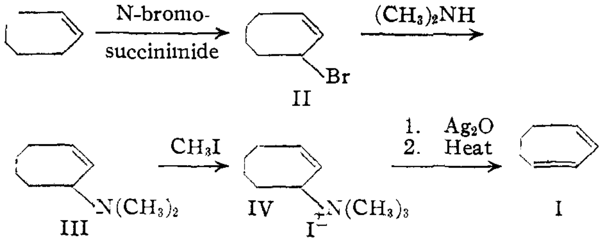

Table I presents a summary of the pertinent reaction data for the various steps of the synthesis.

TABLE I

Compound	Yield,[a] %	B. p. °C.	B. p. Mm.	M. p.	$n^{20}D$
II[b]	48	55-56	8		1.5323
III	69	68-71	13-14		1.4769
IV	77			163-164[c]	
I	29	120-121[d]	Atm.		1.4972

[a] Based on the previous compound in the sequence. [b] Colorless liquid which darkened very rapidly on standing. *Anal.* Calcd. for $C_7H_{11}Br$: C, 48.02; H, 6.33. Found: C, 48.91; H, 6.34. Compound converted immediately to III. [c] Lit. value (ref. 1), 162-163°. *Anal.* Calcd. for $C_{10}H_{20}NI$: C, 42.71; H, 7.17. Found: C, 42.40; H, 6.90. [d] Lit. values: 120-121° (ref. 1); 120-121.5° (ref. 2).

The ultraviolet absorption spectrum of diene I was determined using a Beckman quartz spectrophotometer, model DU, and purified isoöctane as solvent. The results are plotted in Fig. 1, from which the values λ_{max} 248 mμ and log ϵ 3.87 may be obtained.

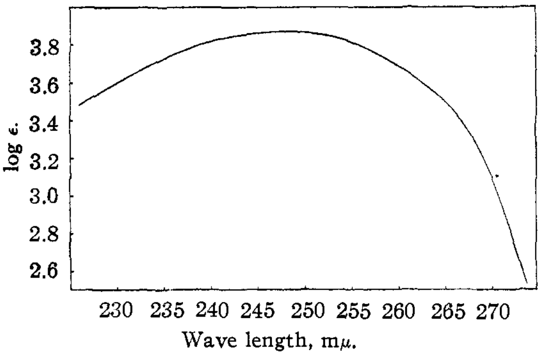

Fig. 1.

Discussion

It is seen in Fig. 1 that, with the degree of resolution furnished by the Beckman instrument, compound I displays the broad absorption band with a single maximum in the ultraviolet that is characteristic[3,4,5] of conjugated cyclic dienes in general.

Since it is known that the position of λ_{max} in the conjugated diene series is virtually independent[7] of the solvent used, over a range from ethyl alcohol to cyclohexane, the present data can be combined with those of previous workers to yield a plot of λ_{max} *vs.* the number of ring members in the cyclic diene. This plot is shown in Fig. 2.

Curiously, the curve is at a maximum for the six-membered diene, and λ_{max} decreases sharply as the ring size is either increased or decreased from this peak value. A satisfactory explanation of this behavior must await a detailed analysis of the relative magnitudes of the strains inherent in both ground and first excited states of these molecules, evaluated as a function of ring size.

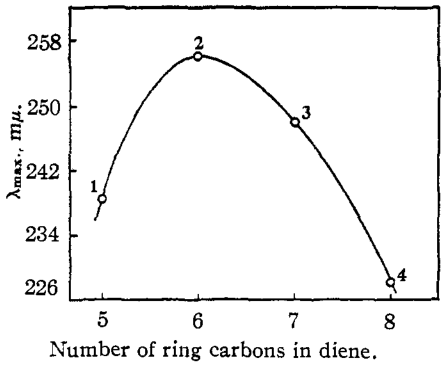

Fig. 2.—1, ref. 3; 2, ref. 4; 3, this work; 4, ref. 5.

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[7] See, for example, the compilation of data in the paper by Booker, Evans and Gillam, *J. Chem. Soc.*, 1453 (1940).

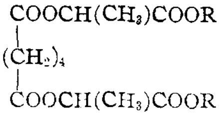
Diesters of Lactic Acid. Adipates of Various Lactates[1,2]

BY C. E. REHBERG AND MARION B. DIXON

The hydroxyl group in esters of lactic acid may be readily esterified by use of carboxylic acids, anhydrides or acyl chlorides. Previous papers from this laboratory have described the acetates,[3] laurates,[4] acrylates,[5] alkyl carbonates[6] and diethylene glycol bis-carbonates[7] of various lactates.

Adipic acid was of special interest in this work because of its availability at low cost and the potential utility of its lactate esters as plasticizers.

The lactate adipates studied (Table I) have the type formula



$$\begin{array}{l}\mathrm{COOCH(CH_3)COOR}\\ |\\ \mathrm{(CH_2)_4}\\ |\\ \mathrm{COOCH(CH_3)COOR}\end{array}$$

where R is the radical of the alcohol from which the lactate was made. These esters were conveniently made from adipyl chloride and the lactates. Less pure products but equally good plasticizers

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[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

[2] Presented in part before the Division of Paint, Varnish and Plastics Chemistry, American Chemical Society, Chicago, Ill., April 1948 and Detroit, Mich., April 1950. Article not copyrighted.

[3] Rehberg and Dixon, THIS JOURNAL, **72**, 1918 (1950).

[4] Fein and Fisher, *J. Org. Chem.*, **15**, 530 (1950).

[5] Rehberg, Dixon and Fisher, THIS JOURNAL, **67**, 208 (1945).

[6] (a) Rehberg, Dixon and Fisher, *J. Org. Chem.*, **13**, 254 (1948); (b) Rehberg and Dixon, *ibid.*, **15**, 565 (1950).

[7] (a) Rehberg, Dixon and Fisher, *ibid.*, **14**, 593 (1949); **15**, 560 (1950); (b) *Ind. Eng. Chem.*, **42**, 1409 (1950).

TABLE I

ADIPATES OF LACTIC ESTERS [$-CH_2CH_2COOCH(CH_3)COOR]_2$

	Yield, %	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Sapn. equiv. Calcd.	Sapn. equiv. Found	$n^{20}D$	$n^{40}D$	d^{20}_4	d^{40}_4	Viscosity, cps. 20°	Viscosity, cps. 40°	Mol. refract. Calcd.	Mol. refract. Found 20°
Ethyl	91	55.5	55.2	7.6	7.6	86.6	86.1	1.4412	1.4340	1.1075	1.0883	49.56	18.83	82.70	82.60
Propyl	62	57.7	57.5	8.1	8.3	93.6	91.1	1.4432	1.4370	1.0865	1.0681	61.53	24.26	91.94	91.38
Butyl	96	59.7	59.9	8.5	8.8	100.6	99.7	1.4432	1.4360	1.0543	1.0365	41.37	16.56	101.18	101.24
Isobutyl	98	59.7	59.8	8.5	8.4	100.6	99.6	1.4410	1.4340	1.0479	1.0299	53.29	20.13	101.18	101.44
***s*-Butyl**	88	59.7	59.5	8.5	8.9	100.6	98.6	1.4410	1.4338	1.0574	1.0394	75.58	27.06	101.18	100.52
2-Ethylhexyl	96	65.3	65.2	9.8	9.8	128.7	128.4	1.4494	1.4420	0.9997	0.9836	67.97	25.63	138.12	138.17
***n*-Octyl**	93	65.3	65.2	9.8	9.6	128.7	127.7	1.4482	1.4414	.9960	.9801	53.71	22.47	138.12	138.37
2-Octyl	85	65.3	65.2	9.8	9.9	128.7	125.6	1.4446	1.4375	.9929	.9769	82.4	23.55	138.12	137.83
3,5,5-Trimethylhexyl	87	66.4	66.3	10.0	10.0	135.7	134.7	1.4500	1.4430	.9881	.9733	117.0	37.75	147.36	147.61
Allyl[a]	85	58.4	58.2	7.1	7.1	92.6	91.8	1.4565	1.4485	1.1085	1.0892	41.98	16.39	91.01	90.92
2-Butoxyethyl	62	58.8	58.7	8.6	8.6	122.6	120.2	1.4472	1.4401	1.0668	1.0508	71.93	26.10	122.93	122.92
2-Hexyloxyethyl	90	61.5	61.3	9.2	9.0	136.7	137.8	1.4490	1.4419	1.0327	1.0161	66.54	24.96	141.41	141.98
2-(2-Butoxyethoxy)-ethyl	60	58.1	58.2	8.7	8.8	144.7	146.0	1.4507	1.4433	1.0725	1.0559	79.19	31.42	144.69	145.19
Tetrahydrofurfuryl	78	57.6	57.1	7.5	7.7	114.6	112.6	1.4680	1.4610	1.1677	1.1516	525.9	123.5	109.30	109.15
1-Carbethoxyethyl[b]	87	53.9	53.9	7.0	6.8	81.8	81.8	1.4462	1.4390	1.1478	1.1285	543.5	95.0	113.72	114.01
1-Carbobutoxyethyl[c]	98	57.1	57.0	7.7	7.7	91.1	91.9	1.4470	1.4400	1.1026	1.0842	283.5	67.9	132.19	132.42

[a] This ester has been reported by Howald and Jones, U. S. Patent 2,462,042, February 15, 1949. Their physical constants are in substantial agreement with ours. [b] Adipate of ethyl acetyllactate. [c] Adipate of butyl lactyllactate.

TABLE II

PREPARATION AND PROPERTIES OF LACTIC ESTERS

Lactate	Yield, %	Boiling point °C.	Boiling point Mm.	$n^{20}D$	d^{20}_4	Mol. refraction Calcd.	Mol. refraction Found	Sapn. equiv. Calcd.	Sapn. equiv. Found	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
2-Octyl	83	54	0.2	1.4300	0.9300	56.18	56.18	202.3	198.0	65.3	65.4	11.0	11.2
3,5,5-Trimethylhexyl	86	80	.3	1.4365	.9236	60.80	61.29	216.3	220.5	66.6	66.6	11.2	11.2
2-Hexyloxyethyl	83	82	.3	1.4362	.9829	57.82	58.09	218.3	223.3	60.5	60.9	10.2	10.6
1-Carbethoxyethyl[a]	25[b]	77	1.0	1.4292	1.1136	43.98	44.05	95.1	94.8	50.5	50.4	7.4	7.5
1-Carbobutoxyethyl[c]	22[b]	94	1.0	1.4329	1.0622	53.21	53.38	109.1	108.8	..	..	..	..

[a] Ethyl lactyllactate. [b] Conversion of lactate to lactyllactate. [c] Butyl lactyllactate.

can be made by the direct esterification of adipic acid with the lactic ester.[8]

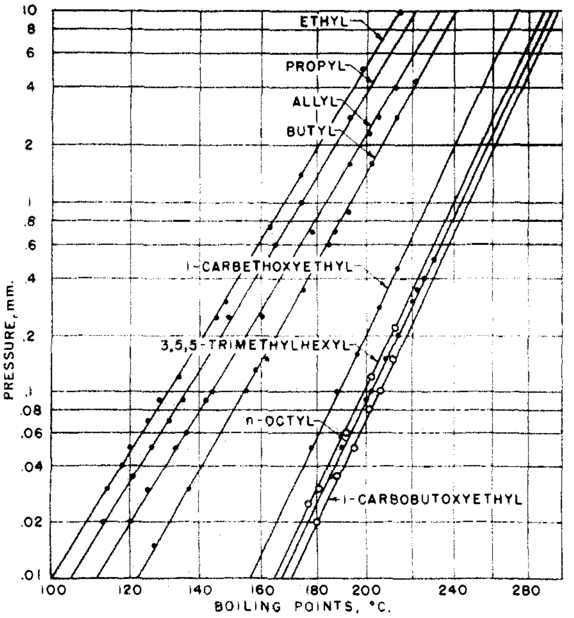

Fig. 1.—Boiling points of lactate adipates.

All of the esters were clear, colorless, oily liquids having little or no odor. Data on their use as plasticizers will be published elsewhere.

Boiling Points.—Each ester was distilled, and constant boiling fractions were used for the deter-

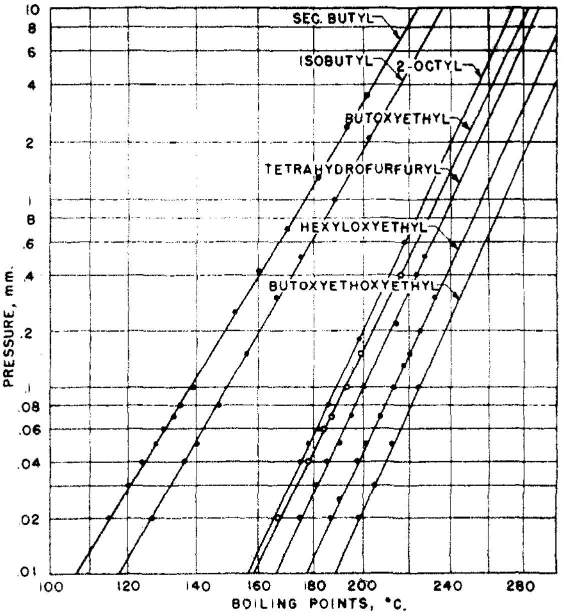

Fig. 2.—Boiling points of lactate adipates.

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[8] Rehberg and Dixon, "Plasticizers from Lactic Acid. Direct Esterification of Butyl Lactate with Adipic Acid," presented before the Division of Paint, Varnish and Plastics Chemistry, American Chemical Society, Atlantic City, N. J., September 1949.

mination of boiling points and other physical properties. Figures 1 and 2 were drawn from boiling points determined with a recently described alembic type tensimeter-still.[9] The temperature coördinates of these figures (Cox charts) were laid off as linear functions of $1/(t^\circ + 223)$. This was easily achieved[10] by adding 50° to each calibration mark on a Cox chart graduated according to $1/(t^\circ + 273)$.

Boiling points of the esters at 1 mm. pressure were taken from Figs. 1 and 2 and plotted *vs.* the normal boiling points of the alcohols ROH. These points fell approximately on a straight line, the equation of which was $B_E = 0.67\ B_A + 115$, where $B_E =$ b. p. of the ester at 1 mm. and $B_A =$ b. p. of ROH at atmospheric pressure. The maximum deviation from this line was 8° and the average was 4°. This equation is convenient for the estimation of the boiling points of lactate adipates for which data are not available.

Acknowledgment.—We are grateful to C. O. Willits, C. L. Ogg and their associates for analytical data; to E. I. du Pont de Nemours and Company, Inc., for 3,5,5-trimethylhexanol, and to Carbide and Carbon Chemicals Corporation for 2-ethylhexyl, butoxyethyl, hexyloxyethyl and butoxyethoxyethyl alcohols.

Experimental

Lactates.—Ethyl and butyl lactates are available commercially. All the others except those in Table II have been reported previously[11] and were prepared by direct esterification[11d] of lactic acid or by the alcoholysis[6a] of methyl or ethyl lactate.

Ethyl and butyl lactyllactates (Table II) have been reported by Claborn[12] who made them by the reaction of lactide with the appropriate alcohol. We prepared these esters by the self-alcoholysis[13] of the corresponding lactate. Briefly, the lactate, containing about 0.2% of sulfuric acid, was refluxed in a still while approximately the theoretical amount of alcohol was distilled out. The catalyst was then neutralized, and the product was distilled at the lowest practicable temperature.

Reaction of Adipyl Chloride with Lactates.—One mole of lactate and one mole of pyridine were dissolved in 200 to 300 cc. of anhydrous ether. This solution was stirred and maintained at 0–10°, while one-half mole of adipyl chloride was added dropwise. After being left for several hours at room temperature, the reaction mixture was washed with water, dried and distilled. For the distillation, a short Vigreux column or an alembic type still[9] was most suitable. The latter was used exclusively for determination of boiling points.

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[9] Ratchford and Rehberg, *Anal. Chem.*, **21**, 1417 (1949).

[10] Rehberg, *Ind. Eng. Chem.*, **42**, 829 (1950).

[11] (a) Smith and Claborn, *ibid.*, **32**, 692 (1940); (b) Fein, Ratchford and Fisher, THIS JOURNAL, **66**, 1201 (1944); (c) Fein and Fisher, *ibid.*, **68**, 2631 (1946); (d) Rehberg, *Org. Syntheses*, **26**, 4 (1946).

[12] Claborn, U. S. Patent 2,350,388, June 6, 1944.

[13] Filachione, Costello and Fisher, "Plasticizers from Lactic Acid. Esters of Polymeric Lactic Acid," presented before the Division of Paint, Varnish and Plastics Chemistry, American Chemical Society, 112th Meeting, New York, Sept. 1947.

New Methods of Preparation of 2-Methy cyclohexen-1-one[1]

BY WALTER W. RINNE, H. R. DEUTSCH, MAX I. BOWMAN AND IRVING B. JOFFE

In investigating the preparation of 2-methyl-2-cyclohexene-1-one,[2] it occurred to us to try a number of methods previously unreported. One method which appears to be very satisfactory is bromination of 2-methylcyclohexanone, followed with dehydrobromination with 2,4-dinitrophenylhydrazine,[3,4] a method previously used only with steroidal compounds.

Bromination of 2-methylcyclohexanone with bromine in acetic acid gives a bromoketone fraction (I) which is different from that (II) obtained by the N-bromosuccinimide method as shown by differences in chemical behavior. (II) was converted virtually quantitatively to the 2,4-dinitrophenylhydrazone of 2-methyl-2-cyclohexen-1-one by the Mattox–Kendall procedure,[3] whereas (I) gives the same product but only in 68% yield. Pyridine dehydrobromination of (II) gave 2-methyl-2-cyclohexene-1-one in good yield, whereas (I) under the same conditions yielded 6-methyl-2-cyclohexen-1-one.[5] This difference could be explained either on the assumption that (I) contains both the 2-bromo and 6-bromo derivatives or that a rearrangement occurs in one of the dehydrobromination steps.

2-Methyl-2-cyclohexen-1-one could also be prepared from the Oppenauer oxidation of 1-methyl-1,2-cyclohexandiol to give 2-methyl-2-hydroxycyclohexanone, which, as has previously been shown,[2] can be readily dehydrated by various methods. Because of the difficulty of purification of the product, this method is less satisfactory than the others.

Bromination of 1-methylcyclohexene with N-bromosuccinimide gave a bromo derivative which could also be converted to this ketone by the Sommelet procedure, but in rather low yield.

Experimental

Bromomethylcyclohexanone (I).—To 20 g. of 2-methylcyclohexanone in 150 ml. of glacial acetic acid kept at 5°, was added with constant stirring 14 g. of bromine dissolved in 50 ml. of acetic acid containing 0.5 ml. of 4 *N* HBr. The bromo compound was separated by addition of water and extraction with ether. After washing with sodium bicarbonate solution, the ether solution was dried over anhydrous calcium sulfate, the ether removed by distillation and the residual liquid distilled. The fraction boiling at 65–97° at 10 mm. was collected as a viscous oil. The yield was 13 g. The bromo compound was not further purified but was used in subsequent reactions as soon as possible to avoid polymerization to a tarry material.

Bromomethylcyclohexanone (II).—From 33.5 g. of 2-methylcyclohexanone, brominated with 53 g. of N-bromosuccinimide in carbon tetrachloride in the usual manner,

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[1] This work was carried out under contract N8onr76201 between the Navy Department, Office of Naval Research and the University of Louisville.

[2] Butz, Davis and Gaddis, *J. Org. Chem.*, **12**, 122 (1947).

[3] Mattox and Kendall, THIS JOURNAL, **70**, 882 (1948).

[4] Djerassi, *ibid.*, **71**, 1004 (1949).

[5] Kotz and Steinhorst, *Ann.*, **379**, 1 (1911).