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Note

Oxidation of adamantane by palladium acetate systems

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Abstract

Only low yields have been found for the oxidative substitution of adamantane catalysed by diacetatopalladium(II) in trifluoroacetic acid. Addition of copper(II) acetate produced a significant increase in conversion, exclusively to 1-adamantanol. The addition of potassium persulfate gave even higher yields, but at the expense of selectivity, with some 2-adamantanol product. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Adamantane has been used by numerous researchers to investigate alkane activation. It is a non-volatile substrate, experimentally more convenient to use than lighter alkanes. With 12 equivalent secondary carbons and four equivalent tertiary carbons, it is a potential probe for regioselectivity, although the interpretation of that selectivity is a matter of continuing controversy [1,2]. Sen et al. have used adamantane to model activation of methane with palladium acetate [3,4]. Reaction in trifluoroacetic acid at 80°C was reported to give > 50% yields of 1-adamantyltrifluoroacetate in 1 h [3]. We have been unable to reproduce this work. Our efforts are described here, together with the observation of significant enhancement of the reaction in the presence of copper acetate.

2. Experimental**2.1. Materials**

Analytical grade solvents were dried and distilled under nitrogen. Heptane (Merck) was distilled from

sodium wire; diethyl ether (BDH) and benzene (Merck) from sodium wire and benzophenone. Adamantane (Aldrich), 1-adamantanol (Merck), 2-adamantanol (Aldrich), 2-adamantanone (Aldrich), biphenyl (Aldrich), chloroform (Prolabo), copper(II) acetate (Univar), copper(II) chloride (Aldrich), decalin (Merck), deuterated chloroform (Aldrich), ethyl acetate (Prolabo), glacial acetic acid (Aldrich), hydrogen peroxide (Pacific), nitric acid (Univar), palladium(II) acetate (Aldrich), palladium(II) chloride (Matthey Garrett), palladium sponge (Johnson Matthey), potassium peroxydisulfate (Univar), spectroscopic grade potassium bromide (Univar), tetramethylsilane (Aldrich), trifluoroacetic acid (Aldrich), trifluoroacetic anhydride (Aldrich) and trifluoromethanesulfonic (triflic) acid (Aldrich) were used as received.

2.2. Syntheses**2.2.1. Diacetatopalladium(II) from palladium(II) chloride**

Diacetatopalladium(II) was prepared following the method of Hausman et al. [5]. Palladium(II) chloride (2.6 g, 0.015 mol) was dissolved in a solution of hydrochloric acid (10 M, 2.7 ml) and water (5.0 ml), by heating in an ethanol bath. Sodium hydroxide (20% w/v, 12 ml) was added dropwise and as quickly as possible (ca. 10 min), without the reaction temperature

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exceeding 80°C, which would cause polymerisation of the hydrous palladium oxide. The hydrous palladium oxide was filtered off, washed with water (4 × 35 ml) and *partially* dried at the pump. Complete drying also can cause polymerisation. The product was dissolved in glacial acetic acid (18 ml) and stirred at 80°C for 2 h. The solvent was removed under vacuum at room temperature (r.t.) over 10 h. The resultant solid was dried over potassium hydroxide under vacuum at 85°C to yield a red–brown powder (2.9 g, 0.013 mol, 88%). The product was characterised by its vibrational spectrum and melting point [6].

Stephenson et al. report that it is possible to recrystallise the product from benzene/acetic acid [7]. However, in the present work, this often led to decomposition to Pd(0). Decomposition occurred even if diacetatopalladium(II) were merely left standing at r.t. in some solvents (methanol, ethanol, chloroform, benzene) from several hours to several days.

2.2.2. Diacetatopalladium(II) from palladium sponge

Palladium sponge (2 g, 0.019 mol) was boiled gently under reflux in a solution of glacial acetic acid (50 ml) and concentrated nitric acid (1.5 ml) until the evolution of brown fumes ceased. A small amount of palladium sponge usually remained undissolved; if this were not the case, a little more sponge was added and reflux continued until no trace of brown fumes was observed. This process was necessary to avoid contamination of the product with Pd(NO₂)(OOCCH₃). The boiling brown solution was filtered and allowed to cool whereupon most of the complex separated as orange–brown crystals. The crystals were washed with acetic acid and water and air dried. The yield was virtually quantitative.

Bis(trifluoroacetato)palladium(II) was prepared following the method of Stephenson et al. [7]. Diacetatopalladium(II) (330 mg, 1.47 mmol) was dissolved in trifluoroacetic acid (15 ml) and the solvent evaporated on a steam bath. More trifluoroacetic acid (7 ml) was added and the process repeated. The product was dried under vacuum at 40°C for 7 h. Bis(trifluoroacetato)-palladium(II) can also be prepared by the method of Hausman et al. [5] for the preparation of diacetatopalladium(II). However, instead of stirring the hydrous palladium oxide in acetic acid, the hydrous palladium oxide is stirred in trifluoroacetic acid for 2 h.

2.2.3. Attempted preparation of palladium–copper acetate species

Sloan and Thornton [8] reported a preparation of mixed palladium(II)–copper(II) acetates, which in our hands gave inconclusive results. Diacetatopalladium(II) (0.6312 g, 2.812 mmol) and copper(II) acetate (1.0239 g, 5.128 mmol) were heated in acetic acid (80 ml) at 50°C for 30 min. An electronic absorption spectrum of

the solution showed a maximum at 350 nm. The solvent was removed under vacuum at r.t. over anhydrous potassium hydroxide. The solid products were extracted with chloroform, the solution filtered and the chloroform removed. The chloroform soluble solid was then extracted with ethyl acetate. Some blue–green solid, reportedly [Cu₂Pd(MeCO₂)₆] [8], was insoluble in ethyl acetate. The ethyl acetate was removed to give a dark green product, reportedly [CuPd₂(MeCO₂)₆]. When the [CuPd₂(MeCO₂)₆] was again extracted with chloroform, a yellow–brown solution resulted. The electronic absorption spectrum of the yellow–brown solution exhibited the same maximum at 350 nm as the initial reaction mixture.

1-Adamantyltrifluoroacetate was prepared by refluxing 1-adamantanol (1.4801 g, 9.722 mmol) in trifluoroacetic anhydride (10 ml) for 3 h. The reaction mixture was allowed to cool and then extracted with heptane. The heptane extracts were dried over anhydrous calcium carbonate and the solvent removed to yield a white crystalline powder (1.689 g, 70%).

2.3. Analyses

Gas chromatographic analyses were performed on a Hewlett–Packard 5890 GC fitted with an SGE 25 m QC2/BP1 0.2 m capillary column and a flame ionisation detector with a 3393A Hewlett–Packard integrator. The GC was operated in split/splitless mode with a 90% rejection. In a typical analysis a helium carrier gas flow of 41 ± 1 ml min⁻¹ was maintained and a column head pressure of 80 KPa was used. The injector and detector ports were set at 270°C since adamantane and derivatives sublime at ~240°C. The temperature program consisted of an initial temperature of 80°C for one min, then a ramp of 20°C min⁻¹ to 200°C held for 5 min. The injected sample size was 0.5 µl. Initially, a type A SGE ‘plunger-in-needle’ graduated 1.0 µl syringe was used for sample injections which gave inconsistent results and was replaced with a series II SGE graduated 5.0 µl syringe to obtain reproducible results.

Adamantane and relevant adamantyl derivatives were identified from their retention times (±0.1 min) by comparison with authentic samples: biphenyl, 8.1; adamantane, 5.7; 1-adamantanol, 7.1; 1-adamantyl trifluoroacetate, 7.2; 2-adamantanol, 7.7; 2-adamantanone, 7.6. A standard solution of known quantities of biphenyl, adamantane, 1-adamantanol, 2-adamantanol and 2-adamantanone was used daily. Neither decalin nor decafluorodecalin were found to be as suitable as biphenyl as an internal standard.

2.4. Procedures

In a typical experiment, adamantane (75.0 mg, 0.550 mmol) and an equimolar amount of a palladium(II)

species were heated under reflux in trifluoroacetic acid for 6 h. Teflon sleeves were used as silicon grease is soluble in trifluoroacetic acid. Adamantane dissolved completely in the trifluoroacetic acid only at reflux. After 6 h, the cooled reaction mixture was diluted with water (10 ml) and then with chloroform (10 ml), which was added to ensure that none of the adamantyl species sublimed at this point or were carried out with the gases. A sodium carbonate solution (20% w/v, 50 ml) was added cautiously to adjust the pH to 9–10. The reaction mixture was extracted with additional chloroform (2 × 50 ml) and the combined chloroform extracts dried over sodium carbonate, filtered and the solvent removed. Biphenyl (approximately 30 mg, accurately weighed) was added as a GC calibrant and the mixture dissolved in chloroform (25 ml) for GC analysis.

For a blank standard adamantane (75 mg, 0.550 mmol) and biphenyl (38.6 mg, 0.250 mmol) were heated under reflux in trifluoroacetic acid (10 ml) for 6 h. The reaction solution remained clear and was analysed in the usual manner. Adamantane and biphenyl were the only species identified from the GC traces, i.e. there was no observable reaction. A mass balance of about 80% was usually obtained, typical of reports of other workers [9–11].

3. Results

Ten different types of experiments were performed. In each case a 10 ml solution of 55 mM adamantane was refluxed for 6 h in the presence of 55–56 mM oxidant or oxidant and co-oxidant(s). In each case, except in the presence of $K_2S_2O_8$ (Exps. 8–10, Table 1), 1-adamantanol was the only product detected by GC and a mass balance of 75–85% was obtained as the sum

of 1-adamantanol and unreacted adamantane. We consider that the missing mass is due to losses in handling and not to non-extractable products such as carboxylic acids, because in the blank process of stirring adamantane with biphenyl only 78% of the material was recovered.

For the reaction of $Pd(OAc)_2$ with adamantane (Exp. 1), we have been unable to reproduce the conversions of greater than 50% reported by Sen et al. [3]. Regardless of the source of palladium acetate (purchased, or prepared by two different methods) the conversion to 1-adamantanol was consistently only about 12% after 6 h. Although variability in results has been ascribed to the ‘freshness’ of the palladium acetate [3], the reproducibility of our results with different sources of the reagent indicates that this is probably not the reason for the low conversions which we observe.

Sen does not describe his method of workup of the reaction, apart from extraction into pentane, but does report that 1-adamantyl trifluoroacetate was the only organic product [4]. It is not stated whether any unreacted adamantane was observed in the GC trace nor what mass balance was observed. In the absence of a description of procedures and the use of standards, it is difficult to account for the differences between Sen’s results and the work reported here. Other workers have also reported conversions of methane with palladium acetate much lower than 50% [12–14].

When palladium trifluoroacetate was used in place of palladium acetate as the oxidant, a similar conversion of 11% was observed. This is perhaps not surprising, if it is assumed that in refluxing trifluoroacetic acid palladium acetate is converted by ligand exchange into palladium trifluoroacetate.

The use of copper complexes as co-catalysts with palladium is well established in the Wacker process.

Table 1
Conversion of adamantane to 1-adamantanol with various oxidants^a

Exp.	Oxidant	Conversion (%)	Original colour	Final colour
1	$Pd(OAc)_2$	12 ± 3	red–brown	darkened, mirror, some black ppt
2	$Pd(TFA)_2$	11 ± 2	red–brown	darkened, mirror, some black ppt
3	$Cu(OAc)_2$	0	green	green
4	$Pd(OAc)_2, CuSO_4$	9 ± 3	blue–brown	blue–black
5	$Pd(OAc)_2, CuCl_2$	10 ± 2	blue–brown	blue–black
6	$Pd(TFA)_2, CuCl_2$	9 ± 2	blue–brown	blue–black
7	$Pd(OAc)_2, Cu(OAc)_2$	40 ± 1	green–brown	green–black
8	$K_2S_2O_8$	5 ± 1 ^{e,f}	clear	clear
9	$Pd(OAc)_2, Cu(OAc)_2, K_2S_2O_8$	85 ± 2 ^{b,c}	green–brown	yellow–grey
10	$Pd(OAc)_2, K_2S_2O_8$	86 ± 2 ^{b,d}	brown	dark brown

^a Reaction conditions: 0.55 mmol adamantane, 0.55–0.56 mmol of each of other oxidants, 10 ml TFA, reflux for 6 h.

^b 11% 2-adamantanol in addition to 1-adamantanol.

^c Mass balance $73 \pm 3\%$.

^d Mass balance 77%.

^e 3% 2-adamantanol.

^f Mass balance $67 \pm 6\%$.

Hence a series of experiments was conducted with the addition of various copper(II) salts to palladium acetate in refluxing trifluoroacetic acid (Exps. 3–7). There was no reaction in the presence of copper acetate alone (Exp. 3). The addition of copper sulfate to palladium acetate (Exp. 4) or copper chloride to palladium acetate or to palladium trifluoroacetate (Exps. 5 and 6) produced no additional conversion over that observed in the absence of copper.

A dramatic increase in conversion to 40% is observed, however, when equimolar quantities of palladium acetate and copper acetate are used together (Exp. 7). The product is exclusively the tertiary isomer 1-adamantanol. Mixed palladium–copper acetate trimers have been described in the literature, both Cu_2Pd and CuPd_2 species having been reported [8].

Even more dramatic effects are observed when potassium persulfate is added to the system. Potassium persulfate alone causes only a minor (5%) amount of oxidation, with both 1- and 2-adamantanol produced (Exp. 8). But in the presence of palladium acetate and copper acetate (Exp. 9) or with just palladium acetate alone (Exp. 10), about 85% conversion occurs. This increase is at the expense of selectivity; however, in contrast to the systems without persulfate, about 11% 2-adamantanol is also formed (as the percentage of the total amount of organics detected).

4. Discussion

In 1987, Sen et al. [3] reported that the reaction of adamantane with diacetatopalladium(II) in trifluoroacetic acid gave > 50% of 1-adamantyl trifluoroacetate when equimolar mixtures of adamantane (0.030 g, 0.223 mmol) and diacetatopalladium(II) (0.050 g, 0.223 mmol) were stirred in trifluoroacetic acid (3–4 ml) at 80°C over 2 h [4]. In our hands, over 6 h only $11 \pm 3\%$ of the adamantane is converted to the ester. Other groups also have reported much lower yields for the related activation of methane [12–14]. A possible source of experimental error might be the small volumes which were used in the previous work.

Both palladium acetate and palladium trifluoroacetate activate adamantane to approximately the same limited extent, presumably because the acetate is converted into the trifluoroacetate in the trifluoroacetic acid solvent. The only product of the adamantane oxidation is 1-adamantanol, with 100% selectivity to the tertiary product in each case.

Copper(II) has been used extensively in Wacker-type chemistry to reoxidise palladium(0) and so complete a catalytic cycle. Hence, in the present work copper(II) chloride, copper(II) sulfate and copper(II) acetate were tested as possible co-oxidants with the palladium(II)

complexes. Copper(II) chloride and copper(II) sulfate did not have any effect on the conversion of adamantane by the palladium(II) complexes. The conversion of adamantane to 1-adamantanol by diacetatopalladium(II), however, increased approximately fourfold when copper(II) acetate was added. The selectivity of tertiary to secondary substitution was not altered; the sole product was the tertiary derivative 1-adamantanol. Copper(II) acetate did not activate adamantane alone.

Potassium peroxydisulfate has also been used to oxidise palladium(0) to palladium(II) [3]. When one equivalent each of adamantane, diacetatopalladium(II) and potassium peroxydisulfate were reacted in trifluoroacetic acid, a conversion of > 90% was achieved. However, this was at the expense of selectivity, which decreased to approximately 90%, with some 2-adamantanol formed as well. The results indicate that the palladium acetate–copper acetate system is a promising one for the controlled oxidation of alkanes. Fujiwara and co-workers have made very similar observations on the carboxylation of gaseous alkanes with CO [15]. Further work is required to determine the optimum conditions for selectivity and conversion, to extend the range of alkanes that can be oxidised and to investigate the possibility of a catalytic cycle, in place of the stoichiometric reactions of the present work.

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