2. The change in the chemical potential of the adsorbent and isosteric heat of adsorption under the conditions studied is identical in nature to the dependence on the amount of adsorption.

3. These results indicate a change in the state of zeolite NaX upon adsorption, which must be taken into account in calculating the thermodynamic indices of the adsorption process.

LITERATURE CITED

1. B. P. Bering, A. L. Maiers, and V. V. Serpinskii, Dokl. Akad. Nauk SSSR, 193, 119 (1970).
2. L. A. Vashchenko and V. V. Serpinskii, Izv. Akad. Nauk SSSR, Ser. Khim., 1248, 1637 (1975).
3. L. A. Vashchenko, V. V. Katal'nikova, and V. V. Serpinskii, Izv. Akad. Nauk SSSR, Ser. Khim., 2396 (1980).
4. A. G. Bezus, A. A. Lopatkin, and A. V. Kiselev, Kolloidn. Zh., 37, 1045 (1975).

SYNTHESIS OF N-(5-TETRAZOLYL)AMIDINES FROM 5-AMINOTETRAZOLE AND NITRILES USING ORGANOBORANES

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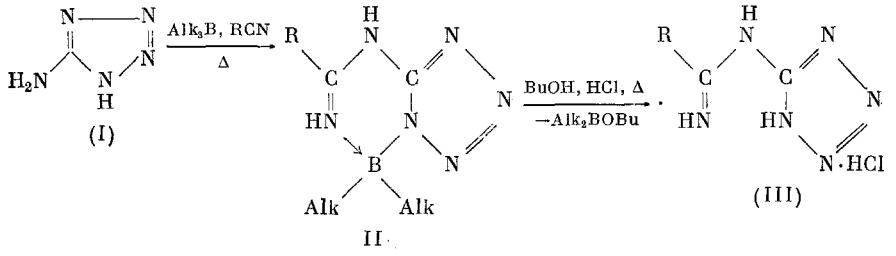
Heterylamidines attracted our attention as potential chelating ligands [1, 2]. These compounds also hold interest as starting reagents for constructing condensed heterocyclic systems [3-5]. However, such compounds are not always readily available. Thus, our attempts to obtain N-(5-tetrazolyl)amidines (TA) from 5-aminotetrazole (I) and nitriles in the presence of $AlCl_3$ proved unsuccessful. The most commonly employed method for the synthesis of amidines proposed by Pinner [6] is not very suitable for amines with low basicity [7] and does not give TA.

We have developed a method for the preparation of TA from (I) and nitriles using organoboranes. Chelate compounds (II), in which TA in the deprotonated form are the ligands, were readily obtained from (I), nitriles and trialkylboranes [8]. Upon the action of HCl in butanol, (II) is cleaved to give hydrochloride salts of TA (III) in 67-85% yield. Thus, the synthesis of (III) from (I) may be carried out by a two-step procedure indicated in (1):



(1)

Alk = Pr, Bu; R = Ph (a), *p*-$CH_3C_6H_4$ (b), *o*-$CH_3C_6H_4$ (c), Me (d).

The trialkylborane (Pr_3B or Bu_3B) thus has an auxiliary role in the formation of (III) from (I) and nitriles.

Another approach which permits us to bypass the difficulties related to the preparation and storage of R_3B entails the use of dicyclohexylborane obtained *in situ* from cyclohexene and BH_3·THF as the borylating reagent. This method was used for the synthesis of hydrochloride salt (IIIa) from (I) in 65% yield:

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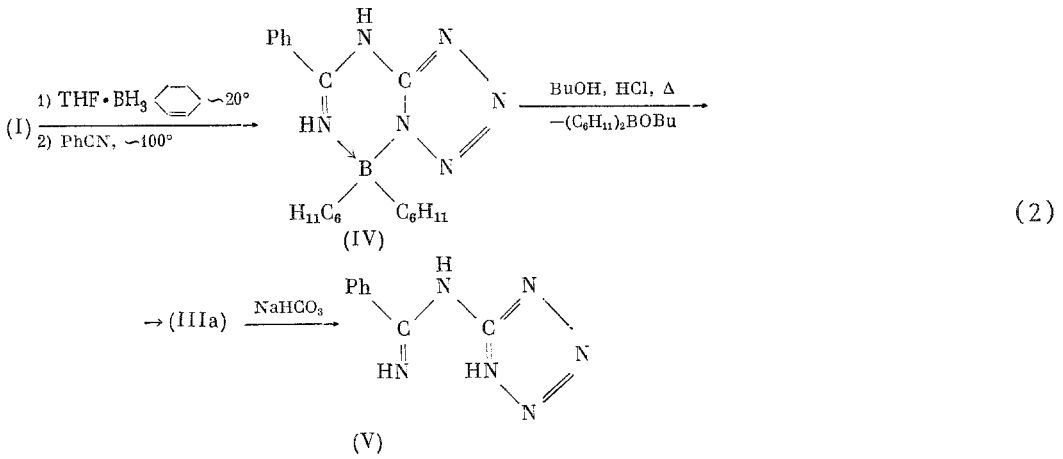

(2)

These amidine derivatives may be isolated as the free bases from salts (III) upon the addition of alkali. Thus, N-(5-tetrazolyl)benzamidine (V) was obtained from (IIIa) in 72% yield.

TA hydrochlorides (IIIa)-(IIId) are colorless crystalline compounds which have good solubility in methanol and DMSO and moderate solubility in acetone and ethanol. Their mass spectra show peaks for $(M-HCl)^+$ or $(M-HCl-H)^+$ ions. The elimination of N_2 or HN_3 is characteristic for the further fragmentation of these compounds.

The IR spectra of (IIIa-d) in KBr pellets show strong absorption at 1670-1695 cm^{-1} which should be ascribed to νC=N of the amidine fragment. A broad band with several maxima (hydrogen bonds) is observed at 2200-3400 cm^{-1} in the region of NH stretching vibrations. The ^{13}C NMR chemical shifts for the carbon atom of the tetrazolyl ring are virtually independent of the substituent R (δ 156.2-157.2 ppm). The amidine carbon gives a downfield signal at 165.1 ppm for (IIId) and δ 162.6-163.6 ppm for (IIIa-c).

EXPERIMENTAL

The operations with the organoboron compounds were carried out in a dry argon atmosphere. The ^{13}C NMR spectra were taken on Bruker WM-250 and Bruker AM-300 spectrometers and given in δ, ppm. The signals were assigned on the basis of their chemical shift, coupling constant, and multiplicity. The signals for the amidine carbon in (IIIa) and (V) were identified relative to the observed $^3J_{C,H}$ (3.7 and 5.0 Hz, respectively). The IR spectra were taken on a UR-20 spectrometer (ν, cm^{-1}). The mass spectra (m/z) were taken on a Varian MAT CH-6 mass spectrometer with direct sample inlet into the ion source at 150-200°C.

Dialkylboryl[N-(5-Tetrazolyl)amidinates] (II) were synthesized by heating a mixture of (I), Alk_3B, and excess nitrile at 120°C according to our previous procedure [8]. For the preparation of (II, R = Me), the reaction was carried out in an autoclave.

Hydrochloride Salts of N-(5-Tetrazolyl)amidines (IIIa-d). A mixture of 0.005-0.015 M of the corresponding (II), 1.5-6 ml 5-8 N HCl in 1-butanol, and 1-3 ml xylene (to reduce the solubility of the reaction product) was heated in a sealed ampul at 100-150°C for 1-3 h. After cooling, the precipitate of (III) was filtered off, washed with benzene and ether, and dried in vacuum.

Hydrochloride salt of N-(5-Tetrazolyl)benzamidine (IIIa) was obtained in 75% yield, mp 221-223°C (dec.). Found, %: C 43.18, H 4.28, Cl 15.54, N 36.62. C_8H_9ClN. Calculated, %: C 42.77, H 4.04, Cl 15.78, N 37.41. Mass spectrum: 187 $[M - HCl]^+$. IR spectrum in KBr: 1670 (C=N). ^{13}C NMR spectrum in DMSO-d_6: 162.6 (Ph-C), 157.2 (C_{tetraz}), 133.6, 129.2, 128,9, 128.8 (Ph).

Hydrochloride salt of N-(5-Tetrazolyl)-p-toluamidine (IIIb) was obtained in 67% yield, mp 242-245°C (dec.). Found, %: C 45.16; H 4.72; Cl 14.70. $C_9H_{11}ClN_6$. Calculated, %: C 45.29, H 4.65, Cl 14.85. Mass spectrum: 201 $[M-HCl-H]^+$. IR spectrum in KBr: 1670 (C=N).

Hydrochloride salt of N-(5-Tetrazolyl)-o-toluamidine (IIIc) was obtained in 68% yield, mp 230-235°C (dec.). Found, %: C 45.45, H 4.52; Cl 14.49%. $C_9H_{11}ClN_6$. Calculated, %: C 45.29, H 4.65, Cl 14.85. Mass spectrum: 187 $[M-HCL-CH_3]^+$. IR spectrum in KBr: 1675 (C=N).

Hydrochloride salt of N-(5-tetrazolyl)acetamidine (IIId) was obtained in 86% yield, mp 235-237°C (dec.). Found, %: C 22.25, H 4.64, Cl 22.33, N 50.90. $C_3H_7ClN_6$. Calculated, %: C 22.16, H 4.34, Cl 21.81, N 51.69. Mass spectrum: 126 $(M-HCl)^+$. IR spectrum in KBr: 1695 (C=N). ^{13}C NMR in DMSO-d_6: 165.1 ($CH_3\underline{C}$), 156.2 (C_{tetraz}), 18.6 (CH_3).

Synthesis of (IIIa) using Dicyclohexylborane. A sample of 1.7 g (0.02 mole) (I) was added in portions with stirring over 0.5 h to a suspension of dicyclohexylborane obtained according to Zweifel et al. [9] from 3.4 g (0.04 mole) cyclohexene and 16.5 ml 1.22 M BH_3 in THF. After no further gas evolution was noted, the mixture was evaporated to dryness in vacuum. A sample of 15 ml benzonitrile was added to the residue and maintained for 3 h at 100°C. The precipitate was filtered off, washed with hexane, and dried in vacuum to give 6.8 g (90%) dicyclohexylboryl[N-(5-tetrazolyl)benzamidinate] (IV), mp 276-277°C (dec.). Found, %: C 66.19, H 7.90, B 2.90. $C_{20}H_{29}BN_6$. Calculated, %: C 65.93, H 8.02, B 2.97. Mass spectrum: 281 $[M-C_6H_{11}]^+$. IR spectrum in KBr: 1640 (C=N), 3382, 3200-2400 (NH).

The cleavage of (IV) with HCl in 1-butanol was carried out as described above to give (IIIa) in 72% yield.

N-(5-Tetrazolyl)benzamidine (V). A sample of 5 ml saturated aqueous $NaHCO_3$ was added to 0.56 g (IIIa) and stirred until no further gas was evolved (about 15 min). The precipitate was filtered off, washed with water, and dried to give 0.34 g (72%) (V), mp 237-238°C (dec.). Found, %: C 51.10, H 4.30, N 44.53. $C_8N_8N_6$. Calculated, %: C 51.05, H 4.28, N 44.66. Mass spectrum: 187 $[M-H]^+$. ^{13}C NMR spectrum in DMSO-d_6: 160.9 (Ph-$\underline{C}$), 159.3 (C_{tetraz}), 133.5, 131.7, 128.4, 127.6 (Ph).

CONCLUSIONS

A method has been proposed for the synthesis of N-(5-tetrazolyl)amidines from 5-aminotetrazole, nitriles, and organoboranes through boron chelate compounds, namely, dialkylboryl[N-(5-tetrazolyl)amidinates].

LITERATURE CITED

1. V. A. Dorokhov, B. M. Zolotarev, and B. M. Mikhailov, Izv. Akad. Nauk SSSR, Ser. Khim., 869 (1981).
2. I. A. Teslya, Z. A. Starikova, and V. K. Trunov, Izv. Akad. Nauk SSSR, Ser. Khim., 2730 (1981).
3. K. T. Potts, H. R. Burton, and J. Bhattacharyya, J. Org. Chem., 31, 260 (1966).
4. T. Novinson, K. Senga, J. Kobe, et al., J. Heterocycl. Chem., 11, 691 (1974).
5. T. Georg and R. Taribramani, Synthesis, 346 (1974).
6. A. Pinner, Chem. Ber., 16, 1654 (1883).
7. L. Baiocchi and G. Palazzo, Ann. Chim. (Rome), 58, 608 (1968).
8. V. A. Dorokhov, A. R. Amamchyan, I. A. Teslya, and Z. A. Starikova, Izv. Akad. Nauk SSSR, Ser. Khim., 2049 (1987).
9. G. Zweifel, H. Arzoumanian, and C. Whitney, J. Am. Chem. Soc., 89, 3652 (1967).