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PALLADIUM(II)-CATALYZED OXIDATION OF SUBSTITUTED BENZENES TO BIARYLS BY TRIS(TRIFLUOROACETATO)THALLIUM(III)

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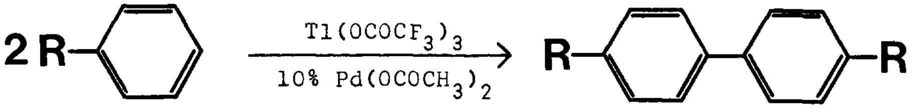
Summary: The method of oxidation of substituted benzenes to 4,4'-biaryls by Tl(III) trifluoroacetate catalyzed by Pd(II) acetate is presented. The reactions proceed in the completely homogeneous solution of arene.

Thallium(III)[1] and palladium(II)[2] compounds are known to be convenient reagents for oxidation of substituted benzenes to biaryls[3]. McKillop and Taylor[1] have shown recently that $Tl(OCOCF_3)_3$ is an efficient oxidant of benzenes to biaryls under rather mild conditions. However, this method is suitable for benzenes with electron donating ring substituents (at least one methoxy group is required) and boron trifluoride etherate is necessary when CCl_4 is used as solvent. The limitations on arene structure are lower in the case of palladium(II) compounds[2], but the reaction conditions are usually more vigorous. The reactions with palladium(II) can be performed in a catalytic regime with respect to Pd(II). Recent results on arylation of olefins[4] and carbonylation of arenes[5] in the presence of Pd(II) using organo-thallium(III) derivatives as starting materials have demonstrated that only catalytic amounts of Pd(II) can be used, e. g. thallium(III) can reoxidize reduced palladium. Very recently van der Ploeg, et. al.,[6] reported the formation of 1:1 complexes of Pd(II) and Tl(III) carboxylates of the formula $PdTl(OCOR)_5$, in which electrophylic properties of both metal ions could be substantially increased. So, on the one hand Tl(III) may be used as palladium reoxidant and on the other a combination of Pd(II) and Tl(III) carboxylates may result in the formation of a promising oxidant of arenes. These findings of other authors prompted us to investigate tha activity of the mixtures of Pd(II) and Tl(III) carboxylates in the oxidative coupling of arenes. Here we wish to report our first results which have demonstrated that $Tl(OCOCF_3)_3$ in the presence of catalytic quantities of $Pd(OCOCH_3)_2$ easily and regiospecifically oxidizes substituted benzenes to biaryls in a solution of oxidizing arene, eq. (1).



(1)

R = MeO; Me; H; F; Cl

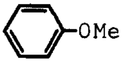
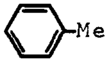
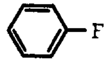
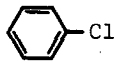
Preliminary experiments were performed using benzene as both substrate and solvent at 80° C. In accordance with the literature data[7] it was found that $Pd(OCOCH_3)_2$[8] does not oxidize benzene under these conditions. The same is true for $Tl(OCOCH_3)_3$[9]; only traces of biphenyl were formed. Treatment of $Tl(OCOCH_3)_3$ in the presence of catalytic amount of $Pd(OCOCH_3)_2$ (10% with respect to thallium) in benzene for 4 h gave biphenyl in very low yield (3%)[10]. Since $Pd(OCOCF_3)_2$ is almost insoluble in all common solvents including aromatic hydrocarbons[11], we did not test this palladium(II) compound in the reaction (1). On the contrary, possessing a rather good solubility $Tl(OCOCF_3)_3$[12] provides the desirable homogeneity of the solution and this compound was studied both alone and in its mixture with Pd(II) acetate. When the solution of $Tl(OCOCF_3)_3$ in benzene was thermostatted at 80° C for 4 h biphenyl formed in a 14% yield; under the same conditions in the presence of $Pd(OCOCH_3)_2$ (14% with respect to thallium) the yield of biphenyl increased up to 69% and no precipitation of palladium metal was observed. The reduction of Pd(II) became noticable only after a prolonged heating of the solution when the yield of biphenyl approached to 90%. When $Tl(OCOCF_3)_3$ was in deficiency (14% with respect to palladium), the precipitation of palladium metal began immediately and after the reaction had ceased ($2\frac{3}{4}$ h), the yield of biphenyl was 100%, but that based on Pd(II) was only 14%. The results obtained convincingly show that Pd(II) acetate and Tl(III) trifluoroacetate really activate each other in this oxidative coupling reaction.

We have tested not only benzene, but some other arenes, namely anisole, toluene, fluorobenzene and chlorobenzene. The results of selected runs are summarized in the Table, where some data for benzene are also included. It is seen from the Table that arenes with electron donating and medium electron withdrawing ring substituents undergo readily the coupling reaction. The process is rather regioselective; after recrystallization pure 4,4'-isomers were obtained The yields are excellent in the case of benzene and toluene, but good for the other arenes.

Our method constituted a simple procedure of isolation of biaryls, which was as follows. The solvent was removed in vacuo, and the residue was extracted

TABLE

Palladium(II)-catalyzed oxidation of substituted benzenes to biaryls by $Tl(OCOCF_3)_3$ in a solution of arene. Conditions: $Tl(OCOCF_3)_3$ - 0.930 mmol; $Pd(OCOCH_3)_2$ - 0.093 mmol; solvent - 25 ml.

Arene	Temperature, °C	Reaction time, h	Yield of 4,4'-Ar_2, %, based on Tl(III)	mp, °C	lit. mp, °C
	room temp.	46	37	173	174[b]
	room temp.	170	45		
	50	46	79		
	105	16	61	122-123	123-124[c]
	105	27	93		
	65	16	64	70	69[d]
	65	70	103		
	65[a]	70	43		
	50	88	54	84-85	88.5[e]
	70	64	86		
	70[a]	64	traces		
	105	16	49	150	148-149[e]
	105	45	66		

[a] No Pd(II) acetate added; [b] G. W. K. Cavill, D. H. Solomon, *J. Chem. Soc.*, *1955*, 1404; [c] Y. Fujiwara, I. Moritani, K. Ikeganai, S. Teranishi, *Bull. Chem. Soc. Japan*, *43*, 863, 1970; [d] R. van Helden, G. Verberg, *Rec. trav. chim. pays-bas*, *84*, 1263, 1965; [e] B. Williamson, W. H. Rodebush, *J. Amer. Chem. Soc.*, *63*, 3018, 1941.

three times with hot hexane or heptane[13]. The organic extracts were combined, concentrated, and then passed through the silica gel column to remove the traces of metals using chloroform-heptane mixtures as an eluant depending on the nature of biaryl. Evaporation of the solvent under reduced pressure gave pure biaryl, which could be additionally purified by recrystallization from EtOH.

Various mechanisms of this process are possible. The thallation of arene may initiate the reaction, followed by substitution of Tl(III) for Pd(II) to form unstable arylpalladium species, since it is known[14] that interaction of palladium(II) and arylthallium compounds as starting materials gives biaryls. However, our spectrophotometric study of $Tl(OCOCF_3)_3$ and $Pd(OCOCH_3)_2$ in benzene reveals the formation of 1:1 adduct. This adduct may be a reactive species, activating the aromatic molecule. Further work is necessary for establishing a true mechanism of the reaction. The scope and limitations of this reaction are also under study in our laboratory.

Acknowledgment

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References and Notes

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   (b) A. K. Yatsimirsky, I. V. Berezin, *Dokl. Akad. Nauk SSSR (Russ.)*, *255*, 1193, 1980.
8. Palladium(II) acetate was prepared according to ref.[11].
9. Thallium(III) acetate was obtained dissolving Tl_2O_3 in acetic acid.
10. The yields of biaryls throughout the paper are given with respect to the initial quantity of Tl(III) in the reaction mixture.
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12. Thallium(III) trifluoroacetate was obtained from Mr. A. Ya. Usiatinsky, Institute of Organo-Element Compounds, Moscow.
13. To the residual oil, which is left after the extraction, a new portion of arene could be added. The reaction starts again, if, of course, thallium(III) is not exhausted completely.
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