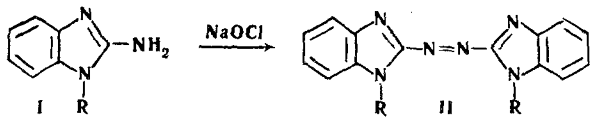
zimidazole (I) [2], which were oxidized in ethanol solution with 30% aqueous sodium hypochlorite solution (3 mole).



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

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.

REFERENCES

1. A. Kreutzberger, J. Org. Chem., 27, 886, 1962.
2. A. M. Simonov, collection: Essays on the Chemistry of Azoles [in Russian], Izd-vo Rostovsk.-na-Donu gos. univ., 1965.

25 February 1966

Rostov-on-Don State University

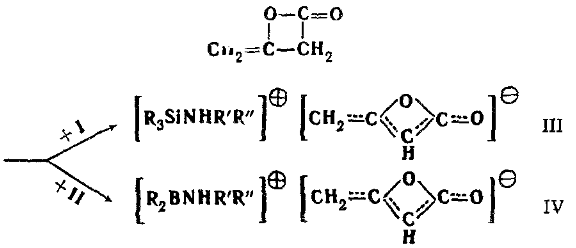
REACTION OF SILYL- AND BORAMINES WITH KETENE AND DIKETENE

V. D. Sheludyakov, V. P. Kozyukov, L. I. Petrovskaya, and V. F. Mironov

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 3, No. 1, pp. 185-186, 1967

UDC 547.71+546.287+543.422+541.67

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



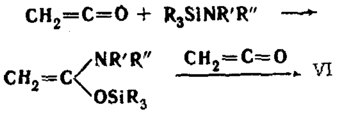
Then these adducts decompose with formation of O and C metallated products:

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

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

$\mathbf{III} \rightarrow CH_3C(O)\text{*}CH(SiR_3)\text{-}C(O)NR'R''$ (**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



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

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.

10 March 1966

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

---

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