[CONTRIBUTION FROM THE CENTRAL RESEARCH DEPARTMENT, MONSANTO CHEMICAL COMPANY]

THE FREE RADICAL ADDITION OF ALDEHYDES TO UNSATURATED POLYCARBOXYLIC ESTERS

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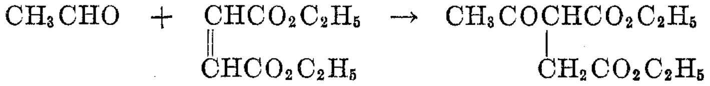
For some years it has been known that free acyl radicals are formed from aldehydes upon exposure to free radicals from another source, or by means of photochemical or thermal decomposition (1).

This observation was put to preparative use by Kharasch, Urry, and Kuderna (2), who reported that simple olefins would add saturated aliphatic aldehydes in the presence of peroxides or ultraviolet light to give ketones, often in good yield. Since this reaction occurred in the presence of only catalytic amounts of decomposing peroxide, a logical chain reaction mechanism, involving free radicals, was advanced.

The present work was initiated in an effort to determine whether ethyl acetylsuccinate could be prepared in similar fashion by the addition of acetaldehyde to ethyl maleate.[1]



$$CH_3CHO \;+\; \begin{array}{l} CHCO_2C_2H_5 \\ \| \\ CHCO_2C_2H_5 \end{array} \;\rightarrow\; \begin{array}{l} CH_3COCHCO_2C_2H_5 \\ \qquad\quad | \\ \qquad\quad CH_2CO_2C_2H_5 \end{array}$$

The desired reaction occurred smoothly in 76–81% yield upon treating ethyl maleate with a two-fold excess of acetaldehyde at 80–95° in the presence of benzoyl peroxide. The mechanism of the reaction is thought to be entirely analogous to that proposed by Kharasch, Urry, and Kuderna (2).

The simplicity and economy of this preparation of ethyl acetylsuccinate, usually obtained from ethyl acetoacetate, sodium, and ethyl chloroacetate (11), prompted further investigation of related materials. Thus, butyraldehyde and enanthaldehyde functioned equally well as addends in the synthesis of homologous ethyl acylsuccinates. On the other hand the reaction of ethyl maleate with 2-ethylcaproaldehyde was much more sluggish, resulting in a 27% conversion and 59% yield under comparable conditions. This behavior is ascribed to the labile tertiary hydrogen atom *alpha* to the carbonyl group. It is presumed that its reactivity toward an acyl radical approaches that of the carbonyl hydrogen. The resulting tertiary free alkyl radical would be more stable than either the acyl radical or the secondary alkyl radical, and, instead of propagating a chain, would be expected to terminate it through dimerization or disproportionation.

Several α,β-unsaturated aldehydes, including crotonaldehyde, furfural, and benzaldehyde, were employed as potential addends with ethyl maleate, but were shown to give little or none of the desired adduct. Of these, only benzaldehyde gave any isolable product. Ethyl benzoylsuccinate was formed in 5% conversion

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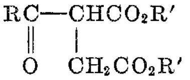
[1] Since the completion of the work described herein, several patents assigned to the U. S. Rubber Co. have appeared on the free radical addition of aldehydes to simple olefins (ref. 3–6) and to unsaturated ethers, carboxylic acids, and esters (ref. 7–10).

and 15% yield. The failure of the α,β-unsaturated aldehydes to give satisfactory yields of adducts was not unexpected because of the opportunity for resonance stabilization of the intermediate acyl radicals.

The dialdehyde, glutaraldehyde, was used satisfactorily with ethyl maleate, and it appears that each of the aldehyde functions combined with a molecule of maleate to give a nearly quantitative yield of ethyl glutarylbissuccinate. The product was of too high molecular weight to distil without decomposition and attempts to hydrolyze it to 4,8-dioxoündecanedioic acid gave a gummy product which could not be purified sufficiently well for analysis.

TABLE I

PREPARATION OF ALKYL ACYLSUCCINATES



$$\underset{\displaystyle O}{\overset{\|}{RC}}-\underset{\displaystyle CH_2CO_2R'}{\overset{|}{CHCO_2R'}}$$

R	R′	MOLE RATIO Ald.: Ester	CATALYST, Wt.—%	TEMP., °C.	TIME (Hrs.)	CRUDE PRODUCT	
						Conv., %	Yield, %
Methyl	Ethyl	3:1	0.1	82–89	4.5	68	78
Methyl	Ethyl	3:1	U.V.	30	16	15	59
Propyl	Ethyl	4:1	1.4	82–88	18	76	76
Propyl	Ethyl	4:1	U.V.	25–30	7	65	73
Propyl	Ethyl	4:1[a]	1.7	82–87	18	26	26
Hexyl	Ethyl	2:1	0.25	84–88	18	76	76
3-Heptyl	Ethyl	3:1	0.4	80–90	17	27	59
Phenyl	Ethyl	4:1	0.6	81–83	23	5	15
Trimethylene	Ethyl	1:3	1.3	80–82	19	100	100
2-Methoxyethyl	Ethyl	3:1	0.2	80–82	21	23	46
2-Methoxyethyl	Ethyl	4:1	U.V.	50–75	18	55	55
Propyl	Hexyl	3:1	0.25	86–96	24	85	85
Propyl	2-Ethylhexyl	3:1	0.2	86–95	18	99	99
Propyl	Tetradecyl	4:1	0.3	83–85	7	94	94
Propyl	Cyclohexyl	3:1	0.5	85–92	21	83	83
Propyl	Benzyl	3:1	0.3	84–93	16	97	97
Hexyl	2-Ethylhexyl	3:1	0.3	85–91	17	97	97

[a] Ethyl fumarate was used in this experiment. Maleates were used in all others.

β-Methoxypropionaldehyde gave a satisfactory yield (46–55%) of ethyl β-methoxypropionylsuccinate, but another substituted aldehyde—chloral—was used unsuccessfully.

At present there appear to be no feasible methods to effect the direct addition of formaldehyde to maleic esters. This may be due, at least in part, to the practical difficulty of obtaining formaldehyde in concentration in an anhydrous, monomeric state. Experiments with aqueous formaldehyde, paraformaldehyde, and nascent formaldehyde (from trioxane) were of no avail in the present work.

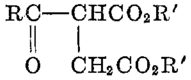
The addition of butyraldehyde and enanthaldehyde to higher maleic esters presented no difficulty. Crude yields approaching theoretical were obtained with hexyl, 2-ethylhexyl, tetradecyl, cyclohexyl, and benzyl maleates.

Table I gives the pertinent data on the preparation of the various acylsuccinates while Table II lists their properties and analytical data.

As in many free radical addition reactions with olefinic materials, the principal by-products obtained in the present work are telomers, *i.e.*, adducts wherein the mole ratio of ester to aldehyde is greater than unity. As might be expected, the reaction may be controlled to favor the formation of telomers by decreasing the ratio of aldehyde to ester in the reaction mixture. This was demonstrated by variation of mole ratios from 4:1 to 1:4 for a series of experiments with butyraldehyde and ethyl maleate as shown in Table III.

TABLE II

PROPERTIES OF ALKYL ACYLSUCCINATES



$$\underset{\displaystyle O}{\overset{\Vert}{RC}}\text{—}\underset{\displaystyle CH_2CO_2R'}{\overset{|}{CHCO_2R'}}$$

R	R′	B.P., °C.	MM.	n_D^{25}	d_{25}^{25}	ANALYSES			
						Calc'd		Found	
						C	H	C	H
Methyl	Ethyl	89–91[a]	0.5	1.4360	1.0783				
Propyl	Ethyl	112–114[b]	1	1.4349	1.0410	59.0	8.25	59.1	8.49
Hexyl[c]	Ethyl	132–133	0.5	1.4392	0.9951	62.9	9.15	63.5	9.23
3-Heptyl	Ethyl	114–120	0.5	1.4400	.9761	64.0	9.39	65.0	9.52
Phenyl	Ethyl	150–160	0.8	1.5028	1.1263	64.8	6.52	64.8	6.42
Trimethylene	Ethyl			1.4652		56.7	7.26	57.1	6.88
2-Methoxyethyl	Ethyl	115–116	0.5–0.6	1.4410	1.0852	55.4	7.75	55.6	7.68
Propyl	Hexyl	155–165	0.3–0.5	1.4440	0.9624	67.4	10.18	66.3	9.94
Propyl	2-Ethylhexyl	182–184	0.5	1.4492	.9472	69.9	10.75	70.0	10.75
Propyl	Tetradecyl	260–265	0.5	1.4563	.9026	74.4	11.80	75.2	11.62
Propyl	Cyclohexyl	175–185	1	1.4728	1.0475	68.2	9.15	68.1	9.01
Propyl	Benzyl	195–220	1	1.5268	1.1209	71.7	6.56	71.6	6.46
Hexyl	2-Ethylhexyl	190–210	0.7	1.4511	0.9329	71.3	11.10	71.5	10.58

[a] B.p. 121–124°/5 mm. (11). [b] B.p. 102–104°/1 mm., n_D^{20} 1.4392 (9). [c] Sulfuric acid hydrolysis of the product gave a 96% crude yield of γ-oxocapric acid, which melted at 69–71° after one recrystallization from 33% aqueous ethanol. Lukěs (18) reports m.p. 71°.

In contrast to the maleates, fumarates tend to give a large proportion of telomer with butyraldehyde. Thus, under comparable reaction conditions, ethyl maleate gave a 76% yield of 1:1 adduct and a weight ratio of 3.8:1 of ethyl butyrylsuccinate to telomer, whereas ethyl fumarate gave a 26% yield of 1:1 adduct and a weight ratio of 0.48:1 of ethyl butyrylsuccinate to telomer. Qualitatively, the tendency for telomer formation appears to be related to the rate at which a given augend will homopolymerize. This hypothesis is supported by the observation that the proportion of telomer formed increases for the series maleate < fumarate < itaconate. Nearly all of the ethyl itaconate was converted to a low telomer when it was treated with butyraldehyde.

Aconitates appear to be entirely comparable to maleates in their reactivity with aldehydes. Good yields of α-acyltricarballylates were obtained with acetaldehyde, butyraldehyde, and enanthaldelyde. That the products were α- rather than β-substituted was indicated by their enolization (solubility in sodium hydroxide, color formation with ferric chloride, and failure to give a positive haloform test), and was confirmed by hydrolysis of ethyl acetyltricarballylate to acetonylsuccinic acid rather than to β-acetylglutaric acid.

TABLE III

ETHYL BUTYRYLSUCCINATE

THE EFFECT OF REACTANT RATIO ON THE RATIO OF PRODUCT TO TELOMER

ALDEHYDE (g.)	ESTER (g.)	MOLE RATIO (Ald.: Ester)	Bz_2O_2 Wt.—%	TEMP., °C.	TIME Hrs.	CRUDE PRODUCT		RESIDUE		RATIO PROD.:RES. (Wt. Basis)
						Conv.	Yield, %	g.	M.W.	
72	43	4:1	1.4	82–88	18	76	76	12.2	298	3.8:1
72	43	4:1	U.V.[a]	25–30	7	65	73	11.4	—	3.5:1
36	86	1:1	0.41	80–82	16	13	50	12.8	370	1.2:1
36	86	1:1	1.2	80–82	64	62	62	36.1	398	2.1:1
36	172	1:2	1.4	80–82	64	44[b]	44[b]	102.3	421	0.52:1
18	172	1:4[c]	0.21	92	65	3[d]	10[d]	14.5	448	0.12:1

[a] No peroxide used. Reaction initiated by 100-watt U.V. lamp. [b] Based on one-half the ester charged. [c] 150 ml. benzene used as solvent. [d] Based on one-fourth the ester charged.

EXPERIMENTAL

Ethyl acetylsuccinate. A 9-gallon, light-gauge, stainless steel tank in the shape of a prolate spheroid served as a reaction vessel. The tank was fitted with a thermowell at one end and a line bearing a valve, pressure gauge, and vent valve in that order at the other end. The vessel was heated by a water-bath whose temperature was controlled by the introduction of live steam or cold water. A solution of 8000 g. (182 moles) of acetaldehyde, 10,430 g. (60.7 moles) of ethyl maleate, and 18.4 g. of benzoyl peroxide was charged to the reactor which was then heated by slowly raising the bath temperature to the maximum of 82°. When the contents of the reactor reached 76°, the reaction appeared to become fairly rapid and the temperature rose to the maximum of 89° where it remained for about 20 minutes before dropping. The bath was maintained at 82° for 4½ hours after the temperature of the mixture reached its maximum. The pressure was 50 p.s.i.g. during the initial heating period when the temperature reached 71°. It reached the maximum of 150 p.s.i.g. during the reaction and was 59 p.s.i.g. at the conclusion of the heating period when the temperature was 82°.[2] The reaction mixture was distilled to give, in addition to recovered acetaldehyde and

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[2] Caution: In a system from which the heat of reaction cannot be removed rapidly, the use of quantities of catalyst substantially greater than this amount should be avoided. When 184 g. of catalyst was employed in a run otherwise identical to that described, the reaction was uncontrollably fast. The temperature reached the maximum of 140° and the pressure would have exceeded 450 p.s.i.g. had the vessel not been vented.

some intermediate fractions, 1400 g. of recovered ethyl maleate and 8805 g. (68% conversion and 78% yield) of ethyl acetylsuccinate, b.p. 110–111°/3 mm., n_D^{26} 1.4340.

Several similar runs have been carried out in the vessel described as well as in Carius tubes and smaller stainless steel pressure vessels using up to 1% by weight of benzoyl peroxide catalyst. Conversions and yields as high as 81% have been obtained.

Ethyl butyrylsuccinate. A mixture of 43.0 g. (0.25 mole) of ethyl maleate, 72.0 g. (1.0 mole) of butyraldehyde, and 2.0 g. of benzoyl peroxide was boiled under reflux for 18 hours. The temperature during this time rose from 82° to 88°. The pale yellow reaction mixture was cooled, extracted with a saturated sodium bicarbonate solution, washed twice with water, and dried over sodium sulfate. Upon distillation there was obtained, in addition to unreacted aldehyde and a small intermediate fraction, 46.5 g. (76% crude yield) of ethyl butyrylsuccinate, b.p. 95–108°/0.5 mm., n_D^{25} 1.4362. The residue was 12.2 g. of a yellow, slightly viscous oil. Redistillation of the crude product gave 31.9 g. of purer material, b.p. 112–114°/1 mm., n_D^{25} 1.4349, d_{25}^{25} 1.0410, which was used for analysis. It gave a faint violet test with ferric chloride, and a positive test with a mercuric chloride–sodium ethoxide reagent.

A similar experiment was conducted with 28.0 g. (0.163 mole) of ethyl fumarate, 47.0 g. (0.65 mole) of butyraldehyde, and 1.3 g. of benzoyl peroxide. In 18 hours the temperature at reflux rose from 82° to 87°. There were obtained 10.3 g. (26% yield) of ethyl butyrylsuccinate, b.p. 139–142°/1 mm. (superheated?), n_D^{25} 1.4358, and 21.3 g. of a cloudy yellow, very viscous residue. On redistillation the product boiled at 104–106°/0.7 mm., n_D^{25} 1.4363.

One-gram samples of each of these two preparations of ethyl butyrylsuccinate were refluxed for two hours with mixtures of 10 ml. of concentrated sulfuric acid and 15 ml. of water. By this time the oil layers had disappeared. Each reaction mixture was cooled, made slightly basic to phenolphthalein with 20% sodium hydroxide, and extracted twice with ether. The aqueous portions were acidified with dilute sulfuric acid and again extracted three times with ether. The latter extracts were dried with calcium sulfate, and then evaporated. Each solid residue weighed 0.5 g. (85% yield). That from the fumarate source melted at 41–46°, and after recrystallization from benzene-hexane, at 48–50°. The acid from the maleate source melted at 44–48° before recrystallization, and at 49–50° afterward. The melting point of a mixture of the two recrystallized samples was 48–50°. γ-Oxoenanthic acid melts at 49.8° (12).

A photochemically-catalyzed reaction was carried out with 72 g. (1.0 mole) of butyraldehyde and 43 g. (0.25 mole) of ethyl maleate. The charge was placed in a one-liter flask fitted with a stirrer, thermometer, condenser, and 100-watt mercury vapor lamp.[3] The lamp did not contact the stirred liquid. The flask was cooled by a running-water bath and the stirred solution was irradiated for seven hours at 25–30°. The slightly yellow reaction mixture was distilled to give 48.5 g. of recovered butyraldehyde, b.p. 72°/atm.—40°/150 mm., 2.7 g., b.p. 72–96°/16 mm.; 4.9 g. of recovered ethyl maleate, b.p. 58°/1 mm.—85°/0.5 mm.; 39.5 g. (65% conversion and 73% yield) of ethyl butyrylsuccinate, b.p. 95–113°/1 mm., n_D^{25} 1.4350; and 11.4 g. of a clear amber viscous liquid residue.

Ethyl benzoylsuccinate. A mixture of 43.0 g. (0.25 mole) of ethyl maleate, 106.0 g. (1.0 mole) of benzaldehyde (freshly redistilled), and 0.3 g. of benzoyl peroxide was held at 81–83° for 23 hours with occasional shaking. Additional 0.3-g. portions of benzoyl peroxide were added after one hour and three hours respectively. The amber reaction mixture was cooled and then extracted twice with small portions of 5% sodium hydroxide, using a little benzene to facilitate layer separation. The solution was washed with water until neutral and dried with sodium sulfate. Distillation gave 82.3 g. of recovered benzaldehyde, b.p. 60°/25 mm.—85°/19 mm., and 25.8 g. of recovered ethyl maleate, b.p. 85°/19 mm.—118°/18 mm. The residue consisted of 18.9 g. of an amber liquid which deposited a few crystals upon cooling. The solid was evidently benzoic acid formed from benzaldehyde during the manipulation. The residue was diluted with benzene, extracted twice with 5% sodium hydroxide,

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[3] This was a General Electric AH-4 lamp whose outer envelope was replaced by a quartz envelope.

washed with water until neutral, dried over calcium sulfate, and distilled from a Claisen flask. There were obtained 1.9 g. of a pale yellow liquid having an odor of ethyl maleate, b.p. 70–150°/0.8 mm., n_D^{25} 1.4578; 3.8 g. (5% conversion and 15% yield) of ethyl benzoylsuccinate, b.p. 150–160°/0.8 mm., n_D^{25} 1.5028, d_{25}^{25} 1.1263; and 7.4 g. of a viscous amber residue.

Two drops of the product were boiled with dilute sulfuric acid until complete solution occurred (*ca.* 15 minutes). Then the solution was cooled to give white crystals, which, after recrystallization from water, melted at 117–118°. β-Benzoylpropionic acid melts at 117–118° (13).

Ethyl glutarylbissuccinate. To a 500-ml. jacketed flask there were added 129.0 g. (0.75 mole) of ethyl maleate, 25.0 g. (0.25 mole) of glutaraldehyde (as a 40% solution in ether) (14), and 1.0 g. of benzoyl peroxide. A slow stream of nitrogen was passed through the mixture and a vacuum was applied to the flask to evaporate the ether. Benzene was boiled in the jacket of the flask in order to maintain a temperature of 80–82°. After three hours an additional 1.0-g. portion of peroxide was introduced. Heating was continued for a total time of 19 hours. Distillation from a Claisen flask gave 31.2 g. of recovered ethyl maleate, b.p. 63–86°/2 mm. (mostly 70–75°/2 mm.), n_D^{25} 1.4387, and 6.5 g. of liquid (probably mostly ethyl maleate) containing a few crystals (probably benzoic acid), b.p. 80°/1.5 mm.—162°/2 mm. The residue, 110.3 g. of light amber, viscous liquid, n_D^{25} 1.4652, evidently was a nearly theoretical yield of crude ethyl glutarylbissuccinate.

Ethyl β-methoxypropionylsuccinate. A mixture of 88.0 g. (1.0 mole) of β-methoxypropionaldehyde and 43.0 g. (0.25 mole) of ethyl maleate was placed in a tubular glass vessel fitted with a thermometer, reflux condenser, and the 100-watt mercury vapor lamp. The lamp was immersed in the solution. The reactor was surrounded by an ice-bath. The heat from the lamp held the reaction mixture at 50–55°. After two hours, the ice-bath was replaced by a running-water bath and the reaction was continued for 16 hours longer at 70–75°. The resulting mixture was a clear yellow solution. Distillation gave 35.5 g. (55% yield) of crude ethyl β-methoxypropionylsuccinate, b.p. 120–134°/1 mm., n_D^{25} 1.4414, and 29.4 g. of a clear dark amber residue. The product was redistilled to give 29.0 g. (45%) of purer material, b.p. 116°/0.6 mm.—115°/0.5 mm., n_D^{25} 1.4410, d_{25}^{25} 1.0852, a pale yellow liquid giving a violet color reaction with ferric chloride.

Butyraldehyde–ethyl itaconate telomer. A mixture of 108.0 g. (1.5 moles) of butyraldehyde, 93.0 g. (0.5 mole) of ethyl itaconate, and 0.5 g. of benzoyl peroxide was boiled under reflux. After four hours an additional 0.5-g. portion of benzoyl peroxide was introduced, and refluxing was continued for a total of 74 hours. During this time the temperature remained constant at 86°. The light yellow solution was distilled to give I, 74.3 g. of recovered aldehyde, b.p. 72° to 48°/150 mm.; II, 5.8 g., b.p. 57°/20 mm.—110°/18 mm., n_D^{25} 1.4060, (probably butyric acid, bibutyryl, and 2-ethyl-2-hexenal); III, 12.6 g. of recovered ethyl itaconate, b.p. 77–86°/2 mm., n_D^{25} 1.4381; and IV, 2.8 g., b.p. 103–120°/1 mm., n_D^{25} 1.4505. The residue (93.0 g.) consisted of a viscous yellow liquid, n_D^{25} 1.4623. Cryoscopic determination of the molecular weight in benzene gave an average value of 597 which corresponds to a 1:2.82 telomer.

Anal. Calc'd for ($C_4H_8O + 2.82\ C_9H_{14}O_4$): C, 59.1; H, 8.02.
Found: C, 58.9; H, 7.96.

Ethyl α-acetyltricarballylate. A solution of 56.3 g. (1.28 moles) of freshly distilled acetaldehyde, 82.6 g. (0.32 mole) of ethyl aconitate (b.p. 121°/2 mm., n_D^{23} 1.4532), and 0.3 g. of benzoyl peroxide was charged to a glass liner of a 1-l. Aminco rocking autoclave and heated with agitation at 82–92° for four hours. The excess acetaldehyde was evaporated from the cooled mixture. The residue was diluted with an equal volume of ether, washed with a saturated sodium bicarbonate solution, and then three times with water. After the solution had been dried over sodium sulfate, it was fractionated to give 82.2 g. (85% yield) of crude ethyl α-acetyltricarballylate, b.p. 127°/2 mm.—139°/1.5 mm., n_D^{19} 1.4538–n_D^{23} 1.4472. The major portion (50.8 g.) boiled at 140–143°/2 mm., n_D^{23} 1.4479. Ruhemann and Browning (15) gave b.p. 187–188°/11 mm. The product was insoluble in water, soluble in 5% aqueous sodium hydroxide, gave a deep violet color with ferric chloride in ethanol solution, and failed to give iodoform when treated with iodine-potassium iodide.

A mixture of 3.0 g. (0.01 mole) of the ester and 5 ml. of conc'd hydrochloric acid was refluxed for one hour. The resulting clear solution was evaporated to one-half its initial volume in an evaporating dish. A quantity of chloroform then was added and the mixture was boiled until the water was removed. Chloroform was added from time to time during this procedure. Several crops of white crystals totalling 1.1 g. (65% yield) were obtained by evaporating the chloroform solution to a small volume, adding carbon tetrachloride, and chilling. The crude acetonylsuccinic acid melted at 90–99°, and a pure product, after three recrystallizations from ether-chloroform-carbon tetrachloride solution, melted at 105.5°. Alder and Söll (16) reported m.p. 108° for acetonylsuccinic acid, while Fittig (17) reported m.p. 58° for β-acetyglutaric acid.

Anal. Calc'd for $C_7H_{10}O_5$: Neut. equiv., 87. Found: Neut. equiv., 87.

Butyl α-butyryltricarballylate. A solution of 75.0 g. (1.04 moles) of butyraldehyde, 85.5 g. (0.25 mole) of butyl aconitate, and 0.5 g. of benzoyl peroxide was boiled under reflux for eight hours. An additional 0.2-g. portion of peroxide had been added after five hours. The temperature rose from 84° to 89°. All volatile matter up to a pot temperature of 165°/1 mm. was distilled from the mixture leaving a residue of 102.7 g. (99% yield) of crude butyl α-butyryltricarballylate, a yellow, slightly cloudy liquid, n_D^{25} 1.4475. A 20.0-g. aliquot of this product was distilled giving 16.7 g. (83% yield) of purer material, b.p. 175–180°/0.5 mm., n_D^{25} 1.4471, d_{25}^{25} 1.0126.

Anal. Calc'd for $C_{22}H_{38}O_7$: C, 63.8; H, 9.24.
Found: C, 63.9; H, 8.90.

Butyl α-enanthyltricarballylate. A mixture of 108.0 g. (0.95 mole) of enanthaldehyde, 108.3 g. (0.317 mole) of butyl aconitate, and 1.5 g. of benzoyl peroxide was heated at about 75–90° for 20 hours. A benzene solution of the cooled reaction mixture was extracted with 200 ml. of 1% aqueous sodium hydroxide, washed twice with water, dried with Drierite, and distilled. The following fractions were obtained: I, 64.4 g. of recovered enanthaldehyde, b.p. up to 54°/20 mm.; II, 8.2 g. of intermediate, b.p. 60–202°/1 mm.; III, 104.2 g. (72% yield) of butyl α-enanthyltricarballylate, b.p. 202–208°/1 mm. (sl. dec.) n_D^{25} 1.4510, d_{25}^{25} 0.9923; and 20.4 g. of a viscous, amber residue.

Anal. Calc'd for $C_{25}H_{44}O_7$: C, 65.7; H, 9.71.
Found: C, 66.1; H, 9.46.

SUMMARY

A variety of aliphatic aldehydes was added to maleate or aconitate esters under free radical conditions to give acylsuccinates or α-acyltricarballylates smoothly and in good yield.

Formaldehyde, chloral, and certain α,β-unsaturated aldehydes failed to undergo this addition.

The ratio of 1:1 adducts to telomers formed was in rough proportion to the mole ratio of aldehyde to maleate used.

Unsaturated esters which tend to homopolymerize more readily than maleates gave low telomers as products in proportion to this tendency.

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REFERENCES

(1) WATERS, *The Chemistry of Free Radicals*, Oxford University Press, 1946, p. 116 *et seq.*
(2) KHARASCH, URRY, AND KUDERNA, *J. Org. Chem.*, **14**, 248 (1949).
(3) LADD, U. S. Patent 2,517,684, Aug. 8, 1950.

(4) LADD, U. S. Patent 2,517,685, Aug. 8, 1950; British Patent 647,971 (Dec. 28, 1950).
(5) STITELER AND LITTLE, U. S. Patent 2,517,732, Aug. 8, 1950.
(6) U. S. RUBBER Co., British Patent 640,479, July 19, 1950.
(7) LADD, U. S. Patent 2,533,944, Dec. 12, 1950.
(8) LADD, U. S. Patent 2,560,770, July 17, 1951.
(9) LADD, U. S. Patent 2,577,133, Dec. 4, 1951.
(10) U. S. RUBBER Co., British Patent 636,287, April 26, 1950.
(11) BLATT, *Org. Syntheses*, Coll. Vol. II, 262 (1943).
(12) FRANKE, *et al.*, *Monatsh.*, **69**, 167 (1936) [*Chem. Zent.*, I, 2606 (1937)].
(13) SUDBOROUGH, *J. Chem. Soc.*, **101**, 1231 (1912).
(14) LONGLEY AND EMERSON, *J. Am. Chem. Soc.*, **72**, 3079 (1950).
(15) RUHEMANN AND BROWNING, *J. Chem. Soc.*, **73**, 727 (1898).
(16) ALDER AND SÖLL, *Ann.*, **565**, 57 (1949).
(17) FITTIG, *Ann.*, **314**, 1 (1901).
(18) LUKĚS, *Collection Czechoslov. Chem. Comm.*, **1**, 119 (1929) [*Chem. Abstr.*, **23**, 4469 (1929)].