acetic acid, 100 ml. of concd. hydrochloric acid, and 50 g. of phenone refluxed for twelve to sixteen hours, with 50-ml. portions of hydrochloric acid added at intervals of four to five hours, 50–70% yields of *p*-dibutylbenzenes were obtained. The products were purified by heating with and distilling from 10 g. of phosphorus pentoxide, followed by repeated distillation from sodium.

B. Alkylation.—This was accomplished in the manner previously described. If *n*-butyl alcohol was used, 0.12 mole of phosphorus pentoxide per 0.5 mole of alcohol was added after saturation with boron fluoride. From 0.5 mole of butylbenzene, 0.5 mole of *n*- or isobutyl alcohol, and 0.5 mole of boron fluoride, yields from 33 to 59% were obtained. Products were purified by fractionation from sodium.

Final determinations of physical properties were made with samples of constant boiling point, density and refractive index. The values are given in Table II.

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Summary

1. The isomeric *p*-di-butylbenzenes have been prepared by direct alkylation of the butylbenzenes or by acylation of the butylbenzenes followed by Clemmensen reduction.

2. The isomerization of *n*- and isobutyl groups to *s*- and *t*-butyl groups, respectively, by boron fluoride in alkylation procedures has been reconfirmed.

3. At temperatures up to 75° no isomerization of a butyl group already in the benzene ring is effected upon further alkylation by boron fluoride either alone or with phosphorus pentoxide.

4. The eight new *p*-butylbutyrophenones have been prepared and described.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MARSHALL COLLEGE]

Some Esters of Normal Aliphatic Alcohols and Acids[1]

BY JOHN H. HOBACK, DENZIL O. PARSONS AND J. F. BARTLETT

In order to obtain further light on the variation in melting point, boiling point, density and refractive index of an homologous series of esters of normal alcohols and acids, we have undertaken the preparation of a number of these esters, some new, and some already known, and have measured their physical properties.

TABLE I

PROPERTIES OF THE ESTERS

Ester	B. p., °C. at 20 mm. (cor.)	M. p., °C. (cor.)	n^{25}_D	d^{25}_0	d^{25}_4	Saponification equivalents Calcd.	Found
Propyl caproate	85.28[a]	−68.7	1.4109	0.8847[c]	0.8632	158.1	156.3
Butyl caproate	99.21[b]	−64.3	1.4153	.8821[d]	.8623	172.2	171.6
Amyl caproate	116.6	−47.0	1.4202	.8801	.8612	186.2	186.7
Nonyl caproate	173.3	−22.3	1.4318	.8767	.8582	242.2	241.4
Undecyl caproate	198.4	−10.5	1.4365	.8749	.8569	270.3	271.6
Dodecyl caproate	221.3	− 4.6	1.4382	.8743	.8562	284.3	282.2
Tridecyl caproate	Decom.	6.9	1.4396	Solid	.8550	298.3	301.4
Tetradecyl caproate	Decom.	2.0	1.4414	Solid	.8543	312.3	313.3
Pentadecyl caproate	Decom.	16.3	1.4422	Solid	.8536	326.3	327.8
Propyl heptylate	98–100	−63.5	1.4158	0.8823	.8610	172.2	172.5
Butyl heptylate	112–114	−67.5	1.4204	.8799	.8592	186.2	185.5
Amyl heptylate	118–119	−49.0	1.4231	.8780	.8580	200.2	198.0
Propyl caprylate	112–113	−45.0	1.4201	.8820	.8616	186.2	185.5
Butyl caprylate	121–122	−43.0	1.4232	.8786	.8584	200.2	202.0
Amyl caprylate	124–126	−34.5	1.4262	.8770	.8562	214.2	213.5
Propyl pelargonate	120–122	−36.0	1.4236	.8744	.8540	200.2	197.0
Butyl pelargonate	122–124	−38.0	1.4262	.8720	.8520	214.2	212.0
Amyl pelargonate	130–132	−27.0	1.4318	.8701	.8506	228.2	228.0

[a] B. p. 760 mm. 185.5°, Gartenmeister, *Ann.*, **233**, 279 (1886) [b] B. p. 760 mm. 204.3°, Gartenmeister. [c] d^0_0 0.8844, Gartenmeister. [d] d^0_0 0.8824, Gartenmeister.

Preparation.—The esters were prepared from the appropriate alcohols and acids[2] by refluxing

(1) Abstracted from Theses presented by John H. Hoback and Denzil O. Parsons for the degree of Master of Science.

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them in the presence of *p*-toluenesulfonic acid as a catalyst and using benzene as a solvent. The benzene was removed by distillation under slightly reduced pressure and the residual esters were washed with water, 1 to 50 ammonia water[3] and again with water, re-dissolved in benzene and then dried over calcium chloride. Fractionation at 20 mm. was carried out and in each case a sample having a boiling range of 0.5° was collected. These samples were further purified by repeated crystallization from pentane until successive crops showed a constant melting point. Such crops were regarded as pure and were used in the determination of the physical properties. The saponification equivalent of each ester was determined using the method of Redemann and Lucas.[4]

Physical Constants.—The physical constants of the esters and their saponification equivalents are listed in Table I.

Melting points of all the esters prepared are plotted in Fig. 1.

It will be observed that the segments of curves II and IV show the same general character, and that curve III and that part of curve I which represents the melting points of the propyl, butyl and amyl caproates, resemble each other very closely. Curves II and IV represent the esters of acids which possess odd numbers of carbon atoms, whereas curves I and III represent the esters of acids which possess even numbers of carbon atoms. These curves indicate that there is a regular variation between esters, the parent acids of which all contain an odd or all an even number of carbon atoms. Work is in progress at the present time to extend the series of the esters of heptylic acid and thus furnish additional data to extend curve II.

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(3) Ruhoff and Reid, THIS JOURNAL, **55**, 3827 (1933).

(4) Redemann and Lucas, *Ind. Eng. Chem., Anal. Ed.*, **9**, 521 (1937).

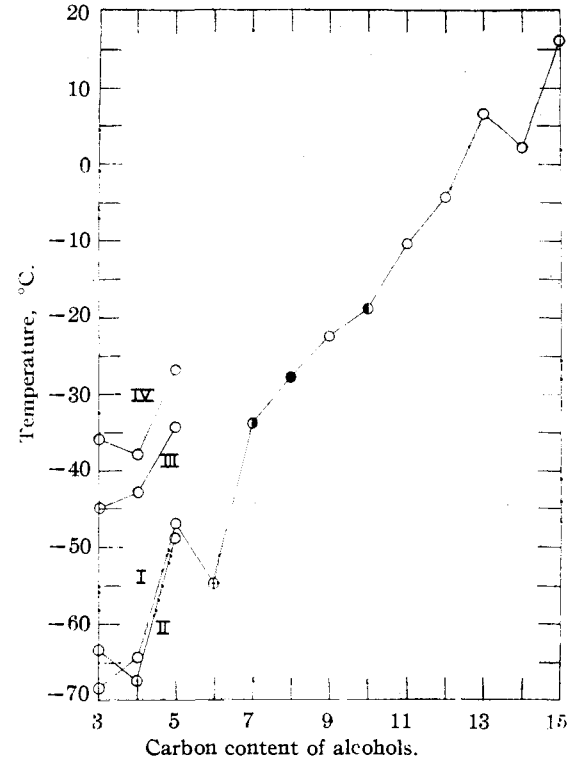

Fig. 1.—Melting points of esters of caproic, heptylic, caprylic and pelargonic acids: I, caproates; II, heptylates; III, caprylates; IV, pelargonates; points ⊕ ◐ ● are from Bilterys and Gissileire, *Bull. soc. chim. belg.*, **44**, 567–586 (1922); **55**, 3815–3818 (1933).

Summary

Nine esters not previously known, namely, nonyl, undecyl, dodecyl, tridecyl, tetradecyl and pentadecyl caproates, and the propyl, butyl and amyl pelargonates, and nine other propyl, butyl and amyl esters, already known, of caproic, heptylic and caprylic acid, have been prepared and their common physical properties determined.

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