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GIACOMELLI G. P., LARDICCI L. *

ON THE MAXIMUM ROTATION OF (S)-1-PHENYL-3-METHYL-PENTANE: DETERMINATION OF THE RELATIONSHIP ROTATORY POWER-OPTICAL PURITY OF (S)-1-PHENYL-3-METHYL-1-PENTANONE

Riassunto — A partire da (—)(S)-2-metil-1-butanolo e mediante sequenze che procedono con ritenzione di configurazione ed esenti da racemizzazione, sono stati preparati il (+)(S)-1-fenil-3-metil-1-pentanone (I) e il (+)(S)-1-fenil-3-metilpentano (II). I poteri rotatori massimi di (I) ($[\alpha]^{25}_D$ 19,06) e di (II) ($[\alpha]^{25}_D$ 17,27) vengono stabiliti ed i valori ottenuti sono confrontati con quelli precedentemente pubblicati. Su questa base vengono corretti i poteri rotatori massimi di alcuni derivati dell'acido 2-metil-4-fenilbutanoico, riportati in letteratura.

Abstract — (+)(S)-1-phenyl-3-methyl-1-pentanone (I) and (+)(S)-1-phenyl-3-methylpentane (II) were prepared from (—)(S)-2-methyl-1-butanol by sequences proceeding with retention of configuration and no racemization. On the basis of the results obtained, $[\alpha]^{25}_D$ 19.06 and $[\alpha]^{25}_D$ 17.27 are established for the maximum rotatory power of (I) and (II) respectively. These data are compared with the ones previously reported in literature and the maximum rotations of some derivatives of 2-methyl-4-phenyl butanoic acid are corrected.

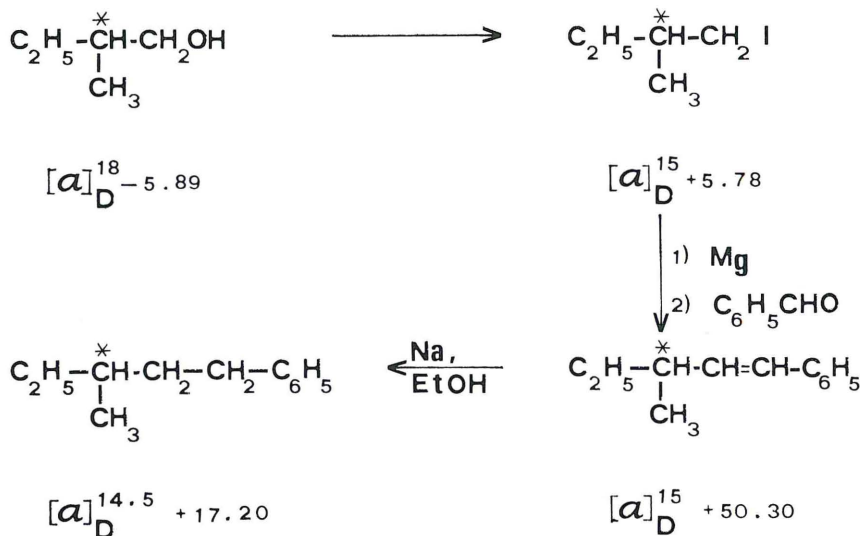
INTRODUCTION

In the course of our investigations on the mechanism of the reaction between alkyl aluminium compounds and aromatic nitriles, it was necessary to know the relationship between optical activity and optical purity of (+)(S)-1-phenyl-3-methyl-1-pentanone (I), which is a product of the reaction between (+)tris-[(S)-2-methylbutyl]-aluminium (L. CONTI et al. [1961]) and benzonitrile.

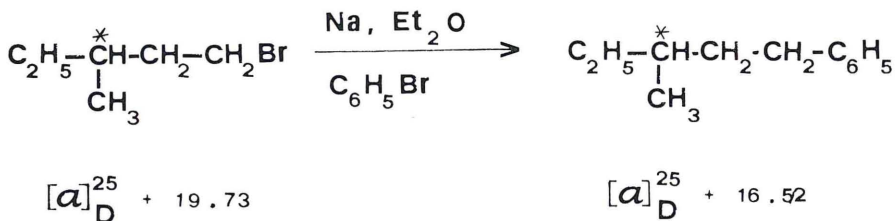
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(I) had been previously prepared by Friedel-Crafts acylation of benzene with (+)(S)-3-methylpentanoyl chloride (K. B. WIBERG and B. I. ROWLAND [1955]) and, more recently, by dithiane method (D. SEEBACH and D. STEINMÜLLER [1968]); its maximum rotatory power

Scheme 1



A. Klages and R. Sautter (1904)



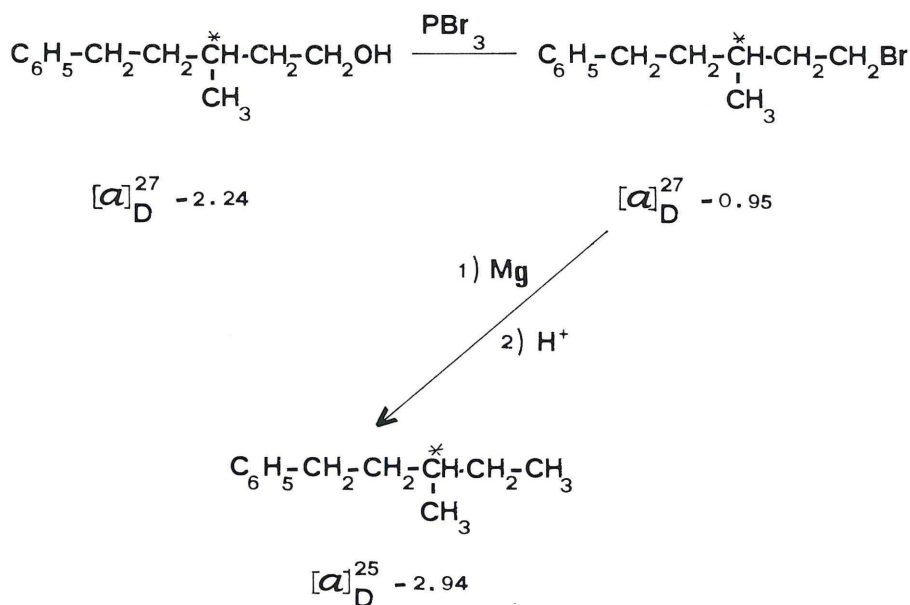
D. Hardin (1908)

was evaluated on the basis of the minimum optical purity of the starting materials. We have performed a new synthesis of (I) and, in order to compare our data with those formerly published, we have related its rotatory power to that of (+)(S)-1-phenyl-3-methyl-

pentane (II), by sequences proceeding without racemization, at least as generally accepted (L. LARDICCI and R. ROSSI [1962], L. LARDICCI et al. [1966]).

The synthesis of (II) had been performed by A. KLAGES and R. SAUTTER [1904], D. HARDIN [1908] (Scheme 1), P. A. LEVENE and R. E. MARKER [1935] (Scheme 2), and P. A. LEVENE and S. A. HARRIS

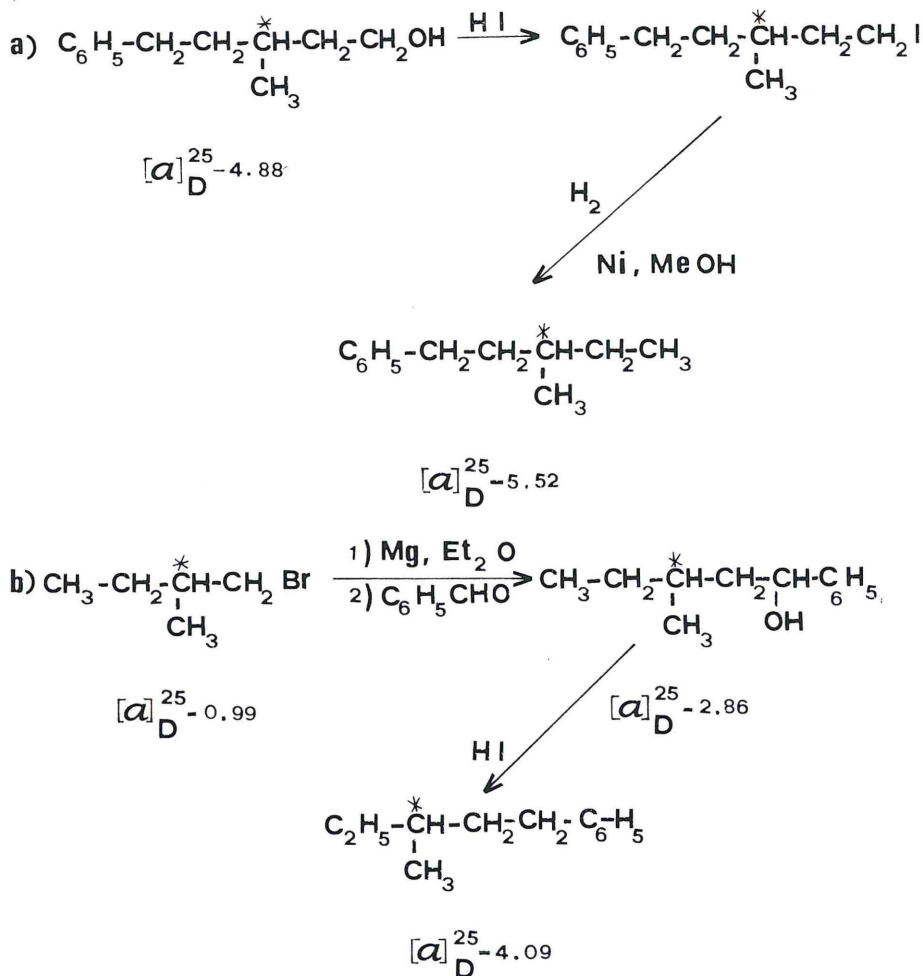
Scheme 2



P.A. Levene and R.E. Marker (1935)

[1935] (Scheme 3), who had also established a maximum rotatory power.

Moreover a detailed analysis indicates a disagreement of the data of A. KLAGES and R. SAUTTER [1904] and D. HARDIN [1908] with those of P. A. LEVENE and S. A. HARRIS [1935]; therefore it seemed necessary to carry out an independent evaluation of the maximum rotatory power of (+)(S)-1-phenyl-3-methyl-1-pentanone (I) and (+)(S)-1-phenyl-3-methylpentane (II) and, at the same time, a more accurate investigation of all the results previously published.

Scheme 3**P.A. Levene and S.A. Harris (1935)****RESULTS AND DISCUSSION**

(+)(S)-1-phenyl-3-methyl-1-pentanone (I) and the corresponding hydrocarbon (II) were obtained as reported in Scheme 4, starting from (—)(S)-2-methyl-1-butanol of known optical purity (R. Rossi et al. [1968]).

(+)(3S)-1-phenyl-3-methyl-1-pentanol (III) was prepared (71.4% yield) by the method of A. TSATSAS [1947], by reacting benzaldehyde with (+)(S)-2-methylbutyl magnesium chloride.

Chromic acid oxidation of (III) (P. E. VERKADE et al. [1964]) yielded (95%) (+)(S)-1-phenyl-3-methyl-1-pentanone (I), which was furthermore purified through the corresponding semicarbazone, according to the procedure of C. DJERASSI and L. E. GELLER [1959].

(I) was converted into (+)(S)-1-phenyl-3-methylpentane (II) by Wolff-Kishner reduction (Huang-Minlon modification) (85.9% yield) (L. LARDICCI and R. ROSSI [1962]).

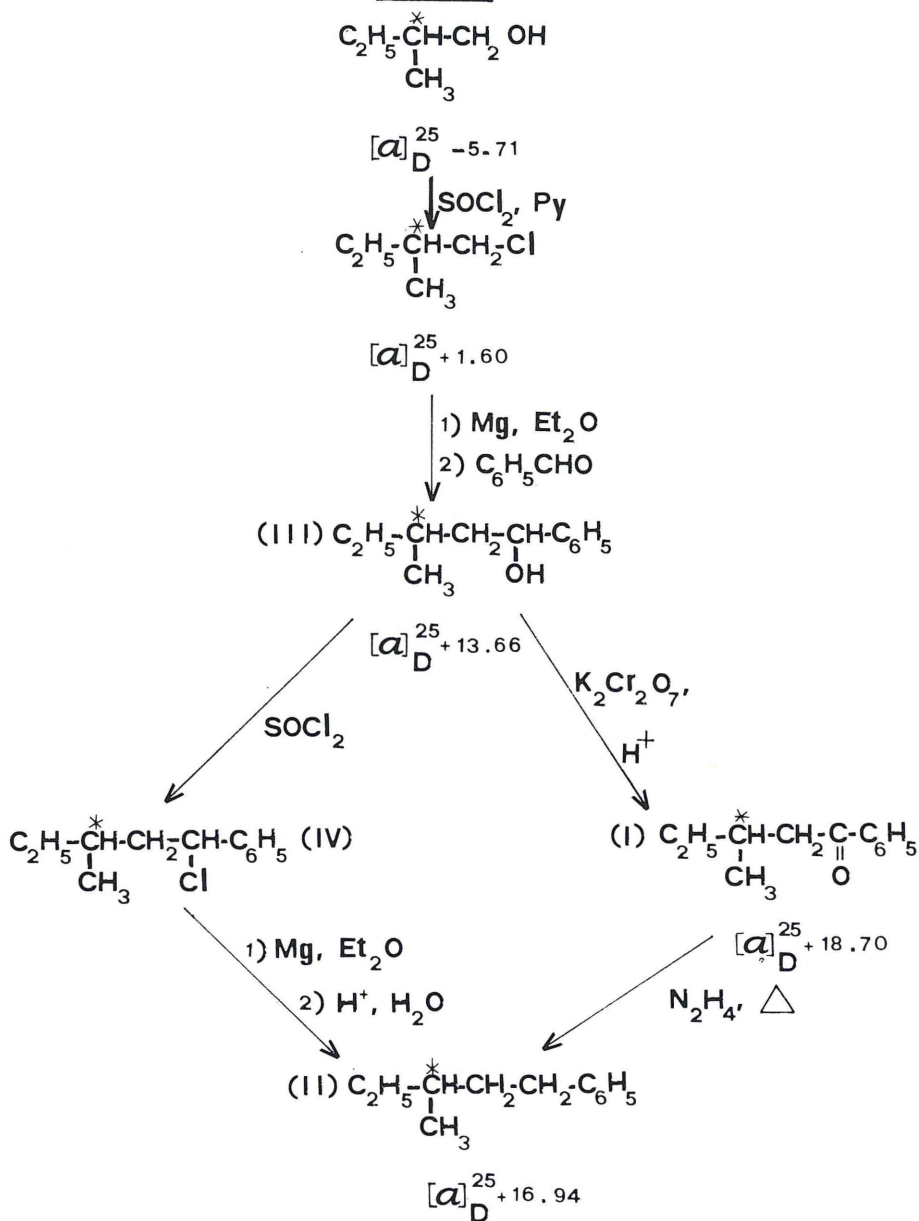
(+)(3S)-1-chloro-1-phenyl-3-methylpentane (IV) was obtained by reacting (III) and thionyl chloride according to a method, analogous to that employed by S. WINSTEIN and B. K. MORSE [1952] for the synthesis of 1-chloro-1-phenyl-2,2-dimethylpropane.

The hydrolysis of the (IV) Grignard reagent afforded a sample of (+)(S)-1-phenyl-3-methylpentane (II) with the same physical constants and rotatory power of that one obtained from (I) (Scheme 4).

On the basis of the results obtained and of the optical purity of the (+)(S)-1-chloro-2-methylbutane (P. PINO et al. [1961]) used in the sequence of Scheme 4, it is possible to establish $[\alpha]^{25}_D + 17.27$ for the maximum rotatory power of (+)(S)-1-phenyl-3-methylpentane (II), and $[\alpha]^{25}_D + 19.06$ for that of (+)(S)-1-phenyl-3-methyl-1-pentanone (I) (Table 1) in good agreement with what reported by K. B. WIBERG and B. I. ROWLAND [1955] and D. SEEBACH and D. STEINMÜLLER [1968] (Table 1). The reliability of this value is confirmed by the identical value of the optical rotatory power of the two specimens of (II) prepared by different routes (Scheme 4), since it is very unlikely that two different synthetic paths could have produced equal amounts of racemization.

As the values of the maximum rotatory power of (II), reported by A. KLAGES and R. SAUTTER [1904] and by D. HARDIN [1908], agree substantially with our data (Table 1), no appreciable racemization should be occurred in their synthetic sequences (Scheme 1), contrary to the considerations of P. A. LEVENE and S. A. HARRIS [1935].

Regard to the results published by these authors, it is to remark that the lowest value of the maximum molar rotation of (II) ($[M]^{25}_D 17.7$) (Table 1), might be explained on the basis i) of a relevant racemization in the adopted reactions (Scheme 3a) or/and ii) of a wrong evaluation of the maximum rotatory power of 3-me-

Scheme 4

thyl-5-phenyl-1-pentanol, directly dependent from that of the 2-methyl-4-phenylbutanoic acid.

TABLE 1

Maximum rotatory power of (S)-1-phenyl-3-methyl-1-pentanone (I) and (S)-1-phenyl-3-methylpentane (II), related to the optically active starting materials.

starting materials		(S)-1-phenyl-3-methyl-1-pentanone (I)				(S)-1-phenyl-3-methylpentane (II)			Reference
$[\alpha]^{25}_D$	optical purity %	$[\alpha]^{25}_D$	$[\alpha]^{25}_{D_{\max}}$	$[M]^{25}_{D_{\max}}$		$[\alpha]^{25}_D$	$[\alpha]^{25}_{D_{\max}}$	$[M]^{25}_{D_{\max}}$	
+ 5.78 ^{a, b}	~ 100	—	—	—		+ 17.2 ^c	+ 17.2 ^c	+ 27.9 ^c	A. KLAGES and R. SAUTTER [1904]
+ 19.73 ^{d, e}	96.5 ^e	—	—	—		+ 16.5 ^e	+ 17.1 ^e	+ 27.8 ^e	D. HARDIN [1908]
— 14.53 ^f	28.4	—	—	—		+ 5.52	+ 10.9	+ 17.7	P. A. LEVENE and S. A. HARRIS [1935]
+ 0.99 ^g	18.8	—	—	—		+ 4.09	+ 21.7	+ 35.1	P. A. LEVENE and S. A. HARRIS [1935]
+ 1.46 ^h	89.6	+ 17.5	+ 19.5	+ 34.4		—	—	—	K. B. WIBERG and B. I. ROWLAND [1955]
+ 4.80 ^{a, i}	~ 85.0	+ 16.7 ⁱ	+ 19.6 ⁱ + 19.0	+ 34.5 ⁱ + 33.6		—	—	—	D. SEEBACH and D. STEINMÜLLER [1968]
+ 1.60 ^h	98.1	+ 20.3 ⁱ + 18.7	+ 20.7 ⁱ + 19.0	+ 36.5 ⁱ + 33.6		+ 16.94	+ 17.3	+ 28.0	present research

a) (S)-1-iodo-2-methylbutane. b) t = 15°. c) t = 14.5°. d) (S)-1-bromo-3-methylpentane. e) interpolated values; based on maximum rotation of (S)-1-bromo-3-methylpentane (P. SALVADORI et al. [1968]). f) (R)-2-methyl-4-phenylbutanoic acid. g) (S)-1-bromo-2-methylbutane. h) (S)-1-chloro-2-methylbutane. i) t = 23°. l) ether, c ~ 5.

i) The maximum racemization encountered in the synthesis of (—)(R)-1-phenyl-3-methylpentane (II) according to Scheme 3a and evaluable from the sequences of Scheme 2 (P. A. LEVENE and R. E. MARKER [1935]) does not exceed 14%: the maximum rotation of (II), corrected on this basis ($[\alpha]^{25}_D$ 12.66), is however still low with respect to our value (Table 1).

Therefore we should conclude that ii) the maximum rotatory power of 2-methyl-4-phenylbutanoic acid, $[M]^{25}_D$ 51.20, established on resolution criteria by P. A. LEVENE and S. A. HARRIS [1935], should be effectively corrected to $[M]^{25}_D$ 69.85 (Table 2).

On the other hand the highest value ($[M]^{25}_D$ 35.1) (Table 1) of the maximum rotation of (II) (prepared from optically active 2-methyl-1-butanol according to Scheme 3b) is erroneous, since it has been deduced by P. A. LEVENE and S. A. HARRIS [1935] assuming, in a clear disagreement with recent literature data ⁽¹⁾, $[\alpha]^{25}_D$ —5.23 for the optically pure (—)(R)-1-bromo-2-methylbutane.

Table 2 reports the maximum molar rotations of some compounds, related by P. A. LEVENE and S. A. HARRIS [1935] to the hydrocarbon (II) and which are corrected on the basis of the previous considerations.

TABLE 2
Maximum rotations of derivatives of 2-methyl-4-phenylbutanoic acid.

$\text{C}_6\text{H}_5-(\text{CH}_2)_2-\overset{*}{\underset{\text{CH}_3}{\text{CH}}}$	$[M]^{25}_D$ max ^{a, b}	$[M]^{25}_D$ max ^{a, c}	$[M]^{25}_D$ max ^d corrected
—COOH	51.20	—	69.85
—CH ₂ OH	23.52	46.60	32.08
—CH ₂ Br	10.81	21.41	14.75
—CH ₂ —COOH	26.60	52.69	36.29
—CH ₂ —CH ₂ OH	17.03	33.72	23.23
—CH ₃ —CH ₂ Br	—	16.26	13.45
—CH ₂ —CH ₃	17.72	35.10	28.02

a) P. A. LEVENE and S. A. HARRIS [1935]. b) based on parent acid. c) based on hydrocarbon. d) based on maximum rotation of 3-methyl-5-phenyl-1-pentanol, from sequence of Scheme 2.

⁽¹⁾ On the accepted maximum rotation of (—)(R)-1-bromo-2-methylbutane ($[\alpha]^{25}_D$ —4.08) (L. LARDICCI and R. ROSSI [1962], L. LARDICCI et al. [1966], P. SALVADORI et al. [1968]), from the sequence of Scheme 3b it is possible to calculate, for the optically pure (II), $[\alpha]^{25}_D$ —17.0, a value which agrees very well with our and other's ones (Table 1).

EXPERIMENTAL SECTION

All boiling and melting points are uncorrected. Microanalyses were carried out by Microanalytical Laboratory of Donegani Institute, Novara, Italy. Glpc analyses were performed on a Carlo Erba Fractovap Mod. GT using a 2-m column filled with 10% butandiol succinate on Chromosorb W (60/80 mesh) and N_2 as carrier gas. The determination of optical activity was carried out using a Schmidt-Haensch polarimeter with sensitivity of $\pm 0.005^\circ$.

(+)(3S)-1-phenyl-3-methyl-1-pentanol. (III) - To a solution of 0.837 moles of (+)(S)-2-methylbutyl magnesium chloride (from (+)(S)-1-chloro-2-methylbutane, n_D^{25} 1.4102, $[\alpha]_D^{25} + 1.60$) in 650 ml of dry ether were added dropwise at -15° with stirring 74.3 g (0.723 moles) of benzaldehyde in 100 ml of anhydrous ether. The mixture was stirred at room temperature for $\frac{1}{2}$ hr, cautiously hydrolyzed with diluted sulphuric acid and then extracted with ether. The ether extracts were washed twice with 10% aqueous sodium carbonate. Distillation of the dried (Na_2SO_4) extracts gave 92.2 g (71.4% yield) of (III) b.p. $89-90^\circ$ (0.7 mm), n_D^{25} 1.5034, d_4^{25} 0.9477, $[\alpha]_D^{25} + 13.66$ (neat). *Anal.* Calcd. for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.42; H, 9.98.

(+)(S)-1-phenyl-3-methyl-1-pentanone. (I) - To a mixture of 24.2 g (0.135 moles) of (III) n_D^{25} 1.5034, $[\alpha]_D^{25} + 13.66$, and a solution of 31.5 g of potassium bichromate in 110 ml of water was added dropwise, while stirring, a mixture of 12.6 ml of concentrated sulphuric acid and 30 ml of water, the temperature gradually rising to 50° . The mixture was heated for $\frac{1}{2}$ hr at 55° , then cooled and extracted with ether. The ether solution was washed with 10% aqueous sodium carbonate and water. Distillation of the dried (Na_2SO_4) extracts afforded 22.8 g (95.5% yield) of (I), b.p. $136-137^\circ$ (20 mm), n_D^{25} 1.5082, which was purified through the semicarbazone derivative

The pure (+)(S)-1-phenyl-3-methyl-1-pentanone had b.p. $79-80^\circ$ (0.7 mm), n_D^{25} 1.5082, d_4^{25} 0.9566, $[\alpha]_D^{25} + 18.70$ (neat), $[\alpha]_D^{25} + 20.31$ (5.170 g/100 ml, ether), $[\alpha]_D^{25} + 20.46$ (5.184 g/100 ml, pentane). *Anal.* Calcd. for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.74; H, 9.09. K. B. WIBERG and B. I. ROWLAND [1955] reported b.p. $118-120^\circ$ (10 mm), n_D^{25} 1.5082, d_4^{25} 0.964, $[\alpha]_D^{25} + 17.39$ (neat).

The semicarbazone (*Anal.* Calcd. for $C_{13}H_{19}N_3O$: N, 18.01. Found: N, 18.19) and the 2,4-dinitrophenylhydrazone (*Anal.* Calcd.

for $C_{18}H_{20}N_4O_4$: N, 15.72. Found: N, 15.75) have m.p. 175° and 138° respectively.

(+)(3S)-1-chloro-1-phenyl-3-methylpentane. (IV) - (III) (38.1 g, 0.214 moles), $n_D^{25} 1.5034$, $[\alpha]_D^{25} + 13.66$ (neat), was added dropwise, with stirring, to 65.2 g (0.548 moles) of thionyl chloride, cooled at -10° . The mixture was kept in a ice-bath overnight and stirred at room temperature until gas evolution was complete (10 hr). The excess thionyl chloride was eliminated under vacuum, the mixture was cooled, poured into ice and then extracted with ether: the ether extracts were washed with saturated sodium bicarbonate solution and water. By rectification of the dried (Na_2SO_4) ether layer, several fractions (39.8 g) of (IV) were obtained. A redistilled sample, b.p. 96° (2 mm), $n_D^{25} 1.5080$, had $\alpha_D^{25} + 18.34^\circ$ (l 1, neat).

(+)(S)-1-phenyl-3-methylpentane. (II) - a) from (+)(S)-1-phenyl-3-methyl-1-pentanone (I) according to Huang-Minlon procedure. - A mixture of 14.6 g (0.083 moles) of (I), $n_D^{25} 1.5082$, $[\alpha]_D^{25} + 18.70$ (neat) and 15 ml of diethylene glycol was cooled at 0° and 12.5 g of hydrazine hydrate in 25 ml of diethylene glycol were added. After stirring at room temperature for 12 hr, 7.5 g of powdered potassium hydroxide and 25 ml of diethylene glycol were added. The mixture was refluxed for 1 hr and then was distilled until its temperature raised to 240° . The combined distillates were washed twice with 100 ml of water and dried (Na_2SO_4). Distillation gave 11.6 g (85.9% yield) of (II), b.p. $104-105^\circ$ (18 mm), $n_D^{25} 1.4853$, $d_4^{25} 0.8581$, $[\alpha]_D^{25} + 16.94$ (neat). *Anal.* Calcd. for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.80; H, 11.23. A. ROTHEN and P. A. LEVENE [1939] reported $n_D^{25} 1.4859$, $d_4^{25} 0.8585$.

b) from (+)(3S)-1-chloro-1-phenyl-3-methylpentane (IV) through Grignard reagent. - To 1.5 g of magnesium turnings were added 8.4 g (0.042 moles) of (IV), $n_D^{25} 1.5080$, $\alpha_D^{25} + 18.34^\circ$ (l 1, neat), in 30 ml of dry ether. The reaction was started with 0.01 ml of ethyl bromide. After refluxing for 2 hr, the mixture was cautiously hydrolyzed with diluted sulphuric acid. The layers were separated, the aqueous phase was extracted with ether and the combined ether solutions were dried (Na_2SO_4). There were recovered 6.7 g of crude product containing 42.8% of hydrocarbon, as shown by glpc analysis. On careful distillation 0.9 g of (II) were obtained: b.p. $102-103^\circ$ (13 mm), $n_D^{25} 1.4853$, $[\alpha]_D^{25} + 16.94$ (neat).

REFERENCES

- CONTI L., LARDICCI L., PINO P. (1961) - Sintesi del (+)tris-[(S)-2-metilbutil]-alluminio. *Chim. Ind. (Milan)*, **43**, 414-416.
- DJERASSI C., GELLER L. E. (1959) - Optical rotatory dispersion studies. XXIV. Effect of distance of a single asymmetric center from an aliphatic carbonyl function. *J. Am. Chem. Soc.*, **81**, 2789-2794.
- HARDIN D. (1908) - Sur la relation entre le pouvoir rotatoire et la constitution chimique. *J. Chim. Phys.*, **6**, 584-591.
- KLAGES A., SAUTTER R. (1904) - Ueber optisch active Benzolkohlenwasserstoffe. *Ber.*, **37**, 649-655.
- LARDICCI L., NAVARI F., ROSSI R. (1966) - Synthesis of some optically active α -alkylacrylic compounds containing a *sec*-butyl group. *Tetrahedron*, **22**, 1991-2001.
- LARDICCI L., ROSSI R. (1962) - Sulla purezza ottica di alcuni metilchetoni alifatici otticamente attivi. *Atti Soc. Toscana Sci. Nat. Pisa, Proc. Verballi Mem.*, **B68**, 23-42.
- LEVENE P. A., HARRIS S. A. (1935) - Maximum rotations of carboxylic acids containing a phenethyl group. *J. Biol. Chem.*, **111**, 725-733.
- LEVENE P. A., MARKER R. E. (1935) - The configurational relationship of acids of the phenethyl series to those of normal series. *J. Biol. Chem.*, **110**, 311-321.
- PINO P., LARDICCI L., CENTONI L. (1961) - Sintesi e determinazione della purezza ottica del (—)(S)-4-metil-1-esene. *Gazz. Chim. Ital.*, **91**, 428-440.
- ROSSI R., DIVERSI P., INGROSSO G. (1968) - On the relationship between the optical rotatory power and the optical purity of (+)(R)-methylsuccinic acid. *Gazz. Chim. Ital.*, **98**, 1391-1399.
- ROTHEN A., LEVENE P. A. (1939) - Rotatory dispersion and absorption spectra of carboxylic acids and hydrocarbons containing a phenyl or cyclohexyl group. *J. Chem. Phys.*, **7**, 975-983.
- SALVADORI P., LARDICCI L., STAGI M. (1968) - Su alcuni tioli e tioeteri alifatici otticamente attivi. *Gazz. Chim. Ital.*, **98**, 1400-1416.
- SEEBACH D., STEINMÜLLER D. (1968) - Preparation of (S)-2-methylbutyl and (S)-*sec*-butyl ketones from optically active 2-methyl-1-butanol by the dithiane method. *Angew. Chem. internat. Edit.*, **7**, 619-620.
- TSATSAS A. (1946) - Structure, transpositions intramoléculaires et absorption de quelques dérivés de l'acide β -butyl-tert. cinnamique. *Ann. Chim. (Paris)*, **12**, 342-394.
- VERKADE P. E., DE VRIES K. S., WEPSTER B. M. (1964) - Reactions of aliphatic halides with solutions of alkali metals in liquid ammonia. III. *Rec. Trac. Chim.*, **83**, 367-378.
- WIBERG K. B., ROWLAND B. I. (1955) - 1,3-Shifts. II. The stereochemistry of the rearrangement of α -alkoxystyrenes. *J. Am. Chem. Soc.*, **77**, 1159-1163.
- WINSTEIN S., MORSE B. K. (1952) - Neighboring carbon and hydrogen. VIII. Solvolysis of optically active α -phenylneopentyl derivatives. *J. Am. Chem. Soc.*, **74**, 1133-1139.

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