[CONTRIBUTION FROM THE INSTITUTE OF POLYMER RESEARCH, POLYTECHNIC INSTITUTE OF BROOKLYN]

The Preparation of 2-Alkyl-1,4-butanediols[1]

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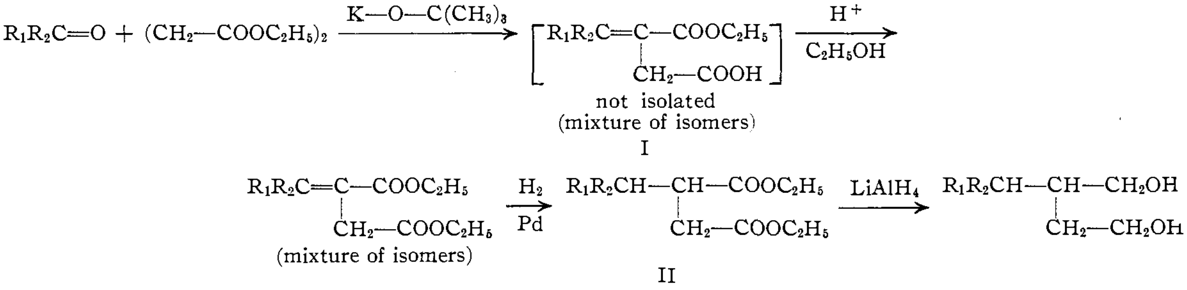
We have undertaken the preparation of a series of 2-alkylbutadienes in order to determine the reactivities of such dienes in the copolymerization reaction,[2] and to study the effects of side-chain alkyl groups, both straight and branched, upon the physical properties of diene polymers. Crystallization of the polymeric backbone and of the side chain are of special interest. Thus, the long alkyl side chains in a polymer of hexadecyl acrylate[3] results in crystallite formation in the side chain. Likewise, a branched alkyl group[4] or a long alkyl group may increase the amount of the 1,4-addition of the diene when forming the polymer, increasing the homogeneity and thus increasing the crystalline properties of the main polymer chain when the chains are oriented by stretching.

This paper will describe the preparation of some 2-alkyl-1,4-butanediols (II, also Table III), intermediates in the preparation of 2-alkylbutadienes. The synthetic route for preparing these diols was similar to that used by Wojcik and Adkins[5] and by Marvel, Myers and Saunders[6] to prepare 2-isopropyl-1,4-butanediol. Our improved procedure is experimentally different, and furnishes a good general method for the preparation of the 2-alkyl-1,4-butanediols. The procedure is outlined below.



$$R_1R_2C{=}O + (CH_2{-}COOC_2H_5)_2 \xrightarrow{K{-}O{-}C(CH_3)_3} \left[\begin{array}{l} R_1R_2C{=}C{-}COOC_2H_5 \\ \qquad\ CH_2{-}COOH \end{array}\right] \xrightarrow[C_2H_5OH]{H^+}$$

not isolated
(mixture of isomers)
I

$$\begin{array}{l}R_1R_2C{=}C{-}COOC_2H_5\\ \qquad\ CH_2{-}COOC_2H_5\end{array} \xrightarrow[Pd]{H_2} \begin{array}{l}R_1R_2CH{-}CH{-}COOC_2H_5\\ \qquad\qquad CH_2{-}COOC_2H_5\end{array} \xrightarrow{LiAlH_4} \begin{array}{l}R_1R_2CH{-}CH{-}CH_2OH\\ \qquad\qquad CH_2{-}CH_2OH\end{array}$$

(mixture of isomers)

II

The crude half-esters (I) obtained by the general procedure of Johnson and co-workers[7] were not isolated by us but were esterified to give high yields of a mixture of isomeric unsaturated 2 alkyl succinate esters (Table I). The yield reported for the condensation of acetone and diethyl succinate to the unsaturated diester according to the original conditions of the Stobbe condensation with sodium ethoxide was 53%[6]; compare 92%, Table I. The unsaturated alkyl diesters were further characterized by saponification to the unsaturated 2-alkylsuccinic acids (Table I).

Hydrogenation of the unsaturated diethyl esters over palladium at low pressures gave the 2-alkylsuccinic esters (Table II), which were similarly characterized by conversion to the 2-alkylsuccinic acids (Table II). Reduction of the diethyl 2-alkylsuccinates to the 2-alkyl-1,4-butanediols (Table III) was accomplished in almost quantitative yields by means of lithium aluminum hydride.[8] The diacetates of these diols are described in Table IV. The preparation and characterization of the dienes will be described in a later paper.

Discussion of the Structure of the Unsaturated 2-Alkylsuccinate Diesters and Diacids.—On the assumption that the extinction coefficient of an α,β-unsaturated ester is similar to that of an α,β-unsaturated acid[9] and is between 11,000 and 13,000 depending on the solvent, between 2200 and 2100 Å., some of the compounds in Table I have the double bond largely in the α,β-position: R_1 = iso-C_3H_7, n-C_9H_{19}, n-$C_{11}H_{23}$ and n-C_6H_{13}; R_2 = H. Those that have a lower extinction coefficient between 2200 and 2100 Å. are the esterified conden-

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[1] This work was supported by a contract from the Office of Naval Research.

[2] Alfrey and Goldfinger, *J. Chem. Phys.*, **12**, 205 (1944); Mayo and Lewis, THIS JOURNAL, **66**, 1594 (1944); Wall, *ibid.*, **66**, 2050 (1944).

[3] Kaufman, Sacher, Alfrey and Fankuchen, *ibid.*, **70**, 3146 (1948).

[4] However, it has recently been shown by Marvel, Williams and Baumgarten (*J. Polymer Sci.*, in press) that the isopropyl group in the 2-position has no effect on the amount of 1,4-addition in an emulsion polymer when compared with polyisoprene.

[5] Wojcik and Adkins, THIS JOURNAL, **55**, 4939 (1933); **56**, 2424 (1934).

[6] Marvel, Myers and Saunders, *ibid.*, **70**, 1694 (1948). Some of our work was done prior to this publication. Professor Marvel kindly furnished us with a copy of his manuscript before publication.

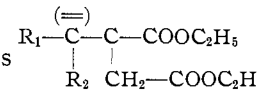
[7] (a) Johnson, Goldman and Schneider, THIS JOURNAL, **67**, 1357 (1945); (b) Johnson, Davis, Hunt and Stork, *ibid.*, **70**, 3021 (1948); (c) Johnson, Johnson and Peterson, *ibid.*, **67**, 1360 (1945).

[8] Nystrom and Brown, *ibid.*, **69**, 1197 (1947). Hydrogenation of diethyl 2-isopropylidenesuccinate at high pressures with a copper chromite catalyst (refs. 5, 6) gave low yields of 2-isopropyl-1,4-butanediol.

[9] (a) Braude, "Ann. Repts. on Progress Chem. (Chem. Soc., London)," 42, 111 (1945); (b) Dimroth, *Angew. Chem.*, **52**, 545 (1939); (c) Mohler and Lohr, *Helv. Chim. Acta*, **21**, 485 (1938); (d) for a comparison of carboxyl and carbalkoxy groups from a resonance viewpoint see Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 73; (e) thus Andrews, Cristol, Lindenbaum and Young, THIS JOURNAL, **67**, 715 (1945), have demonstrated the similarity between the absorption spectrum of α-cyanocrotonic acid, $\lambda_{max.}$ 2150 Å., ϵ 9700 and methyl-α-cyanocrotonate, $\lambda_{max.}$ 2200 Å., ϵ 8400.

TABLE I

UNSATURATED DIETHYL 2-ALKYLSUCCINATES



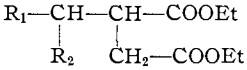
$$\overset{(=)}{R_1\text{—}C}\text{—}C\text{—}COOC_2H_5 \quad R_2,\ CH_2\text{—}COOC_2H_5$$

R_1, R_2	Reac. time, hr.	B. p., °C., mm.	Yield, %	n^{25}_D	Percentage composition Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	$\lambda_{max.}$, Å.	ϵ[h]	M. p. of diacid [i]	Recryst. solvent of diacid
CH_3, CH_3	0.5[b]	76[d] (0.6)	92	1.4504	61.66	61.42[f]	8.47	8.37	2195	9200	161.5–162[j]	W[r]
CH_3, C_2H_5	0.5[b]	93–94 (1.0)	83	1.4500	63.13	62.87[g]	8.83	8.93	2180	6960	179–181[k]	W
C_5H_{10},[a] —	0.3[b]	120–121 (0.8)	72	1.4756	66.11	66.03[g]	8.72	8.85	2200	5050	179–180[l]	W
Iso-C_3H_7, H	1.5[b]	142–143[e] (11.0)	85	1.4410	63.13	62.92[f]	8.83	8.55	2130	11,400	189–189.5[m]	W
n-C_9H_{19}, H	2.0[c]	153 (1.1)	40	1.4530	69.19	69.00[f]	10.32	10.28	2135	10,200	140–140.5[n]	B[s]–PE[t]
n-$C_{11}H_{23}$, H	8.0[c]	164 (0.6)	58	1.4532	70.55	70.37[f]	10.66	10.41	2130	10,100	137–138[o]	B–PE
n-C_6H_{13}, H	14.0[c]	133–134 (1.5)	59	1.4508	66.63	66.64[f]	9.69	9.70	2135	11,200	127–127.5[p]	PE
Iso-C_3H_7, CH_3	7.0[b]	92.5–93 (0.8)	78	1.4490	64.44	64.18[f]	9.15	9.14	2195	7890	178.5–179.5[q]	A[u]–PE

[a] Prepared from cyclohexanone. [b] Prepared by procedure A. [c] Prepared by procedure B. [d] Ref. 6 reported b. p. 100–102° (2 mm.); n^{20}_D 1.4550; d^{20}_4 1.0304. [e] Fittig and Burwell, *Ann.*, **304**, 259 (1899) reported b. p. 282°. [f] Analyses by Mr. H. S. Clark. [g] Analyses by Dr. Francine Schwarzkopf. [h] Purified cyclohexane as solvent. [i] Prepared by saponification of the diester. [j] Fittig and Petkow, *Ann.*, **304**, 208 (1899), reported m. p. 160–161°; assigned α,β-structure because acid did not form lactone. Farmer, Ingold and Thorpe, *J. Chem. Soc.*, 121, 128 (1921), reported m. p. 154–156° or 160° depending upon the rate of heating, and refers to Ssemenoff, *J. Russ. Phys.-Chem. Soc.*, **23**, 430 (1898), who reported m. p. 161–162°. Stobbe, *Ber.*, 26, 2312 (1893); *ibid.*, **36**, 197 (1903), reported m. p. 160–161°; proved alleged α,β-structure by oxidation experiments. [k] Stobbe, *Ann.*, **321**, 105 (1902), reported m. p. 181°, presented evidence for α,β-structure by oxidation experiments; Stobbe, *ibid.*, **282**, 280 (1894), previously reported m. p. 165–167°; we found that heating at the rate of three degrees per minute gives m. p. 179–181°; slow heating, one degree per two minutes gives m. p. 164.5–166° dec. Ref. 10 reported m. p. 186° dec. [l] Ref. 7b reported m. p. 179–180°. [m] Fittig and Burwell, ref. [e], Table I, reported m. p. 189–192°; structure proof see [b]; λ_{max} 2135Å.; ϵ, 11,820, 95% ethanol. [n] *Anal.* Calcd.: C, 65.59; H, 9.44. Found: C, 65.42; H, 9.35; λ_{max}, 2140 Å.; ϵ, 12,340, 95% ethanol. [o] *Anal.* Calcd.: C, 67.57; H, 9.92. Found: C, 67.43; H, 9.89; $\lambda_{max.}$, 2130 Å.; ϵ, 12,130, 95% ethanol. [p] Fittig and Hoeffken, *Ann.*, **304**, 326 (1899), reported m. p. 129–130°. *Anal.* Calcd.: C, 61.66; H, 8.47. Found: C, 61.47; H, 8.37; $\lambda_{max.}$, 2130 Å.; ϵ, 11,587, 95% ethanol. [q] *Anal.* Calcd.: C, 58.05; H, 7.58. Found: C, 58.33; H, 7.47. Analyses by Mr. H. S. Clark. [r] W, water. [s] B, benzene. [t] PE, petroleum ether (90–100°). [u] A, acetone. Water may also be used.

TABLE II

DIETHYL 2-ALKYLSUCCINATES



$$R_1\text{—}CH\text{—}CH\text{—}COOEt \quad R_2,\ CH_2\text{—}COOEt$$

R_1, R_2	B. p., °C.	Mm.	Yield, %	n^{25}_D	d^{25}_4	Mol. ref. diff.	Percentage composition Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	M. p. of diacid[f]	Recryst. solv. of diacid
CH_3, CH_3	105–106[b]	6.5	83	1.4237	0.9869	−0.25	....	...	...	...	115–115.5[g]	W[o]
CH_3, C_2H_5	75–76	0.2	94	1.4293	0.9745	+0.04	62.58[d]	62.86	9.63	9.38	130–130.5[h]	W
C_5H_{10},[a] —	103–104[c]	.5	88	1.4554	1.0284	−0.31	65.59[e]	65.72	9.44	9.39	145–145.5[i]	PE[p]
Iso-C_3H_7, H	84–85	.9	97	1.4259	0.9679	+0.01	62.58[d]	62.28	9.63	9.75	108–108.5[j]	B[q]–PE
n-C_9H_{19}, H	134	.3	91	1.4398	.9341	+ .01	68.75[d]	69.01	10.90	10.89	88.5–90[k]	B–PE
n-$C_{11}H_{23}$, H	159.5	.4	94	1.4412	.9237	+ .07	70.13[d]	70.19	11.18	10.91	96–97.5[l]	PE
n-C_6H_{13}, H	114–115	.7	92	1.4329	.9457	+ .03	66.14[d]	66.17	10.36	10.31	89.5–90.5[m]	W
Iso-C_3H_7, CH_3	86–87	.4	88	1.4400	.9838	+ .10	63.90[d]	64.01	9.90	9.61	90–91.5[n]	A[r]–PE

[a] From cyclohexanone. [b] B. p. also 94–95° (2.4 mm.) (86%). Ref. 6 reported b. p. 65° (10.5 mm.), n^{20}_D 1.4284, d^{20}_4 0.9925. [c] Swain, Todd and Waring, *J. Chem. Soc.*, 548 (1944), reported b. p. 110–120° (10^{-1} mm.). [d] Analysis by H. S. Clark. [e] Analysis by Dr. Francine Schwarzkopf. [f] Prepared by saponification of diesters. [g] Henry and Paget, *J. Chem. Soc.*, 78 (1928), reported m. p. 114°. [h] *Anal.* Calcd. for $C_8H_{14}O_4$: C, 55.16; H, 8.10. Found: C, 55.02; H, 7.97. Analysis by R. Schachat. [i] Ref. C, Table II, reported m. p. 146–147°. [j] Bentley and Perkin, *J. Chem. Soc.*, **73**, 45 (1898), reported m. p. 109°. [k] Barry and Twomey, *Proc. Royal Irish Acad.*, **51B**, 137 (1947), reported m. p. 91–93°. [l] *Ibid.*, reported 97.5–98.5°. [m] Ref. *h*, Table II reported m. p. 90–91°. [n] *Anal.* Calcd. for $C_9H_{16}O_4$: C, 57.43; H, 8.57. Found: C, 57.75; H, 8.29. Analysis by Mr. H. S. Clark. [o] W, water. [p] PE, petroleum ether (90–100°), [q] B, benzene. [r] A, acetone.

sates from methyl ethyl ketone ($R_1 = CH_3$, $R_2 = C_2H_5$) cyclohexanone, ($R_1R_2 = C_5H_{10}$), and methyl isopropyl ketone (R_1 = iso-C_3H_7, $R_2 = CH_3$). The condensate from acetone ($R_1 = CH_3$, $R_2 = CH_3$) has an extinction coefficient at the indicated range between the above two groups.

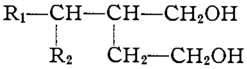
Separation of the unsaturated alkyl esters from unsymmetrical ketones or from aldehydes into possible *cis–trans* isomers has not been attempted. In general, there would only be slight displacements in the intensity and position of the absorption maxima for *cis* and *trans* forms in compounds of this type.

From the close agreement of the absorption spectra of the unsaturated alkyl diacids resulting from the diesters derived from aldehydes (R_1 = iso-C_3H_7, n-C_9H_{19} and n-C_6H_{13}; R_2 = H) it would appear that under the mild conditions of the saponification, no isomerization took place. The maximum absorption compares favorably with other α,β-unsaturated acids.[9b] Small increases of the extinction coefficients are noted, but this may be due to the small increase in resonance through a carboxyl group over the carbalkoxy group.[9e] Here again no attempt has been made to distinguish between *cis* and *trans* forms from aldehydes and unsymmetrical ketones.

The melting points of the diacids reported in

TABLE III

2-ALKYL-1,4-BUTANEDIOLS



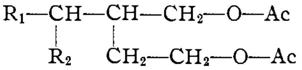
$R_1—CH(R_2)—CH(CH_2—CH_2OH)—CH_2OH$

R_1, R_2	B. p., °C.	Mm.	Yield, %	$n^{25}D$	d^{25}_4	Molecular refraction		Formula	Percentage composition			
									Carbon		Hydrogen	
						Calcd.	Found		Calcd.	Found	Calcd.	Found
CH_3, CH_3	128–129	6.4[c]	96	1.4515	0.9533	37.58	37.41	$C_7H_{16}O_2$	...	...	...	...
CH_3, C_2H_5	143.5	8.9[d]	96	1.4582	0.9536	42.20	41.86	$C_8H_{18}O_2$	65.71	65.59[h]	12.41	12.83
C_5H_{10},[a] —	142.5	1.6[e]	90	1.4915	1.0211	49.24	49.24	$C_{10}H_{20}O_2$	69.72	69.44	11.70	11.52
Iso-C_3H_7, H	110	0.8	88	1.4510	0.9320	42.20	42.23	$C_8H_{18}O_2$	65.71	65.99	12.41	12.41
n-C_9H_{19}, H	161–163	1.1	94	1.4604	0.9018	69.92	70.01	$C_{14}H_{30}O_2$	72.98	73.28	13.13	13.13
n-$C_{11}H_{23}$, H	165[b]	0.4	95	....	....	...	...	$C_{16}H_{34}O_2$	74.36	74.63	13.26	12.98
n-C_6H_{13}, H	143	1.3[f]	93.3	1.4560	0.9164	56.06	55.86	$C_{11}H_{24}O_2$	70.16	70.08	12.85	12.61
Iso-C_3H_7, CH_3	108	0.5[g]	85	1.4688	0.9537	46.82	46.78	$C_9H_{20}O_2$	67.45	67.70	12.58	12.53

[a] From cyclohexanone. [b] M. p. from anhydrous ethyl ether, 40–41.5°. [c] B. p. also 100° (0.2 mm.). Ref. 6 reported b. p. 106° (4 mm.), 145–146° (18 mm.), $n^{20}D$ 1.4535, d^{20}_4 0.9672. [d] B. p. also 106° (0.6 mm.). [e] B. p. also 131.5–134° (0.5–0.6 mm.), 85%. [f] B. p. also 136° (0.7 mm.). [g] B. p. also 116–118° (1.0 mm.). [h] Analysis by H. S. Clark.

TABLE IV

2-ALKYL-1,4-BUTANEDIOL DIACETATES



$R_1—CH(R_2)—CH(CH_2—CH_2—O—Ac)—CH_2—O—Ac$

R_1, R_2	B. p. °C.	Mm.	Yield, %	$n^{25}D$	d^{25}_4	Molecular refraction		Formula	Percentage composition[e]			
									Carbon		Hydrogen	
						Calcd.	Found		Calcd.	Found	Calcd.	Found
CH_3, CH_3	85[b]	1.0	91	1.4331	1.0011	56.72	56.32	$C_{11}H_{20}O_4$	...	...	...	...
CH_3, C_2H_5	95.5–96[c]	0.9	86	1.4364	0.9886	60.94	60.96	$C_{12}H_{22}O_4$	62.58	62.28	9.63	9.71
C_5H_{10},[a] —	115.5	0.7	88	1.4599	1.0353	67.98	67.80	$C_{14}H_{24}O_4$	65.59	65.64	9.44	9.26
Iso-C_3H_7, H	96[d]	1.3	94	1.4303	0.9761	60.94	60.99	$C_{12}H_{22}O_4$	62.58	62.39	9.63	9.82
n-C_9H_{19}, H	155–156	1.1	86	1.4435	.9405	88.66	88.70	$C_{18}H_{34}O_4$	68.75	68.56	10.90	10.70
n-$C_{11}H_{23}$, H	154–155	0.3	92	1.4445	.9308	97.90	97.84	$C_{20}H_{38}O_4$	70.13	70.41	11.18	11.40
n-C_6H_{13}, H	123	0.7	86	1.4374	.9569	74.80	74.66	$C_{15}H_{28}O_4$	66.14	66.35	10.36	10.19
Iso-C_3H_7, CH_3	105–106	1.1	92	1.4417	.9859	65.55	65.51	$C_{13}H_{24}O_4$	63.90	64.16	9.90	9.72

[a] From cyclohexanone. [b] B. p. also 119° (6.9 mm.), 87%. Ref. 6 reported b. p. 96° (1.5 mm.), $n^{20}D$ 1.4349, d^{20}_4 1.0055. [c] B. p. also 132–133° (8.5 mm.), 82%. [d] B. p. also 88–90° (1.1 mm.). [e] Analysis by H. S. Clark.

Table I are dependent on the rate of heating. A sample of the diacid from the cyclohexanone condensate obtained from Professor W. S. Johnson[10] was identical with our acid, mixed m. p. 179–180°, if the rate of heating was 3° per minute whether immersion of the sample was at low temperature or 170°. Heating at the rate of one degree per minute gave a m. p. 164.5-166° dec., mixed m. p. 164–166° dec. This depression may be due to lactone formation or to other decomposition. We used a heating rate of a 2 or 3° rise per minute to obtain our melting points.

Experimental

Preparation of Diethyl 2-Alkyl Unsaturated Succinates. Procedure A.—The compounds listed in Table I were prepared according to modifications of the procedure described by Johnson and co-workers.[7a,7b] We have extended the preparative scheme to the direct preparation of the diethyl esters of 2-substituted unsaturated succinic acids. The following procedure was employed for the compounds in Table I indicated by superscript b.

A mixture of 0.8 mole of the carbonyl compound and 1.0 mole of diethyl succinate was added over fifteen minutes to a refluxing solution of 0.88 mole of potassium in 800 ml. of anhydrous *t*-butyl alcohol. The stirred reaction mixture was heated under reflux for a time depending upon the reactivity of the carbonyl compound (see Table I). The solvent was removed from the reaction mixture under reduced pressure, the residue was made slightly acid to litmus with dilute hydrochloric acid and the remainder of the solvent was removed. The organic layer was dissolved in 200 ml. of ethyl ether and the aqueous layer was separated and extracted with three 200-ml. portions of ether. The combined ether solutions were washed with water and then extracted completely with 10% aqueous carbonate. The ether washing of combined alkaline extracts was added to the original ether layer and the ether solution was dried over anhydrous magnesium sulfate. From this residue it was possible to recover unreacted and excess diethyl succinate.

The alkaline solution was made strongly acid with concentrated hydrochloric acid and chilled. The organic layer was separated, and the aqueous layer was extracted with four 150-ml. portions of ethyl ether. The ether layers were combined with the separated organic layer, washed with water, and dried over anhydrous magnesium sulfate. After removal of the ether from the "half-acid," a chilled solution of the residue in 10 volumes of anhydrous ethyl alcohol was treated with dry hydrogen chloride to give a 5% solution by weight. After twenty-four hours at room temperature, the alcohol was removed under reduced pressure. The residue was poured into an ice–ice-water mixture, and the ester layer was taken up in ethyl ether. The aqueous layer was extracted with four 200-ml. portions of ethyl ether, and the extracts, after combining with the original separation, were neutralized by washing with aqueous sodium bicarbonate and dried over anhydrous magnesium sulfate. The alkaline washes were saved and on subsequent saponification gave a small quantity of 2-alkenesuccinic acid. The residual diester was fractionated through a 30-cm., helices-packed column. The yields of the diesters and physical constants are found in Table I.

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[10] We are indebted to Professor W. S. Johnson for a sample of the half-acid derived from the cyclohexanone condensate and the diacid from its saponification, m. p. 179–180°. Evidence was presented to show that this was the α,β-acid.

Procedure B.—The compounds listed in Table I (superscript c) were prepared by this modified procedure since by-products obtained in the initial condensation and difficulties due to emulsification made it impossible to completely separate the "half-acid" by the usual carbonate extraction. Therefore, the initially acidified reaction mixture was extracted with ether in the usual manner and dried over anhydrous magnesium sulfate. The entire ether-soluble reaction product was esterified as in the previous procedure, and the residue fractionated through a similar column. A typical experiment gave in the case of diethyl 2-*n*-decylidenesuccinate the following fractions: Fraction 1, 25 g., b. p. 80–90° (0.7 mm.); fraction 2, 75 g., b. p. 155–160° (0.6 mm.); fraction 3, 75 g., b. p. 210–220° (0.6 mm.). Fraction 2 was refractionated through the same column to give 60 g. (35%) of pure product.

Saponification of Unsaturated Diesters.—Five grams of the pure diethyl unsaturated 2-alkylsuccinates were saponified in 50 ml. of a refluxing 10% aqueous sodium hydroxide. Acidification of the decolorized and filtered reaction mixtures with concentrated hydrochloric acid gave crystalline succinic acids. The products were air-dried and recrystallized from the appropriate solvent as noted in Table I.

Preparation of Diethyl 2-Alkylsuccinates.—One-tenth mole of our initial condensation product (Table I) was dissolved in 50 ml. of 95% ethyl alcohol containing 0.5 g. of suspended 5% palladium-on-charcoal catalyst, and the mixture shaken in an atmosphere of hydrogen at 55–60 p. s. i. pressure. In all experiments between 95 and 100% of the theoretical quantity of hydrogen was absorbed. The reaction mixture was filtered to remove the catalyst, and the solvent was removed by distillation at atmospheric pressure. The residual ester was distilled under reduced pressure. The data are summarized in Table II.

Preparation of 2-Alkylsuccinic Acids.—Five grams of the diethyl 2-alkylsuccinates was saponified as described for the treatment of the unsaturated esters. The data are summarized in Table II.

Preparation of 2-Alkyl-1,4-butanediols.—Following the general procedure of Nystrom and Brown,[8] 0.1 mole of the diethyl 2-alkylsuccinate was added dropwise to a chilled, stirred anhydrous ether solution of 0.12 mole of lithium aluminum hydride. The reaction mixture was stirred for one hour after the addition was completed and the excess hydride was decomposed by the careful addition of the required amount of water. The reaction mixture was then poured into a mixture of ice and water containing 10% sulfuric acid. The ether layer was separated after the complex had been completely decomposed and the aqueous layer was extracted with five 100-ml. portions of ethyl ether. The combined ether layers were washed with a minimum of water containing bicarbonate and dried over anhydrous magnesium sulfate. The residual diol was fractionated through a 30-cm., helices-packed column. There was usually a forerun of lower boiling material. The data on each of the diols are summarized in Table III.

Preparation of the 2-Alkyl-1,4-butanediol Diacetate.—Each diol was suspended in a threefold excess by weight of acetic anhydride and boiled under reflux for from six to ten hours. The excess anhydride was removed by distillation under reduced pressures, the residue taken up in ethyl ether and the ether solution washed with bicarbonate solution until neutral. The ether solution was dried over anhydrous magnesium sulfate, and the residue was fractionated through a 30-mm., helices-packed column. The data are summarized in Table IV.

Ultraviolet Absorption Spectra.—Ultraviolet absorption spectra were determined with a Beckman quartz ultraviolet spectrophotometer in purified cyclohexane[11] and 95% ethanol as solvents. The cell length used in all experiments was 1 cm. Figure 1 describes the spectra for the esterified condensation product of diethyl succinate and *n*-decylaldehyde and the analogous diacid.

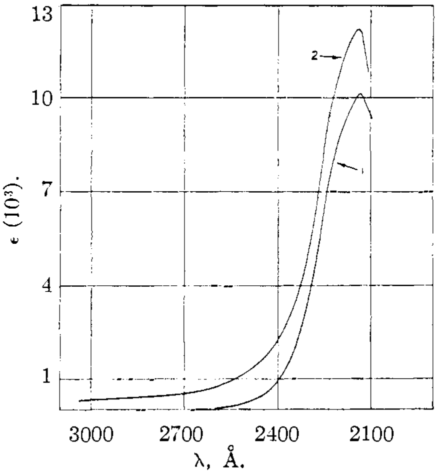

Fig. 1.—Ultraviolet absorption spectrum of: (1) diethyl-2-decylidenesuccinate in cyclohexane; (2) 2-decylidenesuccinic acid in 95% ethanol.

Summary

1. A convenient preparation of 2-alkyl-1,4-butanediols, intermediates in the synthesis of 2-alkyl-1,3-butadienes has been described.

2. Seven new 2-alkyl-1,4-butanediols have been prepared and characterized [$OH-CH_2-CH(CHR_1R_2)-CH_2-CH_2OH$] $R_1 = CH_3$, $R_2 = C_2H_5$; $R_1R_2CH = C_5H_{10}$; $R_1 = iso-C_3H_7$, $R_2 = H$; $R_1 = n-C_9H_{19}$, $R_2 = H$; $R_1 = n-C_{11}H_{23}$, $R_2 = H$; $R_1 = n-C_6H_{13}$, $R_2 = H$; $R_1 = iso-C_3H_7$, $R_2 = CH_3$. The diacetates of these diols have likewise been prepared and characterized.

3. Seven new diethyl 2-alkylsuccinates intermediate in the diol synthesis have been prepared and characterized [$EtOOCCH(CHR_1R_2)CH_2-COOEt$]. Likewise the diacid ($R_1 = iso-C_3H_7$, $R_2 = CH_3$) derived from the corresponding diester is described.

4. The absorption spectra of eight unsaturated 2-alkylsuccinates (see above R_1R_2, also $R_1 = CH_3$, $R_2 = CH_3$) have been measured. The isomeric structures surmised from these data are briefly discussed. Likewise, absorption spectra have been obtained for four new unsaturated 2-alkylsuccinic acids. On the basis of existing data for the absorption spectrum of an α,β-unsaturated acid, the results indicate that the double bond is in the α,β-position.

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[11] Maclean, Jencks and Acree, *J. Research Natl. Bur. Standards*, **34**, 271 (1945).