

ACTIVE ESTERS AS POTENTIAL REACTIVE DYES FOR WOOL*

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All reactive dyes for wool have substituents capable of reacting with primary and secondary amino groups, and the ϵ -amino groups of the lysyl residues in wool provide one of their main sites of binding.¹⁻³ Acrylamido, mono- and di-chlorotriazinyl, and vinylsulphonyl groups are a few examples of such reactive substituents.⁴ Active esters have been widely used in peptide chemistry,⁵ since they react with amino groups to give amides. Therefore active esters of coloured carboxylic acids may be suitable as reactive dyestuffs. The 4-nitrophenyl ester is one of the most commonly used in peptide chemistry⁶ and is usually allowed to react at, or below, room temperature in anhydrous solvents. By contrast, active esters must be applicable to wool from boiling aqueous solutions to be suitable as reactive dyes. This paper describes the synthesis of some water-soluble carboxylic esters and their evaluation as potential reactive dyes for wool.

The esters shown in Table 1 were prepared from monosodium 4-carboxybenzenesulphonate, via the carboxylic acid chloride, by reaction with the appropriate phenol in pyridine. The acid chloride was formed readily by treating the acid with an equimolar amount of thionyl chloride in pyridine, whereas no acid chloride was formed in the absence of pyridine.

The esters reacted readily with cyclohexylamine in aqueous solution, giving the cyclohexylamide in 19–82% yield. Wool fabric was then treated with boiling aqueous solutions of the esters under the usual conditions for applying levelling and milling acid dyes (c. pH 2 and 5, respectively). After treatment for 1 hr the wools were analysed for primary amino groups, and from these results the extent of reaction of the various esters with wool was calculated. The results are shown in Table 1. Only the 4-nitrophenyl and 2,4,5-trichlorophenyl esters reacted appreciably with wool, the extent of reaction being greater at pH 5 than at pH 2. Prolonged treatment with these esters failed to increase the extent of reaction with wool, and spectrophotometric examination of the aqueous phase showed that virtually all of the ester had been destroyed within an hour, either by reaction with amino groups or by hydrolysis. Imidazole has been used as a catalyst for the reaction

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⁴ Zollinger, H., *Rev. Text. Prog.*, 1959, **11**, 215.

⁵ Schröder, E., and Lübke, K., "The Peptides." Vol. 1, p. 97. (Academic Press: London 1965.)

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of 4-nitrophenyl,⁷ methyl,⁸ and thiophenyl⁸ esters with amines. However, it failed to increase the extent of reaction of the 4-methoxyphenyl and thiophenyl esters of sodium 4-carboxybenzenesulphonate with the amino groups of wool. This is perhaps not surprising, since imidazole also catalyses the hydrolysis of esters.⁹

The results with the above model compounds suggest that active esters of carboxy dyestuffs will be unsatisfactory as reactive dyes for wool, since most of the dye will be lost by competitive hydrolysis in the dye-bath. This prediction was substantiated by examination of the dyeing behaviour of the 4-nitrophenyl ester of pyridinium (3'-carboxy-4'-hydroxyphenylazo)benzene-4-sulphonate. Very little of this dye was bound covalently to wool, since at least 95% could be extracted from dyed fabric with boiling aqueous pyridine.

Experimental

Carboxylic Esters of 4-Carboxybenzenesulphonic Acid

Thionyl chloride (3.0 g) was added dropwise to an ice-cooled suspension of anhydrous monosodium 4-carboxybenzenesulphonate¹⁰ (4.5 g) in pyridine (20 ml). The mixture was then allowed to warm to room temperature, and after 30 min a solution of the appropriate phenol (0.02 mole) in pyridine (15 ml) was added. After a further 1 hr the pyridine was evaporated under reduced pressure at c. 35°, and the residue treated with a little water. In two cases the ester separated as a pyridinium salt, but it was generally necessary to add saturated sodium chloride to precipitate the product as a sodium salt.

Analytical samples were prepared by rapid recrystallization of the esters from a little water.

The esters, their yields, and microanalyses are given in Tables 1 and 2.

Reaction of Esters of 4-Carboxybenzenesulphonic Acid with Cyclohexylamine

The pyridinium salt of the 4-nitrophenyl ester (0.5 g) was heated on a steam-bath with a solution of cyclohexylamine (0.5 g) in water (10 ml) for 30 min. On cooling, *cyclohexylammonium 4-cyclohexylamidobenzenesulphonate* (0.39 g, 82%) separated as colourless plates, m.p. 332–335° after recrystallization from water (Found: C, 59.4; H, 8.0; N, 7.3; S, 8.4. $C_{18}H_{26}N_2O_4S$ requires C, 59.6; H, 7.9; N, 7.3; S, 8.4%). Under the same conditions, the corresponding thiophenyl, 2,4,5-trichlorophenyl, 2-methoxycarbonylphenyl, and 4-chlorophenyl esters gave the above amide in 75, 61, 58, and 19% yields respectively.

Application of Esters to Wool

Wool fabric (1.0 g) was added to a boiling solution of the ester (0.05 g), sodium sulphate (0.05 g), and either sulphuric acid (0.04 g) or acetic acid (0.012 g) in water (50 ml). After 1 hr under reflux, the fabric was removed, rinsed with water, and conditioned at 20° and 65% R.H. Subsequently the treated wool samples were analysed for residual amino groups, using a colorimetric ninhydrin procedure,¹¹ and the extent of reaction of the esters with amino groups in the wool was calculated. The results are shown in Table 1.

In experiments with the 4-methoxyphenyl and thiophenyl esters, imidazole (0.04 g) was also added, but had no effect on the extent of reaction of these esters with wool.

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Pyridinium [3'-(4'-Nitrophenyloxycarbonyl)-4'-hydroxyphenylazo]benzene-4-sulphonate

A suspension of 3'-carboxy-4'-hydroxyphenylazobenzene-4-sulphonic acid¹² (0.8 g) in anhydrous pyridine (15 ml) was treated dropwise with thionyl chloride (0.36 g). After 30 min most of the dye had dissolved. A solution of 4-nitrophenol (0.35 g) in pyridine (5 ml) was added, and after another hour the mixture was evaporated to dryness. The 4-nitrophenyl ester separated as the pyridinium salt on adding water (15 ml) and was purified by crystallization from a little water (Found: C, 53.1; H, 3.8; N, 10.2; S, 5.9. $C_{24}H_{18}N_4O_8S$ requires C, 53.3; H, 3.7; N, 10.4; S, 5.9%).

TABLE 1
CARBOXYLIC ESTERS OF 4-CARBOXYBENZENESULPHONIC ACID

Compound	Ester	Salt	Yield (%)	Extent of Reaction with Wool (%)	
				pH 2	pH 5
1	Phenyl	sodium	74	—	2
2	4-Chlorophenyl	sodium	62	—	9
3	4-Methoxyphenyl	sodium	55	—	4
4	2-Carbomethoxyphenyl	pyridinium	66	—	6
5	Thiophenyl	sodium	75	—	10
6	2,4,5-Trichlorophenyl	sodium	63	10	29
7	4-Nitrophenyl	pyridinium	45	9	23

TABLE 2
MICROANALYSES

Compound	Formula	Found (%)					Required (%)				
		C	H	N	S	Cl	C	H	N	S	Cl
1	$C_{13}H_9NaO_6S$	52.2	3.2	—	10.8	—	52.0	3.0	—	10.7	—
2	$C_{13}H_8ClNaO_5S \cdot H_2O$	44.8	3.1	—	9.0	—	44.3	2.9	—	9.1	—
3	$C_{14}H_{11}NaO_6S \cdot 1\frac{1}{2}H_2O$	47.4	4.0	—	9.0	—	47.1	4.0	—	9.0	—
4	$C_{20}H_{17}NO_7S$	58.5	4.4	3.4	7.7	—	57.8	4.1	3.4	7.7	—
5	$C_{13}H_9NaO_4S_2$	49.5	3.2	—	19.7	—	49.4	2.9	—	20.3	—
6	$C_{13}H_6Cl_3NaO_5S$	38.9	1.9	—	8.1	26.2	38.7	1.5	—	7.9	26.4
7	$C_{13}H_{14}N_2O_7S$	53.7	3.5	6.9	8.2	—	53.7	3.5	7.0	8.0	—

3'-Cyclohexylamido-4'-hydroxyphenylazobenzene-4-sulphonic Acid

Pyridinium [3'-(4'-nitrophenyloxycarbonyl)-4'-hydroxyphenylazo]benzene-4-sulphonate (0.5 g) was heated on a steam-bath for 30 min with cyclohexylamine (0.5 g) in water (20 ml). The mixture was then acidified, giving the *amide* (0.37 g, 98%) which crystallized from water containing a little ethanol as orange plates, m.p. 275–276° (Found: C, 51.8; H, 5.7; N, 9.2; S, 7.4. $C_{19}H_{21}N_3O_5S \cdot 2H_2O$ requires C, 51.9; H, 5.7; N, 9.6; S, 7.3%).

¹² Griess, P., *Ber. dt. chem. Ges.*, 1878, 11, 2191.