

Review

Synthesis of Hindered Phenols and Hindered Phenolic Light Stabilizers

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This review contains the synthetic methods of 2,6-dialkylphenols, 2,4,6-trialkylphenols, hindered bisphenolic compounds, and nonvolatile hindered phenolic compounds. These compounds can be effectively used as light stabilizers for polymers and the other components, except for 2,6-dialkylphenols.

KEY WORDS: Hindered phenol/ Light stabilizer/ 2,6-Dialkylphenol/ 2,4,6-Trialkylphenol/ Hindered bisphenolic compound/ Hindered phenolic compound/

I. INTRODUCTION

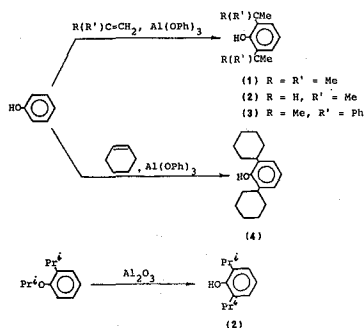
Since the pioneering proposal of Irganox 1010 (trade name by Ciba-Geigy AG, see the compound **56** in Section V) as an effective light stabilizer for agricultural films, many efforts have been devoted toward the synthesis of hindered phenols and hindered phenolic light stabilizers which are able to retard the agings of polymers and the other compositions. At the present time, a large number of researches relating to the synthetic methods of such phenolic compounds as well as those relating to their effective applications to the molding of polymers, dyeing and printing are found in the literature. Therefore it is absolutely impossible to find all of their places in one review. Thus, this review contains only the synthetic methods of 2,6-dialkyl-, and 2,4,6-trialkylphenols, hindered bisphenolic compounds, and nonvolatile hindered phenolic compounds. In spite of such the limitation allowing the numbers of compounds, which should be cited, to minimize, it was impossible to cover all of the compounds belonging to the category above-mentioned. Especially in Section V, a half or more numbers of compounds which are usable light stabilizers have been omitted.

II. SYNTHESIS OF 2,6-DIALKYLPHENOLS

If 2,6-dialkylphenols described in this section are blended with polymers or the other compositions, they would function similarly to the so-called hindered phenolic light stabilizers in preventing the chain reaction of generated active radicals by imparting a hydrogen radical to them. However, 2,6-dialkyl phenols are employed mainly as the starting materials for preparing the hindered phenolic

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light stabilizers which are practically usable. In Section I, the method synthesizing such the 2,6-dialkylphenols, except for the easily available ones such as 2,6-dimethylphenol, are described. A mixture of phenol and 3-4 mol % or less of Al turnings in a pressure resistant vessel is heated to afford Al (III) phenoxide in phenol. After venting the evolved H_2 to the atmosphere, the mixture is allowed to react with an excess of isobutylene in the same vessel affording 2,6-di-*tert*-butylphenol (1) together with 2-*tert*-butylphenol.¹⁾ The yield of 1 can be raised to about 80% or more by regulating the reaction temperature, time, and pressure in vessel¹⁻⁴⁾. This procedure, though relatively higher temperature and pressure inside the vessel are necessitate, can be applied to the reaction with propylene or with cyclohexene instead of isobutylene, where 2,6-diisopropylphenol (2) or 2,6-dicyclohexylphenol (4) is produced.^{1,2,5,6)} The analogous 2,6-dialkylation is also accomplished by using α -methylstyrene instead of isobutylene to afford 2,6-bis(α , α -dimethylbenzyl)phenol (3).⁷⁾ Some alternative methods are proposed concerning the preparation of such the 2,6-dialkylphenols. Thus, when a mixture of phenol

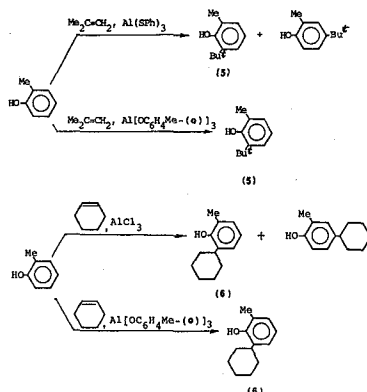


and a catalytic amount of Ga (III) phenoxide, prepared from Ga turnings and phenol, is heated together with an excess of isobutylene at 3 atmospheres in a pressure-resistant vessel, 1 is produced accompanied with 2-*tert*-butylphenol.⁸⁾ Upon heating under nitrogen, isopropyl 2-isopropylphenyl ether is catalytically rearranged to 2 by Al_2O_3 , $AlPO_4$ or silica-modified Al_2O_3 .⁹⁾ Also, a mixture of phenol and transitional Al_2O_3 , prepared by calcination of β - $Al_2O_3 \cdot 3H_2O$, is heated together with an excess of cyclohexene to afford 4 and 2-cyclohexylphenol.¹⁰⁾

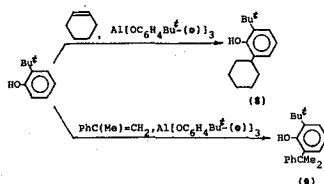
The reactions of 2-alkylphenols with the olefinic compounds above-mentioned in the presence of a catalyst are also found in the literature. Thus, as early as 1955, an excess of isobutylene was introduced to *o*-cresol containing a small amount of $POCl_3$ at 60°C to afford 2-*tert*-butyl-6-methylphenol (5) in moderate yield.¹¹⁾ Later, the reaction of *o*-cresol with isobutylene was carried out under the catalytic action of Al (III) thiophenoxide (about 6 weight % based on *o*-cresol), prepared from Al turnings and thiophenol, in an autoclave at 100°C, where 5 was produced in relatively high yield and was accompanied by small amounts of 4-*tert*-butyl-2-methylphenol.¹²⁾ The analogous reaction using propylene instead of isobutylene provides 2-isopropyl-6-methylphenol.¹²⁾ One year later it has been found that the reaction of *o*-cresol with isobutylene affording 5 is well catalyzed by 3-4 mole %

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(based on *o*-cresol) of Al (III) 2-methylphenoxide in the coexistence of NaCl (or LiCl or BaCl₂) in an autoclave, where the yield of 5 was 80%.¹³⁾ Recently, *o*-cresol was autoclaved with a small amount of Al turnings at high temperature and then the reaction mixture containing Al (III) 2-methylphenoxide was again autoclaved while feeding an excess of isobutylene to afford 5 in 90% yield.¹⁴⁾ The AlCl₃-



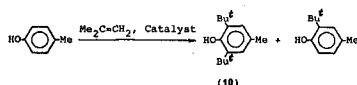
catalyzed reaction¹⁵⁾ of *o*-cresol with cyclohexene at 100°C as well as the reaction¹⁶⁾ of *o*-cresol with cyclohexanol in the presence of cation exchanger KU-2 at 150°C provide a mixture of 2-cyclohexyl-6-methyl- (6) and 4-cyclohexyl-2-methylphenol, which are capable of separating from each other. On the other hand, the reaction of *o*-cresol with cyclohexene in the presence of 3-4 mole % (based on *o*-cresol) of Al (III) 2-methylphenoxide in an autoclave proceeds smoothly affording 6 alone,¹⁷⁾ suggesting that the catalyst promotes only the alkylation occurring at the *o*-position. When α -methylstyrene is used instead of cyclohexene in the above reaction, 2-(α , α -dimethylbenzyl)-6-methylphenol (7) is produced exclusively.¹⁸⁾ The same tendency is found in the reaction of 2-*tert*-butylphenol with cyclohexene or with α -methylstyrene under the catalytic action of Al (III) 2-*tert*-butylphenoxide (3-4 mole % based on 2-*tert*-butylphenol) in an autoclave at high temperature to afford 2-*tert*-butyl-6-cyclohexylphenol (8) or 2-*tert*-butyl-6-(α , α -dimethylbenzyl)phenol (9).^{5, 7)} A patent literature claims that the reaction of 2-cyclohexylphenol with isobutylene in the presence of a catalytic amount of HgCl₂ in a pressure resistant vessel at 200°C provides 8.¹⁹⁾ But, it is not clear that whether HgCl₂-catalyst promotes only the *o*-alkylation without alkylation occurring at the *p*-position or not.



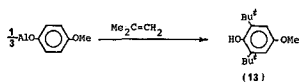
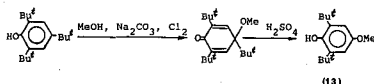
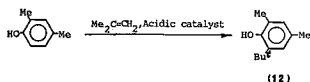
III. SYNTHESIS OF 2,4,6-TRIALKYLPHENOLS AND RELATED COMPOUNDS AS HINDERED PHENOLIC LIGHT STABILIZERS

2,6-Di-*tert*-butyl-4-methylphenol (BHT) (10), which is most famous and widely

used as a light stabilizer, can be synthesized by allowing *p*-cresol containing a catalytic amount or more of any one of concentrated H_2SO_4 ,²⁰⁾ a cation exchanger,²¹⁾ I_2 ,²²⁾ and 5-sulfosalicylic acid dihydrate²³⁾ to react with isobutylene or with a gaseous hydrocarbon mixture containing 35% isobutylene at 60–100°C, where a small amount of 2-*tert*-butyl-4-methylphenol is produced concomitantly. Recently, a few alternative methods synthesizing **10** are proposed. For example,



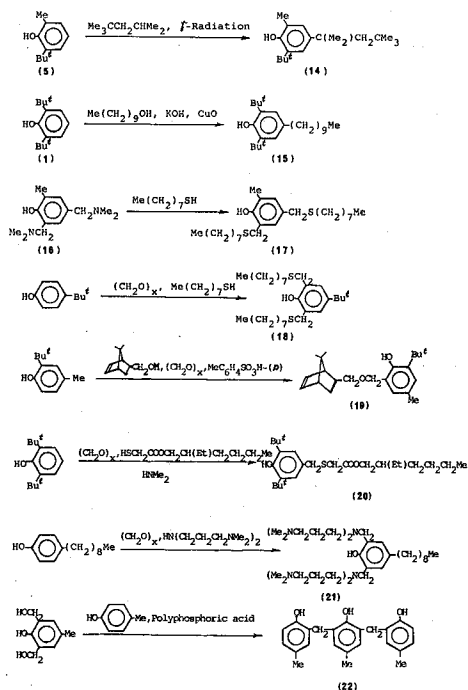
when a mixture of 2,6-di-*tert*-butyl-4-(methoxymethyl)phenol (**11**), methanol, H_2SO_4 , and Pd/C is autoclaved together with high-pressure H_2 at 35°C, **10** is produced in almost quantitative yield.²⁴⁾ This method is not so tedious, because the starting **11** is easily available by heating a mixture of **1**, formaldehyde, and methanol in the presence of dimethylamine.²⁵⁾ Also, a mixture of **1**, 35% aqueous formaldehyde, a catalytic amount of LiOH, 5% Pd/C, and methanol is autoclaved at 90°C together with H_2 at 7 bar to afford **10**.²⁶⁾ 2-*tert*-Butyl-4,6-dimethylphenol (**12**), similarly to **10**, has been used also as a light stabilizer. Thus, isobutylene is bubbled into a mixture of 2,4-dimethylphenol and a cation exchanger at 60°C affording 50% yield of **12**.²⁷⁾ If the reaction temperature is raised to 150°C, an interchange between 4-methyl group of 2,4-dimethylphenol and isobutylene molecule leading to undesirable by-products seems to occur²⁸⁾. As early as 1947, a mixture of 2,4-dimethyl- and 2,5-dimethylphenol was allowed to react with a gaseous hydrocarbon mixture containing isobutylene, *n*-butylene, and butane in the presence of a catalytic amount of 98% H_2SO_4 at 55°C giving **12** accompanied by small amounts of 4-butyl-2,5-dimethylphenol,²⁹⁾ suggesting that only 2,4-dimethylphenol undergoes *o*-alkylation by isobutylene included in the gaseous hydrocarbon mixture under the acidic conditions. Nowadays, the compound **12** is synthesized by a process involving *o*-alkylation of 2,4-dimethylphenol by an analogous hydrocarbon mixture containing isobutylene or pure isobutylene, if possible, in the presence of an acidic catalyst such as concentrated H_2SO_4 . Similarly to **10** or **12**, 2,6-di-*tert*-butyl-4-methoxyphenol (**13**) has been used also as a light stabilizer. When a mixture of 2,4,6-tri-*tert*-butylphenol³⁰⁾ and Na_2CO_3 in methanol is refluxed with introduction of Cl_2 and the resulting solution of 2,4,6-tri-*tert*-butyl-4-methoxycyclohexa-2,5-diene-1-one in methanol is again refluxed with concentrated H_2SO_4 , **13** is produced.³¹⁾ However, the



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compound **13** seems to be available more easily by the reaction of Al (III) 4-methoxyphenoxide, prepared from 4-methoxyphenol with Hg (II) acetate- or HgCl₂-activated Al, with isobutylene.³²⁾

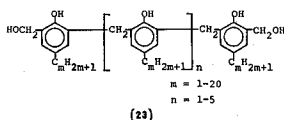
When a solution of **5** in 2,2,4-trimethylpentane is exposed *in vacuo* to γ -radiation for a long time, **14** is produced.³³⁾ The condensation of **1** with 1-decanol in the presence of KOH and CuO provides 4-decyl-2,6-di-*tert*-butylphenol (**15**).³⁴⁾ Allowing the Mannich base **16**, which can be synthesized³⁵⁾ by the Mannich reaction using *o*-cresol together with formaldehyde and dimethylamine, to react with 1-octanethiol at 150°C with evolution of dimethylamine afford **17**.³⁶⁾ Probably, it is difficult to synthesize **17** by direct *o*-cresol-formaldehyde-1-octanethiol interaction. In contrast with this, heating a mixture of 4-*tert*-butylphenol, paraformaldehyde, and 1-octanethiol with separation of H₂O affords **18**.³⁷⁾ Besides, some jointed compounds by formaldehyde such as **19**, **20**, **21**, and **22** are found in the literature. The compound **19** is synthesized by refluxing a mixture of 2-*tert*-butyl-4-methylphenol, paraformaldehyde, 5-norbornene-2-methanol, and a catalytic amount of *p*-toluenesulfonic acid in toluene.³⁸⁾ The compound **20** is synthesized when a mixture of **1**, paraformaldehyde, and 2-ethylhexyl thioglycolate is autoclaved together with



dimethylamine at 130°C.³⁹⁾ The Mannich base **21** is prepared by adding paraformaldehyde in portions to a heating mixture of 4-nonylphenol, *N,N*-dimethyl-*N*'-[3-(dimethylamino)propyl]-1,3-propanediamine, and benzene with separation of H₂O.⁴⁰⁾ The compound **22** is synthesized by the reaction of 2-hydroxy-5-methyl-1,3-benzenedimethanol, which is prepared⁴¹⁾ by the condensation of *p*-cresol with formaldehyde in 1-butanol containing NaOH, with *p*-cresol in the presence of

polyphosphoric acid.⁴²⁾

Recently, several reports concerning oligomeric or polymeric hindered phenolic light stabilizers have successively been presented. In one of these reports, the structure of oligomer resulting from the condensation of 4-alkylphenol with formaldehyde is described.⁴³⁾ This is represented by the formula which is numbered with **23**. An oligomer, which resembles in structure to **23**, is also synthesized by the condensation of 4-phenylphenol with paraformaldehyde in refluxing xylenes in the presence of aqueous NaOH.⁴⁴⁾ Heating a mixture of 4-nonylphenol, 37% aqueous formaldehyde, 1-dodecanethiol, toluene, and a small amount of *p*-toluenesulfonic acid at 140°C with separation of H₂O affords a mixture of oligomers having terminal dodecylthiomethyl groups accompanied by a small amount of 2,6-

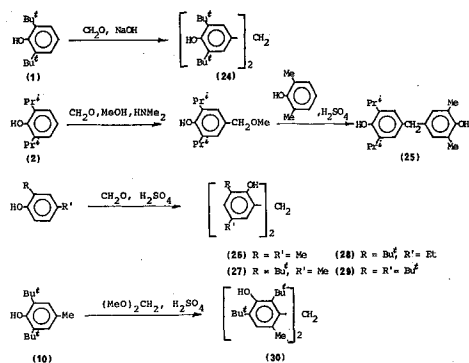


bis(dodecylthiomethyl)-4-nonylphenol.⁴⁵⁾ A mixture of oligomers, prepared by the condensation of *p*-cresol with $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl-1,3-benzenedimethanol in the presence of *p*-toluenesulfonic acid in toluene at 100°C, undergoes *tert*-butylation by *tert*-butanol with *p*-toluenesulfonic acid at 70°C affording an oligomeric light stabilizer.⁴⁶⁾ Further, a mixture of 2,4-dinonyl-, 4-nonylphenol, paraformaldehyde, and small amounts of *p*-toluenesulfonic acid is heated at 85°C to afford a mixture of oligomers, which is used as a nonvolatile liquid light stabilizer.⁴⁷⁾ Two polymeric light stabilizers are proposed.⁴⁸⁾ One is prepared by adding AlCl₃ to a solution of *p*-cresol, styrene, 4-(chloromethyl)styrene, and 3-(chloromethyl)styrene in chlorobenzene and the other is a kind of *p*-cresol-divinylbenzene copolymer.

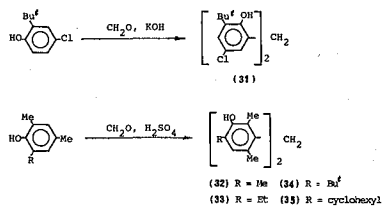
IV. SYNTHESIS OF HINDERED BISPHENOLIC LIGHT STABILIZERS

Most of the hindered bisphenolic compounds described in this section are used commonly as light stabilizers in polymers as well as the other compositions. Firstly, the methods synthesizing 4,4'-methylenebis(2,6-dialkylphenols), 2,2'-methylenebis(4,6-dialkylphenols), and 3,3'-methylenebis(2,4,6-trialkylphenols) are described. Synthesis of 4,4'-methylenebis(2,6-di-*tert*-butylphenol) (**24**) was carried out by the condensation of **1** with 37% aqueous formaldehyde in isopropanol containing a base such as NaOH or KOH at 60°C.⁴⁹⁾ Also, **24** is synthesized by refluxing a mixture of **1**, formic acid, and paraformaldehyde.⁵⁰⁾ A gradual addition of **2** to a hot mixture of formaldehyde and dimethylamine in methanol affords 2,6-diisopropyl-4-(methoxymethyl)phenol. And, it is allowed to react with 2,6-dimethylphenol in H₂SO₄ giving **25**.⁵¹⁾ Some compounds which are classifiable into 2,2'-methylenebis(4,6-dialkylphenols) are found in the literature. By the condensation with formaldehyde or with dimethoxymethane in the presence of H₂SO₄, 2,4-dimethyl-,⁵²⁾ 2-*tert*-butyl-4-methyl-,^{53, 54)} 2-*tert*-butyl-4-ethyl-,^{52, 55)} and 2,4-di-*tert*-butylphenol⁵⁶⁾ can be converted to the corresponding 2,2'-methylenebis(4,6-dialkylphenols) (**26**, **27**, **28**, and **29**, respectively). By the analogous procedure using dimethoxymethane in the

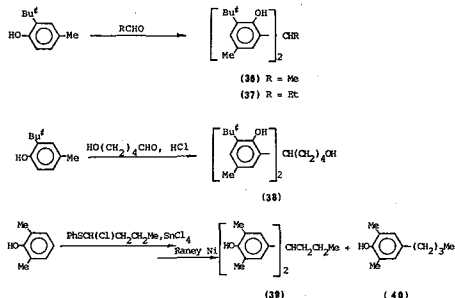
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presence of H₂SO₄, **10** is converted to 3,3'-methylenebis(2,6-di-*tert*-butyl-4-methylphenol) (**30**).⁵⁷⁾ Also, a few modified methods synthesizing 2,2'-methylenebis(4,6-dialkylphenols) are found in the literature. For example, when 2-*tert*-butyl-4-methylphenol in heptane is allowed to react with 1,3,5-trioxane in formic acid at 80°C, **27** is produced.⁵⁸⁾ When a mixture of 2-*tert*-butyl-4-ethylphenol, paraformaldehyde, and SiO₂-Al₂O₃ in hexane is heated with removal of H₂O, **28** is produced.⁵⁹⁾ In this case, cation exchanger or activated clay can be employed instead of SiO₂-Al₂O₃.⁵⁹⁾ Also, heating a solution of 2-*tert*-butyl-4-chlorophenol and 36% aqueous formaldehyde in isopropanol containing KOH at 45°C provides 2,2'-methylenebis(6-*tert*-butyl-4-chlorophenol) (**31**).⁶⁰⁾ Besides, it is found that a successive addition of concentrated H₂SO₄ and 36% aqueous formaldehyde to a cooled solution of 2,4,6-trimethyl-, 2,4-dimethyl-6-ethyl-, 2-*tert*-butyl-4,6-dimethyl- (**12**), or 2-cyclohexyl-4,6-dimethylphenol in chloroform provides 3,3'-methylenebis(2,4,6-trialkylphenol) such as **32**, **33**, **34**, or **35**, respectively.⁶¹⁾

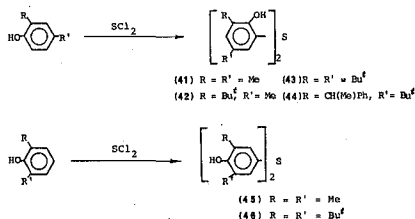


Other alkylidenebisphenolic compounds are also usable as light stabilizers. 2,2'-Ethylidene- (**36**) and 2,2'-propylidenebis(6-*tert*-butyl-4-methylphenol) (**37**) are synthesized by the reactions of 2-*tert*-butyl-4-methylphenol with aqueous acetaldehyde

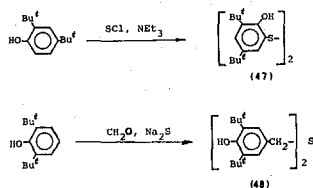


and with aqueous propionaldehyde in isooctane, respectively.⁶²⁾ Also, the compound **38** is synthesized by the condensation of 2-*tert*-butyl-4-methylphenol with 5-hydroxypentanal in concentrated HCl at 60°C.⁶³⁾ When a solution of 2,6-dimethylphenol and 1-chlorobutyl phenyl sulfide in dichloromethane is treated with SnCl₄ followed by desulfurization using Raney Ni in acetone-ethanol, 4,4'-butylidenebis(2,6-dimethylphenol) (**39**) is produced together with 4-butyl-2,6-dimethylphenol (**40**).⁶⁴⁾

Secondary, the methods synthesizing 2,2'-thiobis(4,6-dialkylphenols) and 4,4'-thiobis(2,6-dialkylphenols) are described. By the condensation with SCl₂ in neat or in a solvent such as ether or petroleum ether, 2,4-dimethyl-, 2-*tert*-butyl-4-methyl-, 2,4-di-*tert*-butyl-, and 4-*tert*-butyl-2-(α -methylbenzyl)phenol are converted to the former group of compounds (**41**, **42**, **43**, and **44**, respectively) and 2,6-dimethyl- and 2,6-di-*tert*-butylphenol (**1**) to the latter group of compounds (**45** and **46**, respectively).⁶⁵⁻⁶⁶⁾ Attempts to increase the yields of such the thiobisphenolic compounds have been made. For example, **46** is prepared by treating **1** with SCl₂ in CS₂ in the presence of Fe and heating the product mixture with NaOH in methanol followed by stirring with powdered Zn plus an excess of HCl.⁶⁷⁾ The compound **42** is prepared by a slow addition of SCl₂ to 2-*tert*-butyl-4-methylphenol in CCl₄ containing Me(CH₂)₁₇N[(CH₂CH₂O)₉H]₂ at low temperature.⁶⁸⁾ And, the compound **45** is prepared in 92% yield by adding SCl₂ to a solution of 2,6-dimethylp-



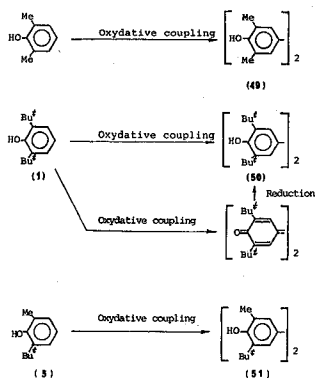
henol in cyclohexane in the presence of I₂ at low temperature followed by heating at 60°C.⁶⁹⁾ The compounds **47** and **48** are proposed as another types of sulfur-containing bisphenolic compounds. The former is synthesized by the condensation of 2,4-di-*tert*-butylphenol with SCl in the presence of triethylamine in toluene at low temperature,⁷⁰⁾ and the latter by the condensation of **1** with formaldehyde in methanol containing Na₂S.⁷¹⁾



Thirdly, the methods synthesizing 3,3',5,5'-tetramethyl- (**49**), 3,3',5,5'-tetra-*tert*-butyl- (**50**), and 3,3'-di-*tert*-butyl-5,5'-dimethyl-1,1'-biphenyl-4,4'-diol (**51**) are described. When 2,6-dimethylphenol in H₂O containing a small amount of Me(CH₂)₁₁OSO₃H is heated under O₂ and then treated successively with aqueous Cu(II) acetate and NaHCO₃, **49** is produced.⁷²⁾ When a mixture of 2,6-dimethylphenol and ZnO in methanol at 50°C is exposed to a 450-W Hg lamp while being fed with O₂,

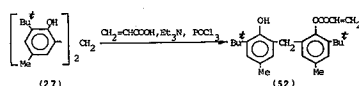
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49 is produced.⁷³⁾ When a solution of 2,6-dimethylphenol and a catalytic Cu chelate of biguanidine sulfate in H₂O, which was adjusted to pH 9, is heated at 80°C, **49** is produced.⁷⁴⁾ The reaction of a mixture of 2,6-dimethylphenol, acetonitrile, and ferrocene with 60% aqueous H₂O₂ at 50°C,⁷⁵⁾ the reaction of 2,6-dimethylphenol with Mn (III) acetylacetonate in refluxing CS₂,⁷⁶⁾ and the reaction of 2,6-dimethylphenol with CuO in a closed vessel at 100°C⁷⁷⁾ provide the same **49**. More recently, a solution of 2,6-dimethylphenol, borax, and a small amount of Me-



(CH₂)₁₁SO₃Na in H₂O is heated together with Cu(II) acetate under O₂ at 70°C followed by additional heating at 95°C without supplying O₂ to afford **49**.⁷⁸⁾ The methods synthesizing **50** can be divided into two types, methods consisting of single reaction step and those involving two reaction steps. The reaction of **1** with 50% aqueous H₂O₂ (or O₂) in the presence of 50% aqueous KOH and methyltributylammonium chloride in an autoclave at 200°C^{79,80)} as well as the reaction of **1** with Pd in nitrobenzene at 190°C⁸¹⁾ providing **50** will belong to the former type of methods. The latter type of methods will be illustrated by the following reactions. Thus, when a mixture of **1** and a catalytic amount of KOH in H₂O is autoclaved at 150°C together with high-pressure O₂ and the resulting 3,3',5,5'-tetra-*tert*-butyldiphenoquinone is again autoclaved at room temperature together with toluene and high-pressure H₂ in the presence of 10% Pd/C, **50** is produced.⁸²⁾ When 3,3',5,5'-tetra-*tert*-butyldiphenoquinone, prepared from **1** in a similar manner, is allowed to react with the starting **1**, itself, in the presence of Pd/C at 60°C, **50** is produced.⁸³⁾ Also, when 4-chloro-2,6-di-*tert*-butylphenol is oxidized by air in the presence of butylamine, H₂O, and a catalytic amount of Cu powder and the resulting 3,3',5,5'-tetra-*tert*-butyldiphenoquinone is reduced by Zn in aqueous acetic acid at room temperature, **50** is produced.⁸⁴⁾ The methods synthesizing **51** are not so many. The air oxidation of **5** in H₂O, adjusted to pH 12 by Na₂HPO₄ and Na₃PO₄, in the presence of small amounts of an anionic surfactant, xylenes, and Cu (II) acetate at 85°C⁸⁵⁾ as well as the irradiation of **5** with γ -radiation of ⁶⁰Co⁸⁶⁾ affording **51** are found in the literature.

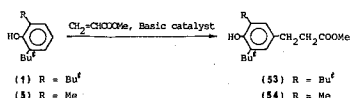
Almost all of hindered bisphenolic compounds described in this section are employed as light stabilizers without any further chemical modification. Several years ago, however, it has been found that a bisphenolic compound **27** is converted



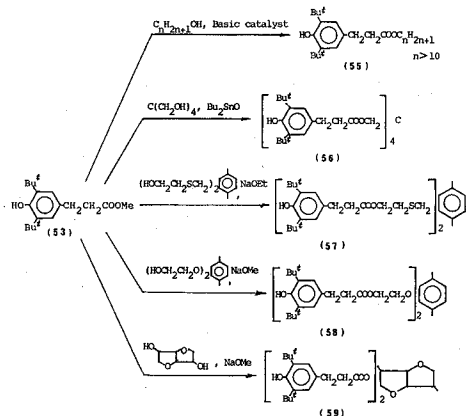
to a polymerizable light stabilizer in almost quantitative yield by treating a solution of **27**, acrylic acid, and triethylamine in toluene with POCl_3 followed by heating the reaction mixture at 80°C .⁸⁷⁾ This suggests that some of hindered bisphenolic compounds described in this section would be as susceptible to such the alteration providing the polymerizable light stabilizers as **27**.

V. SYNTHESIS OF HINDERED PHENOLIC LIGHT STABILIZERS VIA RING-SUBSTITUTIONS OF HINDERED PHENOLS

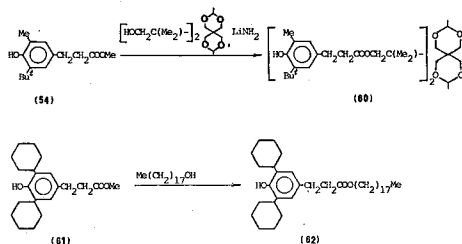
The reaction of **1** with methyl acrylate in the presence of a basic catalyst is well-known. Thus, a mixture of **1** and methyl acrylate is heated together with a small amount of sodium phenoxide or NaBH_4 to afford **53**. The yield being 82 or 96%.^{88, 89)} Cyanoethylation of **1** with acrylonitrile in the presence of *K tert*-butoxide followed by saponification and esterification with methanol provides also **53**.⁹⁰⁾ Adding methyl acrylate to a mixture of **5** and a small amount of *K 2-tert*-butyl-6-methylphenoxide at 140°C provides **54**.⁹¹⁾ The compound **53** undergoes the transesterification by some straight and branched higher alcohols ($n > 10$ in $\text{C}_n\text{H}_{2n+1}\text{OH}$)



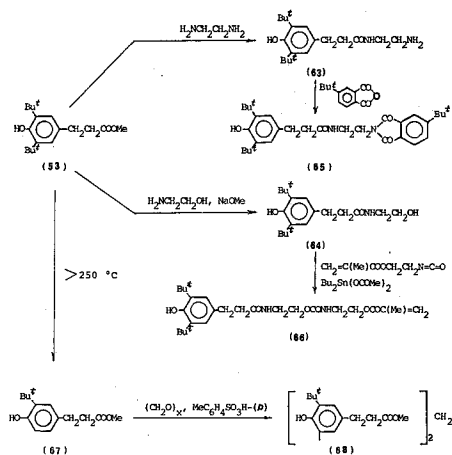
in the presence of a basic catalyst leading to the production of **55**.^{92, 93)} Also, it is converted to **56**, which is known as Irganox 1010, by an analogous transesterification using pentaerythritol in the presence of Bu_2SnO in toluene at 175°C .⁹⁴⁾ Other examples illustrating the transesterification of **53** are found in the reactions of **53** with 2,2'-[1,4-phenylenebis(methylthio)]bisethanol, hydroquinone bis(2-hydroxyethyl) ether, and isosorbide in neat in the presence of sodium ethoxide or methoxide at elevated temperature, where **57**, **58**, and **59** are produced, respectively.⁹⁵⁻⁹⁷⁾ Adding methanolic LiNH_2 to a heated solution of **54** and 3,9-bis(1,1-dimethyl-2-hydroxyethyl)-2,4,8,10-tetraoxaspiro[5.5]undecane in toluene followed by



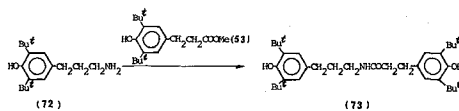
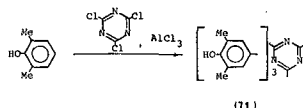
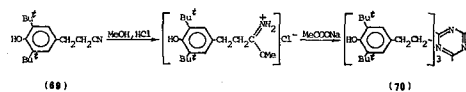
Synthesis of Hindered Phenols and Hindered Phenolic Light Stabilizers



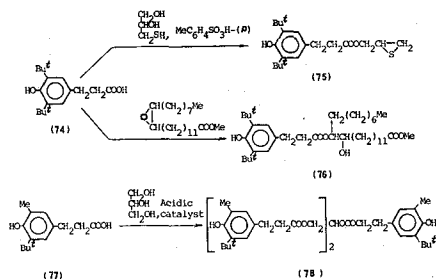
stirring the reaction mixture with azeotropic removal of methanol affords **60**.⁹⁸⁾ Refluxing a solution of **61**, prepared by the reaction of **4** with methyl acrylate in the presence of an appropriate basic catalyst in analogy with the preparation of **53** or **54**, and 1-octadecanol in toluene with azeotropic removal of methanol affords **62**.⁹⁹⁾ Condensation of **53** with ethylenediamine in refluxing toluene as well as that of **53** with ethanolamine in the presence of a basic catalyst such as sodium methoxide in refluxing toluene proceed smoothly to afford **63** and **64**, respectively.^{100, 101)} The former product **63** is converted to **65** by allowing **63** to react with 4-*tert*-butylphthalic anhydride in refluxing toluene¹⁰⁰⁾ and the latter product **64** is converted to **66** by allowing **64** to react with 2-isocyanatoethyl methacrylate in the presence of a catalytic amount of dibutyltin diacetate.¹⁰¹⁾ Several years ago, it has been reported that the compound **67** is formed from **53** upon heating it beyond 250°C.¹⁰²⁾ This report seems to be worth noting. Because, the compound **67** is a valuable material for preparing a new class of 2-(2*H*-benzotriazol-2-yl)phenolic ultraviolet absorbers.¹⁰³⁾ On the other hand, when the compound **67** is refluxed with paraformal-



dehyde in the presence of *p*-toluenesulfonic acid in cyclohexane, **68** is produced.¹⁰⁴⁾ As described in the beginning of this section, the compound **69** is easily available by the cyanoethylation of **1** with acrylonitrile in the presence of *K tert*-butoxide.⁹⁰⁾ When gaseous HCl is bubbled through a solution of **69** in methanol plus benzene at low temperature followed by refluxing the reaction mixture, the corresponding iminoester-HCl is produced. Treatment of the iminoester-HCl in methanol with sodium acetate at room temperature provides **70**.¹⁰⁵⁾ The reaction of 2,6-dimethyl-

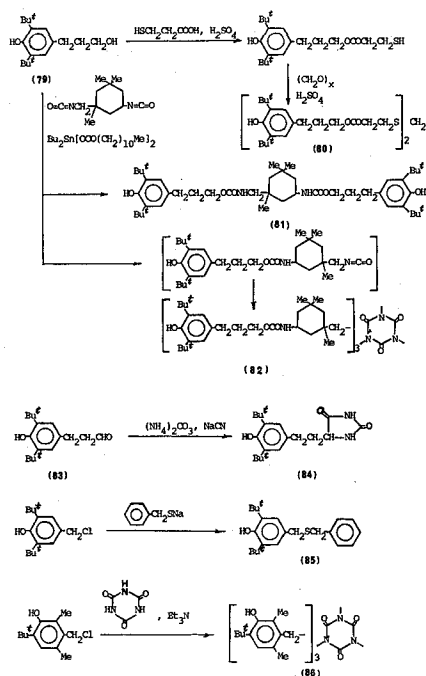


phenol with cyanuric chloride in tetrachloroethylene under the catalytic action of AlCl_3 at room temperature affording **71** is described in the same reference.¹⁰⁵⁾ Condensation of **72**, which is available by the reduction of **69** with LiAlH_4 , with **53** at elevated temperature provides **73**.¹⁰⁶⁾ Also, the compound **74** is synthesized by the saponification of **53** or **69**. It is allowed to react with thioglycerol in the presence of *p*-toluenesulfonic acid and with epoxidized rape-oil ester at $140\sim 180^\circ\text{C}$ affording **75** and **76**, respectively.^{107,108)} A method synthesizing **77** is proposed.¹⁰⁹⁾ Thus, the compound **77** is synthesized *via* a process involving cyanoethylation of *o*-cresol with acrylonitrile under the catalytic action of AlCl_3 , hydrolysis by HCl , and *tert*-butylation with isobutylene in the presence of H_2SO_4 . Also, it would be

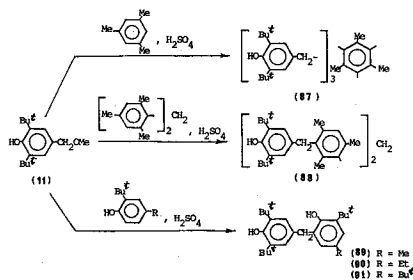


synthesized by the saponification of **54** already described. Ester condensation of **77** with glycerol in the presence of an acidic catalyst provides a light stabilizer **78**.¹¹⁰⁾ The compound **79**, which is available¹¹¹⁾ by LiAlH_4 -reduction of **53**, is utilized for the preparations of high-molecular-weight light stabilizers such as **80**, **81**, and **82**. Thus, **80** is prepared by ester condensation of **79** with 3-mercaptopropionic acid in the presence of H_2SO_4 in toluene and subsequent dithioacetalization of the resulting ester with paraformaldehyde in the presence of the same H_2SO_4 .¹¹²⁾ The compound **81** is prepared by the reaction of **79** with a half molar equivalent of isophorone diisocyanate under the catalytic action of dibutyltin dilaurate in toluene at $60\sim 80^\circ\text{C}$.¹¹³⁾ If equimolar amounts of **78** and isophorone diisocyanate are used in the same solvent containing the same catalyst at $55\sim 60^\circ\text{C}$, the reaction proceeds further to afford **82** *via* the intermediate monoisocyanate.¹¹⁴⁾ Similarly to the reaction of **1** with methyl acrylate, the reaction of **1** with acrolein in the presence of a basic catalyst proceeds smoothly to afford **83**. Thus, adding acrolein to a mixture

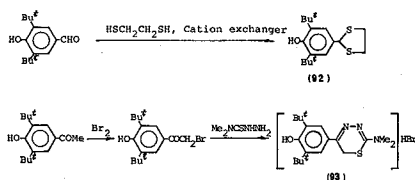
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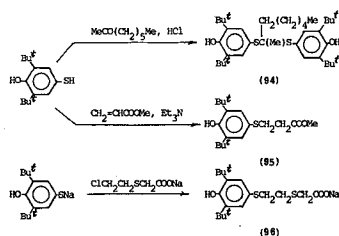
of **1** and a small amount of *K tert*-pentoxide in 2-ethyl-1-hexanol and stirring the reaction mixture at room temperature for an appropriate period provide **83**.¹¹⁵⁾ It is allowed to react with $(\text{NH}_4)_2\text{CO}_3$ in the presence of NaCN in 90% aqueous ethanol to afford **84**.¹¹⁶⁾ The chloromethylation of hindered phenols such as **1** and **12** is found in the literature. For example, when gaseous HCl is bubbled through a mixture of **1** and paraformaldehyde in acetic acid, 4-chloromethyl-2,6-di-*tert*-butylphenol is produced.¹¹⁷⁾ When gaseous HCl is bubbled through a mixture of **12**, concentrated HCl, H_2SO_4 , and dimethoxymethane, **12** is converted to 6-*tert*-butyl-3-(chloromethyl)-2,4-dimethylphenol.¹¹⁸⁾ The condensation of 4-chloromethyl-2,6-di-*tert*-butylphenol with α -toluenethiol sodium salt in refluxing methanol to afford **85**¹¹⁹⁾ as well as that of 6-*tert*-butyl-3-(chloromethyl)-2,4-dimethylphenol with isocyanuric acid in the presence of triethylamine in *N,N*-dimethylformamide affording **86**¹²⁰⁾ will illustrate the usefulness of such chloromethylated hindered phenols for the preparation of light stabilizers. 2,6-Di-*tert*-butyl-4-(methoxymethyl)phenol (**11**) which has already been described in Section III, is also an usable intermediate



for preparing light stabilizers. Thus, the condensation of **11** with mesitylene,¹²¹⁾ methylene dimesitylene,¹²²⁾ 2-*tert*-butyl-4-methyl,¹²³⁾ 2-*tert*-butyl-4-ethyl,¹²³⁾ and 2,4-di-*tert*-butylphenol¹²³⁾ in the presence of concentrated H₂SO₄ in dichloromethane at low temperature afford **87**, **88**, **89**, **90**, and **91**, respectively. Heating **1** together with hexamethylenetetramine in acetic acid provides 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde,¹²⁴⁾ which is converted to **92** by refluxing the aldehyde with 1,2-ethanedithiol in benzene containing a cation exchanger.¹²⁵⁾ Fridel-Crafts acylation of **1** using acetyl chloride plus AlCl₃ at low temperature provides 3,5-di-*tert*-butyl-4-hydroxyacetophenone¹²⁶⁾ which is converted to **93** by a process involving bromination by Br₂ in refluxing dichloromethane and the subsequent cyclocondensation of the resulting 3,5-di-*tert*-butyl-4-hydroxyphenacyl bromide with 4,4-dimethyl-3-thiosemicarbazide in refluxing ethanol.¹²⁷⁾ 2,6-Di-*tert*-butyl-4-mercapto- and 4-amino-2,6-

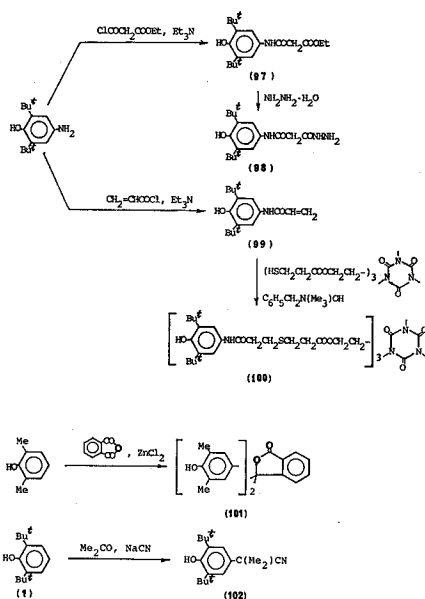


di-*tert*-butylphenol are also employed as intermediates for the preparation of light stabilizers. The former is synthesized by heating **1** together with S and KOH in ethanol followed by stirring the product mixture with Zn dust and 3N HCl at room temperature,¹²⁸⁾ and the latter is synthesized by nitration of **1** with concentrated HNO₃ in hexane at -20°C and the subsequent reduction of the obtained 2,6-di-*tert*-butyl-4-nitrophenol with Zn dust plus concentrated HCl in methanol.¹²⁹⁻¹³⁰⁾ The reaction of 2,6-di-*tert*-butyl-4-mercaptophenol with 2-octanone in methanol under the catalytic action of gaseous HCl at 55°C to afford **94**¹³¹⁾ as well as the reaction of 2,6-di-*tert*-butyl-4-mercaptophenol with methyl acrylate in the presence of triethylamine in acetonitrile affording **95**¹³²⁾ are found in the literature. Also, monoso-



dium salt of 2,6-di-*tert*-butyl-4-mercaptophenol provides **96** upon refluxing the salt together with sodium [(2-chloroethyl)thio]acetate in ethanol.¹³³⁾ On the other hand, 4-amino-2,6-di-*tert*-butylphenol is condensed with ethyl 3-chloro-3-oxopropanoate in the presence of triethylamine and the obtained **97** is further condensed with 85% hydrazine hydrate in refluxing ethanol to give the corresponding hydrazide **98**.¹³⁴⁾ The compound **99**, which is prepared by the condensation of 4-amino-2,6-di-*tert*-butylphenol with acryloyl chloride in the presence of triethylamine, is allowed to react with tris[2-[(3-mercaptopropionyl)oxy]ethyl] isocyanurate in the presence

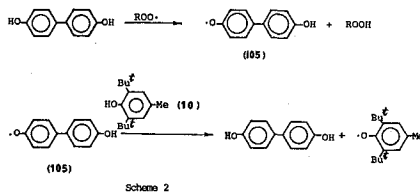
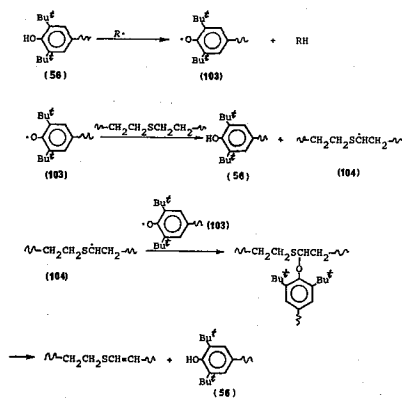
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of benziltrimethylammonium hydroxide in chloroform to afford a practical light stabilizer **100**.¹³⁵⁾ Besides, the reaction of 2,6-dimethylphenol with phthalic anhydride in the presence of $ZnCl_2$ -catalyst at $130^\circ C$ affording **101**¹³⁶⁾ as well as the reaction of **1** with acetone and NaCN in *N,N*-dimethylformamide in a closed vessel at $140^\circ C$ to afford **102**¹³⁷⁾ are found in the literature.

VI. SEVERAL EXAMPLES IN USING HINDERED PHENOLIC LIGHT STABILIZERS

Various combined uses of hindered phenolic light stabilizers and one or more of other additives such as hindered amine light stabilizers, 2-(2*H*-benzotriazol-2-yl)-phenolic compounds, sulfur compounds, phosphorous compounds, and the others in polymers and the other compositions are found in the literature. In these cases, the obtained synergistic effects are described accentually. For example, polyoxymethylene compounded with **56** and didodecyl 3,3'-thiodipropionate is more stable to aging at elevated temperature, compared with the same polyoxymethylene compounded only with **56**.¹³⁸⁾ As is obvious from Scheme 1, the radical species **103**, which has been formed by imparting a hydrogen radical to the initially generated radical species ($R\cdot$), is reformed to the original molecule of **56** by the coexistent didodecyl 3,3'-thiodipropionate and also by the radical species **104** which is a transient intermediate. This rapid regeneration of **56** bring about the synergistic effect. On the other hand, another type of synergism which is promoted by a combination of **10** and an unhindered phenolic compound, 4,4'-biphenyldiol, is described in the literature. Thus, the combination shows a synergistic effect in terms of tensile strength of natural rubber vulcanizates after aging at elevated temperature.¹³⁹⁾ This is explained by Scheme 2, in which the coexistent 4,4'-biphenyldiol molecule imparts a hydrogen radical to the generated peroxy radical ($ROO\cdot$) prior to **10**



and the resulting radical species **105** is reformed to the original molecule of 4,4'-biphenyldiol by a radical interchange with **10**. Gurvich and his co-workers¹⁴⁰⁾ have compared the ability of **27** with that of **28** as stabilizers for polymers and found that the abilities correlate to their molecular configurations. In the molecule of **27**, the two OH groups are *cis* and the molecule of **28** possesses two *trans*-configured OH groups, so that natural rubber vulcanizates containing **27** are more resistant to thermal and mechanistic aging than those containing **28**, and the oxidation induction period of polypropylene containing **27** is longer than that of polypropylene stabilized with **28**. Pchelintsev and his co-workers¹⁴¹⁾ have reported concerning the effectiveness of **87**, **27**, **56**, and **10** as inhibitors of oxidative degradation of *cis*-1,4-polyisoprene. The effectiveness decreases in the order above-mentioned. The time during which polypropylene stabilized with **73** and dioctadecyl 3,3'-thiodipropionate is stable in an oven at 150°C is 812 h. In contrast with this, the time during which the unstabilized polypropylene is stable in the same oven is only 50 h.¹⁰⁶⁾ A polyester jersey is dyed in an aqueous dyebath containing a disperse dye compounded with **56**, a 2-(2*H*-benzotriazol-2-yl)phenolic compound, and a hindered amine light stabilizer to give a dyed jersey with improved lightfastness.¹⁴²⁾ Unstabilized polypropylene decomposes at 150°C within 24 h. However, it takes 522 h for the decomposition of polypropylene containing **59**.⁹⁷⁾ When polyethylene containing **86** and a certain phosphite is submitted to continued heating at elevated temperature, an increase in torque accompanied by crosslinking is recognized after 75 min. In the same test, however, unstabilized polyethylene indicates the same increase after only 8 min.¹⁴³⁾ Polypropylene alone requires 24 h for its failure at 150°C. Such the time is prolonged to 456 h by the addition of **88** and further to 1500 h by a combination

of 88 and dioctadecyl 3,3'-thiodipropanoate.¹²²⁾

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