This review involves the synthetic methods of hindered amine light stabilizers (HALS) having 2,2,6,6-tetramethylpiperidine moieties as functional groups. The most parts of these HALS are synthesized via the initial alteration of 2,2,6,6-tetramethyl-4-piperidinone into 2,2,6,6-tetramethyl-4-piperidinol, -piperidinamine or its N-alkyl derivatives. And, the residual parts of these HALS are synthesized by the chemical modification of 2,2,6,6-tetramethyl-4-piperidinone, itself, without such the initial reductive alteration.

KEY WORDS: Hindered amine light stabilizer/ 2,2,6,6-Tetramethyl-4-piperidinone/ 2,2,6,6-Tetramethyl-4-piperidinol/ 2,2,6,6-Tetramethyl-4-piperidinamine/ N-Alkyl-2,2,6,6-tetramethyl-4-piperidinamine/ Photostabilization mechanism/

I. INTRODUCTION

There are several examples of hindered amine light stabilizers (HALS) having 7,15-diazadispiro(5.1.5.3)-hexadecane, 2,2,4-trimethyl-1,2-dihydroquinoline or 3,3,5,5-tetramethyl-2-piperazinone moieties as functional groups. However, the most parts of well-known HALS are those having 2,2,6,6-tetramethylpiperidine moieties as functional groups and thus are derived from 2,2,6,6-tetramethyl-4-piperidinone. Since the technical performance of manyfacturing 2,2,6,6-tetramethyl-4-piperidinone on a commercial basis, many researches concerning the synthesis of a variety of such the HALS, which are able to improve the lightfastness of polymers and the other compositions, have been reported in the literature. When 2,2,6,6-tetramethyl-4-piperidinone is reduced by an appropriate reducing agent, it provides 2,2,6,6-tetramethyl-4-piperidinol which is often used for the preparation of practical HALS, especially via a process involving the esterification or transesterification. When 2,2,6,6-tetramethyl-4-piperidinone is allowed to react with ammonia, an alkylamine or alkylendiamine in the presence of H₂ and a hydrogenation catalyst, 2,2,6,6-tetramethyl-4-piperidinamine or its N-alkyl derivative is produced. These compounds are also usable intermediates for preparing a variety of practical HALS, especially via a process involving the condensation with chloride such as cyanuric chloride. Also, several or more examples of synthetic methods of practical HALS utilizing 2,2,6,6-tetramethyl-4-piperidinone, itself, without such the initial reductive alteration into 2,2,6,6-tetramethyl-4-piperidinol, -piperidinamine or its N-alkyl deri-
vative are found in the literature. It is well known that the HALS thus obtained possess an excellent ability in retarding the agings of polymers and the other compositions, especially in combined uses with one or more of other additives such as hindered phenols, 2-(2H-benzotriazol-2-yl)phenolic compounds, sulfur compounds and phosphorous compounds.

II. SYNTHESIS OF 2,2,6,6-TEtramethyl-4-PIPERIDINONE

It is somewhat difficult to synthesize 2,2,6,6-tetramethyl-4-piperidinone (1) in a high yield from acetone and ammonia in the presence of an appropriate catalyst. In 1976 Sosnovsky and Konieczny have found that the condensation of acetone and ammonia in the presence of CaCl₂ affords 1 in 89% yield on taking into account the recovered acetone. Thus, into a mixture of acetone (1000 g) and 4~20 mesh anhydrous CaCl₂ (400 g) is introduced, over a period of 4 days, a total 140 g anhydrous ammonia, in six equal portions. Following the last introduction, the reaction mixture is left to stand at room temperature for 3 days. Then, the unreacted acetone is recovered under reduced pressure. From the remaining cake, 1 is obtained in 89% yield by distillation. This method is too time-consuming to process control. If the CaCl₂-catalyzed reaction is carried out in an enclosed vessel, the reaction temperature can be raised in order to complete the reaction in a shorter time. Thus, when a mixture of acetone, CaCl₂ and ammonia is autoclaved at 80~85°C for 6 h, 1 is produced in 72% yield. However, there is no saying whether the yield is obtained on taking into account the recovered acetone or not. Cation exchangers too seem to be the usable catalysts for the reaction. The reaction of acetone with ammonia (mole ratio is 2~2.5:1) in the presence of a cation exchanger at 30~180°C provides 1 in 39~70% yield. The catalytic ability of such the cation exchangers is enhanced by the addition of ethylenediaminetetraacetic acid, its disodium salt or dimethylglyoxime as a cocatalyst. For example, when a mixture of acetone and ammonia (weight ratio is 97 : 3) is made to flow at 8~10 ml/h through a tube which is charged with 100 g cation exchanger and 0.25 g ethylenediaminetetraacetic acid at 50°C, 1 is produced in 83.4% yield. Further, the employment of 1,2-dimethylhydrazine dihydrochloride, hydrazine monohydrchloride or halo acid halides represented by RXₜ (COX')ₙ (R=C₆H₅ alkyl, cycloalkyl, aryl; X, X'=halogen; m=1~6; n=1, 2) with or without I₂ as a cocatalyst is recommended as the catalyst. For example, ammonia is bubbled through a mixture of 180 g acetone, 9 g methanol and 1.8 g 1,2-dimethylhydrazine dihydrochloride at 40~45°C for 5 h to afford 93 g 1. Also, 12 g ammonia is allowed to react with 180 g acetone in the presence of 1.8 g bromoacetyl bromide in methanol at 50~55°C affording 72.5 g 1. When a few organotin halides, phosphonitrilic chloride trimer and cyanuric chloride have been used as the catalyst, the last compound provides the best yield of 1, and the yield is further enhanced by the addition of cocatalyst such as NH₄Cl, hydrazine dihydrochloride, ZnCl₂ or boron.
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trifluoride etherate. Besides, NH₄Cl, ZnCl₂, KI, LiBr and Al(NO₃)₃ seem to be useful as the catalyst. The procedure using NH₄Cl instead of ammonia is also found in the literature. Thus, when a mixture of 110 ml acetone, 50.1 g NH₄Cl and 21 g CaO is heated together with 10 ml H₂O at 50°C for 8 h, 20.5 g 1 is produced.

III. SYNTHESIS OF HINDERED AMINE LIGHT STABILIZERS VIA THE INITIAL ALTERATION INTO 2,2,6,6-TEtramethyl-4-Piperidinol

For the reduction of 1 to give 2,2,6,6-tetramethyl-4-piperidinol (2), LiAlH₄, NaBH₄ or H₂ in the presence of Raney Ni is used as the hydrogenation agent. When a large quantity of 2 is desired, the method using last hydrogenation agent is most economical. Thus, when a solution of 100 g 1 in 700 ml ethanol containing a catalytic amount of Raney Ni is heated together with H₂ at elevated pressure for 10 h in an autoclave, 2 is produced in 96% yield. Later, the reaction has been studied in more detail in order to find the best reaction conditions. The following reaction conditions is recommended: isopropyl alcohol instead of ethanol as the solvent, H₂ at 55~60 atmospheric pressure, reaction temperature maintained at 120°C, reaction period of 40 min.

The transesterification between 2 and several carboxylic esters in the presence of appropriate catalysts affording practical HALS are reported in the literature. Thus, a solution of 2 and dimethyl sebacate in toluene containing dibutyltin oxide is heated at 120~130°C to afford 3 in 97.9% yield. If the transesterification is carried out in the presence of LiNH₂ in solvent naphtha at 160°C/760 mmHg and further at 160°C/400 mmHg, the yield of 3 is 96%. The reaction of 2 with (1,3,5-triazine-2,4,6-triyltrinitrilo)hexaacetic acid hexamethyl ester in the presence of LiNH₂ in boiling ligroin proceeds smoothly to afford 4. The reaction of 2 with 1,3,5-triazine-2,4,6-trionetripropionic acid trimethyl ester in boiling xylenes containing a small amount of Na methylate plus methanol affording 5 proceeds under the removal of generated methanol in the middle of refluxing. Also, the reaction of 2 with diethylenetriaminepentaacetic acid pentamethyl ester in the presence of LiNH₂ in boiling heptane provides 6. The importance of this kind of transeste-
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rification providing HALS will be further demonstrated by the following two examples. Thus, refluxing a mixture of 2 and 1,5-dioxaspiro(5.5)undecane-3,3-dicarboxylic acid diethyl ester, which is available by acetalization of diethyl bis(hydroxymethyl)malonate with an excess of cyclohexanone under the catalytic action of p-toluenesulfonic acid, in the presence of LiNH₂ in ligroin under N₂ provides 7. When 1,4-dioxaspiro(4.5)decane-2,3-dicarboxylic acid diethyl ester, which can be prepared by an analogous p-toluenesulfonic acid-catalyzed acetalization of diethyl tartrate with an excess of cyclohexanone, is used instead of 1,5-dioxaspiro(5.5)undecane-3,3-dicarboxylic acid diethyl ester in the above reaction, 8 is produced.

Both 1,2,2,6,6-pentamethyl- (9) and 1-(2-hydroxyethyl)-2,2,6,6-tetramethyl-4-piperidinol (10) seem to be the typical compounds as simple derivatives of 2. The former is available by the treatment of 2 with 37% aqueous formaldehyde and formic acid, and the latter by the introduction of ethylene oxide into 2 in H₂O at room temperature, heating the reaction mixture under reflux and the second introduction of ethylene oxide at 60°C followed by the second heating. The former is submitted to the transesterification with diethyl butylmalonate in the same manner as described before. And, the obtained bis(1,2,2,6,6-pentamethyl-4-piperidinyl) butylmalonate (11) is allowed to react with 2,6-di-tert-butyl-4-(dimethylamino)methylphenol in the presence of LiNH₂ in boiling toluene to afford 12.

The latter is employed for the preparation of polymeric HALS by the condensations with several dicarboxylic diesters. For example, heating the latter together with dimethyl succinate in the presence of a catalyst such as Na methylate in a solvent such as xylenes provides 13 (the value n is not given). Also, the latter is converted to 14 by a procedure consisting of heating a mixture of the latter and purified methyl methacrylate containing a polymerization inhibitor in the presence of titanium (IV) butoxide under the removal of generated methanol, supplementary addition of purified methyl methacrylate followed by heating at 90°C and supplementary addition of titanium (IV) butoxide followed by heating at the same
The compound 14 is used as a crosslinking HALS for polymers. When 2 is allowed to condense with one of acryloyl, methacryloyl and fumaryl chloride in the presence of triethylamine in an appropriate solvent such as benzene, 2,2,6,6-tetramethyl-4-piperidinyl acrylate (15), methacrylate (16) and bis(2,2,6,6-tetramethyl-4-piperidinyl) maleate (17) are produced, respectively. The former two compounds are homopolymerized or copolymerized with another monomer such as alkyl acrylates, methacrylates or styrene to give some polymeric HALS. For example, 15 is copolymerized with methyl methacrylate in a toluene solution in the presence of azobisisobutyronitrile giving a polymeric HALS. This HALS together with a hindered phenol and Ca stearate is used for the improvement of lightfastness of polypropylene. The last compound 17 is allowed to react with molten polypropylene with the aid of a peroxide. Thus, a mixture of 17 and polypropylene (weight ratio is 1:10) containing the peroxide is kept melting until all of the added peroxide is consumed giving 18. The compound 19 is also a polymeric HALS derived from 9. Thus, when 9 is allowed to react with isocyanate-terminated poly(ethylene adipate), which has been synthesized by the reaction of poly(ethylene adipate) with 1,3-diisocyanatomethylbenzene (mole ratio is 1:2), 19 is produced.

Refluxing a mixture of 3,9-bis(1,1-dimethyl-2-hydroxyethyl)-2,4,8,10-tetraoxa-spiro[5.5]-undecane and PCl₃ in dichloromethane provides 20. It, without the isolation from reaction mixture, is allowed to react with 2 in the presence of triethylamine affording 21. Addition of metallic Na to a solution of 2 in xylene
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and the subsequent heating of the mixture under reflux provide 2,2,6,6-tetramethyl-4-piperidinol Na salt (22). It, without the isolation from xylenes, is treated with cyanuric chloride to afford 23. The compound 22 in toluene, prepared by a similar procedure using metallic Na, 2 and toluene instead of xylenes, is allowed to react with 2,5-dibromohexanedioic acid diethyl ester in the presence of KI at 80–90°C under N₂ to afford 24. Besides, the reaction of 2,2,6,6-tetramethyl-4-piperidinol hydrochloride (25), prepared by introducing gaseous HCl into 2, with benzoyl chloride in 1,1,2,2-tetrachloroethane maintained initially below 140°C and then at 140°C is reported, where 2,2,6,6-tetramethyl-4-piperidinyl benzoate hydrochloride (26) is produced.

IV. SYNTHESIS OF HINDERED AMINE LIGHT STABILIZERS VIA THE INITIAL ALTERATION INTO 2,2,6,6-TETRAMETHYL-4-PIPERIDINAMINE OR ITS N-ALKYL DERIVATIVES

The cycloaddition of 2,6-dimethyl-2,5-heptadien-4-one with ammonia in methanol including Raney Ni or Co under high-pressure H₂ at 110°C give 2,2,6,6-tetramethyl-4-piperidinamine (27). However, 27 is easily obtained by reductive amination of 1 with ammonia and H₂ in the presence of hydrogenation catalyst. Thus, when a mixture of 1, wet Raney Co, ammonia and methanol is autoclaved together with ≤130 atmospheres H₂ at 130°C, 27 is produced in 95% yield. When a mixture of 27 and 1,3-dicyclohexylcarbodiimide is heated at 140°C, 28 is produced. When 2-butenedioic acid dimethyl ester is added to 27 in methanol and the mixture is stirred at room temperature, 29 is produced. When 27 and trimethyl 3-butene-1,2,3-tricarboxylate are allowed to react in boiling methanol, a mixture of 30 and 31 is produced. Also, when a solution of 27 and dimethyl itaconate in methanol is stirred at room temperature and subsequently refluxed, 32 is produced. The reactions of 27 with acryloyl, methacryloyl chloride and 4-chloro-4-oxo-butanoic acid ethyl ester affording 33, 34 and 35, respectively, proceed smoothly in the presence of tert-amine such as triethylamine in an appropriate solvent. For example, 27 is allowed to react with 4-chloro-4-oxo-butanoic acid ethyl ester in the presence of triethylamine in dichloromethane at 5–10°C to afford 35. The compounds 33 and 34 are homopolymerized or copolymerized with another monomer,
for example, such as dodecyl methacrylate or octadecyl acrylate to afford polymeric HALS. And, the compound 35 is converted to the corresponding hydrazide 36 by the condensation with hydrazine hydrate in boiling ethanol. \( N-(2,2,6,6\)-Tetramethyl-4-piperidinyl)glycine methyl ester (37), prepared by the condensation of 27 with methyl bromoacetate, is submitted to the transesterification with 2 under the reaction conditions described in Section III giving 38. A similar transesterification of 37 with neopentyl glycol provides 39. And, it is further converted to an oligomeric HALS (40, the value \( n \) is not given) by refluxing 39 together with 2,4-dichloro-6-tert-octylamino-1,3,5-triazine in dioxane. \( N,N'\)-Bis(2,2,6,6-tetramethyl-4-piperidinyl)formamidine (41), prepared by the condensation of 27 with triethyl orthoformate, is also employed for the preparation of practical HALS. Addition of ethyl chloroformate to a solution of 41 in chloroform at \( <10^\circ C \) followed by neutralization with NaOH at \( 5-10^\circ C \) provides 42. When a mixture of calculated amounts of 41 and cyanuric chloride in xylenes is heated at \( 50-55^\circ C \) and, after addition of powdered Na\(_2\)CO\(_3\), again heated at \( 70^\circ C \), 43 is produced. And, the compound 43, without the isolation from the reaction mixture, is heated under reflux with 4,4'-methylenebiscyclohexylamine in the presence of remaining Na\(_2\)CO\(_3\) in the xylenes affording a condensate 44. When 1 is allowed to react with ammonia (0.4-0.8 molar equivalent based on 1) and H\(_2\) at 50 atmospheric pressure together with methanol and benzyl alcohol in the presence of 5% Pt/C in an autoclave at \( 60^\circ C \), and the resulting reaction...
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mixture consisting of 27 and bis(2,2,6,6-tetramethyl-4-piperidinyl)amine (45) is again treated similarly with all of the reagents and catalyst, except 1, used in the initial reaction together with separately prepared 27, 1 is converted to 45 in 95% yield. The compound 45 is added to cyanuric chloride in xylenes at 0°C and the mixture is stirred at room temperature with an intermediary addition of powdered NaOH to afford 2-N, N-bis(2,2,6,6-tetramethyl-4-piperidinyl)amino-4,6-dichloro-1,3,5-triazine (46). The obtained 46 is converted to 47 by refluxing with N-octyl-2,2,6,6-tetramethyl-4-piperidinamine (48) in xylenes, addition of powdered NaOH and the second refluxing. In this case, the employed 48 has been prepared by heating a reaction mixture resulting from the condensation between 1 and octylamine at 30~40°C together with 5% Pt/C, H2O and 50 atmospheres H2 in an autoclave at 70~80°C. The practical method in converting 45 into 2,4-bis[N,N-bis(2,2,6,6-tetramethyl-4-piperidinyl)amino]-6-chloro-1,3,5-triazine (49) would be easily understood by reference to the literature concerning the conversion of 45 into 46. When a mixture of 49 thus obtained and diethylenetriamine in xylenes is refluxed for 2 h and, after addition of powdered NaOH, again refluxed for 16 h while the H2O formed is removed from the mixture, 50 is produced. It is reported that, when 1 and ethylamine is allowed to react in the presence of 5% Pt/C and H2O in an autoclave at 30~40°C and, after charging 50 atmospheres H2, the autoclave is again heated at 70~80°C, N-ethyl-2,2,6,6-tetramethyl-4-piperidinamine (52) is produced. N,2,2,6,6-pentamethyl-4-piperidinamine (51) would be synthesized similarly by the use of methylamine instead of ethylamine. The obtained compounds 51 and 52 are also used as intermediates for the preparation of practical HALS. For example, the former is derived to 2,4-bis[N-(2,2,6,6-
tetramethyl-4-piperidinyl)methylamino]-6-chloro-1,3,5-triazine (53) by the reaction with cyanuric chloride in the presence of powdered NaOH in xylenes under suitably decided operating condition. And, the compound 53 together with diethylenetriamine in xylenes is refluxed for 2 h and, after addition of powdered NaOH, again refluxed for 14 h with removal of the H₂O formed to afford 54. Further, the compound 54 is methylated with formaldehyde and formic acid at 110°C affording 55. The latter is converted to 56 by a process involving the Michael addition with diethyl ethoxymethylenemalonate in neat at room temperature and the transesterification between the resulting adduct and 2 in the presence of Na ethylate in boiling xylenes where one molecule of ethanol is eliminated.

When a mixture of 1, 5% Pt/C, 1,6-hexanediamine and H₂O is autoclaved together with 41~55 atmospheres H₂ at 80°C, N,N'-bis(2,2,6,6-tetramethyl-4-piperidinyl)-1,6-hexanediamine (57) is produced in 89% yield. If methanol is used instead of H₂O as the reaction medium, the yield increases up to 93%. The compound 57 thus obtained is an important intermediate for the preparation of oligomeric or polymeric HALS. Treatment of 57 in H₂O with a solution of 1,3-benzenedisulfonyl dichloride in dichloromethane in a blender at room temperature provides a polymeric HALS (58, the value n is not given). The dehydrochlorination between 57 and 2-butylamino-4,6-dichloro-1,3,5-triazine in the presence of powdered NaOH in boiling toluene provides a polymeric HALS (59, the value n is
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not given). In the case where 2,4-dichloro-6-morpholino-1,3,5-triazine is used instead of 2-butylamino-4,6-dichloro-1,3,5-triazine, the dehydrochlorination with 57 is carried out in a somewhat tedious manner; 2,4-dichloro-6-morpholino-1,3,5-triazine and Na₂CO₃ are initially slurried in H₂O at low temperature followed by addition of 57. And, the mixture is refluxed carefully and, after addition of an appropriate amount of morpholine, again refluxed to form an oligomeric HALS (60, the value n is not given). Also, the compound 57 is converted to a polymeric HALS (61, n=4-5) by the condensation with 2-(N,N'-bis(2,2,6,6-tetramethyl-4-piperidinyl)formamidino)-4,6-dichloro-1,3,5-triazine in the presence of powdered NaOH in boiling xlenes. In this case, the employed 1,3,5-triazine derivative has been synthesized by mixing the calculated amounts of 41 and cyanuric chloride in xlenes at ≤ −10°C and subsequent stirring of the mixture with an intermediary addition of powdered NaOH at the same temperature.

Recently, N,N'-bis(2,2,6,6-tetramethyl-4-piperidinyl)-N-methyl-1,3-propanediamine (62) has been proposed as an intermediate for the preparation of HALS. Probably, the compound 62 would be synthesized by such the reductive amination of 1 with N-methyl-1,3-propanediamine and H₂ in the presence of 5% Pt/C and H₂O as is illustrated by the alteration of 1 into 52 or 57 before described. Treating 62 with calculated amount of cyanuric chloride and the further treatment of the resulting 2,4-bis[N,N'-bis(2,2,6,6-tetramethyl-4-piperidinyl)amino]propyl-

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N-(2,2,6,6-tetramethyl-4-piperidinyl)amino]-6-chloro-1,3,5-triazine with 1,6-hexandiamine in the presence of powdered NaOH in xlenes under suitably decided operating conditions provide 63. Besides, N-(2,2,6,6-tetramethyl-4-piperidinyl)ethylenediamine (64), symmetric N,N'-bis(2,2,6,6-tetramethyl-4-piperidinyl)diethylenetriamine (65) and N-tetrahydrofururyl-2,2,6,6-tetramethyl-4-piperidinamine (66) are proposed as intermediates for the preparation of HALS. The compound 64 is synthesized by the same method, except the employment of ethylenediamine instead of octylamine, that is proposed for the preparation of 48 from 1. It is derived to 67 by the condensation with diethyl oxalate at 170°C. And, the obtained compound 67 is further derived to 68 by the condensation with 2,4-bis[N,N'-bis(2,2,6,6-tetramethyl-4-piperidinyl)butylamino]-6-chloro-1,3,5-triazine (69) in the presence of K₂CO₃ in 1-methylpyrrolidine at 170°C. The compound 69 employed just now is synthesized in the following manner; the compound 1 is initially converted to N-butyl-2,2,6,6-tetramethyl-4-piperidinamine by the same method, only with changing octylamine to butylamine, that is proposed for the synthesis of 48 from 1. And, the resulting N-butyl-2,2,6,6-tetramethyl-4-piperidinamine is allowed to react with cyanuric chloride in the presence of powdered NaOH in xlenes under suitably
decided operating condition affording 69. The practical method in converting 1 into 65 or 66 by the reductive amination with diethylenetriamine or tetrahydrofurfurylamine and H₂ in the presence of 5% Pt/C would be easily understood by reference to the literature concerning the conversion of 1 into 48 or 57. The former compound 65 is condensed with dimethyl fumarate in boiling trimethylbenzenes affording 70. The latter compound 66 is converted to 71 in the following manner; the compound 66 is added to a solution of cyanuric chloride in xylenes at 10°C followed by stirring at room temperature. Aqueous NaOH is added to the mixture at 10°C, and stirring at room temperature is continued. The resulting organic layer is separated and then mixed with a solution of 9 in xylenes, followed by the first refluxing without any of condensing agent as well as the second refluxing in the presence of powdered NaOH.

V. SYNTHESIS OF HINDERED AMINE LIGHT STABILIZERS UTILIZING 2,2,6,6-TEtramethyl-4-piperidinone, ITSELF, WITHOUT AN INITIAL REDUCTIVE ALTERATION

Treating 1-chlorohexadecane with metallic Na at —5°C and the further treatment with 1 give 72. When 1 is allowed to react with 1,3-diaminoguanidine monohydrochloride in boiling ethanol followed by neutralization with aqueous NaOH, 73 is produced. When a mixture of 1 and 2,6-dimethylphenol is heated in excess polyphosphoric acid at 60°C, 74 is produced. Also, when a mixture of 1, 2,2-bis-(chloromethyl)-1,3-propanediol and β-toluuenesulfonic acid in benzene or xylenes is

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refluxed while the \( \text{H}_2\text{O} \) formed is removed from the mixture, 75 is produced.\(^{69}\) Heating 1 together with diethyl bis(hydroxymethyl)malonate in the presence of \( p \)-toluenesulfonic acid in a solvent such as cyclohexane or ligroin provides 76.\(^{60}\) It is allowed to condense with 2,2-dimethyl-1,3-propanediol in the presence of \( \text{LiNH}_2 \) at 150°C under \( \text{N}_2 \) affording an oligomeric HALS (77, \( n=4 \sim 5 \)).\(^{60}\) Heating 1 with diethyl tartrate in the presence of methanesulfonic acid in 1,2-dichloroethane provides 78.\(^{70}\) It is allowed to react with 2 in the presence of \( \text{LiNH}_2 \) in boiling ligroin affording 79.\(^{70}\) When dimethyl sulfide is treated with dimethyl sulfate in acetonitrile, with \( \text{Na} \) methylate, and then with 1 at low temperature, 5,5,7,7-tetramethyl-1-oxa-6-azaspiro[2.5]octane (80) is produced.\(^{71}\) It is heated with powdered \( \text{KOH} \) at 150°C affording a liquid HALS (81, \( n= \sim 4 \)).\(^{71}\) When 1 is allowed to react with \( \text{Zn} \) powder in the presence of acetic acid and \( \text{TiCl}_4 \) in dioxane at 5 \sim 10°C followed by refluxing the reaction mixture, 82 is produced.\(^{72}\) Only the last process is the one which seems to belong to neither of Sections III–V.

**VI. PHOTOSTABILIZATION MECHANISM OF HINDERED AMINE LIGHT STABILIZERS**

Although various researchers have studied narrow aspects of the photostabilization of polymers and the other components by HALS, there is no report which could provide a clear understanding of the photoprotection by HALS.\(^{73}\) Probably, this is due to that the clear understanding requires a complete knowledge of all important species involved in polymers and the other components throughout these photooxidative lifetimes.\(^{73}\) However, it is obvious that the main function of HALS is to decrease the possibility of chain reaction of polymers and the other components with the generated active radicals by trapping them. According to the reports\(^{73,74}\) published by Carlsson and Chakraborty and their co-workers, the photostabilization mechanism of HALS seems to be explained by Schemes 1 and 2. Scheme 1 indicates that the initial oxidation of HALS leading to the formation
of nitroxide radical proceeds by the interaction between HALS and ROOH. Besides, nitroxide radical could be produced by the reaction of HALS with singlet oxygen. Scheme 2 indicates that the essential active species in the photoprotection by HALS is the nitroxide radical and it allows many radicals such as R• and ROO• to be scavenged under a regenerative cycle. If the employed HALS behaves correctly as is shown in Scheme 2, the HALS can be reproduced by itself, so that its effectiveness in polymers and the other components must be kept in perpetuity. However, such the experimental result that a HALS has kept its effectiveness in perpetuity is not reported. Probably, HALS will be consumed gradually by other chemical reactions than those described in Schemes 1 and 2. Also, the gradual escape of HALS from polymers and the other components will assist the consumption of HALS.

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