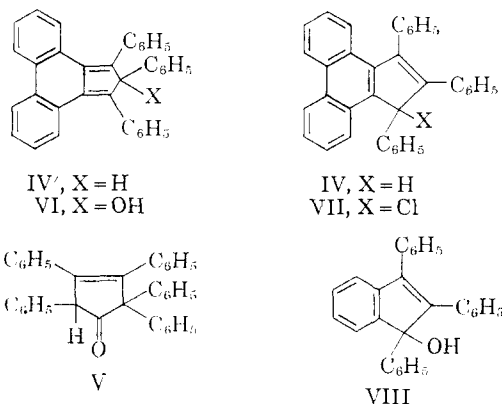


bonium ions, or (b) reversible electron abstraction from III and IV to form cation radicals. These radicals have been detected by strong e.s.r. signals¹¹ from the sulfuric acid solutions of I, III, and IV (width ~ 20 gauss, $g = 2.00$) and considerable line broadening in the n.m.r.; the paramagnetic species, as expected, are not oxidized by bromine.



It seems likely that III and IV are formed *via* II, and indeed a transitory color is seen when I dissolves in sulfuric acid, but II apparently is quite unstable.¹² By contrast, we find that both triphenylindenol (VIII) and 9-phenylfluorenyl give unrearranged carbonium ions in sulfuric acid (of $pK_R^+ = -12.6$ and -10.8 , respectively); these derivatives of the cyclopentadienyl cation, unlike II, are not calculated to have degenerate ground states. Although it is particularly easy to formulate the rearrangement of II to IV in terms of a diradical, it cannot necessarily be concluded that a triplet is involved. Accordingly, the nature of the ground state in such species remains an open question.

Weijland, *J. Chem. Soc.*, 3049 (1959); J. Rooney and R. Pink, *Proc. Chem. Soc.*, 142 (1961).

(11) The e.s.r. spectra were obtained by Mr. Philip Rieger of these laboratories.

(12) Studies of the rate of color development from I and from VIII in solutions of varying H_R show that the pK_R^+ of II is -16 or less.

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A NOVEL HYDRIDE OF VANADIUM¹

Sir:

The group VB metals (V, Nb, Ta) react with hydrogen at moderate temperatures and atmospheric pressure to form hydrides approaching MH.²⁻⁵ The non-stoichiometric monohydrides of tantalum and niobium have a face-centered orthorhombic structure,⁶ while $VH_{0.47-0.81}$ is body-centered tetragonal. Brauer and Müller⁷ recently

reported the preparation of niobium dihydride. We wish to report the synthesis of the corresponding but non-stoichiometric dihydride of vanadium.

For our study of metal-hydrogen systems in the high pressure regions we employed a modified 300-ml., stainless steel, commercial hydrogenation apparatus.⁸ In place of the solenoid-actuated dasher, a 1.25-cm. diameter ball of tungsten carbide brazed to the actuating-rod was used. A stainless steel, mortar-shaped insert reduced the volume to 100 ml. Hydrogen was purified by passing it over a hot uranium bed and the pressure was measured with a 0-5000 p.s.i. Heise gauge. The bomb was charged with 6 g. of $VH_{0.40}$, evacuated and filled with hydrogen to a pressure of 70 atm. The sample was crushed in two 3-hour periods with the greatest hydrogen uptake during the first period ($\Delta P = 12.5$ atm.) and a smaller amount during the second ($\Delta P = 2.0$ atm.). The calculated composition from the drop in pressure was $VH_{1.5}$. Analysis by thermal decomposition and measurement of the hydrogen evolved gave $VH_{1.45} \pm 0.05$.

After hydriding, the sample was removed from the bomb in a protective argon atmosphere and packed into 0.5 mm. thin-walled glass capillaries. Examination by powder X-ray diffraction techniques, using a G.E. XRD-4 unit and copper radiation, showed the presence of a f.c.c. phase along with the b.c. tetragonal monohydride. After correcting for film shrinkage, the lattice parameter of the f.c.c. phase was determined from a plot of *a* versus the Nelson-Riley function,⁹ and was found to be 4.270 ± 0.002 Å. We believe the hydrogen atoms occupy tetrahedral sites in the f.c.c. vanadium lattice giving the new compound a fluorite, C1 type structure at VH_2 . A calculation of the expected internuclear distance (d_{MH}) for this structure using 0.59 Å. for the radius of the vanadium ion,¹⁰ 1.40 Å. for the radius of the hydride ion,¹¹ and applying the proper coordination number corrections¹¹ gave $d_{MH} = 1.89$ Å. The observed distance is 1.85 Å.

Several attempts were made to increase the hydrogen content. These included increasing the pressure in the bomb, lowering the temperature of the bomb by immersion in a thermostatic bath and using up to eleven hours of crushing time. In one of these runs, we succeeded in preparing a material which analyzed as $VH_{1.83}$, but the analysis may not have been carried out on a representative sample. In another run, we obtained $VH_{1.64} \pm 0.05$ (bomb pressure 136 atm., temperature -2° , crushing time eleven hours). An X-ray diffraction powder photograph of this hydride showed a large proportion of the f.c.c. phase ($a_0 = 4.271 \pm 0.002$ Å.) along with the b.c. tetragonal phase.

According to Brauer and Müller,⁴ niobium dihydride can be prepared by electrolysis and also by treating finely divided niobium monohydride (or Nb powder) with 10% HF. We have adopted this latter procedure to prepare vanadium dihy-

(8) Made by Autoclave Engineers, Erie, Pa.

(9) J. B. Nelson and D. P. Riley, *Proc. Phys. Soc., (London)*, **57**, 160 (1945).

(10) Landolt-Börnstein "Tabellen," Vol. I. "Kristalle," Pt. 4, A. Bucken, Ed., Springer-Verlag, Berlin, 6th Ed., 1950, p. 523.

(11) T. R. P. Gibb, Jr., and D. P. Schumacher, *J. Phys. Chem.*, **64**, 1407 (1960).

(1) This research was supported by the U. S. Atomic Energy Commission.

(2) L. Kirschfeld and A. Sieverts, *Z. Elektrochem.*, **36**, 123 (1930).

(3) P. Kofstad and W. E. Wallace, *J. Am. Chem. Soc.*, **81**, 5019 (1959).

(4) W. M. Albrecht, M. W. Mallett and W. D. Goode, *J. Electrochem. Soc.*, **105**, 219 (1958).

(5) A. Sieverts and H. Moritz, *J. anorg. allgem. Chem.*, **247**, 124 (1941).

(6) G. Brauer and R. Hermann, *Z. anorg. Chem.*, **274**, 11 (1953).

(7) G. Brauer and H. Müller, *Angew. Chem.*, **70**, 53 (1958); *J. Inorg. Nucl. Chem.*, **17**, 102 (1961).

dride. A -300 mesh sample of $\text{VH}_{0.87}$ was treated for several hours in a platinum dish with 10% HF. The HF solution then was removed and the product washed in water, alcohol, and finally in ether. An X-ray diffraction powder pattern of the product showed the presence of the f.c.c. vanadium dihydride. Faint lines in the low angle region, however, indicated a small amount of the monohydride. A trace of vanadium oxide also was indicated by faint lines in the diffraction pattern. The value of the lattice constant for the dihydride determined from this film was $4.271 \pm 0.002 \text{ \AA}$. The formula was found to be $\text{VH}_{1.77 \pm 0.05}$ by hydrogen loss *in vacuo*. Vanadium samples of 99.8+ per cent. purity were obtained from the Oregon Metallurgical Company, Albany, Oregon. Additional details of preparation, stability, and physical properties will be given in future publications.

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REDUCTION OF ISOLATED OLEFINIC BONDS BY MEANS OF *p*-TOLUENESULFONYLHYDRAZINE

Sir:

Prompted by Thiele's early work¹ on azodicarboxylic acid, and other considerations, we recently investigated the decomposition of this substance in the presence of olefinic compounds, with the discovery that reduction of isolated carbon-carbon double bonds occurred.² Of the various mechanistic interpretations which might be entertained (including reduction by azomonocarboxylic acid or a related species), involvement of the elusive H_2N_2 or an equivalent is the most direct. We have now found that saturation of isolated olefinic bonds also can be effected through thermal decomposition of another possible H_2N_2 (but not azomonocarboxylic acid) source, *p*-toluenesulfonylhydrazine.^{3,4}

Reductions were carried out by heating under reflux a solution of the olefinic component and a 100% excess of *p*-toluenesulfonylhydrazine in diglyme for one hour under nitrogen.⁵ As typical results, oleic and elaidic acids were reduced to stearic acid (73% and 70%, respectively, both by infrared analysis and bromine titration); in these runs the sulfur-containing by-products were removed by extraction or by oxidation to the water-soluble sulfonic acid. Reduction of allyl alcohol gave 1-propanol (99%), and cyclohexene gave cyclohexane (98%) (both by vapor phase chroma-

(1) J. Thiele, *Ann.*, **27**, 127 (1892). Thiele reported that in the decarboxylation of azodicarboxylic acid, carbon dioxide, nitrogen and hydrazine are formed; and he suggested that the hydrazine and nitrogen arise by disproportionation of the unstable diimide. The comment may be made that reduction of azodicarboxylic acid with H_2N_2 would also lead to hydrazine, *via* decarboxylation of the intermediate hydroazodicarboxylic acid.

(2) E. E. van Tameelen, R. S. Dewey and R. J. Timmons, *J. Am. Chem. Soc.*, **83**, 3725 (1961).

(3) No evidence is available to distinguish between $\text{HN}=\text{NH}$ and

$\text{H}_2\text{N}-\text{N} \leftrightarrow \text{H}_2\text{N}=\text{N}^+$ in this decomposition.

(4) Commercially available from Aldrich Chemical Company, Milwaukee, Wis.

(5) The decomposition of *p*-tosylhydrazine can be accelerated by the addition of hydroxide ion, and to some extent by metal ions. Whether the decomposition is a radical or cyclic process, or involves an α - or β -elimination, is unknown.

tography). The thermal decomposition of *p*-toluene sulfonylhydrazine should give rise to *p*-toluenesulfonic acid as one of the initial products,⁶ and confirmation of this presumption has been obtained by the isolation of the sulfonic acid, along with *p*-tolyl disulfide, from the pyrolysis of the sulfonylhydrazide in diglyme.⁷

Thus, the azodicarboxylic acid and *p*-toluenesulfonylhydrazine reduction methods—insofar as they are compatible with the H_2N_2 hypothesis—involve preparation of a species which, although in itself too unstable to be isolated under ordinary conditions,⁸ nevertheless can be utilized as a reagent in the presence of a substrate.

We wish to take this opportunity for drawing attention to the general possibilities of carrying out new reactions on organic molecules through the use of unstable neutral inorganic reagents, in the same sense that unstable, unisolated organic entities (such as carbenes) are utilized. This field of investigation would appear to be relatively virgin, in that incorporated into the entire body of organic chemistry are only few such examples—virtually all known reactions involving inorganic reagents are executed by means of "shelf" chemicals of normal stability. Further, within the confines of inorganic chemistry, this device may be useful in providing evidence for the existence of such unstable species.

(6) The loss of *p*-toluenesulfonylhydrazine by prolonged heating during recrystallization has been observed by C. H. DePuy and D. H. Froemsdorf, *J. Am. Chem. Soc.*, **82**, 636 (1960).

(7) *p*-Toluenesulfonic acid is converted to *p*-tolyl *p*-toluenethiosulfonate in hot aqueous solution (R. Otto and O. V. Gruber, *Ann.*, **145**, 13 (1868)), and the thioester has been converted to *p*-tolyl disulfide in hot aqueous sodium carbonate (E. Fromm, *Ber.*, **41**, 3409 (1908)).

(8) Some evidence for persistence of H_2N_2 at low temperatures has been presented, for example, by S. N. Poner and R. L. Hudson, *J. Chem. Phys.*, **28**, 719 (1958).

(9) National Institutes of Health Postdoctoral Fellow.

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THE STRUCTURE OF NYBOMYCIN

Sir:

The antibiotic nybomycin has been described in independent reports by Strelitz, Flon and Asheshov,¹ and by Eble, Boyack, Large and DeVries²; apart from strong *in vitro* biological activity, its chief characteristics are its thermal stability (m.p. 325–330°) and its extreme insolubility except in concentrated acids. The report by Eble² showed the molecular formula of nybomycin to be $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_4$ (rather than $\text{C}_8\text{H}_7\text{NO}_2$)¹ and established the presence of an aliphatic hydroxyl group. The present report shows the structure of nybomycin to be represented by I.

On treatment with refluxing 47% hydriodic acid (in which nybomycin is soluble), I is converted to deoxy nybomycin (II, $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_3$,³ dec. >335°), which precipitates from this medium. Deoxy nybomycin differs from the parent I by replacement

(1) F. Strelitz, H. Flon and I. N. Asheshov, *Proc. Natl. Acad. Sci. U. S.*, **41**, 620 (1955).

(2) T. E. Eble, G. A. Boyack, C. M. Large and W. H. DeVries, *Antibiotics and Chemotherapy*, **8**, 627 (1958).

(3) Microanalyses are within accepted limits.