

tion of I occurs by disproportionation, half being dehydrohalogenated to butadiene irontricarbyl by the other half, which in turn decomposes to ferrous chloride, carbon monoxide, and but-2-enes. Such a mechanism is in accord with the stability of I in the melt or in solution.

It is interesting to note that the spectral data indicate that I is not a mixture of isomers, as was found to be the case with the cobalt complex.^{3,5} While such evidence is not definitely conclusive, it seems reasonable, from the mode of formation of I, that the geometry of the C₄ moiety in butadiene irontricarbyl might be maintained on conversion to the π -allyl complex. On this basis, it is suggested that I isolated as described above is the *anti* isomer (IVa).

An X-ray study of the structure of I is currently under way.⁶ Alternate synthetic routes for the preparation of I also are being investigated.

We are indebted to Dr. T. H. Coffield for suggestions leading to the carrying out of the initial reaction.

(6) X-Ray studies are being carried out by Professor L. L. Dahl of the University of Wisconsin.

ETHYL CORPORATION
DETROIT, MICHIGAN

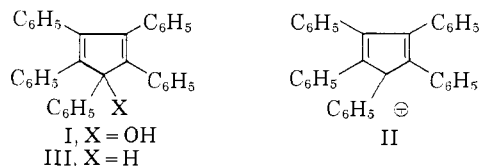
F. J. IMPASTATO
K. G. IHRMAN

RECEIVED JULY 17, 1961

THE REARRANGEMENT OF THE PENTAPHENYLCYCLOPENTADIENYL CATION¹

Sir:

Some time ago Ziegler² reported that the solution of pentaphenylcyclopentadienol (I) in concentrated sulfuric acid contains a purple species which he considered to be the pentaphenylcyclopentadienyl cation (II). He reported that this solution, poured into water, afforded a material which was "evidently the dimeric ether" of I. On the basis of spectroscopic studies Bloom and Krapcho³ concluded that the colored species was indeed II, but they did not further investigate the supposed dimeric ether. Because II is a derivative of the cyclopentadienyl cation in which the five-fold symmetry (D_{5h}) is retained it is of particular interest, since it is also predicted to have a (possible) triplet ground state. The stability and nature of such species is still an open question.⁴ Accordingly we have examined the sulfuric acid solution of I in some detail, and find that after a few seconds none of the cation II is present.



When the solution is poured into water a mixture of products is obtained whose exact composition varies with the strength of the acid and the

(1) This work was supported by a grant from the National Science Foundation, which is gratefully acknowledged.

(2) K. Ziegler and B. Schnell, *Ann.*, **445**, 266 (1925).

(3) S. M. Bloom and A. P. Krapcho, *Chem. and Ind.*, 882 (1959).

(4) For evidence on the possibility that tetraphenylcyclobutadiene has a triplet ground state, cf. H. H. Freedman, *J. Am. Chem. Soc.*, **83**, 2195 (1961).

time of standing, but in a typical run (96% H₂SO₄ for 2 min.) the products are pentaphenylcyclopentadiene (III), 25%, 1,2,3-triphenyl-1H-cyclopenta[1]phenanthrene (IV), 48%, 2,2,3,4,5-pentaphenyl-3-cyclopentene-1-one (V), 5%, and an amorphous oxygen-containing material which has not yet been identified, 21%. This latter does not form pentaphenylcyclopentadienyl chloride with hydrogen chloride in acetic acid under conditions in which I is quantitatively converted to the chloride,² and it gives a brown solution in sulfuric acid.

Compound IV, m.p. 220–221°, has mass 444,⁵ C₃₅H₂₄ (C, 94.26; H, 5.52). In the n.m.r. it has a one-proton singlet at 4.73 τ , a two-proton multiplet at 1.48 τ which is characteristic of the 4,5 hydrogens of a phenanthrene,⁶ and a twenty-proton multiplet at 2.85 τ . All together these data established the structure IV (or, less likely, IV'); the structure was confirmed by synthesis. Phenylcyclo with phenyllithium yielded VI, m.p. 222–223°,⁷ (C, 90.28; H, 5.31), which with thionyl chloride and pyridine yielded VII, m.p. 253–254°, (C, 87.47; H, 5.01). Treatment of VII with zinc in acetic acid afforded IV, identical with the previously obtained material. Structure IV', and an analogous one for the chloride VII, are ruled out by the ultraviolet spectra; $\lambda\lambda_{\text{max}}$ (ϵ): VI, 251 (34,000), 281 (30,000), 415 (3,600); VII 250 (37,000), 352 (4,000); IV, 253 (40,000), 345 (12,000) m μ .⁸ The structure of the ketone (V), m.p. 194–195°, (C, 90.67; H, 5.69), is indicated by the fact that its formation is reversible, since on standing in sulfuric acid it affords III and IV, and by spectroscopic data indicating an unconjugated cyclopentenone⁹: infrared, 5.76 μ , ultraviolet, 261 m μ (13,000); in the n.m.r. it has one proton at 5.25 τ and twenty-five protons in a multiplet at 2.85 τ . Compound III was identified by comparison with an authentic sample.²

The spectrum previously assigned to II is simply the composite spectrum of III and IV in sulfuric acid. Thus III in sulfuric acid forms a bright orange solution, $\lambda\lambda_{\text{max}}$ 502 (32,400) and 445 m μ (18,700) from which III is recovered quantitatively on dilution. The solution of IV in sulfuric acid has $\lambda\lambda_{\text{max}}$ 520 (26,500) and 376 m μ (13,000). The spectrum of I in sulfuric acid, λ_{max} 516 m μ (20,500), can be reproduced quantitatively by an appropriate mixture of III and IV. The spectra are ascribable to one or the other of two possible processes:¹⁰ (a) protonation of III and IV to car-

(5) The mass spectrum was obtained through the courtesy of Dr. B. Dudenbostel of Esso Research Laboratories.

(6) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Company, Inc., New York, N. Y., 1959, p. 248 ff.

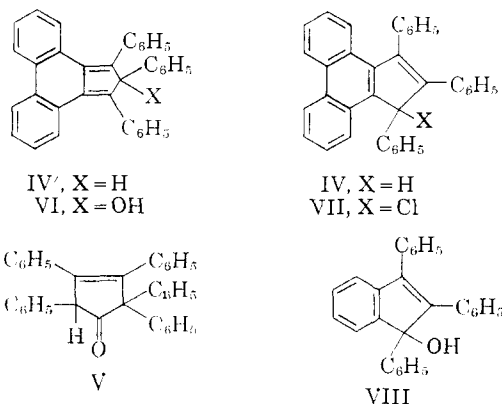
(7) The compound of m.p. 255–257°, prepared by V. Abramov and P. Malskii, *J. Gen. Chem. U.S.S.R.*, **9**, 1533 (1939) by the reaction of phenylcyclo with phenylmagnesium bromide, is a ketone resulting from conjugate addition, and does not have the structure (VI) which they assigned.

(8) This slight change when the chloride is converted to a hydrocarbon is mirrored in the pentaphenylcyclopentadiene series; the ultraviolet spectrum of pentaphenylcyclopentadienol resembles that of the corresponding chloride and hydrocarbon.

(9) Cf. C. F. Allen, J. A. VanAllen and J. F. Tinker, *J. Org. Chem.*, **20**, 1387 (1955).

(10) S. I. Weissman, E. deBoer and J. Conradi, *J. Chem. Phys.*, **26**, 963 (1957); W. Aalbersberg, G. Hoijtink, E. Mackor and W.

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.

DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY
NEW YORK, NEW YORK

RONALD BRESLOW
HAI WON CHANG

RECEIVED MAY 19, 1961

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

(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).

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. Nelsou and D. P. Riley, *Proc. Phys. Soc., (London)*, **57**, 160 (1945).

(10) Landolt-Börnstein "Tabellen," Vol. I. "Kristalle," Pt. 4, A. Eucken, 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).