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A New Direct Esterification Method Using Di-2-pyridyl Sulfite As a New Coupling Agent

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In connection with our continuous studies on the synthetic utility of 2-pyridyl related active carbonates and active esters,¹ we have reported that di-2-pyridyl carbonate (2-DPC) is an efficient coupling agent for the direct esterification of carboxylic acids under mild conditions.² However, the preparation of 2-DPC requires the use of highly toxic phosgene. Therefore, we investigated the possibility of using thionyl

chloride, readily available and easy to handle, instead of phosgene.

Di-2-pyridyl sulfite was easily prepared by treatment of thionyl chloride with 2 equiv of 2-hydroxypyridine and triethylamine in methylene chloride at 0 °C. Di-2-pyridyl sulfite could not be isolated as a pure form due to its instability and so it was used as a crude form.

Table 1. Esterification of Carboxylic Acids Using Di-2-pyridyl Sulfite

Acid RCOOH	Alcohol R'OH	Method ^a	Time, h	Yield, % ^b	
				RCOOR'	RCOO-2-py
CH ₃ (CH ₂) ₆	C ₆ H ₅ CH ₂	A	4	91	0
	CH ₃ CH ₂	A	8	89	0
	CCl ₃ CH ₂	A	2	95	0
	(CH ₃) ₃ C	A	0.3	0	88
		B	24	58	34
C ₆ H ₅ CH ₂	CH ₃ CH ₂	A	6	93	0
	(CH ₃) ₂ CH	A	24	81	9
		B	5	93	0
	CH ₃ CH ₂	A	10	88	0
	C ₆ H ₅ CH ₂	A	5	87	0
	(CH ₃) ₂ CH	A	24	59	36
		B	24	86	0
C ₆ H ₅	CH ₃ CH ₂	A	24	55	36
		B	36	90	0
(C ₆ H ₅) ₂ CH	CH ₃	A	4	90	0
	C ₆ H ₅ CH ₂	A	3	92	0
(CH ₃) ₃ C	C ₆ H ₅ CH ₂	A	0.3	58	23 (9) ^c
		B	30	77	0 (7) ^c

^aMethod A: in CH₂Cl₂ at room temperature. Method B: in CH₃CN at 60 °C. ^bIsolated yields. ^cIsolated yields of pivalic anhydride.

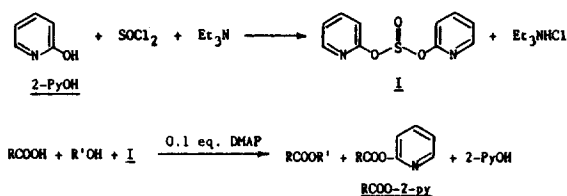


Table 1 shows some experimental results and illustrates the efficiency, the applicability, and the scope of the present method. First, esterification was carried out with equimolar amounts of acids, alcohols, and the reagent in the presence of 0.1 equiv of 4-dimethylaminopyridine (DMAP)³ in methylene chloride at room temperature (Method A). Method A works well with primary and secondary aliphatic carboxylic acids and primary alcohols. Otherwise, the products obtained here were a mixture of the desired esters and 2-pyridyl esters in a variable ratio or exclusively 2-pyridyl esters. Furthermore, in the case of sterically hindered pivalic acid, a small amount of pivalic anhydride was isolated as a byproduct. In general, the scope and limitations of the present method are very similar to those of recently reported method using 2-DPC.²

When the reaction was carried out in acetonitrile at reflux (Method B), better results were obtained as shown in Table 1. Using Method B, most carboxylic acids were smoothly esterified to the corresponding esters with exception of pivalic acid or benzoic acid as an acid component or t-butyl alcohol as an alcohol component.

Several noteworthy features of the present method are ap-

parent as compared with the conventional methods.⁴ First, this method is one-step procedure and requires only a catalytic amount of DMAP in most cases. Second, the reaction proceeds under very mild conditions. Third, this method is much simpler and less laborious than the conventional methods because a byproduct, water-soluble 2-hydroxypyridine, can be completely removed by the usual aqueous workup. Thus, this method does not normally require chromatographic separation of the desired product from the reaction mixture. Furthermore, since it has been reported that 2-pyridyl esters are cleanly converted into the corresponding esters in the presence of cupric bromide in acetonitrile,⁵ we believe that the formation of 2-pyridyl esters from the reaction does not cause serious problems.

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