INTRODUCING A QUINOLINE GROUP INTO THE BENZENE RING OF 1-ALKYL-2, 3-DIHYDROINDOLES

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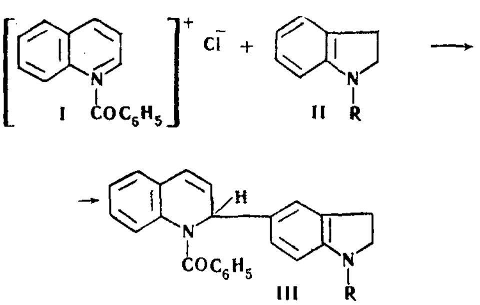
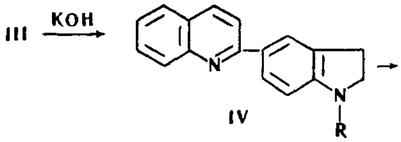
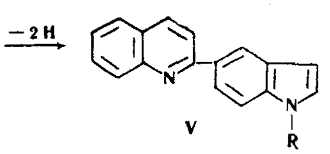
When 1-acylquinolinium salts react with an indole, the quinoline portion enters the pyrrole ring of the indole [1]. To prepare quinolylindoles, substituted in the benzene ring, we made use of our previously described method of preparing pyridylindoles by reacting 1-acylpyridinium salts with 1-alkylinolines [2]. It was found that by this method a quinoline group can be introduced into the benzene ring of 1-alkyl-2, 3-dihydroindoles (II), but that with 1-acylquinolinium salts the reaction proceeds without a catalyst, stopping at the state of formation of 1, 2-dihydroquinolines:



The resultant 1-alkyl-5-(1'-benzoyl-1', 2'-dihydroquinolyl-2')-1, 2-dihydroindoles (III), were smoothly hydrolyzed by alkali to give high yields of 1-alkyl-5-(quinolyl-2')-1, 2-dihydroindoles (IV), from which 5-(quinolyl-2')indoles (V) could be obtained by the usual methods of dehydrogenation.





The UV and IR spectra of all the type III compounds were similar to the spectra of 1-benzoyl-2-p-dialkylaminophenyl-1, 2-dihydroquinolines, which indicates the presence of a quinoline group para to the amino group, and confirms structure III.

By reacting quinoline, benzoyl chloride, and II (2: 1: 1) at 100° for 5 hr, we obtained 1-methyl-5-(1'-benzoyl-1', 2'-dihydroquinolyl-2')-1, 2-dihydroindole (**III**, R = Me), in 57% yield, snow-white crystals, mp 116–117° (ex petrol ether), R_f 0.36 (on alumina, using benzene: hexane: $CHCl_3$ 6: 1: 30), λ_{max}, 265 mμ, ε 17356 (in EtOH). Found: C 81.69; 81.77; H 6.09; 6.11; N 7.37; 7.45%. Calculated for $C_{25}H_{22}N_2O$. C 81.94; H 6.01; N 7.65%.

1-Ethyl-5-(1'-benzoyl-1', 2'-dihydroquinolyl-2')-1, 2-dihydroindole (**III**, $R=C_2H_5$) was prepared similarly, yield 53%, mp 128–130°. Found: C 81.86; 81.91; H 6.60; 6,41; N 7.52; 7,47%. Calculated for $C_{26}H_{24}N_2O$. C 82.11; H 6.32; N 7.37%.

Hydrolysis gave 1-ethyl-5-(quinolyl-2')-1, 2-dihydroindole (**IV**, $R=C_2H_5$), mp 122–123°; picrate mp 193–194° (ex EtOH). Found: N 13.67; 13.81%. Calculated for $C_{19}H_{18}N_2 \cdot C_6H_3N_3O_7$. N 13.91%.

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2, 2'-AZOBENZIMIDAZOLES

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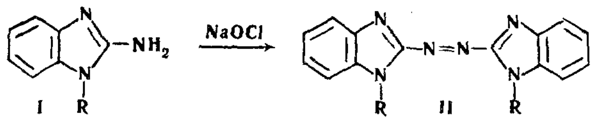
Unlike the recently described symmetrical 2, 2'-azoimidazoles [1], their benzimidazoles (II) have hitherto not been known. We have now prepared the first representatives of this class of compound. The starting materials were the readily accessible N-substituted 2-aminoben-

2, 2'-Azobenzimidazoles (II)

R	Mp, °C	Solvent for crystallizing	Formula	Found, %			Calculated, %			Yield, %
				C	H	N	C	H	N	
CH_3	289–290	EtOH	$C_{16}H_{14}N_6$	65.85	4.86	29.00	66.19	4.86	28.95	20
C_2H_5	197	EtOAc	$C_{18}H_{18}N_6$	68.21	5.95	26.66	67.90	5.70	26.40	17
$C_6H_5CH_2$	279–280	$CHCl_3$-petrol ether	$C_{28}H_{22}N_6$·	75.56	5.29	18.96	75.99	5.01	19.00	36
C_6H_5	260	BuOH	$C_{26}H_{18}N_6$	75.02	4.26	20.23	75.32	4.38	20.30	72

zimidazole (I) [2], which were oxidized in ethanol solution with 30% aqueous sodium hypochlorite solution (3 mole).



$R = CH_3$; C_2H_5; $C_6H_5CH_2$; C_6H_5

The best results were obtained with 1-phenyl-2-aminobenzimidazole. Oxidation of 1-benzyl-, and particularly of 1-alkyl derivatives of 2-aminobenzimidazole was accompanied by side reactions, giving deeply colored resinous materials, with lowering of the yield of azo derivative. Here the azo compounds could only be purified by chromatography.

2, 2'-Azobenzimidazoles (see table) are orange-red compounds, which are decolorized when reduced with tin and hydrochloric acid to give the starting 2-aminobenzimidazoles.

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Rostov-on-Don State University

REACTION OF SILYL- AND BORAMINES WITH KETENE AND DIKETENE

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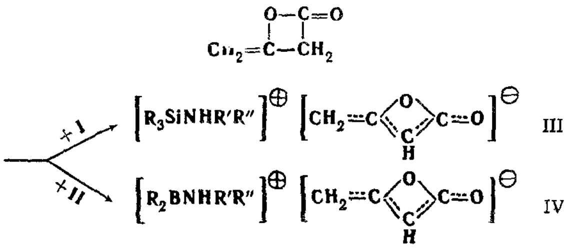
We have found that reaction of trialkylsilyl- and dialkylboramines $R_3SiNR'R''$ (I) and $R_2BNR'R''$ (II), e.g., $(CH_3)_3SiN(CH_3)_2$ (Ia), $(CH_3)_3SiN(C_2H_5)_2$, $(CH_3)_3SiN(C_4H_9)_2$*, $(CH_3)_3SiNHC_3H_7$*, $(CH_3)_3SiNHC_4H_9$*, $(n\text{-}C_3H_7)_2BNHC_4H_9\text{-}n$, $(n\text{-}C_4H_9)_2BN(C_2H_5)_2$, $(n\text{-}C_3H_7)_2BNHC_3H_5$, with methylene-β-propiolactone (diketene) leads to insertion of a molecule of the latter at the Si—N or B—N bond, and formation of derivatives of crotonamide or vinylacetamide. Diketene behaves as a moderately strong acid, and its dissociation gives a bidentate anion. So in the first stage of the reaction under consideration, formation of unstable adducts, type III and IV ammonium salts is possible



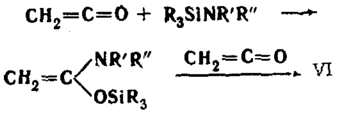
Then these adducts decompose with formation of O and C metallated products:

$$\text{III} \rightarrow CH_3C(OSiR_3)=$$

$$=CHC(O)NR'R''\ (\text{V}) + CH_2=C(OSiR_3)CH_2C(O)NR'R'' \qquad (\text{VI})$$

III → $CH_3C(O)^*CH(SiR_3)\text{-}C(O)NR'R''$ (VII). VII was a mixture of keto and cis-trans enol forms. Raman, IR, and PMR spectra, and determination of active hydrogen, showed the main reaction product to be O derivative forms of V and VI (for Ia the ratio was 2: 3). C derivatives were by-products. PMR spectroscopy showed the presence of cis-trans isomerism.

Reaction of I and II with ketene also gives O derivatives, but the main reaction product is VI, while V is present as an impurity. Formation of VI can be explained in two ways: from the enol form of acetylketene or through the intermediate ketene acetal with insertion of the second molecule of ketene at a C—N bond



$$CH_2=C=O + R_3SiNR'R'' \longrightarrow CH_2=C\begin{matrix}\nearrow NR'R'' \\ \searrow OSiR_3\end{matrix} \xrightarrow{CH_2=C=O} \text{VI}$$

On keeping the compounds obtained underwent substantial changes in refractive index, possibly because of shift of equilibrium between the keto and cis-trans enol forms VII, as well as interconversion between V and VI. The second type of change is more likely.

N-dimethylamide of β-(trimethylsilyloxy)crotonic acid (VIII). a) 24.4 g (0.18 mole) Ia in 50 ml ether and 18.3 g (0.18 mole) diketene gave, by an exothermic reaction, 34.0 g material bp 75-78° (2 mm); n_D^{20} 1.4563, d_4^{20} 0.9609. The PMR spectrum showed it to contain ~40% VIII and ~60% of the N-dimethylamide of β-(trimethylsilyloxy)vinylacetic acid (IX). Found: C 53.60; 53.55; H 9.69; 9.47; Si 14.00; 14.24; active H 0.1% MR_D 56.99; Calculated for $C_9H_{19}SiNO_2$. C 53.68; H 9.51; Si 13.95%; MR_D 57.53 (VIII), 57.16 (IX).

b) Reaction of 27.5 g (0.23 mole) Ia and excess ketene gas gave 31.1 g (66.5%) IX, bp 83—85° (3mm), n_D^{20} 1.4582, d_4^{20} 0.9691. Found: C 53.68; 53.35; H 9,18; 9.32%. VIII was present (according to the PMR spectrum) as an impurity.

More detailed results will be given in future publications.

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State Scientific Research Institute for the Chemistry and Technology of Heteroorganic Compounds of the Elements, Moscow

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*Compounds with an alkyl group of normal or iso structure were studied.