Communications to the Editor

Torsionally Distorted Olefins. Resolution of cis- and trans-4,4'-Bi-1,1',2,2',3,3'-hexahydropenanthyridene

Sir:

Only few examples are known of optically active stereoisomers of alkenes bearing no chiral centers. In principle both the cis as well as the trans form of olefins should be capable of existence as stable optically active stereoisomers, provided bulky substituents cause a permanent out-of-plane distortion of the double bond. This expectation has now been realized by the synthesis and resolution of dl-cis- (II) and dl-trans-4,4'-bi-1,1',2,2',3,3'-hexahydropenanthyridene (III) using a novel method of resolution (as applied to olefins).

When 4.1 g (21 mmol) of 4-keto-1,2,3,4-tetrahydrophenanthrene (I) in 25 ml of dry THF was added, under nitrogen, to the black suspension resulting from mixing 6.5 g of TiCl3 and 0.75 g of LiAlH4 in 20 ml of THF, an immediate reaction occurred. The resulting mixture was stirred and heated for 4 h under reflux and after a normal workup 4.0 g of an oil could be isolated. The apolar fraction of the complex reaction mixture consisted of 0.80 g of colorless crystalline olefins, separable into cis (II, mp 192-193 °C) and trans isomers (III, mp 234-235 °C) via preparative TLC (deactivated alumina) (Scheme I).

The structures of both olefins are based upon the following observations. Correct elemental analysis of both olefins and spectral data in agreement with structures II and III were obtained. The olefins II and III were reconverted into starting ketone I by oxidation using RuO4. Hydrogenation of either olefin gave the same dihydro product (5% Pd/C, 3 atm H2, ethanol solution). Both olefins showed the expected C2 symmetry in their 1H NMR spectra. Assignment of the cis configuration to the lower melting isomer (II) is based upon the 100-MHz 1H NMR spectra and the UV spectra. In the cis isomer an upfield shift was observed for protons in the 5.5', 6.6', 7.7', 8.8' positions. (ABCD system, δ 6.36, 6.48, 6.70, and 6.86). These protons are influenced by the shielding zones of the aromatic rings, indicating a helix-like shape of this isomer. In the 100-MHz 1H NMR spectrum of the trans isomer a multiplet was observed for the protons in the 5.5', 6.6', 7.7', 8.8', 9.9', 10.10' positions (δ 7.1-7.8). A multiplet at δ 8.2 is probably due to the protons in the 5.5' positions, deshielded as a result of steric interaction. A hypsochromic shift is observed for the low energy band in the UV spectrum of the cis isomer (II) compared to that of the trans isomer (III) (Figure 1 and 2). This effect is well known for the cis- and trans-dl-1-naphthylstilbene system. The structural relationship of II and III was clearly demonstrated by the slow isomerization of either pure cis- or pure trans isomer to a cis-trans mixture.

Scheme I

![Scheme I](Image)

Figure 1. UV (--), ORD (- - -), and CD (---) spectra of cis-olefin II.

Both dl-cis and dl-trans olefins could be resolved using HPLC techniques by employing an alumina column impregnated with (+)-TAPA. Partial resolution of the cis isomer was achieved (dl-III: [α]D 22578 +88° c 1.60 x 10⁻³, n-hexane). In addition the trans isomer could be resolved completely (dl-III: [α]D 22578 -508° c 3.14 x 10⁻³, n-hexane). The ORD and CD spectra of II (Figure 1) and of III (Figure 2) showed large rotations and ellipticities.

Recently published CD data and calculations on rotational strength indicate torsion of the olefin chromophore as the dominant contribution in determining the sign of the Cotton effects. However, in this case the entire conjugated system rather than an isolated twisted olefin chromophore must be involved in the interpretation of the spectra. Important features to be taken into consideration are: The direction of the principal C2 axes. Note that in the cis olefin this axis is perpendicular to a plane through the π-orbitals of the double bond, while in the trans olefin the C2 axis lies in the plane of the π-orbitals of the double bond (we realize that it is awkward to speak of a "plane" through the twisted olefin π-orbitals). Thus the relations between the transition moments and the C2 axes in the two olefins differ. This must be evident in the spectra. Whether true exciton splitting is present cannot at this time be answered unequivocally. To a first approximation the fact that we are dealing with a conjugated system would argue against it. The trans isomer could in principle exist in two diastereomeric forms; one dl-trans (III) and one non-dissymmetric form (IV). The resolution of the trans olefin is proof of the structure as III and not IV. The partial stereoselectivity of the reductive dimerization of I, resulting in the formation of dl-trans olefin (III) only, might give an indication about the structure of the intermediate Ti complex. Stereoselective formation of the cis isomer (II) could also been achieved: reaction of I under the
above conditions, but in the presence of (−)-trans-2,3-methylenedioxybutane as solvent gave cis-isomer I1 as the only olefinic product. This product was nevertheless optically inactive.

Some additional aspects of the structures of the cis and trans olefins need to be mentioned. The structure of II resembles that of a heptahelicene (more accurately a tetrahydroheptahelicene) with a double bond replacing an aromatic ring. The olefin III has a double helix structure and resembles a double pentahelicene with a double bond replacing two aromatic rings. Both chiral as well as achiral double helix structures have been reported in the helicene case. The role of π-bond torsion has been the subject of many investigations, although almost all of the attention has been focused on trans-cyclooctene. NMR studies connected with π-bond torsion have been reported for systems such as bisfluorenylidene and bianthrone, but no stable enantiomers have been obtained thus far. To our knowledge, olefins II and III represent the first instance in which a dl-cis and dl-trans form of one inherently dissymmetric olefin have been isolated and resolved into enantiomers.

The isomerization and racemizations of II and III may furnish further information about the torsional distortion in both olefins. This complex series of interconversions will be the subject of further investigations.

Acknowledgment. The authors wish to thank Dr. R. Helder and Dr. H. Numan for their assistance during the HPLC resolutions, Dr. H. Hiemstra for recording and interpreting the NMR spectra, and the Netherlands Organization for Pure Research (Z.W.O.) for a graduate fellowship. We thank Professor A. Moscovitz for a brief but highly valuable discussion.

References and Notes


4. In the case of II and III, only one of the possible enantiomers is shown in Scheme I.

5. In the 100-MHz 1H NMR spectra of both cis-III and trans-III isomers, multiplet signals were observed for the protons in the 1,1',2,2',3,3' positions. The relative positions and nature of the substituent, which imparts chirality of the 1,2-dioxetane. (ii) Condition i requires either the synthesis of an olefin with a functional group allowing resolution, or a novel helical conjugated π-system is a matter of semantics. (b) R. Martin, Angew. Chem., 86, 727 (1974); W. H. L. K. and L. H. M. Cuppen, Tetrahedron Lett., 163 (1971); R. H. Martin, C. Y. Ennield, and N. Defay, ibid., 2731 (1972).

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8. Sir:

Some years ago the synthesis and structure proof of the stable 1,2-dioxyate, derived from adamantylideneadamantane, was reported. Subsequently this molecule has been studied in considerable detail. Using the same olefin moiety, we have now prepared and characterized an optically active 1,2-dioxyate.

In addition to the criteria we enumerated for the successful synthesis of the adamantylideneadamantane-1,2-dioxyate (electron-rich olefin; avoidance of "ene" reaction and no steric hindrance), stereochemical considerations played a crucial role in our present synthetic strategy. (i) The possible difficulties in resolving a 1,2-dioxyate made us decide to prepare an optically active (and if possible optically pure) olefin, as precursor of the 1,2-dioxyate. (ii) Condition i requires either the synthesis of an olefin with a functional group allowing resolution, or the synthesis of an optically active olefin precursor. (iii) The position and nature of the substituent, which imparts chirality...