Base-Catalyzed Reactions of α,β-Unsaturated Esters and Nitriles. 3. Alkali Metal Catalyzed Di- and Trimerization of Acrylates[1]

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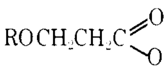
Potassium- or sodium-catalyzed reaction of acrylic acid esters (1) having appropriate alcoholic groups (R = C_4–C_{12} alkyl or cycloalkyl) produces three low molecular weight compounds, i.e., a 3-alkoxypropionate (**2**), an open-chain dimer, 2-methyleneglutarate (**3**), and a cyclic trimer, 1,3,5-cyclohexanetricarboxylate (**4**). **2** is favored (yields up to 66%) only at low temperature (20–70 °C) and low catalyst/1 molar ratios (r_{mol} = 0.12–0.23), whereas dimer **3** is predominant (yields up to 79%) at higher temperatures (100–216 °C) and/or higher r_{mol} levels (0.36–0.40). Trimer **4** is formed only at r_{mol} = 0.7–1.0. Dimerization selectivity, i.e., the dimer **3**/polymer ratio, increases markedly with increase in the size of the R group in the acrylate. The catalytic activity of potassium–benzylpotassium is about 2.4 times higher than that of sodium–benzylsodium, but the latter is more selective since it does not catalyze formation of **2**. It is proposed that formation of dimer **3** is initiated by metalation of the acrylate at the α-vinylic position, while formation of trimer **4** proceeds through a cyclic carbanion precursor, stabilized by charge delocalization. Alkoxy ester **2** is derived by concerted elimination–transfer of an alkoxy anion from the metalated **1** to a second acrylate molecule.

High molecular weight polymerization of acrylates in the presence of base catalysts or initiators, e.g., organolithium and organomagnesium compounds, is usually accompanied by limited formation (<10% by weight) of lower products.[2–4] For instance, small amounts of a cyclic β-keto ester, i.e., 5-(9-fluorenyl)-4-oxocyclohexane 1,3-dicarboxylate, were found in the product of 9-fluorenyllithium-initiated polymerization of acrylates.[5]

The patent literature cites the anionic polymerization of acrylates in aliphatic or aromatic solvents, using dispersed sodium or potassium metals in admixture with an alkali or alkaline-earth salt as catalysts.[6] This process yields products with molecular weights in the range of 90 000 to 1 000 000, depending on the monomer/catalyst molar ratio. Oligomerization of acrylates leading to dimers and/or trimers as main products has not been previously reported. It was recently found, on the other hand, that by applying promoted alkali metal catalysts under appropriate conditions it is possible to attain selective di- and/or trimerization of α,β-unsaturated esters and nitriles possessing a β-methyl substituent. For instance, in the presence of a potassium–benzylpotassium catalyst, ethyl crotonate is dimerized to diethyl 2-ethylidene-3-methylglutarate with 90% selectivity,[7] while 2-butenonitrile yields 20–23% of 2-ethylidene-3-methylglutaronitrile and 67–75% of a cyclic trimer, i.e., 1,3,5-tricyano-2,4,6-trimethylcyclohexane.[1]

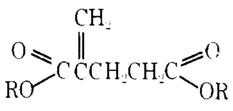
The purpose of the present study was to explore catalyst systems and experimental conditions which could lead to oligomerization of acrylates with suppression of high molecular weight polymerization. Several series of comparative experiments were performed in order to determine the change in product composition as a function of monomer structure (type of alcoholic R group), concentration and type of base catalyst, and reaction temperature. The experimental procedure was similar to that used previously.[1,7] Products were identified and quantitatively analyzed by a combination of gas chromatography, NMR, and mass-spectral methods (see Experimental Section).

It is found that by using promoted alkali metal catalysts, e.g., potassium–benzylpotassium, and acrylate monomers having alcoholic R groups of appropriate size, e.g., 2-ethyl-1-hexyl acrylate (**1**), the formation of high molecular weight polymers is greatly suppressed, and three low molecular weight compounds are obtained as main products, i.e., a 3-alkoxypropionate (**2**), an open-chain dimer, 2-methyleneglutarate (**3**), and a cyclic trimer, the triester of 1,3,5-cyclohexanetricarboxylic acid (**4**).



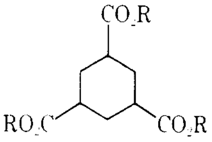
$ROCH_2CH_2C(=O)OR$

2



$ROC(=O)C(=CH_2)CH_2CH_2C(=O)OR$

3



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Results and Discussion

Effect of Catalyst Concentration. Using 2-ethyl-1-hexyl acrylate (**1**) as starting monomer, ethylcyclohexane as solvent, and potassium–benzylpotassium as catalyst, a series of experiments were performed in which the catalyst/monomer molar ratio (r_{mol}) was changed from 0.12 to 1.00 (gram-atom of K/moles of monomer).

Results obtained are summarized in Table I. As seen, the product distribution obtained is very sensitive to the change in the concentration of the catalyst. In experiments with low catalyst/1 ratios (r_{mol} = 0.12–0.32) the alkoxy ester **2** is formed as the principal nonpolymeric product, while at higher ratios (r_{mol} = 0.36–0.44) the predominant reaction is formation of dimer **3**. At the highest ratios employed (r_{mol} = 0.71–1.00) compounds **2** and **3** are absent from the product, while significant amounts of the cyclic trimer **4** are produced. The main products under these conditions are 2-ethyl-1-hexanol (**5**) and high molecular weight polymeric compounds. It is also noted that the overall conversion of monomer **1** increases with increase in r_{mol} from 0.12 to 0.32, but then remains essentially constant at r_{mol} = 0.36–1.00.

The formation of 3-alkoxypropionate (**2**) can be interpreted as occurring through elimination of an alkoxy anion (RO^-) from the metalated monomer **1a**, and transfer of this anion to a second monomer molecule in a subsequent step, or more likely by a concerted mechanism. Removal of the alkoxy group should produce an equimolar amount of 1-oxo-1,2-propadiene (methylene ketene) (**1b**), which could be expected to undergo fast polymerization.

A closely similar type of elimination, leading to formation of a ketene, has been recently reported to result from tri-

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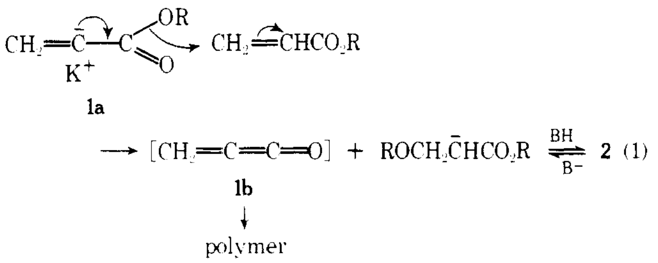
Table I. Composition of Products from $K/C_6H_5CH_2K$ Catalyzed Reaction of 2-Ethyl-1-hexyl Acrylate (1) as a Function of Catalyst Concentration[a,b]

expt no.	1	2	3	4	5	6	7	8
catalyst/1 molar ratio (r_{mol})	0.12	0.23	0.32	0.36	0.40	0.44	0.71	1.0
conversion of 1, mol %	30.4	60.5	71.1	80.4	80.4	80.1	80.2	80.5
product distribution,[c] % by wt								
2	65.2	59.6	50.4	25.4	20.1	9.6	trace	
3	15.0	20.7	33.0	57.0	63.5	42.1	0.5	
4						trace	16.1	19.4
other products[d]				5.6	6.4	24.1	43.4	45.0
polymer[e]	19.8	19.7	16.6	12.0	10.0	20.2	30.0	34.6
mol % 1 converted to:								
3-alkoxy ester (2)	37.2	33.7	28.9	14.3	11.7	5.8		
dimer (3)	17.1	23.4	35.6	54.9	62.9	43.3	0.6	
trimer (4)						trace	17.9	19.5
($CH_2{=}C{=}CO$)[f]	37.3	33.7	28.4	23.8	20.6	42.7	68.2	64.4
"polymer"[g]	8.4	9.2	7.6	7.0	4.8	8.2	13.3	16.0

[a] In each experiment were used 0.05 mol of 1, 0.5 mol of solvent, and the calculated amount of $K/C_6H_5CH_2K$ catalyst. [b] Reaction temperature, 132 °C; total reaction time, 120 min. [c] R = 2-ethyl-1-hexyl. [d] Consisting mostly (>95%) of 2-ethyl-1-hexanol (5). [e] High boiling components. [f] In the form of high boiling products (number of moles of methylene ketene calculated as equal to the number of moles of 2 plus 5; see text). [g] Products of direct polymerization of 1 (calculated by difference).



$$\underset{\mathbf{1a}}{\underset{K^+}{\mathrm{CH_2{=}\bar{C}{-}C({=}O)OR}}}\ \ \mathrm{CH_2{=}CHCO_2R} \longrightarrow \underset{\mathbf{1b}}{[\mathrm{CH_2{=}C{=}C{=}O}]} + \mathrm{ROCH_2\bar{C}HCO_2R} \underset{B^-}{\overset{BH}{\rightleftharpoons}} \mathbf{2} \quad (1)$$

$$\mathbf{1b} \longrightarrow \text{polymer}$$

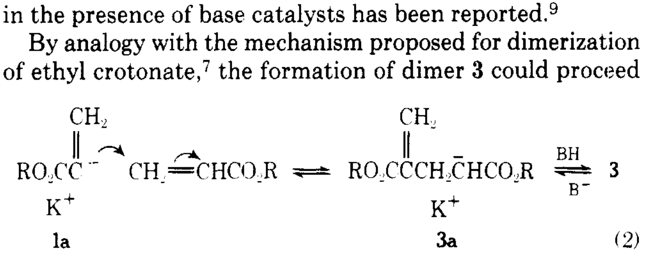
where BH = 1 or other carbo acid

methylamine-initiated dehydrochlorination of 2-butenoyl chloride.[8]

The amounts of polymer formed at low catalyst/monomer ratios (r_{mol} 0.12–0.40) are in approximate agreement with reaction 1, since for each mole of 3-alkoxypropionate (2) formed there is at least 1 mol of the suggested methylene ketene (**1b**) found in the polymeric form (Table I). Further, the amount of polymer in the above range of r_{mol} values decreases with decrease in the concentration of **2**. On the other hand, the marked increase in polymeric products at r_{mol} = 0.4–1.0 is apparently connected with the formation of 2-ethyl-1-hexanol (**5**) by decomposition of the metalated acrylate (vide infra).

The addition of an alkoxide anion at the C-3 position of an α,β-unsaturated ester seems to be limited to acrylates having no substituents at this position. No such reaction was observed with ethyl crotonate,[7] indicating that a β-alkyl substituent hinders this type of addition. Addition of alcohols to acrylates in the presence of base catalysts has been reported.[9]

By analogy with the mechanism proposed for dimerization of ethyl crotonate,[7] the formation of dimer **3** could proceed by metalation of the acrylate at the α-vinylic position, followed by addition of the resulting carbanion to a second monomer molecule.

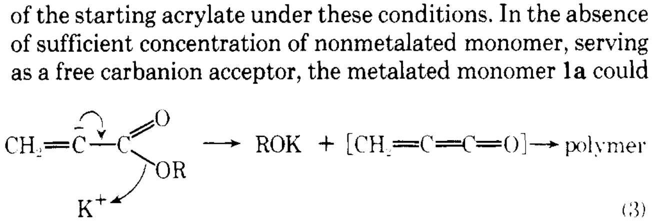


$$\underset{\mathbf{1a}}{\underset{K^+}{\mathrm{RO_2C\overset{CH_2}{\overset{\|}{C}}{}^-}}}\ \ \mathrm{CH_2{=}CHCO_2R} \rightleftharpoons \underset{\mathbf{3a}}{\underset{K^+}{\mathrm{RO_2C\overset{CH_2}{\overset{\|}{C}}CH_2\bar{C}HCO_2R}}} \underset{B^-}{\overset{BH}{\rightleftharpoons}} \mathbf{3} \quad (2)$$

Trimer **4** is most likely formed by addition of the dimeric anion **3a** to another monomer molecule to form a resonance-stabilized cylic precursor, which on protonation yields **4**. A similar mechanism was previously proposed for the high-yield trimerization of 2-butenonitrile to 1,3,5-tricyano-2,4,6-trimethylcyclohexane.[1]

The inversion in the relative importance of sequences 1 and 2, accompanying the increase in conversion from 30 to 80% (Table I), may be partially related to changes in the extent of ionic dissociation of the metalated monomer with the progress of the reaction. It should be noted that, while alkoxide elimination from the ion pair **1a** (reaction 1) may proceed without steric interference by the alkali counterion, the rate of addition of the monomeric carbanion to a second acrylate molecule (reaction 2) may considerably depend on the steric effect of this cation. In the initial low-polar reaction medium, consisting mainly of ethylcyclohexane, the extent of ionization of **1a** is very low and, therefore, reaction 1 is apparently faster than reaction 2. However, with increase in conversion, i.e., with gradual accumulation of the alkoxy ester **2**, the polarity of the reaction medium is expected to be augmented, with consequent increase in the ionization of **1a**. This could facilitate addition of the monomeric carbanion and increase the relative rate of reaction 2.

The absence of compounds **2** and **3**, and the preferential formation of 2-ethyl-1-hexanol (**5**) and high-boiling polymers at high catalyst/monomer ratios (r_{mol} = 0.71–1.00) can be explained in terms of the anticipated high extent of metalation of the starting acrylate under these conditions. In the absence of sufficient concentration of nonmetalated monomer, serving as a free carbanion acceptor, the metalated monomer **1a** could gradually decompose to yield polymeric products and alkoxide **5a**, which upon acidification at the end of the reaction gives the free alcohol **5** (R = 2-ethyl-1-hexyl).



$$\underset{K^+}{\mathrm{CH_2{=}\bar{C}{-}C({=}O)OR}} \longrightarrow \mathrm{ROK} + [\mathrm{CH_2{=}C{=}C{=}O}] \longrightarrow \text{polymer} \quad (3)$$

It is not excluded, however, that part of the alkoxide anion is derived by retrogressive reaction of the alkoxy ester **2**, which might have been formed in the initial stage of the reaction.

Since the concentration of protonating agent available in the reaction system at r_{mol} = 0.7–1.0 should be low, any dimeric anion produced under such conditions may tend to add to another monomer molecule, yielding a cyclic trimeric carbanion prior to the terminating protonation step. This could explain the preferred formation of trimer **4** rather than

Table II. Composition of Products from K/$C_6H_5CH_2K$ Catalyzed Reaction of 2-Ethyl-1-hexyl Acrylate (**1**) as a Function of Reaction Temperature[a,b]

expt no	9	10	11	12	13	14	15
reaction temp, °C	20	70	100	132	150	174	216
conversion of **1**, mol %	84.8	86.4	84.6	80.4	71.1	70.8	65.3
product distribution,[c] % by wt							
2	65.6	56.5	42.2	25.4	10.2	9.7	9.1
3	13.2	25.5	43.5	57.0	65.9	71.9	75.8
other products[d]	21.2	18.0	14.3	17.6	23.9	18.4	15.1

[a] In each experiment were used 0.05 mol of **1**, 0.5 mol of solvent, and the calculated amount of K/$C_6H_5CH_2K$ catalyst (0.018 g-atom of K metal and 0.005 mol of *o*-chlorotoluene). [b] Total reaction time, 120 min. [c] R = 2-ethyl-1-hexyl. [d] Compounds **4** and **5**, plus polymeric products.

Table III. Dependence of Product Composition from K/$C_6H_5CH_2K$-Catalyzed Reaction of Acrylates upon the Type of Alcoholic (R) Group[a,b]

expt no.	16	17	18	19	20	21	22
starting acrylate ($CH_2{=}CHCO_2R$), R =	CH_3 (**1a**)	C_2H_5 (**1b**)	isobutyl (**1c**)	2-ethyl-1-hexyl (**1d**)	cyclohexyl (**1e**)	*n*-$C_{12}H_{25}$ (**1f**)	1-bornyl (**1g**)
registry no.	96-33-3	140-88-5	106-63-8	103-11-7	3066-71-5	2156-97-0	67253-41-2
monomer conversion, mol %	~100	~100	80.2	80.4	79.8	3.2	5.1
product distribution,[c] % by wt							
2		3.0	20.1	21.3	22.3	22.1	18.0
registry no.		763-69-9	67208-80-4	38940-91-9	67208-81-5	67208-82-6	67208-83-7
3		6.0	46.0	58.5	60.2	75.9	79.0
registry no.		5621-43-2	67208-84-8	67208-85-9	23720-24-3	67208-86-0	67208-87-1
polymer	~100	91.0	33.9	20.2	17.5	2.0	2.0
$r_{\text{dimer 3/polymer}}$		0.06	1.35	2.9	3.5	37.9	39.5
mol % **1** converted to:							
3-Alkoxypropionate (**2**)		3	12.8	12.7	14.3	12.8	10.7
Dimer (**3**)		6	46.0	58.4	59.0	74.5	78.6
($CH_2{=}C{=}CO$)[d]		3	12.8	12.7	14.3	12.8	10.7
"polymer"[e]	100	88	28.4	16.2	12.4		
registry no.	9003-21-8	9003-32-1	26335-74-0	9003-77-4	27458-65-7		

[a,b] As in Table I; catalyst/monomer ratio = 0.36. [c] No significant amounts of trimer **4** could be detected under the experimental conditions. [d,e] See footnotes f and g (Table I), respectively.

dimer **3** in experiments 7 and 8.

Effect of Reaction Temperature. The change in product distribution as a function of reaction temperature was investigated in the range of 20–216 °C, using **1** as starting monomer and keeping a constant potassium–benzylpotassium/**1** ratio (r_{mol} = 0.36) in all experiments. Methyl- or ethylcyclohexane was used as solvent for temperatures up to 132 °C, and *n*-decane or *n*-dodecane was used for temperatures in the range of 150–216 °C.

Results obtained are summarized in Table II. As seen, alkoxy ester **2** is the main product at 20 and 70 °C, even at the high conversion levels reached (84.8 and 86.4%, respectively). This seems to indicate that at these relatively low temperatures the alkoxide transfer sequence (eq 1) remains kinetically favored even if the polarity of the solvent is somewhat changed with the progress of the reaction. However, with increase in reaction temperature above 100 °C there is a gradual increase in the relative rate of the competing dimerization reaction (eq 2), and the range of 174–216 °C is adaptable for preparation of dimer **3** in good yields (72–76% by weight). It is also observed that, while dimerization selectivity increases with increase in temperature from 100 to 216 °C, the total monomer conversion somewhat decreases. This can be explained by increased retrogressive reaction of dimer **3**, leading to the monomer (reaction 2).

Influence of the Alcoholic (R) Group. The dependence of product composition upon the type of alcoholic (R) group in the acrylate monomer was investigated by a series of comparative experiments with different acrylates (R = CH_3, C_2H_5, isobutyl, 2-ethyl-1-hexyl, cyclohexyl, *n*-dodecyl, and 1-bornyl), using potassium–benzylpotassium as catalyst.

Results obtained are summarized in Table III. As seen, both monomer conversion and product distribution change considerably with variation in the type of R group. Under the experimental conditions, conversion is quantitative for methyl and ethyl acrylates (**1a** and **1b**, respectively), decreases for monomers with medium size R groups, e.g., compounds **1c**, **1d**, and **1e**, and drops sharply for acrylates with long-chain or bulky R groups, e.g., compounds **1f** and **1g**. In the latter case the deactivation effect seems to be mainly steric, although it is uncertain whether hindrance by a bulky R group affects the first reaction step, i.e., the metalation of the acrylate, or the subsequent addition steps of the process. A deactivating effect of bulky R groups has been also observed in radical type polymerization of acrylates.[11]

The effect of the R group is particularly pronounced in controlling the relative extent of dimerization vs. that of polymerization. Whereas methyl acrylate is exceptional in yielding exclusively high molecular weight polymers, it is found (Table III) that the dimer **3**/polymer ratio increases markedly with increase in the size of the R group. Polymer formation is low with cyclohexyl acrylate and is fully sup-

Table IV. Dependence of Product Composition from the Reaction of 2-Ethyl-1-hexyl Acrylate (1) upon Catalyst Type[a,b]

expt no.	23	24	25	26
catalyst system	$K/KCH_2C_6H_5$	$Na/NaCH_2C_6H_5$	$Li/Li\ CH_2C_6H_5$[c]	Na/Al_2O_3[d]
conversion of 1, mol %	70.8	30.2	<1.0	12.2
product distribution, % by wt				
2	9.7	<0.1		10.7
3	71.9	76.4		24.1
other products	18.4	23.6		65.2

[a] In experiments 23, 24, and 25 were used 0.05 mol of monomer, 0.018 g atom of metal, 0.5 mol of solvent, and 0.005 mol of promoter (*o*-chlorotoluene). [b] Reaction temperature, 174 °C, except in expt 26 (132 °C); reaction time, 120 min. [c] In the preparation of this catalyst, the Li metal (0.18 g atom) was dispersed at 216 °C, instead of 170 °C, as used for the other alkali metals. [d] 0.5 g (0.22 g atom) of sodium and 3 g of alumina were used for preparation of this catalyst.

pressed with *n*-dodecyl and 1-bornyl acrylates. The increase in dimerization selectivity for such compounds indicates that a bulky R group may prevent the growth of a polymeric chain beyond the dimeric stage, i.e., the rate of protonation of a dimeric anion in such cases may be faster than propagation.

Effect of Catalyst Type. The dependence of relative reaction rate and of product composition upon the type of alkali metal catalyst was examined by a series of experiments with 1 in the presence of promoted potassium, sodium, and lithium metal dispersions, as well as sodium supported on alumina. A sufficiently high temperature (174 °C) was used in experiments with the nonsupported catalysts in order to increase dimerization selectivity. The supported sodium–alumina catalyst was employed at 132 °C.

Results obtained are summarized in Table IV. As seen, the relative activity of the nonsupported alkali metal catalysts increases with increase in the electropositivity of the alkali metal, the order being K > Na > Li. Although potassium–benzylpotassium is about 2.4 times more active than sodium–benzylsodium (expt 23 vs. 24), the latter is a more selective dimerization catalyst since it does not catalyze the formation of the alkoxy ester **2**. Lithium–benzyllithium is essentially inactive for this reaction. These results are in agreement with the sharp decrease in ionic character of metal–carbon bonds in passing from potassium to sodium to lithium. It is known that the extent of separation between the counterion and the carbanion end group of an oligomer is the primary factor which determines the rate of reaction propagation.[12,13]

The main reaction in the presence of the supported sodium–alumina catalyst is polymerization, 63.5%, and only 24.1% of dimer **3** is produced, based on reacted monomer.

Experimental Section

Apparatus, Catalysts, and Experimental Procedure. The apparatus consisted of a 250-mL three-neck flask, provided with a high-speed stirrer (10 000 rpm), a reflux condenser, an inlet for dry nitrogen, a thermometer, and a calibrated Sage syringe pump. Heat was provided by means of a thermo-regulated heating mantle. Typical experiments with promoted alkali metal catalysts were performed, using the following procedure.

About 20 mL of solvent, e.g., methylcyclohexane, was introduced in the reaction flask and the desired amount of freshly cut alkali metal was added to it under a stream, ~30 mL/min, of nitrogen. The mixture was heated at the reflux temperature of the solvent for a period of 20 min, and the melted metal was subsequently dispersed into a fine powder form by stirring for a period of at least 1 h. The calculated amount of promoter, usually *o*-chlorotoluene, was then added to the mixture to generate the benzylalkali salt,[6,7] and the stirring was contined for another 2 h. After bringing the mixture to the desired reaction temperature, the monomer solution (monomer/solvent molar ratio 1:10) was added dropwise to the flask at a constant feed rate. At the end of the selected reaction period, the mixture was cooled to −10 °C, and the alkali metal catalyst was decomposed by adding absolute ethanol. This was followed by consecutive washing of the mixture with 10% aqueous hydrochloric acid, 10% aqueous sodium bicarbonate, and, finally, with water. The product obtained was dried on anhydrous magnesium sulfate, filtered, and examined by gas chromatography, usually without removal of the solvent. In some cases, gas chromatography was preceded by flash distillation of the product at 0.1 Torr.

The supported sodium–alumina catalyst was prepared and used in situ according to a general procedure described previously.[14]

Quantitative gas chromatographic analysis of product components was performed with the following types of columns: (a) a 6 ft × 1/8 in. tube packed with 10% silicone gum rubber on 80–100 mesh Diatoport S; (b) a 6 ft × 1/8 in. tube packed with 10% of diethylene glycol succinate on 80–90 mesh Anakrom A; and (c) a 300 ft × 0.01 in. Golay column coated with trifluoropropylmethylsilicone. Preparative 6 ft 3/8 in. columns packed as in a and b were also employed.

Individual product components were isolated by fractional distillation and/or preparative gas chromatography, and subsequently identified by a combination of NMR, infrared, and mass spectral methods.

Preparation of Starting Materials. Acrylic acid esters (purity >98%) were prepared by sulfuric acid catalyzed alcoholysis of methyl acrylate[15,16] with an excess of the desired alcohol (isobutyl alcohol, cyclohexanol, 2-ethyl-1-hexanol, 1-borneol, or 1-dodecanol) followed by distillation at 15 Torr.

Isolation and Identification of Products. Alkyl 3-Alkoxypropionate (2). The isolation and identification of 3-alkoxypropionates obtained from different acrylates is illustrated by the following example.

Isobutyl 3-isobutoxypropionate (2c) was isolated by fractional distillation of the combined product from several experiments. Repurification by preparative gas chromatography gave a sample of 98% purity: bp 74–75 °C (0.5 mm); IR (CS_2) 2945–2860 (CH_3 stretching), 1735 (C=O stretching), 1374–1360 (CH deformation in $(CH_3)_2C$),[17] 1105 and 1065 (C–O–C strecthing) cm^{-1}; NMR (CCl_4) δ 3.80 (d, 2 H, *J* = 6.5 Hz, $CO_2C\mathbf{H}_2CH(CH_3)_2$, 3.63 (t, 2 H, *J* = 6.5 Hz, $OC\mathbf{H}_2CH_2CO_2R$), 3.16 (d, 2 H, *J* = 6.5 Hz, $(CH_3)_2CHC\mathbf{H}_2OCH_2$), 2.47 (t, 2 H, *J* = 6.0 Hz, $OCH_2C\mathbf{H}_2CO_2R$), 2.15–1.44 (m, 2 H, two $C\mathbf{H}(CH_3)_2$), 0.95 (d, 12 H, *J* = 3 Hz, two $(C\mathbf{H}_3)_2CH$); *m/e* 202 (M$^+$). Complete separation of all NMR absorption bands was achieved by using tris[1,1,1,2,2,3,3-heptafluoro-7,7,-dimethyl-4,6-octanedionato]europium [Eu(fod)$_3$] as a shift reagent. This included separation of the two closely spaced doublets (δ 3.80 and 3.63), and resolution of the multiplet (δ 2.15–1.44) into two simpler multiplets, corresponding to the two different types of methine groups.

Anal. Calcd for $C_{11}H_{22}O_3$: C, 65.70; H, 11.04. Found: C, 65.60; H, 11.07.

The other 3-alkoxypropionates (**2b–g,** Table III) were analyzed by the same methods, and their identity was confirmed by mass spectrometry.

Dialkyl α-Methyleneglutarate (3). The isolation and identification of the series of dimers **3** produced from different acrylates is illustrated by the following example.

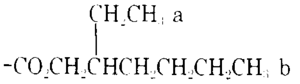
Diisobutyl α-methyleneglutarate (3c) was obtained in 93% purity by fractional distillation. Further purification by preparative gas chromatography gave a sample of 99% purity: bp 118–120 °C (0.5 mm); IR (CS_2) 2940–2860 (CH_3 stretching), 1744 (C=O stretching in CH_2CO_2R),[17] 1720 (C=O stretching in $C{=}CCO_2R$),[17] 1632 (conjugated C=C) cm^{-1}; NMR (CCl_4) δ 6.15 (s, 1 H, *trans*-$\mathbf{H}CH{=}C(CO_2R)CH_2CH_2CO_2R$),[7] 5.60 (s, 1 H, *cis*-$HC\mathbf{H}{=}C(CO_2R)CH_2CH_2CO_2R$),[7] 3.90 (d, 2H, *J* = 6.5 Hz, $C{=}CCO_2C\mathbf{H}_2CH$), 3.80 (d, 2 H, *J* = 6.5 Hz, $OC\mathbf{H}_2CH$), 2.53 (t, 4 H, *J* = 3.5 Hz, $C\mathbf{H}_2C\mathbf{H}_2CO_2R$), 1.00 (d, 6 H, *J* = 2.5 Hz, $(C\mathbf{H}_3)_2CH$), 0.93 (d, 6 H, *J* = 2.5 Hz, $(C\mathbf{H}_3)_2CH$); *m/e* 256 (M$^+$).

Anal. Calcd for $C_{14}H_{24}O_4$: C, 65.59; H, 9.44. Found: C, 65.52; H, 9.50.

The identity of the other α-methyleneglutarates (**3b, 3d–g,** Table III) was determined by the same methods and confirmed by mass spectrometry.

Tris(2-ethyl-1-hexyl) 1,3,5-Cyclohexanetricarboxylate (4d). Liquid chromatography of the product from experiments 7 and 8 gave a 0.4-g sample of compound **4d** in 98% purity. The chromatographic column, 40 in. × 1/4 in., was packed with 200 g of kieselgel 60, 70–230 mesh ASTM. Compound **4d** shows R_f 0.5 (hexane/ethyl acetate 9:1, silica gel precoated aluminum plates; UV lamp development); NMR (CCl_4) δ 3.98 (m, 6 H, superposition of three doublets of $\mathbf{OCH_2}$ groups), 2.5–2.0 (m, 6 H, **CH** of the 2-ethyl-1-hexyl group and **CH** of the ring), 1.67–1.10 (br signals, 30 H, ring $\mathbf{CH_2}$, and esteric $\mathbf{CH_2}$ groups), 0.83 (m, 18 H, superimposed triplets of the $CH_2\mathbf{CH_3}$ groups); IR ($CHCl_3$) 2980 ($\mathbf{CH_3}$ stretching), 2915 ($\mathbf{CH_2}$ stretching), 2890–2880 (CH stretching), 1735 (C=O stretching, saturated CO_2R),[17] 1265–1000 (cyclohexane ring deformation bands);[17] *m/e* 552 (M^+).

The ^{13}C NMR spectrum of compound **4d** is composed of nine major signals corresponding to the different types of carbons, as the anticipated tenth carbon is apparently not sufficiently resolved. A definite broadening of certain signals, e.g., those centered at 30.35, 23.86, and 10.98 ppm, may be due to dynamic equilibrium between different conformations of **4d** under the conditions of measurement (25 °C). For chair–chair interconversion compound **4d** should be preferably in an axial–equatorial–equatorial (a,e,e) conformation, whereas for the energetically less likely chair–boat interconversion, all the ester groups should be equatorially disposed (e,e,e conformation). Examination of the spectrum indeed shows the presence of several narrow signals at 63.94, 31.95, 29.30, 23.40, 22.70, 19.76, and 14.47 ppm, which may be due to the presence of small amounts of the e,e,e conformer. Assignment of the major signals in the ^{13}C NMR spectrum of **4**, based on assignments in the spectrum of the starting monomer **1d**, is as follows: 10.97 ($\mathbf{CH_3}$ b), 14.01 ($\mathbf{CH_3}$ a), 23.86 ($\mathbf{CH_2CH_2}CH_3$), 28.96 ($\mathbf{CH_2}CH_3$ a), 30.35 ($\mathbf{CH_2}CH$), 38.74 (–**CH**–), 67.11 ($\mathbf{OCH_2}$), the designation of the a and b positions of CH_3 in the ester group being



$$\begin{array}{l} \qquad\qquad CH_2CH_3\ \text{a} \\ \qquad\qquad | \\ -CO_2CH_2CHCH_2CH_2CH_2CH_3\ \text{b} \end{array}$$

1,3,5-Cyclohexanetricarboxylates obtained from other acrylates were analyzed by the same methods.

Registry No.—**4d**, 67208-88-2; benzylpotassium, 2785-29-7; potassium, 7440-09-7; isobutyl alcohol, 78-83-1; cyclohexanol, 108-93-0; 2-ethyl-1-hexanol, 104-76-7; 1-borneol, 507-70—; 1-dodecanol, 112-53-8.

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Base-Catalyzed Alkylation of Cyclopentadiene Rings with Alcohols and Amines

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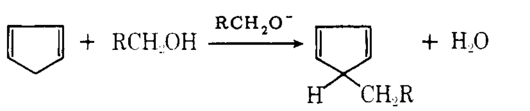
Multiple alkylations of several compounds possessing cyclopentadiene rings were accomplished by the action of alcohols in the presence of their corresponding alkoxides. Several new 1,3-dialkylindenes and 3,5-dialkyl-1,2,4-triphenylcyclopenta-1,3-dienes were synthesized. 1,2,3,4,5-Pentabenzylcyclopenta-1,3-diene was prepared for the first time. It was also demonstrated that 9-benzylfluorene resulted from the action of benzylamine and sodium amide on fluorene.

Since active methylene groups of cyclopentadienes were shown to be alkylated by alcohols and base,[3,4] a research program was undertaken to expand the scope of this reaction. In general form the reaction may be depicted as shown in eq 1, a simplified formulation which disguises informative aspects of the mechanism.[3] However, an examination of this mechanism suggested that more than one, but not necessarily all, of the unsubstituted ring carbon atoms of variously constituted cyclopentadiene moieties should be capable of substitution.



(1)

It has already been demonstrated that each hydroxyl group of certain glycols will alkylate a fluorene molecule to afford bis(9-fluorenyl)alkanes[5,6] and that benzyl alcohol will benzylate indene at both the 1 and 3 positions.[4] Douris and Mathieu,[7] however, isolated only a mixture of 1,3-dibenzylindene and 1-benzyl-3-benzalindene from treatment of indene with benzyl alcohol in the presence of sodium alkoxide or potassium hydroxide, although methanol, ethanol, and 2-propanol gave only the corresponding monoalkylated derivatives under the same conditions. Fritz et al.,[6] using less than molar equivalents of potassium hydroxide, were able to obtain a 74% yield of the dialkylated product with 2-ethylhexanol and indene and 26% yield of dialkylated product with cyclohexanol; however, only a monoalkylate derivative was obtained with 2-propanol.

It was desirable, therefore, to increase the applicability of the reaction to "multifunctional" cyclopentadienes (i.e., cyclopentadienes possessing more than one potentially active methylene group) to provide groundwork for the possible synthesis of a new class of all-hydrocarbon condensation polymers, some of which would be expected to possess a high order of thermal stability. It was further of interest to determine whether amines (which are considerably more basic than alcohols) could be similarly employed. Such a reaction would make possible alkylation by a similar route of methylene or methyl groups much less acidic than those present in cyclopentadienes.

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