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Preliminary communication

The synthesis and properties of phenylsilver

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With the aim of preparing phenylsilver, the reaction of phenylmagnesium bromide with silver chloride in diethyl ether was carried out in 1923[1,2]. The solid dark-brown reaction product was reported to decompose violently upon evaporation of the ether. Other authors subsequently prepared ether suspensions of "phenylsilver" in this way at low temperatures and studied the thermal decomposition[3,4] and chemical reactivity[3], but in no case was phenylsilver isolated and identified as such.

We now report the synthesis and characterization of phenylsilver, which is one of the most stable unfluorinated σ-bonded organosilver compounds known at present[5].

A solid yellow bis(phenylsilver)–silver nitrate complex was obtained in 1919 from the reaction of ethyltriphenyltin or -lead with silver nitrate in ethanol[6]. We studied this type of reaction at $-30°$, $0°$ and $25°$, using saturated solutions of silver nitrate in ethanol to which mixed alkylphenyltin and -lead compounds were added as phenylating agents, in molar ratios $R_nPh_{4-n}M/AgNO_3 \leqslant 1$. Bright-yellow precipitates were isolated, which analyzed correctly for the composition 5 PhAg·2 $AgNO_3$.

However, very slow addition of a solution of silver nitrate in ethanol to a solution of a large excess of trialkylphenyltin or -lead compounds in the same solvent above $15°$ and $-10°$, respectively, afforded a white precipitate of pure phenylsilver in 80–95% yield, which analyzed correctly for C_6H_5Ag. We did not succeed in obtaining pure phenylsilver under similar conditions from alkyltriphenyltin or -lead compounds. In this case the formation of phenylsilver always was accompanied by complexation with silver nitrate.

Phenylsilver can be obtained from the yellow phenylsilver–silver nitrate complex in two ways. First, by treating the complex, suspended in ethanol, with a large excess of trialkylphenyltin or -lead compounds above $15°$ and $-10°$, respectively. Secondly, by treating the complex with special ligands, such as acetonitrile or methylisocyanide, which do not appreciably coordinate with phenylsilver under the reaction conditions. A large excess of pure acetonitrile at $-30°$ to $-10°$ gave phenylsilver and an acetonitrile–silver nitrate complex[7] which could be removed by extraction with ether. A similar reaction occurred upon addition of a slight excess of methylisocyanide to a suspension of the

phenylsilver–silver nitrate complex in ether at –60° to –40°. Extraction at –40° with a 1/1 ethanol/ether mixture gave insoluble phenylsilver, and a solution from which the new complex, bis(methylisocyanide)–silver nitrate, was isolated.

Phenylsilver is more stable at room temperature than its silver nitrate complex, and does not decompose during one day in dry air or during several days under nitrogen. We observed a very exothermic initial decomposition stage of phenylsilver and of its silver nitrate complex by TGA (5°/min) at 67° and 47° (explosive), and by DTA* (10°/min) at 86° and 72° (explosive at 79°), respectively. Proton NMR spectra of solutions of phenylsilver and its complex in pyridine, *N,N*-dimethylformamide and *N,N*-dimethylacetamide at –30° to 0° show somewhat broadened multiplets of the *ortho*-protons, which are shifted downfield, and of the *meta*- and *para*-protons, which are slightly shifted upfield with respect to the singlet of benzene. This feature has been observed also in the spectra of substituted phenylcopper[8] compounds. ^{1}H and ^{13}C NMR spectra of several arylsilver compounds will be published in the near future. The IR absorptions of solid phenylsilver and its silver nitrate complex are nearly identical, and comparable with the absorptions of monosubstituted phenyl groups[9,10]. The presence of a very strong absorption at about 1340 cm^{-1} and of a weak single absorption at 1753 cm^{-1} in the spectrum of the phenylsilver–silver nitrate complex indicates that this complex contains ionic nitrate[11].

We have found that organotin and -lead compounds of the type RR'_3M are very suitable for the preparation of organosilver compounds generally. Further details of this work will be published shortly.

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*TGA = thermogravimetric analysis; DTA = differential thermal analysis.