HETEROCYCLES, Vol. 65, No. 6, 2005, pp. 1393 - 1401
Received, 10th December, 2004, Accepted, 15th April, 2005, Published online, 19th April, 2005

SYNTHESIS OF NEW ULTRAVIOLET LIGHT ABSORBERS BASED ON 2-ARYL-2*H*-BENZOTRIAZOLES

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Abstract - A procedure for the synthesis of some new ultraviolet absorbers of the benzotriazole series is reported. The compounds bear a carboxylic or a formyl group *para* to the hydroxy group, and these functionalities impart to the absorbers improved compatibility with certain disperse dyes on polyester fibers.

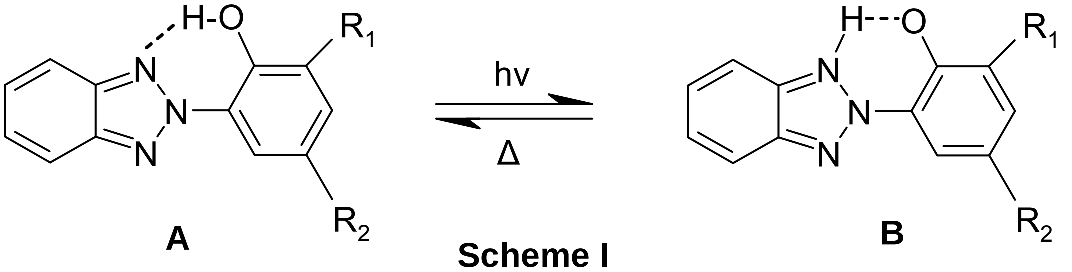
INTRODUCTION

A wide variety of additives have been developed as stabilizers for polymers against degradation[1]. Without stabilizing additives,[2-4] extended exposure of the polymer backbone to solar radiation often leads to photodegradation and oxidation of the surface of polymeric materials. Stabilization of these polymers against photooxidation is accomplished by addition of ultraviolet light absorbers. UV absorbers which have the basic 2-(2-hydroxyphenyl)-2*H*-benzotriazole structure are a very important class of such photostabilizers.[5] These additives protect polymers as well as organic pigments from UV radiation helping to preserve the original appearance and physical integrity of the polymeric system during outdoor weathering.

The photostabilization effect of photostabilizers based on 2-(2-hydroxyphenyl)-2*H*-benzotriazole is explained as being due to an excited-state intramolecular proton transfer[6] through hydrogen bond formation between the hydroxyl group of the phenyl ring and the nitrogen atom of the benzotriazole moiety,[7] Scheme I. In addition, these compounds have the ability to dissipate the electronic excitation energy into a less harmful vibrational energy, through a series of photochemical processes.[8,9]

Throughout the years,[10,11] compounds that contain the 2-(2-hydroxyphenyl)-2*H*-benzotriazole unit have been synthesized and used as UV absorbers in the dye industry. Although there are many kinds of commercially available UV stabilizers, it appears that there is yet room for the synthesis of certain 2-(2-

hydroxyphenyl)-2*H*-benzotriazole derivatives bearing functional groups which might impart to the stabilizers improved properties. We reasoned that a functional group that is capable of interacting with the absorbed dye in the polymer, would be less prone to diffuse away from the molecule of the dye. In such a case, one can reasonably expect that the stabilizer will perform its function more effectively. Given that many dyes contain NH groups, we chose the carboxylic and formyl groups as promising candidates. We have therefore developed a new general method for the preparation of 2-(2-hydroxyphenyl)-2*H*-benzotriazole derivatives, which have a COOH or a CHO *para* to the hydroxy group. It should be mentioned that our approach is somewhat analogous to that described in a patent,[12] in which the synthesis of a number of 2-(1,4-dicarboxy-6-hydroxyphenyl)-2*H*-benzotriazoles is described. These compounds are copolymerized to polyesters and polyamides, which exhibit ultra violet light-absorbing properties.



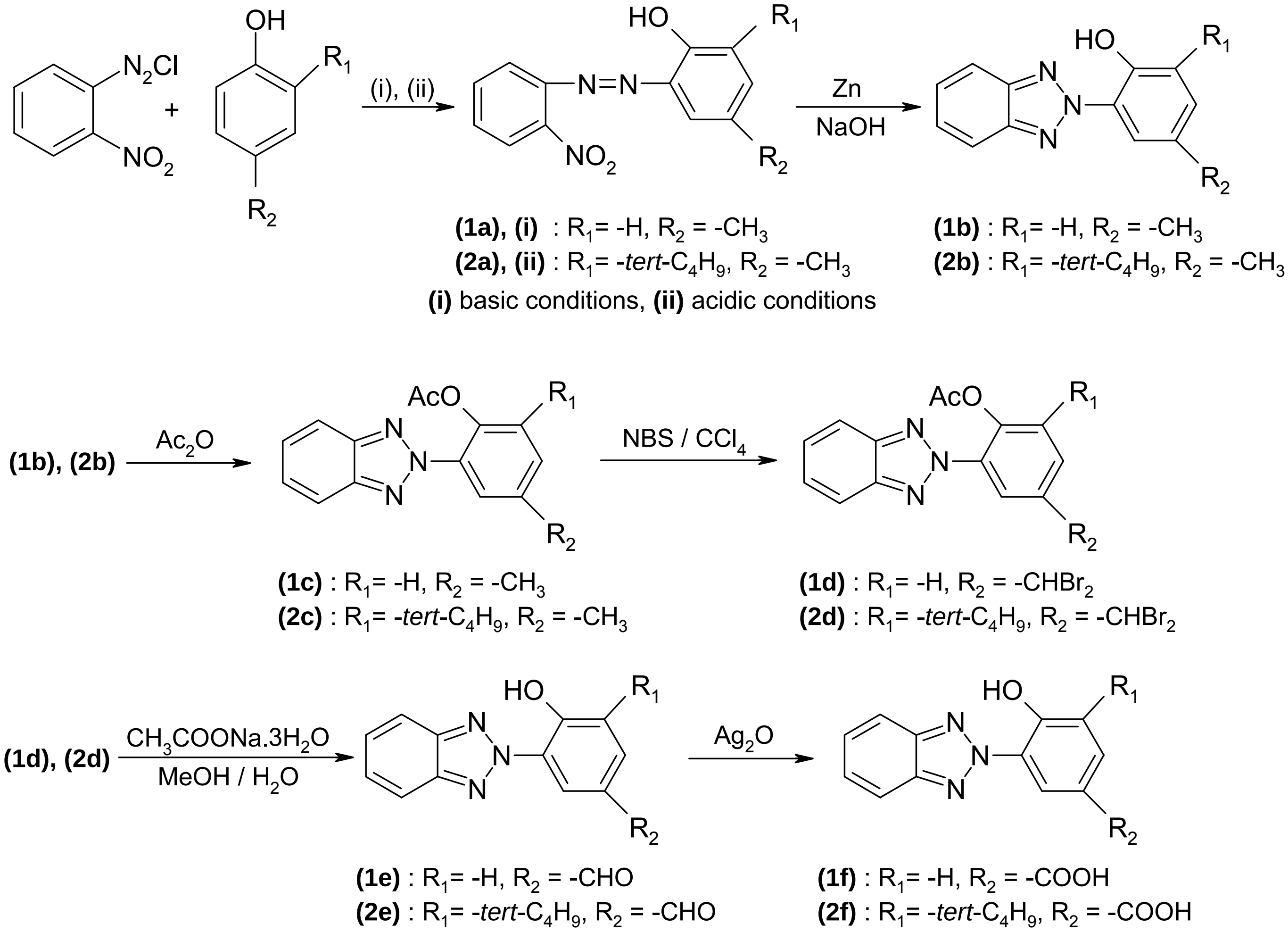
Scheme I

Based on the work of Heller,[13] we became interested in producing derivatives of 2-(2-hydroxyphenyl)-2*H*-benzotriazole which have a bulky alkyl group, such as the *tert*-butyl group, located *ortho* to the hydroxy group. The introduction of this group shields the intramolecular hydrogen bond from being broken and enhances the photoprotective capability[14-17] of these derivatives.

RESULTS AND DISCUSSION

A simple six-step process for the preparation of 2-(2-hydroxyphenyl)-2*H*-benzotriazoles is reported in Scheme II. In the first step, the synthesis of these compounds involves the diazotization of *o*-nitroaniline and coupling of the diazonium salt with the appropriate phenol and produces the corresponding azo-compounds **(1a)** and **(2a)**. The coupling reaction may be carried out under either basic or acidic conditions.

For the synthesis of 2-(2-hydroxyphenyl)-2*H*-benzotriazole derivatives **(1b)** and **(2b)**, the azo-compounds **(1a)** and **(2a)** are subsequently reduced with zinc powder in a strongly basic medium of aqueous sodium hydroxide. This reductive cyclization is a two stage process. In the first stage, the nitro and diazo nitrogens join to form benzotriazole *N*-oxide. Subsequently a marked color change from deep red to green occurs indicating that the reductive-cyclization reaction has been completed and the benzotriazole *N*-oxide moiety has been reduced.



(1a), (i) : R_1= -H, R_2 = -CH_3
(2a), (ii) : R_1= -*tert*-C_4H_9, R_2 = -CH_3
(i) basic conditions, **(ii)** acidic conditions

(1b) : R_1= -H, R_2 = -CH_3
(2b) : R_1= -*tert*-C_4H_9, R_2 = -CH_3

(1c) : R_1= -H, R_2 = -CH_3
(2c) : R_1= -*tert*-C_4H_9, R_2 = -CH_3

(1d) : R_1= -H, R_2 = -$CHBr_2$
(2d) : R_1= -*tert*-C_4H_9, R_2 = -$CHBr_2$

(1e) : R_1= -H, R_2 = -CHO
(2e) : R_1= -*tert*-C_4H_9, R_2 = -CHO

(1f) : R_1= -H, R_2 = -COOH
(2f) : R_1= -*tert*-C_4H_9, R_2 = -COOH

Scheme II

In the next step, compounds **(1b)** and **(2b)** were acetylated with acetic anhydride in the presence of sulfuric acid as catalyst. The acetylated products **(1c)** and **(2c)** were then brominated with *N*-bromosuccinimide (NBS) to give compounds **(1d)** and **(2d)** which subsequently were hydrolyzed to afford the desired formyl derivatives of 2-(2-hydroxyphenyl)-2*H*-benzotriazole **(1e)** and **(2e)**, which have a carbonyl group located *para* to the hydroxy group. Finally the desired **(1f)** and **(2f)** derivatives of 2-(2-hydroxyphenyl)-2*H*-benzotriazole were obtained by oxidation of **1e** and **2e** compounds with silver oxide in a strongly basic medium of aqueous sodium hydroxide. It should be stressed that many attempts to oxidize the carboxaldehyde **(2e)** to the corresponding carboxylic acid by a large number of conventional oxidants led to the displacement of the formyl group by a phenolic hydroxy group. Our method of synthesis is an indirect method as compared to the claims of ref. 12, which leads more directly to benzotriazoles bearing carboxylic groups.

The results[18] of the use of 2-[(2-hydroxy-5-carboxy)phenyl]-2*H*-benzotriazole **(1f)** in the dyeing of polyester fibers with disperse dyes showed that light fastness values of the dyed samples were improved using low light fastness disperse dyes, thus establishing its usefulness as a UV-absorber of the benzotriazole series. Another study of the application of 2-[(2-hydroxy-5-carboxy)phenyl]-2*H*-benzotriazole **(1f)** resulted in a significant increase in dye uptake. Duplication of this UV-absorber quantity (molar ratio dye/UV-absorber=1/2) resulted in a further increase in dye uptake. This could be related to the molecular structure of both the UV- absorber and the dye. Addition of the 2-[(2-hydroxy-5-carboxy)phenyl]-2*H*-benzotriazole **(1f)** with the carboxylic group in the molecule could enhance the uptake of disperse dye containing a weakly basic group, such as -NHPh.

In conclusion, the synthesis of several 2-(2-hydroxyphenyl)-2*H*-benzotriazole derivatives are reported. The compounds described in this paper can be employed as UV stabilizers in the dyeing of polyester fibers. The proposed route allows the introduction of the carboxy or carbonyl group located *para* to the hydroxy group in the benzotriazole ring. The presence of these groups provides the advantage of adsorption on polyester fibers and, even more importantly, compatibility with specific disperse dyes.

EXPERIMENTAL

Chemical reagents were commercial products and used without purification in most cases. Solvents were dried by standard methods. GC analyses were performed on a Varian Analytical Instruments model Star 3400CX. GC-MS analyses were performed on a Varian Analytical Instruments model SATURN 2000 mass spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on 300 MHz Bruker instrument. IR spectra were recorded on a Nicolet Analytical Instruments model Impact 420 FT-IR. Melting points were determined on an Electrothermal apparatus and are uncorrected. Products were isolated by column chromatography on Merck silica gel (230-400 mesh).

4-Methyl-2-[(*E*)-2-(2-nitrophenyl)diazenyl]benzenol (1a) : 2-Nitroaniline (27.6 g , 200 mmol) was added to concentrated hydrochloric acid (75 mL) in a 500 mL beaker and the resulting mixture was warmed to 70°C whilst stirring mechanically. The beaker was placed in an ice-salt bath and cooled to 0-5°C. To this suspension was added a cold solution of sodium nitrite (20.7 g, 300 mmol) in 40 mL of distilled water slowly with vigorous stirring. These conditions were maintained for 1 h and then a small quantity of urea was added to eliminate the unreacted nitrous acid. The reaction mixture of the diazonium salt was added slowly with stirring, over a 1 h period, to a solution of *p*-cresol (21.6 g, 200 mmol), sodium hydroxide (8 g, 200 mmol) and sodium carbonate (63.6 g, 600 mmol) in 600 mL of distilled water at rt. A red azo-compound precipitated and the reaction mixture was stirred for 3 h, the suspension was filtered and the bright red azo-compound was washed several times with cold water and dried. The yield of the crude product was 46.1 g (90%) and melted at 99-101°C. Two recrystallizations from isopropanol afforded the title compound with 73% recovery and a melting point of 109-111°C. (lit.,[19] mp 108-110°C).

2-(*tert*-Butyl)-4-methyl-6-[(*E*)-2-(2-nitrophenyl)diazenyl]benzenol (2a) : 2-Nitroaniline was diazotized according to a literature method[20] and the filtered diazonium salt solution added dropwise to a stirred warm suspension of 4-methyl-2-*tert*-butylphenol (8.2 g, 50 mmol) in 125 mL of 1N hydrochloric acid, containing 1.5 g of sodium laurylsulfate.[21] After the addition was complete, the mixture was stirred at 45°C for 6 h. The resulting red dye was filtered, washed thoroughly with warm water and dried. The yield of product, which was used without further purification for the subsequent steps, was 10.5 g (67%) with a melting point of 170-172°C (lit.,[21] mp 170-172°C).

2-(2*H*-1,2,3-Benzotriazol-2-yl)-4-methylbenzenol (1b) : To a stirred mixture of 12.85 g (50 mmol) of **(1a),** 125 mL of ethanol and 2N sodium hydroxide (190 mL) was added in small portions zinc dust 16.3 g (250 mmol) over a 1 h period. The reaction was allowed to proceed at 100°C for 4 h. The initial deep red color of the mixture was replaced by a green color. The suspension was then filtered to remove zinc, washed with 5% aqueous solution of sodium hydroxide and the combined dark green filtrate was carefully acidified with concentrated hydrochloric acid to a pH of 1. A pale yellow precipitate was removed by filtration and the filter cake was washed several times with distilled water and dried. A total of 10.6 g of crude product was obtained. Recrystallization from ethanol gave white crystals of 2-[(2-hydroxy-5-methyl)phenyl]-2*H*-benzotriazole 9.6 g (85%), melting at 127-129°C. (lit.,[22] mp 129-131°C). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 11.13 (s, 1H), 8.20 (s, 1H), 7.92-7.95 (m, 2H), 7.46-7.49 (m, 2H), 7.06-7.10 (m, 2H), 2.32 (s, 3H). GC-MS m/z 225.

2-(2*H*-1,2,3-Benzotriazol-2-yl)-6-*tert*-butyl-4-methylbenzenol (2b) : To a stirred mixture of 9.4 g (30 mmol) of **2a**, in 65 mL of ethanol, was added dropwise a cold solution of 2N sodium hydroxide (100 mL). After the addition was completed, zinc dust 9.6 g (147 mmol) was added in small portions over a 1 h period. This mixture was heated at 100°C for 5 h and the initial deep red color of the mixture was replaced by a green color. A yellow precipitate was slowly formed, which dissolved on adding 135 mL of ethanol. The suspension was then filtered to remove zinc, washed with 5% aqueous sodium hydroxide and the combined dark green filtrate was carefully acidified with concentrated hydrochloric acid to a pH of 1. The resulting pale yellow precipitate was filtered, washed with water and dried. The yield of the product, which was used without further purification for the subsequent steps, was 6.8 g (81%) with a melting point of 139-140°C (lit.,[21] mp 139-140°C). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 11.61 (s, 1H), 8.31 (s, 1H), 8.04-8.08 (m, 2H), 7.58-7.60 (m, 2H), 7.29 (s, 1H), 2.36 (s, 3H), 1.39-1.41 (m, 9H). GC-MS m/z 281.

2-(2*H*-1,2,3-Benzotriazol-2-yl)-4-methylphenyl acetate (1c) : 30 g (133 mmol) of 2-[(2-hydroxy-5-methyl)phenyl]-2*H*-benzotriazole **(1b)** were suspended in 90 mL (0.95 mol) of acetic anhydride and 2 mL of concentrated sulfuric acid. The reaction was allowed to proceed at rt for 1 h and then heated on a steam bath for further one hour. The reaction mixture was poured into a beaker with ice-water, resulting in formation of a yellow solid. After stirring for 2 h the yellow solid was isolated by filtration, washed with cold water and dried. Purification was carried out by column chromatography using CH_2Cl_2 as eluant, yielding 33.2 g (94%) of white crystals of 2-[(2-acetoxy-5-methyl)phenyl]-2*H*-benzotriazole with a melting point of 104-106°C which was pure enough to be used without further recrystallization. GC-MS m/z 267. (lit.,[22] mp 104-106°C).

2-(2*H*-1,2,3-Benzotriazol-2-yl)-6-(*tert*-butyl)-4-methylphenyl acetate (2c) : The 2-[(2-acetoxy-3-*tert*-butyl-5-methyl)phenyl]-2*H*-benzotriazole was synthesized following the procedure[22] already described above for **1c** starting with 10.4 g (37 mmol) of 2-[(2-hydroxy-3′-*tert*-butyl-5-methyl)phenyl]-2*H*-benzotriazole **(2b).** Purification was carried out by column chromatography using CH_2Cl_2 as eluant, yielding 11.1 g (93%) of 2-[(2-acetoxy-3-*tert*-butyl-5-methyl)phenyl]-2*H*-benzotriazole as a white crystalline solid mp 117-118^{o}C, which was used without further purification. ^1H NMR (300 MHz, $CDCl_3$) δ: 7.88-7.65 (m, 3H), 7.56-7.34 (m, 2H), 7.08 (s, 1H), 2.20 (s, 3H), 2.15 (s, 3H)1.41,(s, 9H). GC-MS m/z 324.

2-(2*H*-1,2,3-Benzotriazol-2-yl)-4-dibromomethylphenyl acetate (1d) : A mixture of 10.7 g (40 mmol) 2-[(2-acetoxy-5-methyl)phenyl]-2*H*-benzotriazole **(1c)**, 15 g (84 mmol) of *N*-bromosuccinimide and 0.1 g of α,α′-bis-azo-isobutyronitrile in 150 mL of carbon tetrachloride was refluxed for 24 h. The mixture was cooled to ambient temperature and the insoluble succinimide removed by filtration. The filtrate was washed with cold water and dried over anhydrous sodium sulfate. Evaporation of the CCl_4, after removing the drying agent, left a yellow product solid. Recrystallization of this product from isopropanol afforded 14.3 g (84%) of yellow crystals of 2-[(2-acetoxy-5-dibromomethyl)phenyl]-2*H*-benzotriazole melting at 140-142°C (lit.,[22] mp 140-142°C). GC-MS m/z 426.

2-(2*H*-1,2,3-Benzotriazol-2-yl)-6-*tert*-butyl-4-dibromomethylphenyl acetate (2d) : 2-[(2-acetoxy-3-*tert*-butyl-5-dibromomethyl)phenyl]-2*H*-benzotriazole was synthesized following the procedure already described above for **1d** starting with 10.7 g (33 mmol) of 2-[(2-acetoxy-3-*tert*-butyl-5-methyl)phenyl]-2*H*-benzotriazole **(2c).** The product was recrystallized from isopropanol, at –15°C yielding 10.5 g (66%) yellow crystals, which melted at room temperature to a viscous liquid of 2-[(2-acetoxy-3-*tert*-butyl-5-dibromomethyl)phenyl]-2*H*-benzotriazole. ^1H NMR (300 MHz, $CDCl_3$), δ: 8.80 (s, 1H), 7.88-7.71 (m, 3H), 7.51-7.45 (m, 2H), 6.61 (s, 1H), 1.45 (s, 9H). GC-MS m/z 481.

2-(2*H*-1,2,3-Benzotriazol-2-yl)-4-hydroxybenzenecarboxaldehyde (1e) : A mixture of 4.25 g (10 mmol) of 2-[(2-acetoxy-5-dibromomethyl)phenyl]-2*H*-benzotriazole, 4.25 g (31 mmol) of sodium acetate trihydrate, 40 mL of methanol and 20 mL of water was heated at reflux for 6 h. 10 mL of concentrated hydrochloric acid were then added and refluxing continued an additional 12 h. The reaction mixture was cooled in an ice bath and the resulting precipitate was isolated by filtration, washed with water and dried. Purification was carried out by column chromatography using CH_2Cl_2 as eluant, yielding 2.2 g (94%) as pale yellow crystals of 2-[(2-hydroxy-5-carbonyl)phenyl]-2*H*-benzotriazole and melting at 170-172°C. The product was 99% pure by GC and was not purified further. ^{1}H NMR (300MHz, $CDCl_3$) δ: 12.06 (s, 1H), 10.0 (s, 1H), 8.95 (s, 1H), 7.90-7.98 (m, 3H), 7.51-7.54 (m, 2H), 7.31-7.34 (d, 1H, *J*= 8.6 Hz); IR (KBr disc): 3433, 3052, 1687, 1598, 1478, 1262, 739 cm^{-1}; GC-MS m/z 239.

2-(2*H*-1,2,3-Benzotriazol-2-yl)-5-*tert*-butyl-4-hydroxybenzencarboxaldehyde (2e) : 2-[(2-Hydroxy-3-*tert*-butyl-5-carbonyl)phenyl]-2*H*-benzotriazole was synthesized following the procedure already described above for **1e** compound starting with 9.6 g (20 mmol) of 2-[(2-acetoxy-3-*tert*-butyl-5-dibromomethyl)phenyl]-2*H*-benzotriazole **(2d).** Purification was carried out by column chromatography using hexane/ether 90/10 as eluant, yielding 5.2 g (88%) pale yellow glassy solid, which on trituration with hexane gave white crystals. Recrystallization from hexane afforded the title compound, mp 134-135°C. GC-MS m/z 295. ^{1}H NMR (300 MHz, $CDCl_3$) δ : 10.01 (s 1H), 8.47 (s, 1H), 806-7.89 (m, 3H), 7.40-7.36 (m, 2H), 1.43 (m, 9H).

2-(2*H*-1,2,3-Benzotriazol-2-yl)-4-hydroxybenzenecarboxylic acid (1f) : A solution of 19.5 g (115 mmol) of silver nitrate in 120 mL of water was treated with a solution of 5.04 g (126 mmol) of sodium hydroxide in 46 mL of water. The mixture was stirred for 10 min and the silver oxide[23] was collected by filtration and washed free of nitrates with water. The wet, freshly precipitated silver oxide was transferred to 0.5 L beaker, covered with 230 mL of water and treated with 23 g (0.575 mol) of sodium hydroxide pellets with vigorous stirring. The temperature of the mixture was adjusted to 55-60°C and with stirring 27 g (113 mmol) of 2-[(2-hydroxy-5-carbonyl)phenyl]-2*H*-benzotriazole **(1e)** was added. Stirring was continued further for 1 h without heating. The precipitated silver was separated by filtration, the precipitate was washed with hot water and the filtrate was carefully acidified with concentrated hydrochloric acid to pH 1. The precipitated 2-[(2-hydroxy-5-carboxy)phenyl]-2*H*-benzotriazole was isolated by filtration and washed with cold water. Recrystallization from CH_2Cl_2 gave white crystals of 2-[(2-hydroxy-5-carboxy)phenyl]-2*H*-benzotriazole 25.7 g (89%) with a melting point of 283-285°C. ^{1}H NMR (300 MHz, DMSO) δ: 8.39 (s, 1H), 8.04-8.11 (m, 3H), 7.59-7.62 (m, 2H), 7.32(d, 1H, *J*= 8.6 Hz); IR (KBr disc) cm^{-1}: 3407, 3000, 1694, 1598, 1471, 1296, 739 cm^{-1}. Anal. Calcd for $C_{13}H_9N_3O_3$: C, 61.17; H, 3.55; N, 16.47. Found : C, 61.19; H, 3.53; N, 16.46.

2-(2*H*-1,2,3-Benzotriazol-2-yl)-5-*tert*-butyl-4-hydroxybenzenecarboxylic acid (2f) : 2-[(2-Hydroxy-3-*tert*-5-carboxy)phenyl]-2*H*-benzotriazole was synthesized following the procedure already described above for **1f** starting with 4 g (13.5 mmol) of 2-[(2-hydroxy-3-*tert*-butyl-5-carbonyl)phenyl]-2*H*-benzotriazole **(2e).** Purification was carried out by column chromatography using CH_2Cl_2:CH_3COOEt (2:1) as eluant, yielding 2.6 g (62%) white crystals of 2-[(2-hydroxy-3-*tert*-butyl-5-carboxy)phenyl]-2*H*-benzotriazole and melting at 284-286°C (CH_2Cl_2-hexane). ^{1}H NMR (300 MHz, CD_3COCD_3) δ: 9.03 (s, 1H), 8.08-8.11 (m, 3H), 7.60-7.64 (m, 2H), 1.52-1.55 (m, 9H); IR (KBr disc) : 1680, 1602, 1416, 1305, 743 cm^{-1}. Anal. Calcd for $C_{17}H_{17}N_3O_3$: C, 65.58; H, 5.50; N, 13.50. Found: C, 65.54; H, 5.47; N, 13.54.

ACKNOWLEDGEMENTS

The financial support for this project was provided by the General Secretariat for Science and Technology (YPER 94YP2-115) and Institute of Organic and Pharmaceutical Chemistry, National Hellenic Research Foundation (NHRF).

Thanks are also due to Professor E. G. Tsatsaroni, Laboratory of Organic Chemical Technology and Industrial Chemistry, Department of Chemistry, Aristotle University of Thessaloniki for measuring the light fastness and adsorption of the UV-absorber on the fabric.

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