

NOTES

UV-Spectral Behaviour of Some Newly Synthesised Half-Esters†

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As an application of the newly devised an efficient method of selective esterification several new half-esters were prepared. For their identification and characterisation spectral data become very helpful. The UV-spectral data of several half-esters, prepared by selective esterification of the aliphatic primary carboxylic groups of carboxy phenoxyacetic acids (*o*, *m* and *p*) and carboxy phenylacetic acids (*o*, *m* and *p*) were collected. The isomeric half-esters, prepared by partial hydrolysis of the corresponding dialkyl esters, were also examined.

Studies were made on the physico-chemical properties of some newly synthesised half-esters. A convenient and efficient method of selective esterification of the aliphatic primary carboxylic groups of carboxy-phenoxyacetic acids (*o*, *m* and *p*) and carboxyphenylacetic acids (*o*, *m* and *p*), each possessing both aromatic and aliphatic primary carboxylic groups, was developed¹. This led to the preparation of several half-esters (I to VI and XIII). A detailed study was needed for their identification and characterisation. For a comparative study the isomeric half-esters (VII to XII and XIV) were prepared by partial hydrolysis of the corresponding dialkyl esters.

PMR spectral data² are very suggestive and they are also helpful for their characterisation. IR spectral data have been collected as a routine work but they could not give any clear out distinctive information regarding their identification. The UV-spectral data of seven pairs of such compounds are presented in this paper. Collection of other physical and chemical data, such as dissociation constants, relative stabilities, inter convertibilities etc. are yet to be completed. Some chemical change over has been carried on with such compounds and they will come out in forthcoming publications.

The UV absorption spectra of these half-esters are nonetheless important as the supplied a very useful information. Absorption maxima (λ_{\max}) with molar extinction co-efficient ($\log \epsilon_{\max}$) have been summarised in the table. Those half-esters having carboxy groups directly attached to

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the aromatic ring (as in I to VI and XIII) showed hypsochromic shifts when a drop of sodium hydroxide solution was added to each one of the cell containing the half-ester in ethanol. The half-esters (VII to XII and XIV in which the free carboxy groups are aliphatic in nature, showed slight bathochromic shifts under similar condition. Only the compound III behaved in a different way. These findings are in accordance with the behaviour of benzoic and phenylacetic acids when they were examined separately in the presence of a drop of alkali.

An intimate mixture of anhydrous copper sulphate, anhydrous sodium sulphate and phosphorus pentoxide in the ratio of 5 : 5 : 1 by weight was prepared and was used for esterification reaction under the name 'reagent'. Pure methanol was distilled and stored over anhydrous copper sulphate for 3 days at room temperature, and decanted just before esterification. Rectified spirit was heated under reflux for 6 hrs in presence of sodium hydroxide and then distilled for spectral studies and the UV spectra were recorded in ethanol in Hitachi 200-20 spectrophotometer.

Preparation of the Half-Esters (I to VI and XIII)

The following general procedure had been adopted for the preparation of these half-esters.

A mixture of dicarboxylic acid (0.1 mol), dry alcohol (50 ml) and the reagent (4 g) as mentioned above was heated under reflux at moisture-free conditions for 4 hrs. on a steam-bath. On usual work-up the neutral part was separated from the acidic part and rejected. The acidic part (isolated through sodium bicarbonate extraction) was crystallised to furnish the pure desired half-ester, the half-esters I to VI were obtained through selective esterification of the corresponding dicarboxylic acid with methanol (for I to VI) and with ethanol (for XIII). Yields varied from 65-80%.

Preparation of the Half-Esters (VII to XII and XIV)

The following general procedure had been practical for the selective hydrolysis of aliphatic primary carboxylic ester group of dialkyl ester of the corresponding dicarboxylic acid.

A mixture of dialkyl ester (2 g), alcohol (20 ml), potassium carbonate (2g) and water (20 ml) was heated on a steam-bath for 5 min. Then removed from the steam-bath and stirred for 1 hr. when the reaction mixture gradually attained room temperature (35°C). It was diluted with water (150 ml) and the usual work-up with a mixture of ether and benzene separated the unhydrolysed ester. The aqueous alkaline solution was acidified with concentrated hydrochloric acid and the precipitated solid on the usual work-up with ether furnished the desired isomeric half-ester. The half-esters VII to XII were obtained from the corresponding dimethyl esters and XIV from its diethyl ester. Yields varied from 80-90%.

TABLE I
UV-ABSORPTION SPECTRAL DATA (VIDE EXPERIMENTAL)

Sl. No.	Name of the compound m.pt. (°C)	No.	λ_{\max} in nm		Shift*
			in EtOH (log ϵ)	in EtOH + a drop of alkali	
1.	Benzoic acid ³		228	223	-5
2.	Phenylacetic acid		225	227	+2
			258	258	± 0
3.	Methyl 2-carboxyphenoxy- acetate (100°)	I	232(3.73)	<220	<-12
			289(3.24)	276	-13
4.	Methyl 3-carboxyphenoxy- acetate (117°)	II	231(4.14)	<220	<-20
			291(3.60)	284	-7
5.	Methyl 3-carboxyphenoxy- acetate (174°)	III	212(3.73)	214	+2**
			249(4.08)	253	+4**
6.	Methyl 2-carboxyphenyl- acetate ⁴ (98°)	IV	228(3.79)	209	-19
			276(2.83)	209(270)	-6
7.	Methyl 3-carboxyphenyl- acetate (92°)	V	231(3.93)	228	-3
			277(2.56)	274	-3
8.	Methyl 4-carboxyphenyl- acetate (136°)	VI	236(4.09)	232	-4
9.	2-Carbomethoxyphenoxy- acetic acid (108°)	VII	232(3.86)	235	+3
			291(3.41)	295	+4
10.	3-Carbomethoxyphenoxy- acetic acid (115°)	VIII	235(3.86)	236	+1
			293(3.35)	296	+3
11.	4-Carbomethoxyphenoxy- acetic acid ⁵ (159°)	IX	214(3.83)	215	+1
			253(4.15)	259	+6
12.	2-Carbomethoxyphenyl- acetic acid ⁶ (142°)	X	230(3.82)	233	+3
			278(2.79)	282	+4
13.	3-Carbomethoxyphenyl- acetic acid (80°)	XI	232(3.93)	236	+4
			276(2.24)	286	+10
14.	4-Carbomethoxyphenyl- acetic acid ⁷ (110°)	XII	237(4.01)	245	+8
15.	Ethyl 2-carboxyphenoxy- acetate	XIII	231(3.84)	<210	<-20
			289(3.43)	277	-12
16.	2-Carboethoxyphenoxy- acetic acid (84°)	XIV	232(3.85)	232	± 0
			291(3.49)	296	+5

*Values indicate bathochromic shifts and - values indicate hypsochromic shifts.

**This is the only exception where the normal course is not followed.

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