

The density of 3,3-diaminodiphenyl is 1.102, which gives a calculated value of 3.993 (or 4) molecules in the unit cell. The reference to Caspari is *J. Chem. Soc.* 573, 2944 (1926); 1093 (1927); *Phil. Mag.*, 1, 1276 (1927).

We are indebted to Dr. Huggins for calling attention to these omissions which occurred as a result of condensing the paper and a typographical error.

The remaining criticisms of the communications require no comment,

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URBANA, ILLINOIS  
RECEIVED AUGUST 24, 1931  
PUBLISHED OCTOBER 5, 1931

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF LOUISVILLE]

## THE REACTIONS OF SOME INORGANIC VANADIUM COMPOUNDS WITH PHENYLMAGNESIUM BROMIDE<sup>1</sup>

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RECEIVED APRIL 10, 1931

PUBLISHED OCTOBER 5, 1931

### Introduction

The Grignard reagent reacts with several metallic halides to give organo-metallic compounds of the type  $R_nM$ , in which the organic radical (R) is directly attached to the metal (M). In some cases oxides of certain metals react with this reagent<sup>2</sup> to give compounds of the same type. Vanadium in some of its states of valence may be considered analogous to some metals whose halides and oxides are known to behave in this fashion.

Organic vanadium compounds of the ester, alcoholate and complex types are known, and some have reputed therapeutic value<sup>3</sup> but no true organovanadium compound of the type discussed is mentioned in the literature. On the basis of related known compounds it might be expected that organovanadium compounds would be highly unstable.<sup>4</sup>

On the other hand, certain salts of heavy metals have been found to cause a coupling of the organic radicals, when allowed to react with the Grignard reagent.<sup>5</sup> Probably this difference in behavior is due to the manner in which the equilibria discussed by Gilman and St. John<sup>6</sup> are

<sup>1</sup> Presented before the Organic Division of the American Chemical Society, Indianapolis, Indiana, April 1, 1931.

<sup>2</sup> Blicke and Smith, *THIS JOURNAL*, 51, 1558-1565 (1929).

<sup>3</sup> A. Grippa, *Ann. Chem. Appl.*, 20, 244-248 (1930), [*C. A.*, 24, 5288 (1930)]; *Vancoram Review*, 2, 43-46 (1931). This reference summarizes the uses of vanadium in medicine and also gives data on toxicity.

<sup>4</sup> Bennett and Turner, *J. Chem. Soc.*, 105, 1057-1062 (1914).

<sup>5</sup> Gilman and Parker, *THIS JOURNAL*, 46, 2823-2827 (1924); Gardner and Borgstrom, *ibid.*, 51, 3375-3377 (1929).

<sup>6</sup> Gilman and St. John, *ibid.*, 52, 5017-5023 (1930). This article contains leading references to the work of others along the same line.

affected by the compounds used. Supniewski<sup>7</sup> has reported that vanadium tri- and tetrahalides caused coupling of the organic radicals of various organomagnesium halides.

In this study, the halides and oxides of vanadium not previously studied were allowed to react with phenylmagnesium bromide, and the products examined, particular search being made for true organovanadium compounds. For this reason it is probable that the yields of diphenyl, the coupling product formed, might well be higher than those reported, under more nearly optimum conditions. A part of the work reported on by Supniewski was repeated in order to check the technique used in the present study. The reaction between vanadium oxytrichloride and phenylmagnesium bromide was also further studied.

### Experimental Part

**Metallic Vanadium with Alkyl, Aryl and Acyl Halides.**—Each of the following compounds, with ether as a solvent, was sealed in a glass tube with a small amount of metallic vanadium which had been crushed until it was less than forty mesh in size: ethyl bromide, ethyl iodide, isopropyl bromide, *n*-butyl chloride, *n*-butyl iodide, bromobenzene, iodobenzene, *sym*.-dibromoethane, *p*-dibromobenzene and benzene sulfonyl chloride. Benzyl chloride, benzoyl chloride, acetyl chloride and dimethyl sulfate were used without a solvent. After eight months at room temperature in the dark, no change was apparent in any of the tubes containing alkyl or aryl halides, the metal remaining untarnished in every case. When opened, the content of each tube was poured into water, with no evidence of any reactions, save hydrolysis in those cases where acyl halides were used. After the unchanged vanadium had been filtered out, the water solutions were acidified, and again no reactions were shown. In the tube containing acetyl chloride, there was a very small amount of green, water-soluble coating on the metal, and an unpleasant odor, but most of the metal and acetyl chloride appeared unchanged. In the tube containing benzoyl chloride, a small amount of gray water-insoluble coating was present on the metal, which was easily shaken off, leaving the metal untarnished. A similar gray coating was noticed in the tube containing dimethyl sulfate. In no case could anything identifiable be isolated. The conclusion was reached, therefore, that no reaction of any magnitude had occurred.

**Metallic Vanadium with Phenylmagnesium Bromide.**—A mixture composed of 2.51 g. (0.05 atom) of metallic vanadium (40-mesh, 92% pure) and 0.1 mole of phenylmagnesium bromide in ether was refluxed over a water-bath for thirty-four hours, being in contact for a total of fifteen days. Ammonium chloride solution was added to hydrolyze the unchanged organomagnesium halide, and a vigorous reaction indicated that some still remained. The ether layer yielded 0.5 g. (6.5%) of diphenyl. The aqueous layer gave a negative test for vanadium, and when evaporated to dryness and the residue extracted with chloroform, showed no organic compounds present. A total of 2.0 g. of unchanged vanadium was recovered, representing 80% of the original amount.

**Qualitative Test for Vanadium in the Presence of Organic Material.**—The qualitative test discussed by Meyer<sup>8</sup> was used. In order to test its effectiveness under the conditions applying to this study, small amounts of each of the vanadium compounds used were mixed with diphenyl and bromobenzene, the two substances most likely to be pres-

<sup>7</sup> Supniewski, *Roczniki Chem.*, **7**, 172-175 (1927) [*C. A.*, **22**, 766 (1928)].

<sup>8</sup> J. Meyer, *Chem.-Ztg.*, **53**, 366 (1929) [*C. A.* **23**, 4640 (1929)].

ent. This mixture was strongly ignited on porcelain for fifteen minutes, the residue cooled and dissolved in 20% sulfuric acid. One drop of 3% hydrogen peroxide was then added to the solution. In every case, the color appeared against the white background within one minute.

### Vanadium Halides and Oxyhalide with Phenylmagnesium Bromide

TABLE I  
PHENYLMAGNESIUM BROMIDE WITH VANADIUM COMPOUNDS

V compd.	Quantities		C <sub>6</sub> H <sub>5</sub> Br mole	Time		Yield (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> Wt., g.	V comps. reco- vered, g.	Indica- tions of organic V comp.	Notes		
	Wt., g.	Mole		Re- flux, hrs.	Stand- ing, days						
VCl <sub>3</sub>	I	5.0	0.03+	0.1	1	..	4.8	62.4	2.0	..	Distilled before hydrolysis
	II	0.2	....	.1	5	..	0.75	7.8	...	..	
VCl <sub>4</sub>	I	4.0	.04+	.1	5	4	1.6	20.9	2 (App.)	..	Protected from light
	II	4.0	.04+	.1	10	6	2.0	25.9	2 (App.)	..	Unprotected from light
VOCl <sub>2</sub>	I	5.8	.03	.1	..	2	4.4	57.2	...	..	Cold
	II	8.2	.047	.1	..	4	4.3	55.9	...	+	Room temp., very slow addn.
V <sub>2</sub> O <sub>3</sub>	I	5.0	.03	.1	25	20	0.3	3.8	4.5 (App.)	..	V <sub>2</sub> O <sub>3</sub> apparently unchanged before hydrolysis
	II	5.0	.03	.1	10	30	0.7	9.09	...	..	
V <sub>2</sub> O <sub>4</sub>	I	16.6	.1	.1	10	5	1.1	14.28	...	..	
V <sub>2</sub> O <sub>5</sub>	I	3.7	.02	.1	15	10	..	...	...	..	

The results of the experiments with phenylmagnesium bromide and vanadium compounds are included in Table I. For the most part, the procedures were alike, so a typical run is described. Any variations have been indicated in the last column of Table I.

The ether solution of phenylmagnesium bromide was prepared in the usual manner in a three-necked flask equipped with a mechanical stirrer and adequate protective devices. This solution was cooled with an ice-salt mixture, and the cold vanadium compound slowly added, the whole being rapidly stirred and cooled so that the temperature was never above 10° and usually much lower. If the vanadium compound did not dissolve in dry ether or toluene, it was added as a suspension. If a temperature higher than the boiling point of ether was desired for later refluxing, dry toluene was added. After the initial reaction subsided, stirring was continued and the mixture slowly allowed to come to room temperature. Usually it was allowed to stand for a time and finally refluxed.

In some cases distillation was attempted without hydrolysis with dilute hydrochloric acid, but the residues and distillates were eventually shaken with the hydrolyzing solution. In cases where there appeared to be considerable unchanged vanadium compound, this was recovered by decantation and washed several times with dry ether. Careful fractional distillation of the ether solutions followed, the last fractions being collected *in vacuo*, if a sufficient residue remained after the ether had been collected. After testing for the presence of organic vanadium compounds in these fractions and residues, they were finally steam distilled to collect the diphenyl. The aqueous solutions, after being washed with ether, were extracted with chloroform and benzene or toluene. In no case did these extracts yield an organic compound, so they were discarded.

The initial reaction, in the case of the halides and oxyhalide, was very vigorous. It subsided gradually until there was little or no apparent reaction during the addition of the last half of the vanadium compound,

In the second run of vanadium oxytrichloride, approximately 1.0 g. of a dark green crystalline solid appeared, adhering to the walls of the reaction flask at that point where the vanadium oxytrichloride had been introduced. This solid, washed with dry ether and dried rapidly on a porous plate, darkened at 85–100°, but did not melt, even though heated to 220°. Exposed to air for thirty minutes, it lost its crystalline form and green color and became a dark gray powder. When ignited, it burned in flashes of sooty yellow flame, and left a white amorphous residue which gave a positive test for vanadium. This green solid could not be recrystallized from any organic solvents. It reacted with water to form diphenyl. This may be regarded as evidence of a phenyl-metal combination, on the basis of similar results in analogous cases.<sup>9</sup> In addition to this, in both runs with vanadium oxytrichloride, a considerable amount of insoluble black tar appeared before hydrolysis. This tar readily hydrolyzed, yielding diphenyl. It may have been the green crystalline compound in an impure form, or else a compound similar in character. A further study of these compounds will be made.

While there was no apparent evidence of reaction in the cases of the oxides studied, in at least two runs the yield of diphenyl was distinctly above that which would have been the normal yield (4%) expected from the preparation of phenylmagnesium bromide.<sup>10</sup>

The author wishes to thank the Vanadium Corporation of America for the vanadium compounds used in this research. He also wishes to acknowledge his indebtedness to Dr. F. E. Brown, whose suggestions concerning a reaction between vanadium oxytrichloride and the Grignard reagent led to this study.

### Summary

1. All the halides and oxyhalides of vanadium studied reacted with phenylmagnesium bromide to give diphenyl, apparently in direct proportion to the amount of vanadium compound used.

2. Vanadium oxytrichloride gave in one case an unstable organic solid which showed a positive vanadium test, and which gave diphenyl on hydrolysis.

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<sup>9</sup> Gilman and Kirby, *Rec. trav. chim.*, **48**, 155 (1929). This article contains leading references to the work of others along similar lines.

<sup>10</sup> Gilman and McCracken, *THIS JOURNAL*, **45**, 2462 (1923); Gilman and Kirby, *Rec. trav. chim.*, **48**, 157 (1929).