[CONTRIBUTION FROM THE MULTIPLE FELLOWSHIP OF THE SUGAR INSTITUTE, INC., AT MELLON INSTITUTE OF INDUSTRIAL RESEARCH]

Some Alkyl Esters of Levulinic Acid

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The demonstration by Thomas and Schuette[3] that the yield of levulinic acid from cane sugar can be increased from 22 to 42% of the theoretical by raising the reaction temperature from 100 to 162° has encouraged us to attempt the practical manufacture of the esters of levulinic acid. As a part of our study we have prepared twelve alkyl levulinates and examined them for possible utility,[4] and have developed a more efficient method of preparation of the esters.

Sah and Ma[5] have described seven aliphatic esters of levulinic acid, and Schuette and Cowley[6] and Cowley and Schuette[7] have investigated the series, notably all straight chain compounds up to and including *n*-decyl levulinate. The esters which we have prepared and studied include four which have not been previously described: namely, secondary butyl, 2-methylbutyl, methylpropyl carbinol and diethylcarbinol levulinates. We have determined the surface tensions of the esters and have reëxamined the physical properties of most of those previously known.

McKenzie[8] has shown that in the preparation of levulinic acid from sucrose at atmospheric pressure, 22% of the theoretical yield can be obtained. We have found that the *crude sirup* of levulinic acid as prepared by McKenzie yields 29–37.3% of pure esters when esterified with various alcohols. The superior efficiency of recovery of the levulinic values by esterification of crude levulinic acid is further shown by our yield of 40% of *n*-butyl levulinate from crude levulinic acid prepared at temperatures near 146° compared with the 34.3% yield of acid reported by Thomas and Schuette[3] at 145°.

We have obtained small yields (maximum, 11.0%) of *n*-butyl levulinate by boiling a mixture of *n*-butyl alcohol, sucrose and hydrogen chloride. We have also found that *n*-butyl alcohol will extract levulinic acid from crude solutions and that the ester can be prepared in good yield from such extracts. But these methods yield *n*-butyl formate and *n*-butyl chloride as additional products and are not as convenient as direct esterification of crude levulinic acid *sirup* as described below.

Experimental

We have prepared levulinic acid by two methods, which are essentially those of

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(1) Senior Industrial Fellow.

(2) Industrial Fellow.

(3) Thomas and Schuette, THIS JOURNAL, **53**, 2324 (1931).

(4) Cox and Dodds, *Ind. Eng. Chem.*, in press.

(5) Sah and Ma, THIS JOURNAL, **52**, 4880 (1930).

(6) Schuette and Cowley, *ibid.*, **53**, 3485 (1931).

(7) Cowley and Schuette, *ibid.*, **55**, 387 (1933).

(8) McKenzie, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1932, Collective Vol. I, p. 328.

McKenzie[8] and Thomas and Schuette.[3] We have prepared only *n*-butyl levulinate from crude levulinic acid obtained by the autoclave method.

Levulinic Acid.—To 6000 cc. of water in a 12-liter flask were added 3000 g. of cane sugar and 1500 cc. of concentrated hydrochloric acid. The mixture was boiled in an oil-bath with continuous stirring for twenty-four hours. Humus material, average weight 660 g., was filtered off and washed. The filtrate and washings were evaporated *in vacuo* to a sirup, weighing 1400–1500 g.

A two-gallon Pfaudler enameled still was used as an autoclave for preparing levulinic acid at higher temperatures. The raw material consisted of 1800 g. of cane sugar, 3500 cc. of water and 885 cc. of concentrated hydrochloric acid. With steam pressure of 75 lbs. per sq. in. in the jacket, the mixture was heated for one hour after a temperature of 120° had been reached. A maximum temperature of 146° was attained. The preparation was completed by the same procedure as used for levulinic acid made at atmospheric pressure. The yield was 650–750 g. of sirup.

Levulinic Esters.—The preparation of 2-methylbutyl levulinate is typical of the esterification of crude levulinic acid. The crude levulinic acid sirup was washed into a two-necked, 5-liter round-bottomed flask with 2000 g. of 2-methylbutanol[9] and 100 cc. of concentrated hydrochloric acid. The flask was equipped with a motor stirrer and with a water separator in series with a reflux condenser. Esterification was effected by boiling over a free flame. When most of the water had been separated, the mixture was cooled and the alcohol solution decanted from a gummy material. The heating was then continued until water separation was negligible. The alcohol was distilled and the ester recovered by distillation *in vacuo*. The ester so obtained was yellow and contained free acid. The acid was removed by shaking the ester with anhydrous sodium carbonate and most of the color by means of "norit." The yield from cane sugar treated at atmospheric pressure was 1175 g., or 36.0% of the theoretical. Yields of 29.0 to 37.3% of the theoretical were obtained from other alcohols treated similarly.

From one lot of levulinic acid made in the autoclave from 1800 g. of sugar, 725 g. of *n*-butyl levulinate or 40.0% of the theoretical, was obtained.

Physical Constants.—The samples used for the determination of the physical constants were obtained from the middle fractions in two successive redistillations of the respective esters. Vapor pressure was determined in the apparatus of Ramsay and Young.[10] Anschütz thermometers, calibrated by the Bureau of Standards, were used. Pressures were read on a closed manometer, which was checked for accuracy by comparison with a standard barometer. An accessory long-stem thermometer was used with its bulb placed below the delivery tube of the boiling flask but above the mercury column of the Anschütz thermometer. Readings of the Anschütz thermometer were recorded when the readings on the accessory thermometer were constant, thus insuring total immersion of the short-stem thermometer in the vapor. The constants A, B and C in the vapor pressure–temperature equation, $\log P = A + B \log T + C/T$, were calculated from ten pairs of observations for the four new esters. The formulas are shown in Table I. The boiling points of all the esters were observed in the Ramsay and Young[10] apparatus. A pressure equivalent to 760 mm. of mercury at 0° was maintained as the boiling temperature was observed.

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[9] Alcohols of the amyl series were supplied by the Sharples Solvents Corporation.

[10] Ramsay and Young, *J. Chem. Soc.*, **47**, 42 (1885).

TABLE I

VAPOR PRESSURE–TEMPERATURE EQUATIONS AND BOILING POINTS OF ALKYL LEVULINATES

Alkyl	Log *P*	Boiling point, °C., 760 mm. Observed	Calculated
Methyl		196.0	197.7[a]
Ethyl		205.8	206.2[a]
n-Propyl		221.2	221.2[a]
Isopropyl		209.3	208.2[a]
n-Butyl		237.8	237.8[a]
Isobutyl		230.9	229.9[a]
Sec-butyl	$12.0748 - 1.2307 \log T - 2928.8/T$	225.8	225.5
n-Amyl		253.4	253.2[a]
Isoamyl		248.8	247.9[a]
Methylpropylcarbinol	$30.2454 - 7.0487 \log T - 4236.6/T$	239.6	239.6
Diethylcarbinol	$40.2863 - 10.2810 \log T - 4890.3/T$	239.0	239.3
2-Methylbutyl	$17.8985 - 3.0375 \log T - 3515.8/T$	247.2	246.2

[a] Calculated by Schuette and Cowley, Ref. 6.

TABLE II

SPECIFIC GRAVITY, SURFACE TENSION AND PARACHORS OF ALKYL LEVULINATES

	Specific gravity, 20/4°			Surface tension and parachors		
Alkyl	Observed	Sah and Ma	Schuette and Cowley	Surface tension, dynes, cm.	Parachor observed	Parachor theoretical
Methyl	1.04945	1.05113	1.05145	38.8	309.9	304.2
Ethyl	1.01114	1.01336	1.01346	35.7	347.7	344.2
n-Propyl	0.98955	0.98988	0.99007	34.2	386.7	384.2
Isopropyl	.98724	.98422	.98005	32.7	386.3	381.2
n-Butyl	.97353	.97452	.97350	34.4	427.9	424.2
Isobutyl	.96770	.97047	.96926	33.0	426.9	421.2
Sec-butyl	.96698			32.7	425.4	421.2
n-Amyl	.96136		.96357	34.0	468.6	464.2
Isoamyl	.96029	.95921	.95827	32.6	463.3	461.2
Methylpropylcarbinol	.95569			32.4	465.5	461.2
Diethylcarbinol	.95905			33.1	465.8	461.2
2-Methylbutyl	.96072			33.1	465.0	461.2

TABLE III

INDEX OF REFRACTION AND MOLECULAR REFRACTION OF ALKYL LEVULINATES

	Index of refraction at 20°			Molecular refraction, Lorenz–Lorentz		
Alkyl	Authors	Sah and Ma	Schuette and Cowley	Observed Authors	Sah and Ma	Calculated
Methyl	1.42333	1.4231	1.4223	31.58	31.52	31.77
Ethyl	1.42288	1.4225	1.4218	36.28	36.17	36.38
n-Propyl	1.42576	1.4255	1.4251	40.92	40.88	40.98
Isopropyl	1.42088	1.4220	1.4211	40.98	40.83	40.98
n-Butyl	1.42905	1.4290	1.4283	45.59	45.53	45.58
Isobutyl	1.42677	1.4264	1.4251	45.65	45.48	45.58
Sec-butyl	1.42499			45.51		45.58
n-Amyl	1.43192		1.4316	50.21		50.19
Isoamyl	1.43102	1.4310	1.4294	50.18	50.23	50.19
Methylpropylcarbinol	1.42808			50.12		50.19
Diethylcarbinol	1.42890			50.03		50.19
2-Methylbutyl	1.43100			50.16		50.19

The specific gravities of the esters at 20/4° were determined by means of a calibrated 25-cc. pycnometer. Surface tension was measured by means of the du Noüy tensiometer. The parachors were calculated by the formula $M\gamma^{1/4}/d$, in which M is the molecular weight, γ is the surface tension in dynes per centimeter and d is specific gravity. The theoretical values are based on the constants of Mumford and Phillips,[11] namely, C = 9.2, H = 15.4, O = 20, double bond = 19, branched chain = −3 and carbonyl in ester = −3. Indices of refraction were measured by means of the Zeiss immersion refractometer. The molecular refraction for each ester was calculated from the Lorenz–Lorentz atomic values.

Summary

1. The yield of levulinic esters from cane sugar has been improved by esterification of *crude* levulinic acid and purification of the resulting esters.
2. Four new alkyl esters of levulinic acid have been prepared.
3. Observations have been made of corrected boiling point, specific gravity, surface tension and index of refraction of twelve alkyl esters of levulinic acid.

(11) Mumford and Phillips, *J. Chem. Soc.*, 2112 (1929).

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1-Diphenylene-3-phenylindene

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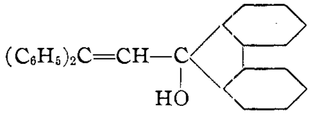
In a recent paper by E. Bergmann and others[1] α-diphenylene-γ,γ-diphenylallyl alcohol (I) is described as a solid melting at 118–121° with gas evolution. In the same paper it is noted that when this alcohol is warmed with acetic acid or with acetyl chloride there is formed a hydrocarbon melting at 139–140°, and this compound is formulated as α-diphenylene-γ,γ-diphenylallene (II).



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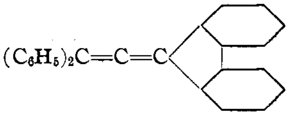

II

Experiments carried out in this Laboratory, which are the subject of the present communication, have led to somewhat different results and conclusions. α-Diphenylene-γ,γ-diphenylallyl alcohol obtained by the reaction of fluorenone with β,β-diphenylvinylmagnesium bromide, the same method as that used by the German investigators, melts at 98–99°; its dehydration by warming with acids results in the formation of a colorless

(1) Bergmann, Hoffmann and Meyer, *J. prakt. Chem.*, [2] **135**, 253 (1932).