

SYNTHESIS OF ISO-CIS AND ISO-TRANS PERHYDROTRIPTYCENE

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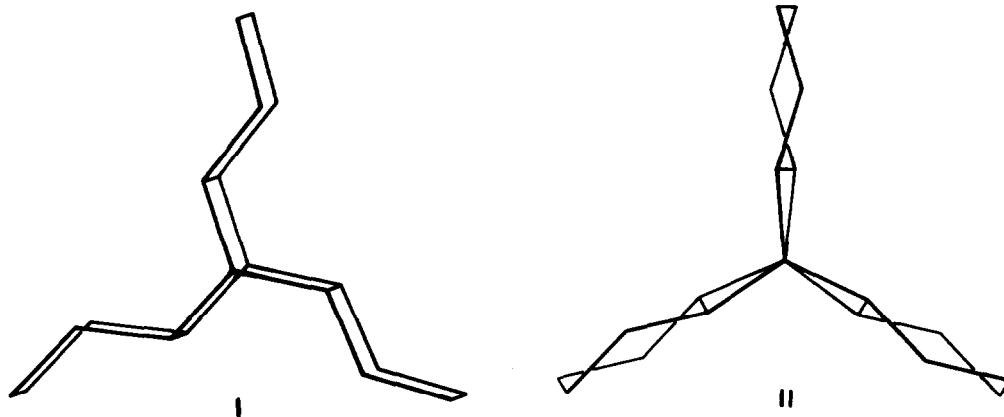
Within a program concerned with the synthesis of high-symmetry chiral compounds(1), we have examined a series of compounds with the skeleton of 2, 2, 2 bicyclooctane.

We have found that among them the pentacyclic compounds obtained by hydrogenation of triptycene are particularly attractive from the synthetic standpoint. Depending on the hydrogenation conditions (temperature ranging between 100 and 200°C, pressure of H<sub>2</sub> between 30 and 100 atm, time from one day to one month, catalyst Pd/C or Ru/C, solvent n-heptane or none), a mixture was obtained of either partial or total hydrogenation products, characterized by gas-chromatographic and mass-spectrometric analyses.

Some stereoisomers of perhydrotriptycene were separated by preparative g.l.c. and studied more extensively. Among them, A and B deserve particular attention. Both have the formula C<sub>20</sub>H<sub>32</sub>, molecular weight 272 (by mass spectrometry) and have a hexagonal crystal lattice (m.p. 165 and 199°C respectively). A was obtained in high yield (up to 60%) after short reaction times, the yield then falling off with increasing time; on the contrary, B was the predominant product after longer times (after one month it reached 60%). The different thermodynamic stabilities also affect the gas-chromatographic behavior, the retention time of B being much shorter than that of A.

The <sup>1</sup>H-NMR spectra of A and B revealed the presence of two uncoupled or weakly coupled hydrogens, at 0.88 and 0.80 δ respectively (those in positions 9 and 10); the <sup>13</sup>C-NMR spectra showed only four signals thus indicating a high degree of molecular symmetry. When the <sup>13</sup>C spectra were run under off-resonance conditions, the multiplicity of the signals were in agreement with the structures foreseen. The simplicity of the spectrum is not accidental; in fact, other low-symmetry isomers exhibit the twenty foreseeable signals. The spectral data do not allow a unique attribution of the ternary symmetry structure I (iso-cis) and II (iso-trans) to compounds A and B; the term iso indicates that the substituents exhibit the same spatial arrangement around the bicyclooctane nucleus. Kinetic and gas-chromatographic data suggest that A corresponds to I and B to II. Such a hypothesis is substantiated by the mass spectra which show a base peak at m/e 190 in A and at 189 in B. The peak at m/e 190 (272-82) may be attributed to elimination of cyclohexene via a mechanism similar to a retro Diels-Alder

reaction; such an elimination would occur more easily with the compound having a cis arrangement.



Conclusive data concerning the structure have been obtained by X-ray analysis of the two compounds (2).

Compound A. Space group  $P6_3/m$   $a=b=9.129 \text{ \AA}$ ,  $c=11.482 \text{ \AA}$ ,  $z=2$ ,  
calculated density  $1.092 \text{ gr/cm}^3$ , experimental  $1.08$ .

Compound B. Space group  $R3_c$   $a=b=9.12 \text{ \AA}$ ,  $c=34.78 \text{ \AA}$ ,  $z=6$ ,  
calculated density  $1.08 \text{ gr/cm}^3$ , experimental  $1.067$ .

Both unit cells have three-fold axes coincident with the molecular symmetry axis. At the present state of tridimensional refinement, we may state that the formula of compound A is iso-cis I and of compound B is iso-trans II. As a result of this investigation, B is the high symmetry chiral compound (point group  $D_3$ ) we looked for.

Preliminary data on the equilibrium between A and B, carried out on Pd/C at  $190^\circ\text{C}$ , indicates a  $\Delta G$  value ranging between 2500 and 3500 cal/mol. This value is exceptionally low in view of the fact that A possesses the three outer cyclohexane rings in the boat conformation, as shown by X-ray and low temperature  $^{13}\text{C}$  studies.

The synthesis and structure of the perhydrotriptycene stereoisomers will be described more extensively in the near future.

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- 1) C. Morandi, graduation thesis, University of Milan, 1970-71;  
C. Morandi and M. Farina, to be published.
- 2) A. Colombo and A. Immirzi, independently, private communications.