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CARBONYLATION OF NITROSOBENZENES TO CARBAMATE ESTERS CATALYZED BY PALLADIUM AND CUPRIC ACETATES UNDER AMBIENT CONDITIONS

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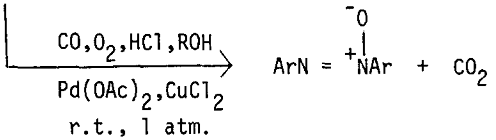
Summary: Palladium acetate and cupric acetate are effective catalysts for the reaction of nitrosobenzenes with carbon monoxide and alcohol at room temperature and one atmosphere.

Palladium chloride, in the presence of cupric chloride, hydrochloric acid, oxygen, and alcohol is a useful catalyst for the hydroesterification of unsaturated hydrocarbons[2,3] and amines[4]. In the latter case, carbamate esters are obtained from aromatic amines by operating at room temperature and atmospheric pressure.

A more difficult transformation to achieve is the conversion of nitrosobenzenes to carbamate esters. We now find that such a reaction occurs under remarkably mild conditions, provided the appropriate palladium and copper salts are used.

Nitrosobenzene was recovered unchanged after attempted reaction with carbon monoxide and oxygen in methanol using palladium chloride as the catalyst [room temperature, one atmosphere, 16-18 hours]. In the absence of oxygen, azoxybenzene was isolated in 61% yield and azobenzene in 18% yield. When one applies the conditions employed in the amine hydroesterification reaction to nitrosobenzene [i.e. $CO/O_2/PdCl_2/CuCl_2/HCl/CH_3OH$], azoxybenzene (51%) was obtained, together with azobenzene (22%) and aniline (25%), but no carbamate ester was detected. However if one simply substitutes palladium acetate and cupric acetate for the chloride salts, then methyl N-phenylcarbamate [2,Ar=Ph,R=CH_3] was formed from nitrosobenzene [1,Ar=Ph] in 57% yield after 12 hours and in 89% yield after 48 hours. The ratio of 1/$Pd(OAc)_2$/ $Cu(OAc)_2$ used was 10/1/2.

$$\underset{(1)}{ArNO} + ROH + 2CO \xrightarrow[O_2,\text{HCl},\text{r.t.},1\text{ atm.}]{Pd(OAc)_2,\ Cu(OAc)_2} \underset{(2)}{ArNHCOOR} + CO_2 \qquad \text{(eq. 1)}$$



$$(1)\xrightarrow[\substack{Pd(OAc)_2,CuCl_2\\ \text{r.t., 1 atm.}}]{CO,O_2,HCl,ROH} ArN=\overset{\overset{{}^{-}O}{|}}{{}^{+}N}Ar + CO_2 \qquad \text{(eq. 2)}$$

Both palladium and cupric carboxylates are critical to the success of the reaction. No reaction occurs without the palladium catalyst while the absence of cupric acetate leads to 2 (35%), azoxybenzene (35%) and aniline (8%). Note that azoxybenzene is formed in quantitative yield when palladium acetate and cupric chloride are used to catalyze the reaction [$PhNO/CO/O_2/HCl/CH_3OH$ (eq. 2) - 2.5 hr., r.t., 1 atm]. These conditions compare favorably with those reported for the same conversion of nitroso - to azoxybenzene at higher temperatures and/or pressures[5,6]. In addition to the requirement for the use of acetates of palladium and copper, the nature of the acid is important since substitution of acetic acid for hydrochloric acid results in a decrease of the yield of methyl N-phenylcarbamate from 89% to 29% [48% recovered PhNO].

Other alcohols can be used for the reaction described in equation 1, affording carbamate esters in good yields [e.g. $PhNHCOOC_2H_5$ (81%), $PhNHCOOC_3H_7$-n (76%), $PhNHCOOC_3H_7$-i (57%)]. The reaction is also applicable to other nitrosoarenes including 1, Ar=o-$CH_3C_6H_4$, p-$(CH_3)_2NC_6H_4$, and 1-$C_{10}H_7$.

The following general procedure was used; Carbon monoxide was bubbled through the alcohol (60 ml.). Palladium acetate [0.112 g., 0.50 mmol] was added to the magnetically stirred solution, followed by two drops (≈ 0.07 ml.) of hydrochloric acid. After three minutes, cupric acetate [0.18 g., 1.0 mmol] was added and then 5.0 mmol of the nitroso compound. Oxygen was bubbled through the solution, together with carbon monoxide, and the mixture was stirred overnight at ambient temperature. The solution was subjected to rotary evaporation, the residue was triturated with ether, the ether extract was dried and concentrated to give the carbamate ester (2). Analytically pure 2 was obtained by silica gel column or thin-layer chromatography.

In conclusion, the palladium acetate and cupric acetate catalyzed conversion of nitrosobenzenes to carbamate esters occurs under remarkably mild conditions. This research also illustrates the significant influence of the anionic component of the catalyst on the reaction course.

Acknowledgments

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