

LETTERS TO THE EDITORS

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Reactions of Carboxylic Esters

ALTHOUGH, as pointed out in a recent review¹, acid or alkali catalysed hydrolysis or esterification and, it may be added, alkoxy interchange, usually take place by mechanisms in which the bonds of the alkoxy carbon atom are not disturbed (mechanism I), the alternative mechanism (II) does, however, occur, and probably to a greater extent than has previously been recognized, when the alkoxy group R" has electron-releasing properties.



This fact was brought to our notice during the preparation of some optically active α -disubstituted allyl alcohols. Whereas in the alkaline hydrolysis of the hydrogen phthalates of a large number of optically active saturated aliphatic alcohols under varying experimental conditions no racemization has ever been observed, the optically pure hydrogen phthalic esters of the substituted allyl alcohols, when submitted to hydrolysis with only a slight excess of alkali, yield the partly racemized alcohols; when larger proportions of alkali are used optically pure alcohols are obtained². Mechanism (II) implies dissociation of the ester into a carbonium cation and an anion. If the cation is mesomeric, as it is in the esters of the substituted allyl alcohols, rearrangement is to be expected³, leading to a mixture of alcohols when mechanism (II) is operative. This has, in fact, been observed: α -phenyl- γ -methylallyl hydrogen phthalate, on hydrolysis by means of a slight excess of 5*N* aqueous sodium hydroxide, yields a mixture of α -phenyl- γ -methyl- and γ -phenyl- α -methylallyl alcohols³.

We have further observed that esters of these optically active unsaturated alcohols, when warmed with carboxylic acids or with alcohols, yield esters or ethers with extensive loss of optical purity and therefore, presumably by mechanism (II)⁴. This behaviour is in marked contrast to that of esters of saturated aliphatic alcohols: the hydrogen phthalate of octan-2-ol, for example, can be recrystallized unchanged from hot glacial acetic acid⁵. We also find that esters of phenylmethylcarbinol and of the naphthylmethylcarbinols react in a similar way with acids and with alcohols; we have not, however, observed the occurrence of racemization during the alkaline hydrolysis of the hydrogen phthalates of these carbinols.

The powerful electron-releasing effect of the *p*-methoxy group causes the above-mentioned reactions to occur very readily with esters of anisylmethyl- and anisylphenylcarbinols. These esters, moreover, are easily decomposed, yielding *p*-methoxystyrene and $\alpha\alpha'$ -di-*p*-methoxyphenyldiethyl ether and $\alpha\alpha'$ -di-*p*-methoxyphenyldibenzyl ether respectively. The hydrogen phthalic esters of these two carbinols when warmed with dilute alkali yield the neutral esters (di-anisylmethylcarbinyl- and di-anisylphenylcarbinylphthalate).

All these observations are explainable on the assumption that the esters dissociate according to mechanism (II), and detailed descriptions of the reactions are in preparation. An analogous reaction is the racemization, without any observable evidence of decomposition or side-reaction, of the acetate of octan-2-ol, when heated in acetic acid solution with one molecular proportion of a strong acid (for example, *p*-toluenesulphonic or sulphuric acids). This reaction, which may be due either to dissociation or to a continued series of Walden inversion reactions, is at present the subject of further study.

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¹ Watson, *Ann. Repts. Progress of Chemistry*, 27, 229 (1940).

² Arcus and Kenyon, *J. Chem. Soc.*, 1912 (1938).

³ Kenyon, Partridge and Phillips, *J. Chem. Soc.*, 216 (1937).

⁴ Reference (2) and unpublished results.

⁵ "Organic Syntheses", 6, 68.

Errors of Observation due to Instrument Scale Limitations

IN the course of a recent investigation, of the lightning discharge¹, it was found that scatter diagrams showing the variation with distance of the field changes set up by lightning flashes are liable to misinterpretation owing to a limitation in the recording apparatus which misses all records falling below a certain level. The effect of this limitation has been partly recognized by C. T. R. Wilson² in his investigations of the lightning flash, but has been overlooked in later publications on this subject³. The misleading effect due to this limitation is demonstrated below, and it is shown that a similar error of interpretation is liable to occur in many other cases in which a statistical analysis is based on data obtained with apparatus having a similar limitation.

The accompanying graph shows as an example the variation of the electrostatic field changes due to comparatively near lightning flashes. The recording electrometer, which was set to reproduce accurately the highest field changes that might be expected from nearby strokes, has a minimum recording limit which, as can be shown, excludes an increasing number of small values as the distance increases. This is shown directly by the fact that, assuming a uniform distribution of flashes, the number of records should from geometrical considerations increase with distance, whereas it decreases rapidly in the diagram reproduced. Again, while the spread of the data at any distance up to about 10 km. shows a ratio of about 50 : 1 between the maximum and minimum values recorded, this ratio decreases to about 10 : 1 at a distance of 20 km., though such variation has no foundation in the mechanism of the lightning