# ATTI
DELLA
# SOCIETÀ TOSCANA
DI
# SCIENZE NATURALI
RESIDENTE IN PISA

MEMORIE - SERIE A
VOL. LXXX - ANNO 1973

ARTI GRAFICHE PACINI MARIOTTI - PISA - 1973

# INDICE

MEMORIE

*Atti Soc. Tosc. Sci. Nat., Mem.*, Serie A, **80** (1973),
*pagg. 40-58, tabb. 2.*

A. M. CAPORUSSO, G. P. GIACOMELLI, L. LARDICCI *

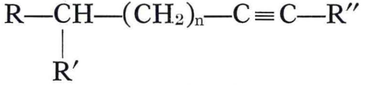
# (+)(S)-3,4-DIMETHYL-1-PENTYNE AND (+)(S)-3,4,4-TRIMETHYL-1-PENTYNE: SYNTHESIS AND ENANTIOMERIC PURITY

**Riassunto** — Viene descritta la preparazione del (+)(S)-3,4-dimetil-1-pentino (I) e del (+)(S)-3,4,4-trimetil-1-pentino (II) a partire dagli acidi (+)(S)-2,3-dimetilbutanoico e (+)(S)-2,3,3-trimetilbutanoico attraverso le corrispondenti α-olefine (+)(S)-3,4-dimetil-1-pentene (III) e (+)(R)-3,4,4-trimetil-1-pentene (IV). Sulla base dei risultati ottenuti nella determinazione della relazione potere rotatorio-purezza ottica di (I), (II), (III) e (IV) si conclude che le sequenze di sintesi adottate non comportano apprezzabili fenomeni di racemizzazione.

**Summary** — (+)(S)-3,4-dimethyl-1-pentyne (I) and (+)(S)-3,4,4-trimethyl-1-pentyne (II) were prepared from (+)(S)-2,3-dimethylbutanoic acid and (+)(S)-2,3,3-trimethylbutanoic acid respectively, through the corresponding α-olefins (+)(S)-3,4-dimethyl-1-pentene (III) and (+)(R)-3,4,4-trimethyl-1-pentene (IV) via bromination-dehydrobromination procedure. The relationship rotatory power-optical purity of (I), (II), (III) and (IV) was determined and, on the basis of the obtained results, it was concluded that all the reactions involved in the synthesis proceed without significant racemization.

## INTRODUCTION

During investigations on the mechanism of the reactions between unsaturated substrates and organometallic compounds of 2nd and 3rd Group elements, in the absence or in the presence of transition metal complexes, we have prepared some optically active acetylenic hydrocarbons of general formula:



$$R-\underset{\displaystyle R'}{\underset{|}{\overset{*}{C}H}}-(CH_2)_n-C\equiv C-R''$$

$$n = 0,1,2$$

$$R = Me, Et;\ R' = Et, Pr^i, Bu^t;\ R'' = H, Me, Pr^i, Bu^t.$$

---

* Istituto di Chimica Organica, Facoltà di Scienze M.F.N., Università di Pisa.

These compounds represent also i) new models to investigate the relationship between optical activity and structure in series of compounds containing a chromophoric system absorbing at wavelength ⩽220 nm (P. PIRRO [1971]), ii) monomers for the preparation of optically active polymers containing coniugate double bonds (F. CIARDELLI et al. [1967], O. PIERONI et al. [1972], O. PIERONI and F. CIARDELLI [1972]) and iii) useful synthetic intermediates.

Up to date only 1-alkynes containing an optically active *sec*-butyl group (L. LARDICCI et al. [1966]) and (—)(R)-3,7-dimethyl-1-octyne (P. PIRRO [1971]) have been described.

In the present paper we report the synthesis of some alkynes of different steric requirements, such as (+)(S)-3,4-dimethyl-1-pentyne (I) and (+)(S)-3,4,4-trimethyl-1-pentyne (II), and the evaluation of their minimum enantiomeric purity.

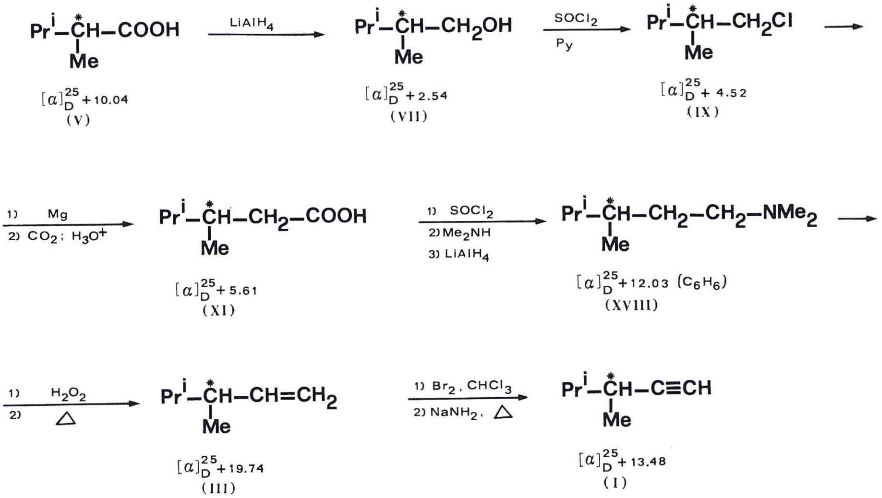
## PREPARATION AND PURIFICATION OF (I) AND (II)

According to general methods reported in the literature (L. LARDICCI et al. [1966], P. PIRRO [1971]), we have carried out the synthesis of (I) and (II) from the corresponding optically active 1-alkenes through a bromination-dehydrobromination procedure.
(+)(S)-3,4-dimethyl-1-pentene (III) and (+)(R)-3,4,4-trimethyl-1-pentene (IV) were prepared from (+)(S)-2,3-dimethylbutanoic acid (V) and (+)(S)-2,3,3-trimethylbutanoic acid (VI) respectively.
(V) and (VI) were converted, by usual procedures (L. LARDICCI et al. [1972], P. PIRRO [1971]), via the pentanoic acids (XI) and (XII), into (+)(R)-N,N-3,4-dimethylpentylamine (XVIII) and (+)(R)-N,N-dimethyl-3,4,4-trimethylpentylamine (XIX) (Schemes 1, 2): their corresponding N-oxides were finally pyrolyzed to (III) and (IV) (L. LARDICCI et al. [1972], P. PIRRO [1971]).

In order to check the suitability of the procedure adopted, racemic materials have been previously employed in the sequences of Scheme 1 and 2.
(III) and (IV) were prepared in 40-50% overall yield; their chemical purity, evaluated by glc analyses, was ⩾ 99,9%. The structure of the olefins obtained was confirmed by nmr spectroscopy and by mass spectrometry (see expt. section).
Some physical properties of (III) and (IV) are reported in Table 1.

While (R)(S)-(V) was easily prepared in 75% overall yield by the malonic ester synthesis (S. SAREL and S. M. NEWMAN [1956])

SCHEME 1



SCHEME 2

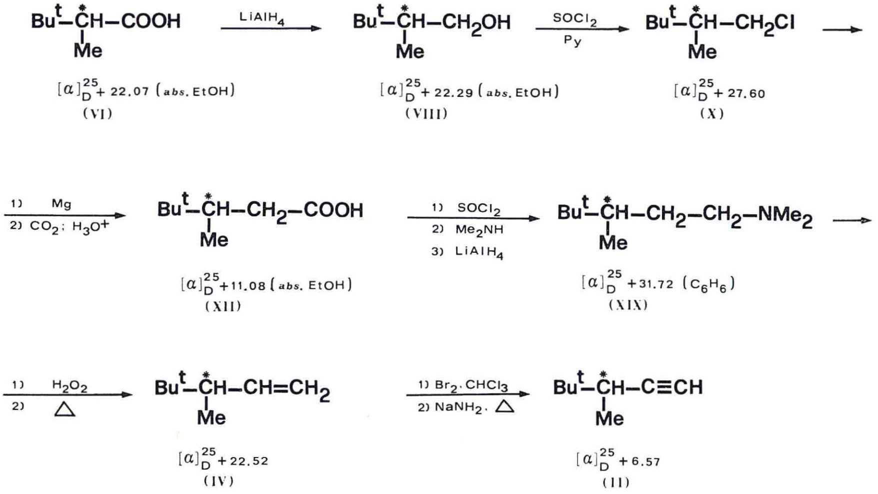


TABLE 1

*Physical properties of the optically active 1-alkynes and of the corresponding alkenes and alkanes of general formula:* $R\text{—}\overset{*}{C}H(Me)\text{—}X$ ($R = Pr^i$, $Bu^t$).

| R | X | b.p. °C | $n^{25}_D$ | $d^{25}_4$ | $[\alpha]^{25}_D$ | ref. |
|---|---|---|---|---|---|---|
| $Pr^i$ | $C\equiv CH$ | 81 | 1.4007 | 0.7187 | +13.48 | — |
| | $CH{=}CH_2$ | 81 | 1.3963 | 0.697 | +19.74 | *a*) |
| | $CH_2\text{—}CH_3$ | 89-90 | 1.3898 | 0.6909 | + 5.06 | *b*) |
| $Bu^t$ | $C\equiv CH$ | 99 | 1.4095 | 0.7350 | + 6.57 | — |
| | $CH{=}CH_2$ | 100 | 1.4066 | 0.7150 | +22.52 | *c*) |
| | $CH_2\text{—}CH_3$ | 109 | 1.4007 | 0.7120 | +19.87 | *d*) |

*a*) R. R. Dreisbach [1959a]; *b*) L. Lardicci et al. [1968]; *c*) R. R. Dreisbach [1959b]; *d*) R. R. Dreisbach [1959c].

the preparation of (R)(S)-(VI) appeared more difficult, at least in the light of the literature data.

Although M. Farina and E. Mostardini Peronaci [1966] reported the synthesis of this compound from 2,3,3-trimethyl-1-butene, we have preferred to employ the Favorskii rearrangement of bromomethylneopentyl ketone (J. G. Aston et al. [1942], S. Sarel and S. M. Newman [1956]).

This compound was satisfactorily prepared (⩾ 90% yield) by bromination of methylneopentyl ketone in absolute methanol, according to a recent report of M. Gaudry and A. Marquet [1970], and it was stored at —30° in the dark before use, in order to prevent the eventual dismutation (F. Kröhnke [1936]).

(R)(S)-2,3-dimethylbutanoic acid (V) and (R)(S)-2,3,3-trimethylbutanoic acid (VI) were resolved into the enantiomers by fractional crystallization of their dehydroabietylamine salts from acetone and methanol-chloroform mixture respectively.

Similar procedure has been previously applied by M. Farina and E. Mostardini Peronaci [1966] to the resolution of (R)(S)-(VI) while (R)(S)-(V) had been resolved by P. A. Levene and L. W. Bass [1926] via brucine salt. The method we have adopted seems however to be more suitable for preparative purposes, since convenient amounts of optically active (V) (ca. 50% optical purity) were obtained after 4-5 crystallizations of its diastereoisomeric salts.

The α-olefins (III) and (IV) were converted into the corresponding 1,2-dibromides by addition of bromine in chloroform at —80°, in a quantitative yield (P. Pirro [1971]).

Among the several methods of dehydrohalogenation (G. Köbrich and P. Buck [1969]) we have preferred that one based on the dehydrobromination by commercial sodium amide in mineral oil at 150-160° (L. Lardicci et al. [1966], P. Pirro [1971]). Although the yields were very good (70-80%), the crude products contained also the corresponding olefins (10%) (1). Therefore it was always necessary to purify the crude (I) and (II) through their silver salts according to the literature suggestions (L. Lardicci et al. [1966]).

Because of this purification, the yields in (I) and (II) (with respect to the corresponding 1,2-dibromoalkanes) decreased therefore to 50-60%.

The chemical purity of (I) and (II) so prepared ($\geqslant$ 99,5%) was checked by glc analyses; nmr and mass spectra were in accordance with their structures (see expt. section).

Some physical properties of (I) and (II) are collected in Table 1.

## RESULTS AND DISCUSSION

The absolute configuration of the acids (V) and (VI) has been previously determined in relation to that of (S)-2-methyl-1-butanol (L. Lardicci et al. [1973]).
As the alkynes (I) and (II) were prepared using (V) and (VI) by sequences not affecting the asymmetric carbon atom (Schemes 1, 2), they have been attributed with the same absolute configuration as these acids.

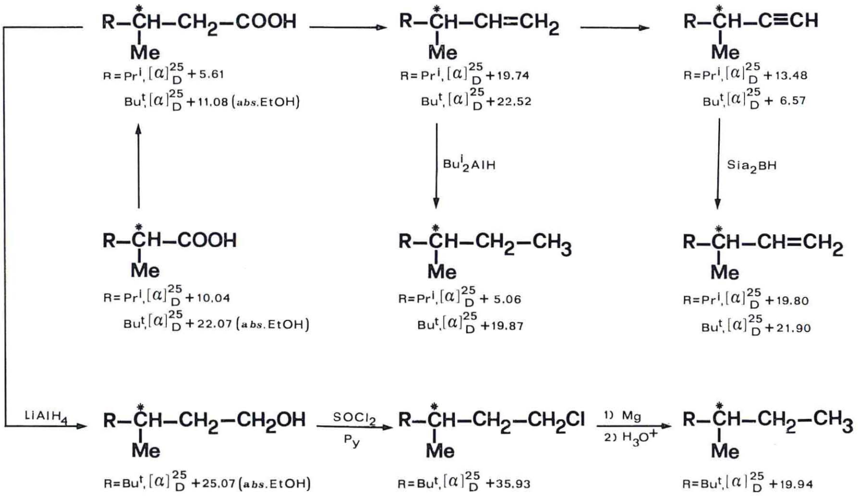
The synthesis of the α-olefins (III) and (IV) from (V) and (VI) does not involve racemization phenomena (L. Lardicci et al. [1973]), while the bromination-dehydrobromination procedure we have adopted might have affected in principle the asymmetric centre.
The enantiomeric purity of (I) and (II) was therefore determined by converting these compounds into the corresponding alkenes (III) and (IV) by monohydroboration with disiamylborane and

---

(1) The dehalogenation reaction represents the well-known disadvantage of the use of alkali metal amides in the dehydrohalogenation of 1,2-dibromides (H. T. Vaughn et al. [1934], R. N. Renaud and L. C. Leitch [1964]).

subsequent protonolysis with acetic acid at room temperature (H. C. BROWN and C. ZWEIFEL [1961]) (Scheme 3).

SCHEME 3



The results obtained indicate that no racemization takes place in the dehydrobromination with sodium amide in spite of the fact that the triple bond of the acetylenic compounds is in the α-position with respect to the asymmetric carbon atom.

In order to interrelate the maximum rotations of (I), (II), (III) and (IV) with those of the corresponding alkanes (XXI) and (XV), samples of (III) and (IV) were converted by diisobutylaluminium hydride (L. LARDICCI and R. MENICAGLI [1970]) into (+)(R)-2,3-dimethylpentane (XXI) and (+)(R)-2,3,3-trimethylpentane (XV) (L. LARDICCI et al. [1973]).

To verify the maximum rotation of (XV), this was prepared from (VI) by an independent scheme of sequences not affecting the asymmetric carbon atom (Scheme 3).

The lack of racemization in the synthesis of the α-olefins (III) and (IV) (Table 2) is in agreement with previous findings in analogous cases (L. LARDICCI et al. [1972], P. PIRRO [1971]) and indicates that the optical yield is independent from the structure of the alkyl group bound to the asymmetric carbon atom.

TABLE 2

*Relationship optical rotatory power-optical purity of 1-alkynes, 1-alkenes and alkanes of general formula:*

$R—\overset{*}{C}H(Me)—X$ (R = $Pr^i$, $Bu^t$).

| R | starting acid | | | prepared compound | | recovered compound | | | Racemization % |
|---|---|---|---|---|---|---|---|---|---|
| | X | $[\alpha]^{25}_D$ | o.p. % | X | $[\alpha]^{25}_D$ | X | $[\alpha]^{25}_D$ | o.p. % | |
| $Pr^i$ | COOH | 10.04 | 45.6 [a] | $CH=CH_2$ | 19.74 | $CH_2—CH_3$ | 5.06 | 44.4 [b] | 2.6 |
| $Bu^t$ | | 22.07<br>(*abs.* EtOH) | 53.8 [c]<br>(*abs.* EtOH) | | 22.52 | | 19.87 | 53.7 [d] | 0.2 |
| $Pr^i$ | COOH | 10.04 | 45.6 [a] | $C\equiv CH$ | 13.48 | $CH=CH_2$ | 19.80 | 44.5 [b] | 2.4 |
| $Bu^t$ | | 22.07<br>(*abs.* EtOH) | 53.8 [c]<br>(*abs.* EtOH) | | 6.57 | | 21.90 | 52.2 [d] | 3.0 |

Calculated assuming for optically pure: *a*) 2,3-dimethylbutanoic acid, $[\alpha]^{25}_D$ 22.0; *b*) 2,3-dimethylpentane, $[\alpha]^{25}_D$ 11.4 (L. LARDICCI et al. [1968]); *c*) 2,3,3-trimethylbutanoic acid, $[\alpha]^{25}_D$ 41.0 (M. FARINA and E. MOSTARDINI PERONACI [1966]); *d*) 2,3,3-trimethylpentane, $[\alpha]^{25}_D$ 37.0 (*this paper*).

The results we have obtained show that the stereospecificity of the dehydrobromination procedure with sodium amide (Schemes 1, 2) is very high, as well as that encountered in the dehydrohalogenation of (3S)-1,2-dibromo-3-methylpentane at 250° by solid potassium hydroxide (L. LARDICCI et al. [1966]) (²).

The maximum molecular rotations of optically active 1-alkynes prepared, evaluated on the basis of the present data, are reported in Table 3 together with those of the corresponding alkenes and alkanes. The alkane and the alkyne have molecular rotation lower than that of the corresponding alkene, although the trend in the two series investigated is rather different and dependent on the structure of the alkyl group R.

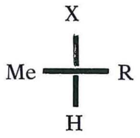
While the molecular rotations of the alkanes, alkenes and (R)-3,4-dimethyl-1-pentyne (I), evaluated according to the rules proposed by J. H. BREWSTER [1961] for open-chain compounds and for endocyclic olefins (J. H. BREWSTER [1959]), agree substantially with those of Table 3 taking into account the approximation of the method, no calculation of molecular rotation of (R)-3,4,4-trimethyl-1-pentyne (II) is possible, since every conformation is optically inactive according to BREWSTER's method [1959], [1961].

On this basis, only a lower molecular rotation than that of the corresponding hydrocarbon is to be predicted. Effectively, the experimental results (Table 3) seem to confirm this suggestion.

ACKNOWLEDGMENT. This work was supported by the C.N.R., Rome.

TABLE 3

*Maximum molecular rotations of optically active alkanes, 1-alkenes and 1-alkynes of general formula*



| R | X | absolute configuration | $[M]^{25}_{D\,\max}$ |
|---|---|---|---|
| | $CH_2$—$CH_3$ (XXI) | S | — 11.4 |
| Pr^i | $CH{=}CH_2$ (III) | R | — 43.6 |
| | $C{\equiv}CH$ (I) | R | — 29.1 |
| | $CH_2$—$CH_3$ (XV) | S | — 42.2 |
| Bu^t | $CH{=}CH_2$ (IV) | S | — 47.0 |
| | $C{\equiv}CH$ (II) | R | — 13.9 |

---

(²) In this last case the crude product contains also allenic hydrocarbons in addition to the olefins.

## EXPERIMENTAL SECTION

Melting points (determined by a Kofler apparatus) and boiling points are uncorrected. Glc analyses were performed on a C. Erba Fractovap Mod. GT instrument, with flame ionization detector, using the columns and the temperatures specified. Elemental analyses were performed by Microanalytical Laboratory of the Faculty of Pharmacy at the University of Pisa. Nmr spectra were recorded on a Varian Associates Model T-60 at 60 MHz instrument. Chemical shifts are reported in p.p.m. (δ) downfield from tetramethylsilane as internal standard. Mass spectra were taken at 70 eV on a Hitachi Perkin-Elmer RMU-6D instrument. The determination of rotations was carried out using a Schmidt-Haensch polarimeter with tubes thermostatted at 25°.

*(R)(S)-2,3-dimethylbutanoic acid.* (V) - (R)(S)-(V), b.p. 90° (15 mm), $n^{25}_{D}$ 1.4136, was prepared in 75% yield from diethylmethylmalonate by the malonic ester synthesis.
L. LARDICCI et al. [1968] reported b.p. 94-95° (17 mm), $n^{25}_{D}$ 1.4136, $d^{25}_{4}$ 0.9220.

*Resolution of (R)(S)-2,3-dimethylbutanoic acid* (V) *with dehydroabietylamine.* - (R)(S)-(V) (132.0 g, 1.136 moles) was dissolved with dehydroabietylamine (396.0 g, 1.140 moles), previously purified (W. J. GOTTSTEIN and L. C. CHENEY [1965]), in 3700 ml of boiling acetone. The obtained salt, after five crystallizations from acetone (g salt: ml acetone = 1:10), according to the «triangular» scheme of fractional recrystallization (R. STUART TIPSON [1956]) gave six salt fractions (A - F). Every fraction was treated with cold sodium hydroxide solution and the dehydroabietylamine extracted by ether. The acid was then liberated from the aqueous solution with dilute sulphuric acid and extracted by ether. Yields and optical rotations of (V) from the salt are shown below:

| Fraction . . . | A | B | C | D | E | F |
|---|---|---|---|---|---|---|
| g salt . . . . | 123 | 50 | 65 | 106 | 90 | 20 |
| g (V) . . . | 33.7 | 13.5 | 17.8 | 29.2 | 24.7 | 5.5 |
| $[\alpha]^{25}_{D}$ (neat) . . | —11.39 | —5.94 | —3.00 | +5.75 | +12.25 | +15.14 |

*(R)(S)-methyl-2,3,3-trimethylbutanoate.* (VIa) - (R)(S)-(VIa), b.p. 147-148°, $n^{25}_{D}$ 1.4092, was prepared in 58-60% yield by a Favor-

skii rearrangement of bromomethylneopentyl ketone according to the procedure of J. G. ASTON et al. [1942]. S. SAREL and M. S. NEWMAN [1956] reported b.p. 150-152° (740 mm), $n^{25}_D$ 1.4092.

*Bromomethylneopentyl ketone* was obtained following two different procedures:

A) *in the absence of solvent according to* S. SAREL *and* M. S. NEWMAN [1956]. - Bromine vapor (0.394 moles) in dry nitrogen was bubbled through methylneopentyl ketone (³) (45.0 g, 0.394 moles) at 0° in 45 min. The reaction mixture was treated with water, the organic layer separated and dried over potassium carbonate. Fractionation of the crude product gave 18.2 g (24% yield) of monobromomethylneopentyl ketone, b.p. 77-82° (16 mm), in addition to 26% of the starting ketone, and 34% of dibromomethylneopentyl ketone, b.p. 110-113° (16 mm).

B) *in absolute methanol according to* M. GAUDRY *and* A. MARQUET [1970]. - Bromine (151.2 g, 0.946 moles) was added rapidly to a solution of methylneopentyl ketone in 1800 ml of absolute methanol at 0°. The reaction mixture was stirred at room temperature, and after decoloration (ca. 1 hr) added with water, neutralized with sodium bicarbonate and extracted with ether. The ethereal extracts were washed four times with water and dried ($Na_2SO_4$). After elimination of the solvent at reduced pressure, 175.0 g (96% yield) of bromomethylneopentyl ketone, b.p. 78-82° (16 mm) were recovered. The compound was stored at —30° in the dark. S. SAREL and M. S. NEWMAN [1956] reported b.p. 91° (32 mm).

*(R)(S)-2,3,3-trimethylbutanoic acid.* (VI) - Saponification of (VIa) was accomplished in 94% yield by prolonged reflux (10 hr) with 20% potassium hydroxide in diethylenglycol to give (R)(S)-(VI), m.p. 53-54°, b.p. 105° (15 mm). J. G. ASTON et al. [1942] reported m.p. 53.5°, b.p. 132° (55 mm).

*Resolution of (R)(S)-2,3,3-trimethylbutanoic acid* (VI) *with dehydroabietylamine.* - (R)(S)-(VI) (59.0 g, 0.453 moles) in 50 ml of ether was gradually added to a solution of dehydroabietylamine (131.0 g, 0.459 moles) in 950 ml of ether. The salt obtained after stirring for 2 hr at 15° was filtered off and washed with ether:

---

(³) This ketone was prepared in large quantities by the oxidation of diisobutylene, according to E. H. MAN et al. [1952].

187.0 g, $[\alpha]^{25}_{D}+27.96$ ($c = 2.5$, $CHCl_3$) were recovered and recrystallized several times from ethanol-chloroform. The progress of the resolution was followed as described below:

| Crystallization | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| ml ethanol | 830 | 660 | 470 | 275 |
| ml chloroform | 470 | 340 | 230 | 185 |
| g salt | 114.0 | 70.0 | 52.5 | 40.5 |
| $[\alpha]^{25}_{D}$ of the salt ($c \sim 2$, $CHCl_3$) | — | +20.30 | +18.20 | +16.95 |

The last salt fraction, $[\alpha]^{25}_{D}$ +16.95 ($c \sim 2$, $CHCl_3$), was treated with cold sodium hydroxide solution and the dehydroabietylamine extracted by ether. From the acidification of the aqueous solution and extraction with ether, 12.5 g of (—)(R)-(VI), $[\alpha]^{25}_{D}$ —37.6 ($c \sim 2.2$, *abs.* EtOH) were recovered.
81.5 g of salt, having $[\alpha]^{25}_{D}$ +35.53 ($c \sim 2$, $CHCl_3$), from which 25.1 g of (+)(S)-(VI), $[\alpha]^{25}_{D}$ +25.90 ($c \sim 2.2$, *abs.* EtOH) were recovered, and 57.6 g of salt, having $[\alpha]^{25}_{D}$ +25.28 ($c \sim 2$, $CHCl_3$), which gave 17.8 g of (—)(R)-(VI), $[\alpha]^{25}_{D}$ —9.15 ($c \sim 2.3$, *abs.* EtOH), were obtained from the mother liquors of the successive recrystallizations.

*(R)(S)- and (+)(S)-2,3-dimethyl-1-butanol.* (VII) - (R)(S)-(V) (120.0 g, 1.033 moles) was reduced with $LiAlH_4$ (67.6 g, 1.783 moles) in anhydrous ether at reflux temperature over 10 hr. Rectification gave 97.9 g (93% yield) of (R)(S)-(VII), b.p. 142°, $n^{25}_{D}$ 1.4191.

(+)(S)-(V), b.p. 108° (26 mm), $n^{25}_{D}$ 1.4136, $[\alpha]^{25}_{D}$ + 10.04, yielded 97% of (+)(S)-(VII), b.p. 62-63° (21 mm), $n^{25}_{D}$ 1.4195, $[\alpha]^{25}_{D}$ +2.54, following the same procedure. The product was shown to be pure by glc (10% BDS on 60-80 mesh Chromosorb W, 200 x 0.30 cm, 90°). L. Lardicci et al. [1968] reported b.p. 58° (18 mm), $n^{25}_{D}$ 1.4191, $d^{25}_{4}$ 0.8249.

*(R)(S)- and (+)(S)-2,3,3-trimethyl-1-butanol.* (VIII) - (R)(S)-(VI) (63.0 g, 0.484 moles) was reduced as above with $LiAlH_4$ (44.1 g, 1.126 moles). Rectification yielded 98% of (R)(S)-(VIII) (55.0 g), b.p. 80° (25 mm), $n^{20}_{D}$ 1.4298, $n^{25}_{D}$ 1.4280.

(+)(S)-(VI), m.p. 53-54°, $[\alpha]^{25}_{D}$ +22.07 ($c=2.2$, *abs.* EtOH) gave in a 97% yield (+)(S)-(VIII), b.p. 80° (25 mm), $n^{25}_{D}$ 1.4279, $[\alpha]^{25}_{D}$

+22.29 (c=2.557, *abs.* EtOH). (VIII) was shown to be pure by glc (5% SE 30 on 80-100 mesh HMDS-Chromosorb W, 200x0.30 cm, 70°). M. FARINA and E. MOSTARDINI PERONACI [1966] reported b.p. 161-162° (740 mm), $n^{20}_D$ 1.4297.

*(R)(S)- and (+)(S)-2,3-dimethyl-1-chlorobutane.* (IX) - Thionyl chloride (166.8 g, 1.402 moles) was added dropwise, with stirring, to (R)(S)-(VII) (95.0 g, 0.930 moles) in pyridine (147.5 g, 1.864 moles) at —10°. The mixture was kept in an ice-bath overnight and stirred at 80-90° for 10 hr (4), and then treated in the usual manner. (R)(S)-(IX) (82.6 g, 74% yield), b.p. 94-100° (300-350 mm), $n^{25}_D$ 1.4202 was obtained.

Analogously (+)(S)-(VII), $[\alpha]^{25}_D$ +2.54 gave (+)(S)-(IX) (76% yield), b.p. 79-80° (200 mm), $n^{25}_D$ 1.4202, $[\alpha]^{25}_D$ +4.52. (IX) showed only a peak by glc (10% BDS on 60-80 mesh Chromosorb W, 200x 0.30 cm, 75°). L. LARDICCI et al. [1968] reported b.p. 83° (210 mm), $n^{25}_D$ 1.4202, $d^{25}_4$ 0.8846.

*(R)(S)- and (+)(S)-2,3,3-trimethyl-1-chlorobutane.* (X) - (R)(S)-(VIII) (25.0 g, 0.215 moles) in pyridine was reacted with thionyl chloride (38.4 g, 0.322 moles) following the above procedure (4). (R)(S)-(X) (20.2 g), b.p. 43° (18 mm), $n^{20}_D$ 1.4313, $n^{25}_D$ 1.4288 was obtained in 70% yield.

(+)(S)-(VIII), $[\alpha]^{25}_D$ +22.29 (c=2.557, *abs.* EtOH) yielded 65% of (+)(S)-(X), b.p. 78° (95 mm), $n^{25}_D$ 1.4288, $[\alpha]^{25}_D$ +27.60. The product was shown to be pure by glc (5% SE 30 on 80-100 mesh HMDS-Chromosorb W, 200 x 0.30 cm, 70°). S. PUCCI et al. [1970] reported b.p. 83° (112 mm), $n^{20}_D$ 1.4313, $d^{25}_4$ 0.8861.

*(R)(S)- and (+)(R)-3,4-dimethylpentanoic acid.* (XI) - (R)(S)-(IX) (77.4 g, 0.643 moles) was converted into the corresponding Grignard reagent, which was then carbonated by the usual technique. (R)(S)-(XI) (72.8 g, 87% yield with respect to (R)(S)-(IX)) b.p. 111° (16 mm), $n^{25}_D$ 1.4241 was obtained.

From (+)(S)-(IX), $[\alpha]^{25}_D$ +4.52, (+)(R)-(XI), b.p. 117° (18 mm), $n^{25}_D$ 1.4241, $[\alpha]^{25}_D$ +5.61 was recovered in a 87% yield. L. LARDICCI et al. [1968] reported b.p. 67° (0.6 mm), $n^{25}_D$ 1.4242, $d^{25}_4$ 0.9230.

---

(4) The course of the reaction was followed by glc analysis.

*(R)(S)- and (+)(R)-3,4,4-trimethylpentanoic acid.* (XII) - (R)(S)-(X) (38.5 g, 0.286 moles) was converted into the corresponding Grignard reagent, which was then carbonated, over a period of 60 hr, to (R)(S)-(XII) (28.8 g, 70% yield), b.p. 126° (18 mm), $n^{25}_D$ 1.4311.

(+)(S)-(X), $[\alpha]^{25}_D$ +27.60 yielded 80% of (+)(R)-(XII), b.p. 120° (14 mm), $n^{25}_D$ 1.4312, $[\alpha]^{25}_D$+11.08 (c=2.573, *abs.* EtOH). The purity of the product was checked by glc analysis (10% BDS on 60-80 mesh Chromosorb W, 200 x 0.30 cm, 110°) of the corresponding methyl ester, obtained by treating (XII) with an ethereal solution of diazomethane. *Neutralization equivalent.* Calcd. for $C_8H_{16}O_2$: 144.21. Found: 144.28. *Anal.* Calcd. for $C_8H_{16}O_2$: C, 66.63; H, 11.18. Found: C, 67.10; H, 11.20.

*(R)(S)- and (+)(R)-N,N-dimethyl-3,4-dimethylpentanamide.* (XVI) - (R)(S)-(XI) (72.0 g, 0.553 moles) was reacted with thionyl chloride in anhydrous ethyl ether to the corresponding acid chloride. The crude product, in ethyl ether (100 ml), was treated with dimethylamine (49.9 g, 1.106 moles) in ethyl ether (100 ml) at —5°. The reaction mixture was stirred at room temperature for 30 hr and then treated in the usual manner. Distillation gave (R)(S)-(XVI) (78.6 g, 90% yield), b.p. 112° (16 mm), $n^{25}_D$ 1.4499.

From (+)(R)-(XI), $[\alpha]^{25}_D$ +5.61, (+)(R)-(XVI), b.p. 115° (17 mm), $n^{25}_D$ 1.4499, $[\alpha]^{25}_D$ +7.59 (c=3.360, EtOH) was obtained (95% yield). *Anal.* Calcd. for $C_9H_{19}NO$: C, 68.74; H, 12.18; N, 8.91. Found: C, 68.86; H, 12.23; N, 8.95.

*(R)(S)- and (+)(R)-N,N-dimethyl-3,4,4-trimethylpentanamide.* (XVII) - Using the procedure above described, (R)(S)-(XII) (25.0 g, 0.173 moles) yielded 96% (28.3 g) of (R)(S)-(XVII), b.p. 124° (15 mm), $n^{25}_D$ 1.4539 and (+)(R)-(XII), $[\alpha]^{25}_D$ +11.08 gave 96% of (+)(R)-(XVII), b.p. 119° (13 mm), $n^{25}_D$ 1.4540, $[\alpha]^{25}_D$ +16.64 (c=2.705, EtOH). *Anal.* Calcd. for $C_{10}H_{21}NO$: C. 70.12; H, 12.36; N, 8.18. Found: C, 70.19; H, 12.40; N, 7.98.

*(R)(S)- and (+)(R)-N,N-dimethyl-3,4-dimethylpentylamine.* (XVIII) - (R)(S)-(XVI) (75.0 g, 0.477 moles) in anhydrous ethyl ether (200 ml) was reduced with $LiAlH_4$ (20.0 g, 0.527 moles) in anhydrous ethyl ether (300 ml). The reaction mixture was heated for 36 hr at reflux temperature. The crude product recovered and purified

through the corresponding hydrochloride yielded 95% of (R)(S)-(XVIII) (64.9 g), b.p. 53° (14 mm), $n^{25}_D$ 1.4200.

(+)(R)-(XVI), $[\alpha]^{25}_D$ +7.59 (c = 3.360, EtOH) yielded 89% of (+)(R)-(XVIII), b.p. 55° (17 mm), $n^{25}_D$ 1.4202, $[\alpha]^{25}_D$ +12.03 (c=3.116, $C_6H_6$). *Anal.* Calcd. for $C_9H_{21}N$: C, 75.44; H, 14.77; N, 9.78. Found: C, 75.42; H, 14.75; N, 9.81.

*(R)(S)- and (+)(R)-N,N-dimethyl-3,4,4-trimethylpentylamine.* (XIX) - According to the above procedure, (R)(S)-(XVII) (26.5 g, 0.154 moles) gave (R)(S)-(XIX) (23.7 g, 80% yield), b.p. 68° (15 mm), $n^{25}_D$ 1.4260 and (+)(R)-(XVII), $[\alpha]^{25}_D$ + 16.64 (c = 2.227, EtOH) afforded (+)(R)-(XIX) (97% yield), b.p. 63° (13 mm), $n_D^{25}$ 1.4260, $[\alpha]^{25}_D$ +31.72 (c = 3.058, $C_6H_6$). *Anal.* Calcd. for $C_{10}H_{23}N$: C, 76.35; H, 14.74; N, 8.91. Found: C, 76.11; H, 14.48; N, 8.90.

*(R)(S)- and (+)(S)-3,4-dimethyl-1-pentene.* (III) - (R)(S)-(XVIII) (58.5 g, 0.408 moles) was converted by 35% hydrogen peroxide (120 ml) into the corresponding N-oxide which was pyrolyzed within 90 min at 125° (0.8 mm). The crude olefin was purified and distilled to yield (R)(S)-(III) (33.4 g, 84% yield).

Analogously, the N-oxide of (+)(R)-(XVIII), $[\alpha]^{25}_D$ +12.03 (c = 3.116, $C_6H_6$) was pyrolyzed to (+)(S)-(III), $[\alpha]^{25}_D$ + 19.74 in a 90% yield. The product was shown to be pure by glc (Squalane capillary column, 100 m, 60°, 2.5 ml/min $N_2$ flow rate). Mass spectrum m/e (rel. intensity) 98 (1.7, parent), 83 (11.3), 70 (58.2), 69 (10.4), 56 (100), 55 (71.3), 43 (61.7), 41 (50.4), 29 (12.2), 27 (19.1); nmr ($CCl_4$) 0.87 (d, 6, $Me_2$CH-), 0.97 (d, 3, -CH*Me*-), 1.18-2.28 (m, 2, $Me_2$*CH*-*CH*Me-), 4.72-5.02 (m, 2, -CH=$CH_2$), 5.42-6.00 (m, 1, -*CH*=$CH_2$).

*(R)(S)- and (+)(R)-3,4,4-trimethyl-1-pentene.* (IV) - (R)(S)-(XIX) (22.5 g, 0.143 moles) was treated with 35% hydrogen peroxide (45 ml) to the corresponding N-oxide, which was pyrolyzed within 100 min at 150° (5 mm) ([5]). After the usual procedure, (R)(S)-(IV) (13.2 g, 82% yield) was obtained.

From (+)(R)-(XIX), $[\alpha]^{25}_D$ +31.72 (c=3.058, $C_6H_6$), through the N-oxide, (+)(R)-(IV), $[\alpha]^{25}_D$ +22.52 was recovered in a 88% yield. The product showed only a peak by glc (Squalane capillary column,

---

([5]) The pyrolysis was carried out in a different way since the N-oxide of (XIX) was shown to sublimate, without pyrolyzing, under the conditions generally used.

100 m, 60°, 2.5 ml/min $N_2$ flow rate). Mass spectrum m/e (rel. intensity) 112 (1.5, parent), 97 (7.0), 84 (1.1), 83, 70 (2.2), 69 (4.1), 57 (100), 56 (12.6), 55 (19.3), 41 (24.1), 29 (15.2) 27 (4.8); nmr ($CCl_4$) 0.87 (s, 9, *Me*$_3$C-), 0.93 (d, 3, -CH*Me*), 1.63-2.13 (m. 1, -*CH*Me), 4.72-5.02 (m, 2, -CH=*CH*$_2$), 5.44-6.04 (m, 1, -*CH*=$CH_2$).

*(R)(S)- and (+)(S)-3,4-dimethyl-1-pentyne.* (I) - (R)(S)-(III) (9.5 g, 0.097 moles) in 30 ml of chloroform was treated at —80° with 0.102 moles of bromine in 25 ml of chloroform. After keeping the mixture at —80° overnight, the solvent was removed at reduced pressure (20 mm). Distillation afforded (R)(S)-1,2-dibromo-3,4-dimethylpentane (24.0 g, 96% yield), b.p. 96° (14 mm), $n^{25}_D$ 1.5044. *Anal.* Calcd. for $C_7H_{14}Br_2$: Br, 61.94. Found: Br, 61.59.
The dibromide was added dropwise to a suspension of commercial powdered sodium amide (17.0 g) in 105 ml of mineral oil at 150°. The mixture, stirred at 160° until evolution of ammonia was complete (1hr), and then cooled, was cautiously hydrolyzed with diluted hydrochloric acid. The ethereal extracts were washed with saturated sodium bicarbonate solution and water. The crude product was rectified. The alkyne thus obtained (8.1 g) was treated with a solution of silver nitrate (34.6 g) in 90 ml of water and successively with ethanol until a precipitate was observed to form. The white product obtained after filtration was then washed with water and acetone and finally dried (15.4 g). The salt was suspended in a solution of sodium cyanide (48.8 g) in 320 ml of water. (R)(S)-(I) (4.5 g, 50% yield) was recovered by steam distillation.

(+)(3S)-1,2-dibromo-3,4-dimethylpentane, $[\alpha]^{25}_D$ +9.73 (c=3.545, *n*.heptane), prepared in a 97% yield from (+)(S)-(III), $[\alpha]^{25}_D$+19.74, yielded 53% of purified (+)(S)-(I), $[\alpha]^{25}_D$ +13.48 after the above procedure. The product was shown to be pure by glc (Squalane capillary column, 100 m, 60°, 2.5 ml/min $N_2$ flow rate). Mass spectrum m/e (rel. intensity) 96 (3.9, parent), 95 (6.4), 81 (96.8), 68 (20.9), 67 (16.1), 54 (100), 53 (40.3), 43 (51.6), 41 (56.7), 39 (51.6), 29 (6.4), 28 (22.6), 27 (33.9); nmr (neat) 0.95 (d, 6, *Me*$_2$CH-), 1.11 (d, 3, -*Me*CH-), 1.36-1.78 (m, 1, $Me_2$*CH*-CH-), 2.05 - 2.50 (m, 1, -CH-*CH*Me-), 1.92 (d, 1, -CH-C≡*CH*). *Anal.* Calcd. for $C_7H_{12}$: C, 87.42; H, 12.58. Found: C, 87.20, H, 12.42.

*(R)(S)- and (+)(S)-3,4,4-trimethyl-1-pentyne.* (II) - (R)(S)-(IV) (10.0g, 0.089 moles) was converted into the corresponding dibromide

which was added, without any purification (⁶), to a suspension of powdered sodium amide (15.3 g) in mineral oil (95 ml) at 150°. The crude alkyne was purified through its silver salt. (R)(S)-(II) was obtained in a 56% yield.

From (+)(R)-(IV), $[\alpha]^{25}_{D}$ +22.52, (+)(S)-(II), $[\alpha]^{25}_{D}$ +6.57 was recovered in a 51% yield. The product showed only a peak by glc (Squalane capillary column, 100 m, 60°, 2.5 ml/min $N_2$ flow rate). Mass spectrum m/e (rel. intensity) 110 (parent), 109, 95 (24.7), 82 (1.7), 81 (3.9), 68 (2.8), 67 (10.1), 57 (100), 53 (6.7), 41 (34.8), 39 (10.1), 29 (21.3), 27 (8.9); nmr (neat) 0.95 (s, 9, $Me_3$C-), 1.10 (d, 3, -*Me*CH-), 2.00-2.40 (m, 1, -*CH*Me-), 1.93 (d, 1, -CH-C≡*CH*). *Anal.* Calcd. for $C_8H_{14}$: C, 87.18; H, 12.81. Found: C, 87.38; H, 12.65.

*(—)(S)-3,4,4-trimethyl-1-pentanol.* (XIII) - (—)(S)-(XII) (22.0 g, 0.152 moles), $[\alpha]^{25}_{D}$ —17.32 (c = 2.771, *abs.* EtOH), from (—)(R)-(VI), $[\alpha]^{25}_{D}$ —34.45 (c = 2.236, *abs.* EtOH), was reduced with $LiAlH_4$ (13.9 g, 0.336 moles) in anhydrous ethyl ether at reflux temperature over 8 hr. Distillation gave 19.7 g (99% yield) of (—)(S)-(XIII), b.p. 84° (14 mm), $n^{25}_{D}$ 1.4334, $[\alpha]^{25}_{D}$ —39.14 (c = 3.283, *abs.* EtOH), which was shown to be pure by glc (5% SE 30 on 80-100 mesh HMDS-Chromosorb W, 200x0.30 cm, 100°). *Anal.* Calcd. for $C_8H_{18}O$: C, 73.78; H, 13.92. Found: C, 73.77; H, 13.75.

*(—)(S)-3,4,4-trimethyl-1-chloropentane.* (XIV) - Thionyl chloride (23.9 g, 0.201 moles) was added dropwise with stirring to (—)(S)-(XIII) (17.5 g, 0.134 moles), $[\alpha]^{25}_{D}$ —39.14 (c = 3.283, *abs.* EtOH) in pyridine (21.2 g, 0.268 moles) at —10°. After the usual procedure (⁴), (—)(S)-(XIV) (15.6 g, 78% yield), b.p. 84° (60 mm), $n^{25}_{D}$ 1.4347, $d^{25}_{4}$ 0.8853, $[\alpha]^{25}_{D}$ —56.08 was obtained. The product showed only a peak by glc (5% SE 30 on 80-100 mesh HMDS-Chromosorb W, 200x 0.30 cm, 80°). *Anal.* Calcd. for $C_8H_{17}Cl$: C, 64.63; H, 11.52; Cl, 23.85. Found: C, 64.86; H, 11.36; Cl, 23.72.

*(—)(S)-2,2,3-trimethylpentane.* (XV) - The Grignard reagent (0.083 moles) from (—)(S)-(XIV), $[\alpha]^{25}_{D}$ —56.08 was cautiously hydrolyzed with saturated ammonium chloride solution. (—)(S)-(XV), $[\alpha]^{25}_{D}$ —31.12 was obtained (6.4 g, 68% yield). (XV) was shown to

---

(⁶) The 1,2-dibromo-3,4,4-trimethylpentane was observed to decompose during the distillation.

be pure by glc (10% Squalane on 60-80 mesh Chromosorb W, 200x 0.30 cm, 80°).

*(+)(R)-2,3-dimethylpentane* (XII): *hydroalumination of (+)(S)*-(III). (+)(S)-(III) (3.0 g, 0.030 moles), $[\alpha]^{25}_{D}$ +19.74 was added to diisobutylaminium monohydride (0.049 moles). The mixture was kept at room temperature for 4 days and then heated at 100° for 12 hr. After careful hydrolysis, (+)(R)-(XXI) (2.0 g, 67% yield), $[\alpha]^{25}_{D}$ +5.06, pure by glc (10% Squalane on 60-80 mesh Chromosorb W, 200x0.30 cm, 80°), was obtained.

*(+)(R)-2,2,3-trimethylpentane* (XV): *hydroalumination of (+)(R)*-(IV). - From (+)(R)-(IV) (3.4 g, 0.030 moles), $[\alpha]^{25}_{D}$ +22.52, by analogous procedure (+)(R)-(XV) (2.6 g, 76% yield) was recovered. (+)(R)- (XV), having $[\alpha]^{25}_{D}$ +19.87, was shown to be pure by glc (10% Squalane on 60-80 mesh Chromosorb W, 200x0.30 cm, 80°).

*(+)(S)-3,4-dimethyl-1-pentene* (III): *hydroboration of (+)(S)*-(I). - Boron trifluoride etherate (7.4 g, 0.052 moles) was added dropwise at 0° under dry nitrogen, to a well-stirred mixture of 2-methyl-2-butene (4.4 g, 0.062 moles) and sodium borohydride (0.023 moles) in diglyme (13 ml). After completion of the addition, the mixture was kept at 0° for 2 hr. To the disiamylborane so prepared was added (+)(S)-(I) (2.5 g, 0.026 moles), $[\alpha]^{25}_{D}$ +13.48, at —10°. The mixture was stirred at 0° for 0.5 hr and then for 2 hr at room temperature. A small quantity (0.5 ml) of ethylene glycol was added to decompose residual hydride. At last glacial acetic acid (13 ml) was added and, after standing for 2 hr at 0°, the reaction mixture was poured into ice-water. The upper layer was separated, washed with sodium hydroxide solution, with a saturated sodium chloride solution, dried ($K_2CO_3$) and then distilled. The fraction (1.8 g) with boiling point 60-80° was redistilled over sodium and gave (+)(S)-(III), $[\alpha]^{25}_{D}$ +19.80, pure by glc (10% Squalane on 60-80 mesh Chromosorb W, 200x0.30 cm, 50°).

*(+)(R)-3,4,4-trimethyl-1-pentene* (IV): *hydroboration of (+)(S)*-(II). - (+)(S)-(II) (3.0 g, 0.027 moles), $[\alpha]^{25}_{D}$ +6.57, was hydroborated with 0.035 moles of disiamylborane following the above procedure. (+)(R)-(IV) (1.8 g), $[\alpha]^{25}_{D}$ + 21.90, thus obtained was

shown to be pure by glc (10% Squalane on 60-80 mesh Chromosorb W, 200x0.30 cm, 70°).

## REFERENCES

ASTON J. G., CLARKE J. T., BURGESS K. A., GREENBURG R. B. (1942) - The new acid synthesis. II. The effect of hindrance. Methyltertiarybutyl- and Methylethylpropylacetic acids. *J. Amer. Chem. Soc.*, **64**, 300-302.

BREWSTER J. H. (1959) - A useful model of optical activity. *J. Amer. Chem. Soc.* **81**, 5475-5500.

BREWSTER J. H. (1961) - Some applications of the conformational dissymetry rule. *Tetrahedron*, **13**, 106-122.

BROWN H. C., ZWEIFEL G. (1961) - Hydroboration. XI. The hydroboration of acetylenes. A convenient conversion of internal acetylenes into *cis*-olefins and terminal acetylenes into aldehydes. *J. Amer. Chem. Soc.*, **83**, 3834-3840.

CIARDELLI F., BENEDETTI E., PIERONI O. (1967) - Polymerization of racemic and optically active 4-methyl-1-hexyne. *Makromol. Chem.*, **103**, 1-18.

DREISBACH R. R. (1959a) - *Physical properties of chemical compounds*. Adv. Chem. Ser., ACS Appl. Publ., **2** (22), 271.

DREISBACH R. R. (1959b) - *Physical properties of chemical compounds*. Adv. Chem. Ser., ACS Appl. Publ., **2** (22), 364.

DREISBACH R. R. (1959c) - *Physical properties of chemical compounds*. Adv. Chem. Ser., ACS Appl. Publ., **2** (22), 46.

FARINA M., MOSTARDINI PERONACI E. (1966) - Antipodi ottici del 2,3,3-trimetilbutanolo-1 e dell'acido 2,3,3-trimetilbutirrico. *Chimica e Industria*, **48**, 602-605.

GAUDRY M., MARQUET A. (1970) - Enolisation des cetones dissymetriques. III. Acces facile aux bromomethylcetones par bromation en presence de methanol. *Tetrahedron*, **26**, 5611-5615.

GOTTSTEIN W. J., CHENEY L. C. (1965) - Dehydroabietylamine. A new resolving agent. *J. Org. Chem.*, **30**, 2072-2073.

KÖBRICH G., BUCK P. (1969) - Synthesis of acetylenes and polyacetylenes by elimination reactions. «*Chemistry of acetylenes*». Viehe H.G. ed., (Dekker M. Inc.), New York, 99-134.

KRÖNKE F. (1936) - Zur theorie und praxis der halogenierung aktiver methyl- und methylengruppen. *Chem. Ber.*, **69**, 921-935.

LARDICCI L., BOTTEGHI C., BENEDETTI E. (1966) - Synthesis of some 1-alkynes containing an optically active *sec*-butyl group. *J. Org. Chem.*, **31**, 1534-1538.

LARDICCI L., ROSSI R., PUCCI S., AGLIETTO M., BOTTEGHI C., PINO P. (1968) - Sul potere rotatorio massimo del (—)(S)-2,3-dimetilpentano e di alcuni composti alifatici ad esso collegati. *Chimica e Industria*, **50**, 227-230.

LARDICCI L., MENICAGLI R. (1970) - Sulla correlazione tra il (—)(S)-2-metil-1-butanolo e composti otticamente attivi contenenti gruppi fenilici: determinazione della relazione potere rotatorio-purezza ottica. *Atti Soc. Toscana Sci. Nat. Pisa, Proc. Verbali Mem.*, A**77**, 25-39.

LARDICCI L., SALVADORI P., CAPORUSSO A. M., MENICAGLI R., BELGODERE E. (1972) - Optically active phenyl-α-olefins: preparation and structure/optical activity relationship in homologous series. *Gazz. Chim. Ital.*, **102**, 64-84.

LARDICCI L., MENICAGLI R., CAPORUSSO A. M., GIACOMELLI G. P. (1973) - A new configurational assignment of (—)2,3,3-trimethylbutanoic acid and some related compounds. *Chem. Ind. (London)*, 184-185.

LEVENE P. A., BASS L. W. (1926) - The configurational relationships of dialkylacetic acids. *J. Biol. Chem.*, **70**, 211-217.

MAN H. E., FROSTICK F. C., HAUSER C. R. (1952) - Proportions of isomeric ketone enol acetates from o-acetylations of methyl- methylene ketones with isopropenyl acetate. *J. Amer. Chem. Soc.*, **74**, 3228-3230.

PIERONI O., MATERA F., CIARDELLI F. (1972) - Chiroptical properties of linear non-planar polyenes. *Tetrahedron Letters*, 597-600.

PIERONI O., CIARDELLI F. (1972) - Chiroptical properties and conformation in solution of polymers of optically active 1-alkynes. *International symposium on macromolecules, Helsinki*, preprint, **3** (**2**), 77-82.

PIRRO P. (1971) - Su alcuni idrocarburi acetilenici otticamente attivi: relazione attività ottica-struttura. *Thesis*. Pisa.

PUCCI S., AGLIETTO M., LUISI P. L. (1970) - Sintesi di paraffine a basso peso molecolare conformazionalmente rigide. *Gazz. Chim. Ital.*, **100**, 159-174.

RENAUD R. N., LEITCH L. C. (1964) - Synthesis of 1-phenylpropyne-2,3-$^{13}C_2$. *Can. J. Chem.*, **42**, 2089-2092.

SAREL S., NEWMAN S. M. (1956) - The synthesis of branched primary and secondary alkyl acetates. *J. Amer. Chem. Soc.*, **78**, 5416-5420.

STUART TIPSON R. (1956) - Crystallization and recrystallization. *Tecnique of organic chemistry*. Weissberger A. ed. (Interscience Publishers, Inc.), New York, 2nd Ed., **3** (1), 395-562.

VAUGHN H. T., VOGT R. R., NIEUWLAND J. A. (1934) - A rapid catalytic preparation of sodamide in liquid ammonia and some of its uses in the preparation of acetylenic materials. *J. Amer. Chem. Soc.*, **56**, 2120-2122.

NOTE ADDED IN PROOF. - In this paper, for the configurations of the optically active compounds, we have adopted the «IUPAC 1968 *Tentative Rules for the Nomenclature of Organic Chemistry, Section E, Fundamental Stereochemistry*». According to these rules, chirality (S) is to be established for (+)-3-phenyl-4-methyl-1-pentene (L. LARDICCI, R. MENICAGLI [1970]).

(*ms. pres. il 10 gennaio 1973; ult. bozze il 21 maggio 1973*)