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PALLADIUM-CATALYZED PHENYLATION OF ALLYLIC 1-PERFLUOROALKYL ALCOHOLS

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Summary

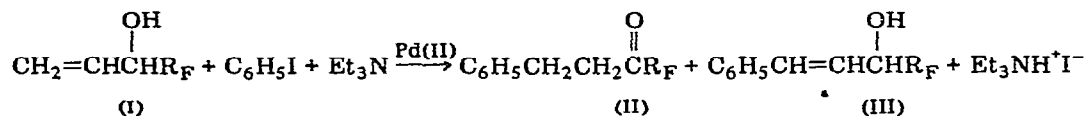
The palladium salt catalysed phenylation of alcohols of the type $\text{CH}_2=\text{CH}-\text{CH}(\text{R}_F)\text{OH}$ (R_F = perfluoroalkyl) with iodobenzene occurs regioselectively at the terminal olefinic carbon.

Introduction

Heck [1] and Chalk [2] have recently described the palladium-assisted addition of aryl halides to allylic alcohols, which, in the presence of base, led to the formation of carbonyl compounds. In order to gain some additional insight into the scope and mechanism of this interesting reaction, we have now studied its applicability to related alcohols having a strongly electron-withdrawing F-alkyl group attached to carbon-1.

Results and discussion

When an alcohol of type I was heated with iodobenzene, triethylamine and a palladium(II) catalyst in acetonitrile, ketone II formed as the major product, along with the unsaturated alcohol III.



(a: $\text{R}_F = \text{C}_2\text{F}_5$, b: $\text{R}_F = \text{C}_6\text{F}_{13}$)

Compounds II and III were easily separated by fractional distillation. The highest ratio of ketone to alcohol was obtained with palladium acetate. The results of some preparative scale experiments are summarized in Table 1. The use of bromo- instead of iodo-benzene decreased the reaction rate by a factor

TABLE 1
PHENYLATION OF COMPOUNDS I WITH IODOBENZENE

Alcohol	Catalyst	Method	Yield (%)	
			Ketone	Alcohol
Ia	Pd(OAc) ₂	a	56.9	29.1
Ib	Pd(OAc) ₂	a	52.9	34.0
Ia	Pd(OAc) ₂ (PPh ₃) ₂	a	49.3	33.2
Ia	PdCl ₂	a	50.6	34.0
Ia	PdCl ₂	b	4.0	37.7

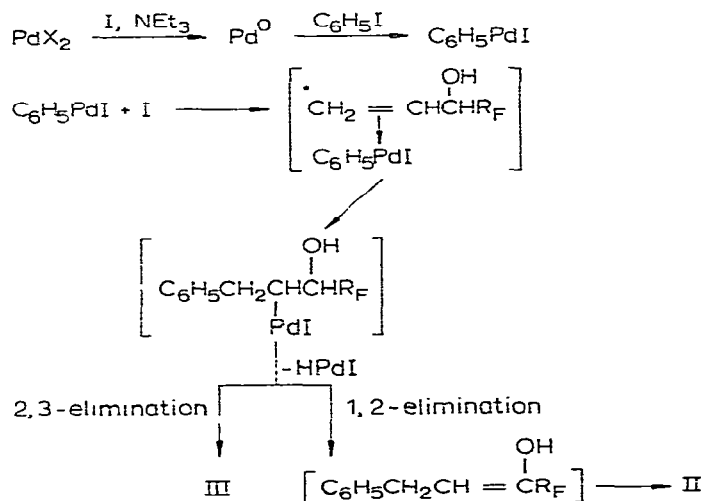
^a A solution containing 0.5 mol of I, 0.5 mol of C₆H₅I, 0.6 mol of NEt₃, 1.5 mmol of catalyst and 160 ml of CH₃CN was heated under reflux for 20 h. ^b The same quantities of I, C₆H₅I and catalyst as in method a were heated with 0.6 mol of sodium bicarbonate and 200 ml of HMPT at 130°C for 5 h. Ketone II proved to be unstable under these conditions in a blank experiment.

of approximately 10². Similarly, a very low degree of conversion was observed with the catalyst RhCl(CO)(PPh₃)₂.

A remarkable feature of these reactions is their strict regioselectivity. The observed 3-arylation is probably caused by the inductive influence of the R_F group, which will tend to produce a partial positive charge on the terminal olefinic carbon in I. Non-fluorinated allylic alcohols invariably give 5–20% 2-arylation [1].

The formation of II and III can be accounted for by the reaction sequence shown in Scheme 1.

SCHEME 1



Both palladium acetate and chloride, on heating in a mixture of I and triethylamine, gave a precipitate of palladium metal. The palladium(0), which in the early stages of reaction probably exists as a solvated species, oxidatively adds iodobenzene to form phenylpalladium iodide; this can then add to the double bond of I via an intermediate π -complex. Finally, β -elimination of

hydride either from carbon-1 or -3 followed by loss of HPdJ affords the isolatable compounds II or III. It is reasonable to assume that the R_F-substituent will hamper the ease of abstraction of the adjacent hydrogen, thus slowing down the 1,2-elimination but leaving the 2,3-route virtually unaffected. It may serve as support for this view that, under comparable conditions, the reaction of the 1-methyl compound 3-buten-2-ol [1] shows a higher over-all rate and almost exclusively yields a ketone analogous to II.

Experimental

Procedure for the phenylation of I: Preparation of 1,1,1,2,2-pentafluoro-5-phenyl-3-pentanone (IIa) and (E)-4,4,5,5,5-pentafluoro-1-phenyl-1-penten-3-ol (IIIa)

A mixture of 88 g of CH₂=CHCH(C₂F₅)OH, 102 g of iodobenzene, 84 ml of triethylamine, 160 ml of acetonitrile and 0.35 g of palladium acetate was refluxed for 20 h under nitrogen. The boiling point rose slowly from 78 to 83°C. The mixture was cooled to 20°C, diluted with 1 l of water and extracted with two 200 ml portions of diethyl ether. The ether layer was washed five times with 100 ml of water, then dried over sodium sulfate. After evaporation of the solvent, the residue was distilled through a 60 cm slotted tube column. 71.7 g of IIa were obtained as a colorless liquid (b.p. 39–41°C/0.3 Torr) and 36.7 g of IIIa (b.p. 78°C/0.3 Torr, m.p. 56°C), which rapidly solidified. The data for the C₆F₁₃ compounds, which were prepared by the same method, were: IIb: b.p. 55–56°C/0.03 Torr, (E)-IIIb: b.p. 82°C/0.03 Torr, m.p. 58°C. The purity of all compounds was greater than 99% (from GLC) and satisfactory elemental analyses were obtained.

Compound IIa rapidly formed a 2,4-dinitrophenylhydrazone melting at 153°C (yellow needles from methanol/dioxane).

Spectroscopic data

IIa: IR: ν(C=O) 1754 cm⁻¹. ¹H NMR (CCl₄, i-TMS, 60 MHz): δ(CH₂) 2.87, δ(C₆H₅) 7.12; ¹⁹F NMR (CF₃CO₂H, 56.45 MHz): δ(CF₂) 45.1, δ(CF₃) 4.1 ppm.

IIb: IR: ν(C=O) 1761 cm⁻¹. ¹H NMR: δ(CH₂) 2.93, δ(C₆H₅) 7.17; ¹⁹F NMR: δ(CF₂) 42.2, 43.5, 44.4 (4F), 48.4; δ(CF₃) 3.4 ppm.

Compounds III are known and their IR and NMR spectra have been reported [3].

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