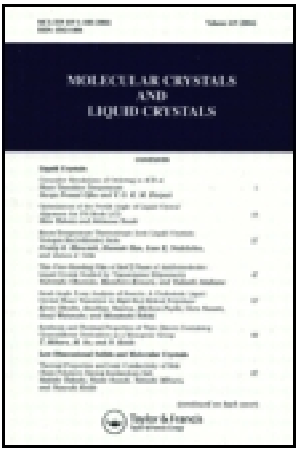

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Photochemical Generation, Photochromism and Photocyclization of 2-Norbornadenyl Substituted Benzo-1,3-Oxazoles

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PHOTOCHEMICAL GENERATION, PHOTOCHROMISM AND PHOTOCYCLIZATION OF 2-NORBORNADIENYL SUBSTITUTED BENZO-1,3-OXAZOLES

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Abstract Under UV-irradiation (365 nm) of their solutions Schiff bases (**I**) undergo the oxidative photocyclization to give 2-(3'-aryl-norbornadien-2-yl)-benzo-1,3-oxazoles (**II**) (λ_{max} = 337 nm, hexane), which then convert to the quadricyclane isomers (**III**) (λ_{max} = 287 nm). The back thermal reaction proceeds on heating the solution ($\tau_{1/2}^{70°C}$ = 2340 s).

Under prolonged UV-irradiation a further ($2\pi+2\pi+2\pi$) photocyclization of the triene moiety of (**II**) followed by 1,5-sigmatropic migration of a hydrogen atom occurs. The resulting photoproduct (**IV**) possesses by an intense fluorescence (λ^{fl}_{max} = 390 nm).

INTRODUCTION

One goal of the applied photochemistry is a search for novel photochromic compounds whose molecular fragments are susceptible of reversible photoinduced transformations.

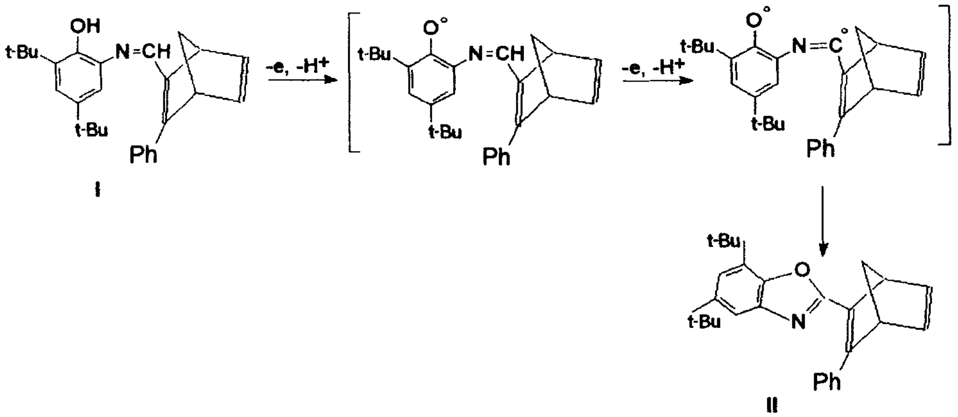
In the present work the study has been undertaken of photochemical reactivity of sterically crowded phenols which are known as efficient antioxidants of thermo- and photodestruction of polymeric materials. The phenols under study contained photochemically active C=N-group [1-3] and a norbornadiene fragment capable of photoinduced valence isomerisation to quadricyclane [4].

EXPERIMENTAL

Absorption spectra of the compounds were recorded with a spectrophotometer Specord M-40 (Germany) equipped with an irradiation device supplied with a high pressure mercury lamp DRSh-250. Photochemical reactions were carried out in hexane or methanol solutions in a photoreactor equipped with a xenone lamp. The characterization of the initial compounds and their photoproducts was made by means of UV-, IR- and ^{1}H-NMR spectroscopy and by elemental analyses as well.

N-2'-(1'-hydroxy-4',6'-di-tert.butyl)-phenyl]-3-phenyl-norbornadiene-2-carbaldimine (**I**) was prepared by coupling of 3,5-di-tert.butyl-2-aminophenol and 3-phenyl-norbornadiene-2-carbaldehyde in acetonitrile. A mixture of 3,5-di-tert.butyl-2-aminophenol (2.21 g) in 5 ml acetonitrile and 3-phenyl-norbornadiene-2-carbaldehyde (1.96 g) in 5 ml acetonitrile was refluxed for 5 min. The risen precipitate was filtered off and recrystallized from hexane. The yield of (**I**) was 2.12 g. (53%). Yellow crystal powder, m.p. 124-125°C (from hexane). ^{1}H NMR ($CDCl_3$), δ, ppm : 1.22 (9H, s, t-Bu), 1.42 (9H, s, t-Bu), 2.16-2.19 (1H, m, H^7-norbornadiene), 2.24-2.27 (1H, m, $H^{7'}$-norbornadiene), 3.93-3.97 (1H, m, H^4-norbornadiene), 4.40-4.45 (1H, m, H^1-norbornadiene), 6.90-7.00 (3H, m, H^5- and H^6-norbornadiene and $H^{3'}$-phenol), 7.20 (1H, s, $H^{5'}$-phenol, 7.35-7.45 (5H, m, Ph), 7.85 (1H, s, OH), 8.60 (1H, s, -CH=N-). I.R. (nujol), ν : 3470, 1630 cm^{-1}.

The sterically crowded phenol (**I**) as well as other similar compounds [1] is readily oxidized through one electron mechanism (-e, -H^+) to give benzoxazole (**II**) in good yield (Scheme 1).



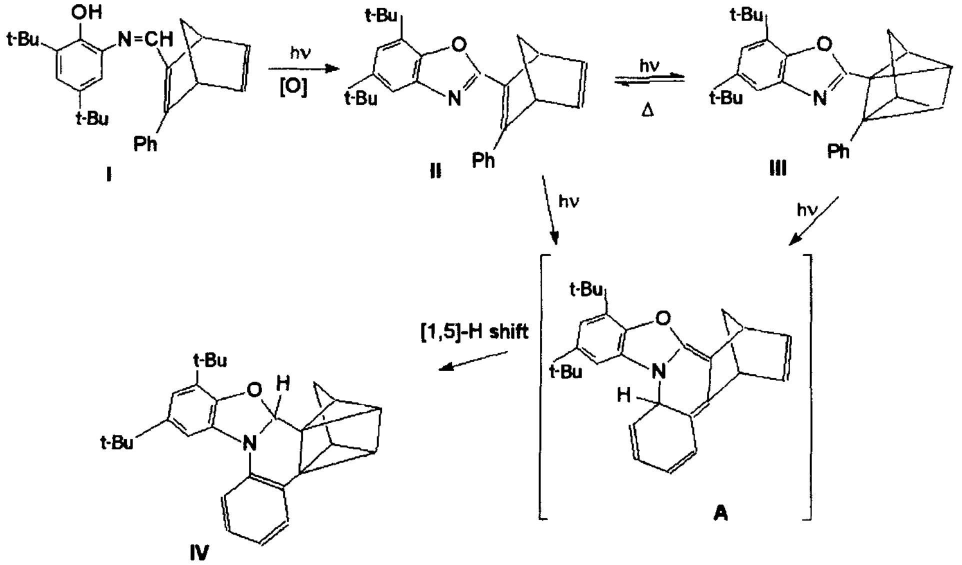
Scheme 1.

2-(4',6'-di-tert.butyl)-benzoxazolil-3-phenyl-norbornadiene (**II**). A mixture of the azomethine (**I**) (0.3 g) and PbO_2 (1.5 g) in hexane (20 ml) was stirred at room temperature as long as yellow colour of the solution disappeared (about 5 hours). The solid sediment was separated and solvent evaporated to give colourless crystals of (II) (0.3 g, yield 100%). M.p. 128-129°C (from methanol). ^{1}H NMR (CDCl$_3$), δ, ppm: 1.25 (9H, s, t-Bu), 1.35 (9H, s, t-Bu), 2.10-2.15 (1H, m, H^7-norbornadiene), 2.20-2.25 (1H, m, H$^{7'}$-norbornadiene), 3.90-3.95 (1H, m, H^4-norbornadiene), 4.45-4.50 (1H, m, H^1-norbornadiene), 6.95-7.00 (1H, m, H^6-norbornadiene and H$^{3'}$-phenol), 7.05-7.10 (1H, m, H^5-norbornadiene), 7.20-7.60 (7H, m, Ph and two meta-H of phenol). I.R. (nujol), ν : 1630, 1620 cm^{-1}.

RESULTS AND DISCUSSION

The use of UV- and NMR ^{1}H-spectroscopy as well as a preparative obtaining of novel compounds arising from the photochemical conversion of compound (I) irradiation (λ= 360 nm) hexane or methanol solution makes it possible to discover and to investigate some sequence intramolecular photoprocesses in phenol (I).

Scheme 2 features the transformations occurring on UV-irradiation (λ=365 nm) of solutions of (I) and leading to the formation of the benzoxazole derivative (II).

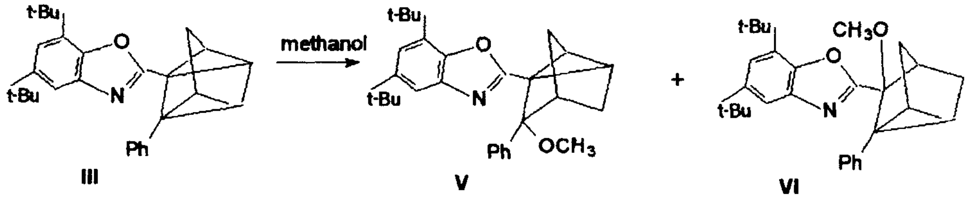


Scheme 2

The process of the photochemical cyclization is detected by decolouration of the yellow solution of the compound (I) (λ_{max}= 394 nm). The first stage of the reaction is associated with the oxidative cyclization of (I) to (II), the origin of the primary photoproduct being proven by UV- and ^{1}H NMR spectral data and its identify with the compound (II) prepared by chemical oxidation of (I) with PbO_2 in benzene solution. The subsequent irradiation of the reaction mixture containing (II) initiates a reversible intramolecular cyclization of the norbornadienyl fragment of (II) into the quadricyclane form (III). This process is accompanied with a hypsochromic shift of the longwave absorption (λ_{max}= 287 nm). The appearance of (III) in of the reaction mixture was witnessed by ^{1}H NMR spectrum which contained the signals inherent in the quadricyclane form (III)*.

The rate of the dark back reaction (III)→ (II) was measured using ^{1}H NMR technique at 70°C in benzene-d_6 solution : $k = 3\cdot10^{-4}$ s^{-1} ($\tau_{1/2}^{70°C}$ = 2340 s).

It should be noted that UV-irradiation of methanol solution of (II) was gives the rise to the formation of adducts (V) and (VI). Their formation is the result of an addition of methanol to which were arisen as the a cyclopropane ring of the quadricyclane fragment of the compound (III) facilitated by the electron withdrawing benzoxazol substitutient, see [5].



Scheme 3.

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^{1}H NMR ($CDCl_3$), δ : 1.18 (9H, s, t-Bu), 1.32 (9H, s, t-Bu), 1.81 (1H, m, H^4-quadricyclane), 2.26 (1H, d, H^7-quadricyclane), 2.38 (1H, m, H^1- quadricyclane), 2.55 (1H, d, H$^{7'}$-quadricyclane), 2.61 (2H, m, H^5- and H^6-quadricyclane), 7.10 (1H, 1, meta-H-phenol), 7.12-7.30 (5H, m, Ph), 7.42 (1H, 1, meta-H-phenol).

The structure of the compounds (V) and (VI) was determined on the basis of their ^{1}H NMR spectra.

Under prolonged UV-irradiation (100-120 min, summary light) of the solutions (**I**) or (**II**) in hexane the ultimate product (**IV**) of the photoreaction was formed as the result of the 2π+2π+2π photocyclization involving a double bond of the phenyl substituent. Examples of similar type can be found in the literature [6].

A peculiar feature of the compound (**IV**) is the intensive fluorescence (λ_{fl}= 390 nm) of its solutions which fact may be associated with the rigid molecular structure of (**IV**).

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