

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.

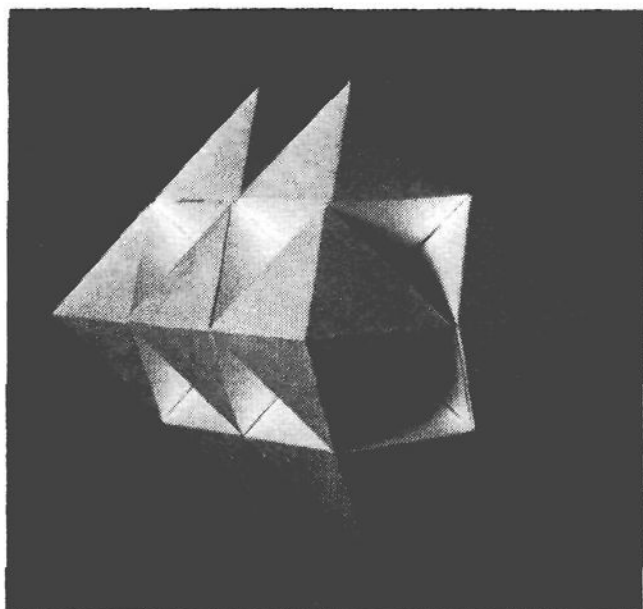


Fig. 1. Model of the decavanadate ion, $\text{V}_{10}\text{O}_{28}^{6-}$, in terms of its ten constituent VO_6 octahedra.

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:

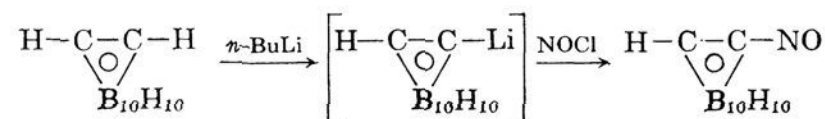
Reaction of alkylmetals with nitrosyl chloride usually gives either alkylnitrosohydroxylamines¹ or dialkylhydroxylamines,² although nitrosobenzene has been prepared³ by passing nitrosyl chloride into phenylmagnesium bromide. We have found that the addition

(1) E. Muller and H. Metzger, *Ber.*, **89**, 396 (1956).

(2) I. Bewad, *J. prakt. Chem.*, [2] **76**, 62 (1907).

(3) B. Oddo, *Gazz. chim. ital.*, **139**, 659 (1909).

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

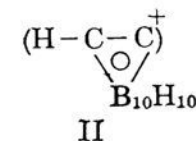
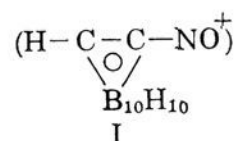
EFFECT OF REACTION TEMPERATURE ON THE PER CENT YIELD OF NITROSOCARBORANES

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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(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).

to leave a white, rubbery polymer containing 10.4% boron with ν_{min} 2620 cm^{-1} (B-H stretching). Under identical conditions no terpolymer was formed when 1-methyl-2-nitrosocarborane was used.

Acknowledgment.—We are indebted to the Atomic Energy Commission, Lawrence Radiation Laboratory, Livermore, Calif., for the support of this work under Contract No. W-7405-ENG 48, and to Mr. Richard Crooker, Mr. Raymond Storey, and Mr. Fred G. Hoffman of this laboratory for analyses and spectra.

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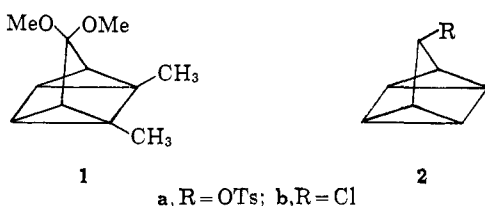
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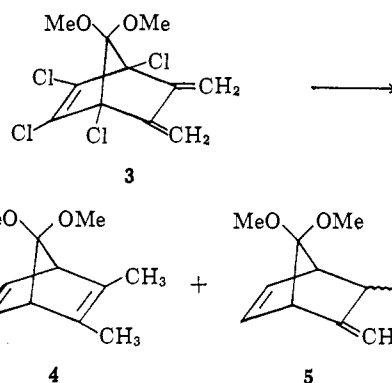
2,3-Dimethyl-7,7-dimethoxyquadracyclo- [2.2.1.0^{2,6}.0^{3,5}]heptane

Sir:

Although numerous publications have been devoted to the one-step syntheses of quadracyclane derivatives,¹⁻⁶ relatively little is known about the chemical reactions of this highly strained system. As part of a general program in the area of quadracyclane chemistry we desired to elucidate the nature and ultimate fate of carbonium ions generated on this quadracyclic skeleton. This communication reports the synthesis of 2,3-dimethyl-7,7-dimethoxyquadracyclo[2.2.1.0^{2,6}.0^{3,5}]heptane (**1**) and the subsequent acid-catalyzed rearrangement of this tetrasubstituted quadracyclane. This rearrangement gives the first positive evidence for the type of bond cleavage postulated by Richey and Buckley⁵ and by Story and Fahrenholtz⁶ in accounting mechanistically for the conversion of 7-substituted quadracyclanes (**2**) to 7-substituted norbornadienes in the solvolysis of **2**.



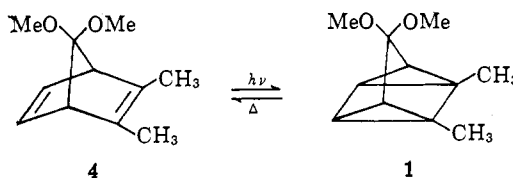
The synthesis of **1** originated with the known triene **3**.⁷ Dehalogenation according to published procedures⁸ yielded **4** through a novel 1,4 reduction. The structure of **4** was substantiated in several ways. Catalytic hydrogenation over palladium on carbon resulted in the rapid uptake of one mole of hydrogen and the relatively slow uptake of a second mole of hydrogen. Near-infrared spectroscopy confirmed the presence of a norbornadiene structure with two olefinic hydrogens as indicated by the absorption at 1.655 μ with a molar absorptivity of 0.676.^{9,10} The final defini-



tive proof was the nuclear magnetic resonance spectrum of **4** which showed the six allylic methyl hydrogens as a singlet at τ 8.30, two methoxy methyls as singlets at τ 7.02 and 6.92, two bridgehead hydrogens as a triplet at τ 6.81, and the two olefinic hydrogens as a triplet at τ 3.42. In addition to this major product, the diene **5** was isolated as the principal side product.

2,3-Dimethyl-7,7-dimethoxybicyclo[2.2.1]heptadiene (**4**) is extremely unstable to acidic conditions. Reaction with dilute acid at -20° gave violent gas evolution with *o*-xylene being formed in high yield. This transformation probably occurs through the initial formation of 2,3-dimethylnorbornadienone (**6**) and subsequent decarbonylation. All attempts to trap **6** have been unsuccessful. It is interesting to note that *o*-xylene also results from the pyrolysis of **4**. This possibly occurs through the expulsion of dimethoxycarbene.¹¹

Photolysis at *ca.* 10° of a pentane solution of 2,3-dimethyl-7,7-dimethoxybicyclo[2.2.1]heptadiene and 2,4-dimethylbenzophenone¹² with a 150-watt Sylvania "blacklite" source gave good conversion of **4** to the



tetrasubstituted quadracyclane, **1**. The photolysis product exhibited less thermal stability than previously reported quadracyclane derivatives. Although **1** is stable at Dry Ice temperature, it slowly reverts to the starting diene at 0° and rapidly isomerizes at more elevated temperatures.¹³ Very pure samples, m.p. $18-19^\circ$, could be prepared by low temperature recrystallization from pentane. The quadracyclane could also be distilled at low temperature but this resulted in considerable thermal isomerization. In addition to the thermal reversal of **1** to **4** and the low boiling point of **1** (indicative of its monomeric character) there exists conclusive spectral evidence for the structure of **1**. The nuclear magnetic resonance spectrum showed the six methyl protons as a singlet at τ 8.78, three methoxy protons as a singlet at τ 6.70, three methoxy protons at

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(2) S. J. Cristol and R. L. Snell, *ibid.*, **80**, 1950 (1958).
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(5) H. G. Richey, Jr., and N. C. Buckley, *ibid.*, **85**, 3057 (1963).
(6) P. R. Story and S. R. Fahrenholtz, *ibid.*, **86**, 527 (1964).
(7) P. E. Hoch, *J. Org. Chem.*, **26**, 2066 (1961).
(8) P. G. Gassman and P. G. Pape, *ibid.*, **29**, 160 (1964).
(9) P. G. Gassman and W. M. Hooker, unpublished work.
(10) The ultraviolet spectrum of **4** showed end absorption at 214 μ (ϵ 1350). Norbornadiene gives an end absorption at 214 μ (ϵ 1480).

(11) J. Diekmann, *J. Org. Chem.*, **28**, 2880 (1963); R. W. Hoffmann and H. Hauser, *Tetrahedron Letters*, **No. 4**, 197 (1964); D. M. Lemal, E. P. Gosselink, and A. Ault, *ibid.*, **No. 11**, 579 (1964); P. G. Gassman and T. H. Koch, unpublished work.

(12) We have found that 2,4-dimethylbenzophenone is an excellent photosensitizer for low temperature photolyses.

(13) Because of the lability of this compound we did not obtain a carbon-hydrogen analysis on **1**. Correct analyses have been obtained on all other compounds.