Tetrahedron. Vol. 26, pp 4067 to 4071. Pergamon Press 1970. Printed in Great Britain

SYNTHESIS AND SPECTRAL PROPERTIES OF *cis-* AND *trans*-(S)-4-METHYL-2-HEXENE†

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(*Received in the UK* 22 *December* 1969; *Accepted for publication* 2 *February* 1970)

Abstract—*cis-* and *trans*-(*S*)-4-Methyl-2-hexenes have been prepared and their minimum optical purity determined. The UV and CD spectra of these compounds are discussed.

BY REACTION of alkyllithium compounds with oxiranes, alcohols and alkenes are obtained. In fact Crandall and Lin[1] have recently reported that t-butyloxirane reacts with t-butyllithium to give *trans*-di-t-butylethylene (64% yield). We have observed that the reaction of (*R*)-1-lithium-2-methylbutane with ethylene oxide[2] (in light petroleum at 35–40°) yields appreciable amounts of (*S*)-4-methyl-1-hexene, *cis*- and *trans*-(S)-4-methyl-2-hexene‡ in addition to the expected primary alcohol.

In order to investigate the mechanism of this anomalous reaction by using stereochemical information also, it was necessary to prepare samples of *cis-* and *trans*-(S)-4-methyl-2-hexene and to determine their minimum optical purity.

The present paper reports the synthesis of alkenes not yet described,§ the relationship between optical purity and [α]; and a discussion of their UV and CD spectra.

The preparation of a mixture of the geometrical isomers of (*S*)-4-methyl-2-hexene was carried out according to the Scheme 1.

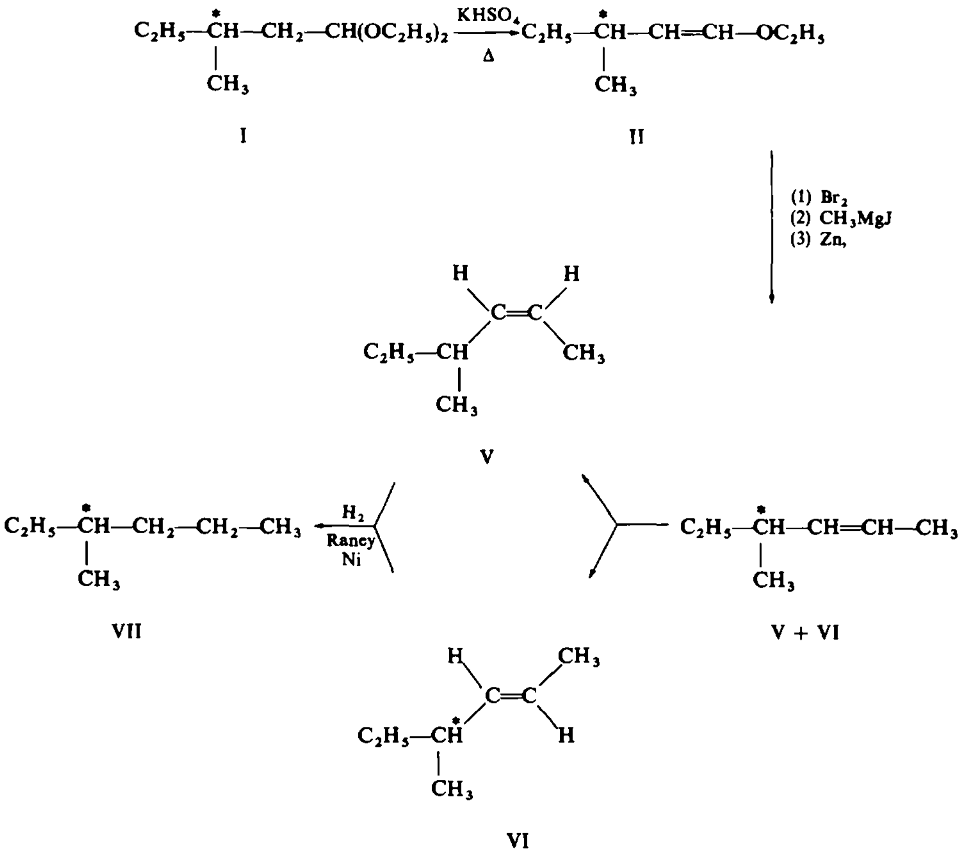
By preparative VPC of the reaction mixture using ODPN (β, β′-oxydipropionitrile) columns, two samples were obtained: the former containing 98·5% of an alkene and 1·5% of its isomer with higher retention time on $AgNO_3$ columns, the latter containing 96·5% of the component with higher retention time and 3·5% of its isomer. The stereoisomers present in the samples were identified by comparison of their VPC retention times on ODPN and their IR spectra with the ones reported for the corresponding racemic alkenes.[3,4] The compound having higher retention time (on $AgNO_3$ or ODPN columns) corresponds to *cis*-(*S*)-4-methyl-2-hexene (V), the other being the *trans* isomer (VI).

[†] The study is a part of a more extensive investigation on the optical properties of simple aliphatic and alicyclic compounds having a 1,2-disubstituted double bond in α position with respect to the asymmetric carbon atom.

[‡] The presence of these alkenes is not in keeping with the mechanism proposed by Crandall and Lin.[1]

[§] By dehydration of (*S*)-4-methyl-2-hexanol over Al_2O_3, G. S. Gordon and R. L. Burwell [*J. Am. Chem. Soc.* **71**, 2355 (1949)] obtained a mixture of heptenes having α_D^{25} (l = 1) + 13·70°.

SCHEME 1



The physical properties of these compounds are summarized in Table 1.

On the basis of the experimental data and assuming that the rotatory power of the mixture (V) + (VI) depends linearly on molar ratio, it is possible to calculate for V and VI $[\alpha]_D^{25}$ +29·34 and +38·87 respectively.

TABLE 1. PHYSICAL PROPERTIES OF *cis*- AND *trans*-(*S*)-4-METHYL-2-HEXENE

Compound	Stereoisomeric purity (%)	n_D^{25}	d_4^{25}	$\alpha^{25}(l = 1)$	I.R (cm^{-1})
cis (V)	96·5	1·4002	0·6951	+20·63°	1661; 720
trans (VI)	98·5	1·3999	0·6932	+26·85°	1667; 970

Minimum optical purity of V *and* VI

The relationship between optical purity and $[\alpha]_D$ of V and VI has been established by catalytic hydrogenation over Raney Ni of these compounds to (*S*)-3-methylhexane (VII) (Scheme 1).

By comparison of the rotatory power of the samples of VII thus obtained with the maximum value given by Levene *et al.*[5,†] for VII, it was possible to attribute a 85% minimum optical purity both to *trans*-(*S*)-4-methyl-2-hexene (VI) ($[\alpha]_D^{25}$ +38·87) and to *cis*-(*S*)-4-methyl-2-hexene (V) ($[\alpha]_D^{25}$ +29·34) prepared.

Since (*S*)-1-chloro-2-methylbutane used for preparing I was 98·8% optically pure,[2] the maximum racemization encountered in the conversion of V and VI to VII is 13%.[‡]

The maximum values of $[\Phi]_{D\max}^{25}$ of V and VI are given in Table 2.[§]

TABLE 2. OPTICAL PROPERTIES OF *cis*- AND *trans*-(*S*)-4-METHYL-2-HEXENE

Alkene	$[\Phi]_{D\max}^{25}$	CD[a]		
		λ(mμ)	$\Delta\varepsilon$[b]	$[\theta]$[c]
cis-(*S*)-4-methyl-2-hexene (V)	+33·8	197	−1·59	−5250
		200[d]	−1·04	−3430
		201	−1·65	−5440
trans-(*S*)-4-methyl-2-hexene (VI)	+44·2	192	+1·70	+5610
		194[d]	+0·81	+2670
		197	+1·36	+4490

[a] at 27° (c = 0·9/1·3 g/l; heptane)
[b] values calculated for 85% optical purity
[c] molecular ellipticity, calculated as $[\theta] = 2{\cdot}303\,(4500/\pi)\,\Delta\varepsilon$
[d] minimum.

UV and CD spectra

The UV spectra of *cis*- and *trans*-(*S*)-4-methyl-2-hexene (V) and (VI), in heptane solution at room temperature, show a strong and broad absorption band at 183–188 mμ. Moreover, in heptane solution and in the vapour phase, three shoulders of lower intensity in the spectral region 190–195 mμ are observed.

While it is possible to assign the principal absorption band to a $\pi_z \rightarrow \pi_z^*$ (N → V, $^1Ag \rightarrow {}^1B_{1u}$) transition,[10,11] the assignment of the absorptions in the region 190–220 mμ is still controversial.[11,12]

[†] It is to be noticed that this value ($[\alpha]_D^{25}$ +9·9) is dependent on the maximum rotatory power of (*S*)-2-methyl-1-butanol ($[\alpha]_D^{25}$ −5·82). Recently it has been demonstrated that this last value is to be truly referred to the optically pure alcohol.[6]

[‡] In our opinion this racemization occurs principally in the Boord synthesis; the catalytic hydrogenation over Raney Ni of compounds having a double bond in α to the asymmetric C atom appears to take place with small racemization (1–2·5%)[7,8], at least at room temp.

[§] As *cis*-V and *trans*-(*S*)-4-methyl-2-hexene (VI) are optically active model compounds of the monomeric unit of *cis*- and *trans*-(*S*)-1,4-poly-penta-1,3-diene, the value of maximum molar rotatory power of V and VI can be used to evaluate the influence exerted by the stereoregularity of isotactic-1,4-poly-penta-1,3-diene on its optical activity.[9]

However the absorption of moderate intensity in the vapour phase of V and not easily detectable both in its solution spectrum and in the vapour phase or solution spectra of VI, is probably to be assigned to an allowed $\pi_z \rightarrow \sigma_g^*$ (N → R) transition.[13]

The CD of V, in heptane or methanol solution, results in a double-humped curve showing a negative maximum at around 201 mμ, a minimum at 200 mμ and a second negative maximum at around 197 mμ (Table 2).

The CD curve of VI, heptane or methanol solution, is also double-humped, with a positive maximum at around 197 mμ, a minimum at 194 mμ and a second maximum at around 192 mμ. Moreover for both the compounds V and VI it is possible to observe the beginning of a positive band of considerable intensity at higher energies.

By comparing these data with what is reported in literature for the UV and CD spectra[11,13–16] of mono-olefins it is possible to draw some conclusions.

Optically active alkenes having a 1,2-disubstituted double bond near the asymmetric C atom show in solution Cotton effects in the region 190–205 mμ; similar Cotton effects have been reported for Δ^4- and Δ^5-steroidal mono-olefins[14] and some cycloalkenes.[11,13,16]

The CD bands in this region can be accounted in terms of singlet-singlet $\pi \rightarrow \pi^*$ rather than $\pi_z \rightarrow \sigma_g^*$ transition.[11] In fact, the latter excitation associated with the absorption of moderate intensity at around 202 mμ, having almost zero magnetic moment,[15] should be weakly rotating and its contribution to CD would be negligible.

The sign of the Cotton effect in the investigated region seems to be correlated with geometrical isomerism of the C=C double bond near the asymmetric center, at least for V and VI.

In our opinion this can be interpreted in terms of different conformational possibilities for the geometrical isomers, the *cis*-isomer being more "conformationally rigid" than the *trans*-isomer. Thus the olefinic chromophore should be exposed to very different asymmetric environments.

At 589 mμ the sign of the rotatory power of V and VI is dependent on optically active bands at $\lambda < 190$ mμ.

EXPERIMENTAL

B.ps are uncorrected. Rotatory powers were taken by a Schmidt–Haensch polarimeter. Gas chromatographic analyses were performed by a Perkin Elmer model 810 Vapor Fractometer equipped with columns containing $AgNO_3$ on diethylene glycol.

PGC was performed at 40° with N_2 gas. The column used was β,β'-oxydipropionitrile on 80–100 mesh Chromosorb P (4 m × 5 mm i.d.). IR spectra were recorded with a Perkin Elmer 225 spectrophotometer. UV spectra were measured with a Cary Model 14 spectrophotometer. CD curves were obtained with a Jouan Roussel CD Dichrograph.

(S)-1,1-*Diethoxy-3-methylpentane* (I). An ethereal Grignard soln was prepared in an atmosphere of dry N_2 from (*S*)-1-chloro-2-methylbutane (136 g, 1·27 mole, $[\alpha]_D^{25}$ +1·61).

This reagent, as described elsewhere,[17] was added dropwise with stirring to boiling ethyl orthoformate (177·8 g, 1·10 mole).

The reaction mixture yielded I (166·3 g, 73%), b.p. 72°/17 mm, n_D^{25} 1·4068, $[\alpha]_D^{25}$ +7·41 (pure liquid) [lit,[18] b.p. 71–72°/15 mm; n_D^{25} 1·4067–68, $[\alpha]_D^{25}$ +7·37 (pure liquid)].

cis- *and* trans-(S)-1-*Ethoxy*-3-*methyl*-1-*pentene* (II). Thermal decomposition at 140° of I (166·3 g, 0·93 mole) in the presence of fused $KHSO_4$ (0·48 g) gave a colourless liquid (b.p. 92–140°). Fractionation produced II (87·37 g, 70·5%), b.p. 135–150°, n_D^{25} 1·4139, $[\alpha]_D^{25}$ +38·61 (pure liquid) [lit,[18] b.p. 144–145°, n_D^{25} 1·4142, $[\alpha]_D^{25}$ +38·72 (pure liquid)].

cis-(S)-4-*Methyl*-2-*hexene* (V) *and* trans-(S)-4-*methyl*-2-*hexene* (VI). (a) Bromine (101 g, 0·644 mole) was added slowly to an ethereal soln (100 ml) of II (81·3 g, 0·644 mole) cooled to −50°. After addition the mixture was stirred for 1 hr while the temp was allowed to increase to +10°.

(b) To an ethereal soln (300 ml) of MeMgI (0·810 mole) cooled to 0°, the above ethereal soln of III was added. The reaction mixture was stirred for 24 hr. Part of the solvent (200 ml) was evaporated and the residual liquid was stirred for 4 hr at room temp. The liquid was poured into water and extracted with ethyl ether. Distillation of the extracts yielded IV (67·5 g), b.p. 91–92°/17 mm, n_D^{25} 1·4535–1·4536, α_D^{25} (1 = 1) +0·41° (pure liquid).

(c) A soln of IV (67·5 g) in 95% EtOH (75 ml) was refluxed with Zn (47·04 g) with stirring for 30 hr. The reaction mixture was distilled collecting a fraction having b.p. to 80°. The liquid obtained was washed several times with cold water, dried and distilled to give a mixture of V and VI (22·4 g), b.p. 87–88°, n_D^{25} 1·4001.

VPC analysis on $AgNO_3$/diethylene glycol columns showed the presence of two components in ratio 62·5/37·5. Two samples were obtained by PGC: the former contained 98·5% of *trans*-VI and 1·5% of V; UV (heptane) λ_{max} 188 mμ (log ε 3·83), shoulders at 191, 193, 195 mμ (lit,[19] b.p. 87·60, n_D^{25} 1·3997).

The latter contained 96·5% of *cis*-V and 3·5% of VI (pure liquid); UV (heptane), λ_{max} 188 mμ (log ε 3·86), shoulders at 191, 193, 195 mμ (lit,[19] b.p. 87·37, n_D^{25} 1·3997).

(S)-3-*Methylhexane from* V. Compound V (1·2 g, 0·012 mole) by catalytic reduction over Raney Ni at room temp was converted to VII (1·0 g, 81·9%), b.p. 91–92°, n_D^{25} 1·3869, $[\alpha]_D^{25}$ +7·82 (*c*, 4·091, iso-octane) (lit,[5] $[\alpha]_{D\,max}^{25}$ +9·9).

(S)-3-*Methylhexane from* VI. Compound VI by catalytic reduction over Raney Ni was converted to VII, b.p. 91–92°, n_D^{25} 1·3862, $[\alpha]_D^{25}$ +7·88 (*c*, 4·184, isoctane), $[\alpha]_D^{25}$ +8·49 (pure liquid).

Acknowledgements—We thank Dr. F. Ciampelli, of Istituto Ricerche "G. Donegani"—Montecatini—Edison S.p.A., for preparative gas chromatography. We are indebted to Dr. P. Salvadori, of Istituto di Chimica delle Macromolecole del C.N.R., Nucleo di Pisa, for determining the CD spectra and for comments upon the interpretation.

REFERENCES

[1] J. K. Crandall and Luan-Hoc. Lin, *J. Am. Chem. Soc.*, **89**, 4527 (1967).
[2] L. Lardicci and P. Pino, *Gazz. Chim. Ital.*, **91**, 441 (1961).
[3] R. A. Hively, *Anal. Chem.*, **35**, 1921 (1963).
[4] American Petroleum Institute Research Project 44, "Infrared Spectral Data", Carnegie Institute of Technology, Serial No. 1897–2666
[5] P. A. Levene and R. E. Marker, *J. Biol. Chem.*, **103**, 3203A (1933)
[6] R. Rossi, P. Diversi and G Ingrosso, *Gazz. Chim. Ital.*, **98**, 1391 (1968).
[7] D. J. Cram, *J. Am. Chem. Soc.*, **74**, 5518 (1952).
[8] F. Giardelli and P. Pino, *Gazz. Chim. Ital.*, **95**, 1201 (1965).
[9] P. Pino, *Adv. Polymer Sci.*, **4**, 393 (1965).
[10] K. Stich, G. Rotzler and T. Reichstein, *Hellv. Chim. Acta*, **42**, 1480 (1959)
[11] M. Yaris, A. Moscowitz and R. S. Berry, *J. Chem. Phys.*, **49**, 3150 (1968)
[12] M. Robin, H. Basch, N. A. Kuebler, B. E. Kaplan and J. Meinwald, *Ibid*, **48**, 5037 (1968)
[13] N. B. Robin, R. R. Hart and N. A. Kuebler, *Ibid.*, **44**, 1803 (1966)
[14] N. Legrand and R. Viennet, *Compt. Rend.*, **252** C, 1290 (1966)
[15] S. F. Mason and G. W. Vane, *Chem. Comm.*, 540 (1965)
[16] A. I. Scott and A. D. Wrixon, *Ibid.*, 1182 (1969).
[17] L. Lardicci, F. Navari and R. Rossi, *Tetrahedron*, **22**, 1991 (1966)
[18] L. Lardicci, C. Botteghi and P. Salvadori, *Gazz. Chim. Ital.*, **98**, 760 (1968)
[19] F. D. Rossini *et al.*, "Selected values of properties of hydrocarbons and related compounds", Carnegie Press, Pittsburg Penn., page 56 (1953)