β-Alkoxypropionates. Addition of Alcohols to the Olefinic Linkage of Alkyl Acrylates

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In 1891 Purdie and Marshall[2] prepared methyl β-methoxypropionate and ethyl β-ethoxypropionate by the addition of alcohol (methanol or ethanol) to methyl and ethyl acrylates in the presence of the corresponding sodium alkoxide. Thus far the alcohols used in the reaction have apparently been limited to methanol and ethanol.[3] Although this reaction provides a convenient method for preparing various β-alkoxypropionates (I) from the commercially available acrylic esters,[4] it has received little attention. Earlier investigators frequently have preferred other methods,[5] such as metathesis[6] between sodium alkoxide and alkyl β-halopropionate, for making β-alkoxypropionates (I)

$$\mathrm{RONa} + \mathrm{XCH_2CH_2COOR} \longrightarrow \underset{\mathrm{I}}{\mathrm{ROCH_2CH_2COOR}}$$

The primary purpose of the work reported here, in which various primary, secondary, tertiary and unsaturated alcohols were studied, was to obtain information on the types of alcohol that can be added to alkyl acrylates.

It was observed that primary alcohols, including those of relatively high molecular weight and those having branched chains, can be added to alkyl acrylates, but the ease of addition decreased with increase in molecular weight of the alcohol. *s*-Butyl alcohol could be added to both methyl acrylate and *s*-butyl acrylate, but *t*-butyl alcohol did not react under comparable conditions. The result of the experiment with *t*-butyl alcohol is in harmony with its known behavior in esterification and alcoholysis reactions and as a solvent in the addition of various chemicals to the olefinic linkage of acrylonitrile.[7] Allyl alcohol, the one unsaturated alcohol studied, was added satisfactorily. Our results indicate that the reaction of alcohols with acrylic esters can be used conveniently to prepare many β-alkoxypropionates (Table I).

By using an excess of the alcohol and somewhat more drastic conditions, both alcoholysis and addition to the olefinic linkage occurred as major reactions. This procedure was used conveniently to convert methyl acrylate into ethyl ethoxypropionate, propyl propoxypropionate, butyl butoxypropionate, ethylbutyl ethylbutoxypropionate, and allyl β-allyloxypropionate (Table II).

Table I

Addition of Alcohols to Acrylic Esters

Acrylate, moles	Alcohol, moles	Temp., °C.	Time, hr.	Yield, % of theory[a]
Methyl, 0.8	Methyl, 0.8	27	16	91
Methyl, 1.5	Methyl, 3.0	Reflux	0.5	87
Methyl, 5.0	Methyl, 6.0	0–10	16	86
Methyl, 1.0	Ethyl, 1.1	27	16	91
Methyl, 1.0	*n*-Butyl, 2.0	Reflux	8	49
Methyl, 1.1	*n*-Butyl, 1.0	27	4	48
Methyl, 3.0	*s*-Butyl, 1.0	Reflux	1	27
Ethyl, 1.0	Methyl, 1.1	27	16	27
Ethyl, 1.0	Ethyl, 1.1	27	16	84
Propyl, 1.0	Methyl, 1.0	27	2.5	41
Propyl, 0.5	Propyl, 1.0[b]	27	16	59
		90	3	
n-Butyl, 1.0	*n*-Butyl, 2.0[b]	16	27	70
		100	3	
s-Butyl, 1.3	*s*-Butyl, 2.6[b]	27	16	54
		100	3	
i-Amyl, 0.5	*i*-Amyl, 1.0[b]	27	40	61
		105	3.5	

[a] Based on reactant present in lesser amount. [b] Reaction periods are consecutive.

Table II

Reaction of Alcohols with Methyl Acrylate

Alcohol	Mole ratio, alcohol/acrylate	Time of reflux, hr.	Conversion to alkoxypropionates, %[a] Alkyl	Methyl
Butyl	4	16	44	28
Butyl	1	0.5	7	21
Butyl[b]	3.6	17	54	0
Allyl	4	18	33	0
Allyl[b]	3.6	16	55	22
Ethyl	3	14	53	20
2-Ethylbutyl	4	20	37	0
Propyl	3	16	35	26

[a] Based on methyl acrylate originally in the reaction mixture. [b] The methanol produced by the reaction was continuously distilled from the mixture (as the methanol–methyl acrylate azeotrope).

Methyl β-methoxypropionate was transformed satisfactorily by alcoholysis into several higher alkyl β-methoxypropionates (Table III). This general method has been used by Harrower[8] to make menthyl methoxypropionate.

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

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(7) H. A. Bruson and T. W. Riener, This Journal, **65**, 23 (1943).

(8) J. Harrower, *J. Chem. Soc.*, 2048 (1931).

TABLE III

ALCOHOLYSIS OF METHYL β-METHOXYPROPIONATE

Alcohol	Yield, %[a]
n-Butyl	77
s-Butyl	91
n-Amyl	94
i-Amyl	83
2-Ethylbutyl	89
Allyl	95
n-Decyl	71

[a] Alkyl β-methoxypropionate, based on methyl methoxypropionate consumed.

$$M/d = 16.5x + 41.4 - 28.5/x$$
$$M/n = 9.551x + 36.78$$

When the *n*-alkyl groups R and R′ in the formula $ROCH_2CH_2COOR'$ were the same, the density and refractive index were lower than those of the isomeric esters having *n*-alkyl groups (Table IV and equations 1 and 2). Alkoxypropionates containing secondary or branched-chain alkyl groups had lower densities, refractive indices, and boiling points than their isomers with *n*-alkyl groups.

TABLE IV

PHYSICAL CONSTANTS OF β-ALKOXYPROPIONATES

Formula	$ROCH_2CH_2COOR'$ R	R′	°C.	B. p., mm.	d^{20}_4	n^{20}_D	Mol. ref. Calcd.	Mol. ref. Observed	Sapn. equiv. Calcd.	Sapn. equiv. Found	Carbon, % Calc.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
$C_5H_{10}O_3$	Me	Me	55	23	1.0088	1.4022	28.59	28.53	118.2	118.3				
$C_6H_{12}O_3$	Me	Et	60	20	.9754	1.4049	33.21	33.21	132.2	132.5				
$C_6H_{12}O_3$	Et	Me	60	20	.9751	1.4050	33.21	33.23	132.2	132.2	54.52	54.59	9.16	9.02
$C_7H_{14}O_3$	Me	*n*-Pr	114	100	.9564	1.4098	37.82	37.85	146.2	147.1	57.51	57.44	9.65	9.62
$C_7H_{14}O_3$	*n*-Pr	Me	70	15	.9560	1.4090	37.82	37.80	146.2	148.6				
$C_7H_{14}O_3$	Et	Et	67	17	.9490	1.4070	37.82	37.89	146.2	144.7	57.51	57.90	9.65	9.86
$C_8H_{16}O_3$	Me	*n*-Bu	76	8	.9411	1.4150	42.44	42.62	160.2	161.5				
$C_8H_{16}O_3$	*n*-Bu	Me	97	23	.9423	1.4152	42.44	42.58	160.2	160.9				
$C_8H_{16}O_3$	Me	*s*-Bu	99	50	.9341	1.4104	42.44	42.53	160.2	160.2				
$C_8H_{16}O_3$	*s*-Bu	Me	73	15	.9384	1.4112	42.44	42.40	160.2	158.6				
$C_9H_{18}O_3$	Me	*n*-Am	92	10	.9335	1.4191	47.06	47.17	174.3	177.8				
$C_9H_{18}O_3$	Me	*i*-Am	84	9	.9295	1.4179	47.06	47.23	174.3	175.5				
$C_9H_{18}O_3$	*n*-Pr	*n*-Pr	53	2	.9255	1.4148	47.06	47.11	174.3	174.4				
$C_{10}H_{20}O_3$	Me	2-EtBu	86	4	.9269	1.4240	51.68	51.84	188.3	190.1	63.80	63.87	10.71	10.26
$C_{11}H_{22}O_3$	*n*-Bu	*n*-Bu	101	5	.9103	1.4221	56.30	56.49	202.3	202.4	65.31	65.22	10.96	10.97
$C_{11}H_{22}O_3$	*s*-Bu	*s*-Bu	55	1	.9031	1.4172	56.30	56.36	202.3	200.3				
$C_{13}H_{26}O_3$	*i*-Am	*i*-Am	106	3	.8971	1.4231	65.53	65.39	230.3	229.4				
$C_{14}H_{28}O_3$	Me	*n*-Decyl	176	20	.9042	1.4339	70.43	70.38	244.4	243.9	68.78	68.31	11.55	11.09
$C_{15}H_{30}O_3$	2-EtBu	2-EtBu	125	3	.9020	1.4350	74.78	74.75	258.5	256.2				
$C_7H_{12}O_3$	Me	Allyl	76	17	.9884	1.4260	37.36	37.36	144.2	144.4				
$C_7H_{12}O_3$	Allyl	Me	75	15	.9900	1.4268	37.36	37.39	144.2	144.4	58.31	58.23	8.39	8.52
$C_9H_{14}O_3$	Allyl	Allyl	124	46	.9777	1.4421	46.13	46.05	170.2	169.9				

The straight lines obtained by plotting M/n^{20}_D against the molecular weight (M) for three homologous series are defined by the following equations (R = *n*-alkyl; first member of series excluded)

$$\left.\begin{array}{c} ROCH_2CH_2COOCH_3 \\ \text{and} \\ CH_3OCH_2CH_2COOR \end{array}\right\} \quad M/n = 0.681M + 4.08 \quad (1)$$

$$ROCH_2CH_2COOR \quad M/n = 0.6839M + 3.92 \quad (2)$$

Huggins and Davis[9] used the equation $V = 16.50\,x + A + B/x$ to describe the relation between molal volume and number of carbon atoms (x) for several homologous series. This general equation is applicable to the densities determined in the present work for members of the two homologous series, $ROCH_2CH_2COOCH_3$ and $CH_3OCH_2CH_2COOR$ (R = *n*-alkyl group). The relations between M/d and M/n and the total number of carbon atoms (x) for these two homologous series may be expressed as follows

(9) M. L. Huggins and D. L. Davis, "Densities of Some Simple Aliphatic Compounds in the Liquid State," presented before the Division of Physical and Inorganic Chemistry at the 107th Meeting of the American Chemical Society, Cleveland, Ohio, April 3, 1944.

Allyl β-allyloxypropionate readily polymerized in the presence of benzoyl peroxide, producing an insoluble, hard, colorless and bubble-free casting. Little or no polymerization occurred when allyl methoxypropionate and methyl allyloxypropionate were similarly treated.

Allyl β-allyloxypropionate was polymerized to an insoluble gel (presumably cross-linked) by passing a fine stream of air through it at 100°. Allyl methoxypropionate and methyl allyloxypropionate became viscous after several days of the same treatment, the latter finally solidifying. The air-polymerized allyl methoxypropionate was insoluble in a toluene–methanol mixture, whereas the air-polymerized methyl allyloxypropionate was soluble.

Irradiation with ultraviolet light transformed allyl allyloxypropionate and methyl allyloxypropionate, respectively, into an insoluble solid and a soluble, viscous liquid, but failed to polymerize allyl methoxypropionate within five days. The slowness with which the mono-allyl compounds polymerized is in agreement with the

observations made previously[10] with methallyl acetate and similar esters.

Allyl allyloxypropionate was copolymerized with methyl acrylate in ethyl acetate solution, and the minimum proportion of the allyl ester required to produce gelation was determined. On the basis of these and earlier experiments,[11] it was concluded that the tendency of allyl allyloxypropionate to form cross-linked copolymers with methyl acrylate is less than that of allyl and methallyl acrylate but approximately equal to that of crotyl acrylate.

Experimental

Methyl and ethyl acrylates were commercial samples and were redistilled through a simple still. The other acrylic esters were prepared from methyl acrylate by alcoholysis.[12]

Addition of Alcohols to Acrylic Esters. General Procedure.—Ratios of alcohol to ester ranging from 1:3 to 10:1 were tested, no advantage being found in using a large excess of either reagent. The practice finally adopted was to use a 10% excess of the alcohol, since it was generally cheaper and more readily available than the acrylate.

Sodium alcoholates, aluminum alcoholates, concentrated aqueous sodium hydroxide and trimethylbenzylammonium hydroxide were tested as catalysts, none of the desired products being obtained with the latter three. The sodium alcoholate was always freshly prepared by dissolving sodium in a portion of the reactant alcohol. From 0.5 to 3.0 g. of sodium was used for each mole of the acrylic ester, the smaller amount being preferred when using alcohols of low molecular weight.

The temperature and time of the reaction may be varied inversely over a rather wide range. Satisfactory results were obtained when the reaction mixture was left overnight at room temperature, though more than two to four hours at reflux temperature appeared to be detrimental. On the other hand, refluxing for one-half to two hours resulted in yields as high as those obtained by allowing the mixture to stand overnight at room temperature.

When the reaction mixtures were refluxed, it was found desirable to add an alkaline polymerization inhibitor to the reaction mixture to prevent polymerization of some of the acrylic ester. Phenyl-β-naphthylamine was generally used as inhibitor although *p*-phenylenediamine was also satisfactory. Cuprous chloride was unsatisfactory.

In some experiments, the catalyst was neutralized with acetic acid before distillation of the reaction mixture. This proved to be of doubtful value. Likewise, little if any increase in yield was produced by filtering the flocculent precipitate from the reaction mixture before distillation.

In general, the procedure for a one-mole batch was to dissolve 1 to 3 g. of sodium in about 25 cc. of the alcohol and add this solution to the mixture of the acrylic ester and the remainder of the alcohol, the mixture being stirred and kept below 40° by a cooling bath. When all the catalyst solution had been added and no more heat was evolved, the mixture was either refluxed for one-half to two hours or left overnight at room temperature. After neutralization of the catalyst the reaction mixture was distilled, preferably at a pressure such that the still pot was never heated above 100°. As a rule, little if any acrylate was recovered, though a resinous mass, probably an acrylic polymer, was sometimes left as a distillation residue. Numerous intermediate and high-boiling fractions were often obtained in the distillation, indicating that a complex mixture of byproducts was produced. These were most abundant when the reaction mixtures were heated for long periods (three to seventeen hours), or when they were refluxed after being left overnight at room temperature.

Yields and other data from selected experiments are shown in Tables I and IV.

Simultaneous Alcoholysis and Addition of Alcohols to Methyl Acrylate.—The general procedure was the same as that outlined above for the addition reaction except that a 4:1 molar ratio of alcohol to acrylate was used, and the reaction mixtures were always refluxed, preferably for six to twelve hours. The product was a mixture of the methyl and the higher esters of the β-alkoxypropionic acid. Conversion to the higher ester was increased if the methanol produced in the reaction was removed continuously. This was done in some experiments by removing the methanol-methyl acrylate azeotrope[13] from the reaction mixture by distillation as fast as methanol was produced.

Only the lower primary alcohols reacted satisfactorily in this process (Table II).

Alcoholysis of Methyl β-Methoxypropionate.—Methyl methoxypropionate, three times the theoretical amount of the alcohol, and 1–2% of sulfuric or toluenesulfonic acid were refluxed in a still from which methanol was removed as fast as formed. Generally, five to ten hours were required for complete removal of methanol. In a few experiments a product distilling above the alkyl methoxypropionate was obtained in small amount. Possibly, it was the alkyl alkoxypropionate formed by simultaneous alcoholysis and ether interchange, but identification was not conclusive because of the difficulty of adequately purifying the small amounts.

Yields and conversions are shown in Table III.

Polymerization.—Copolymers of allyl allyloxypropionate and methyl acrylate were prepared[11] in ethyl acetate solution (20% total monomer). Two per cent. (based on total monomer) of the allyl ester caused no gelation, 3% yielded a slightly stringy solution, and 4% produced a firm gel.

Summary

Primary, secondary, branched-chain and unsaturated alcohols added satisfactorily to the olefinic linkage of acrylic esters, producing β-alkoxypropionates; *t*-butyl alcohol did not add. By simultaneous addition and alcoholysis, methyl acrylate was converted into ethyl ethoxypropionate, propyl propoxypropionate, *n*-butyl butoxypropionate, ethylbutyl ethylbutoxypropionate and allyl β-allyloxypropionate. The higher alkyl β-methoxypropionates were prepared in high yields by alcoholysis of methyl methoxypropionate.

Allyl β-allyloxypropionate polymerized readily, yielding a hard, colorless, transparent and insoluble resin. The tendency of allyl allyloxypropionate to form cross-linked methyl acrylate copolymers was approximately equal to that of crotyl acrylate.

(10) J. D. Ryan and F. B. Shaw, Jr., This Journal, **62**, 3469 (1940).

(11) C. E. Rehberg, M. B. Dixon and C. H. Fisher, *ibid.*, **67**, 208 (1945).

(12) C. E. Rehberg, W. A. Faucette and C. H. Fisher, *ibid.*, **66**, 1723 (1944).

(13) C. E. Rehberg and C. H. Fisher, *ibid.*, **66**, 1203 (1944).