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THE SYNTHESIS AND CHIROPTICAL PROPERTIES OF THE TWO DIASTEREOMERIC 2-BORNANYLIDENE-BORNANES

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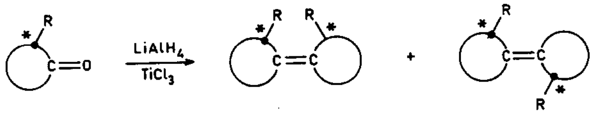
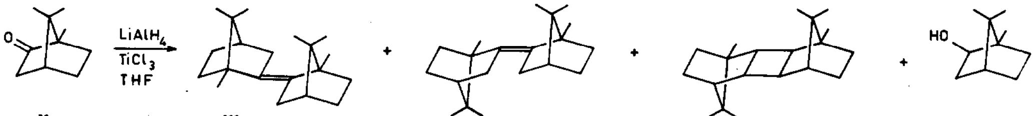
Our current interest in dissymmetric chromophores[1] and non-conjugated as well as spiroconjugated chiral olefins[2,3] was stimulated by the recently reported reductive dimerization reaction of McMurry and Fleming.[4] In effect, starting with a chiral ketone of known absolute configuration two diastereomeric olefins result from this dimerization reaction. If these diastereoisomers are separable and can be characterized stereochemically the olefin octant rule of Scott and Wrixon[5] can be put to a careful test. Very recently Barton et al. has reported the preparation of fenchylidene fenchane.[6] Unfortunately, only one isomer was apparently obtained pure and spectroscopic details are lacking which would allow configurational assignment and comparison with our olefins.

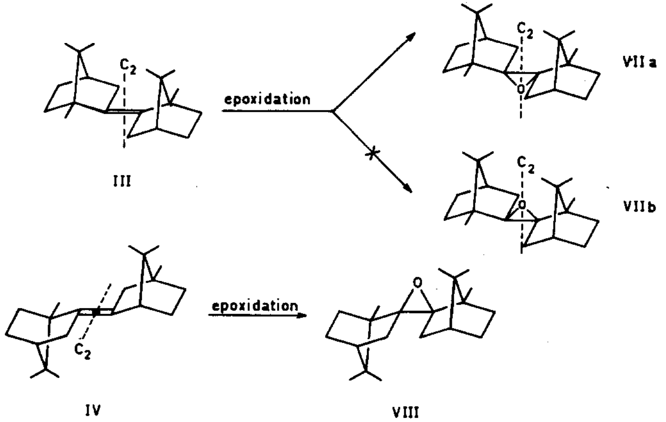


We chose d-(+)-camphor as starting material because of its ready availability, its known optical purity and absolute configuration. This paper reports the preparation of the two dimers which result when d-(+)-camphor (II)[7] is subjected to the reductive dimerization reaction.[4]



II III IV V VI

When 3.2 g (21 mmol) of d-(+)-camphor ($[\alpha]_{578}$ + 70.0°, $[\alpha]_{365}$ + 439.6°, c 4.4,n-hexane) in 50 ml of dry THF was added - under nitrogen - to the black suspension resulting from mixing 6.5 g of $TiCl_3$ and 0.75 g of $LiAlH_4$ in 50 ml of THF an immediate reaction occurs. Fifteen minutes stirring at room temperature followed by heating for 4 hours under reflux allowed the isolation, following a normal work-up, of 2.9 g of semisolid. This crude product contained no starting material as shown by GLC and IR. The two olefins III and IV were separated using HPLC-techniques (Waters Liquid Chromatograph, 100 cm x 3/8" adsorbosil column impregnated with 25% silver nitrate, 100-140 mesh). Nearly equal amounts of the two isomers were isolated, namely 430 mg of analytically pure crystalline dimer (mp 100.1-102.6°) to which we have assigned the transoid structure III and 405 mg of analytically pure liquid dimer for which the cisoid structure IV seems appropriate. Traces of V and VI could be identified. Large rotations and ellipticities were found for the bornanylidene-bornanes III and IV. When the crystalline dimer was oxidized with m-chloroperbenzoic acid to the epoxide VII only one product (mp 117-118°) was obtained which showed C_2 symmetry on the basis of ^{13}C-NMR spectroscopy. Dreiding models indicate that steric hindrance of the geminal methyl groups on the bridge prevents conversion to VIIb. When on the other hand the liquid dimer was epoxidized similarly to VIII again one product could be isolated exhibiting no symmetry according to its ^{13}C-NMR spectrum. These data can be rationalized by assigning structures III and IV to the crystalline and liquid dimer, respectively. Moreover, this identification corresponds with that derived from ^{13}C-NMR data of the olefines III and IV (see Table). The ^{13}C signals of the methyl in the β position with respect to the double bond and the olefinic carbons in the liquid dimer (cisoid structure IV) are shifted further downfield than those in the crystalline dimer. This phenomenon was also observed in cis-di-tert-butyl ethylene compared to the corresponding trans-isomer.[8,9]



C_2-axis perpendicular to plane of the ethylene moiety.

C_2-axis in plane of the ethylene moiety.

On the other hand, the nature of the ^{1}H-NMR spectra did not allow structural assignment to III and IV using NOE techniques. Addition of silver perfluoroborate to both dimers failed to establish the individual structures unambiguously on the basis of chemical shift differences in ^{13}C-NMR spectra (see Table).

Laser-Raman spectroscopy (Cary 81, Raman spectrophotometer with Ne-He Laser source) revealed a significant difference in the olefinic stretching frequencies of both isomers. The liquid dimer showed an olefinic absorption at 1653 cm^{-1} and the crystalline dimer at 1673 cm^{-1}.[10] Force field calculations[12] did not allow structural assignment. Calculations showed that the twist in the cisoid isomer IV was approximately 60°. Therefore, a reliable comparison between the calculated stretching frequencies and structure could not be made.

The transoid dimer III could be reconverted into camphor by a simple quantitative oxidation reaction using RuO_4. This proves the bicyclo[2.2.1]heptane skeleton to retain its stereochemical integrity during the dimerization reaction.

The assignment of structure III to the crystalline isomer is also in agreement with the olefin octant rule of Scott and Wrixon.[5] Knowledge of the absolute configuration of d-(+)-camphor by application of the ketone octant rule[13] laid the basis for a test of the olefin octant rule[5] of the dimer. It can be seen from figure 1 that most of the substituents lie in negative octants which makes a negative contribution to the Cotton effect due to the π-π^* transition at 210 nm.

However, a careful study of the stereochemistry of structure IV (liquid dimer) using Dreiding models revealed that the olefinic linkage should be highly strained and presumably twisted because of the

Table. Spectroscopic data of both isomers.

technique	liquid (cisoid) isomer (IV)	crystalline (transoid) isomer (III)
UV (n-hexane) Cary 15	λ_{max} 206 nm (ϵ 12,700) endabsorption 189 nm (ϵ 8,100) no fine structure ($c = 9.5 \times 10^{-4}$ mol/l).	λ_{max} 214 nm (ϵ 10,600) endabsorption 193 nm (ϵ, 5,600) fine structure, shoulder at 218 nm (ϵ, 10,200) ($c = 10^{-3}$ mol/l).
CD (n-hexane) Cary 60	$[\theta]_{202}$ - 74,000 $[\theta]_{186}$ 0 ($c = 1.9 \times 10^{-4}$ mol/l	$[\theta]_{212}$ - 94,000 $[\theta]_{186}$ + 66,000 ($c = 10^{-3}$ mol/l).
ORD (n-hexane) Cary 60	$[\phi]_{250}$ - 7,900°, $[\phi]_{227}$- 47,620° (trough), $[\phi]_{212}$ 0°, $[\phi]_{200}$ + 38,360°, $[\phi]_{190}$ + 90,000° (± 13,000), $c = 5.14 \times 10^{-5}$ gr/ml	$[\phi]_{250}$ - 8,500°, $[\phi]_{227}$ - 55,000° (trough), $[\phi]_{215}$ 0°, $[\phi]_{200}$ + 80,000°, $[\phi]_{190}$ + 142,000°, $c = 2.7 \times 10^{-4}$ gr/ml
Zeiss polarimeter 005	$[\phi]_{578}$ - 178.2°, $[\phi]_{365}$ - 718.1° (c 1.0, n-hexane)	$[\phi]_{578}$ - 180.9°, $[\phi]_{365}$ - 723.5° c 1.0, n-hexane)
^{1}H-NMR (CCl_4) Varian Xl-100	δ 0.70 (s, 6H), 0.78 (s, 6H), 1.09 (s, 6H) remaining signals: broad multiplet	δ 0.78 (12H), 1.01 (s, 6H) remaining signals: broad multiplet
^{13}C-NMR Varian XL-100	137.7 (olefinic C), 50.6 (two C), 43.8 (CH), 40.1 (CH_2), 35.7 (CH_2), 28.5 (CH_2), 20.5 (CH_3), 19.6 (CH_3), 17.0 (CH_3), carbon tetrachloride.	135.5 (olefinic C), 52.4 (C), 47.4 (C), 44.7 (CH), 37.1 (CH_2), 34.0 (CH_2), 27.8 (CH_2), 19.8 (CH_3), 18.6 (CH_3), 14.6 (CH_3), chloroform.
^{13}C-NMR Varian XL-100 $AgBF_4$ added	137.1 (olefinic C), 48.5 (C), 45.7 (CH), 39.0 (CH_2), 34.8 (CH_2), 28.3 (CH_2), 20.5 (CH_3), 19.1 (CH_3), 15.1 (CH_3), mixture of methylene chloride and carbon tetrachloride.	141.4 (olefinic C), 49.4 (C), 46.2 (CH), 40.8 (CH_2), 34.3 (CH_2), 28.1 (CH_2), 20.9 (CH_3), 19.4 (CH_3), 16.6 (CH_3), mixture of methylene chloride and carbon tetrachloride.

close vicinity of the β methyl substituents. Provided that the olefin octant rule[5,14] is applicable in this particular case then it predicts also for structure IV the correct chirality (Figure 2). In order to account for the smaller long wavelength Cotton effect (Table, $[\theta]_{202}$ - 74000 vs. $[\theta]_{212}$ - 94000 for the crystalline isomer) two factors may be responsible. From figure 2 it can be seen that in a possible twisted form a part of the molecule moves away in the octants with opposite signs, thus giving rise to a smaller resulting negative contribution to the Cotton effect.[15] On the other hand, figure 2 indicates the presence of a helical configuration of the CH_3-C-C=C-C-CH_3 moiety, which is right-handed. This typical feature is absent in the other isomer and might give rise to an extra positive contribution to the Cotton effect.

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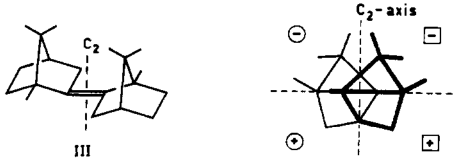
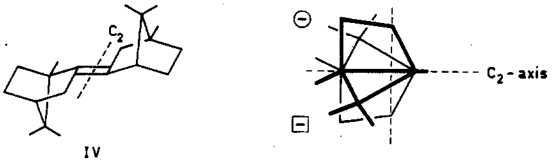


III

Fig. 1. The absolute configuration of (−)-transoid-2-bornanylidene bornane (crystalline dimer) shown in the olefin octant diagram. The corresponding octant signs are given (the backs octants on the left side of the figure and the front octants on the right).



IV

Fig. 2. The absolute configuration of (−)-cisoid-2-bornanylidene bornane (liquid dimer) predicted by the olefin octant rule. The corresponding octant signs are indicated in the figure (the back octant above and the front octant below).

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