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COBALT(II) CHLORIDE CATALYZED SYNTHESES OF ACID ANHYDRIDES FROM ACID CHLORIDES

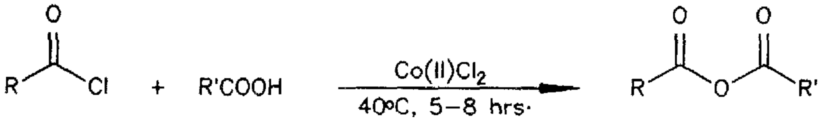
Rajiv R. Srivastava and George W. Kabalka*
Departments of Chemistry and Radiology
University of Tennessee, Knoxville, TN 37996-1600

Abstract: Acid anhydrides were synthesized by reacting acid chlorides with carboxylic acids in the presence of catalytic quantities of cobalt(II) chloride.

Several methods are available in the literature for the syntheses of acid anhydrides which are common intermediates in the preparation of esters, amides and peptides. The syntheses of anhydrides are routinely carried out by the reaction of a carboxylic acid with a dehydrating agent.[1] Other methods are available to effect the transformation[2,3] but each of these methods has one or more of the following shortcomings: unstable or difficult to handle reagents are necessary, complex workups are required, or reactions are limited to the preparation of symmetrical anhydrides. Our interest in transition metals led us to explore the possibility of using a transition metal catalyst to synthesize anhydrides. There is precedence in literature for the transition metal mediated synthesis of anhydrides[3] but catalytic transformations are unknown. We utilized cobalt(II) chloride in these initial investigations.

The following procedure is representative. A mixture of acid chloride (10 mmol) and the corresponding carboxylic acid (10 mmol) in dry CH_2Cl_2 (10 mL) is added to a stirred solution of anhydrous cobalt(II) chloride (25 mg) in dry CH_2Cl_2 (50 mL) containing 5% CH_3CN. The resulting mixture is stirred at 40 °C under nitrogen for 5-8 hrs.[4] Removal of the acetonitrile yields a residue which is then dissolved in ether (80 mL). The ether solution is washed successively with aqueous saturated sodium bicarbonate and water and then dried over $MgSO_4$. Evaporation of the ether yields the crude product which is purified by recrystallization.

Our results are summarized on the next page. The method is suitable for the preparation of mixed anhydrides since a variety of acid chlorides and acids can be utilized. The modest yield of **3f** is probably due to the highly unstable nature of the acid chloride **1f**. The synthesis of **3e** is interesting since classical methods are ineffective;[1b,2a] **3e** has been prepared by treatment of triethylammonium-*p*-nitrobenzoate with phosgene,[2e] by using a phase transfer catalyst,[2f] and by using agents such as chlorosulfonyl isocyanate[2a] or phenyl N-phenylphosporamidochloridate.[1b]



1 2 3

		Yield^{a,b}
a)	$R = R' = C_6H_5$	91%
b)	$R = C_6H_5$; $R' = p\text{-}CH_3OC_6H_4$	89%
c)	$R = R' = p\text{-}CH_3C_6H_4$	79%
d)	$R = R' = p\text{-}CH_3OC_6H_4$	88%
e)	$R = R' = p\text{-}NO_2C_6H_4$	76%
f)	$R = R' = p\text{-}{}^tBuC_6H_4$	51%
g)	$R = R' = CH_3CH{=}CH$	90%
h)	$R = CH_3CH{=}CH$; $R' = p\text{-}CH_3OC_6H_4$	81%
i)	$R = R' = CH_3(CH_2)_2$	87%^{c}

[a] All compounds exhibited spectral data and m.p. consistent with assigned structures.
[b] Isolated yield.
[c] Glpc yield.

We have developed a new method for preparing acid anhydrides. The method appears to be suitable for the preparation of a variety of mixed anhydrides.

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4. Control experiments reveal that less than 20% of the desired products are formed after 8 hrs. in the absence of $CoCl_2$.

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