic radicals into it, N-aryl- and N-acyl-1,3-dimethyl-2-iminobenzimidazolines (**VI**) are formed directly. In order to exclude the binding by the initial imine of the HX formed, in some cases it is desirable to carry out the reaction in the presence of Na_2CO_3. The action of nitrous acid on **I** in a weakly acid medium leads to the N-nitroso derivative (**VII**), which is cleaved by the action of zinc dust in acetic acid (1:1) with the formation of the initial imine (**I**), which confirms its structure as an N-Nitroso compound.



R = alkyl (see table); R′ = acyl or aryl

EXPERIMENTAL

Synthesis of N-substituted 1,3-dimethyl-2-iminobenzimidazolines. A. A mixture of **I** (0.01 mole) and the appropriate alkyl, aryl, or acyl halide* (0.011 mole) was heated in a glycerol bath for 1–3 hr (see table) or until the melt solidified. Exactly 0.01 mole of dibromoethane was used. To obtain **VId–f** (see table), 1 g of sodium carbonate was previously added to the mixture. After cooling, the melt was triturated with a mixture of ethanol and ether (1:5) or with ethanol (**VIa** and **VIb**). When mineral salts were present in the melt, it was treated with hot water. Compound **VIc** was isolated by distilling off the excess of acetic anhydride.

B. With shaking, a solution of 0.015 mole of acyl chloride in 10 ml of benzene was added to a solution of 0.01 mole of **I** and 2 g of sodium bicarbonate in 50 ml of water, and shaking was continued for another 2 hr. The precipitate was filtered off and washed with water, benzene, and a small amount of ethanol.

C. A suspension or aqueous solution of a benzimidazolium salt was treated with an excess of alkali and the precipitate of **V** was filtered off, while **IIIa** and **IIIb** were extracted with ether.

N-Nitroso-1,3-dimethyl-2-iminobenzimidazoline (VII). With stirring at 30–40°C, 1.03 g (15 mM) of dry sodium nitrite was added during 5 min to a solution of 1 g (5 mM) of the hydrochloride of **I** (obtained by adding concentrated HCl to a saturated ethanolic solution of **I**) in 10 ml of water acidified with 3 drops of glacial acetic acid, and stirring was continued for another 30 min. The N-nitroso compound was filtered off and dried at 50–60°C. Yield 0.81 g (85%). Yellow needles (from ethanol) with mp 126°C (with explosive decomposition). Found, %: N 29.15; 29.50. Calculated for $C_9H_{10}N_4O$, %: N 29.45.

2-Amino-1,3-dimethylbenzimidazolium nitrite precipitated when the reaction of **I**·HCl with $NaNO_2$ was carried out without heating or the solution was not acidified with acetic acid. Colorless needles (from ethanol) with mp 194°C (decomp.). The substance gave a reaction for the nitrite ion. Found, %: N 26.79; 26.71. Calculated for $C_9H_{12}N_4O_2$, %: N 26.91.

*Methylation was carried out with methyl benzenesulfonate and acetylation with acetic anhydride (3 moles).

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16 October 1966 Rostov-on-Don State University

FORMYLATION OF 1-METHYLBENZIMIDAZOLE

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Khimiya Geterotsiklicheskikh Soedinenii, Vol. 3, No. 6, pp. 1123–1124, 1967

UDC 547.785.5+542.957

The formylation of 1-methylbenzimidazole in position 2 has been effected by the use of dimethylformamide in the presence of sodium.

Because of the presence in the μ-position of benzimidazole of a positive charge, the direct introduction of an aldehyde group taking place through the stage of the electrophilic replacement of an H atom by a formylating compound is unsuitable for the production of benzimidazole-2-aldehydes. The existing methods for the synthesis of 2-formylbenzimidazoles are based mainly on the oxidation of derivatives of benzimidazole containing a methyl group [1] or a hydroxymethyl group [2] in position 2 and the oxidative degradation of 1,2-dihydroxy-1,2-di(2′-benzimidazolyl)ethane [3] and its N-substituted derivatives [4] and of 2-(d-arabo)-benzimidazole [5]. The production of 2-formylbenzimidazoles from o-arylenediamines and from 1,2-dichloro-1,2-diethoxyethane [6], from the acetal of ethyl glyoxylate [7], and from dichloroacetic acid [8] has been reported.