

UV Absorber Progenitors: Photo-Fries Rearrangements of Sulfonate Esters of Hydroxyphenylbenzotriazoles*

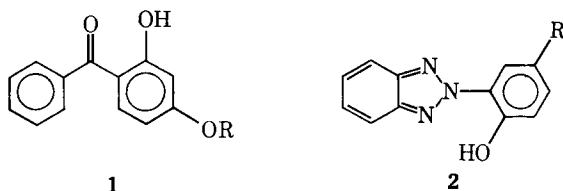
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Synopsis

Benzenesulfonate esters of hydroxyphenylbenzotriazole UV absorbers are described as UV absorber progenitors which can be used in UV-curable coating formulations. During UV exposure, they undergo a photo-Fries rearrangement to form the corresponding *o*-benzenesulfonyl phenol derivatives. These derivatives are formed in good chemical yield during bulk solution photolyses and are also readily formed in polymer films during exposure to sunlight. The reaction is specific for benzenesulfonate esters; little or no rearrangement takes place with benzyl, naphthyl, or alkyl-sulfonate esters or with benzoate esters.

INTRODUCTION

The curing of coatings by ultraviolet light, "UV curing," offers the potential to react solventless formulations at high speeds with minimal energy usage.¹⁻³ Generally, the temperature of substrates is raised to only a small extent, making it attractive to use UV curing on thermally sensitive materials such as plastics. To protect plastics from degradation by long wavelength ultraviolet light and prevent autoacceleration of aging by color bodies formed during thermal aging,⁴ it is often desirable to incorporate UV absorbers such as hydroxybenzophenones 1 or hydroxyphenylbenzotriazoles 2 in coatings for plastics.



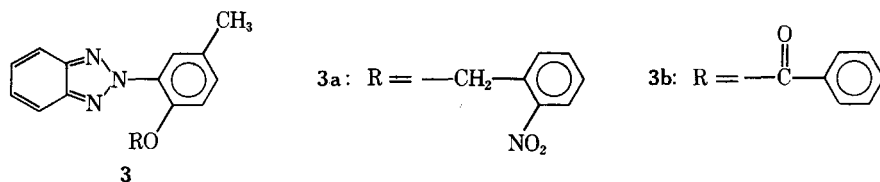
Using UV light to cure formulations which are also highly UV protective presents an inherent problem when common UV initiators such as benzoin derivatives are used. When UV absorbers such as 1 or 2 are incorporated in UV-curable formulations, satisfactory cures cannot be obtained even when the concentration of absorbers is low.⁵ The absorbers, rather than the UV initiators, absorb incident UV light, thereby preventing UV-initiated polymerization. Phenolic derivatives of hydroxybenzophenones and hydroxyphenylbenzotriazoles do not absorb as strongly in the 350–400 nm region as their parent compounds,⁶ and formulations containing relatively high concentrations of these derivatives

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undergo efficient UV cures. It was previously shown that with urethane derivatives, the parent UV absorbers can be regenerated in the coating by heating.⁵ This method is restricted to articles that are coated and then subjected to heat. The goal of this work was to find other derivatives which would be compatible with a UV cure and which would not require subsequent heat treatment to regenerate the UV absorber. In principle, a photochemically reactive progenitor such as a compound which rearranges to a UV absorber or a phenolic derivative that loses its protecting group to regenerate a UV absorber could be used. Examples of the former type are the well-known aromatic salicylates which photorearrange to benzophenone UV absorbers. Unfortunately, many salicylates turn yellow when exposed to UV light.⁷ This report describes photolabile phenolic derivatives of hydroxyphenylbenzotriazole UV absorbers.

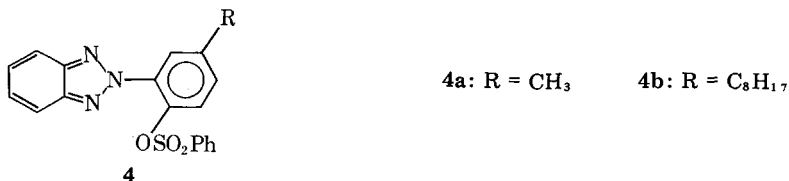
RESULTS AND DISCUSSION

The *o*-nitrobenzyl group has been used as a photolabile protecting group for amines, carboxylic acids, thiols, and alcohols.⁸ Since it appeared that it could also serve as a phenolic protecting group, *o*-nitrobenzyl ether 3a was made and photolyzed in an acrylic film. After 20 min of intense UV irradiation, 65% of UV absorber 2 (R = CH₃) was generated. Unfortunately, the by-product, *o*-nitrosobenzaldehyde, is yellow and imparted color to the film:



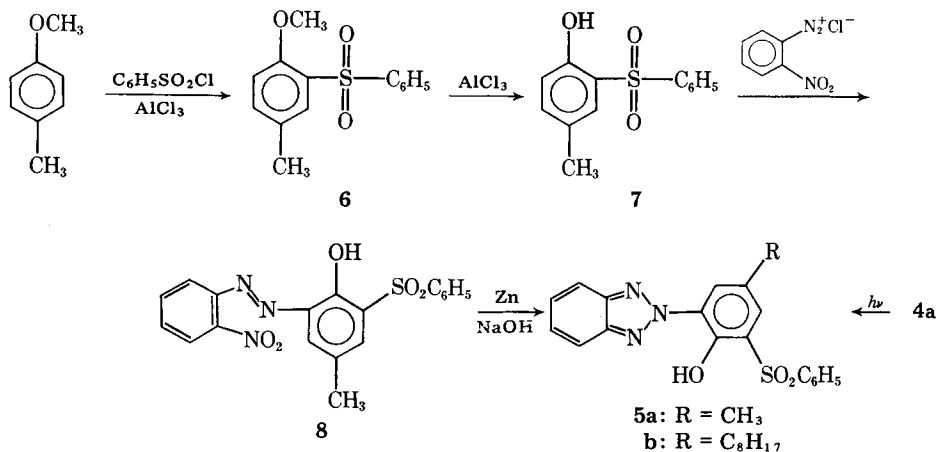
A variety of aromatic esters undergo a Fries rearrangement upon exposure to UV light.⁹ Accordingly, benzoate ester 3b was made and photolyzed in an acrylic film. The product was not identified, but it had low absorption in the 330–400 nm range and imparted a pronounced yellow color to the film.

Sulfonate esters of hydroxyphenylbenzotriazoles were examined as possible UV absorber progenitors, and it was found that benzenesulfonate esters are efficiently and conveniently converted to UV absorbers in good chemical yields on exposure to UV light. They are easily prepared by the reaction of commercial hydroxyphenylbenzotriazoles 2 with benzenesulfonyl chloride to give the corresponding sulfonate ester derivatives 4:



An ethyl acetate solution of the benzenesulfonate ester 4a was photolyzed for 12 h with 300 nm light during which time a white solid precipitated. Analysis by mass spectrometry and elemental analysis established that the precipitated

product was isomeric with the starting material. The infrared spectrum had absorptions at 7.70 and 8.78 μ , consistent with the presence of a sulfone group. The position of the benzenesulfonyl group and the identity of the photolysis product were established by an independent synthesis in which the synthesized material 5a and the photolysis product were identical in all respects (scheme I). The product is the result of a photo-Fries rearrangement of a sulfonate ester, a reaction which has received only scant attention in the literature¹⁰:



Scheme I

Photolysis of the benzenesulfonate ester 4b gave a 66% isolated yield of photolysis product 5b. The UV spectrum of the photolysis product is particularly interesting since it has an ϵ value greater than 20,000 at 345 nm as compared with an ϵ value of only 15,000 for its parent UV absorber 2 (R = C₈H₁₇) at the same wavelength (Fig. 1). Since the effectiveness of a UV absorber is dependent upon

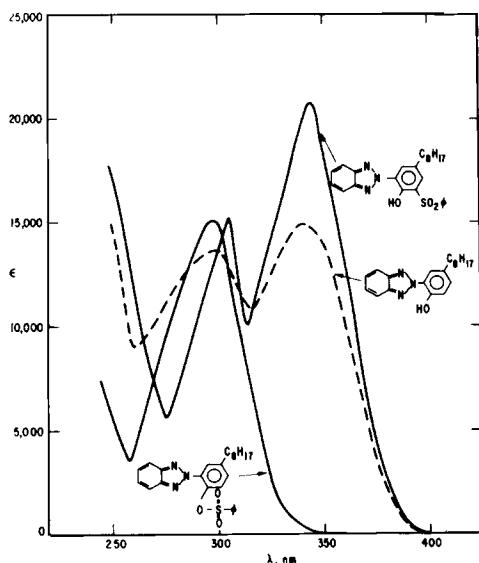


Fig. 1. UV spectra of parent UV absorber 2 (R = C₈H₁₇), sulfonate ester 4b and Fries rearrangement product 5b.

TABLE I
Yield of Photo-Fries Rearrangement Product from Benzenesulfonate Ester 4b as a Function of Irradiation Time with Intense 200–400 nm Light

Irradiation time (min)	0	10	60
% yield	0	60	82

the amount of light that it absorbs, the photolysis product is expected to be a highly effective light stabilizer.

For the sulfonate esters to function as UV absorber progenitors, they must efficiently undergo rearrangement in polymeric films. As shown in Table I, the photo-Fries rearrangement of the benzenesulfonate ester 4b takes place in good yield in an acrylic film. To see if UV absorber regeneration occurs at a sufficient rate during actual weathering to afford protection from UV light to a coated article, benzenesulfonate ester 4a was incorporated in an acrylic film and exposed to outdoor sunlight. The data in Table II show that the UV absorber is generated rapidly during the initial exposure to UV light and then is generated slowly during prolonged exposure. This indicates that the UV absorber is generated at the surface of the film and screens the light from reaching unreacted sulfonate ester. In essence, the UV absorber is generated "as needed."

The photo-Fries reaction of these esters is very specific for benzenesulfonate esters; methanesulfonate esters of hydroxyphenylbenzotriazoles do not rearrange efficiently during UV exposure. This could imply that the acid moiety must absorb light in order for the reaction to occur, and the 1-naphthalenesulfonate ester of 2 ($R = C_8H_{17}$) was made with the reasoning that a better chromophore in the acid moiety might lead to a more efficient reaction. However, after prolonged irradiation with intense UV, only about 25% reaction occurred, and it was accompanied by yellowing. To determine the effect of insulating the benzene chromophore from the sulfonate functionality, the benzenesulfonate ester of 2 ($R = CH_3$) was made and photolyzed in an acrylic film, but less than 10% reaction occurred after prolonged exposure. Thus, in the case of sulfonate esters of hydroxyphenylbenzotriazoles, the most efficient photoarrangement takes place when benzenesulfonate esters are used.

An attempt was made to extend the use of the photo-Fries reaction to hydroxybenzophenones. The benzenesulfonate and methanesulfonate esters of 2-hydroxy-4-methoxybenzophenone were made and photolyzed in ethyl acetate solutions and in acrylic films using 300 nm light. The photolysis products from both esters had only a low absorption in the 315–325 nm range indicating that sulfonate ester derivatives of hydroxybenzophenones are not useful UV absorber progenitors.

TABLE II
Yield of Photo-Fries Rearrangement Product Generated from Benzenesulfonate Ester 4a as a Function of Time in Sunlight

Time (h in Sunlight)	0	1/2	1	2	3	4	8	15	29	42
% yield	0	20	22	25	22	31	29	35	40	39

EXPERIMENTAL

Synthesis

[2-(2H-Benzotriazole-2-yl)-4-Methylphenyl Benzenesulfonate] 4a: A solution of 2-(2'-hydroxy-5'-methylphenyl)benzotriazole (9.0 g, 0.040 mol), benzenesulfonyl chloride (8.3 g, 0.047 mol), and triethylamine (4.4 g, 0.043 mol) in 10 mL of dichloromethane was stirred 20 h at room temperature. The solvent was evaporated and the residue after being taken up in 50% benzene-ether was washed with 5% KOH, 5% HCl, water, and brine. Evaporation of the dry (MgSO_4) solvent followed by recrystallization from ethyl acetate/hexane gave 11.84 g (81%) of 2-(2H-benzotriazole-2-yl)-4-methylphenyl benzenesulfonate, mp 98–100°C. Infrared (KBr) absorptions at 7.28 and 8.53 μ ($-\text{SO}_3-$); NMR (CDCl_3) δ 2.37 (3H) and 6.8–8.0 ppm (complex, 12H); UV (CHCl_2) λ_{max} 298 nm (17,600).

ANAL. Calcd for $\text{C}_{19}\text{H}_{15}\text{N}_3\text{O}_3\text{S}$: C, 62.5%; H, 4.1%; N, 11.5%. Found: C, 62.9%; H, 4.4%; N, 11.7%.

[2-(2H-Benzotriazole-2-yl)-4-*t*-Octylphenyl Benzenesulfonate] 4b: Benzenesulfonyl chloride (44 g, 0.25 mol) was added dropwise to a stirred solution of 2-(2'-hydroxy-5'-*t*-octylphenyl) benzotriazole (64.3 g, 0.20 mol) and sodium hydroxide (8.0 g, 0.20 mol) in 250 mL of acetone plus 25 mL of water. After stirring 1 h at room temperature, the solution was poured into 2 L of water. The precipitated solid was collected and recrystallized from ethyl acetate/hexane to give 78.3 g (85%) of 2-(2H-benzotriazole-2-yl)-4-*t*-octylphenyl benzenesulfonate, mp 94–96°C. Infrared (KBr) absorptions at 7.24 and 8.44 μ ($-\text{SO}_3-$); UV (CHCl_3) λ_{max} 298 nm (15,100); NMR (CDCl_3) δ 0.92, 1.55, and 1.93 (three singlets, 17H) and 6.9–8.1 (complex, 12H).

ANAL. Calcd for $\text{C}_{26}\text{H}_{29}\text{N}_3\text{O}_3\text{S}$: C, 67.4%; H, 6.3%; N, 9.1%. Found: C, 67.8%; H, 6.4%; N, 9.2%.

{2-[2'-(2-Nitrobenzyloxy)-5'-Methylphenyl]Benzotriazole} 3a: The potassium salt of 2-(2'-hydroxy-5'-methylphenyl)benzotriazole (5.6 g, 20 mmol) and 3.43 g (20 mmol) of *o*-nitrobenzyl chloride were dissolved in 15 mL of dry DMF and stirred 2 h at room temperature. The resulting mixture was dissolved in benzene (~400 mL) and washed with dilute KOH, water, and brine. Evaporation of the dry benzene (MgSO_4) gave a solid which was recrystallized from ethyl acetate/hexane to give 5.09 g of fine white needles, mp 155–157°C in two crops. Yield 70%.

ANAL. Calcd for $\text{C}_{20}\text{H}_{16}\text{N}_4\text{O}_3$: C, 66.7%; H, 4.5%; N, 15.5%. Found: C, 67.0%; H, 4.4%; N, 15.5%.

Independent Synthesis of Photo-Fries Product 5a (Yields Are Not Optimized) 2-Methoxy-5-Methyldiphenyl Sulfone, 6: By a variation of the method of Simons et al.¹¹ 0.3 mol of *p*-cresol methyl ether and 0.3 mol of benzenesulfonyl chloride were dissolved in 150 mL of dry 1,2-dichloroethane. To this solution was added 45 g of AlCl_3 in portions. When all the AlCl_3 had been added, the solution was refluxed for 1 h. Dilute HCl was added after cooling and the solvent was removed by steam distillation. The remaining solid was recrystallized from methanol to give 48 g (61% of sulfone 6, mp 135–138°C).

2-Hydroxy-5-Methyldiphenyl Sulfone 7: By the method of Simons et al.¹¹ 48 g of sulfone 6 were mixed with 96 g of AlCl_3 , and the mixture was heated at

150 ± 10°C for 2 h. After cooling, the mass was cautiously treated with dilute HCl until it appeared the Al salts were dissolved. The organic material was filtered and dissolved in 5% KOH solution which was filtered and then reacidified. The precipitate was filtered and recrystallized from methanol to give 42 g (93%) of hydroxysulfone 7 in two crops, mp 136–138°C.

2-(2'-Hydroxy-3'-Benzenesulfonyl-5'-*t*-Octylphenyl)Benzotriazole 5a: *o*-Nitroaniline (1.38 g, 10 mmol) was dissolved in 10 mL of glacial acetic acid containing 5 mL of 3*N* HCl. The solution was cooled in an ice bath and NaNO₂ (0.7 g, 10 mmol) in 8 mL of H₂O was added dropwise. This cold solution was added dropwise to an ice-cold stirred solution of hydroxysulfone 7 (2.48 g, 10 mmol) in 30 mL of aqueous NaOH. (The solution should be slightly basic after completion of the addition.) The dark red azo compound and 0.65 g of Zn powder were slurried with stirring in 10 mL of methanol plus 5 mL of 30% sodium hydroxide solution. After heating to reflux, the solution was cooled and washed with H₂O into ether–benzene. The organic layer was washed with concentrated HCl until the Zn salts were dissolved. After washing with water and brine, the dry (MgSO₄) organic layer was evaporated to give a yellow solid. After two recrystallizations from ethyl acetate, there was obtained 0.35 g (10% from hydroxysulfone 6) of yellow prisms, mp 252–254°C, identical in all respects (TLC, ir, mixture mp) with the photolysis product described below.

Photolyses

Benzenesulfonate ester 4a (1.5 g) was dissolved in 50 mL of ethyl acetate and photolyzed through quartz tubes in a Rayonette merry-go-round with 3000 Å light for 12 h. A precipitate which formed was filtered to give 0.6 g of white solid, mp 250–252°C, identified as 2-(2'-hydroxy-3'-benzenesulfonyl-5'-methyl)benzotriazole (5a). Infrared (KBr) absorptions at 7.70 and 8.78 μ (—SO₂—); UV (CHCl₃) λ_{max} 344 (20,700) and 304 nm (13,900); mass spectrum *m/e* = 365.

ANAL. Calcd for C₁₉H₁₅N₃O₃S: C, 62.5%; H, 4.1%; N, 11.5%. Found: C, 63.0%; H, 4.3%; N, 11.7%.

Benzenesulfonate ester 4b (2.4 g) was dissolved in 80 mL of ethyl acetate and photolyzed through quartz tubes in a Rayonette merry-go-round with 3000 Å light for 24 h. The solvent was evaporated and the product was chromatographed on silica gel to give 1.6 g of a white solid, mp 220–223°C, identified as 2-(2'-hydroxy-3'-benzenesulfonyl-5'-*t*-octyl) benzotriazole (5b). Infrared (KBr) absorptions at 7.69, 7.73, and 8.78 μ (—SO₂—); NMR (CDCl₃) δ 0.78, 1.53, and 1.92 (three singlets, 17H), 7.5–8.9 (complex, 11H), and 12.56 ppm (singlet, 1H); mass spectrum *m/e* = 463; UV (CHCl₃) λ_{max} 345 (20,800) and 305 nm (15,200).

ANAL. Calcd for C₂₆H₂₉N₃O₃S: C, 67.4%; H, 6.3%; N, 9.1%. Found: C, 67.6%; H, 6.6%; N, 9.2%.

A film was prepared by casting on glass a dichloromethane solution containing 39.5 mg of 2-(2H-benzotriazole-2-yl)-4-*t*-octylphenylbenzenesulfonate and 1.20 g of Elvacite® 2042 (registered trademark of the E. I. DuPont de Nemours Co.), a commercial high molecular weight poly(ethyl methacrylate). After the solvent had evaporated, the resultant film was floated from the glass with water. The film was cut in strips and exposed to intense (21,000–27,000 μW/cm²) 200–400 nm light for various amounts of time. The photolyzed strips were dissolved in

chloroform and quantitatively analyzed by UV spectroscopy. Yields of the generated UV absorber in the various strips were calculated from the amount of absorption at 345 nm. Results are listed in Table I.

A film was prepared as above using 41.3 mg of benzenesulfonate ester 4a in 1.20 g of Elvacite 2042. Strips of the film were exposed to May outdoor sunlight in Schenectady, New York. Yields of generated UV absorber were calculated as above. Results are listed in Table II.

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