This article was downloaded by: [Tomsk State University of Control Systems and

Radio]

On: 18 February 2013, At: 13:24

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

http://www.tandfonline.com/loi/gmcl19

Helioghromic Fulgides of Indole Species

Oieg Y. Fedorovskiy $^{\rm a}$, Yriy M. Chunaev $^{\rm a}$, Lidiya N. Kurkovskaya $^{\rm a}$, Nina M. Prghiyalgovskaya $^{\rm a}$ & Nikolay O. Pirogov $^{\rm a}$

^a Russian Chemical Technological University by D. I. Mendeleev, 125190, Moscow, Russia Version of record first published: 24 Sep 2006.

To cite this article: Oieg Y. Fedorovskiy, Yriy M. Chunaev, Lidiya N. Kurkovskaya, Nina M. Prghiyalgovskaya & Nikolay O. Pirogov (1994): Helioghromic Fulgides of Indole Species, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 246:1, 63-66

To link to this article: http://dx.doi.org/10.1080/10587259408037789

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever

caused arising directly or indirectly in connection with or arising out of the use of this material.

Mol. Cryst. Liq. Cryst. 1994, Vol. 246, pp. 63-66 Reprints available directly from the publisher Photocopying permitted by license only © 1994 Gordon and Breach Science Publishers S.A. Printed in the United States of America

HELIOCHROMIC FULGIDES OF INDOLE SPECIES

Oleg Y.Fedorovskiy, Yriy M.Chunaev, Lidiya N.Kurkovskaya Nina M.Prghiyalgovskaya, Nikolay O.Pirogov Russian Chemical Technological University by D.I.Mendeleev, 125190 Moscow, Russia.

ABSTRACT For three fulgides photochromic behaviour was described. Also synthesis of this fulgides was described.

INTRODUCTION

Well-known heliochromic fulgides of furan, thiofen, pyrrol species present interest for utilization as photo-reactiv lenses^{1,4}. In connection with it we decided to synthesize similar fulgides of indole species.

EXPERIMENTAL

experiments (Bruker-200-SY) carried out in were with deuterated chloroform and benzene tetramethylsilan (TMS) as internal standard. We used EPS-3T "HITACHI" spectrophotometer to measure the absorption spectra.

RESULTS

From 1-methyl-2-formylindole and adamantylidensuccinate in toluene using sodium hydride by the Stobbe reaction fulgide 1 (λ =415nm) was synthesized which had E-configuration (fig.1) because the signal of vinyl's proton (7.60ppm) in H-spectrum appeared. Short-time irradiation (λ =415nm) of the E-isomer 1 in toluene leads to Z-isomer 1(λ =420nm). When we irradiate Z-isomer sunglight it reverses to the original form. Long-time

irradiation (λ =415nm) towards the ring closure reaction to form cycle product 2 (λ =534nm). Cycle product 2 of indolic fulgide undergoes a termal 1,5-H shift to form 3 which under conditions of experiment (irradiation $\lambda=415-420$ nm., toluene, $t=60^{\circ}$ C) produced coloured form 4 ($\lambda=552$ nm) reversibly.If we break irradiation and keep the solution in the dark during 3-4 hours, coloured product 4 transforms into cycle form 3. Heliochromic properties of compound 3 displays on sunglight irradiation during 0.5-1.5 sec., which produced reversibly red-cherry coloured form 4. The reverse reaction occurred in the dark. In ¹H-NMR-spectrum of coloured solution signals are observed from form 4, which can undergo E, Z-isomerisation on sunglight. By means of flash-photolysis there was determined the time of semitransformation for coloured form 2 T=200sec. and for coloured form 4 $\tau > 10^4 sec$, (toluene, $t = 20^0 c$). In this case role of E, Z-isomerisation of form 4 may be considerable.

Other indolic fulgide synthesised from 1-ethyl-3-formyl indole did not possess heliochromic properties.On irradiation (λ =403nm.)leads to E-isomer.Revers reaction ouccured on sunlight.On boiling of the fulgide in o-dichlorbenzene using ALCL3,SnCL4(0.001mol.) coloured cyclic product does not form.

It is observed that the isopropylidene derivative of 1^5 was colouring on sunglight ($\Delta\lambda$ =95nm) during 0.2-1 min.Reverse reaction occurred in the dark during 1.5-3.0 min.These properties allow to use it as heliochromic material.

APPENDIX

²⁻Adamantyliden-E(1methyl-2indolylmethylen)succinic anhydride 1.6g.(0.01mol.) 1-methyl-2-formylindole was condensed with diethyl adamantylidensuccinate 3.1g. (0.011mol.)in toluene (100cm.³) using sodium hydride 0.8g.(0.03mol) as condensing agent. After saponification by the 10% ethanolic potassium hydroxide and cyclisation by the 10% ethereal acetic anhydride gave E-fulgide 1 to yield 95%,after recrystalisation from CCl₄, m.p. 215-216°C.

irradiation (λ =415nm) towards the ring closure reaction to form cycle product 2 (λ =534nm). Cycle product 2 of indolic fulgide undergoes a termal 1,5-H shift to form 3 which under conditions of experiment (irradiation λ=415-420nm., toluene, $t=60^{\circ}C$) produced coloured form 4 ($\lambda=552$ nm) reversibly.If we break irradiation and keep the solution in the dark during 3-4 hours, coloured product 4 transforms into cycle form 3. Heliochromic properties of compound 3 displays on sunglight irradiation during 0.5-1.5 sec., which produced reversibly red-cherry coloured form 4. The reverse reaction occurred in the dark. In ¹H-NMR-spectrum of coloured solution signals are observed from form 4, which can undergo E, Z-isomerisation on sunglight. By means of flash-photolysis there was determined the time of semitransformation for coloured form 2 T=200sec. and for coloured form 4 T>104 sec, (toluene, t= 20°C). In this case role of E, Z-isomerisation of form 4 may be considerable.

Other indolic fulgide synthesised from 1-ethyl-3-formyl indole did not possess heliochromic properties. On irradiation (λ =403nm.)leads to E-isomer. Revers reaction outcoured on sunlight. On boiling of the fulgide in o-dichlorbenzene using ALCL3, SnCL4 (0.001mol.) coloured cyclic product does not form.

It is observed that the isopropylidene derivative of 1^5 was colouring on sunglight ($\Delta\lambda$ =95nm) during 0.2-1 min.Reverse reaction occurred in the dark during 1.5-3.0 min.These properties allow to use it as heliochromic material.

APPENDIX

²⁻Adamantyliden-E(1methyl-2indolylmethylen)succinic anhydride 1.6g.(0.01mol.) 1-methyl-2-formylindole was condensed with diethyl adamantylidensuccinate 3.1g. (0.011mol.)in toluene (100cm.³) using sodium hydride 0.8g.(0.03mol) as condensing agent. After saponification by the 10% ethanolic potassium hydroxide and cyclisation by the 10% ethereal acetic anhydride gave E-fulgide 1 to yield 95%, after recrystalisation from CCl₄, m.p. 215-216°C.

2-Adamantyliden-E(1ethyl-3indolylmethylen)succinic anhydride 1.72g. (0.01mol.) 1-ethyl-3-formylindole was condensed with diethyl adamantylidensuccinate 3.1g. (0.011mol.) in toluene (100cm.) using sodium hydrid 0.8g (0.03mol.) as condensing agent. After saponification by the 10% ethanolic potassium hydroxide and cyclisation by the 10% ethereal acetic anhydride gave E-fulgide 5 (λ =403nm., Z-isomer λ =415nm.) to yield 96% after recrystalisation from CCl_A, m.p. 165-166°C.

REFERENCE

- 1. H.G.Heller, S.N.Oliver, J.Whittal, W.Johnoock, P.J. Daroy, C.Trundle (USA), Photochromic fused-ring organic compounds and their use in photoreactiv lenses, U.K.P.A.2146327A GB.

 2. K.Ulrich, H.Port, H.C.Wolf, J.Wonner, F.Effenberger, H.d.Ilge, Photochromic thiofenefulgides. Photokinetics of two isopropyl derivatives., Chemical Physics 154, 311-312, (1991)

 3. Tanaka Takashi, Tanaka Kenji, Imura Satoshi, Kida Yasuji, Novel photochromic compounds, process for production thereof use thereof and composition contaning said photochromic compound, E.P.A. 0315112 (1989).
- 4. Tanaka Takashi, Imura Satoshi, Kida Yasuji, Photochromic compounds, E.P.A 0316179.
- 5 .I.Y. Grishin,,N.M. Przhiyalgovskaya,Y.M. Chunaev, V.F. Mandzhikov, L.N. Kurkovskaya, N.N. Suvorov, Photochromic fulgides on base 1-methyl-2-formylindole,Chimiya Geterocicl. Soedin. (RUSS.),1989, # 7 s.907-910.