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REVIEW

Preparation and Utilization of 2-(2*H*-Benzotriazol-2-yl)-phenolic Compounds

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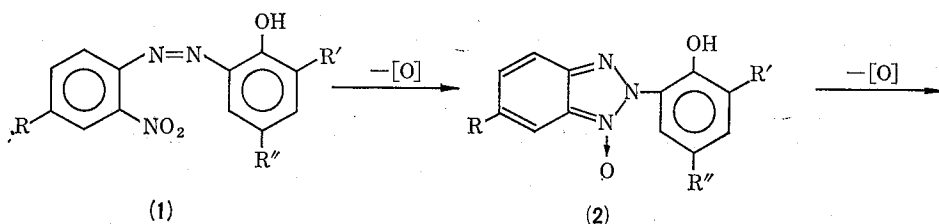
The present article involves the preparation and reaction of 2-(2*H*-benzotriazol-2-yl)phenolic compounds, which are useful as ultraviolet absorbers, as well as their utilization in polymers, dyes and cosmetics.

KEY WORDS: Preparation of 2-(2*H*-Benzotriazol-2-yl)phenols/ Reaction of 2-(2*H*-Benzotriazol-2-yl)phenols/ Antioxidant/ Use of 2-(2*H*-Benzotriazol-2-yl)phenols/

I. PREPARATION OF 2-(2*H*-BENZOTRIAZOL-2-YL)PHENOLIC COMPOUNDS

In 1959 the chemists of Ciba-Geigy AG initially found that 4-methyl-2-[(2-nitrophenyl)azo]phenol (**1**, R = R' = H, R'' = CH₃), prepared by diazotation of 2-nitroaniline and subsequent coupling with *p*-cresol, easily undergoes reductive cyclization affording 2-(2*H*-benzotriazol-2-yl)-4-methylphenol (**3**, R = R' = H, R'' = CH₃) and that it is available as light stabilizer in organic polymers. Since the pioneering proposal by the chemists of Ciba-Geigy AG a variety of 2-(2*H*-benzotriazol-2-yl)phenolic compounds (**3**) have been synthesized for the same purpose. The literatures for the high yield preparation of **1** are only concerned with controlling pH and temperature of the reaction mixture and selecting the dispersing agent and solvent for a phenolic compound used in the coupling reaction. It can be said that there is no variation in methodology for preparing **1**. However, many methods effecting the reductive cyclization of **1** to **3** have been found and reported in the literature. The reducing agents used in these methods are zinc¹⁾ in aqueous methanol containing alkali hydroxide, hydrazine hydrate^{2,3)} in the presence of alkali hydroxide, hydrogen under pressure over palladium⁴⁻⁷⁾ on carbon or platinum sulfide⁸⁾ on carbon or molybdenum modified Raney Nickel^{9,10)} together with sodium hydroxide or diethylamine, and paraformaldehyde¹¹⁾ suspended in isopropyl alcohol containing sodium hydroxide and small amounts of 2,3-dichloro-1,4-naphthoquinone. Recently, thiourea *S,S*-dioxide dissolved in aqueous isopropyl alcohol containing sodium hydroxide has been used as a new reducing agent.¹²⁾ The method involving the electrolytic reduction of **1** at a mercury electrode in aqueous sodium hydroxide has also been proposed.^{13,14)} In a few reports the preparation of **2**, which are the

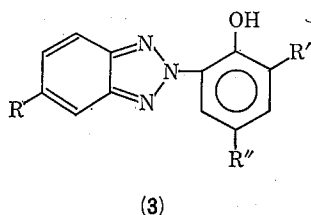
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R = H, Cl, NO₂, straight alkyl

R' = H, straight and branched alkyl

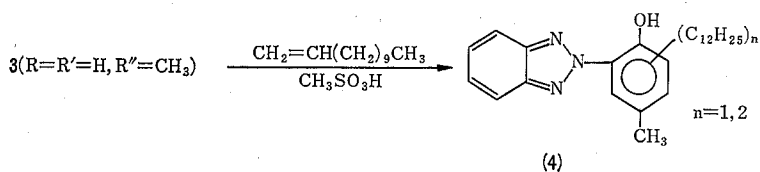
R'' = straight or branched alkyl, alkoxy



intermediates in the reductive cyclization above-mentioned, is described. The employment of glucose in ethanolic alkali hydroxide¹⁵⁾ or a mixture of sodium hydrosulfide and sodium hydroxide in toluene plus water¹⁶⁾ as reducing agent is necessary for the partial reduction of **1** affording **2**. The reduction of **1** with a limited amount of hydrazine hydrate in aqueous methanol containing sodium hydroxide and small amounts of 2,3-dichloro-1,4-naphthoquinone also provides **2**.¹⁷⁾ In the production of **3** in industrial scale, **1** are initially reduced to **2** by the lastly described procedure using a limited amount of hydrazine hydrate and the obtained **2** are again reduced to **3** by zinc in aqueous methanol containing alkali hydroxide.

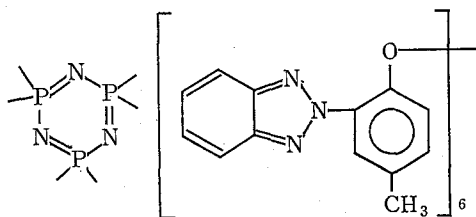
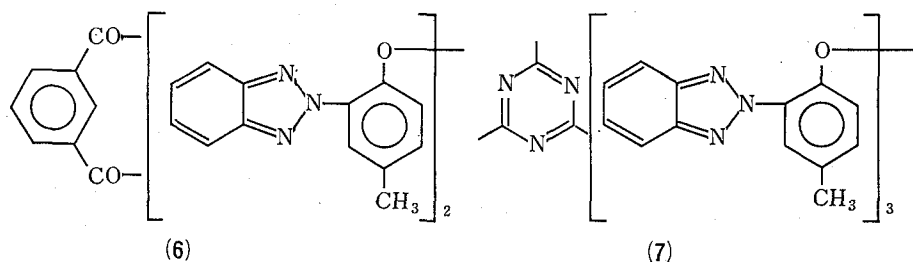
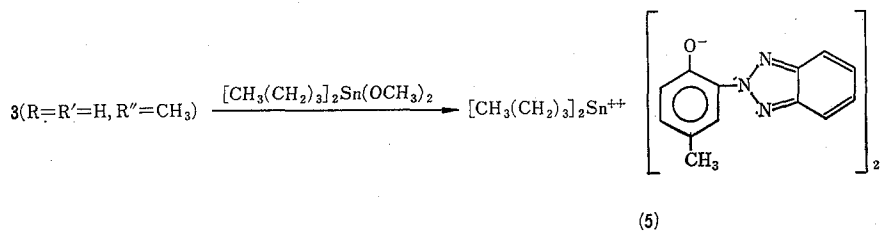
II. REACTION OF 2-(2H-BENZOTRIAZOL-2-YL)PHENOLIC COMPOUNDS

Even though the compounds **3** seem to be relatively unreactive toward chemicals, there are many reports concerning the chemical modifications of **3**. Recently, the compounds **3** of liquid state have been needed, because their blending with polymers and related substances are easy to perform. In 1990 Shipuro Kasei K.K. in Japan marketed 2-(2H-benzotriazol-2-yl)-4,6-dinonylphenol [**3**, R=H, R'=R''=(CH₂)₉CH₃] as a liquid ultraviolet absorber. Before this proposal a method by which the compound **3** (R=R'=H, R''=CH₃) can be liquefied has been devised.¹⁸⁾ When a mixture of **3** (R=R'=H, R''=CH₃) and CH₃SO₃H was agitated at 175°C while 1-dodecene was added below the liquid surface, a liquid mixture of dodecylated compound **4**, which bears dodecyl groups of ≥ 3 isomeric forms, was obtained. When

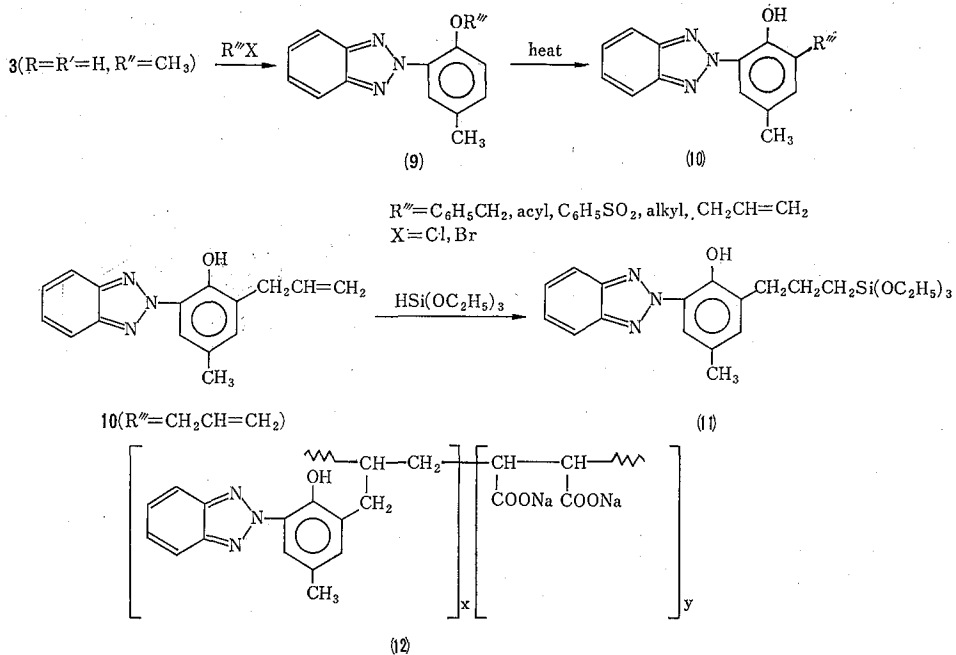


the same reaction using $\text{CH}_3\text{SO}_3\text{H}$ was carried out at 160°C for 4 h, only 2-(2*H*-benzotriazol-2-yl)-4-methyl-6-(1-methylundecyl)phenol [**3**, $\text{R}=\text{H}$, $\text{R}'=\text{CH}(\text{CH}_3)-(\text{CH}_2)_9\text{CH}_3$, $\text{R}''=\text{CH}_3$], which is also a liquid compound, was obtained as a single product.¹⁹ The same method using $\text{CH}_3\text{SO}_3\text{H}$ catalyst was further applied to a combination of 2-(2*H*-benzotriazol-2-yl)-4,6-di-*tert*-butylphenol [**3**, $\text{R}=\text{H}$, $\text{R}'=\text{R}''=\text{C}(\text{CH}_3)_3$] and *n*-octadecene. The obtained octadecylated compound, although its detailed structure is not shown, is useful as a liquid light stabilizer in coatings, photographic elements and polymers.²⁰ The isopropylation of **3** ($\text{R}=\text{R}'=\text{H}$, $\text{R}''=\text{CH}_3$) by propylene (or isopropyl alcohol) in polyphosphoric acid at 120°C or by isopropyl ether in sulfuric acid at 70°C is reported²¹ in the literature. But, these reactions have limited value because the obtained product **3** [$\text{R}=\text{H}$, $\text{R}'=\text{CH}(\text{CH}_3)_2$, $\text{R}''=\text{CH}_3$] is not liquid.

A patent literature²² claims that the refluxing **3** ($\text{R}=\text{R}''=\text{H}$, $\text{R}'=\text{CH}_3$) with dibutyltin dimethoxide in toluene affords a 2*H*-benzotriazol-2-yl phenoxytin derivative such as **5**. The compound **5** was added to styrene and the mixture was polymerized to give a polystyrene sheet with a greatly diminished yellowing degree compared with that of the polystyrene sheet without **5**. The condensations of **3** ($\text{R}=\text{R}'=\text{H}$, $\text{R}''=\text{CH}_3$) with isophthaloyl dichloride, cyanuric chloride and hexachlorocyclotriphosphazene proceed smoothly with release of hydrogen chloride to afford

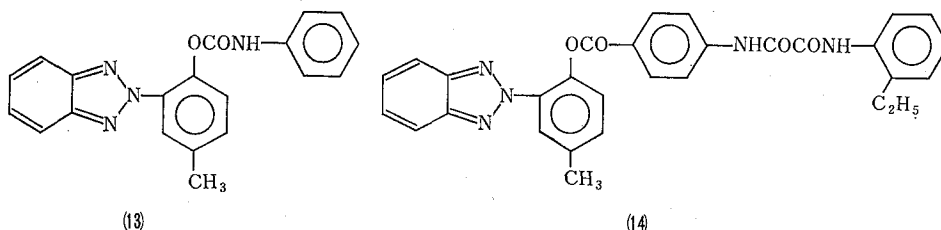


the corresponding condensates (**6**, **7** and **8**), respectively.²³⁾ These compounds are excellent light stabilizers for a certain polyester. The antioxidative mechanism by which **5**, **6**, **7** or **8** operate is not understandable. However, the antioxidative mechanism by which 2-(2*H*-benzotriazol-2-yl)-4-*tert*-octylphenyl benzenesulfonate,²⁴⁾ proposed as an antioxidant, operate is undoubtedly clear. This benzenesulfonate, when it was blended with polymers or related substances, initially undergoes the Fries rearrangement by light and/or heat and then the resulting 2-(2*H*-benzotriazol-2-yl)-4-*tert*-octyl-6-(phenylsulfonyl)phenol operate under the same antioxidative mechanism as **3**. The occurrence of the Fries rearrangement with the benzenesulfonate will be supported by an experimental fact that the benzenesulfonate was photochemically converted to 2-(2*H*-benzotriazol-2-yl)-4-*tert*-octyl-6-(phenylsulfonyl)phenol in 66% yield.²⁵⁾ The compounds **9**, prepared by the condensations of **3** ($R=R'=H$, $R''=CH_3$) with some halides represented with $R'''X$, undergo the Fries rearrangement by heat to afford the compounds **10**.²⁶⁾ Some of **10** seem to be difficult

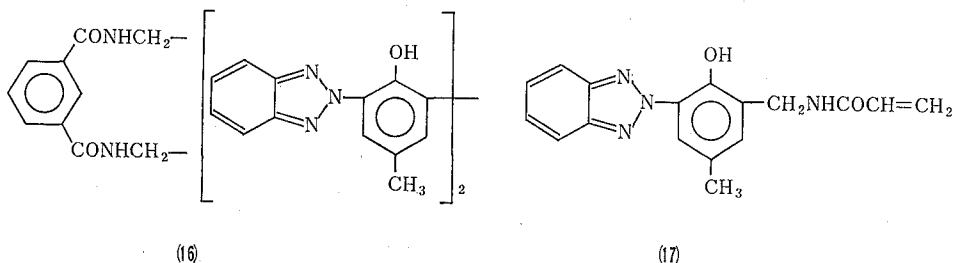
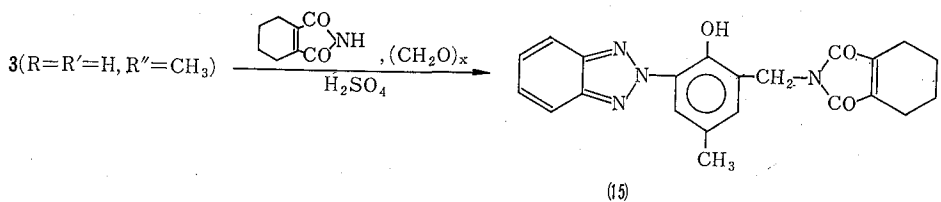


to synthesize by the method described in Section I. The compound **10** ($R'''=CH_2CH=CH_2$) was further allowed to react with triethoxysilane in the presence of a catalyst to afford the compound **11**.²⁷⁾ Also, the compound **10** ($R'''=CH_2CH=CH_2$) is copolymerized with sodium maleate affording a copolymer represented with **12**, which is used as a nonvolatile and nonextractable light stabilizer for polyolefins.²⁸⁾ On the other hand, the compound **9** ($R'''=CH_2CH=CH_2$) is copolymerized with vinylpyrrolidone. The obtained copolymer is usable as light stabilizer, suggesting that the Fries rearrangement with the **9** ($R'''=CH_2CH=CH_2$) unit of the copolymer above-mentioned can occur.²⁹⁾ Two patent literatures^{30,31)} claim that the com-

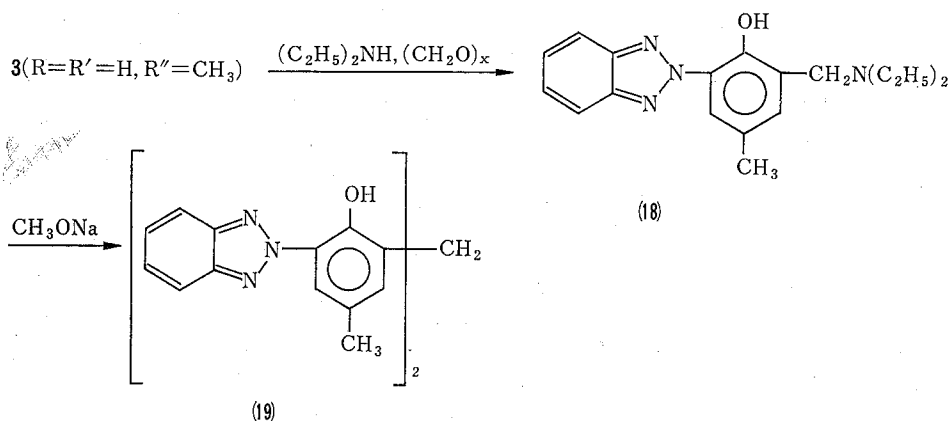
pounds **13** and **14**, which would be derived from **3** ($R=R'=H$, $R''=CH_3$), are useful as antioxidant for color fabrics and for acrylic resin, respectively. But, none is described concerning that whether the Fries rearrangement with these compounds occur or not.



The chemical modification of relatively low molecular weight of **3** is regarded as significant in rendering them less-volatile and more-miscible with polymers and related substances. When a mixture of **3** ($R=R'=H$, $R''=CH_3$) and 3,4,5,6-tetrahydrophthalimide in sulfuric acid is treated slowly with paraformaldehyde, the compound **15** is isolated.³²⁾ The reaction of **3** ($R=R'=H$, $R''=CH_3$) with *N,N*-bis-(hydroxymethyl)-1,3-benzenecarboxamide and with *N*-(hydroxymethyl)acrylamide in sulfuric acid at low temperature afforded **16** and **17**, respectively.^{33,34)} The former compound is useful as light stabilizer for polymers while the latter compound,

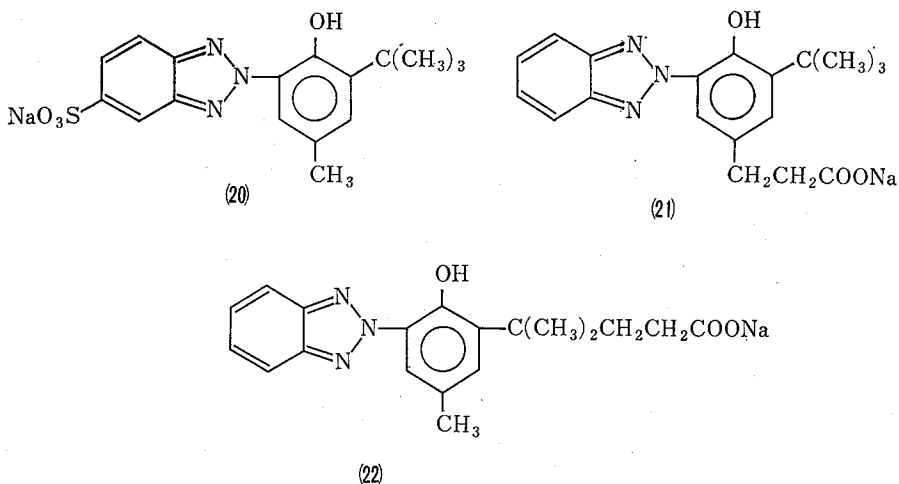


which was copolymerized with octadecyl acrylate, is usable as ultraviolet absorber in cosmetics. When **3** ($R=R'=H$, $R''=CH_3$) is allowed to react with aqueous formaldehyde in sulfuric acid, the compound **19** in a moderate yield is formed.³⁵⁾ For the high yield synthesis of **19**, **3** is initially diethylaminomethylated with diethylamine and paraformaldehyde in butyl alcohol and then the resulting 2-(2*H*-benzotriazol-2-yl)-6-[(diethylamino)methyl]-4-methylphenol (**18**) is heated with sodium methoxide in xylenes, where an excellent yield of **19** is obtained.³⁶⁾ In the conversion of **3** [$R=R'=H$, $R''=C(CH_3)_2CH_2C(CH_3)_3$] to the corresponding methylenebis compound, a somewhat different procedure is adopted; the compound **3** [$R=R'=H$,



$\text{R}''=\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_3$ is initially diethylaminomethylated in a similar manner as the case with **3** ($\text{R}=\text{R}'=\text{H}$, $\text{R}''=\text{CH}_3$) and the resulting 2-(2*H*-benzotriazol-2-yl)-6-[(diethylamino)methyl]-4-*tert*-octylphenol is condensed with the starting compound itself in the presence of sodium methoxide in xylenes.³⁷⁾

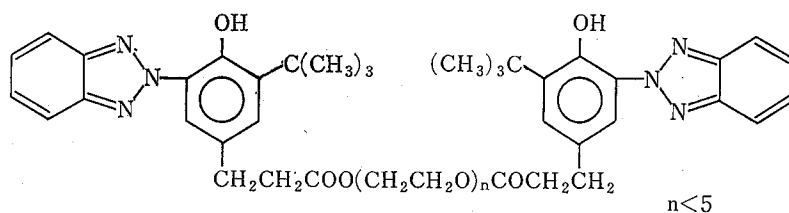
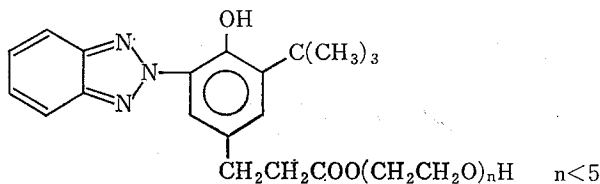
The rendering ultraviolet absorbers water-soluble is of significance, because they occasionally are used in the hydrophilic systems. The compound **3** ($\text{R}=\text{H}$, $\text{R}'=\text{C}(\text{CH}_3)_3$, $\text{R}''=\text{CH}_3$) is sulfonated to sodium 2-(3-*tert*-butyl-2-hydroxy-5-methylphenyl)-2*H*-benzotriazol-5-sulfonate (**20**), by which the yellowing degree of wool can be greatly diminished.³⁸⁾ In the molecule of **20**, the SO_3Na group and OH group are positioned apart from each other. This is associated with that the compound **20** is



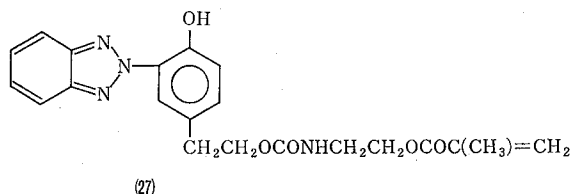
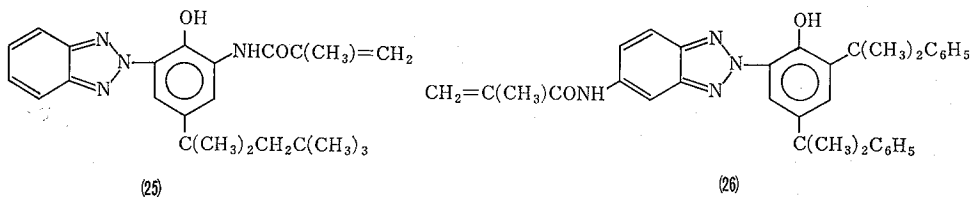
an excellent ultraviolet absorber in wool.³⁹⁾ When **3** ($\text{R}=\text{H}$, $\text{R}'=\text{R}''=\text{C}(\text{CH}_3)_2\text{C}_6\text{H}_5$) is sulfonated with about 5% fuming sulfuric acid, the SO_3Na group is introduced to both benzene nuclei of the α , α -dimethylbenzyl groups.⁴⁰⁾ When sodium 3-(3-*tert*-butyl-4-hydroxyphenyl)propionate and sodium 4-(2-hydroxy-5-methylphenyl)-4-methylpentanoate were used as the coupling component in the method described in

2-(2*H*-Benzotriazol-2-yl)phenolic Ultraviolet Absorbers

Section 1, the compounds **21** and **22** are produced, respectively.^{41,42} These compounds **21** and **22** are used in the hydrophilic systems. For example, the compound **21** is used for diminishing the decoloration of dyed wool.⁴¹ Also, it was converted to the compounds **23** and **24** by the condensations with relatively low molecular weight of poly(ethylene glycol). A polyether-polyurethane with a minimized increase in yellowing index is obtained by the combined use of these compounds and a hindered amine together with α -tocopherol and a phosphite.⁴³



The compound **3** ($R=R'=H$, $R''=CH_3$) and **3** ($R=R'=H$, $R''=C(CH_3)_2-CH_2C(CH_3)_3$) undergo nitration at their 6-position leading to the formation of corresponding nitro compounds.^{44,45} The latter nitro compound is converted to the corresponding **25** *via* a process involving reduction and condensation with methacryloyl chloride.⁴⁵ The compound **26** is also obtained by the same type of condensation of 2-(5-amino-2*H*-benzotriazol-2-yl)-4,6-bis(α , α -dimethylbenzyl)phenol with methacryloyl chloride.⁴⁶ When 2-(2*H*-benzotriazol-2-yl)-4-(2-hydroxyethyl)phenol, prepared from 2-nitroaniline and 4-(2-hydroxyethyl)phenol by the method

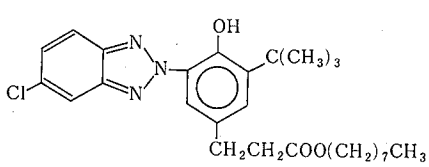
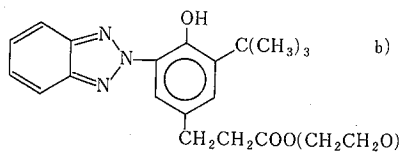


described in Section I, is allowed to react with 2-isocyanatoethyl methacrylate the compound **27** with preserving the desirable longer ultraviolet wavelength band is obtained.⁴⁷⁾

III. THE MAIN 2-(2*H*-BENZOTRIAZOL-2-YL)PHENOLIC ULTRAVIOLET ABSORBERS

The compound **3** (R=R'=H, R''=CH₃), proposed initially as 2-(2*H*-benzotriazol-2-yl)phenolic ultraviolet absorber, is the one which was synthesized with a combination of 2-nitroaniline and *p*-cresol. Instead of 2-nitroaniline other primary aromatic amines such as 4-chloro-2-nitro-, 2,4-dinitro- and 4-methyl-2-nitroaniline have been employed. On the other hand, some 4-alkyl- and 2,4-dialkylphenols have been employed instead of *p*-cresol. A few alkylphenol derivatives, in which one of the alkyl groups bears a OH or COOH group, have also been used instead of *p*-cresol (see the compounds **21**, **22** and **27**). At the present time, it seems to be possible to synthesize a variety of 2-(2*H*-benzotriazol-2-yl)phenolic compounds.

Table 1. 2-(2*H*-Benzotriazol-2-yl)phenolic Ultraviolet Absorbers

Compound	Trade name	Reference
3 (R = R' = H, R'' = CH ₃)	Tinuvin P, Seesorb 701, Mark LA-32	12)
3 [R = R' = H, R'' = C(CH ₃) ₃]	Tinuvin PS	12)
3 [R = R' = H, R'' = C(CH ₃) ₂ CH ₂ C(CH ₃) ₃]	Seesorb 709, Cyasorb UV5411	48)
3 [R = H, R' = R'' = C(CH ₃) ₃]	Tinuvin 320, Seesorb 702	12)
3 [R = H, R' = R'' = C(CH ₃) ₂ CH ₂ CH ₃]	Tinuvin 328, Seesorb 704	49)
3 [R = H, R' = R'' = C(CH ₃) ₂ C ₆ H ₅]	Tinuvin 234	40)
3 [R = Cl, R' = C(CH ₃) ₃ , R'' = CH ₃]	Tinuvin 326, Seesorb 703, Mark LA-36	12)
3 [R = Cl, R' = R'' = C(CH ₃) ₃]	Tinuvin 327, Mark LA-34	12)
3 [R = (CH ₂) ₁₁ CH ₃ , R' = H, R'' = CH ₃]		50)
3 [R = R' = H, R'' = -OC(CH ₃) ₂ CH ₂ C(CH ₃) ₃] ^{a)}	Tinuvin 510	51)
	Tinuvin 109	52)
	b)	53)

a) 2-(2*H*-Benzotriazol-2-yl)-4-*tert*-octyloxyphenol is synthesized from 2-nitroaniline and hydroquinone mono-*tert*-octyl ether according to the method described in Section I.

b) The value n is not given.

However, not so many compounds are put in the market. Here, about ten compounds, which seem to be relatively familiar, are gathered in Table I.

IV. THE USE OF THE ULTRAVIOLET ABSORBERS IN POLYMERS, DYES, AND COSMETICS

When 2-(2*H*-benzotriazol-2-yl)phenolic ultraviolet absorbers are mixed with polymers or the other substances, the weight of formers are usually <1% of that of the latters. This quantitative proportion is kepted also when the ultraviolet absorbers are used together with one or more of the other antioxidants such as hindered phenols, hindered amines, sulfur compounds and phosphorous compounds in expectation of synergism. Even if the ultraviolet absorbers are used beyond the 1% above-mentioned, no additional effect has been found. Thus, it is easy to compare the abilities of two ultraviolet absorbers in any case where they are used. For example, when the compound $3[R=R'=H, R''=C(CH_3)_2CH_2C(CH_3)_3]$ and the corresponding methylenebis compound were used in a certain polycarbonate film prepared from bisphenol A, the latter was better.⁵⁴⁾ When the compound $3(R=R'=H, R''=CH_3)$ and the compound $3[R=H, R'=C(CH_3)_3, R''=CH_3]$ were used in an acrylic-modified acrylonitrile-styrene copolymer, which is in contact with Cu in water, the latter was better.⁵⁵⁾ However, such the results may be altered by changing the used polymers, with which the ultraviolet absorbers were blended, to the other sorts of polymer also by changing the environmental factors of used polymers. Further, an additional complication may arise from the coexistence of other antioxidants than those under consideration. Thus, it is impossible to determine previously which 2-(2*H*-benzotriazol-2-yl)phenolic ultraviolet absorber is best for the given polymers (or the other substances such as dyes). It can be said that the researches relating to the usefulness of 2-(2*H*-benzotriazol-2-yl)phenolic antioxidants have been carried out independently from each other.

As early as 1962, the synergistic effect was discussed in a paper described by the chemists of J.R. Geigy AG.⁵⁶⁾ Thus, they found that the time during which polypropylene containing $3(R=R'=H, R''=CH_3)$, a certain hindered phenol and a certain sulfur compound is stable to accelerated aging in a 150°C oven is >300 h and it greatly exceeds the sum of times during which the polypropylene containing each of the antioxidants above-mentioned is stable to the same aging (7, 56 and 92 h, respectively). At present, 2-(2*H*-benzotriazol-2-yl)phenolic ultraviolet absorbers are used commonly together with the other antioxidants, where the synergistic effect is observed. The compounds $3(R=R'=H, R''=CH_3)$ together with a hindered amine was added to a maleic anhydride-styrene copolymer affording a composition with good weatherability and mechanical strength.⁵⁷⁾ Also, the compound $3(R=R'=H, R''=CH_3)$ together with an oligoepichlorohydrin derivative is used in polyolefin films to impart light stability and antistatic property.⁵⁸⁾ In this case, however, such a compound as that provides the synergistic effect is not added. The compound $3[R=Cl, R'=R''=C(CH_3)_3]$ together with a hindered amine was added to the modified copolymers prepared by grafting polyamide oligomers on Zn-crosslinked ethylene-acrylic acid copolymers to afford the weather-resistant compositions

for automobile exteriors.⁵⁹⁾ A combination of the compound $\mathbf{3}$ ($R=R'=H$, $R''=CH_3$) and a certain hindered amine is used for the improvement of lightfastness of a isoprene-styrene block copolymer.⁶⁰⁾ On the other hand, a combination of the compound $\mathbf{3}$ ($R=R'=H$, $R''=CH_3$) and a special hindered phenol having a SH group was not concerned with the synergism when it was blended with an acrylonitrile-butadiene-styrene copolymer. This means that the compound $\mathbf{3}$ ($R=R'=H$, $R''=CH_3$) is consumed mainly for protecting the latter hindered phenol from ultraviolet photolysis.⁶¹⁾ A branched polycarbonate derived from bisphenol A with which the compound $\mathbf{19}$ and 3,3-bis(4-hydroxy-3-methylphenyl)-2-oxo-2,3-dihydroindole were blended can resist embrittlement during long period of accelerated weathering in ultraviolet light. In the case where the compound $\mathbf{3}$ [$R=H$, $R'=R''=C(CH_3)_3$] was used instead of $\mathbf{19}$, not so good result was obtained.⁶²⁾ As described in Section II,³⁸⁾ the compound $\mathbf{20}$ is useful for diminishing photoyellowing of wool. When this compound was used together with a certain water-soluble hindered phenol, wool is converted to the one with the best protection against photoyellowing in sunlight, behind window-glass.⁶³⁾ A combination of the compound $\mathbf{3}$ [$R=H$, $R'=R''=C(CH_3)_2C_6H_5$] and a polymeric hindered amine can convert a certain urethane polymer to the one with good antiweathering.⁶⁴⁾ Besides, the compound $\mathbf{3}$ [$R=Cl$, $R'=C(CH_3)_3$, $R''=CH_3$], when it was used together with a hindered phenol, a cyclic phosphite and a hindered amine, can convert an ethylene-propylene block copolymer to the one with good antiweathering at elevated temperature.⁶⁵⁾

When cellulose-containing fibers were dyed with reactive dyes and further treated with a solution of the compound $\mathbf{3}$ [$R=H$, $R'=R''=C(CH_3)_2C_6H_5$] in ethylene glycol monoethyl ether plus water, the obtained dyed fibers were lightfast.⁶⁶⁾ A poly(butylene terephthalate) fabric, in which a small amount of a phosphite is included, was dyed with disperse dyes together with the compound $\mathbf{15}$ to afford the dyed fabric with improved lightfastness.⁶⁷⁾ Such the lightfastness would be more improved by the synergistic effect when the 2-(2*H*-benzotriazol-2-yl)phenolic compounds are used together with hindered phenols and hindered amines. Thus, polyester fibers were dyed with disperse dyes containing the compound $\mathbf{3}$ [$R=Cl$, $R'=R''=C(CH_3)_3$], a hindered phenol and hindered amine to afford the dyed polyester fibers with greatly improved lightfastness.⁶⁸⁾ Also, when jet-printing ink, with which sodium 2-(5-chloro-2*H*-benzotriazol-2-yl)-4,6-di-*tert*-butylphenol-3-sulfonate is blended, was applied to jet-printing, light-resistant image was obtained.⁶⁹⁾ Besides, the compound $\mathbf{3}$ [$R=R'=H$, $R''=C(CH_3)_2CH_2C(CH_3)_3$] has been blended with cosmetics.⁷⁰⁾

V. SUMMARY

The contents of this article are focused only on the 2-(2*H*-benzotriazol-2-yl)phenolic compounds which seem to be practically usable as ultraviolet absorbers. These compounds in most cases are used together with the other antioxidants such as hindered phenols and hindered amines. This never means that the study of 2-(2*H*-benzotriazol-2-yl)phenolic compounds is not so important. The function of these

compounds is to change the energy of ultraviolet light to heat energy and it differs from that of hindered phenols or hindered amines to make the chain reaction of generated active radicals impossible. Both functions are necessary for the performance of antioxidation. This means that the study of 2-(2H-benzotriazol-2-yl)phenolic compounds is as important as the study of hindered phenols or hindered amines. This review deals with the chemistry of 2-(2H-benzotriazol-2-yl)phenolic compound, and the chemistry of hindered phenols and hindered amines will be reviewed elsewhere. The contents of Sections I and II will serve for the chemists who engage in the synthesis of 2-(2H-benzotriazol-2-yl)phenolic ultraviolet absorbers. And, the contents of Section IV will serve for the chemists who are concerned with manufacturing and specification of polymers or with dyeing.

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