Tetrahedron Letters No.11, pp. 551-554, 1964. Pergamon Press Ltd.
Printed in Great Britain.

STUDIES IN TRANSESTERIFICATION [1]. THE REACTION OF 4-METHYL-4-METHOXY-2-PENTANOL AND METHYL ACRYLATE [2].

J. K. Haken

Department of Polymer Science, University of New South Wales,
Kensington, New South Wales, Australia.

(Received 27 January 1964)

The application of transesterification to the synthesis of acrylic esters has been reviewed recently [3] and while one example of anomolous behavious is included, the formation of saturated products have not been previously reported.

De Benneville and his co-workers [4] in 1958, showed that the olefinic oxazoline 4,4-diethyl-2- isopropenyl-oxazoline was produced by reaction of 2-amino-2-methyl propanol with methyl methacrylate using an aluminium isopropoxide catalyst. With similar compounds, where the functional groups are widely separated the primary amino ester was formed.

It has also been observed [3] that α-ethoxyethanol forms two products on reaction with methyl methacrylate, (a) α-ethoxyethyl ester, and (b) ethylene glycol dimethacrylate, to the extent of about 10 percent because of a partial decomposition of the starting alcohol.

To produce a methoxy ester for the possible preparation of a cross-linked ether polymer, the transesterification of 4-methyl-4-methoxy-2-pentanol was attempted. The reactant concentrations, catalyst (p-toluene sulphonic acid) and inhibitor (phenol) were as previously reported [5]. Here, with both acrylate and methacrylate, a rapid and apparently normal reaction commenced. When about three-quarters of an equivalent of methanol was removed, the binary began to separate into two layers, (a) acrylic ester plus some methanol, and (b) a water-methanol mixture. Subsequent gas chromatographic examination showed that from the beginning, the distillate contained a significant amount of water which was not apparent because the method of analysis involved washing with brine. In all the distillates, there was present a trace of another low boiling material [6].

While both methacrylate and acrylate behaved similarly, the following examination deals only with the acrylate ester.

The reaction residue on gas chromatographic examination showed the presence of a number of minor peaks and five main peaks, the last three being partially superimposed. Fractionation using a Griffin and George High Efficiency Unit operating at a reflux ratio of 100 to 1 allowed separation without polymer formation of the four main peaks in a fraction boiling over the range 202-220°C.

The products of the reaction are shown in Table 1 and the results of the examination of the principal peaks are detailed below.

Peak 11.

This compound separated by preparative gas phase chromatography has been subjected to micro-analysis and has been examined by infrared spectrophotometry and found to be the expected ester, 4-methyl-4-methoxy-2-pentyl acrylate.

Peaks 12, 13, 14.

These compounds have not been identified principally because of superimposition of the peaks of three compounds. Gas chromatography has allowed peak 12 to be separated with some of 13, and peak 13 with some of 14, while 14 has been isolated in a purer state. The infrared spectra of the three compounds are very similar, each being a typical saturated ester, the first two probably having identical spectra while the last has a higher methyl content [7].

The saturated equivalent of the acrylate ester is the propionate but when 4-methyl-2-pentanol was esterified with propionic acid the product did not have the retention time of any of the products. (RT 5.20).

When satisfactory chromatographic separation can be achieved, identification of these compounds will be undertaken.

REFERENCES.

1 Part III. For Part II see J.K. Haken and T.R. McKay, Aust. J. Applied Science. In press.

2 Presented at Australian Polymer Symposium, Mildura, August 1963.

3 J.K. Haken, Thesis, University of New South Wales (1961).

4 P.L. De Benneville, L.S. Luskin, H.J. Sims, J. Org. Chem., **23**, 1355 (1958).

5 J.K. Haken, J. Appl. Chem., **13**, 168 (1963).

6 This compound has been identified as 2-methyl-1,3-pentadiene.

7 The author is indebted to Professor R.L. Werner for assistance with the interpretarion of the infrared spectra.

TABLE 1.

Peak	Concentration (Percent)	Type of Compound	Compound	Retention time (a) (relative to benzene).
1	0.2	diene	2-methyl-1,3-pentadiene	0.142
2	0.6	methanol		0.150
3	trace	water		0.45
4	8.0	methyl acrylate		0.7
5	6.0	alcohol	4-methyl-2-pentanol	1.67
6	VS (b)	olefin	dimers of 2-methyl-1,3-pentadiene	2.10
7	VS	olefine		2.69
8	8.0	alcohol	4-methyl-4-methoxy-2-pentanol	4.2
9	4.0	ester	4-methyl-2-pentyl acrylate	4.76
10		phenol		5.32
11	ca 15	ester	4-methyl-4-methoxy-2-pentyl acrylate	12.78
12	ca 20 (b)	ester	saturated esters	15.48
13	ca 20	ester	saturated esters	16.76
14	ca 20	ester	saturated esters	17.75

(a) Determined at 130°C. with SE30 25 percent on Celite 50 mesh.

(b) Partially superimposed.