LETTERS TO THE EDITOR

REACTION OF TRICHLOROGERMANE WITH ALKENYLCARBORANES

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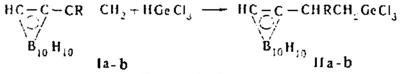
Carborane derivatives containing germanium have been obtained previously via organometallic derivatives [1, 2]. We have found another route for the preparation of germanium-containing carboranes:



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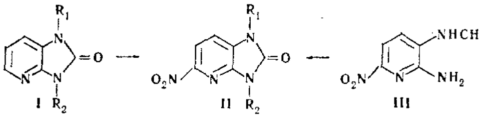
Continuing a study of substitution in the imidazo[4, 5-b]pyridine nucleus, we have investigated the behavior of 2-oxoimidazo[4, 5-b]-pyridines (I) under nitration conditions.

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.