C₃H₆

(structure) M → M—CH=CH—CH₃

pathways seem equally plausible, particularly one involving the participation of a cyclopropylcarbinylnickel derivative.[10]

Carbon–metal β-elimination products have been reported in the pyrolyses of neopentyl derivatives of sodium,[11] potassium,[12] and aluminum,[13] systems in which a β elimination of M–H is precluded. The rearrangements of cyclobutylcarbinyl[8b] and cyclopropylcarbinyl[10] Grignard reagents can be pictured as formally involving intramolecular C–M eliminations.

Further study of the 1,4-diene rearrangements and the extention of the investigation to other transition metal systems are in progress.

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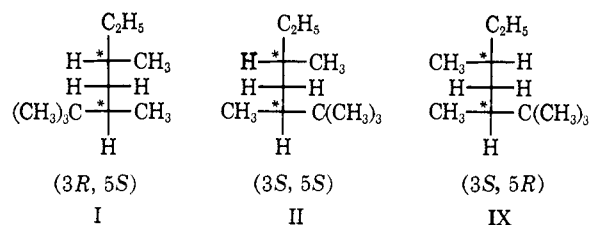E. I. du Pont de Nemours & Company, Inc., Wilmington, Delaware

Conformational Rigidity[1,2] in Aliphatic Paraffins. Synthesis and Determination of Absolute Configuration of (3S,5S)- and (3R,5S)-2,2,3,5-Tetramethylheptane

Sir:

The high optical activity in solution of some stereoregular polymers obtained from optically active α olefins[3] has been attributed[2,4] substantially to the fact that few conformations having high optical rotation of the same sign are allowed for the monomeric unit of such polymers in solution.

As no low molecular weight paraffins were known having [M] of the same order of magnitude of the one found for the monomeric unit of these polymers, we have synthesized (3R,5S)- and (3S,5S)-2,2,3,5-tetramethylheptane (I and II, respectively); for I the existence of two conformations having [M] +180 and +60°, and for II the existence of one conformation having [M] −180° can be foreseen by the Brewster method[5] (Chart I).

Chart I

C₂H₅
H—*—CH₃
H—+—H
(CH₃)₃C—*—CH₃
H

(3R, 5S)
I

C₂H₅
H—*—CH₃
H—+—H
CH₃—*—C(CH₃)₃
H

(3S, 5S)
II

C₂H₅
CH₃—*—H
H—+—H
CH₃—*—C(CH₃)₃
H

(3S, 5R)
IX

A mixture of the two diastereoisomers I and II has been prepared starting with (−)(S)-3-methylpentanal,

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(2) P. Pino, Advan. Polymer Sci., 4, 443 (1965).
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bp 120–121° (760 mm), n^{25}D 1.4002, [α]^{25}D −7, 10°, having an optical purity of 97%,[6] and allowing it to react with t-butylmagnesium chloride.

The (−)(5S)-2,2,5-trimethylheptan-3-ol (III) thus obtained, bp 85° (20 mm), n^{25}D 1.4350, d^{25}_4 0.8305, [α]^{25}D −2.17° (neat) (Anal. Calcd for C₁₀H₂₂O: C, 75.88; H, 14.01. Found: C, 75.91; H, 13.80), was oxidized according to Brown[7] to (+)(S)-2,2,5-trimethylheptan-3-one (IV), bp 75° (22 mm), n^{25}D 1.4193, d^{25}_4 0.8183, [α]^{25}D +19.16° (neat) (Anal. Calcd for C₁₀H₂₀O: C, 76.86; H, 12.90. Found: C, 76.64; H, 12.96), which was allowed to react with methylmagnesium bromide, yielding (+)(5S)-2,2,3,5-tetramethylheptan-3-ol (V), bp 90° (20 mm), n^{25}D 1.4390, d^{25}_4 0.8387, [α]^{25}D +10.13° (neat) (Anal. Calcd for C₁₁H₂₄O: C, 76.67; H, 14.04. Found: C, 76.21; H, 14.06).

V was dehydrated by distillation in the presence of I₂ and the mixture of olefins thus obtained was finally hydrogenated at 120° by H₂ in the presence of Raney nickel, yielding a mixture of I and II, bp 61–62° (18 mm), n^{25}D 1.4202, d^{25}_4 0.7465, [α]^{25}D −0.69° (neat), [α]^{25}D −0.83° (c 15, n-pentane). Anal. Calcd for C₁₁H₂₄: C, 84.52; H, 15.48. Found: C, 84.73; H, 15.59.

The mixture was analyzed by vpc (50-m squalane capillary column); only two components were present, the one with the higher retention time prevailing (60 ± 3%).

By fractional crystallization from propane at −80°, mixtures of I and II having different compositions have been obtained; a sample having a diastereoisomeric purity of 95% showed bp 54–55° (14 mm), n^{25}D 1.4208, [M]^{25}D −87.47 ± 0.1° (neat), [M]^{25}D −87.52 ± 1° (c 20.47, n-pentane). Anal. Calcd for C₁₁H₂₄: C, 84.52; H, 15.48. Found: C, 84.81; H, 15.22.

By plotting the composition of such mixtures vs. their optical rotation and extrapolating at 100% of diastereoisomeric purity, the optical rotation has been calculated for both diastereoisomers.

Taking in account the optical purity of the starting material we have assigned [M]^{25}D +137.8 ± 3° (c 20.47, n-pentane)[8] to the lower retention time diastereoisomer, [M]^{25}D −97.5 ± 4° to the higher retention time diastereoisomer.

In order to establish the relationship between the sign of the optical rotatory power and the absolute configuration of the two asymmetric carbon atoms of the diastereoisomers we have prepared a mixture of (3S,5S)- and (3S,5R)-2,2,3,5-tetramethylheptane (II and IX, respectively), starting with (−)(R)-2,3,3-trimethylbutan-1-ol, [α]^{25}D −15.5° (c 3.41, ethanol), optical purity 37.4%.[9] (−)(R)-1-chloro-2,3,3-trimethylbutane (VI), bp 89–91° (158 mm), n^{20}D 1.4313, d^{25}_4 0.8872, [α]^{25}D −19.93° (neat) (Anal. Calcd for C₇H₁₅Cl: C, 62.44; H, 11.23; Cl, 26.33. Found: C, 62.39; H, 11.15; Cl, 26.44), was obtained from the alcohol by reaction with SOCl₂ in pyridine, and its Grignard reagent was allowed to react with propanal.

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(7) H. C. Brown and C. P. Garg, J. Am. Chem. Soc., 83, 2952 (1961).
(8) Standard deviation calculated by the least-squares method.
(9) The optical purity has been calculated on the basis of the pure (−)(R)-2,3,3-trimethylbutan-1-ol, [α]^{25}D −41.4°: M. Farina and E. M. Peronaci, Chim. Ind. (Milan), 48, 602 (1966); Chem. Abstr., 65, 12091a (1966).

(5S)-5,6,6-Trimethylheptan-3-ol thus obtained was not isolated and was oxidized according to Brown[7] to the (−)(S)-5,6,6-trimethylheptan-3-one (VII), bp 128–130° (126 mm), $n^{25}D$ 1.4277, $\alpha^{25}D$ −7.00° (neat, l = 1) (Anal. Calcd for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found: C, 75.97; H, 12.44), which was purified through its semicarbazone, mp 159–160°.

VII was allowed to react with methylmagnesium bromide, and (−)(5S)-3,5,6,6-tetramethylheptan-3-ol (VIII), bp 89–92° (18 mm), $n^{25}D$ 1.4435, $\alpha^{25}D$ −7.00° (neat, l = 1) (Anal. Calcd for $C_{11}H_{24}O$: C, 76.67; H, 14.04. Found: C, 76.28; H, 13.89), was obtained.

VIII was dehydrated by distillation in the presence of I_2, and the olefins thus obtained were hydrogenated by H_2 at 120° in the presence of Raney nickel, yielding a mixture of (3S,5R)- and (3S,5S)-2,2,3,5-tetramethylheptane (IX and II, respectively), $n^{25}D$ 1.4202, $[\alpha]^{25}D$ −26.19° (c 20.58, n-pentane). Anal. Calcd for C_{11}-H_{24}: C, 84.52; H, 15.48. Found: C, 84.24; H, 15.43.

Acid-catalyzed rearrangements in the dehydration and acid oxidation steps have to be considered improbable on the basis of published data[10,11] on similar compounds.

As I and II have optical activity of opposite sign, IX must have optical activity of the same sign as II; therefore II must have optical rotation of the same sign as the mixture of II and IX and possess therefore negative optical rotation. Consequently the diastereoisomer I, (3R,5S), has positive optical rotation.

The mixture of II and IX was analyzed by vpc, as in the case of the mixture of I and II; it contained 55 ± 3% II which has negative optical rotation and higher retention time; taking into account the optical purity of VI, a value of $[M]^{25}D$ −108.28 ± 1.30° (c 20.58, n-pentane) can be calculated for the molar rotation of the mixture of IX and II. Comparing such a value with the one calculated for the same composition on the basis of the absolute value of the molar rotations of I and II ($[M]^{25}D$ 115.6 ± 4°), a satisfactory agreement is obtained. This agreement can be taken as an indication that both in the synthesis of the mixtures of I and II and of II and IX no extensive racemization occurs at the two asymmetric centers.

Comparing the values found with the value calculated by the Brewster method,[5] a substantial agreement has been found both concerning the sign and the order of magnitude of the optical rotation of I and II, the discrepancy between the values calculated and found being larger in the case in which a single conformation is allowed (see Table I).

Table I

Compd	Max $[M]^{25}D$ found (c 20.47, n-pentane)[a]	$[M]D$ calcd by Brewster method[a]
I	+137.8 ± 3	+120
II	−97.5 ± 4	−180

[a] In degrees.

Our data confirm the previous hypothesis[4] that, in aliphatic hydrocarbons containing a hydrogen atom

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attached to the asymmetric carbon atoms,[12] when the presence of a few conformations having high optical rotation of the same sign can be foreseen by conformational analysis[5] a relatively high optical rotation can be found. This shows the substantial soundness but also the limits of conformational analysis in investigating the conformation of both low and high molecular weight hydrocarbons.

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The Configuration of Vinyl Radicals. The Generation and Trapping of Each Member of a Configurationally Isomeric Pair of Vinyl Radicals

Sir:

We wish to report evidence that vinyl radicals derived from symmetrically disubstituted alkenes exist in a nonlinear configuration capable of facile isomeric interconversion. In addition we are pleased to communicate the results of the first successful attempt to trap the cis and trans isomers of a vinyl radical prior to their complete equilibration.

Several investigations bearing on the structure of vinyl radicals have been reported recently.[1–7] Under conditions of kinetic control, free-radical additions to terminal acetylenes yield predominantly the product of trans addition.[1–3] Skell and Allen[1] attribute this stereoselectivity to the configurational stability of the intermediate vinyl radical. Others[2,3] have suggested that the intermediate radical undergoes rapid cis–trans equilibration, but that the product-forming abstraction reaction involves stereoselective capture of one isomer of this pair.

Elegant electron spin resonance investigations have shown that at low temperatures in liquid ethylene-ethane[4] or in an argon matrix[5] the unsubstituted vinyl radical possesses a nonlinear configuration which undergoes facile inversion. The minimum activation energy for inversion is estimated to be approximately 2 kcal/mole.[4] The 1-methylvinyl radical generated by irradiation of allene in ethane at −172° is also nonlinear.[4] The inversion rate of the 1-methylvinyl radical is less than that for the unsubstituted vinyl radical. Since inversion of the vinyl radical presumably involves

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(3) J. A. Kampmeier and G. Chen, ibid., 87, 2608 (1965).

(4) R. W. Fessenden and R. H. Schuler, J. Chem. Phys., 39, 2147 (1963).

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(7) L. A. Singer and N. P. Kong, ibid., 88, 5213 (1966); Tetrahedron Letters, 2089 (1966).