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DIRECT CONVERSION OF CARBOXYLIC ACIDS INTO ACYL CHLORIDES AND ESTERS USING 9-CHLOROACRIDINE

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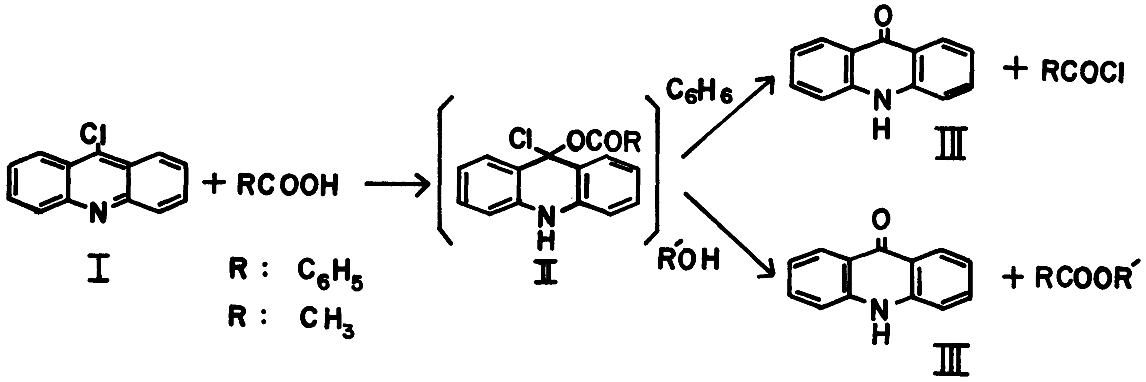
9-Chloroacridine reacted with carboxylic acids in benzene to give acridone and acyl chlorides in satisfactory yields. In the presence of alcohols, the carboxylic acids were converted to the corresponding esters.

We now report on the action of 9-chloroacridine (I) as a reagent converting carboxylic acids into acyl chlorides in benzene and esters in alcohols in a high yield, although acridine shows no reaction with carboxylic acids under identical condition. In such process, I is transformed to acridone (III).



A solution of 0.55 mmol of I and 0.5 mmol of benzoic acid in 5 ml of benzene in a sealed tube was heated under a nitrogen atmosphere at 70°C for 40 hr. During the reaction, 0.46 mmol (83% yield based on I) of the brown precipitate of III deposited. III was converted readily to I by phosphorus oxychloride.1) After removing III′ from the reaction mixture by filtration, the reaction solution was subjected to the gas chromatography. Benzoyl chloride was obtained in 83% yield based on benzoic acid (83% conversion of I) (Table 1). Furthermore, it was confirmed that benzoyl chloride does not react with I or III under identical condition described above. That is, III is not acylated with benzoyl chloride. The yield of benzoyl chloride increased as the reaction time increased. The presence of oxygen in the reaction system did not affect the yield of benzoyl chloride. When a 1 : 4 ethanol-benzene solution (25 ml) containing 2.5 mmol of I and 2.5 mmol of benzoic acid was heated at 70°C for 40 hr, ethyl benzoate and III were produced in 98 and 96% yields respectively. Under this condition I did not react with ethanol.

The reaction of I with acetic acid in benzene was carried out under the similar condition to the case of benzoic acid. After III deposited in 65% yield, 1 ml of isoamyl alcohol was added to the reaction mixture, and the resulting solution was heated at 70°C for 1 hr. Isoamyl acetate was obtained in 87% yield, based on acetic acid (Table 1). The reaction of I with acetic acid in a 1 : 4 isoamyl alcohol-benzene solution gave isoamyl acetate and III in 85 and 100% yields respectively. The decarboxylation of acetic acid by I was not observed at all, although the photoreactions of acridine with the aliphatic carboxylic acids gave 9-alkylacridans as the products through the decarboxylation of the carboxylic acids.²⁾

Table 1. The reactions of I with carboxylic acids (molar ratio of 1 : 1)

RCOOH (R)	Solvent	% Yield of product		
		II	RCOCl	RCOOR'
C_6H_5	Benzene	83	83	-
C_6H_5	Ethanol-Benzene	96	-	98
CH_3	Benzene	65	87[a)]	-
CH_3	Isoamyl alcohol-Benzene	85	-	100

a) Determined as isoamyl acetate.

These reactions would proceed via an addition compound (II) which subsequently decomposes to acyl chloride and III in benzene. The addition process is much more in accord with other reactions of acridines, for example, the reaction of I with phenol forming 9,9-diphenoxyacridan hydrochloride[3)] and the oxidation of acridine with peroxybenzoic acid yielding 2-(2-hydroxyanilino)benzaldehyde.[4)] Thus, I is a convenient reagent for the preparations of acyl chlorides and esters from carboxylic acids, the behavior being analogous to that of the well-known reagents, such as thionyl chloride, phosphorus pentachloride, aluminium chloride, and carbodiimides. Further works on the reactions using acridine derivatives as reagents are currently in progress.

References

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