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CATALYTIC ROLE OF DIORGANOTIN DICHLORIDE IN ESTERIFICATION OF CARBOXYLIC ACIDS

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SUMMARY : Various carboxylic acids were converted into corresponding esters in fair to good yields by diorganotin dichloride-catalysed reaction with alcohols.

In connection with our interest in synthetic, structural and biocidal studies of organotin carboxylates[1], we have observed that some organotin halides act as efficient catalysts for esterification of carboxylic acids. A search of the literature reveals that boric acid[2], polymer protected anhydrous $AlCl_3$[3] have been used as catalyst in esterification reactions and many patents cover the use of dibutyltin oxide and dibutyltin diacetate for the preparation of terylene and related polyesters on an industrial scale[4].

In this Letter we report the catalytic use of diphenyltin dichloride and dimethyltin dichloride by which various carboxylic acids have been converted into the corresponding esters using alcohol as solvent (Table I). The yield (40-97%) was found to be proportional to the Lewis acidity of the organotin chloride. The reaction, in every case, is rapid, convenient to carry out, and the mild acidic condition provides its general use. The derived esters were characterized by IR and ^{1}HNMR data.

As a general procedure, a mixture of the organic acid (0.05 mole), anhydrous alcohol (50 ml) and the diorganotin dichloride (0.002 mole) was heated under gentle reflux for 2 hrs. Concentration of the reaction mixture followed by usual workup with ether and a sodium bicarbonate wash furnished the desired ester. The organotin compounds were generally hydrolysed into insoluble diorganotin oxide during alkali treatment and could not be isolated as such. In a few cases, the organotin component was found to be recoverable to the extent of 90%. For example, in the preparation of n-propyl propionate in the presence of Me_2SnCl_2 the reaction mixture, after refluxing, was distilled off at reduced pressure whereupon the organotin compound was found to remain in the distilling flask. Recrystallization from benzene and petroleum ether (60-80) afforded the catalyst back.

The catalytic role of R_2SnCl_2 may be tentatively explained on the basis

Table I

Acid	Alcohol	Catalyst used	Yield of Ester (%)[a]
1. Propionic acid	Ethanol	Me_2SnCl_2	63
2. Propionic acid	Ethanol	Ph_2SnCl_2	77
3. Propionic acid	1-Propanol	Ph_2SnCl_2	91
4. Phenylacetic acid	Ethanol	Me_2SnCl_2	56
5. Phenylacetic acid	Ethanol	Ph_2SnCl_2	63
6. Phenylacetic acid	Ethanol	No catalyst[b]	5
7. Phenylacetic acid	1-Propanol	Me_2SnCl_2	53
8. Phenylacetic acid	1-Propanol	No catalyst[b]	7
9. Methoxyacetic acid	1-Propanol	Ph_2SnCl_2	97
10. Methoxyacetic acid	2-Propanol	Ph_2SnCl_2	60
11. Methoxyacetic acid	2-Propanol	No catalyst[b]	13
12. 2,4-Dichioro phenoxyacetic acid	1-Propanol	Me_2SnCl_2	75
13. Benzoic acid	Methanol	Me_2SnCl_2	41
14. Benzoic acid	Methanol	No catalyst[b]	3

a Yields after 2 hr. reflux determined by g.l.c. analysis

b Value included for comparison

of the formation of an intermediate weak donar-acceptor complex formed between the acid and the organotin compound through the carbonyl oxygen. Subsequent nucleophilic attack of the alcohol oxygen atom on the electron-deficient carboxyl carbon results in the formation of the ester. The approach of more bulky alcohol to the electrophilic carboxyl carbon is sterically hindered thereby minimising the yield of the corresponding ester (Table I).

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