Chiroptical Molecular Switches 1; Principles and Syntheses.

Lange, Ben de; Jager, Wolter F.; Feringa, Bernard

Published in:
Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liq

Publication date:
1992

Mol. Cryst. Liq. Cryst. 1992, Vol. 217, pp. 129–132
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

CHIROPTICAL MOLECULAR SWITCHES 1; PRINCIPLES AND SYNTHESES.

BEN DE LANGE, WOLTER F. JAGER AND BEN L. FERINGA*
Department of Organic Chemistry, University of Groningen,
Nyenborgh 16, 9747 AG Groningen, The Netherlands.

Abstract The concept and the synthesis of the basic molecules for a chiroptical molecular switch are described. This molecular switch is based on photochemical interconversion of two bistable forms of chiral sterically overcrowded olefins. A large variety of these alkenes with different properties have been prepared by the use of a coupling reaction between a thioketone and a diazo compound.

INTRODUCTION

Photochemically switchable bistable molecules have recently attracted much attention due to possible applications in reversible optical data storage[1,2]. Important advantages are large increase in information storage density theoretically to the molecular level and potential applications as components in molecular computing should be possible. The use of organic molecules in this field is stimulated by the notion that a large variety of photophysical properties might be achieved by small changes in the molecular structure. So far research has focused on cis-trans isomerization of (aza)stilbenes[3,4] and reversible photocyclization reactions[5,6].

PRINCIPLES

The aim of our research is to design and synthesize the molecular components for a chiroptical molecular switch, i.e. a system where it is possible to switch photochemically between two chiral forms of an organic molecule (equation 1).

$$\underset{(+)}{P} \; \underset{\lambda_2}{\overset{h\nu \atop \lambda_1}{\rightleftharpoons}} \; \underset{(-)}{M'}$$

EQUATION 1

This project is based on two bistable forms of inherent dissymmetric alkenes. These compounds are helically shaped chiral molecules with a twisted structure. This class of compounds was first reported by Feringa and Wynberg[7]. A representative of this type of molecules is shown in figure 1.

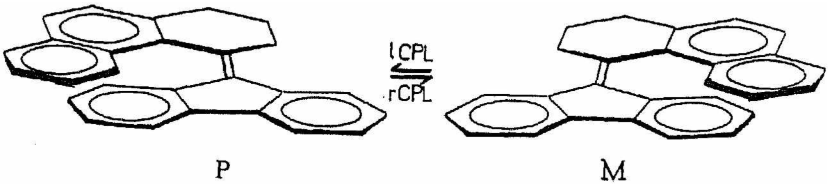


FIGURE 1

These sterically overcrowded structures can exist in two chiral forms, a P and M form. By irradiation of a racemic mixture with right or left-handed circularly polarized light (CPL), we expect to obtain a small enrichment in one of the two enantiomers. The enantiomeric excess can be detected by the use of linearly polarized light. Detection of even a small enantiomeric excess will be possible due to the large optical rotations of these helicene type molecules. Important requirements for these chiroptical molecular switches are:

a) both isomers should be thermally stable

b) both forms should be photochemically interconvertable

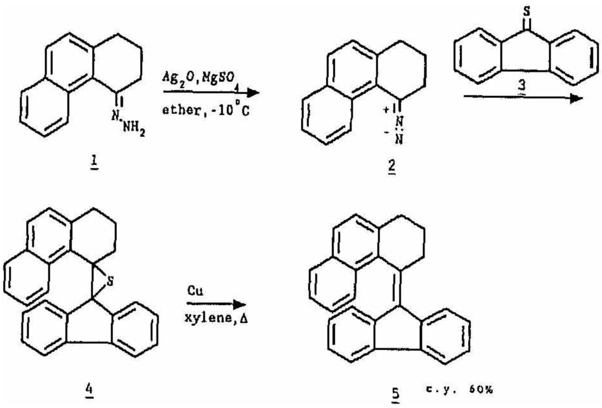
This paper will deal with the synthesis of various structural types of these sterically hindered molecules[8].

SYNTHESIS

A synthetic route to some members of this class of alkenes was reported in 1978 by Feringa and Wynberg[9] using a titanium mediated McMurry coupling between two different ketones as a key step to form the central double bond. Major disadvantages of this route are. i: the selectivity as mixtures of alkenes are obtained which are difficult to separate and ii: the strong reducing power of the titanium reagent will prevent the introduction of various groups e.g. nitro or carboxylic acid functionalities.

Wittig type reactions and Petersons olefination procedures failed to give these sterically hindered alkenes even in low yield. These results urged the need for a selective and mild synthesis.

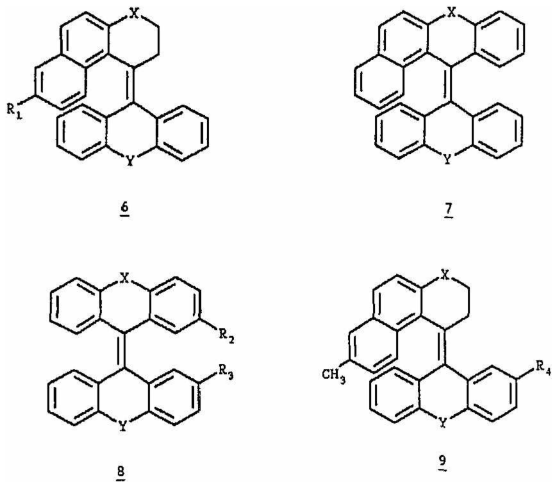
The alkenes could be obtained by using the Kellogg-Barton[10,11] method for the formation of the central double bond. The key step is the coupling between a diazo compound (2) and a thioketone (3) as exemplified in scheme 1.



SCHEME 1

Addition of the darkgreen fluorenone-9-thione (3) to the deep purple diazocompound (2), in situ prepared by Ag_2O oxidation of 4-keto-1,2-,3,4-tetrahydrophenanthrene hydrazone (1) afforded the episulfide (4). The episulfide could be easily desulphurized with copper in boiling xylene to afford the yellow alkene (5) (60% overall yield). The structure of the inherent dissymmetric alkene (5) was established by NMR techniques and X-ray analysis.

This methodology proved to be highly flexible and valuable in the synthesis of a large variety of target compounds. Typical examples of new inherent dissymmetric alkenes are shown in scheme 2. The synthetic route allowed also easy introduction of various functional groups. For instance hydroxyl groups, which can be used for attachment of these alkenes to polymers, and electron donating and accepting functionalities enabling us to tune the electronic properties of these compounds. A chiroptical switch based on molecules of type 9 is described in the following paper in this issue.



$X = CH_2, O, S, SO_2$

$Y = -, O, S, SO_2, C(CH_3)_2, CO, NCH_3$

$R_1 = H, CH_3, OCH_3$

$R_2, R_3 = H, CH_3, CH(CH_3)_2$

$R_4 = H, CH_3, tBu, OCH_3, NO_2$

SCHEME 2

REFERENCES

1. M. Emmelius, G. Pawlowski and H. W. Vollmann, Angew.Chem.Int. Ed.Engl., 28, 1445, (1989).
2. E. M. Engler, Adv. Mater., 2, 166, (1990).
3. H.-W. Losensky, H. Spelthann, A. Ehlen, F. Vögtle and J. Bargon, Angew.Chem., Int.Ed.Engl., 27, 1189 (1988).
4. H. Tachibana, T. Nakamura, M. Matsumoto, H. Komizu, E. Manda, H. Niino, A. Yabe and Y. Kawabata, J.Am.Chem.Soc., 111, 3080, (1989).
5. Y. Nakayama, K. Hayashi and M. Irie, J.Org.Chem., 55, 2592, (1990).
6. J. Daub, J. Salbeck, T. Knöchel, C. Fischer, H. Kunkely and K.M. Rapp, Angew.Chem., Int.Ed.Engl., 28, 1494, (1989).
7. B.L. Feringa and H.Wynberg, J.Am.Chem.Soc., 99, 602, (1977).
8. See for applications and a chiroptical molecular switch the following paper in this issue.
9. B.L. Feringa and H. Wynberg, Recl.Trav.Chim.Pays-Bas, 97, 249, (1978).
10. D.H.R. Barton and B.J. Willis, J.Chem.Soc., Perkin Trans., 305 (1972).
11. J. Buter, S. Wassenaar and R.M. Kellogg, J.Org.Chem., 37, 4045 (1972).