Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

THE NATURE OF THE DECOMPOSITION OF PHENYLVANADIUM OXIDE DICHLORIDE

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(Received March 9th, 1970)

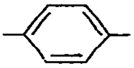
SUMMARY

The reaction of diphenylmercury and vanadium oxide trichloride in cyclohexane solution at 25° initially yielded phenylmercuric chloride and the unstable phenylvanadium oxide dichloride whose decomposition has been studied. When a diphenylmercury/vanadium oxide trichloride ratio >1 was employed, the biphenyl formation rate was accelerated and more than one chlorine on the vanadium was replaced by a phenyl group. When this ratio was <1, the rate of biphenyl appearance was retarded and, on acid hydrolysis, benzene, phenol and biphenyl were recovered. It was shown that all cyclohexane-soluble, phenyl-bearing species (*e.g.* Ph_nVOCl_{3-n}, Ph_2Hg) interchanged phenyl groups very rapidly. The appearance of biphenyl was thought to be due to the concerted decomposition of an unstable di-σ-phenylvanadium intermediate.

INTRODUCTION

In 1955, a review by Cotton[1] on σ-bonded alkyl and aryl transition metal compounds indicated that few authentic compounds of that type had been prepared up to that time. Since then, many compounds with transition metal–carbon σ-bonds have been prepared. However, organovanadium compounds having a σ-carbon–metal bond are still relatively rare. The reaction of phenylmagnesium halide[2] or phenyllithium[3] with vanadium halides in ether solvents seemed to yield σ-bonded phenylvanadium species which rearranged to the π-benzene–vanadium compounds. And the very stable σ-phenyldi-π-cyclopentadienylvanadium (III) is known[4].

Very recently, unstable σ-tetraphenylvanadium and σ-diphenylvanadium have been prepared in impure state by reaction of phenyllithium with vanadium tetrachloride at low temperatures[5]. Previously[6], we described the preparation of an unstable organovanadium compound, believed to be phenylvanadium oxide dichloride, by reaction of diphenylmercury and vanadium oxide trichloride in cyclohexane. The present work utilizes *p*-deuterium labeled diphenylmercury in order to examine the nature of this reaction more carefully. The initial reaction occurring is believed to be*:

In this and subsequent eqns., Ph=  and Ph = D— 

$$Ph_2Hg + VOCl_3 \xrightarrow{C_6H_{12}} PhVOCl_2 + PhHgCl\downarrow \quad (1)$$

This phenylvanadium compound ultimately decomposed to give biphenyl in quantitative yield. The decomposition was shown to be a concerted, non-homolytic process. Both chemical and kinetic evidence suggested the intermediacy of diphenylvanadium oxide chloride as the unstable species which leads to biphenyl:

$$2\,PhVOCl_2 \rightleftarrows Ph_2VOCl + VOCl_3 \quad (2)$$

$$Ph_2VOCl \rightarrow PhPh + VOCl \quad (3)$$

$$VOCl + VOCl_3 \rightleftarrows 2\,VOCl_2 \quad (4)$$

EXPERIMENTAL

All experiments were conducted under dry nitrogen and with dried and purified reagents. $(p\text{-}DC_6H_4)_2Hg$ was prepared by reaction of *p*-dibromobenzene with one equivalent of n-butyllithium in ether, followed by hydrolysis with deuterium oxide. The resulting distilled *p*-deuteriobromobenzene was converted, via its Grignard reagent, to $(p\text{-}DC_6H_4)_2Hg$, m.p. 127.5–128.5° (resublimed).

Preparation and decomposition of phenylvanadium oxide dichloride

A 200-ml, dry, nitrogen-flushed bottle was charged with 2.5 mmoles of diphenylmercury, 150 ml of dry cyclohexane, and a magnetic stirring bar. The bottle was sealed with a serum cap and purged with dry nitrogen to remove all air. Gas inlet and outlet were through hypodermic needles. A cyclohexane solution of 2.5 mmoles of vanadium oxide trichloride was then quickly injected into the bottle with rapid stirring. A heavy precipitate of phenylmercuric chloride formed immediately. Stirring was continued for the desired reaction time, during which a dark precipitate of reduced vanadium compounds formed. At the end of the reaction, the precipitated phenylmercuric chloride and other insolubles were removed by filtration, and the solution was evaporated to give the crude biphenyl which was purified by sublimation. In other experiments which were carried out for short reaction times, the reaction was quenched with dilute sulfuric acid and the biphenyl was recovered from the cyclohexane layer. Recovered phenylmercuric chloride was recrystallized once or twice from acetone/methanol. In the experiments with the deuterated species, no effort was made to obtain quantitative recovery of the various products since the conclusions sought here related only to the *relative* concentrations of the labeled species and are not dependent on quantitative recovery. In the experiments described in Table 1, the biphenyl concentration was determined by vapor phase chromatographic analysis of the cyclohexane solution at the end of the reaction.

Analysis of deuterium content in diphenylmercury and phenylmercuric chloride samples

Synthetic mixture of deuterated (93% phenyl groups contain one deuterium) and non-deuterated phenylmercuric chloride were prepared by solution blending in acetone/methanol. The concentration of labeled phenylmercuric chloride in an unknown sample was determined by comparing the ratio of IR absorptions (1389 and

1440 cm^{-1} or, alternately, 855 and 692 cm^{-1}) with the known calibration curve (KBr disk technique). The percent of bis(*p*-deuteriophenyl)mercury in the recovered diphenylmercury was determined similarly (1385 and 1430 cm^{-1}). The analytical numbers for percent *p*-deuteriophenylmercuric chloride and bis(*p*-deuteriophenyl)-mercury (which were carried out by IR, Table 2) do not include the 93% labeling efficiency. No IR bands attributable to *o*- or *m*-deuteriophenyl groups were ever observed in the reaction products (including the biphenyls).

Formation of phenol from phenylvanadium oxide dichloride

By use of a hypodermic syringe, a solution of 4 mmoles of diphenylmercury in 20 ml of cyclohexane was added to a solution of 8 mmoles vanadium oxide trichloride in 15 ml cyclohexane over a 5 min interval with frequent shaking. After a reaction period of 1 h at room temperature, 30 ml of 1 *N* sulfuric acid was added to stop the reaction. IR examination of the cyclohexane layer showed the presence of absorption bands due to phenol (major), benzene (minor), and biphenyl (minor). The presence of phenol was rigorously established by bromination to give the 2,4,6-tribromophenol, which had the same IR spectrum as a known sample prepared under the same reaction conditions. The phenol concentration in the organic layer was obtained by comparison of the IR absorption at 3620 cm^{-1} (hydroxyl) or 868 cm^{-1} with that of known solutions of phenol in cyclohexane. In computing the yield of phenol, a correction was included to account for the phenol which was soluble in the aqueous phase. In the specific experiment described above, the yield of phenol was 3 mmoles or 75% of theory.

RESULTS AND DISCUSSION

When the diphenylmercury/vanadium oxide trichloride ratio (Hg/V) was increased from one to ten, then almost all the chlorine was replaced by phenyl groups. The transient phenylvanadium species eventually formed biphenyl (Table 1).

TABLE 1

EFFECT OF $(C_6H_5)_2Hg/VOCl_3$ RATIO ON BIPHENYL FORMATION[a]

$(C_6H_5)_2Hg$ / $VOCl_3$	C_6H_5 found as biphenyl / $VOCl_3$ charged	C_6H_5HgCl found / $VOCl_3$ charged
0.98	0.93	1.00
1.95	1.39	1.32
3.54	1.67	1.68
10.2	1.40	—

[a] All mole ratios.

The rate of biphenyl appearance was substantially increased with increase in the Hg/V ratio which suggests that the vanadium center was arylated twice or more, resulting in a higher concentration of the diphenylvanadium oxide chloride, a more rapid appearance of biphenyl, and a lower average oxidation state of the final vanadium species. On the other hand, when an excess of vanadium oxide trichloride

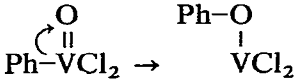
TABLE 2

RESULTS OF DIPHENYLMERCURY/VANADIUM OXIDE TRICHLORIDE REACTIONS USING DEUTERIUM LABELED PHENYL GROUPS

Sample no.	(A)[a], initial reagents (mmole)			Reaction time[b] (min)	(B), added reagents (mmole)			Reaction time[c] (min)	Biphenyls[d] (%)			Ph* content of recovered[e]	
	$\mathrm{Ph_2Hg}$	$\mathrm{Ph_2^*Hg}$	$\mathrm{VOCl_3}$		$\mathrm{Ph_2Hg}$	$\mathrm{Ph_2^*Hg}$	$\mathrm{PhVOCl_2}$		PhPh	Ph*Ph	Ph*Ph*	Ph*HgCl	$\mathrm{Ph_2^*Hg}$
E-1		5.0	5.0	120					0.8	13.5	85.6		
									0.7	13.3	86.0	100	
E-2	1.25	1.25	2.5	120					27.6	51.5	20.7		
									28.1	50.8	21.0	50	
E-3		2.5	2.5	1			2.5		29.3	49.3	21.4		
		2.5	3				2.5	240	29.6	45.6	24.8	47	
E-4	2.5		2.5	2		2.5		120	23.4	56.3	20.3	36	
E-5		2.5	2.5	1	5.6			5	31.6	58.8	9.5	58	11.5
E-6		2.5	2.5	5	5.6			60	37.9	49.2	12.9	54	19

[a] Solution (A) prepared as above in dry cyclohexane. To this added solution (B) prepared as above in dry cyclohexane. [b] Time for reaction (A) to proceed. [c] Total reaction time after mixing (A) and (B). [d] Mass spectral analysis. [e] IR analyses; the factor for 93% Ph* purity of $\mathrm{Ph_2^*Hg}$ was not included in analyses calibrations.

was employed, *e.g.*, Hg/V < 0.5, then phenol as well as biphenyl appeared and the rate of decomposition of the phenylvanadium species was decreased greatly. When the Hg/V ratio was one, no phenol was detected; when this ratio was progressively decreased to 0.5, a yield of about 75% of phenol was obtained. When the Hg/V ratio was lowered further, no significant increase in the phenol yield was observed. A reasonable explanation for the formation of phenol involves the simple migration of the phenyl group from vanadium to oxygen:



$$\overset{O}{\overset{\|}{Ph{-}VCl_2}} \rightarrow \overset{Ph{-}O}{\overset{|}{VCl_2}} \qquad (5)$$

with reduction of vanadium to the trivalent state. Atempts to determine the specific vanadium valence by permanganate titration and polarography gave inconclusive results because of interference by phenol.

In order to learn more about these reactions, *p*-deuterio-labeled phenyl groups were introduced into the system since they provide an easily recognizable tag (IR, mass spectroscopy) to determine the fate of these groups from various sources. The deuterium atom in the *para* position was far removed from the reaction site, therefore, no substantial isotope effect would be expected, and the labeled and unlabeled phenyl groups should have had equal reactivity.

When the labeled diphenylmercury (92.8% Ph^*_2Hg) was treated with vanadium oxide trichloride, the results (Table 2, E-1) show that most (86%) of the biphenyl was present as the dilabeled form $(p\text{-}DC_6H_4)_2$ (all *para*, no other isomers were detected by IR) and some was the monolabeled (13%) product, along with a trace of unlabeled material (0.7%). When a 1/1 mixture of labeled and unlabeled diphenylmercury was allowed to react (E-2) with vanadium oxide trichloride (Hg/V 1.0), then the expected statistical mixture of un-, mono-, and dilabeled biphenyl was obtained (28/51/21). Half of the recovered phenylmercuric chloride was derived from the labeled species. The duplicate experiments give an indication of the fair degree of precision which this technique allowed.

The subsequent four experiments related to various combinations of reacting labeled and unlabeled diphenylmercury with vanadium oxide trichloride or with the phenylvanadium oxide dichloride intermediate of this reaction sequence. Thus, when (E-3), a solution of phenylvanadium oxide dichloride (from Ph_2Hg and $VOCl_3$. aged 3 min), was mixed with a solution of Ph^*VOCl_2 (prepared similarly), then a ratio of un-, mono-, and dilabeled biphenyl resulted (29.6/45.6/24.8) which, as expected, was not unlike that of the second experiment (E-2). The increase of un- and dilabeled concentrations at the expense of the monolabeled product no doubt was due to decomposition of the preformed $PhVOCl_2$ and Ph^*VOCl_2 prior to mixing and preferential accumulation of Ph_2 and Ph^*_2 at the expense of $PhPh^*$. About 47% of the recovered phenylmercuric chloride was derived from the labeled diphenylmercury.

These facts indicated that each $PhVOCl_2$ reacted in a random manner with a labeled or unlabeled partner to yield a statistical mixture of biphenyls. If each species of $PhVOCl_2$ had decomposed discretely to its own biphenyl, then a 50.5/6.5/43 ($Ph_2/PhPh^*/Ph^*_2$) mixture of biphenyls would have resulted. It seemed most reasonable to accomodate these facts by the assumption that the biphenyls arose from a common intermediate in which the phenyl groups had scrambled.

$$3\ \mathrm{PhVOCl_2} + 3\ \mathrm{Ph^*VOCl_2} \xrightleftharpoons{\text{rapid}} \left\{\begin{array}{l}\mathrm{PhPhVOCl}\\ \mathrm{PhPh^*VOCl}\\ \mathrm{Ph^*Ph^*VOCl}\end{array}\right\} + 3\ \mathrm{VOCl_3} \tag{6}$$

$$\left\{\begin{array}{l}\mathrm{PhPhVOCl}\\ \mathrm{PhPh^*VOCl}\\ \mathrm{Ph^*Ph^*VOCl}\end{array}\right\} \xrightarrow[\text{determining}]{\text{rate}} (\mathrm{PhPh} + \mathrm{PhPh^*} + \mathrm{Ph^*Ph^*}) + 3\ \mathrm{VOCl} \tag{7}$$

$$\mathrm{VOCl} + \mathrm{VOCl_3} \rightarrow 2\ \mathrm{VOCl_2} \tag{8}$$

Eqn. (6) represents a rapid reaction (probably an equilibrium) of the two $\mathrm{PhVOCl_2}$ species to yield diphenylvanadium oxide chloride in which the phenyl groups had paired in a random manner. The subsequent rate determining decomposition [eqn. (7)] then yields the equilibrated biphenyls.

When next (E-4) a solution of $\mathrm{Ph_2^*Hg}$ was added to a prepared solution of $\mathrm{PhVOCl_2}$ ($\mathrm{Ph_2Hg}$, $\mathrm{VOCl_3}$, 1/1, aged 2 min), then slightly over half (56.3%) of the resulting biphenyl was the PhPh*. A reaction such as this should have resulted in polyphenylated-vanadium species (Table 1, total Hg/V = 2.0), *e.g.*:

$$\mathrm{Ph_2^*Hg} + \mathrm{PhVOCl_2} \rightarrow \mathrm{Ph^*PhVOCl} + \mathrm{Ph^*HgCl} \tag{9}$$

If this polyphenylated species had decomposed at once to biphenyl and phenyl-scrambling reactions, such as:

$$3\ \mathrm{PhPh^*VOCl} \rightleftarrows \left\{\begin{array}{l}\mathrm{PhPhVOCl}\\ \mathrm{PhPh^*VOCl}\\ \mathrm{Ph^*Ph^*VOCl}\end{array}\right\} \tag{10}$$

had been *absent*, then a predominance (>90%) of PhPh* would have been expected.

This clearly was not the case, and the formation of biphenyl by a direct, bimolecular reaction between $\mathrm{Ph_2^*Hg}$ and $\mathrm{PhVOCl_2}$ is also excluded. The amount of PhPh* actually found (56.3%) was only slightly larger than the quantity expected (~50%) based upon a statistical scrambling of the phenyl groups prior to decomposition to the variously labeled biphenyls [eqn. (7)]. The relative quantities of PhPh and Ph*Ph* formed (23.4 and 20.3%, respectively) were approximately equal and also reflected near statistical mixing of phenyl groups prior to decomposition to biphenyls.

From the 36% label of the recovered Ph*HgCl (E-4), it can be calculated ($x/(2.5+x) = 0.36$) that 1.37 mmoles of the 2.50 mmoles $\mathrm{Ph_2^*Hg}$ added had reacted to yield a diphenylated vanadium species,

$$\mathrm{Ph_2^*Hg} + \mathrm{PhVOCl_2} \rightarrow \mathrm{Ph^*PhVOCl} + \mathrm{Ph^*HgCl} \tag{11}$$

This compared favorably with the 32–40% additional reaction predicted by the data of Table 1, sample 2. If phenyl exchange reactions such as:

$$\mathrm{Ph_2^*Hg} + \mathrm{PhPh^*VOCl} \rightleftarrows \mathrm{PhPh^*Hg} + \left\{\begin{array}{l}\mathrm{PhPhVOCl}\\ \mathrm{PhPh^*VOCl}\\ \mathrm{Ph^*Ph^*VOCl}\end{array}\right\} \tag{12}$$

had *not* taken place, then the biphenyls which resulted from this reaction [eqn. (11)]

should have contained:

$$[\mathrm{Ph}^*/(\mathrm{Ph{-}V}+\mathrm{Ph}^*{-}\mathrm{V})]\times 100\% =$$
$$[(1.37\times 0.93)/(2.50+1.37)]\times 100\% = 33\%\ \mathrm{Ph}^*\ \text{groups}$$

The actual analysis showed the biphenyls of this experiment to contain 48.5% Ph* groups. This is much greater than these non-exchange [eqn. (12)] calculations predict. The increase in labeled phenyl groups must have arisen from an exchange between the soluble Ph^*_2Hg and $PhVOCl_2$ [eqn. (12)] species. (Phenylmercuric chloride does not exchange phenyl groups with diphenylmercury under these reaction conditions; 25°, 4 h, cyclohexane slurry).

The total soluble phenyl groups in this experiment (E-4) are: 2.50 mmoles Ph from the initial reaction (A, Table 2), 1.37 mmoles (93% labeled) Ph from the second reaction (B, Table 2) with Ph^*_2Hg and 1.13 mmoles (93% labeled) unreacted Ph^*_2Hg (*e.g.*, 2.26 mmoles Ph).

This represents a total of 2.76 mmoles (2.50+0.26) Ph and 3.37 mmoles (2.10+1.27) Ph* or 55.0% Ph* groups; therefore, a complete scrambling of all soluble phenyl groups would have resulted in a biphenyls mixture which contained 55% Ph* groups. The actual analysis showed the biphenyls to contain 48.5% Ph*; hence the system was almost completely equilibrated. The last two experiments (E-5 and E-6) involved the preparation of Ph^*VOCl_2 solutions (aged 1 and 5 min, respectively) and the addition of Ph_2Hg solutions to them (total Hg/V 3.24). In effect, this is the reverse of E-4, except that a larger amount of Ph_2Hg is used to react with the preformed Ph^*-$VOCl_2$. The PhPh* content was again relatively low, for reasons discussed above, the decrease of this PhPh* concentration from 58.8% (E-5) to 49.2% (E-6) was due to the increase in aging time of the preformed Ph^*VOCl_2 (which decomposes mainly to Ph^*_2, thereby increasing the Ph^*_2 concentrations from 9.5 to 12.9%). The 58% and 54% Ph* (averaged 56%) in the recovered PhHgCl showed that 1.96 mmole of the 5.6 mmoles Ph_2Hg added for the second reaction (B, Table 2) had reacted*.

By these methods it was calculated that, in the absence of phenyl group exchanges [such as eqn. (12)], the biphenyls from E-5 and E-6 should have had 52% Ph*. On the other hand, if complete scrambling of all soluble phenyl groups had occurred, then the biphenyls should have contained 19.8% Ph*. The experimental results show values somewhat in between (38.9 and 37.0% for E-5 and E-6, respectively). Additional evidence of these exchange rections was indicated by the Ph* assay of the recovered diphenylmercury (in E-5, 11.5% and E-6, 19%).

In summary, while no phenylvanadium species were isolated**, considerable evidence for their existence has been produced. These phenylvanadium compounds participate in a complex set of equilibria, the rates of which are greater than the decomposition of the phenylvanadium compounds to diphenyl. Biphenyl appeared to be formed in a concerted process involving coupling of two phenyl groups attached to the same vanadium center in a di- or polyphenylvanadium compound.

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* {[Ph* from 1st reaction]/[(Ph+Ph*) from all reactions]} × 100% = [2.50/(2.50+x)] × 100% = 56%. x = 1.96 mmoles Ph_2Hg reacted.

** The addition of a bipyridyl solution in cyclohexane to a phenylvanadium oxide dichloride solution yielded a brown precipitate for which only very poor analyses could be obtained. The $PhVOCl_2\cdot$Bipy complex is, therefore, not a stable one at room temperature.

ACKNOWLEDGEMENT

We would like to thank Mr. W. S. Tamplin of the South Charleston, West Virginia Laboratories, Union Carbide Corporation, for the mass spectroscopic analysis of the biphenyls.

REFERENCES

1 F. A. COTTON, *Chem. Rev.*, 55 (1955) 560.
2 E. KURRAS, *Angew. Chem.*, 72 (1960) 635.
3 E. KURRAS, *Z. Anorg. Allg. Chem.*, 351 (1967) 268.
4 H. J. DE LIEFDE MEIJER, M. J. JANSSEN AND G. J. M. VAN DER KERK, *Chem. Ind. (London)*, (1960) 119.
5 G. A. RAZUVAEV, V. N. LATAYAEVA, B. G. ZATEEV AND G. A. KILYAKOVA, *Dokl. Akad. Nauk SSSR*, 172 (1967) 1337; (Engl. transl. p. 180).
6 W. L. CARRICK, W. T. REICHLE, F. PANNELLA AND J. J. SMITH, *J. Amer. Chem. Soc.*, 82 (1960) 3887.