Chirality solely due to the presence of an excited state

Citation for published version (APA):
Meijer, E. W., & Wynberg, H. (1988). Chirality solely due to the presence of an excited state. *Angewandte Chemie - International Edition*, *27*(7), 975-975. https://doi.org/10.1002/anie.198809751

DOI:
10.1002/anie.198809751

Document status and date:
Published: 01/01/1988

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

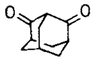
providing details and we will investigate your claim.

Download date: 08. Feb. 2024

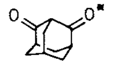
Chirality Solely Due to the Presence of an Excited State[**]

By *E. W. Meijer*[*] and *Hans Wynberg*

One of the most fascinating challenges in the study of optical activity is the synthesis of a compound in which the optical activity is solely due to the presence of an excited state. This property is available in *meso* compounds with two identical chromophores, in which one of the chromophores is selectively excited. In the case of diketones with a plane of symmetry in the ground state, the chirality in the excited state is due to the out-of-plane geometry of one of the two carbonyl groups. We have focused our attention on 2,4-adamantanedione **1**, whose chiral excited state is **1***.



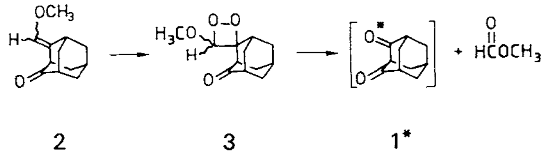
1



1*

The only way to obtain **1*** in a high enantiomeric excess is by selective excitation of one of the two carbonyl groups of **1** by chemical conversion. The enantiomeric excess via a photochemical process is expected to be low, since the difference in absorption of right (or left) circular polarized light by the two carbonyls is governed by the dissymmetry factor in absorption. Obviously, resolution of an excited-state diketone belongs in the realm of fantasy.

Chemiexcitation of ketones is well known to occur via the decomposition of 1,2-dioxetanes.[1-3] A high yield of singlet-excited-state adamantanone is obtained from the 1,2-dioxetane of 2-(methoxymethylene)adamantane.[4] The chemical route towards optically active **1*** via the optically active 1,2-dioxetane **3** is based on our previous work.[5-8]



The optically active precursor of **3** is enol ether **2**. The latter is prepared in several steps from adamantanone via the resolution of *endo*-bicyclo[3.3.1]non-6-ene-3-carboxylic acid.[8] A photooxygenation with $^1O_2$ at −50°C, followed by rapid low-temperature column chromatography, afforded a solution of 1,2-dioxetane **3** in dichloromethane.

The ketodioxetane **3** was not stable enough to allow a structure determination. However, dilute solutions of **3** in *n*-heptane yielded chemiluminescence, ($\lambda_{max} = 420$ nm, characteristic of ketone fluorescence) when heated. The product, which could be isolated in almost quantitative yield proved to be 2,4-adamantanedione **1**. It is reasonable to assume that the chemiluminescence is obtained from the decomposition of **3**, which generates **1** in the excited state (**1***). The enantiomeric excess of **3** is assumed to be identical to that of the resolved starting material, to wit $ee = 69\%$. Therefore it is expected that in the formation of **1*** one of the two carbonyls is excited in favor over the other in an enantiomeric excess of 69%.

This synthesis of chiral **1*** is, to the best of our knowledge, the first example of a chemical route to a chiral compound (with high *ee*) whose chirality is solely due to the presence of an excited state.

The synthesis of **1*** is one challenge, the detection of optical activity in this short-lived molecule is another. It seemed obvious to measure the circular polarization of chemiluminescence (CPCL) in the thermal activation of **3**.[9] However, the CPCL measurements of **3** (10^{-3}–10^{-6} mol L^{-1} in *n*-heptane) showed complete lack of optical activity at the moment of emission ($g_{chemlum} = 0 \pm 3 \times 10^{-3}$).

This is probably caused by a fast racemization in the singlet-excited state. This racemization occurs by an energy transfer between the two carbonyls in the rigid conformation of **1***. This fast energy transfer in **1*** is reasonable due to the close proximity of the two carbonyls. The UV spectrum of **1** and the CD spectrum of its mono-^{18}O analogue even indicate some π overlap of these chromophores.[7] The intramolecular n,π* energy transfer is fast relative to the lifetime of a singlet-excited-state ketone, pointing to a rate of energy transfer of $k_{ET} = 1 \times 10^{10}$ s^{-1}. Energy transfer between carbonyl n,π* excited states is a very intriguing phenomenon and several systems have been investigated,[10-13] showing both efficient and slow processes. Recently, the circular polarization in fluorescence was studied after excitation of *meso* diketones with circular polarized light,[13] indicating a very efficient energy transfer for carbonyl groups in close proximity to each other. Although triplet–triplet annihilation can be regarded as another source of racemization in the excited state, it is assumed to be of minor importance. This is based on both the reaction conditions used and the fact that up to now the occurrence of this phenomenon in 1,2-dioxetane chemiluminescence has not been reported.

From the preliminary results presented here we can conclude that a synthesis of a compound that is chiral solely in its excited state can be performed by chemiexcitation of a *meso* diketone via an optically active 1,2-dioxetane. In order to obtain stability with respect to racemization it is necessary to increase the distance between the two chromophores. This type of compound would enable us to investigate the rate of intramolecular energy transfer.

Received: February 29, 1988 [Z 2637 IE]
German version: *Angew. Chem. 100* (1988) 1004

---

[1] T. Wilson, *Int. Rev. Sci. Phys. Chem. Ser. Two 9* (1976) 265.
[2] P. D. Bartlett, M. E. Landis in H. H. Wasserman, R. W. Murray (Eds.): *Singlet Oxygen*, Academic Press, New York 1979, p. 243.
[3] A. L. Baumstark in A. A. Frimer (Ed.): *Singlet O_2, Vol. II*, CRC Press, Boca Raton, FL, USA 1985, p. 1.
[4] E. W. Meijer, H. Wynberg, *Tetrahedron Lett. 1979*, 3997.
[5] H. Wynberg, H. Nyman, *J. Am. Chem. Soc. 99* (1977) 603.
[6] H. Numan, H. Wynberg, *J. Org. Chem. 43* (1978) 2232.
[7] E. W. Meijer, H. Wynberg, *J. Am. Chem. Soc. 104* (1982) 1145.
[8] H. Numan, C. B. Troostwijk, J. H. Wieringa, H. Wynberg, *Tetrahedron Lett. 1977*, 1761.
[9] H. Wynberg, H. Numan, H. P. J. M. Dekkers, *J. Am. Chem. Soc. 99* (1977) 3870.
[10] P. J. Wagner, T. Nakahira, *J. Am. Chem. Soc. 95* (1973) 8474.
[11] P. Lechtken, N. J. Turro, *Angew. Chem. 85* (1973) 300; *Angew. Chem. Int. Ed. Engl. 12* (1973) 314.
[12] E. A. Lissi, M. V. Encinas, F. Castaneda, F. A. Olea, *J. Phys. Chem. 84* (1980) 251.
[13] P. H. Schippers, H. P. J. M. Dekkers, *J. Am. Chem. Soc. 105* (1983) 145.

---

[*] Dr. E. W. Meijer
Philips Research Laboratories
P.O. Box 80000, NL-5600 JA Eindhoven (The Netherlands)
Prof. Dr. H. Wynberg
Dept. of Organic Chemistry, University of Groningen
NL-9747 AG Groningen (The Netherlands)

[**] The authors gratefully acknowledge Dr. *H. P. J. M. Dekkers* and Dr. *P. H. Schippers* for measuring the CPCL spectra and for stimulating discussions.