CATALYST FOR HETEROAROMATIZATION OF ALIPHATIC IMINO COMPOUNDS

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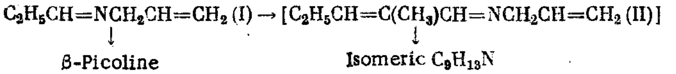
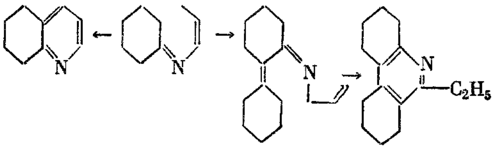
UDC 542.97:547.415.3

The catalytic heteroaromatization of imino derivatives AlkCH=NAlk' in the presence of Al–K (AK) and Al–Cr–K (ACK) catalysts leads to a mixture of pyridine bases that differ in both structure and composition, for example:



$$\begin{array}{ccc} C_2H_5CH{=}NCH_2CH{=}CH_2\ (I) & \rightarrow & [C_2H_5CH{=}C(CH_3)CH{=}NCH_2CH{=}CH_2\ (II)] \\ \downarrow & & \downarrow \\ \beta\text{-Picoline} & & \text{Isomeric } C_9H_{13}N \end{array}$$

In the present paper we studied the transformations of (I) and cyclohexylideneallylamine (III) in the presence of 5% Ni/Al_2O_3, which is a new catalyst for this reaction. It is known that Ni-containing catalysts are quite inactive in aromatization processes, but the Ni/Al_2O_3 catalyst exhibited a higher activity in the formation of pyridines from (I) and (III) than do the known AK and ACK catalysts. The catalyzates, obtained from (I) under various conditions, contained only β-picoline and 3,5-dimethyl-2-ethylpyridine (IV) and none of the isomeric $C_9H_{13}N$ compounds, and the overall yield of the pyridines reached 50% (in a helium stream). 5,6,7,8-Tetrahydroquinoline (V) and 6-ethyl-1,2,3,4,7,8,9,10-octahydrophenanthridine (VI) were obtained in a similar manner from (III):



(V) (III) (VII) (VI)

The intermediate products of the transformations (I) → (IV) and (III) → (VI) [imino compound (II) and N-allylimino-2-cyclohexylidenecyclohexanone (VII)] were also isolated.

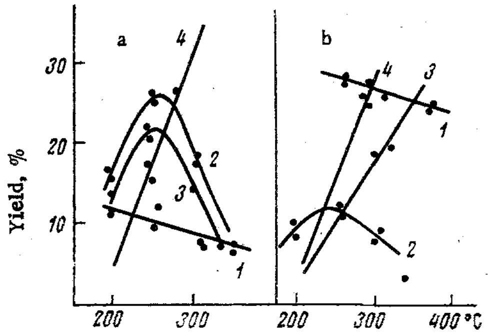


Fig. 1. Yields of transformation products of propylidene-allylamine as a function of the temperature and carrier gas (a) He, b) NH_3): 1) unreacted imine; 2) β-picoline; 3) 3,5-dimethyl-2-ethylpyridine; 4) propionitrile.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1446-1447, June, 1978. Original article submitted November 18, 1977.

0568-5230/78/2706-1263$07.50

EXPERIMENTAL

The catalytic aromatization method is described in [1]. The results of transforming (I) at 200-400°C and a space velocity of 1 h^{-1} in either a He or NH_3 atmosphere are plotted in Fig. 1. The constants and analytical data for the obtained picoline and (II) correspond to the literature data. Compound (IV), bp 85-90° (13 mm). PMR spectrum (δ, ppm, CD_3OD, standard = TMS): 1.2 t (3H); 2.2 d (6H); 2.68 qu (2H). Picrate, mp 152°; cf. [3]. The transformations of (III) were studied at 250-400° in a He stream and a space velocity of 1 h^{-1}. At 275° the yield of (V) was 14.5%, and that of (VI) was 20%. Compound (VI), bp 160-164° (3 mm). PMR spectrum (δ, ppm, neat, standard = TMS): 1.13 t (2H); 1.7 m (8H); 2.25 m (8H); 2.6 qu (2H). Ultraviolet spectrum: λ_{max} 218, 225, 230, 275 nm. Found: C 83.06; H 10.15%. $C_{15}H_{21}N$. Calculated: C 83.66; H 9.83%. Oxidation of (VI) with $KMnO_4$ gave pyridine-3,4,5-tricarboxylic acid [4] with mp 261°. Compound (VII) was isolated from the fraction with bp 200-210° (22 mm). PMR spectrum (δ, ppm, neat, TMS): 1.07 m (10H); 2.25 m (4H); 3.90 d.d (2H); 5.03 m (2H); 5.75 t (1H).

CONCLUSIONS

Ni/Al_2O_3 is an active catalyst for the heteroaromatization of aliphatic imino compounds; the selectivity of forming the pyridine bases on Ni/Al_2O_3 is higher than in the presence of Al–K and Al–Cr–K catalysts.

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CRYSTAL AND MOLECULAR STRUCTURE OF BIS(o-CARBORANYL)DIMETHYLGERMANE

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UDC 541.6:547.1'127:547.246

A number of structure studies of "tetrahedral" molecules with a central Ge atom is described in the literature [1-5].

The purpose of the present paper was to ascertain the effect of bulky substituents on the geometric characteristics of the Ge coordination sphere.

EXPERIMENTAL

The crystals of bis(o-carboranyl)dimethylgermane are monoclinic, $a = 6.950(6)$ Å, $b = 19.05(2)$ Å, $c = 15.81(1)$ Å, $\beta = 95.80(7)$, space group $P2_1/c$, $V = 2083$ Å^3, $Z = 4$, $d_{calc} = 1.246$ g/cm^3, and $d_{meas} = 1.238$ g/cm^3. The parameters, determined by the photo method, were made more precise using the method of least squares (MLS) on a four-circle automatic Syntex $P2_1$ diffractometer. The intensities of 1539 independent reflections with $F^2 > 2\sigma$ (λ MoK_α radiation, graphite monochromator, $\theta/2\theta$ scanning, $\theta \leq 21°$) were measured on it.

The structure was deciphered by the heavy-atom method. The coordinates of the Ge atom were determined from the Patterson function. The other atoms were developed by successive approximations of the electron-density syntheses. The structure was refined by the MLS as the isotropic approximation. The anisotropic temperature factor was introduced only for Ge. The final R factor was 8.6%. The C atoms in the o-carborane nuclei were distinguished on the basis of analyzing the bond lengths and temperature factors. All of the calculations were made on a NOVA 1200 electronic computer on the basis of XTL programs.

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1447-1450, June, 1978. Original article submitted November 29, 1977.