mμ, ε 8300.[11] The ketone was unreactive toward semicarbazide acetate.

$\Delta^{9,11:8,14:22,23}$-Stigmastatrienol-3-one-7 Acetate (VI).—The acetylated ketonic fraction of the preceding section was chromatographed and 1.2 g. of the trienone VI was isolated. It was recrystallized from aqueous acetone. m. p. 190–192°, $[\alpha]^{23}\text{D}$ $-24 \pm 2°$ (0.82% in chloroform).

Anal. Calcd. for $C_{31}H_{46}O_3$: C, 79.78; H, 9.95. Found: C, 79.92; H, 10.10.

The substance had an absorption maximum at 299 mμ, ε 5300.

The same product (VI) was obtained from either of the pure ketoxides III or IV by refluxing them with hydrochloric acid in ethanol followed by acetylation in pyridine–acetic anhydride.

$\Delta^{8,14}$-Stigmastenol-3-one-7 Acetate (V).—Palladium black (50 mg.) in ethanol was saturated with hydrogen, and 100 mg. of the trienone VI dissolved in ethanol was added. In one hour 11 cc. (2.1 moles) of hydrogen had been adsorbed. The product was recrystallized from 80% ethanol, m. p. 140–141°; $[\alpha]\text{D}$ $-53 \pm 1.5°$ (0.87% in chloroform).

Anal. Calcd. for $C_{31}H_{50}O_3$: C, 79.10; H, 10.71. Found: C, 79.03; H, 10.48.

The substance had an absorption maximum at 260 mμ, ε 7800.

When the trienone V was hydrogenated with palladium black or platinum oxide in acetic acid, the sole product was α-spinastenyl acetate, m. p. 117°; $[\alpha]\text{D}$ $13 \pm 1°$ (0.61% in chloroform).

Anal. Calcd. for $C_{31}H_{52}O_2$: C, 81.52; H, 11.48. Found: C, 81.28; H, 11.40.

Summary

Mild oxidation of α-spinasteryl acetate yielded three pure products, the α,β-unsaturated ketone II, and two isomeric α,β-ketoxides III and IV. When heated with hydrochloric acid in ethanol both ketoxides were converted into the same trienone VI, which was reduced catalytically to the $\Delta^{8,14}$-7-ketone V. The compounds II, III, IV, V and VI are entirely analogous to the corresponding derivatives obtained by the same procedures from α-dihydroergosteryl acetate. The two series are homologous and differ only by one carbon atom in the side chain.

Comparison of these two series with the compounds obtained by the same procedures from $\Delta^{8,14}$-ergostenol-3(α-ergostenol) leads to the conclusion that the nuclear double bond of α-spinasterol, like that of α-dihydroergosterol, lies between carbon atoms 8 and 9, rather than 8 and 14, as proposed by Fernholz and Ruigh.[6] Therefore α-spinasterol is $\Delta^{8,9:22,23}$-stigmastadienol-3.

A $\Delta^{7,8}$ or $\Delta^{8,9}$ steroid double bond will not invariably shift to the 8,14 position when a $\Delta^{7,8}$- or $\Delta^{8,9}$-steroid is shaken with a hydrogenating catalyst and nitrogen. It is unsafe to conclude from a negative result obtained in the absence of hydrogen that the double bond occupies the 8,14 position.

NEW BRUNSWICK, N. J. RECEIVED APRIL 29, 1943

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[11] All spectrographic measurements were made in absolute ethanol.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

The Isomeric p-Dibutylbenzenes[1]

BY G. F. HENNION AND LAWRENCE A. AUSPOS

Introduction

Investigations[2,3,4] conducted in this Laboratory on the alkylation of benzene and alkylbenzenes with alcohols and boron fluoride, alone or with a co-condensing agent such as phosphorus pentoxide, sulfuric acid, or benzenesulfonic acid, have led to the conclusions (a) that the dialkylbenzenes so obtained are almost exclusively of the *para* constitution and (b) that isomerization of *n*- and isobutyl groups occurs, thus introducing *s*- and *t*-butyl groups, respectively. The present investigation was undertaken in order to make available for comparison purposes all the possible p-di-butylbenzenes. By means of these data we hope to extend our alkylation studies, especially in connection with isomerizations and rearrangements. Authentic reference compounds are needed since no other means are available for determining the structure of a butyl group in a complex hydrocarbon.

Only two of the ten possible p-dibutylbenzenes are well known. The di-tertiary isomer has been reported many times,[2,3,5] while the di-secondary

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[1] Paper XXVIII on organic reactions with boron fluoride; previous paper THIS JOURNAL, **64**, 2751 (1942).

[2] McKenna and Sowa, *ibid.*, **59**, 470 (1937).

[3] Toussaint and Hennion, *ibid.*, **62**, 1145 (1940).

[4] Welsh and Hennion, *ibid.*, **63**, 2603 (1941).

[5] (a) Goldschmidt, *Ber.*, **15**, 1067 (1882); (b) Meyer and Bernhauer, *Monatsh.*, **53-54**, 721 (1929); (c) Ipatieff and Pines, THIS JOURNAL, **58**, 1056 (1936); (d) Simons and Archer, *ibid.*, **60**, 986, 2952, 2953 (1938); (e) Potts and Dodson, *ibid.*, **61**, 2553 (1939).

compound is more recent.[2,3,4,5b,6] The *p*-di-*n*-butylbenzene was reported[7] as having been obtained from a Wurtz–Fittig reaction between *p*-dichlorobenzene and *n*-butyl chloride. The boiling point given (225°), however, is much lower than that found in this work. In the previously reported instances the *p*-dibutylbenzenes are of symmetrical structure and apparently no isomer containing unlike butyl groups was ever prepared.

In this research the second butyl group was introduced in the *para* position of the various butylbenzenes by two methods: (a) *n*- and isobutyl groups by Friedel–Crafts acylation and Clemmensen reduction, and (b) *s*- and *t*-butyl groups by alkylation with *n*- and isobutyl alcohols by means of boron fluoride, phosphorus pentoxide being used as an assistant in the former case. All of the unsymmetrical *p*-dibutylbenzenes were thus prepared in two ways, depending upon which of the two groups was introduced first, while the symmetrical compounds could be obtained in but one.

There are slight discrepancies in some of the physical properties of like compounds made by reduction and by alkylation. This is attributed to the presence of a small amount of *ortho* isomer in the latter cases. The experimental evidence indicates that the product obtained by the reduction method is purer than the corresponding compound prepared by direct alkylation. The following disagreements in physical properties were noted: *p*-*n*-butyl-*s*-butylbenzene by reduction, d^{20} 0.8570, by alkylation, 0.8585; *p*-*s*-butyl-isobutylbenzene by reduction, d^{20} 0.8511, by alkylation, 0.8534; *p*-*t*-butyl-isobutylbenzene by reduction, d^{20} 0.8547, $n^{20}\text{D}$ 1.4875, by alkylation, d^{20} 0.8543, $n^{20}\text{D}$ 1.4867. The atmospheric boiling points of *p*-*n*-butyl-*s*-butylbenzene and *p*-*s*-butyl-isobutylbenzene prepared by alkylation were 2° lower than for the same compounds prepared by Clemmensen reduction. The symmetrical dibutylbenzenes were obtained crystalline on cooling with solid carbon dioxide. The unsymmetrical compounds, with the exception of *p*-*n*-butyl-*t*-butylbenzene, could not be induced to crystallize because of glassing. Of the two samples of *p*-*n*-butyl-*t*-butylbenzene the one obtained by Clemmensen reduction had the higher freezing point.

Oxidation of each of the compounds by the method of Welsh and Hennion[4] gave terephthalic acid, identified as the dimethyl ester, m. p. 140°. Fusion of the acid with resorcinol gave no appreciable fluorescein although the samples prepared from dibutylbenzenes made by alkylation procedures gave a somewhat more definite test than the corresponding compounds made by reduction.

Attempts to prepare the *p*-dibutylbenzenes by Wurtz–Fittig reactions resulted in reduction of the halobenzenes employed. Thus from *p*-*s*-butylbromobenzene[1] and *n*-butyl bromide, a 36% yield of *s*-butylbenzene was obtained while from the reaction between *p*-dibromobenzene and *n*-butyl bromide, a 31% yield of *n*-butylbenzene resulted.

In no case of direct alkylation with boron trifluoride, either alone or aided by phosphorus pentoxide, was there any isomerization of a butyl group already in the ring.

Experimental

Materials.—Boron trifluoride was obtained from the Harshaw Chemical Company and used as received. The butyl alcohols were obtained from the Commercial Solvents Corporation and were carefully fractionated through a helix packed column, and only those fractions of proper boiling point and index of refraction used. The bromobenzene, and *n*- and isobutyryl chlorides were supplied by the Eastman Kodak Company and were fractionated before use. The alkyl bromides were prepared in the conventional manner[8] and were purified with the usual care. The benzene was of C. P. quality and was dried over sodium and fractionated.

Equipment.—All reaction products were fractionated through either a 40 cm. glass-helix packed, partial take-off column or a 45 cm. modified Podbielniak total take-off column containing a no. 23 Nichrome wire spiral.

Preparation of the Four Isomeric Monobutylbenzenes.—*n*-Butylbenzene was prepared in a variety of ways. Yields of 15–58% were obtained by the Wurtz–Fittig reaction[9] using 2.3 gram atoms of sodium, 1.15 moles of *n*-butyl bromide, and 1 mole of bromobenzene. As proof of structure, *n*-butylbenzene was prepared also in small yield by the reaction of benzyl chloride with *n*-propylmagnesium bromide in ether solution, and by the Wurtz reaction, equimolar quantities of benzyl chloride and *n*-propyl bromide being heated at 100–130° with excess sodium for twenty hours. The best method from the standpoint of ease of procedure and yields obtained was the reduction of *n*-butyrophenone,[10] obtained in 86% yield, b. p. 120° at 28 mm., $n^{20}\text{D}$ 1.5191, semicarbazone m. p. 188.5–189°, by the method of Clemmensen as modified by Martin.[11] The reduction gave a 73% yield of *n*-butylbenzene which could be increased to 85% by retreating the higher boiling residues. The crude hydrocarbon was purified by heating

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(6) Koch and Steinbrink, *Brennstoff-Chem.*, **19**, 277 (1938).

(7) Morgan and Hickinbottom, *J. Chem. Soc.*, **119**, 1879 (1921).

(8) "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., 1932, Coll. Vol. 1, p. 26.

(9) Read and Foster, THIS JOURNAL, **48**, 1606 (1926).

(10) Schmidt, Hopp and Schoeller, *Ber.*, **72B**, 1893 (1939).

(11) Martin, THIS JOURNAL, **58**, 1438 (1936).

TABLE I

PHYSICAL PROPERTIES AND ANALYSES OF THE *p*-BUTYLBUTYROPHENONES

Butyl-	Butyro-	B. p. °C.	Mm.	$n^{20}D$	d^{20}_4	Mol. wt.[a] Obsd.	Carbon[b] Obsd., %	Hydrogen[c] Obsd., %
n-	*n*-	138	6	1.5129	0.9450	204	82.28	9.91
n-	*i*-	118	3	1.5106	.9437	202	82.45	10.16
s-	*n*-	125	3	1.5130	.9453	199	82.21	10.08
s-	*i*-	116	3	1.5114	.9418	201	82.20	10.01
i-	*n*-	142	8	1.5110	.9398	200	82.22	9.68
i-	*i*-	121	7	1.5096	.9355	202	82.50	9.98
t-	*n*-	128	5	1.5130	.9456	201	82.49	10.12
t-	*i*-	140	4	1.5116	.9436	206	82.41	9.77

[a] Calcd., 204.26. [b] Calcd., 82.36%. [c] Calcd., 9.88%.

TABLE II

PHYSICAL PROPERTIES AND ANALYSES OF *p*-DIBUTYLBENZENES

p-Butyls	B. p. °C.	Mm.	B. p., °C. at 15 mm.	$n^{20}D$	d^{20}_4	M. p., °C.	Mol. wt.[a] Obsd.	Carbon[b] Obsd., %	Hydrogen[c] Obsd., %
Di-*n*-	259	745	124	1.48792	0.8556	−24	187	88.09	11.61
n-*s*-	250	739	117	1.48849	.8570		188	88.62	11.74
n-*i*-	251	743	118	1.48580	.8508		190	88.57	11.74
n-*t*-	248	743	116	1.48984	.8595	−46	188	88.56	11.81
s-*i*-	241	739	113	1.48560	.8511		190	88.63	11.76
Di-*s*-	239	739	108	1.48782	.8573	−58	186	88.47	11.70
s-*t*-	235	745	108	1.48916	.8607		187	88.56	11.72
Di-*i*-	242	739	109	1.48338	.8456	−21	189	88.49	11.84
i-*t*-	239	751	109	1.48753	.8547		186	88.54	11.67
Di-*t*-	237	743	109	.....	....	77.7	190	88.47	11.84

[a] Calcd., 190.32. [b] Calcd., 88.34%. [c] Calcd., 11.65%.

with 15 g. of phosphorus pentoxide for five hours and then distilling therefrom. This was followed by redistillation from sodium. The acetamino derivative was prepared by the procedure of Ipatieff and Schmerling,[12] m. p. 104–104.5°.

All of the isobutylbenzene was prepared by the reduction of isobutyrophenone. This compound was made in the same manner as the *n*-isomer: yield 84%, b. p. 105° at 15 mm., $n^{20}D$ 1.5175; semicarbazone m. p. 167–167.5°. The reduction was carried out in the manner cited above; over-all yield, 80%. The acetamino derivative had m. p. 124–125.5°. As this is approximately the same as that of the corresponding derivative of *s*-butylbenzene, a mixed melting point was taken and found to be 101–106°, thus proving the non-identity of the two compounds.

s-Butylbenzene was best prepared in 84% yield by the direct alkylation of benzene with *n*-butyl alcohol using boron fluoride assisted by phosphorus pentoxide as reported previously.[3] The acetamino derivative melted at 124–125°. Using *s*-butyl alcohol no phosphorus pentoxide was required and a 52% yield of *s*-butylbenzene and 17.3% yield of *p*-di-*s*-butylbenzene were obtained. The acetamino derivative of the mono compound melted at 124.5–125°, and a mixed m. p. with the first sample, 124–125°. The density of the *s*-butylbenzene made from *s*-butyl alcohol was slightly lower than that from *n*-butyl alcohol probably due to the presence of a small amount of olefin polymer.

t-Butylbenzene was prepared in the same manner as the *s*-compound, using either iso- or *t*-butyl alcohol. Better yields and purer product were obtained from isobutyl alcohol. The yield from isobutyl alcohol was 41% with 8% *p*-di-*t*-butylbenzene, while with the tertiary alcohol the apparent yield was higher (48%), but the product had a low index of refraction, evidently due to isobutylene polymer which could not be separated by distillation. The best samples were purified by fractionation from sodium. The acetamino derivative melted at 168–169°.

The monobutylbenzenes had the following constants: *n*, b. p. 79° at 23 mm., $n^{20}D$ 1.4900, d^{20} 0.8608; *s*, b. p. 69° at 20 mm., $n^{20}D$ 1.4900, d^{20} 0.8623 from *n*-butyl alcohol and 0.8618 from *s*-butyl alcohol; *iso*, b. p. 59.5° at 12 mm., $n^{20}D$ 1.4871, d^{20} 0.8540; *t*, b. p. 62° at 16 mm., $n^{20}D$ 1.4914, d^{20} 0.8658.

Preparation of the Ten Isomeric *p*-Di-butylbenzenes.—The various *p*-di-butylbenzenes were prepared by one or both of two general methods, namely, by reduction of the butylbutyrophenones or by alkylation of the butylbenzenes. As the procedures are nearly identical for the specific applications of the general methods, only a typical example is given for each method.

A. Clemmensen Reduction.—The butylbutyrophenones were made as previously cited[10] with the exception that carbon disulfide was used as a solvent. From 0.4 mole of butylbenzene, 0.4 mole of butyryl chloride, 200 ml. of carbon disulfide, and 120 g. of aluminum chloride, the eight new *p*-butylbutyrophenones were obtained in yields from 76–91%. The physical constants and analyses are given in Table I.

The same method of reduction was used as previously described[11] with the exception that glacial acetic acid was substituted for the toluene in order to increase the solubility of the ketone in the aqueous layer. From 100 g. of zinc amalgam, 100 ml. of water, 15 ml. of glacial

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(12) Ipatieff and Schmerling, THIS JOURNAL, **59**, 1056 (1937).

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.

Acknowledgment.—The junior author (L.A.A.) gratefully acknowledges assistance given by the Organic Chemicals Division of the du Pont Company.

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.

NOTRE DAME, INDIANA RECEIVED MARCH 15, 1943

[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^{20}_D	d^0_4	d^{20}_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

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

[2] The authors are indebted to Sharples Chemicals, Inc., for the amyl alcohol and to Carbide and Carbon Chemicals Corporation for the caproic acid and butyl alcohol used in this work.