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# OXONIUM SALT INTERMEDIATES FROM HALF ESTER ACID CHLORIDES

M. Vishnumurthi Rao, Shaker H.El. Ashry and M. Vivekananda Bhatt*
Department of Organic Chemistry, Indian Institute of Science
Bangalore-560012, INDIA.

Summary:- Isomeric half ester acid chlorides derived from 1,2-and 1-3-carboxylic acids give rise to the same oxonium salt with Lewis acids.

The use of half ester acid chlorides derived from unsymmetrical 1,2-and 1,3-carboxylic acids in synthesis has been severely limited by occurrence of rearrangements and formation of unexpected products[1-6]. A number of previous reports[4,7,8] and a publication from this laboratory[9] had drawn attention to the complications arising because of the participation of the neighbouring alkoxy carbonyl group. The nature and consequences of the carbonyl group participation has been a matter of considerable amount of speculation and discussion[7,8].

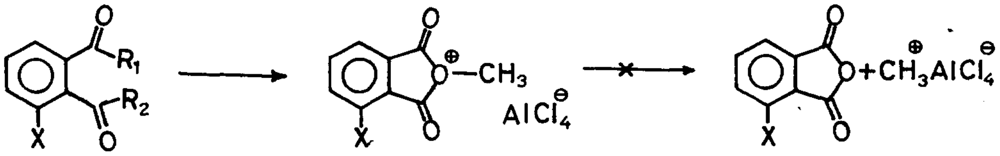
We have shown[9] that participation during solvolysis of half ester acid chlorides need not necessarily lead to isomerisation of the half ester acid chlorides themselves or to the formation of a common intermediate.

In the present communication we present evidence for the formation of oxonium type intermediates by the reaction of half ester acid chlorides with some of the Lewis acids (Scheme 1). Table 1 contains the n.m.r. spectral data of the oxonium salt intermediates derived from two pairs of isomeric half ester acid chlorides (1-4). It can be seen that the isomeric pair which have different chemical shifts for ester methyl protons give identical n.m.r. spectra upon treatment with Lewis acids, thus providing evidence for the formation of a common oxonium salt intermediate. This pattern is found in the case of $AlCl_3$, $TiCl_4$ and $SnCl_4$, but not in the case of the weaker Lewis acid $ZnCl_2$. The poor Lewis acidity of $ZnCl_2$ is well documented[11] and is further corroborated by our own independent experiments[11]. The magnitude of the shift of the methyl protons depends upon the relative strengths of the Lewis acid.

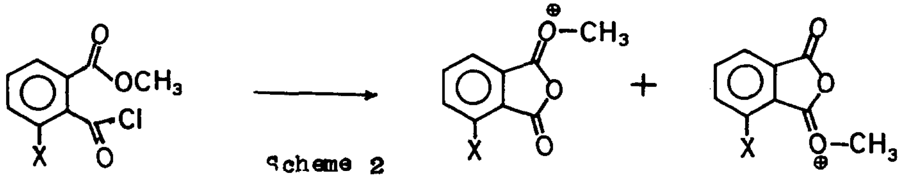
The $^{13}C$ n.m.r. spectrum of the complex obtained from $AlCl_3$ and methyl hydrogen phthalate gives only three sets of signals for the aromatic carbons (140.68 δ, 130.51δ, and 128.90δ) and a single signal for both the carbonyl carbons (167.96δ) and one signal for the methyl carbon (53.72δ). The data is consistant only with the structure suggested for the oxonium salt and does not agree with the alternate formulations. Variable temperature spectra of complexes of $AlCl_3$ and 1 did not show any detectable variation further ruling out the alternate formulations(Scheme 2)

It is pertinent to mention that $CH_3Cl$-$AlCl_3$ complex has a chemical shift much different from the one observed for the oxonium salts. Moreover the signal of $CH_3Cl$-$AlCl_3$ complex does not shift in the presence of phthalic anhydride. This clearly rules out the possibility of the observed values being derived from methyl tetrachloroaluminium ion pair.

1. X = $NO_2$ $R_1$ = $OCH_3$ $R_2$ = Cl 3. X = Cl $R_1$ = $OCH_3$ $R_2$ = Cl
2. X = $NO_2$ $R_1$ = Cl $R_2$ = $OCH_3$ 4. X = Cl $R_1$ = Cl $R_2$ = $OCH_3$



Scheme 1



Scheme 2

**Table 1***

Chemical shifts of the ester methyl signal (in δ values)

| Compound | Uncomplexed methyl signal | $AlCl_3$ | $TiCl_4$ | $SnCl_4$ | $ZnCl_2$ |
|---|---|---|---|---|---|
| 1 | 4.09 | 4.60 | 4.40 | 4.13 | 4.09 |
| 2 | 4.01 | 4.60 | 4.40 | 4.13 | 4.01 |
| 3 | 4.00 | 4.60 | 4.40 | 4.10 | 4.00 |
| 4 | 3.90 | 4.60 | 4.40 | 4.10 | 3.90 |

*errors of the order of 0.01δ

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