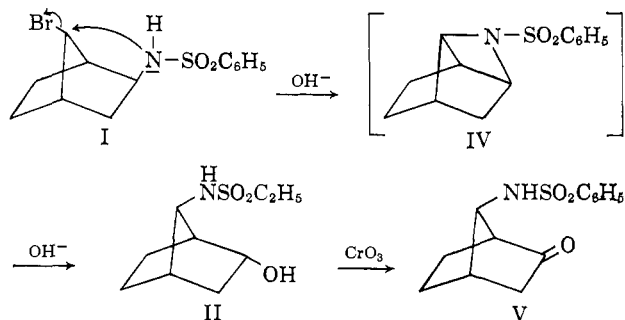
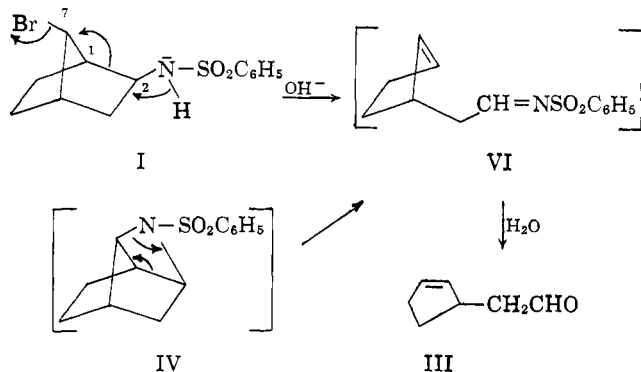


azetidine (IV) which under the reaction conditions is opened by hydroxide ion to give II. Participation of a suitable 2-*exo* group in the solvolysis of 7-*anti* substituents might be expected in view of the known pronounced acceleration of solvolysis shown in 7-*anti*-norbornenyl systems.² However, the 2-methylene substituent was ineffective in this regard.³ II was characterized by its oxidation with Jones reagent⁴ to give



the known ketone V⁵ and the hydroxyl group in II is assumed to be in the *endo* configuration.

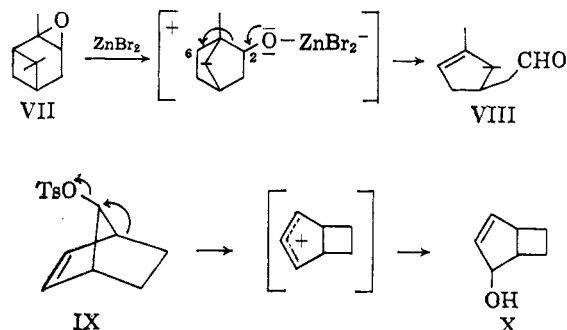
The major product III undoubtedly arises by hydrolysis of VI, the latter presumably being produced either directly from I by cleavage of the C₁-C₂ bond as depicted, or from intermediate IV, which may suffer collapse of the strained azetidine ring under the re-



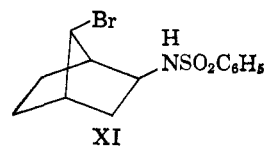
action conditions. The former path is analogous to solvolytic fragmentation reactions of amines studied by Grob.⁶ Aldehyde III was identified by elemental analysis of its 2,4-DNP (C₁₃H₁₄N₄O₄, m.p. 100-101°, lit.⁷ m.p. 98-99°) and by the characteristic n.m.r. spectrum of the 2,4-DNP which showed six methylene protons (δ 1.2-2.6), one methinyl proton (δ 3.0), two olefinic protons (δ 5.75), and one aldehydic proton (δ 8.84).

Berson² has pointed out that formal cleavage of a bicyclo[2.2.1]heptane has been reported in only a few cases and this is believed to be the first example in which cleavage occurs by displacement at C₇ giving a double bond at the C₁-C₇ position of the original norbornane skeleton. The reported conversion⁸ of α -pinene oxide (VII) to campholenic aldehyde (VIII) is somewhat

analogous, but involves displacement at C₆. Internal displacement at C₇ has been observed in the hydrolysis of *syn*-7-norbornenyl *p*-toluenesulfonate (IX) to yield 2-bicyclo[3.2.0]heptenol-4 (X). In the latter case, the formation of a stabilized intermediate allylic carbonium ion provides a strong driving force for the ring cleavage.



In contrast to the solvolysis of I, as described above, the isomeric 7-*syn*-bromo-2-*exo*-benzenesulfonamidobicyclo[2.2.1]heptane¹ (XI) was quantitatively recovered



unchanged after refluxing in 5% aqueous alcoholic sodium hydroxide for 60 hr.; thus it is apparent that participation by the benzenesulfonamido group must occur in the cleavage of the C-Br bond in I.

(9) National Defense Education Act Fellow, 1962-1965.

DEPARTMENT OF CHEMISTRY
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RECEIVED JULY 24, 1964

The Structure of the Decavanadate Ion¹

Sir:

When vanadate solutions (V₂O₅ dissolved in alkali) are acidified to a pH value between 2 and 6, they turn orange in color because of the formation of the isopolycomplex ion, V₁₀O₂₈⁶⁻. Salts of this decavanadate ion are readily crystallized from such solutions by evaporation, and at least two, Ca₃V₁₀O₂₈·16H₂O (pascoite) and K₂Mg₂V₁₀O₂₈·16H₂O (hummerite) occur naturally in the Colorado Plateau vanadium-uranium ore deposits.² The devanadate ion in solution has been established chemically³ to be a 10-nucleate molecular group. Its structure has now been revealed for the first time by simultaneous and entirely independent crystal structure analysis of pascoite (at N.R.C.) and of the zinc analog of hummerite, K₂Zn₂V₁₀O₂₈·16H₂O (at U.S.G.S.). Crystals of pascoite are monoclinic, I2/m, while those of the zinc analog of hummerite are triclinic, P $\bar{1}$. Both structures have been solved by three-dimensional Patterson and Fourier methods and are being refined by least-squares procedures.

In both crystals the decavanadate group may be described in terms of a portion of the rock salt type

(2) J. A. Berson, "Carbonium Ion Rearrangements in Bridged Bicyclic Systems," in "Molecular Rearrangements," Part I, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 3.

(3) E. van Tamelen and C. I. Judd, *J. Am. Chem. Soc.*, **80**, 6305 (1958).

(4) A. Bowers, T. H. Halsall, E. R. H. Jones, and A. J. Lemm, *J. Chem. Soc.*, 2555 (1953).

(5) L. H. Zalkow and A. C. Oehlschlager, *J. Org. Chem.*, **28**, 3303 (1963).

(6) C. A. Grob, *Gazz. chim. ital.*, **92**, 902 (1962).

(7) C. W. Whitehead, et al., *J. Org. Chem.*, **26**, 2814 (1961).

(8) B. Arbusov, *Ber.*, **68**, 1430 (1935).

(1) Publication approved by the Director, U. S. Geological Survey.

(2) H. T. Evans, Jr., M. E. Mrose, and R. Marvin, *Am. Mineralogist*, **40**, 314 (1955); in this abstract, for pascoite, C2/M should read I2/m.

(3) F. J. C. Rossotti and H. Rossotti, *Acta Chem. Scand.*, **10**, 957 (1956).

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.

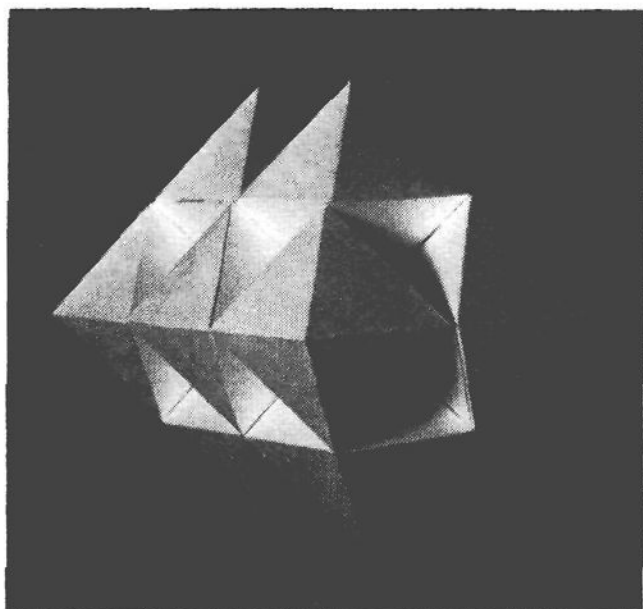


Fig. 1. Model of the decavanadate ion, $\text{V}_{10}\text{O}_{28}^{6-}$, in terms of its ten constituent VO_6 octahedra.

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.

(4) National Research Council Postdoctorate Fellow 1963-1964.

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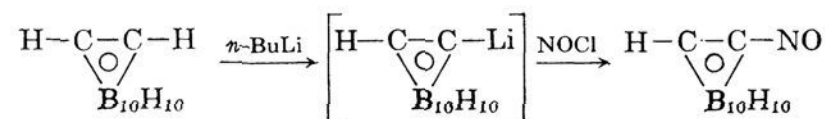
RECEIVED AUGUST 7, 1964

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

(4) T. L. Heying, J. W. Ager, Jr., S. L. Clark, R. P. Alexander, S. P. Papetti, J. A. Reid, and S. I. Trotz, *Inorg. Chem.*, **2**, 1097 (1963).

(5) D. Grafstein, J. Bobinski, J. Dvovak, H. Smith, N. Schwartz, M. S. Cohen, and M. Fein, *ibid.*, **2**, 1120 (1963).

(6) M. F. Hawthorne, unpublished information.

(7) N. Mayes, private communication.

(8) D. A. Barr, R. N. Haszeldine, and C. J. Willis, *Proc. Chem. Soc.*, 230 (1959).

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