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Influence of the catalyst on the Pd^0-mediated reactions of $BrZnCH(CH_3)COO^tBu$ with vinyl and aryl triflates

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Abstract

A series of Pd^{II} complexes containing various Group V-donors were reduced with diisobutylaluminum hydride and the products screened as potential catalysts for the coupling of representative vinyl- and aryl-trifluoromethanesulfonate substrates to the Reformatsky reagent $BrZnCH(CH_3)COO^tC_4H_9$. The desired coupling product was obtained only with "reduced" dichlorobis(1,1-diphenylphosphino)ferrocene as catalyst and 2-naphthyl triflate as the substrate. These results are discussed in terms of the structural features of the reactants and catalyst.

Introduction

We have previously reported [1] the Pd^0-mediated cross-coupling of vinyl- and aryl-trifluoromethylsulfonates (triflates) with the Reformatsky reagent bromozinc-t-butoxyacetate, $BrZnCH_2COO^tC_4H_9$. We were interested in extending this type of cross-coupling reaction to alkyl-substituted bromozinc esters, $BrZnCH(R)COO^tC_4H_9$, because the formation of asymmetric carbon–carbon bonds might allow synthesis of optically active compounds when mediated by chiral transition metal complexes. As a model for this type of reaction we investigated the coupling of $BrZnCH(CH_3)COO^tC_4H_9$ with two unsaturated substrates, the triflate **1** derived from (+)dehydroisoandrosterone acetate and naphthyl triflate (**2**), using as catalysts a series of "reduced palladium" species prepared in situ by the action of diisobutylaluminum hydride on palladium(II) complexes.

In the present work, the complexes used as catalysts precursors were varied in respect of the nature of the donor atoms (P, As, or Sb) and for the phosphine series in respect of the substituents on the phosphorus: PPh_3, $P(OPh)_3$, and

$[Ph_2PCH_2P(CH_2Ph)Ph_2]^+$. A complex containing the strongly chelating asymmetric ligand, *R*-(+)-1,2-bis(diphenylphosphine)propane was also used in order to introduce a chiral center while minimizing palladium–phosphine dissociation, and thus reduce the tendency of the catalyst to promote β-hydrogen migration. Finally, 1,1′-bis(diphenylphosphino)ferrocene was included in this study because of its ability to efficiently catalyze the coupling of primary and secondary Grignard reagents with alkylzinc organic halides [2].

Experimental

Materials and procedure

Diisobutylaluminum hydride (1.2 *N* solution in toluene) was purchased from Aldrich Chem. Co. The trifluoromethylsulfonate (triflate) of **1** was prepared from the corresponding ketone by treatment of trifluoromethylsulfonic anhydride and 2,6-t-butylpyridine in dichloromethane [1]. 2-Naphthyltrifluoromethylsulfonate (**2**) was prepared similarly from 2-naphthol, with pyridine as the base. The Reformatsky reagent was prepared as previously described [3]. The following palladium complexes (catalyst precursors) were purchased from Aldrich Chem. Co. or prepared by published methods: **A**, *trans*-$[PdCl_2\{P(C_6H_5)_3\}_2]$ (Aldrich); **B**, *trans*-$[PdBr_2\{[P(C_6H_5)_2CH_2P^+(CH_2C_6H_5)(C_6H_5)_2\}_2]Br_2$ [4]; **C**, *trans*-$[PdBr_2\{P(OC_6H_5)_3\}_2]$ [4]; **D**, *trans*-$[PdCl_2\{As(C_6H_5)_3\}_2]$ [4]; **E**, $[PdCl_2\{Sb(C_6H_5)_3\}_2]$ [4]; **F**, dichloro[1,1-bis(diphenylphosphino)ferrocene}palladium(II) (Aldrich); **G**, *R*(+)-1,2-bis(diphenylphosphino)propane (Aldrich). Tetrahydrofuran was distilled from lithium aluminum hydride. Zinc wool was activated as previously described [5]. Microanalyses were carried out with a Perkin–Elmer 240 Elemental Analyzer; the results were consistent with the assigned formulas. Infrared (IR) spectra were measured on a Perkin–Elmer 681 Spectrophotometer. Mass spectra (MS) were recorded on a VG 7070 EQ spectrometer. ^1H nuclear magnetic resonance (NMR) spectra were obtained at 80 MHz on a Brucker WP80 Spectrometer; chemical shifts are reported as δ values in ppm relative to internal tetramethylsilane internal standard; coupling constants are in Hz. ^{13}C NMR spectra were obtained at 200 MHz on a Varian FT 200 Spectrometer; chemical shifts are reported in ppm relative to TMS.

Reaction of triflate 1 with $BrZnCH(CH_3)COO^tC_4H_9$ in the presence of "reduced" trans-$[PdCl_2\{P(C_6H_5)_3\}_2]$

Diisobutylaluminum hydride (1.2 *M* in toluene, 0.5 ml) was added to a stirred suspension of the finely-powdered precursor **A** (0.21 g, 0.3 mmol) in THF (8 ml) at 0 °C in a nitrogen-flushed apparatus. The suspended yellow solid dissolved and a deep red-brown colour developed. A solution of triflate **1** (0.920 g, 2 mmol) in THF (2 ml) was added, and the mixture stirred for 5 min. The Reformatsky reagent $BrZnCH(CH_3)COO^tC_4H_9$ (1.73 g, 5 mmol) was added dropwise and the mixture was stirred overnight at room temperature. The resulting red-brown solution was diluted with diethyl ether (6 ml) and then with hydrochloric acid (1.2 *N*, 6 ml). The nitrogen flow was discontinued and the aqueous phase was extracted with diethyl ether (3 × 4 ml).The organic layer and the ether extracts were combined, washed with water, until neutral, and dried over sodium sulfate. The solvent was evaporated under reduced pressure and the residue was flash-chromatographed on silica gel with 9/1 ethylacetate/n-hexane as the eluent [6]. Compound **3** was obtained as the major product (50% yield) together with 4 (16%).

Characterization of the products. **3**: m.p. 82–83° C (ethyl acetate/n-hexane); IR ($CHCl_3$), ν(C=O) 1720 cm^{-1}; ^1H NMR ($CDCl_3$): 5.75 (2H,m), 5.38 (1H,bz,d,*J* 5 Hz) 4.55 (1H,m), 2.1 (3H,s), 1.05 (3H,s), 0.75 (3H,s). ^{13}C NMR: 170.5 (s), 143.8 (d), 139.9 (s), 129.3 (d), 126.7 (d), 73.9 (d), 56.1 (d), 50.8 (d), 45.4 (s), 38.1 (t), 36.9 (t), 36.9 (s), 35.8 (t), 32.1 (t), 31.7 (t), 30.4 (d), 27.8 (t), 21.4 (q), 20.8 (t), 19.2 (q), 16.8 (q). MS: *m/z* 254 (M^+ – AcOH). **4**: m.p. 120–121° C (ethyl acetate/n-hexane); IR ($CHCl_3$) 3610, 3440 sh cm^{-1}; ^1H NMR ($CDCl_3$): 5.80 (1H,m). 5.35 (1H,m), 3.55 (1H,m), 1.10 (3H,s), 0.8 (3H,s). MS: *m/z* 272 (M^+).

Reactions of $BrZnCH(CH_3)COO^tC_4H_9$ with triflate 1 or triflate 2 in the presence of various catalysts

All reactions were carried out by the general procedure described for reaction of triflate **1** with catalyst precursor **A**, unless otherwise indicated. The following results were obtained with a 1/10 molar ratio of catalyst precursor to substrate.

*Triflate 1, "Reduced" precursor **B**.* Triflate **1** was added 1 h after the initial mixing of **B** with diisobutylaluminum hydride, because the initial step of the reaction was slow. Unchanged triflate **1** (25%), and products **3** (32%) and **8** (26%) were obtained. Characterization of **8**: m.p. 102–104° C (isopropyl ether/n-hexane); IR ($CHCl_3$): 1725 cm^{-1}. ^1H NMR ($CDCl_3$): 5.4 (1H,d,*J* 4 Hz), 5.28 (1H,m), 4.6 (1H,m), 2.02 (3H,s), 1.04 (3H,s), 0.9 (6H,d,*J* 7 Hz); MS: *m/z* 310 (M^+ – AcOH).

*Triflate 1, "Reduced" precursor **C**.* Unchanged **1** (67%) and products **5** (11%) and **6** (3%) were obtained.

Characterization of new products: **5**: thick oil. IR ($CHCl_3$) (cm^{-1}) ν(C=O) 1735–1730, 1590–1460. ^1H NMR: 7.35–7.00 (10H), 6.95 (1H,ddd,*J*(P–C) 9 Hz; *J*(C–H) 4, 2.6 Hz), 5.38 (1H,d,*J* 5 Hz), 4.55 (1H,m), 2.1 (3H,s), 1.05 (3H,s). ^{13}C NMR ($CDCl_3$): 170.5 (s), 150.53 (dd,*J*(P–C) 16.9 Hz), 144.98 (s), 141.24 (s), 140.08 (s), 129.60 (s), 129.60 (d), 129.60 (d), 29.58 (d), 129.59 (d), 124.90 (dd,*J*(P–C) 3 Hz), 124.80 (dd,*J*(P–C) 3 Hz), 121.95 (d), 120.52 (dd,*J*(P–C) 6 Hz), 120.51 (dd,*J*(P–C) 6 Hz), 120.38 (dd,*J*(P–C) 6 Hz), 120.38 (dd,*J*(P–C) 6 Hz), 73.70 (d), 57.40 (dd,*J*(P–C) 13.5 Hz), 50.14 (d), 48.41 (d,*J*(P–C) 13.5 Hz), 38.11 (t), 36.85 (t), 36.77 (s), 34.39 (t), 33.43 (dt, *J*(P–C) 18.8 Hz), 31.56 (t), 30.39 (d), 27.73 (t), 21.41 (q), 20.66 (t), 19.21 (q), 16.72 (q); ^{31}P NMR: 10.12 (d, *J*(P–H) 9 Hz). MS: *m/z* 486 (M^+ – AcOH).

6: m.p. 175–177° C (ethyl acetate/n-hexane); IR ($CHCl_3$): 1720, 1590, 1490 cm^{-1}; ^1H NMR ($CDCl_3$): 7.3–7 (10H), 5.55 (1H,m), 5.35 (1H,brd,*J* 5 Hz), 2.98 (1H,dd,*J* 8,2.5 Hz), 2.03 (3H,s), 1.42 (9H,s), 1.05 (3H,d,*J* 7 Hz), 0.9 (3H,s). ^{13}C NMR ($CDCl_3$): 174.87 (s), 170.50 (s), 150.70 (d,*J*(P–C) 7.5 Hz), 150.50 (d, *J*(P–C) 7.5 Hz), 139.78 (s), 129.6 (dd,*J*(P–C) 4 Hz), 129.60 (dd, *J*(P–C) 4 Hz), 129.59 (dd, *J*(P–C) 4 Hz), 129.61 (dd,*J*(P–C) 4 Hz), 124.82 (d), 124.82 (d), 122.09 (d), 120.62 (dd,*J*(P–C) 5 Hz), 120.72 (dd,*J*(P–C) 5 Hz), 120.51 (dd,*J*(P–C) 5 Hz), 120.2 (dd,*J*(P–C) 5 Hz), 80.23 (s), 73.83 (d), 56.83 (dd,*J*(P–C) 20.6 Hz), 52.33 (d), 49.68 (dd,*J*(P–C) 16.9 Hz), 44.46 (s), 41.02 (d), 38.98 (d), 38.43 (t), 38.06 (t), 36.97 (t), 36.60 (s), 31.81 (t), 31.64 (dd,*J*(P–C) 3.75 Hz), 28.12 (q), 27.69 (t), 27.05 (dt,*J*(P–C) 13.1 Hz),21.41 (q), 20.57 (t), 19.25 (q), 15.00 (dq, *J*(P–C) 3.7 Hz), 9.66 (q); ^1H NMR (C_6D_5N): 7.6–7.2 (10H), 5.48 (1H,d,*J* 5 Hz), 4.9 (1H,m), 4.0 (1H,m), 3.8 (1H,m), 3.48 (1H,dd,*J* 8, 2.5 Hz), 2.15 (3H,s), 1.6 (9H,s), 1.38 (3H,d,*J* 7 Hz), 1.35

(3H,s), 1.1 (3H,s). ^{13}C NMR (C_6H_5N): 175.44 (s), 170.74 (s), 151.69 (dd,J(P–C) 7 Hz), 151.7 (dd,J(P–C 7 Hz), 140.71 (s), 130.70 (d), 130.71 (d), 130.70 (d), 130.69 (d), 125.86 (d), 125.86 (d), 122.91 (d), 121.80 (dd,J(P–C) 5 Hz), 121.79 (dd,J(P–C) 5 Hz), 121.74 (dd,J(P–C) 5 Hz), 121.74 (dd,J(P–C) 5 Hz), 80.65 (s), 74.54 (d), 57.43 (dd,J(P–C) 20 Hz), 53.43 (d), 50.51 (dd,J(P–C) 10 Hz), 45.36 (s), 42.13 (d), 40.26 (d), 39.06 (t), 38.97 (t), 37.67 (t), 37.35 (s), 32.50 (t) 32.40 (dd,J(P–C) 5 Hz), 28.50 (q), 28.50 (t), 27.80 (dt,J(P–C) 15 Hz), 21.78 (q), 21.34 (t), 19.80 (q), 15.83 (dq,J(P–C) 4 Hz), 10.49 (q); ^{31}P NMR; 25.71 (dd,J(P–H) 17 Hz): MS m/z 604 ($M^+ + 1 - OC(CH_3)$) 467 (527 – AcOH).

Triflate 1, "reduced" precursor D. The products isolated were **3** (62) and **4** (20%).

Triflate 1, "reduced" precursor E. Unchanged **1** (69%) and product **8** (10%) were isolated. Characterization of **8**: m.p. 130–132 °C (ethyl acetate/n-hexane); IR ($CHCl_3$): 3619, 3450 sh, 1630 cm^{-1}. ^{1}H NMR ($CDCl_3$) 5.58 (1H,dd,J 2.6, 2.5 Hz), 5.35 (1H,br,J 5 Hz), 3.45 (1H,m), 1.03 (3H,s), 0.95 (3H,s). MS: m/s 420 (M^+).

Triflate 1, "reduced" precursor F. The mixture after reaction consisted chiefly of unchanged **1**.

Triflate 1 with "non-reduced" precursor F. The products isolated were **3** (40%) and **4** (25%).

Triflate 1, "reduced" precursor G. The products isolated were **3** (48%) and **4** (22%).

Triflate 2, "reduced" precursor F. Unchanged **2** (61%) and the product **9** (18%) were obtained. Characterization of **9**: m.p. 50–52 °C (ethyl acetate/n-hexane); IR ($CHCl_3$) 1720, 1606 cm^{-1}; ^{1}H NMR ($CDCl_3$): 7.8–7.3 (7H, aromatic H), 3.7 (1H,q,J 7.5 Hz), 1.55 (3H,d,J 7.5 Hz), 1.4 (9H,s). MS: m/z 256 (M^+).

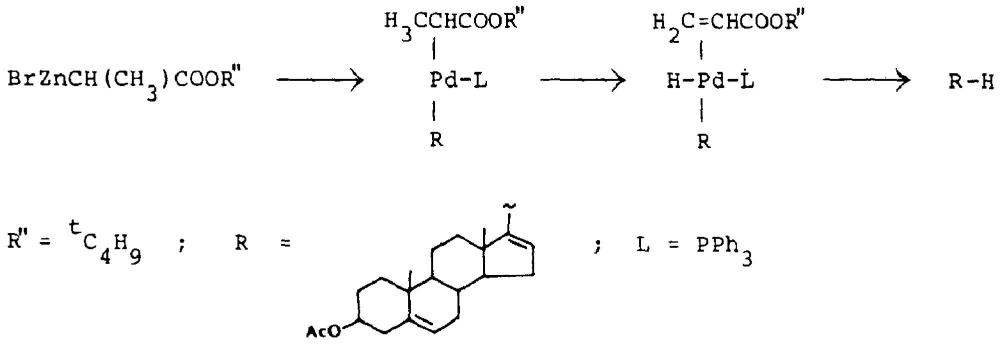
Triflate 2, "non-reduced" precursor E. The mixture after reaction contained chiefly unchanged **2**.

Triflate 2, "reduced" precursor A. The products isolated were **10** (20%) and **11** (10%). Characterization of the products: **10**: b.p. 265–270 °C; IR ($CHCl_3$): 1600, 1500, 1480 cm^{-1}. ^{1}H NMR ($CDCl_3$): 7.8–7.2 (7H), 2.65 (2H,d,J 7.5 Hz), 2.0 (1H,qqt,J 7.5,7.5,7.5 Hz), 0.98 (6H,d,J 7.5 Hz). MS: m/z high resolution: 184.1253 (M^+).

11: ^{1}H NMR ($CDCl_3$): 7.8–7.2 (aromatic protons of the naphthalene dimer). MS: m/z 254 (M^+).

Results and discussion

Whereas the Reformatsky reagent $BrZnCH_2COO^tC_4H_9$ gives high yields of the cross-coupling products with (+)-dehydroisoandrosterone acetate **1** in the presence of bis(triphenylphosphine)palladium(0) [1], under the same conditions use of $BrZnCH(CH_3)COO^tC_4H_9$ gives the reduction products **3** and **4**. Reduction was previously observed as a side reaction in the cross-coupling of sec-alkyl reagents of magnesium and zinc. It involves a β-hydride elimination of a σ-alkyl metal species, generated in the catalytic cycle, to afford a hydrido-olefin complex, as shown in Scheme 1. Cross-coupling products uncontaminated by side products could possibly be achieved by the choice of a catalyst that, in the oxidative addition–reductive elimination process, makes the reductive elimination of the coupling product much faster than the β-elimination.



Scheme 1

To this objective we investigated the reactions of the Reformatsky reagent $\mathrm{BrZnCH(CH_3)COO_4^tH_9}$ with the two substrates, the triflate **1**, derived from (+)-dehydroisoandrosterone acetate and 2-naphthyl triflate **2**, in the presence of various "reduced" and "non-reduced" palladium catalysts. The results obtained are summarized in Fig. 1 and 2. Since all experiments were carried out under closely similar conditions, discussion of the observed product distributions is justified.

The isobutyl-substituted product **8** [7] probably results from a cross-coupling reaction of **1** with a diisobutylaluminum halide formed from the corresponding hydride and precursor **B** ($\mathrm{L = \{C_6H_5\}_2PCH_2P^+\{(CH_2C_6H_5)(C_6H_5)_2\}}$. We found that **8** was obtained in even higher yields (78%) when **1** was treated with the reduced precursor **B** and diisobutylaluminum hydride (mole ratio, 1/1/2), in the absence of the Reformatsky reagent. A parallel experiment with the reduced precursor **A** gave products **8** (15%) and **3** (45%). When these results are compared with those from the reaction carried out in the presence of both reduced **A** and $\mathrm{BrZnCH(CH_3)COO^tC_4H_9}$ namely, no **8** and a total of 66% of the reduced products **3** and **4**, is clear that the alkylaluminum halide system promotes the cross-coupling reaction much more effectively than the Reformatsky reagent, which apparently favors reductive elimination.

With the catalyst precursor **C** ($\mathrm{L = P(OC_6H_5)_3}$) some products were isolated along with unchanged **1**. On the basis of their spectroscopic data they are tentatively assigned structures **5** and **6**. Work is in progress to elucidate the mechanism of their formation.

Comparisons of the product distributions for series of related catalyst precursors suggests a relative order for the overall reactivity of these systems. Thus, when the catalyst precursors involve the ligands, $\mathrm{P(C_6H_5)}$ and $\mathrm{\{C_6H_5\}_2PCH_2P^+\{(CH_2C_6H_5)(C_6H_5)_2\}}$, the yields of the reduced products **3** (50 and 32%, respectively) decrease in the same order as the ease of dissociation of the ligands from $\mathrm{Pd^{II}}$, as estimated from their π-bonding ability and steric hindrance. This suggests that dissociation of a L ligand may be important for these species in the β-hydrogen migration step. The observation that appreciable yields of reduced product **3** are formed in the case of the catalyst precursors *trans*-$\mathrm{[PdCl_2L_2]}$ with $\mathrm{L = P(C_6H_5)_3}$ or $\mathrm{As(C_6H_5)_3}$, whereas none are obtained when $\mathrm{L = Sb(C_6H_5)}$, suggests that with this last species the reduction of the precursor to the "reduced" active catalyst is unfavourable. This is consistent with the reported behaviour of $\mathrm{PdCl(SbR_3)}$ complexes towards reducing agents [8].

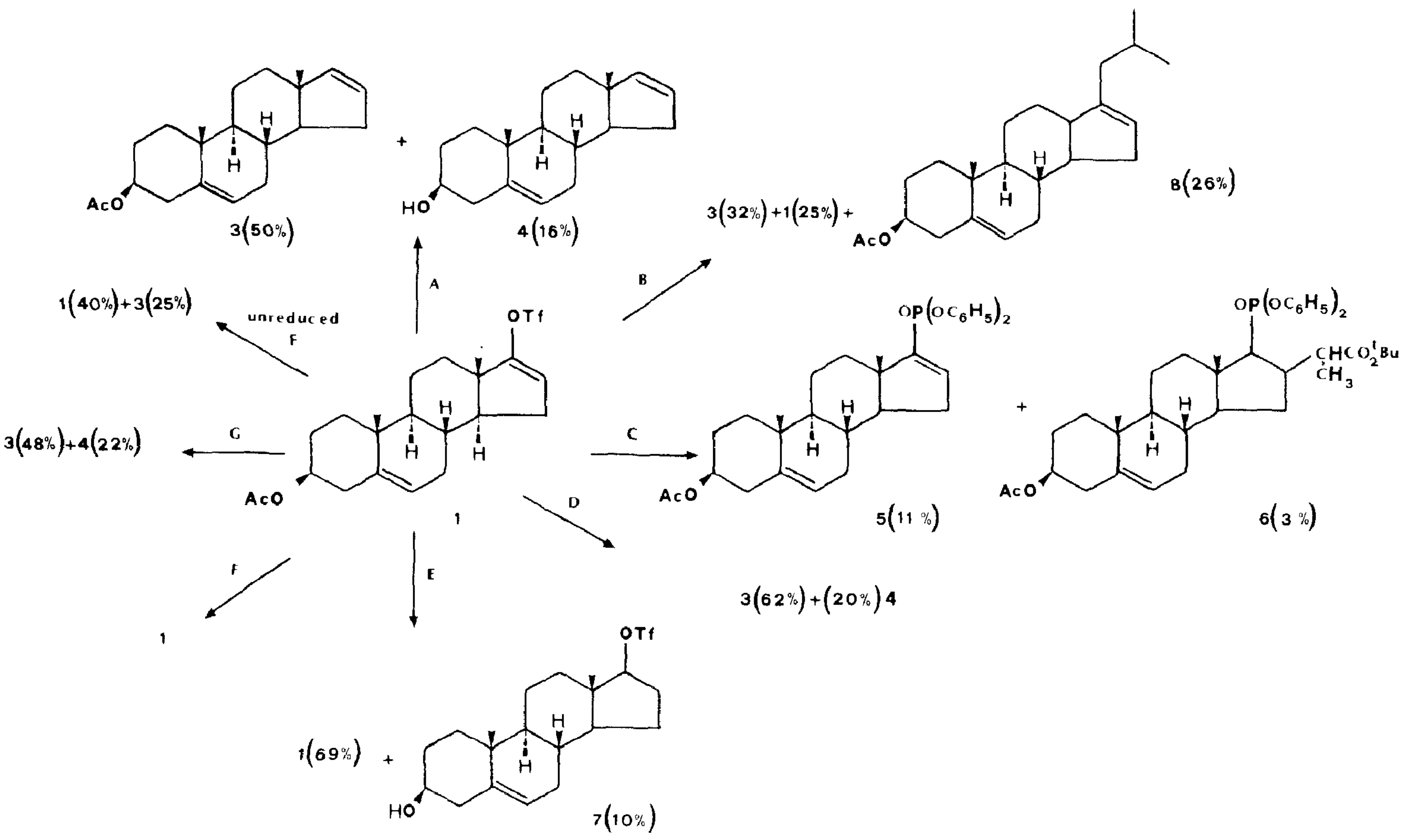


Fig. 1. Summary of products obtained in the reaction of the Reformatsky reagent, $BrZnCH(CH_3)COO^tC_4H_9$, with the triflate derived from (+)-dehydroisoandrosterone in the presence of various "reduced palladium" catalysts obtained from the following precursors: **A**, *trans*-$[PdCl_2\{P(C_6H_5)_3\}_2]$; **B**, *trans*-$[PdBr_2\{[P(C_6H_5)_2CH_2P^+(CH_2C_6H_5(C_6H_5)_2\}_2]Br_2$; **C**, *trans*-$[PdBr_2\{P(OC_6H_5)_3\}_2]$; **D**, *trans*-$[PdCl_2\{As(C_6H_5)_3\}_2]$; **E**, $[PdCl_2\{Sb(C_6H_5)_3\}_2]$; **F**, dichloro-[1,1-bis-(diphenylphosphino)ferrocene]palladium(II); **G**, *R*(+)-1,2-bis(diphenylphosphino)propane.

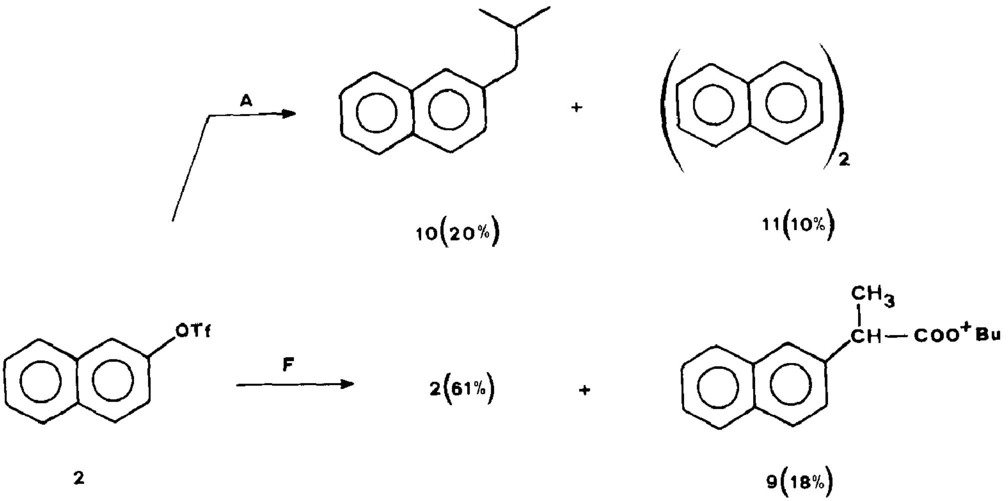


Fig. 2. Summary of the products obtained in the reaction of the Reformatsky reagent, BrZnCH(CH$_3$)COO^{t}C$_4$H$_9$), with 2-naphthyl trifluoromethylsulfonate in the presence of various "reduced palladium" catalysts obtained from the precursors indicated in Fig. 1.

The desired coupling product was obtained from substrate **2** only in the presence of the reduced complex of 1,1-bis(diphenylphosphino)ferrocene. Since this substrate is recovered unchanged when the reaction is performed with the unreduced complex (Precursor **F**), reported by Hayashi to be the most effective and selective catalyst for the reaction of sec-butylzinc bromide with bromobenzene, it may be concluded that the reduced species is, indeed, the active catalyst for this Reformatsky coupling process.

The effectiveness of a palladium catalyst in promoting the coupling of a secondary alkyl (*R′*) of a Reformatsky reagent to an organic substrate (R = vinyl or aryl) originally present as triflate, means that the R and R′ groups must be linked to the palladium(II) center in *cis*-positions and be sufficiently close to interact and bind to one another at a rate competitive with that of other possible processes, especially β-hydrogen migration from R′ to R via an agostic intermediate. Such a situation is favoured by the rigidly chelating structure and by the large P–Pd–P angle of the bis(diphenylphosphino)ferrocene complex, which forces together the other ligands of the {PPd(R)(R′)} species. Indeed for the corresponding *cis*-dichloro complexes, the Cl–Pd–Cl angle was found to decrease by 6.4 from the complex of 1,2-bis(diphenylphosphino)ethane (Cl–P–Cl, 94.2; P–Pd–P, 85.8) to that of bis(1,1′-diphenylphosphino)ferrocene complex (Cl–P–Cl, 87.8; P–Pd–P, 99.07) [2]. A similar compression of the angle opposite to the *cis*-bis(diphenylphoshino)ferrocene moiety may be expected to be present in the [PPd(R)(R′)] reaction intermediate provided the group R (substrate) is not so sterically hindered as to prevent a sufficiently close approach to the R′ (Reformatsky) group.

Conclusions

The results shows that "secondary" Reformatsky reagents, similar to the "primary" reagents previously reported, can couple with triflates in the presence of

Pd^0-phosphine catalysts prepared in situ by reduction of Pd^{II} precursors with diisobutylaluminum hydride. The efficiency of the coupling reaction, however, appears to be subject to rather stringent requirements. Thus the catalyst must contain a rigidly chelating diphosphine, such as bis(1,1′-diphenylphosphinoferrocene), which gives rise to an exceptionally large P–Pd–P angle and thus forces together the Pd-bound partners-to-be organic groups of the Reformatsky and substrate reagents. For the same reasons, substrates may have to be chosen from species that present limited steric hindrance, at least in respect of the internal direction of the R–Pd–R′ angle.

Our results have shown that when either the palladium catalyst or the substrate do not favour (or permit) the close approach required for the coupling, either no reaction occurs or β-hydrogen migration from R to R′ take place, leading to reduction products. These generalization provide a useful background for future work aimed at identifying substrate/catalyst pairs suitable for coupling with secondary Reformatsky reagents.

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