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A NEW, EASY SYNTHESIS OF PHENYLSILVER

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Summary

The reaction of diphenylzinc with silver salts yields stable phenylsilver in almost quantitative yield. The phenylsilver has been characterized by IR, and ^{1}H and ^{13}C NMR spectroscopy. The properties of phenylsilver made in this way have been compared with those of phenylsilver prepared from phenyltin- or phenyllead compounds.

Introduction

The first synthesis of pure phenylsilver, not stabilized by additional ligands, was reported in 1972 by Beverwijk and van der Kerk [1]. Several earlier attempts at preparing phenylsilver had resulted in impure products which decomposed spontaneously at room temperature or below [2,3,4]. In those preparations, silver salts were treated with phenylmagnesium compounds, but in all cases the resulting phenylsilver was contaminated with either magnesium salts or silver salts. The presence of such contaminants, which could not be easily removed, generally resulted in products of low thermal stability. Only in special cases, viz. when the arylgroup carried one or more substituents containing a heteroatom, did the organolithium route yield stable products (pentafluorophenylsilver [5], 2-(dimethylaminomethyl)phenylsilver [6], 2,6-dimethoxyphenylsilver [6] and 2,4,6-trimethoxyphenylsilver [6]).

The method used by Beverwijk and van der Kerk uses trialkylaryl-lead or -tin species as arylating agents. Although this route yielded pure, stable phenylsilver, it is cumbersome and restricted to small scale preparations (0.2—1.0 g) because of the special reaction conditions required and of the thermal lability of phenylsilver in the reaction medium.

We describe below a new simple synthesis of phenylsilver which has no scale limitations.

Results and discussion

Stirring finely divided solid silver nitrate for 2 h at 0° with an ethereal diphenylzinc solution in 1/2 molar ratio gives pure phenylsilver quantitatively as a colourless suspension.

$$Ph_2Zn + AgNO_3 \xrightarrow[0^\circ C]{Et_2O} PhAg\downarrow + [PhZnNO_3]$$

In the same reaction with ether-soluble silver tetrafluoroborate, $AgBF_4$, or silver trifluoromethane sulfonate, $AgSO_3CF_3$, phenylsilver is precipitated immediately, but in an impure and so unstable form. The IR spectrum of the phenylsilver obtained in this way from $AgBF_4$ shows absorptions attributable to a tetraphenyl boride species, apparently formed by arylation of the anion. These homogeneous reactions yield pure phenylsilver, however, when carried out at −30° C.

When Ph_2Zn is treated with $AgNO_3$ in a 1/1 molar ratio, an orange-coloured compound analyzing as $PhAg \cdot 2\ AgNO_3$ can be isolated, although in a low yield. The stoechiometry of this complex differs from that observed by Krause [7] and Beverwijk [1] for phenylsilver—silver nitrate complexes ($5\ PhAg \cdot 2\ AgNO_3$). The transient orange colours, which are also observed in the other reactions, may be attributed to intermediate phenylsilver–silver salt complexes. Apparently there is a rapid further arylation of these complexes to phenylsilver by diphenylzinc, in contrast to the corresponding reactions with phenyltin and phenyllead compounds which require up to a thirty-fold excess of the arylating agents for the same purpose.

When the diphenylzinc/silver salt ratio was lowered to 1/1 in the reactions with $AgBF_4$ and $AgSO_3CF_3$, only non-stoechiometric mixtures of phenylsilver and silver salts were obtained and in no case were well-defined complexes isolated.

Similar experiments were carried out with triphenylaluminium instead of diphenylzinc. In all cases formation of metallic silver was observed, even at low temperatures. Triphenylboron did not react with silver salts not even at 25° C.

Characterization of phenylsilver

The IR spectrum of the phenylsilver obtained in this work, recorded as a Nujol mull between polyethylene films, is superimposable upon that of phenylsilver made by the tin or lead route. The thermal stability of the phenylsilver obtained in this new way is slightly lower than that obtained by Beverwijk. The decomposition temperatures, as measured by DTA at a heating rate of 2° C/min, were 44 and 50° C, respectively.

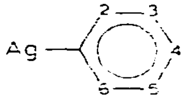
The solubility in chloroform of the phenylsilver made from diphenylzinc, in contrast to that of the phenylsilver described by Beverwijk, is just sufficient to allow the recording of both ^1H and ^{13}C NMR spectra. Unfortunately the thermal instability of solutions of phenylsilver in boiling chloroform prevented an ebulliometric molecular weight determination. The solubility in benzene was to small to permit determination of the molecular weight by cryoscopy. The results of NMR measurements are compiled in Table 1, together with some reference data.

The ^1H NMR spectrum of PhAg in deuterated chloroform at −10° C shows two well-defined multiplets centered at δ 7.67 and δ 7.13 ppm with a 2 : 3 integral ratio, assigned to *meta/para* protons and *ortho* protons, respectively. No change in the spectrum was observed over the temperature range 0 to −60° C and no Ag—^1H coupling was detected.

The proton-decoupled ^{13}C NMR spectrum of phenylsilver in deuterated chloroform at −45° C shows three sharp peaks at δ 131.2, δ 127.2 and δ 146.4 ppm.

TABLE 1

^{1}H AND ^{13}C NMR DATA OF PHENYLSILVER COMPOUNDS AT −30°C



Resonance positions in ppm relative to external TMS

Compound	H(2,6)	H(3,5)	H(4)	C(1)	C(2,6)	C(3,5)	C(4)
PhAg [a]	7.67 [c]	7.13 [c]	7.13 [c]	[e]	146.4	127.2	131.2
PhAg [b]	8.05 [d]	7.28 [d]	7.28 [d]	[f]	[f]	[f]	[f]
2 PhAg · 2 $AgNO_3$ [b]	7.88 [d]	7.28 [d]	7.28 [d]	148.52	144.40	128.94	133.07

[a] Prepared from diphenylzinc, deuterochloroform solution. [b] Prepared according to ref. 1, deuterated pyridine solution. [c] Estimated mean of well-defined multiplets. [d] Unresolved, broad signal. [e] Not detected. [f] Solubility to low.

These signals all split up into doublets in the undecoupled spectrum and must therefore be assigned to carbon atoms bearing a hydrogen substituent. No signal attributable to the silver-substituted carbon atom was detected. This may be due mainly to exchange broadening of the signal, which would in any case be of low intensity because of lack of NOE enhancement and splitting by ^{109}Ag—^{13}C and ^{107}Ag—^{13}C couplings.

The absence of a detectable Ag-substituted carbon signal, considered along with the absence of silver—hydrogen and silver—carbon couplings, indicates the occurrence of rapid exchange of phenylgroups between magnetically unequivalent sites. This exchange is apparently very fast, even at −60°C. Similar observations were made by Beverwijk [8]. In fact, only in one case have silver—hydrogen and silver—carbon couplings been detected [9].

When the sample used for recording the ^{1}H-spectrum was heated from 0 to 25°C, the original pattern disappeared completely and the spectrum of pure biphenyl appeared showing that phenylsilver decomposes cleanly into biphenyl and metallic silver:

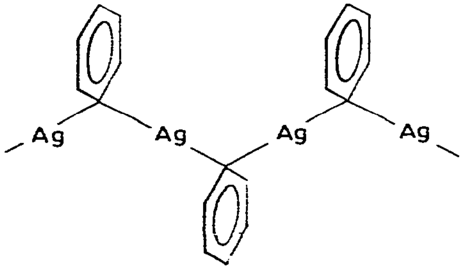
$$\text{PhAg} \xrightarrow{\Delta} \text{Ph—Ph} + \text{Ag metal}$$

Conclusion

Diphenylzinc is a good reagent for arylation of silver because it has better arylating properties than aryl-tin and aryl-lead compounds, and at the same time lacks the reducing effects observed with aryllithium, arylmagnesium and arylaluminium compounds.

The solubility of the phenylsilver obtained in this work is higher than that of phenylsilver obtained from phenyltin or phenyllead compounds. No explanation for this difference, except that traces of impurities may be responsible, can be offered.

In the light of the structure proposed by Van Koten [10] for the similarly insoluble phenylcopper it is tempting to suggest an analogous structure for phenylsilver, viz.:



However, the available data do not suffice to confirm this hypothesis. We are currently determining the scope of this synthetic route and seeking to elucidate the molecular structures of the resulting arylsilver compounds.

Experimental

All experiments were carried out under dry, purified nitrogen using Schlenk-type glassware. Liquids were handled by syringe techniques. Solvents were purified, distilled under nitrogen, and stored under nitrogen over molecular sieves.

NMR spectra were recorded with a Varian XL-100-15 spectrometer system and IR spectra were recorded on a Perkin—Elmer 457 spectrometer.

Decomposition temperatures were determined by DTA using samples sealed under nitrogen in glass ampoules. The reproducibility of the decomposition temperatures appeared to be ±1°C.

Diphenylzinc was prepared as described by Strohmeier [11]. The silver salts were of AR quality and were used without further purification.

Elemental analyses were carried out under the supervision of W.J. Buis in the Analytical Department of the Institute for Organic Chemistry TNO at Utrecht.

Synthesis of phenylsilver from silver nitrate

1.0 g (5.9 mmol) of finely ground $AgNO_3$ was added with stirring to a solution of 2.41 g (11.0 mmol) of Ph_2Zn in 40 ml of diethyl ether at 0°C. A part-orange, part-white precipitate formed immediately. The orange colour disappeared after 2 h stirring and the amount of white precipitate correspondingly increased. After decantation of the green supernatant liquid, the solid was washed five times with 25 ml of diethyl ether and dried in vacuo. Yield 1.02 g (5.5 mmol) (93% calcd. on $AgNO_3$). Analyses: found: C, 38.9; H, 2.9; Ag, 57.6. C_6H_5Ag calcd.: C, 38.96; H, 2.72; Ag, 58.32%.

Synthesis of phenylsilver from silver tetrafluoroborate and silver trifluoromethylsulfonate

These preparations were carried out similarly, solutions of the silver salts in diethyl ether being added dropwise during 15 min to a diphenylzinc solution in diethylether, at −30°C. The mixture was then stirred for 2 h at −30°C and worked up as described above. Yields were generally over 90%.

Synthesis of the phenylsilver—silver nitrate complex $PhAg \cdot 2\ AgNO_3$

A suspension of 0.37 g (2.15 mmol) of $AgNO_3$ in a solution of 0.47 g (2.15

mmol) of Ph_2Zn in 30 ml of diethyl ether was stirred for 6 h at 0°C. An orange precipitate formed, which after decantation of the supernatant liquid, was washed three times with 15 ml of diethyl ether and dried in vacuo. Yield 0.03 g. Analyses: found: C, 13.7; H, 1.0; Ag 61.6; N, 5.4; O, 18.3. $C_6H_5Ag_3N_2O_6$ calcd.: C, 13.73; H, 0.96; Ag 61.67; N, 5.34; O, 18.29%.

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References

1 C.D.M. Beverwijk and G.J.M. van der Kerk, J. Organometal. Chem., 43 (1972) C11.
2 E. Krause and B. Wendt, Chem. Ber., 56 (1923) 2064.
3 H. Gilman and J.M. Stralev, Rec. Trav. Chim. Pays-Bas, 55 (1936) 821.
4 H. Hashimoto and T. Nakano, J. Org. Chem., 31 (1966) 891.
5 V.B. Smith and A.G. Massey, J. Organometal. Chem., 23 (1970) C9.
6 A.J. Leusink, G. van Koten and J.G. Noltes, J. Organometal. Chem., 56 (1973) 379.
7 E. Krause and M. Schmitz, Chem. Ber., 52 (1919) 2159.
8 C.D.M. Beverwijk, Ph.D. thesis, Utrecht, 1974.
9 A.J. Leusink, G. van Koten, J.W. Marsman and J.G. Noltes, J. Organometal. Chem., 55 (1973) 419.
10 G. van Koten, Ph.D. thesis, Utrecht, 1974.
11 W. Strohmeier, Chem. Ber., 88 (1955) 1218.