LETTERS TO THE EDITOR

REACTION OF TRICHLOROGERMANE WITH ALKENYLCARBORANES

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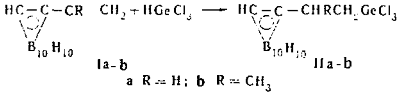
Carborane derivatives containing germanium have been obtained previously via organometallic derivatives [1, 2]. We have found another route for the preparation of germanium-containing carboranes:



$$\underset{B_{10}H_{10}}{HC{-}C{-}CR}{=}CH_2 + HGeCl_3 \longrightarrow \underset{B_{10}H_{10}}{HC{-}C{-}CHRCH_2GeCl_3}$$

Ia-b IIa-b

a R = H; b R = CH$_3$

However, the addition of HGeCl$_3$ to unsaturated carboranes, in contrast to the majority of other unsaturated compounds, takes place with difficulty and gives low yields of the adducts. This is probably due to the deactivation of the double bond of the initial compounds through the powerful electron-accepting nature of the carborane nucleus.

2-Trichlorogermylethylcarborane (IIa). To a solution of 9.3 g (0.055 mole) of **Ia** in 19 ml of benzene was added 11.4 g (about 0.045 mole) of HGeCl$_3$ [3]. The mixture was boiled for 12 hr and vacuum-distilled to give 4.5 g of **Ia** and 7.6 g of a fraction with bp 167–200° C (2 mm) which partially crystallized. Filtration yielded 3.1 g of **IIa** with mp 115–117° C (sublimation). Yield 31% on the **Ia** that had reacted. Found, %: C 13.52; H 4.41; Cl 30.10; B 31.30; Ge 20.80. Calculated for $C_4H_{15}B_{10}Cl_3Ge$, %: C 13.71; H 4.32; Cl 30.36; B 30.88; Ge 20.72.

1-Methyl-2-trichlorogermylethylcarborane (IIb). Under the conditions of the preceding experiment, 8.9 g of HGeCl$_3$ (about 0.035 mole) and 10.3 g (0.056 mole) of **Ib** in 10 ml of petroleum ether gave 8.1 g of **IIb** (64%) with mp 75–76.5° C (sublimation). Found, %: C 16.43; H 4.51; B 29.50; Cl 28.60; Ge 19.80. Calculated for $C_5H_{17}Cl_3B_{10}Ge$, %: C 16.48; H 4.70; B 29.69; Cl 29.20; Ge 19.92.

The IR spectra of **IIa** and **IIb** (UR-20 spectrometer) have bands characteristic for the vibrations of the Ge–Cl bond (432–437 cm^{-1}) and of the carborane nucleus (2600 and 3065 cm^{-1}).

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NITRATION OF 2-OXOIMIDAZO[4, 5-b]PYRIDINE AND ITS N-METHYL DERIVATIVES

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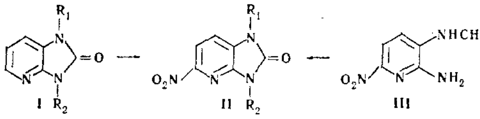
Continuing a study of substitution in the imidazo[4, 5-b]pyridine nucleus, we have investigated the behavior of 2-oxoimidazo[4, 5-b]-pyridines (I) under nitration conditions.

As was found, I readily undergoes nitration even in the cold but, in contrast to 3-methylimidazo[4, 5-b]pyridine [1], the nitro group is directed into position 5, i.e., into the free α-position of the pyridine ring.

The structure of the nitro derivatives (II) obtained was shown by their independent synthesis from 2-amino-3-methylamino-6-nitropyridine (III), which was obtained by the reduction of the product of the replacement of the methoxy group by a methylamino group (see [2]) in 3-methoxy-2, 6-dinitropyridine [3]. Fusing III with urea led to IIc. The methylation of the latter (just as in the case of **IIa** and **IIb**) gave **IId** [4].



I II III

a R$_1$=R$_2$=H; b R$_1$=H, R$_2$=CH$_3$; c R$_1$=CH$_3$, R$_2$=H; d R$_1$=R$_2$=CH$_3$

5-Nitro-2-oxoimidazo[4, 5-b]pyridine (IIa). Yield 72%. Mp 388–339° C (water). Found, %: C 40.24; H 2.39. Calculated for $C_6H_4N_4O_3$, %: C 40.01; H 2.24.

3-Methyl-5-nitro-2-oxoimidazo[4, 5-b]pyridine (IIb). Yield 76%. Mp 278–278.5° C (long colorless needles from ethanol). Found, %: C 43.22; H 3.06. Calculated for $C_7H_6N_4O_3$, %: C 43.30; H 3.11.

1-Methyl-5-nitro-2-oxoimidazo[4, 5-b]pyridine (IIc). Yield 83%. Mp 358–360° C (fine yellow needles from dimethylformamide). Found, %: C 43.28; H 3.02. Calculated for $C_7H_6N_4O_3$, %: C 43.30; H 3.11.

1, 3-Dimethyl-5-nitro-2-oxoimidazo[4, 5-b]pyridine (IId). Yield 80%. Mp 230.5–231.5° C (long pale yellow needles from ethanol). Found, %: C 46.30; H 4.21. Calculated for $C_8H_8N_4O_3$, %: C 46.15; H 3.87.

3-Methyl-2, 6-dinitropyridine. Yield 95%. Mp 199–200° C (long bright yellow rods from acetone). Found, %: N 28.20. Calculated for $C_6H_6N_4O_4$, %: N 28.27.

2-Amino-3-methyl-6-nitropyridine (III). Yield 43%. Mp 234–236° C (rhombic orange crystals from dioxane). Found, %: C 42.65; H 4.51. Calculated for $C_6H_8N_4O_2$, %: C 42.86; H 4.79.

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MAGNETIC SUSCEPTIBILITY AND EFFECTIVE MAGNETIC MOMENTS OF METALLOATRANE-3, 7, 10-TRIONES

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In the course of a study of internally complexed alkoscides and inorganic esters of triethanolamine and its C-substituted derivatives—the metalloatranes $N(CH_2CH_2O)_3M$ (where M is a tervalent metal or a group of atoms containing a multivalent metal) [1, 2]—it appeared to us to be of interest to study the internally complexed salts and mixed inorganic anhydrides of aminotriacetic acid $N(CH_2COO)_3M$, with apparently analogous structures, which we have formally named metalloatrane-3, 7, 10-triones. It might have been expected that the appearance of three carbonyl groups in the atrane skeleton would lead to an anomalous change in the physicochemical properties of these compounds due to the increased polarity of the M—O bond, to the change in the strength of the M←N bond, and to the nature of the intermolecular interaction.

With this object, we have determined the effective magnetic moments of a number of metalloatranetriones, mainly in the form of the hydrates $N(OCOCH_2)_3M \cdot nH_2O$. A comparison of the values of μ_{eff} obtained with the calculated moments for "pure spin" paramagnetism determined by the total number of unpaired electrons [3] is given in the table.

In all cases, the experimental figures obtained (μ_{exp}) are of the same order as the calculated figures (μ_{calc}). The fact that the values of μ_{exp} are greater than μ_{calc} for the compounds of cobalt, iron, and manganese is explained by the contribution of the spin-orbital coupling, which is characteristic for the formation of complexes [3]. In the case of intermolecular interaction in the crystal lattice of the metalloatrane-3, 7, 10-triones due to the carbonyl groups, a deviation of μ_{exp} from μ_{calc} is possible—in particular, a lowering in μ_{exp} as a consequence of the exchange interaction, as has been observed for copper complexes [4]. As was to be expected, the lanthanum compound is diamagnetic. A comparison of the experimental magnetic susceptibility with the value calculated by Pascal's new scheme ($\chi_{calc} = -0.2335 \cdot 10^{-6}$) [5]

Magnetic Susceptibilities and Effective Magnetic Moments of the Metalloatrane-3, 7, 10-triones $N(CH_2COO)_3M \cdot nH_2O$

M	n	T°, K	$\chi_g \cdot 10^{-6}$	$\chi_{mol} \cdot 10^{-6}$	μ_{exp}	μ_{calc}
La	3	298	−0.1599			
Cr	3	299	20.42	6094	3.83	3.88
Mn	0	296	32.60	8013	4.37	4.90
Mn	1	296	32.20	10844	5.09	4.90
Fe	1	299	62.17	16375	6.28	5.92
Co	3	298	40.95	12418	5.46	4.90
Ni	3	298	20.25	6182	3.82	3.88