

structure. Thus the ten vanadium atoms may be visualized as forming two octahedra which share one horizontal edge. Each of these vanadium atoms in turn is surrounded octahedrally by six atoms of oxygen. Of the resulting ten VO_6 octahedra, six are condensed into a 2×3 rectangle by sharing horizontal O-O edges, and two are inserted symmetrically above and two below the rectangle and share sloping O-O edges with octahedra of the rectangular array (see Fig. 1). The symmetry of the decavanadate group, therefore, is orthorhombic mmm.

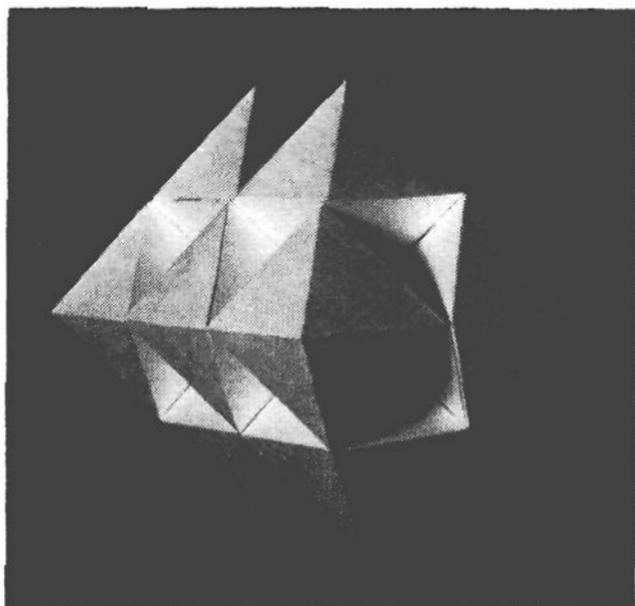


Fig. 1. Model of the decavanadate ion, $\text{V}_{10}\text{O}_{28}^{6-}$, in terms of its ten constituent VO_6 octahedra.

In pascoite, two of the calcium ions are coordinated to the two apical oxygen atoms above and below the decavanadate group shown in Fig. 1 and to five water molecules each to form a $[\text{Ca}(5\text{H}_2\text{O})_2\text{V}_{10}\text{O}_{28}]^{2-}$ complex ion, and the third calcium ion is octahedrally coordinated to the remaining six water molecules in a separate $\text{Ca}(\text{H}_2\text{O})_6^{2+}$ ion which probably is hydrogen bonded to certain oxygen atoms of the decavanadate ion. In the zinc analog of hummerite, the zinc ion is octahedrally coordinated to six water molecules, and the potassium ion is in contact with ten oxygen atoms, namely, three H_2O from two $\text{Zn}(\text{H}_2\text{O})_6^{2+}$ ions, five oxygen atoms from three neighboring $\text{V}_{10}\text{O}_{28}^{6-}$ ions, and two additional H_2O molecules which fill the remaining space in the structure.

Full details of the two independent structure investigations will be published separately.

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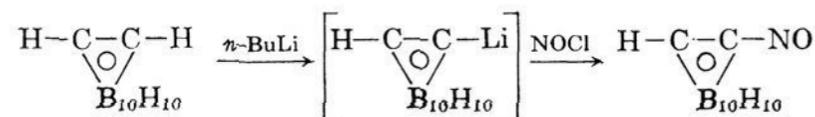
RECEIVED AUGUST 7, 1964

Nitrosocarboranes from Nitrosyl Chloride

Sir:

Reaction of alkylmetals with nitrosyl chloride usually gives either alkylnitrosohydroxylamines¹ or dialkylhydroxylamines,² although nitrosobenzene has been prepared³ by passing nitrosyl chloride into phenylmagnesium bromide. We have found that the addition

of 1-carboranyl lithium^{4,5} to excess nitrosyl chloride forms 1-nitrosocarborane in good yield if the reaction is performed at low temperatures. The product, a blue, volatile solid, is identical with material prepared by a



conventional route from carborane-1-carboxyl chloride⁴ through the azide, amine, and then peracid oxidation of the amine.⁶ Similarly, 1-methyl-2-carboranyl lithium and nitrosyl chloride gave 1-methyl-2-nitrosocarborane, which also has been prepared by the conventional route.^{6,7} Table I shows the influence of reaction temperature on the yield of nitroso compound obtained.

TABLE I

EFFECT OF REACTION TEMPERATURE ON THE PER CENT YIELD OF NITROSOCARBORANES

Temperature, °C	0	-70	-125
$\text{H}-\text{C}-\text{C}-\text{NO}$ $\text{B}_{10}\text{H}_{10}$..	21	49, 39
$\text{CH}_3-\text{C}-\text{C}-\text{NO}$ $\text{B}_{10}\text{H}_{10}$	13	26, 27, 21	...

A typical procedure involved the addition of 1-carboranyl lithium (from 0.01 mole of carborane) in ether-hexane to 2 ml. of nitrosyl chloride in 11 ml. of ether at -125° during a 25-min. addition period. The reaction mixture was then poured into ice-cold sodium carbonate solution, and the blue organic layer was dried, freed of solvent, and leached with ligroin. The extract was passed through a column containing 50 g. of silica gel. Evaporation of the blue ligroin eluate gave 49% of 1-nitrosocarborane, m.p. $196.5-197.5^\circ$, lit.⁶ m.p. $195-197^\circ$.

Anal. Calcd. for $\text{C}_2\text{H}_{11}\text{B}_{10}\text{NO}$: C, 13.87; H, 6.40; B, 62.38. Found: C, 13.60; H, 6.40; B, 62.00.

The mass spectrum shows m/e 175 (I) as the highest



molecular species, while the base peak is m/e 145 (II). The infrared and visible spectra have ν_{min} 719, 1018, 1075, 1169, 1562, 2580, 3080, 15,150, and 16,700 cm^{-1} .

We suggest that this addition of alkylmetals to nitrosyl chloride at very low temperatures will be of general utility in the preparation of stable nitroso compounds.

A nitroso rubber⁸ terpolymer containing 10 mole % 1-nitrosocarborane, 40 mole % nitrosotrifluoromethane, and 50 mole % tetrafluoroethylene has been prepared by bulk polymerization of 37, 13, and 50 mole %, respectively, of the above monomers. The polymerization was conducted in a sealed tube for 24 hr. at -25° followed by 120 hr. at $50-70^\circ$. The crude product was washed with methylene chloride

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