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Description

The invention concerns halogenated coupled aromatic phenolic compounds, with a process to prepare them. These compounds are useful flame retardants, fungicides and monomers, especially for polymers such as engineering thermoplastics and epoxy thermosets. The invention integrally thus concerns such polymeric compositions.

Halogenated phenols are generally useful fungicides, monomers and flame retardants. Certain of the halogenated phenols and their derivatives, for example, brominated aromatic epoxy thermosets, are especially useful in the electronics industry.

However, bromination of most phenols and also certain novolacs is known to provide ringbromo-substitution at positions ortho or para to the phenolic hydroxyl group. See, for example, Jouannetaud et al., U S-A-4,447,660 (1984) and also JP-A-60-210615 (85/210615).

Certain meta-halogenated phenols, for example, meta-brominated phenols, are generally known to be more thermally stable than their ortho-halogenated counterparts. See, for example, copending U.S. Patent Application Serial No. 851,996, filed April 14, 1986. Unfortunately, only a few meta-brominated bisphenols have been described in the literature. K. Auwers & H. Allendorf, *Ann.*, 302, 76-98 (1898), reported the preparation of 2,2',6,6'-tetrabromo-3,3',5,5'-tetramethyl-4,4'-dihydroxystilbene from 4-bromomethyl-3,5-dibromo-2,6-dimethylphenol. However, this solid is extremely insoluble, which limits its utility.

A more soluble solid is 2,2',6,6'-tetrabromo-3,3',5,5'-tetramethyl-4,4'-dihydroxydiphenylmethane, reported by Auwers et al., *Ann.*, 344, 95-141 (1906) and *Ann.*, 356, 124-51 (1907). It is reported to have been prepared by disproportionation in base of 4-aminomethyl-3,5-dibromo-2,6-dimethylphenol.

More recently, a number of meta-brominated biphenols have been prepared by the bromination of tetraalkyldiphenylquinones. See, for example, Orlando et al., U S-A-3,929,908 (1975) and 3,956,403 (1976) and Kinson et al., U S-A-4,058,570 (1977). Using this approach, bromination is the last step in the reaction sequence, and yields are only modest.

In the art of rendering flame-retardant otherwise more flammable materials, for example, thermoplastic polymeric substances such as polystyrenes, concerns include flame-retardant efficiency, formulation simplicity, ease of processability, retention of favorable structural properties and discoloration effects. Flame-retardant efficiency is typically related to the weight ratio of the flame-retardant rendering moiety such as, for example, weight of halogen of an organic halide, to the otherwise more flammable material. Flame-retardant efficiency can be decreased by ongoing processes such as, for example, oozing of the flame retardant. Typically, large amounts of the flame retardant may be thus added to increase the flame-retardant efficiency. In addition, typically large amounts of a flame-retardant synergist such as, for example, an antimony oxide, may be added to increase the flame-retardant efficiency of the flame retardant, for example, the organic halides. A typical formulation to obtain a UL 94 V-O rating may require 12 weight percent bromine in an aromatic bromide and 3.5 weight percent antimony oxide (Sb_2O_3). Moreover, the flame retardant itself may be difficultly processable into, or more importantly, adversely affect the structural properties of, the otherwise more flammable material, for example, the thermoplastics. See, for example, GB-A-1,356,508 (1974). In addition, discoloration effects, for example, so-called "scorch" in a polyurethane, especially in flexible polyurethane foams, may be encountered in commercial production and are undesirable.

From JP-A-60 115 543 brominated p-phenylphenol derivatives are known which are useful as a flame-retardant. The bromine atoms are at one or both aromatic nuclei.

GB-A-885 005 refers to bisphenol compounds and their preparation by reacting bis-chloromethyl-xylene with a phenol or a substituted phenol. The compounds are useful as antioxidants, fungicides and as intermediates for polyesters and epoxy resins. The reference does not disclose phenols containing only meta-halogens at the aromatic nuclei.

US-A-3 232 993 relates to halogenated bisphenols and their preparation, wherein three aromatic rings are coupled via methylene groups. They are prepared by reacting halogenated p-xylene derivatives with phenol. This reference does not disclose phenols containing halogens only in the meta-position.

From EP-A-214 722 which is a document according to Article 54(3) EPC, brominated derivatives of tetraalkyldihydroxy diaromatic compounds are known wherein the brominated aromatic rings are polymethylene bridged. The bisphenols have at least one ethane linkage between the aromatic ring. The compounds are useful as intermediates for the preparation of valuable chemical compounds such as epoxy derivatives which can be cured to epoxy resins.

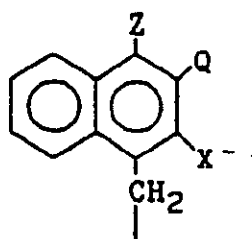
In the art of epoxy thermosets, for example, such as in electrical encapsulations and laminates, certain properties of the thermosets are desirable. For example, a higher glass transition temperature (T_g) coupled with higher hydrolytic stability such as measured by a low hydrolyzable halide content and with high flame-retardant efficiency is desirable in electrical encapsulations. However, presently available commercial electrical encap-

sulation systems derived from cresol epoxy novolacs and bis(4-(2,3-epoxypropoxy)-3,5-dibromophenyl)isopropylidene with bromo moieties ortho to the 4-oxy moiety, although of high flame-retardant efficiency (UL 94 V-O rating) and good thermal stability (T_g 155°C, by T.M.A., Thermo Mechanical Analyzer), are hydrolytically unstable (hydrolyzable bromide 180 parts per million (ppm) as measured by total hydrolyzable halide method herein). For example, this hydrolytic instability, even when coupled with the moderately high thermal stability, is problematical because when coupled with moisture penetration, can result in internal corrosion of the encapsulated device, thereby reducing or destroying the effectiveness especially of microelectric circuitry. The moderately high thermal stability itself is also a property needing improvement. A major reason for this is the miniaturization in the art of so-called "microchip" technology. As the scale of these microchips becomes increasingly smaller, the localized heat problems become increasingly greater, and thus, the present encapsulation formulation properties may not be as suitable as desired. In the art of electrical laminates, many of these same considerations apply.

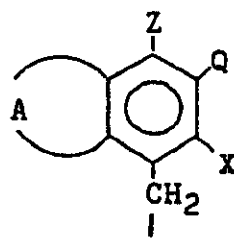
The present invention, in one aspect, concerns a coupled aromatic compound represented by the formula



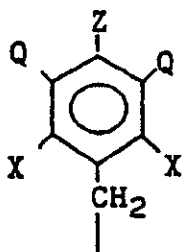
wherein Ar is an aromatic moiety different from Y and Y is an aromatic moiety represented by one of the formulae :



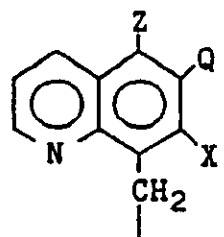
II,



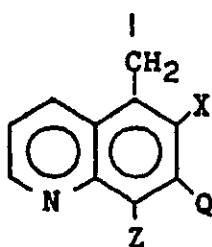
III,



IV,

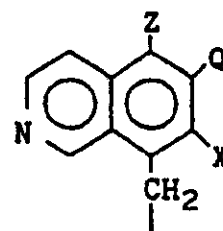


V,



VI

or



VII

wherein the Y moiety is coupled to a ring carbon in the Ar moiety and wherein

A is an aliphatic ring system bonded to the aromatic ring ;

Q is separately at each occurrence hydrogen, alkyl or inertly-substituted alkyl with proviso that the carbon atom bonded to the aromatic ring is a primary or secondary carbon atom. Preferably Q is an alkyl having 1 to 12 carbon atoms, most preferably methyl ;

X is separately at each occurrence a halogen moiety, preferably X is chloro, bromo or fluoro, more preferably chloro or bromo and most preferably bromo ;

Z is a nitrogen- or chalcogen-containing moiety, preferably the corresponding oxygen-containing moiety, most preferably OH.

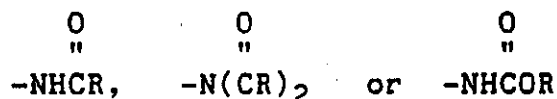
In another aspect the present invention concerns a process for the preparation of the coupled aromatic compound of Formula I above which process comprises contacting an aromatic compound with an alkylating aromatic agent represented by the formula (hm)-Y wherein hm is Br, Cl, OH or C_{1-4} alkoxy group and Y is defined

as hereinbefore, under conditions sufficient to form the coupled aromatic compound.

The coupled aromatic compounds of this invention range in form from monomers useful for example, for engineering thermoplastics and epoxy thermosets, for example, in electronics, to polymers which are, for example, the engineering thermoplastics and epoxy thermosets therefrom or which are polymers modified with the coupled aromatic compounds.

For the purpose of this invention the inertly-substituted alkyl denotes an alkyl group having a substituent such as hydroxyl group, alkoxy group and halogen on a carbon atom(s) which is not directly bonded to the aromatic ring.

The nitrogen- or chalcogen-containing moiety represented by the Z substituent in the foregoing formula is -NH₂, -NHR, -NR₂, -OH, -OR, -SH, -SR,



wherein R is, separately at each occurrence, a C_{1-r} organic group (organic group with from one to r carbon atoms. Preferably the organic (R) group is hydrocarbonyl. The r is an integer, preferably from 2 to 12 in the case of a generally monomeric coupled aromatic compound, and otherwise up to the number of carbons found in a particular generally polymeric material. More preferably the organic (R) group is C₁₋₈ hydrocarbonyl for example C₁₋₈ aryl such as phenyl, tolyl, xylyl and ethylphenyl, and C₁₋₈ aliphatic radical, especially alkyl such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl and branched chain isomers thereof.

In case of Z being -OR moiety, R is suitably an alkyl, preferably having 1 to 4 carbon atoms such as methyl, ethyl, propyl and butyl or an alkylene, preferably methylene substituted, for example, with additional ether linkage methylene chains, methyl capped, or with hydroxyl group or an ester moiety (O-CO-R) such as acetoxy moiety.

Preferably, the coupled aromatic compound contains at least 0.3 percent by weight from the aromatic moiety present, more preferably at least 2 percent by weight and most preferably at least 7 percent by weight. It is especially preferred that at least 10 percent by weight of the aromatic moiety is present in the coupled aromatic compound and more especially at least 20 percent by weight.

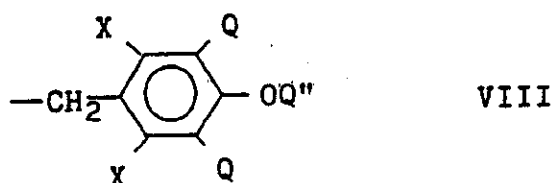
Preferably the compound of the invention is a novolac resin containing at least 1 percent by weight of the moiety represented by Y.

Also within the scope of the Y aromatic moiety are moieties such as substituted fused or cycloaliphatic ring variants of the moieties of the formulae (II), (III), (V) and (VI) such as substituted with other fused or cycloaliphatic ring systems, also hydrocarbonyl groups, for example, methyl and ethyl. However, such are preferably methyl-substituted such as at the ortho position in relation to the Z moiety of the aromatic moieties of the formulae (II), (V) and (VI).

Preferred Y aromatic moieties are those represented by formulae (II), (III) and (IV), more preferred are those of formula (IV), especially the ones wherein Z is oxygen-containing moiety.

Preferably, halogen substituents are at both meta positions to the nitrogen or chalcogen singly bonded to the aromatic nucleus. Preferably, the meta halogen substituents are selected from the group consisting of fluoro, chloro and bromo, more preferably, chloro and bromo, and most preferably the meta halogen substituents are each bromo.

More preferably, the Y aromatic moiety is represented by the formula :



wherein Q and X are as hereinbefore defined and

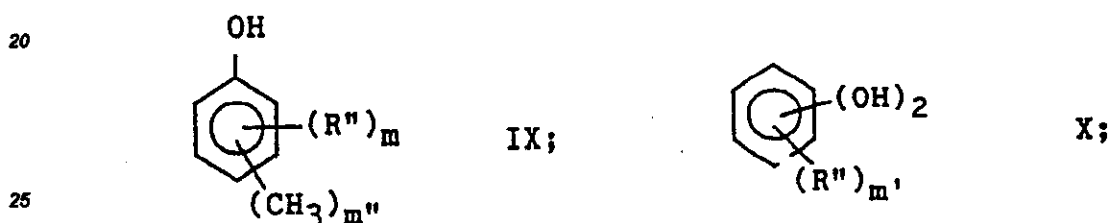
Q'' is hydrogen or the R group, such as 2,3-epoxypropyl or 2-hydroxy-3-halogenpropyl ; preferably hydrogen.

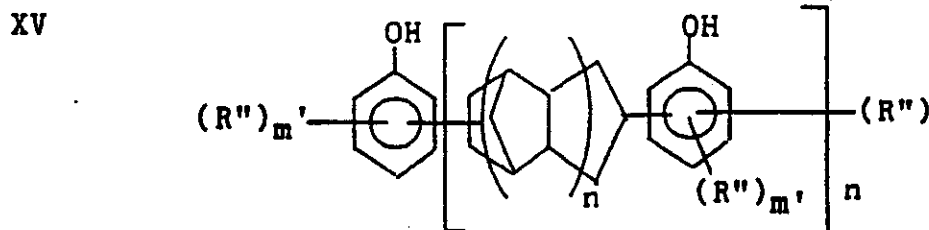
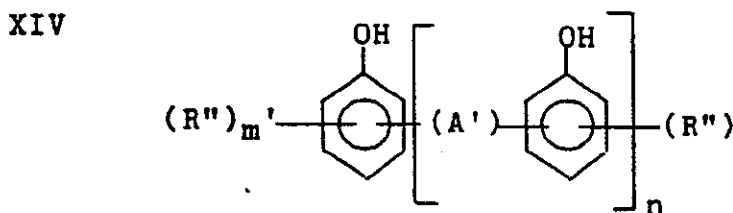
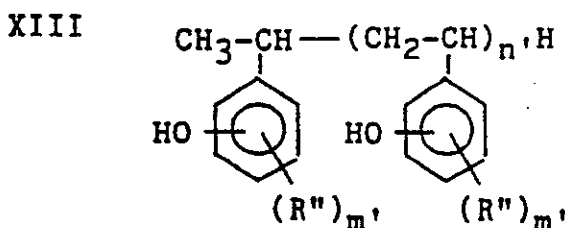
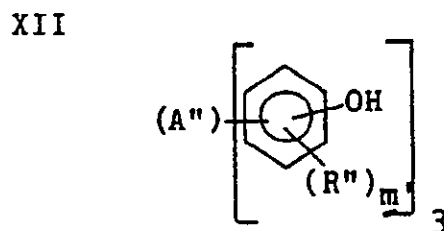
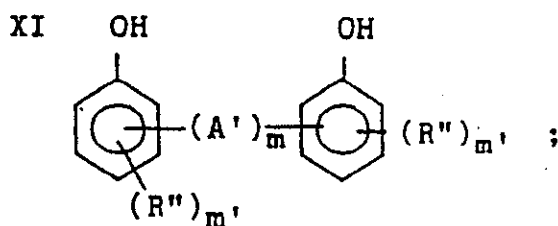
Thus, especially preferred are 4-hydroxy-3,5-dimethyl-2,6-dibromobenzyl or such as 4-(2,3-epoxypropoxy)-3,5-dimethyl-2,6-dibromobenzyl, or 4-(2-hydroxy-3-halogenpropoxy)-3,5-dimethyl-2,6-dibromoben-

zyl.

The Y aromatic moiety is bonded (coupled) to a ring carbon in the other mentioned aromatic ring which can be heterocyclic such as, for example, 2-pyridinol, or carbocyclic such as, for example, benzene ring, naphthalene ring, anthracene ring or cyclopentadiene ring systems, and the like. Thus, the Y aromatic moiety is generally coupled to an aromatic carbon of all aromatic-containing compounds for monomers, and to polymers such as, for example, polystyrenes, or modified polystyrenes such as, for example, polymer blends with polystyrene or chloromethylated polystyrenes, copolymers containing polystyrenes such as, for example, ABS resins, styrene-divinylbenzene copolymers and styrene-acrylonitrile copolymers, polycarbonates and copolymers thereof such as polyester carbonates and polyether carbonates and polymer blends therewith, polyphenylene sulfides and copolymers thereof and polymer blends therewith, aromatic polyesters and copolymers thereof and polymer blends therewith, polyether sulfones and copolymers thereof and polymer blends therewith, polyphenylene oxides and copolymers thereof and polymer blends therewith and polyaryl ether ketones and copolymers thereof and polymer blends therewith and so forth.

Preferably, the Y aromatic moiety is attached to an aromatic ring system which itself contains at least one aromatic hydroxy moiety such as, for example, in phenols (IX), aromatic diols (X), diphenolics (XI), trisphenols (XII), polyvinyl phenols (XIII), novolac resins (XIV), polycyclopentadiene polyphenols (XV), each of the following formulae





45 wherein in each of the substances of the formulae (IX through XV, inclusive), as appropriate,
A' is a divalent organic group, more preferably a divalent hydrocarbyl group, for example, such as methylene (-CH₂-) radical;
A'' is a trivalent organic group, more preferably a trivalent hydrocarbyl group, for example, such as methylidyne

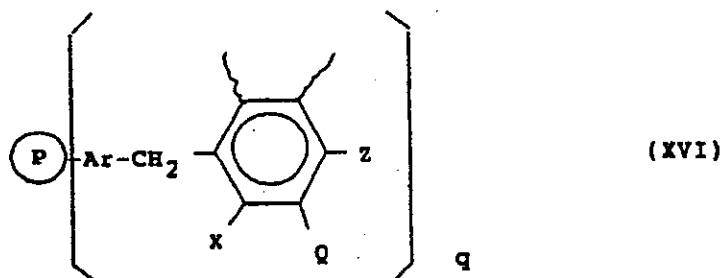
50 (-CH-) radical;

55 R'' is hydrogen or an alkyl or aryl group, more preferably the alkyl group, halogen or organo-oxy group;
m is separately at each occurrence an integer from zero to 4, more preferably zero to 2;
m' is separately at each occurrence an integer from zero to 2, more preferably one;
m'' is zero or one;

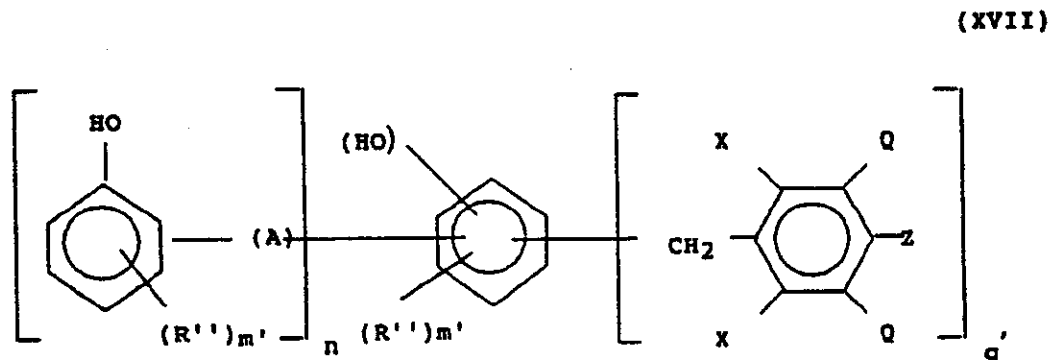
n is separately at each occurrence an integer from one to 10, more preferably one to 6 ; and
n' is an integer from one to 100, more preferably to 50 and most preferably is 25.

Also, the Y organic moiety is attached to the aromatic ring system of the appropriately substituted aromatic rings of compounds disclosed in US-A-4,649,181, issued March 10, 1987, and derivatives thereof in which the aromatic groups contain sulfur or nitrogen atoms. Example of such, is 1,4-bis(4-hydroxybenzoyl)benzene.
Epoxidation can follow if desired.

The so-called alkylated products thus can be illustrated by the following exemplary formulae



especially such as, for example,



wherein

Q, R'', X, Z, m' and n are as hereinbefore defined ;

Ar is an aromatic ring ;

Ⓟ is a polymeric substance to which the Ar is bonded ;

q is an integer from one to a number limited by the length of any polymer chain as represented ; and

q' is an integer from one to 4, especially one to 3, representing the number of Y aromatic moieties bonded to each other aromatic ring.

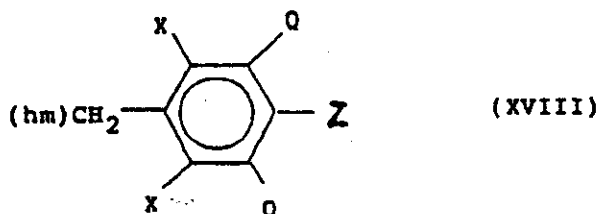
The parenthetical recitation "hm" hereinafter means a "hetero moiety" substituted onto the paramethyl group. For example, the hetero moiety can be HALO, that is, a halogen selected from bromo (Br) and chloro (Cl), preferably bromo, and the resulting para-(hm)methyl group would thus be para-HALOmethyl (4-HALOmethyl). Or, the hetero moiety can be hydroxy group, and the resulting para-(hm)methyl group would thus be para-hydroxymethyl. Other of such suitable hetero moieties are those such as, for example, methoxy, ethoxy and acetoxy. In general, the hetero moiety is one which can form a by-product such as a hydrogen-adduct, (H(hm)) with a moiety such as the hydrogen moiety of the other aromatic ring in the preparation of the meta-halogenated-phenylic-coupled aromatic compound. The para-(hm)methyl-meta-halogen-phenylic is a suitable source of the Y aromatic moiety.

The para-(hm)methyl-meta-halogenatedphenylic compound also contains at least one moiety such as a halogen moiety in a position meta to nitrogen or chalcogen singly-bonded onto an aromatic nucleus such as a six-membered aromatic ring. Preferably, said nitrogen or chalcogen, and preferably oxygen, is a part of a moiety such as a, for example, an amino, mercapto or hydroxy moiety and more preferably the hydroxy moiety, although, for example, said oxygen can be part of an organo-oxy moiety, especially such as, alkoxy, for example, methoxy or inertly-substituted variant thereof, wherein inertly refers to a substituted moiety which does not generally interfere with the process for preparing the meta-halogenated-phenylic-coupled aromatic compound. Similarly, said nitrogen or other chalcogen can be part of a moiety such as secondary amino or,

for example, organo-thiol (R-SH).

Preferably, halogenated moieties of the para-(hm)methyl-meta-halogenated phenylic compound are at both meta positions of a six-membered aromatic carbon ring. Preferably, the meta-halogen moieties are selected from the group consisting of fluoro, chloro and bromo, more preferably, chloro and bromo, and most preferably, the meta-halogen moieties are each bromo.

More preferably, the para-(hm)methyl-meta-halogenatedphenylic compound is a para-(hm)methyl-dimeta-halogenatedphenolic compound such as represented by the formula



wherein Q and X and Z are as hereinbefore defined, (hm) is the hetero moiety, preferably hydroxy, the HALO or methoxy, most preferably hydroxy or bromo.

The most preferred of the para-(hm)methyl-dimeta-halogenatedphenolic compounds include, for example, 4-bromomethyl-3,5-dibromo-2,6-dimethylphenol and 4-hydroxymethyl-3,5-dibromo-2,6-dimethylphenol.

The para-(hm)methyl-meta-halogenatedphenylic compounds can be prepared by known procedures or by a procedure disclosed or referenced herein. For example, ortho alkylation of phenols is well-known in the art. The ortho alkylation of 1-naphthol or tetrahydro-1-naphthol or the quinolines (commercial materials available from Aldrich Chemical Company) affords a 2-alkyl phenol or appropriately corresponding alkyl quinoline; 2-methyl-1-naphthol is readily available. Bromination of these phenols or alkylated quinolines in superacids using the general procedure of Jacquesy et al., *J. C. Soc. Chem. Comm.*, 110-11 (1980), affords the meta-brominated phenols or quinolines. Further functionalization of these phenols or quinolines to prepare hydroxymethyl or chloromethyl derivatives uses well established procedures.

Also, para-HALOmethyl-dimeta-halogenated-diortho-substituted phenols (that is, 4-HALOmethyl-3,5-dihalo-2,6-disubstituted phenols) are preferably prepared by the process of US-A-4,684,752, issued August 4, 1987. The para-hydroxymethyl-dimeta-halogenated-2,6-disubstituted phenols can then be prepared by reacting the para-HALOmethyl-dimeta-halogenated-diortho-substituted phenols with water in acetone such as by the general procedure of K. Auwers & H. Allendorff, *Ann.*, 302, 76-98 (1898) or by reacting such as, for example, 3,5-dibromo-2,6-dimethylphenol with formaldehyde by the general procedure of K. Auwers & F. A. Trawn, *Ber.*, 32, 3309-17 (1899).

Corresponding ortho-hydro phenolic compounds can be prepared by isomerizing ortho-bromophenols into corresponding meta-brominated derivatives in the presence of a liquid superacid as generally described by Jouannetaud et al., US-A-4,447,660 (1984). Corresponding organo-oxy compound (including, of course, organo-oxy moieties of the "hetero moiety") can be prepared from the para-hydroxymethyl-meta-halophenolic compound by standard Williamson ether synthesis or by the general procedure of K. Auwers & H. Allendorff, *Ann.*, 302, 76-98 (1898).

The other aromatic can be virtually any aromatic compound to which the para-(hm)methyl-meta-halogenatedphenylic compound is contacted with to prepare the meta-halo-phenylic-coupled aromatic compound such as would contain the other mentioned aromatic rings to which the Y aromatic moiety is coupled. Preferred are the hydroxy aromatic compounds such as of the formulae (IX) through (XV), especially alkyl phenols and cresol formaldehyde novolacs.

The meta-halogenated-phenylic-coupled aromatic compounds are prepared by contacting the para-(hm)methyl-meta-halogenatedphenylic compound with the other aromatic compound. Conditions are those sufficient to carry out the coupling reaction.

The conditions of the coupling can appropriately be those generally encountered in known alkylation couplings. For example, conditions can be those generally encountered in Friedel-Crafts alkylations.

Preferably the alkylation reaction is carried out at elevated temperatures.

More preferably the reaction is carried out at temperatures from 20°C to 150°C in the presence of a suitable catalyst.

The Friedel-Crafts alkylation is suitably carried out at elevated temperatures. Typically, Friedel-Crafts alkylation is carried out at temperatures from 20°C to 220°C or higher depending whether or not a catalyst is present.

Friedel-Crafts alkylation conditions can include employment of a Lewis acid or Bronsted acid catalyst such

as, for example, aluminum tribromide, aluminum trichloride or ferric chloride, or a protic acid, an inert organic diluent such as a haloalkane, for example, dichloromethane, temperatures from 20°C to 150°C, typically ambient pressures and times from 10 minutes to 14 hours depending on the conditions, for example, by an increase in temperature or by an increase in the level of catalyst.

In general, a by-product such as the corresponding H(hm) compound is prepared from the coupling. For example, with 4-hydroxymethyl-3,5-dibromo-2,6-dimethylphenol employed as the para-(hm)methyl-meta-halogenatedphenylic compound, a by-product of water is thus typically produced, and the corresponding halide from the para-HALOmethyl group appears as a by-product of the Friedel-Crafts alkylation, most typically as HCl or HBr. Other H(hm) compounds such as, for example, methanol or acetic acid, as is appropriate for each hetero moiety, methoxy or acetoxy, respectively, are also typically produced as a useful by-product.

Preferably and even more unexpectedly, the para-(hm)methyl-meta-halogenatedphenylic compounds, especially the para-(hm)methyl-dimeta-halogenatedphenolic compounds, do not generally require the addition of catalysts, for example, Lewis acid or Bronsted acid catalysts. The alkylation may thus be acatalytic, self-catalytic or catalyzed by minute amounts of impurities normally present in the reaction mixture or on the reaction vessel.

More preferred temperature ranges include those such as from 20°C to 100°C with the employment of additional Bronsted or Lewis acid catalyst. Temperatures from 80°C to 220°C are generally preferred when the alkylation is carried out without added catalyst. Typically, temperatures such as from 80°C to 150°C are more preferred without added catalyst in the case of alkylation of the lower molecular weight other aromatics, for example, pyridinols, phenolics and novolacs, and typically even higher temperatures are preferred when thus alkylating the higher molecular weight polymeric materials, for example, polystyrenes.

An inert diluent is preferably present. Preferably, the inert diluent is one which can form a low-boiling azeotrope with the by-product such as the H(hm) by-products. For example, benzene, toluene or methyl isobutylketone (MIBK), with an aqueous by-product.

Etherification of meta-halogenated-phenylic-coupled aromatic compounds, for example, the hydroxy-containing ones (that is, meta-halogenated-phenylic-coupled aromatic compounds), for example, 4-hydroxy-3,5-dimethyl-2,6-dibromobenzyl moiety containing coupled benzenes and phenols up through the novolacs can be next carried out, if desired, to prepare hydroxy-containing organo-oxy moieties by reacting an oxirane therewith by generally known procedures such as, for example, that of Jackson, US-A-3,402,169 (1968). Preferably, the etherification is carried out with an epihalohydrin such as, for example, epichlorohydrin or epibromohydrin. The amino- and mercapto-containing meta-halogenated-phenylic-coupled aromatic compounds react similarly to the hydroxy-containing ones, generally preparing amino- or mercapto-containing epoxy resins.

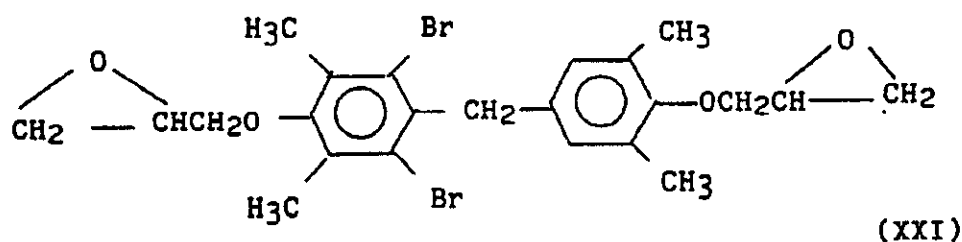
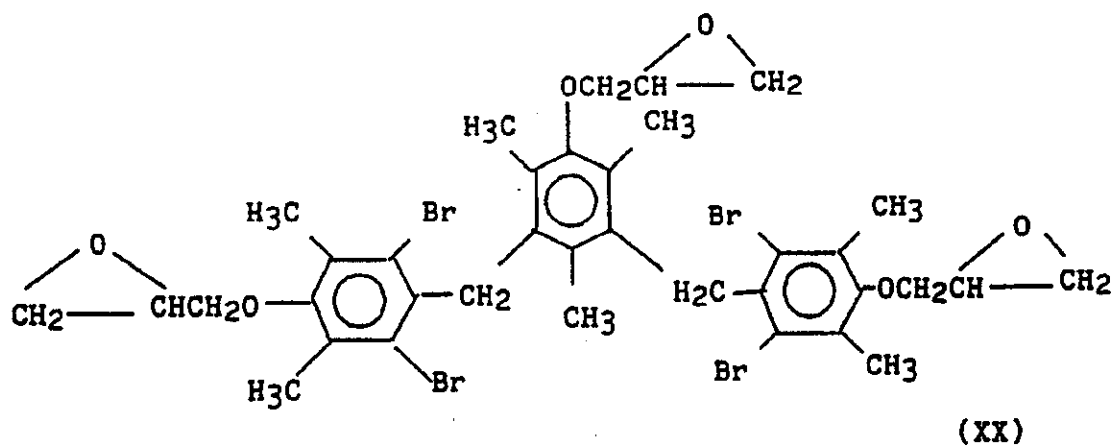
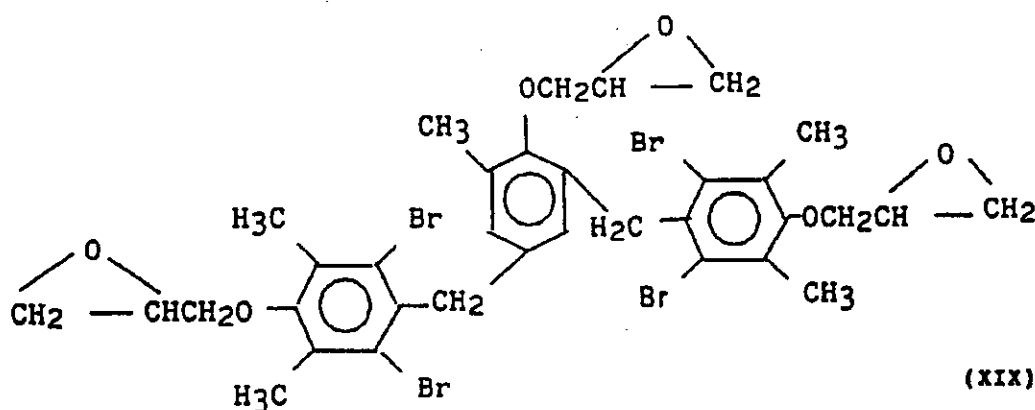
When the oxirane employed to carry out the etherification is such as the epihalohydrins, a vicinal halohydrin organo-oxy moiety is preferably obtained, wherein halogen and hydroxy moieties are on adjacent terminally ended carbons such as, for example, in a 3-chloro-2-hydroxypropoxy moiety. Preferably, the vicinal halohydrin organo-oxy moiety-containing meta-halogenated-phenylic-coupled aromatic compound is epoxidized to obtain a meta-halogenated-phenylicoxypoxy-coupled aromatic compound such as containing a terminally ended epoxy group, for example, 2,3-epoxypropoxy.

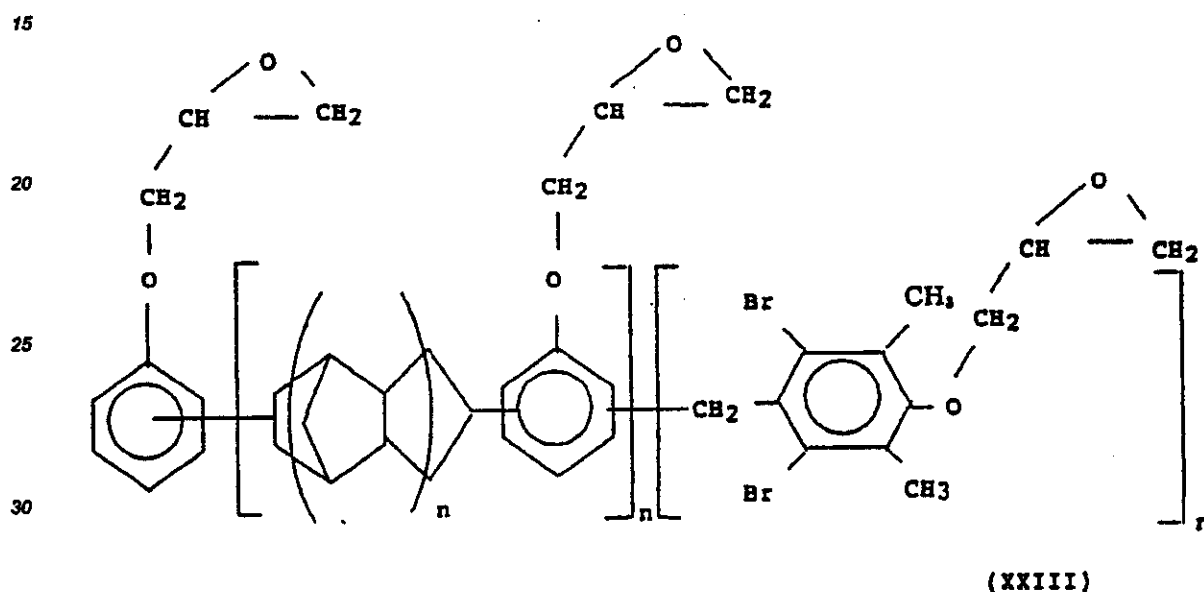
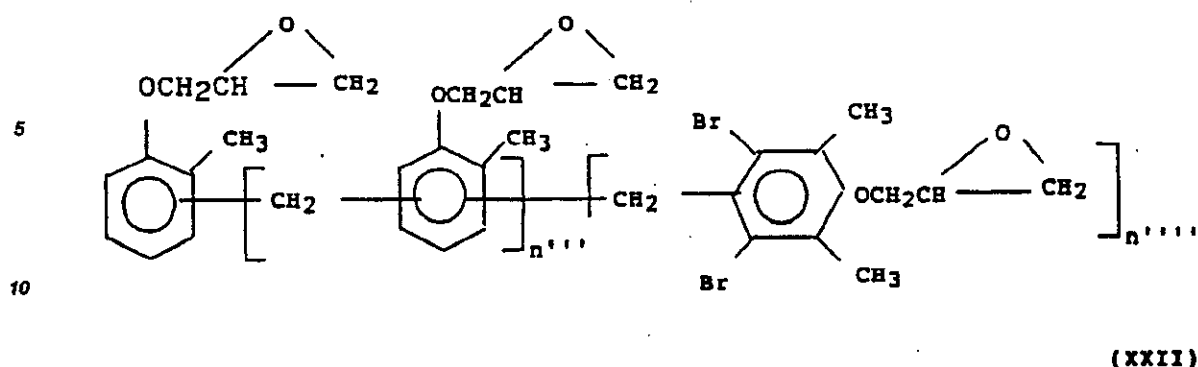
The epoxidation can be carried out with epoxidizing agents such as an aqueous alkali metal hydroxide in a biphasic reaction system, such as by the general procedure of Wang et al., US-A-4,499,255 (1985) or by the general procedure of Au, US-A-4,266,054 (1981). Preferably, the epoxidation is carried out with aqueous sodium hydroxide employing as the organic phase diluent an inert organic diluent such as a saturated ether or ether-alcohol. The ether-alcohol is preferably one such as, for example, 1-methoxy-2-hydroxypropane.

The meta-halogenated-phenylicoxypoxy-coupled aromatic compounds can be cured into meta-halogenated-phenylic-coupled aromatic epoxy thermosets by employment of a curing agent, for example, a hydroxy-containing organic compound. Preferably, the curing agent contains one or more of compounds such as primary aliphatic and aromatic amines, guanidines, biguanides, polycarboxylic acids and anhydrides thereof, amides, sulfones, sulfonamides and polyhydric phenols, with preferred species also including bis-(4-aminophenyl)sulfone, aminophenyl sulfonamide, dicyandiamide, phenylenediamide and phthalic anhydride. The phenol formaldehyde novolacs, including meta-halogenated-phenolic-coupled aromatic novolacs, are preferred curing agents in formulations such as for electronic encapsulation. These novolacs herein preferably contain from 1 to 20 percent by weight bromine, more preferably from 5 to 15 percent by weight bromine, especially as from meta-bromo moieties, or at least half that from the lighter molecular weight halogens. The curing agent, thus more preferably contains a phenol formaldehyde novolac or a hydroxy-containing compounds such as, for example, 4-hydroxymethyl-3,5-dibromo-2,6-dimethylphenol and/or meta-halogenated-phenylic-coupled aromatic novolacs. Alternatively, the meta-halogenated-phenoxy-coupled aromatic compound can be used as the curing agent to cure a thermosettable epoxy such as a cresol epoxy novolac to afford a cured epoxy thermoset composition containing the Y organic moiety.

Preferably the compound of the invention is a cured epoxy thermoset containing at least $\frac{1}{2}$ percent by weight of the Y moiety.

In general, the meta-halogenated-phenylic-coupled aromatic compounds typically possess unusually high hydrolytic and thermal stability. Thus, for example, the meta-halogenated-phenylic-coupled aromatic compound cured epoxy thermosets can be generally employed as part of an electronic encapsulation material which preferably has flame-retardant capability and very low hydrolyzable halide content upon heat or moisture exposure. For example, when used in electronic encapsulation formulations, these materials can provide a substantial increase in electronic device reliability. Preferably, the electronic encapsulation material is prepared with the meta-bromo-phenylic-coupled aromatic compound cured epoxy systems. Preferred electronic encapsulation formulations include those employing the following meta-bromo-phenylic-coupled aromatic compounds :





35 wherein n is separately at each occurrence an integer from one to 10, more preferably one to 6; n'' is generally from zero to 100, preferably from 2 to 10; and n''' is the same as n'' but preferably is less, more preferably from one to 5.

Of these compounds of the formulae, the compounds of the formulae (XXI through XXIII) are more preferred, and even more preferred are the compounds of the formulae (XXII and XXIII).

40 Preferably, the amounts of the hydroxy-(or other such active hydrogen) containing compounds (e.g., novolac; thiol; amino) as "curing agents" are employed with the epoxy compound in a ratio of the stoichiometric ratio. The stoichiometric ratio is one molar equivalent of such active hydrogen-containing moieties in the compound (e.g., one molar equivalent of $-OH$ or $-SH$ or one-half equivalent of $-NH_2$) with one molar equivalent of the epoxy moieties, generally as a glycidyl ether moiety, in the other compound. Preferably herein, final bromine

45 content of the encapsulation formulation is from 0.5 to 3 percent by weight, more preferably from 1 to 2 percent by weight.

The following examples further illustrate the invention. Parts and percentages are by weight unless otherwise noted.

50 Examples 1-14

Alkylations with 4-bromomethyl-3,5-dibromo-2,6-dimethylphenol (tribromomesitol):

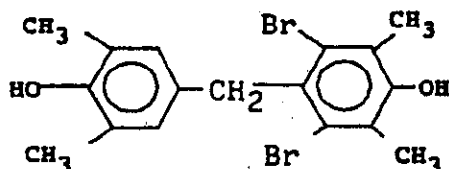
Example 1 - Monoalkylation of 2,6-Dimethylphenol

55

A 372.9 g (1.0-mole) portion of 4-bromomethyl-3,5-dibromo-2,6-dimethylphenol (tribromomesitol) and 122.2 g (1.0 mole) of 2,6-dimethylphenol were dissolved in 3.0 liters of methylene chloride at 20°C and 0.15 g of ferric chloride was added. The solution was gently heated to 40°C over a period of one hour. Subsequent

to heating for a few minutes, a precipitate begun to form. HBr gas was evolved during the heating period. At the moment the temperature reached 40°C, the slurry was refluxed for 0.5 hour, cooled to 25°C, and the insoluble solid was filtered and dried. This afforded 372.7 g of crude, white solid which was analyzed as 99 + percent purity dibromotetramethylbisphenol F as determined by gas chromatography (90 percent yield) which has the following nuclear magnetic resonance spectrum :

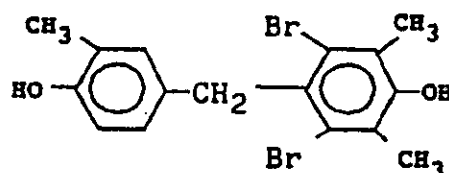
(acetone d_6), delta : 2.20 (s, 6H), 2.40 (s, 6H), 4.30 (s, 2H), 6.60 (s, 2H). This is consistent with the structure of the product. Recrystallization from 2.0 liters of toluene afforded 335.0 g of solid of 99.9 + percent purity as determined by gas chromatography. This latter solid melts at 210°C-211°C and is represented by the following formula



Example 2 - Monoalkylation of ortho-Cresol

A 175.0-g (0.47-mole) portion of tribromomesitol and 150 g (1.39 moles) of ortho-cresol were dissolved in 1.5 liters of carbon tetrachloride at 20°C, and 0.20 g (0.0012 mole) of ferric chloride was added. The solution was heated to 45°C over a period of one hour. During this time a precipitate appeared. The slurry was heated to 70°C to complete the evolution of HBr gas, and was held there for 0.5 hour. Cooling to 25°C and filtering of the insoluble solid afforded 139.0 g (74 percent yield) of dibromotrimethyl-bisphenol F, identified by liquid chromatography as 99 + percent purity para-alkylated material. The solid has the following H nuclear magnetic resonance spectrum :

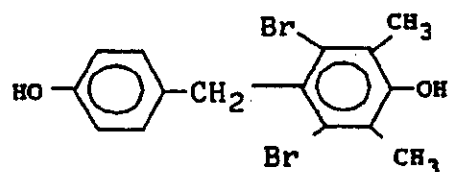
(acetone d_6), delta : 2.20 (s, 3H), 2.40 (s, 6H), 4.30 (s, 2H), 6.60 (s, 2H), 6.80 (s, 1H), and melts at 197°C-199°C. The insoluble solid is represented by the following formula



Example 3 - Monoalkylation of Phenol

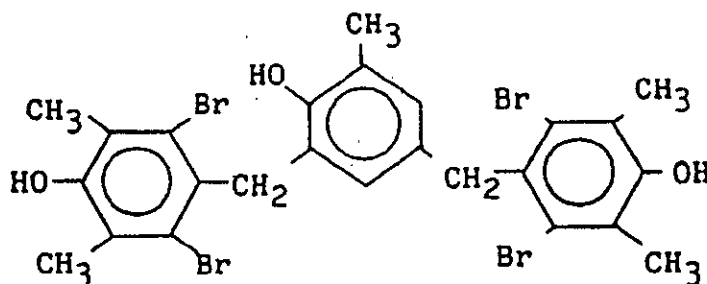
A 372.9-g (1.0-mole) portion of tribromomesitol and 282.0 g (3.0 moles) of phenol were dissolved in 2.5 liters of carbon tetrachloride at 20°C, and 0.3 g (0.0018 mole) of ferric chloride was added. The solution was heated to 45°C over a period of one hour. A solid precipitated during this period. The slurry was heated to reflux temperature, and 1.0 liter of solvent was removed. Cooling to 25°C afforded 203.2 g of a slightly yellow solid which, when analyzed by liquid chromatography, has the following composition :

2 percent tribromomesitol, 4 percent phenol, 90 percent monoalkylated phenol as a mixture of isomers, and 4 percent dialkylated phenol. Further purification of the crude solid from 1.0 liter of hot carbon tetrachloride, by refluxing for 0.5 hour afforded 180.0 g of a product which contained 92 percent of the para-alkylated phenol. The solid has the following H nuclear magnetic resonance spectrum : (acetone d_6), delta : 2.40 (s, 6H), 4.30 (s, 2H), 6.6-7.2 (m, 4H), and melts at 168°C-175°C. The latter solid is represented by the following formula

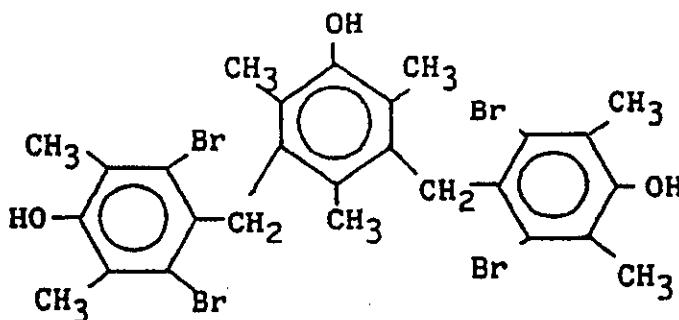


Example 4 - Dialkylation of ortho-Cresol

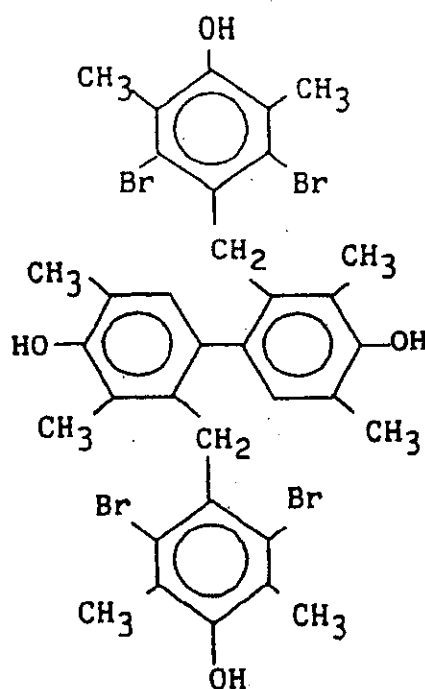
A 313.0-g (0.84-mole) portion of tribromo-mesitol and 43.2 g (0.40 mole) of o-cresol were dissolved in 3.5 liters of methylene chloride at 20°C, and 0.3 g (0.0018 mole) of ferric chloride was added. The solution was heated to 40°C over a period of one hour, and the slurry which was obtained was refluxed for one more hour. Removing 1.0 liter of solvent and cooling to 25°C afforded 255.0 g of solid, which analyzed by liquid chromatography as 98 percent dialkylated product, with 1 percent monoalkylated and 1 percent trialkylated o-cresol. The solid has the following H nuclear magnetic resonance spectrum : (acetone d₆), delta : 2.20 (s, 3H), 2.30 (s, 6H), 2.40 (s, 6H), 4.20 (s, 2H), 4.40 (s, 2H), 5.80 (s, 1H), 6.80 (s, 1H), and melts at 224°C-226°C. The solid was as represented by the following formula

**Example 5 - Dialkylation of 2,4,6-Trimethylphenol**

A 392.0-g (1.03-mole) portion of tribromo-mesitol and 68.1 g (0.50 mole) of 2,4,6-trimethylphenol were dissolved in 3.0 liters of carbon tetrachloride at 20°C, and 1.0 g (0.006 mole) of ferric chloride was added. The solution was heated to reflux and held there for 7.0 hours. Some solid precipitated during this time. Removing 1.0 liter of solvent and cooling to 25°C afforded 286.3 g of solid (76 percent yield) of 96 percent purity by liquid chromatography, containing 4 percent monoalkylated product. The solid has the following H nuclear magnetic resonance spectrum : (acetone d₆), delta : 1.80 (s, 3H), 2.10 (s, 6H), 2.30 (s, 12H), 4.40 (s, 4H). The solid was purified by slurrying in hot methylene chloride, cooling to 25°C, and filtering to afford 99 percent purity dialkylated mesitol, which melts at 164°C-166°C. The latter solid is represented by the following formula

**Example 6 - Dialkylation of Tetramethylbiphenol**

A 7.50-g (0.020-mole) portion of tribromo-mesitol and 2.40 g (0.010 mole) of tetramethylbiphenol were suspended in 100 ml of carbon tetrachloride, and 0.10 g (0.0006 mole) of ferric chloride was added. The mixture was heated to reflux and held there for 5.0 hours. Cooling of the slurry and filtration of the insoluble solid afforded 6.04 g of product. Analysis by liquid chromatography indicated 84 percent dialkylated product and 16 percent monoalkylated material. The solid melts at 221°C-226°C, and has the following H nuclear magnetic resonance spectrum : (acetone d₆), delta : 1.90 (s, 6H), 2.10 (s, 6H), 2.20 (s, 12H), 4.10 (s, 4H), 4.30 (small s), 6.20 (s, 2H). The solid represented by the following formula

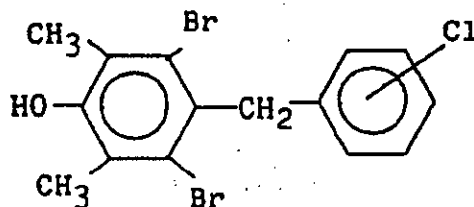


Example 7 - Alkylation of Dicyclopentadienebisphenol Novolac

A 3.7-g (0.01-mole) portion of tribromomesitol and 3.5 g of dicyclopentadienebisphenol novolac of 2.2 hydroxy functionality was dissolved in 100 ml of methylene chloride, and 0.008 g (0.05 mmole) of ferric chloride was added. The solution was refluxed for 8.0 hours, cooled, and the solvent was removed in a rotary evaporator. This affords 6.5 g of product. Complete reaction of the tribromomesitol to alkylation products was shown when it was analyzed by nuclear magnetic resonance spectroscopy: a singlet of 4.3 delta for the methylene group of the alkylated products. The methylene singlet for tribromomesitol appears at 4.90 delta.

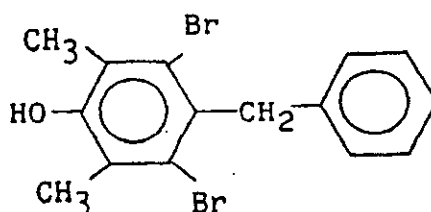
Example 8 - Monoalkylation of Chlorobenzene

A 7.46-g (0.02-mole) portion of tribromomesitol was suspended in 100 ml of chlorobenzene (0.98 mole), and 0.02 g (0.00012 mole) of ferric chloride was added. The mixture was heated to reflux and held there for 4 hours. The solution was cooled, and the solvent was removed in a rotary evaporator. A brown oil was obtained which was recrystallized from hexane, which affording 4.7 g of solid which was identified by H nuclear magnetic resonance and mass spectrometry as the monoalkylated product. H nuclear magnetic resonance spectrum: (CDCl₃), delta: 2.34 (s, 6H), 4.44 (s, 2H), 7.12 (m, 4H). The oil is identified as a mixture of isomers represented by the following formula



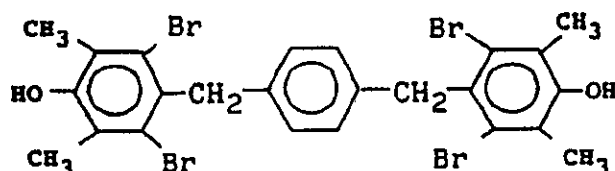
Example 9 - Monoalkylation of Benzene

A 9.30-g (0.025-mole) portion of tribromomesitol was added to 100 ml of benzene (1.12 moles), and 0.02 g (0.00012 mole) of ferric chloride was added. The mixture was heated to reflux and held there for 1.5 hours. Cooling of the solution, filtration of insoluble solid and removing the solvent by a rotary evaporator afforded 8.10 g of crude product which was identified by its H nuclear magnetic resonance spectrum as the monoalkylated product. H nuclear magnetic resonance spectrum: (CDCl₃), delta: 2.33 (s, 6H), 4.48 (s, 2H), 7.16 (m, 5H). The product is represented by the following formula



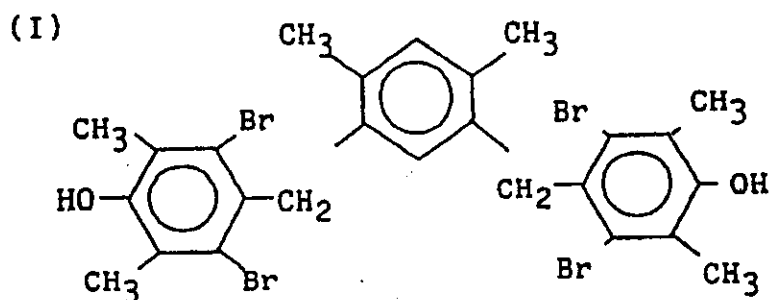
Example 10 - Dialkylation of Benzene

A 112.0-g (0.30-mole) portion of tribromomesitol and 13.0 ml (0.146 mole) of benzene were dissolved in 1.2 liters of methylene chloride, and 0.10 g (0.0006 mole) of ferric chloride was added. The solution was heated to reflux and held there for 2.0 hours. A solid precipitates during the refluxing period. The slurry was cooled to 25°C, and the insoluble solid was filtered. This afforded 85.6 g of white solid. The crude solid was purified by slurrying in 250 ml of acetone and filtering, which afforded 81.7 g (96 percent yield) of solid which was identified as the dialkylated benzene by liquid chromatography. The purified solid has the following H nuclear magnetic resonance spectrum : (DMSO d_6 + CCl_4 , 1:1), δ : 2.31 (s, 12H), 4.34 (s, 4H), 6.92 (s, 4H). The solid does not melt at temperatures at or below 300°C. The purified solid is represented by the following formula



Example 11 - Dialkylation of meta-Xylene

A 198.0-g (0.53-mole) portion of tribromomesitol was dissolved in 2.0 liters of methylene chloride at 20°C, and 0.20 g (0.0012 mole) of ferric chloride was added. The solution was heated to 35°C, and 30.6 ml (0.25 mole) of meta-xylene was added over a period of 10 minutes. HBr gas was evolved during the addition, and a precipitate appeared. The slurry was refluxed for 1.5 hours, 1.0 liter of solvent was removed, and the insoluble solid was filtered after cooling to 25°C. This afforded 136.0 g of dialkylated product (79 percent yield) of 99+ percent purity as determined by liquid chromatography. The solid has the following H nuclear magnetic resonance spectrum : (DMSO d_6), δ : 2.20 (s, 12H), 2.30 (s, 6H), 4.10 (s, 4H), 5.40 (s, 1H), 6.90 (s, 1H), and it melts at from 295°C to 297°C. The solid is represented by the following formula



Example 12 - Alkylation of Polystyrene

A one-liter resin kettle, fitted with a reflux condenser and overhead stirrer, was charged with 50.0 g of general purpose heat-resistant polystyrene resin (STYRON® 685D, The Dow Chemical Company), 300 ml of methylene chloride and 0.030 g of anhydrous $FeCl_3$. The resulting solution was stirred continuously at room temperature while 22.0 g of tribromomesitol which was dissolved in 300 ml of methylene chloride was added over a 4-hour period. The reaction mixture was left to stir overnight at room temperature under a nitrogen atmosphere. The thus alkylated polystyrene was next recovered by precipitation into methanol and was washed three

times with methanol. The product was next dried at 60°C in vacuo overnight which yielded 66.7 percent the alkylated polystyrene. Instrumental neutron activation analysis of the the alkylated polystyrene showed the polymer containing 12 (\pm 0.3) weight percent bromine.

5 Example 13 - Modification of Styrene-Divinylbenzene Copolymer Beads

A creased 500-ml three-neck round-bottom flask, which was fitted with a reflux condenser, was charged with 20.8 g of macroporous 6/42 styrene-divinylbenzene copolymer beads, 20 mg of anhydrous FeCl₃ solid, and 250 ml of 1,2-dichloroethane. The mixture was stirred continuously and heated to reflux temperature. Upon
10 establishment of reflux, 37.3 g of solid tribromomesitol was added over a 30-minute period via a solid addition funnel. Upon completing the addition of the tribromomesitol, the mixture was stirred and maintained at reflux for 4 hours. Next, the heating was terminated, and the mixture allowed to cool to 40°C. The thus modified copolymer beads were next collected on a medium porosity fritted glass funnel with vacuum filtration. The thus isolated beads were next transferred to a 500-ml Erlenmeyer flask and washed by stirring as a slurry in 250 ml
15 of 2-propanol at 50°C for 15 minutes. Next, the wash liquor was removed by vacuum filtration through a fritted funnel. The copolymer beads were returned to the Erlenmeyer flask and washed in the same fashion two additional times. Upon completion of the third washing, the thus isolated beads were rinsed with an additional 250 ml of 2-propanol at 25°C while on the glass frit. Upon drying in vacuo at 40°C for 16 hours, 39.9 g of modified copolymer beads were obtained. The thus modified copolymer beads gained weight to indicate that 36 percent
20 of the benzene rings in the copolymer contain the 2,6-dibromo-4-hydroxy-3,5-dimethylbenzyl moiety.

Example 14 - Alkylation of Bisphenol A Polycarbonate

A 6.35-g portion of bisphenol A polycarbonate, having an inherent viscosity of 0.525 deciliters/gram in methylene chloride at 25°C at an approximate concentration of 0.5 g/deciliter, was dissolved in 35 ml of 1,2-dichloroethane. The solution was heated to reflux, and 2.0 mg of anhydrous FeCl₃ was added. Next, 2.35 g of tribromomesitol was added via a solid addition funnel. The mixture was maintained at reflux for 90 minutes, during which time HBr evolution was observed. Upon the completion of the 90 minutes, the heating was terminated, and the hot polymer solution poured into 500 ml of well stirred methanol. The resulting polymer precipitate next was washed with methanol, chopped three times in methanol in a blender and dried in vacuo at room
30 temperature overnight. Instrumental neutron activation analysis shows the alkylated polycarbonate contains 4.9 (\pm 0.2) percent bromine.

Example 15 - Monoalkylation of 2,6-Dimethylphenol with 3,5-Dibromo-4-methoxymethyl-2,6-dimethylphenol

A 6.48-g (0.02-mole) portion of 3,5-dibromo-4-methoxymethyl-2,6-dimethylphenol and 2.44 g (0.02 mole) of 2,6-dimethylphenol were suspended in 100 ml of carbon tetrachloride, and 0.2 g (0.001 mole) of p-toluene sulfonic acid was added. The mixture was heated to reflux and held there for 8.0 hours. Methanol was produced as a by-product. Cooling of the mixture and filtering of the insoluble solid afforded 8.3 g of the monoalkylated
40 product identical with the product of Example 1. The product has 99+ percent purity as determined by gas chromatography.

Examples 16-23

45 Alkylations with 3,5-dibromo-4-hydroxymethyl-2,6-dimethylphenol :

Examples 16-17

With added catalyst :

50

Example 16 - Monoalkylation of 2,6-Dimethylphenol

A 3.1-g (0.01-mole) portion of 3,5-dibromo-4-hydroxymethyl-2,6-dimethylphenol was suspended in 100 ml of toluene, and 1.22 g (0.01 mole) of 2,6-dimethylphenol was added, followed by 4.0 g of acidic DOWEX® ion-exchange resin beads. The mixture was heated to reflux, and the distillate boiling below 110°C, containing some water, was removed. During the distillation, 100 ml of toluene was added to keep the amount of solvent constant. Upon removal of water, the mixture was kept at 110°C for 1 hour, and the solution is filtered to separate the beads. Cooling of the solution to 25°C affords a precipitate which was analyzed as 93 percent purity by gas
55

chromatography. The solid was slurried in 20 ml of CH_2Cl_2 and filtered to afford 1.4 g (34 percent yield) of 3,5-dibromo-2,2',6,6'-tetramethylbisphenol F, which identified by nuclear magnetic resonance spectroscopy as being identical with the product of Example 1. It melts at 206°C-208°C.

5 Example 17 - Monoalkylation of 2,6-Dimethylphenol

A 6.2-g (0.02-mole) Portion of 3,5-dibromo-4-hydroxymethyl-2,6-dimethylphenol was slurried in 100 ml of carbon tetrachloride, and 2.4 g (0.02 mole) of 2,6-dimethylphenol was added, followed by 0.19 g (0.001 mole) of p-toluene sulfonic acid. The mixture was heated to reflux, 75°C, and held there for 0.5 hour. Upon completion
10 of this heating interval, the reaction was complete as determined by nuclear magnetic resonance spectroscopy. Cooling to 25°C and filtration of the solid afforded 6.0 g (73 percent yield) of dibromotetramethylbisphenol F as a white solid, identical with the product of Example 1.

Examples 18-23

15

Without added catalyst :

Example 18 - Monoalkylation of 2,6-Dimethylphenol

20 In a 100-ml round-bottom flask, 6.2 g (0.020 ml) of 3,5-dibromo-4-hydroxymethyl-2,6-dimethylphenol and 2.6 g of 2,6-dimethylphenol were suspended in 25 ml of nitrobenzene. The mixture was stirred continuously and was heated over a 30-minute period to 175°C. The stirring of the mixture was maintained, and the temperature maintained at 175°C for 1 hour. Next, the stirring mixture was cooled to room temperature. The resulting precipitate was collected by filtration and dried overnight in vacuo. Liquid chromatographic analysis and ^1H
25 nuclear magnetic resonance and ^{13}C nuclear magnetic resonance spectroscopic analyses showed the resulting product to be identical with the product of Example 1.

Example 19 - Alkylation of Cresol Formaldehyde Novolac

30 To a one-liter reaction vessel equipped with temperature control and indicating means and a Dean-Stark trap with a reflux condenser, were added 227.5 g (1.96 eq.) of cresol formaldehyde novolac (softening point 78°C), 80 g (0.258 eq.) of 3,5-dibromo-4-hydroxymethyl-2,6-dimethylphenol and 100 g of toluene. Upon stirring at room temperature and atmospheric pressure to thoroughly mix the contents, the temperature was raised to 115°C. During the course of reaction, the water by-product of the reaction was removed by azeotrope with
35 toluene. The distillate was condensed, thereby forming two distinct phases, an aqueous (bottom) phase and a toluene (top) phase. The aqueous phase was cumulated inside the Dean-Stark trap, and the toluene phase overflow from the Dean-Stark trap was recycled back into the reactor. Completion of reaction was checked by liquid chromatography for the disappearance of the reactant, 3,5-dibromo-4-hydroxymethyl-2,6-dimethylphenol, in the reaction mixture. The reaction was completed in 2 hours as was indicated by the complete disappearance of said reactant in the liquid chromatograph and by the cumulation of the theoretical amount of
40 water in the Dean-Stark trap.

The resulting solution was next distilled under vacuum at a temperature of 160°C to generally remove all toluene. The resulting novolac contains 13.1 percent bromine and has a softening point of 99°C.

45 Example 20 - Alkylation of Phenol Formaldehyde Novolac

Phenol formaldehyde novolac (150 g, 1.47 eq., softening point 60°C), 52.5 g (0.169 eq.) of 3,5-dibromo-4-hydroxymethyl-2,6-dimethylphenol and 100 g of toluene were reacted in the same manner as Example 19. Upon removal of toluene, the resulting novolac contained 13.2 percent bromine and has a softening point of
50 83.7°C.

Example 21 - Alkylation of Dicyclopentadiene Phenol Novolac

Dicyclopentadiene phenol novolac (200 g, 1.21 eq., softening point 90°C), 70 g (0.226 eq.) of 3,5-dibromo-4-hydroxymethyl-2,6-dimethylphenol and 150 g of toluene were reacted in the same manner as Example 19. Upon removal of solvent, the resulting novolac contained 13.43 percent bromine and has a softening point of
55 108.7°C.

Example 22 - Alkylation of 1,1,1-Tri-(hydroxyphenyl)methane

1,1,1-Tri(hydroxyphenyl)methane (196 g, 2.0 eq., softening point 112°C), 70 g (0.226 eq.) of 3,5-dibromo-4-hydroxymethyl-2,6-dimethylphenol and 150 g of methyl isobutyl ketone were reacted in the same manner as Example 19. Upon removal of methyl isobutyl ketone, the resulting novolac contained 15.23 percent bromine and has a softening point of 134°C.

Example 23 - Alkylation of PolystyreneA. Neat Preparation

A Brabender mixer (Model R.O.6.), which was heated to 200°C and was operating at 63 rpm, was charged with 37.4 g of general purpose heat-resistant polystyrene (STYRON® 685D, The Dow Chemical Company). Upon the completion of 3 minutes, a homogeneous melt phase was obtained, and 13.8 g of 3,5-dibromo-4-hydroxymethyl-2,6-dimethylphenol was added over a 5-minute period. Mixing was continued an additional 25 minutes, during which time steam evolution was evident. The resulting polymer was next recovered and cooled to room temperature on a stainless steel table. The polymer subsequently was dissolved in methylene chloride, filtered, recovered by precipitation into methanol and washed three times in methanol. The product was dried overnight at 60°C *in vacuo*. Instrumental neutron activation analysis showed the resulting alkylated polystyrene to contain 8.4 (± 0.4) percent bromine.

B. Testing for Improved Ignition Resistance

A sample of the alkylated polystyrene of Part A was blended with Sb_2O_3 (3.5 weight percent of total). Vertical burning tests (UL Standard 94) were conducted with compression molded samples of the Sb_2O_3 -doped polymer. The polymer exhibited combustion behavior consistent with a UL 94 V-O classification. This showed improved flame-retardant efficiency was obtained.

Examples 24-27Epoxidation of alkylated novolac resins :Example 24 - Epoxidation of 2,6-Dibromo-4-hydroxy-3,5-dimethylbenzyl containing Cresol Formaldehyde Novolac

To a 2-liter reaction vessel which was equipped with temperature and pressure control and indicating means, a means for the continuous addition of aqueous sodium hydroxide, a means for condensing and separating water from a codistillate mixture of water, solvent and epichlorohydrin and means for returning the solvent and epichlorohydrin to the reaction vessel, was added 393.1 g (2.7995 eq.) of 2,6-dibromo-4-hydroxy-3,5-dimethylbenzyl containing cresol formaldehyde novolac as from Example 19, 1554 g (16.8 eq.) of epichlorohydrin and 1035 g of the methyl ether of propylene glycol (1-methoxy-2-hydroxypropane) as a solvent. Upon stirring at room temperature and atmospheric pressure to thoroughly mix the contents, the temperature was raised to 55°C and the pressure was reduced to 105 mm Hg absolute. To the resulting solution was continuously added 220.6 g (2.7575 eq.) of 50 percent aqueous sodium hydroxide solution at a constant rate over a period of 3 hours.

During the addition of the sodium hydroxide, the water was removed by codistilling with epichlorohydrin and solvent. The distillate was condensed, thereby forming two distinct phases, an aqueous phase (top) and an organic epichlorohydrin solvent phase (bottom). The organic phase was continuously returned to the reactor. Upon completion of the sodium hydroxide addition, the reaction mixture was maintained at a temperature of 55°C and a pressure of 105 mm Hg absolute for an additional 30 minutes. The resulting glycidyl ether next was distilled under full vacuum and at a temperature of up to 160°C to generally remove all epichlorohydrin and 1-methoxy-2-hydroxypropane. The molten glycidyl ether product was diluted to 20 percent resin concentration with a 75/25 methyl ethyl ketone/toluene solvent mixture, and the diluted product was next washed with deionized water several times to remove NaCl. The organic phase from the water washes was placed on a rotary evaporator under a vacuum and at a temperature of 160°C to remove the solvent. The resulting polyglycidyl ether has an epoxide content of 19.4 percent and contains 9.53 percent bromine, and has a softening point of 75.6°C. This is the most preferred epoxy for use in an electronic encapsulation formulation.

Example 25 - Epoxidation of 2,6-Dibromo-4-hydroxy-3,5-dimethylbenzyl containing Phenol Formaldehyde Novolac

The general procedure of Example 24 was used to prepare this epoxy resin. The phenol formaldehyde novolac was as from Example 20. The resulting epoxy resin has an epoxide content of 21.5 percent, containing 8.62 percent bromine, and has a softening point of 62°C.

Example 26 - Epoxidation of 2,6-Dibromo-4-hydroxy-3,5-dimethylbenzyl containing Dicyclopentadiene Phenol Novolac

The general procedure of Example 24 was used to prepare this epoxy resin. The dicyclopentadiene phenol novolac was as from Example 21. The resulting epoxy resin has a softening point of 74.9°C containing 16.27 percent epoxide and 9.91 percent bromine.

Example 27 - Epoxidation of 2,6-Dibromo-4-hydroxy-3,5-dimethylbenzyl-containing 1,1,1-Tri(hydroxyphenyl)methane

The general procedure of Example 24 was used to prepare this epoxy resin. The 2,6-dibromo-4-hydroxy-3,5-dimethylbenzyl-containing 1,1,1-tri(hydroxyphenyl)methane is as from Example 22. The resulting epoxy resin has a softening point of 89.7°C, containing 20.87 percent epoxide and 9.6 percent bromine.

Example 28 - Use in Encapsulation with Comparative Formulation

I. Total Hydrolyzable Halide

The sample to be analyzed was saponified by KOH reflux, and the resulting halides which were extracted were titrated argentometrically by a potentiometric technique, as follows : weigh into a 250 Erlenmeyer flask 2 g of sample, add 30 ml of 1,4-dioxane and stir until the sample dissolves. Preset a heat source which permits the sample to begin reflux in 4-6 minutes (240-360 seconds). Add 30 ml of 3N ethanolic KOH solution, and next attach a condenser to the flask, and heat to reflux with constant stirring. Reflux 30 minutes, with the initial time as the moment the first condensed drop of liquid falls back into the flask from the condenser. Add 20 ml of 20 percent nitric acid to the flask. Add 50 ml of deionized water ; next cool the solution to room temperature. Calibrate an ion meter with a Ag/AgCl and KNO₃-type electrodes to read 0 mV against a NaCl reference solution. Titrate the sample mixture with standard silver nitrate solution (0.025 N aqueous), insuring that the sample mixture is spinning and the electrodes are free of resin. From the volume of titrant used, calculate the hydrolyzable chloride and hydrolyzable bromide.

II. Formulation

Each of the products of Examples 24 and 26 and a control resin were formulated into an electrical encapsulating formulation. The formulations were each cured at 175°C for 4 hours. The encapsulating formulations are given in Table I.

The properties of the cured encapsulating formulations were determined by the following procedures, except the total hydrolyzable halides which were determined on the epoxy resins themselves. The results are given in Tables II, III and IV.

III. Moisture Absorption

The moisture pick-up was determined by placing preweighed 0.16 cm (1/16") thick x 10 cm (4") diameter cured disks in an autoclave at of 103 kPa (15 psig (gauge pressure)) steam, 121°C, for 500 hours. The disks were removed and were cooled at ambient temperature (25°C) for 15-30 minutes, and next the disks were wiped dry and were again weighed to determine any weight difference. The results are given in Table III.

IV. Dielectric Constant

The dielectric constant was determined by the use of a Gen Rad 1689 bridge and LD-3 cell. Coupons approximately 76.2 mm x 76.2 mm x 1.6mm (3" x 3" x 1/16") were cut from each cured formulated disk and were measured with the Gen Rad 1689 bridge and LD-3 cell at the ambient temperature. The frequencies used

were 1×10^3 Hz, 10×10^3 Hz, and 100×10^3 Hz.

V. Device Reliability Testing

- 5 The device testing was determined by a highly accelerated stress test, which involved the following conditions: 121°C , 15 psig steam, and 25 volts bias. The device was a 14-pin LM 324 quad operational amplifier with a single passivation layer. The percentage of devices that fail as a function of time are given in Table IV.

TABLE I

Encapsulation Formulation

	<u>Component</u>	<u>Co.*</u>	<u>A</u>	<u>B</u>
15	Epoxy Resin I Type/g	174.7	59.3	0.0
20	Epoxy Resin II Type/g	Control/ 26.3	Ex.24/ 136.7	Ex.26/ 201.0
25	Curing Agent, g	89.75	94.75	72.50
	triphenyl-phosphine, g	2.25	2.25	2.50
30	Mold release agent, g	4.0	4.0	6.0
	Epoxy silane, g	4.0	4.0	4.0
35	Fused silica, g	685.0	685.0	700.0
40	Antimony Oxide (Sb2O3), g	10.0	10.0	10.0
	Carbon Black, g	4.0	4.0	4.0
45	% Bromine in Formulation	1.25	1.25	2.00

*Comparative

50 Epoxy Resin I is Quatrex® 3410, a cresol epoxy novolac having an epoxide equivalent weight (equiv. wt.) of 216 and a viscosity of $372 \text{ mm}^2/\text{s}$ (372 centistokes) at 150°C .

Epoxy Resin II is as listed, with the control Quatrex® 6410, a solid generally ortho-brominated epoxy resin.

55 The curing agent is a phenol-formaldehyde novolac resin with an average hydroxyl functionality of 6 and a phenolic hydroxyl equiv. wt. of 104. (Schenectady Chemical, HRJ-2210).

The mold release agents are refined Montan waxes (OP ; E) as available from Hoechst.

The epoxy silane is Z-6040 available from Dow Corning Corp.

TABLE II

Total Hydrolyzable Halide Analysis

<u>Sample Number</u>	<u>Hydrolyzable Chloride, ppm</u>	<u>Hydrolyzable Bromide, ppm</u>
Co. *	240	180
A	209	0
B	254	0

*Comparative

TABLE III

Moisture Absorption

<u>Sample Number</u>	<u>% Weight Gain</u>
Co. *	0.93
A	0.83
B	0.75

*Comparative

Dielectric constant in each of the Comparative, the A, and the B formulations is generally equivalent.

TABLE IV

Device Reliability

<u>Sample Number</u>	<u>% Device Failure</u>		
	<u>400 hrs</u>	<u>600 hrs</u>	<u>800 hrs</u>
Co*	25	75	100
A	3	7	28
B	0	2	15

*Comparative

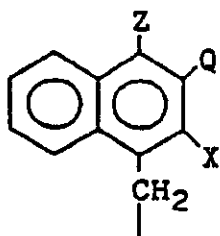
Thus, it can be seen that these stable meta-bromine-containing formulations give substantially better performances than the conventional systems.

Claims

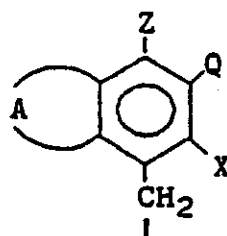
1. A coupled aromatic compound represented by the formula

Ar-Y (I)

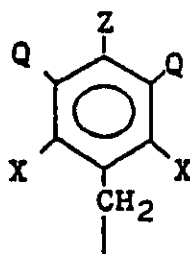
wherein Ar is an aromatic moiety different from Y and Y is an aromatic moiety represented by one of the formulae



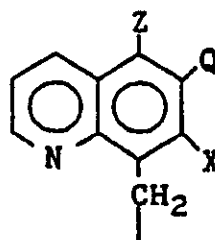
II,



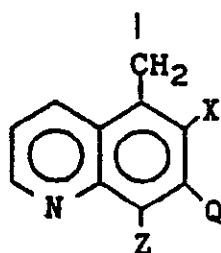
III,



IV,

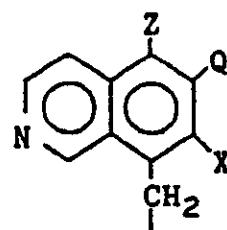


V,



VI

or



VII

wherein the Y moiety is coupled to a ring carbon in the Ar moiety and

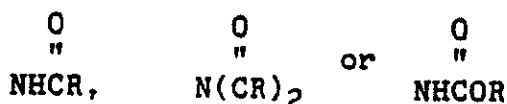
wherein A is an aliphatic ring system bonded to the aromatic ring ;

Q is separately at each occurrence hydrogen, alkyl or inertly-substituted alkyl with proviso that the carbon atom bonded to the aromatic ring is a primary or secondary carbon atom ;

X is separately at each occurrence a halogen moiety ;

Z is a nitrogen- or chalcogen-containing moiety.

2. The compound of Claim 1 wherein X is Br or Cl and Z is NH₂, NHR, NR₂, OH, OR,



wherein R is hydrocarbyl having from 1 to 12 carbons.

3. The compound of Claim 1 wherein Q is alkyl having 1 to 12 carbons, Z is OH and X is Br.

4. The compound of Claim 1 which is a novolac resin containing at least $\frac{1}{2}$ percent by weight of the moiety represented by Y.

5. The compound of Claim 4 wherein the Y moiety is a 2,6-dihalogenated-4-hydroxy-3,5-di(C₁₋₁₂ alkyl)benzyl moiety.

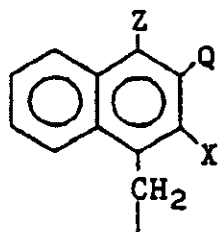
6. The compound of Claim 5 wherein the weight percent of halogen attributable to 2,6-dihalogenated-4-hydroxy-3,5-dimethylbenzyl moieties is from one to 20 percent.

7. The compound of anyone of Claims 1 to 6 which is a cured epoxy thermoset containing at least $\frac{1}{2}$ percent

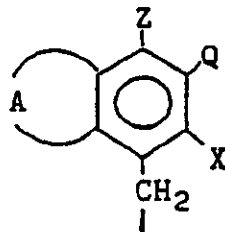
by weight of the Y moiety.

8. The compound of anyone of Claims 1 to 6 which is an aromatic-containing polymeric resin which contains at least 1 percent by weight of the Y moiety.

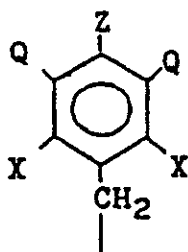
9. A process for the preparation of the coupled aromatic compound of Claim 1 which process comprises contacting an aromatic compound with an alkylating aromatic agent represented by the formula (hm)-Y wherein hm is Br, Cl, OH or C₁₋₄ alkoxy and Y is represented by the formulae :



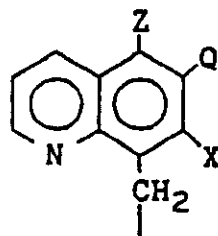
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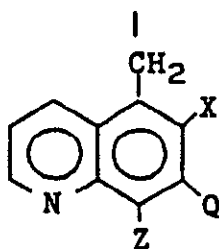
III,



IV,

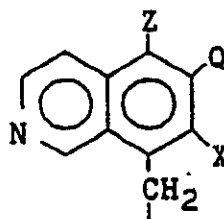


V,



VI

or

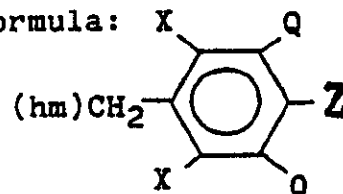


VII

wherein Q, X and Z are as defined in Claim 1, under condition sufficient to form the coupled aromatic compound.

10. The process of Claim 9 wherein the

alkylating agent is represented by the formula:



wherein (hm) is as defined in Claim 9 ;

X is separately at each occurrence a halogen moiety selected from the group consisting of fluoro, chloro and bromo ;

Q is separately at each occurrence hydrogen, or C₁₋₁₂ alkyl or inertly-substituted alkyl, each with at most a secondary carbon atom attached to the six-membered ring ; and

Z is as defined in claim 9.

11. The process of Claim 10 wherein the alkylating agent is 4-bromo-methyl-3,5-dibromo-2,6-dimethylphenol or 3,5-dibromo-4-hydroxymethyl-2,6-dimethylphenol.

12. The process of Claim 11 wherein Ar is selected from the group consisting of alkyl phenols and novolacs.

13. The process of Claim 10 wherein Ar is a hydroxy-containing aromatic and further wherein etherification with an epichlorohydrin is carried out to prepare a vicinal halohydrin organo-oxy containing meta-halogen-phenoxy-coupled aromatic compound.

14. The process of Claim 13 further wherein epoxidation of the vicinal halohydrin organo-oxy moiety is carried out to prepare a meta-halogen-phenoxyepoxy-coupled aromatic compound.

15. The process of any one of Claims 9 to 12 wherein the reaction is carried out at elevated temperatures.

16. The process of any one of Claims 9 to 12 wherein the reaction is carried out at temperatures from 20°C to 150°C in the presence of a suitable catalyst.

17. The process of any one of Claims 9 to 12 wherein the reaction is carried out at temperatures from 80°C to 220°C.

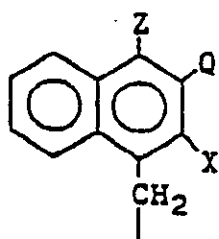
18. The process of any one of Claims 9 to 12 wherein the reaction is carried out in the presence of an inert organic diluent.

15 Revendications

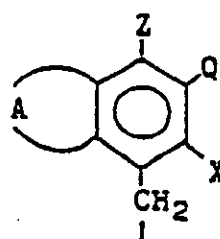
1. Composé aromatique couplé, représenté par la formule

Ar-Y (I)

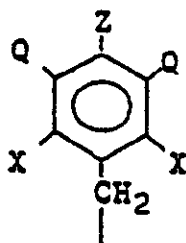
dans laquelle Ar est un groupe aromatique différent de Y et Y est un groupe aromatique représenté par l'une des formules



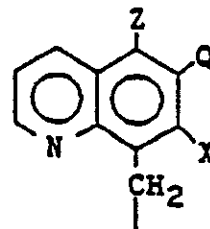
II,



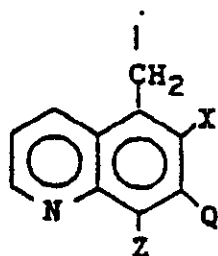
III,



IV,

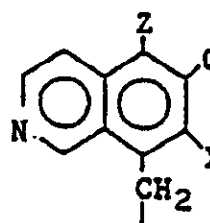


V,



VI

ou



VII

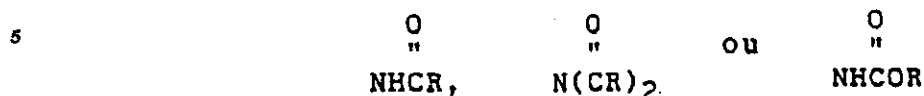
le groupe Y étant couplé à un carbone du cycle du groupe Ar, et dans lesquelles A est un système cyclique aliphatique lié au cycle aromatique ;

Q représente séparément dans chaque cas un atome d'hydrogène, un groupe alkyle ou un groupe alkyle portant un substituant inerte, étant entendu que l'atome de carbone lié au cycle aromatique est un atome de carbone primaire ou secondaire ;

X représente séparément dans chaque cas un atome d'halogène ;

Z représente un groupe contenant de l'azote ou un chalcogène.

2. Composé selon la revendication 1, dans lequel X représente Br ou Cl et Z représente NH_2 , NHR , NR_2 , OH, OR,



où R représente un groupe hydrocarboné comportant 1 à 12 atomes de carbone.

10 3. Composé selon la revendication 1, dans lequel Q est un groupe alkyle comportant 1 à 12 atomes de carbone, Z représente OH et X représente Br.

4. Composé selon la revendication 1, qui est une résine novolaque contenant au moins 1/2 % en poids du groupe représenté par Y.

15 5. Composé selon la revendication 4, dans lequel le groupe Y est un groupe 2,6-dihalogéno-4-hydroxy-3,5-di(alkyl(C_{1-12}))-benzyle.

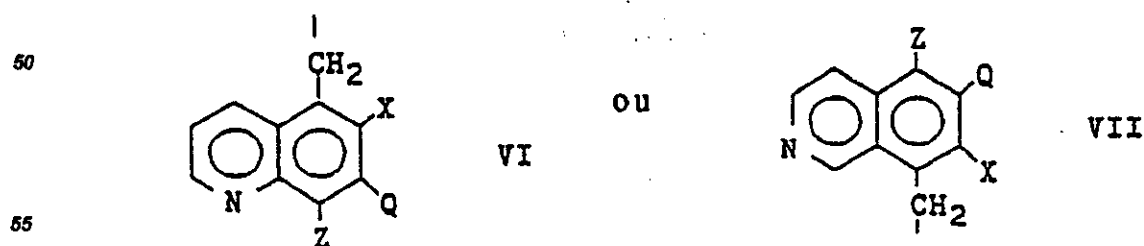
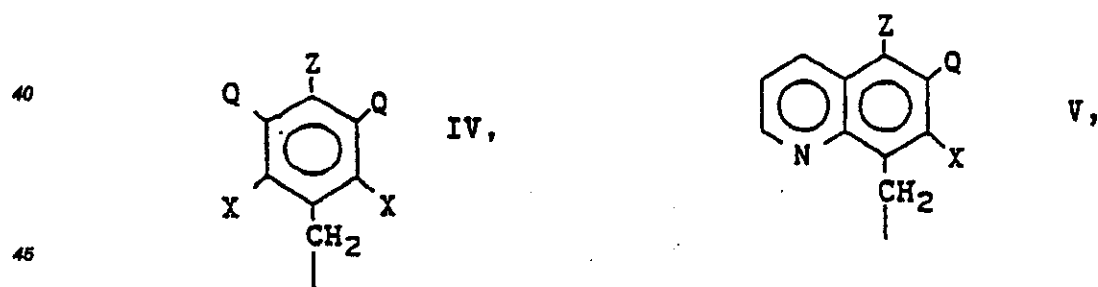
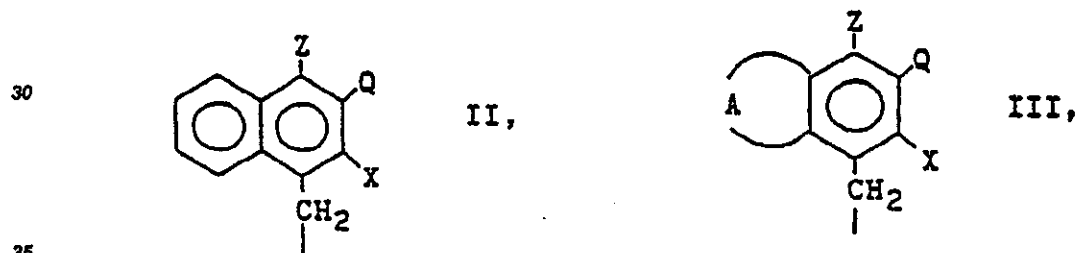
6. Composé selon la revendication 5, dans lequel le pourcentage en poids d'halogène attribuable aux groupes 2,6-dihalogéno-4-hydroxy-3,5-diméthylbenzyle vaut de 1 à 20 %.

7. Composé selon l'une quelconque des revendications 1 à 6, qui est un composé époxy thermodurcissable durci contenant au moins 1/2 % en poids du groupe Y.

20 8. Composé selon l'une quelconque des revendications 1 à 6, qui est une résine polymère contenant des groupes aromatiques, qui contient au moins 1/2 % en poids du groupe Y.

9. Procédé de préparation du composé aromatique couplé de la revendication 1, comprenant les étapes consistant à mettre un composé aromatique en contact avec un agent aromatique d'alkylation représenté par la formule (hm)-Y, dans laquelle hm représente Br, Cl, OH ou un groupe alcoxy en C_{1-4} , et Y est représenté par les formules :

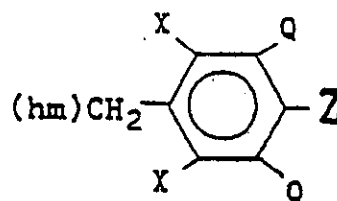
25



dans lesquelles Q, X et Z sont tels que définis dans la revendication 1, dans des conditions suffisantes pour

former un composé aromatique couplé.

10. Procédé selon la revendication 9, dans lequel l'agent d'alkylation est représenté par la formule :



dans laquelle (hm) est tel que défini dans la revendication 9 ;

X représente séparément dans chaque cas un reste halogéno choisi dans le groupe composé des restes fluoro, chloro et bromo ;

Q représente séparément dans chaque cas un atome d'hydrogène ou un groupe alkyle (C₁₋₁₂) ou un groupe alkyle portant un substituant inerte, comportant dans chaque cas au plus un atome de carbone secondaire attaché au cycle à six chaînons ; et

Z est tel que défini dans la revendication 9.

11. Procédé selon la revendication 10, dans lequel l'agent d'alkylation est le 4-bromométhyl-3,5-dibromo-2,6-diméthylphénol ou le 3,5-dibromo-4-hydroxyméthyl-2,6-diméthylphénol.

12. Procédé selon la revendication 11, dans lequel Ar est choisi dans le groupe composé des alkylphénols et des résines novolaque.

13. Procédé selon la revendication 10, dans lequel Ar est un groupe aromatique hydroxylé et dans lequel une étherification à l'aide d'une épichlorhydrine est réalisée pour préparer un composé aromatique couplé méta-halogéno-phénoxy contenant un groupe organo-oxy à fonction halogénhydrine vicinale.

14. Procédé selon la revendication 13, dans lequel l'époxydation du groupe organo-oxy à fonction halogénhydrine vicinale est réalisée pour préparer un composé aromatique couplé méta-halogéno-phénoxy-époxy.

15. Procédé selon l'une quelconque des revendications 9 à 12, dans lequel la réaction est effectuée à des températures élevées.

16. Procédé selon l'une quelconque des revendications 9 à 12, dans lequel la réaction est effectuée à des températures de 20°C à 150°C, en présence d'un catalyseur approprié.

17. Procédé selon l'une quelconque des revendications 9 à 12, dans lequel la réaction est effectuée à des températures de 80°C à 220°C.

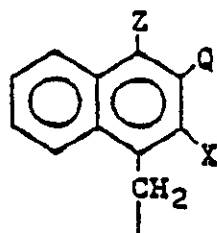
18. Procédé selon l'une quelconque des revendications 9 à 12, dans lequel la réaction est effectuée en présence d'un diluant organique inerte.

Patentansprüche

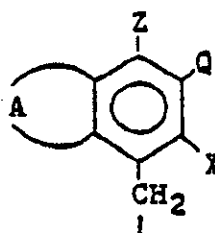
1. Gekuppelte, aromatische Verbindung der Formel

Ar-Y (I),

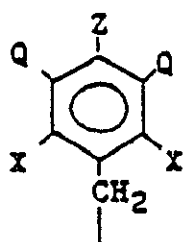
in der Ar eine von Y unterschiedliche aromatische Gruppe ist und Y eine aromatische Gruppe nach einer der Formeln ist



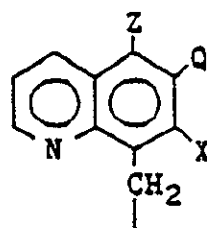
II,



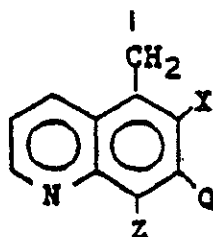
III,



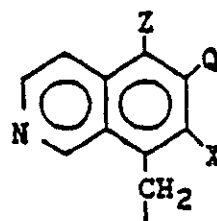
IV,



V,



VI oder



VII

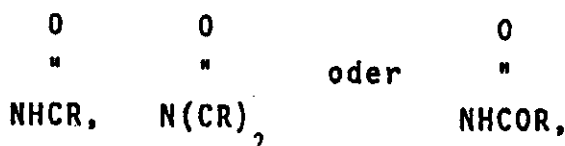
wobei die Y-Gruppe an einen Ringkohlenstoff in der Ar-Gruppe gekuppelt ist und wobei A ein an den aromatischen Ring gebundenes aliphatisches Ringsystem ist,

Q ist getrennt bei jedem Auftreten Wasserstoff, Alkyl oder inert substituiertes Alkyl, mit der Bedingung, daß das an den aromatischen Ring gebundene Kohlenstoffatom ein primäres oder sekundäres Kohlenstoffatom ist,

X ist getrennt bei jedem Auftreten eine Halogensgruppe,

Z ist eine Stickstoff oder Chalcogen enthaltende Gruppe.

2. Verbindung nach Anspruch 1, dadurch gekennzeichnet, daß X Brom oder Chlor ist und Z ist NH_2 , NHR , NR_2 , OH , OR ,



wobei R eine Kohlenwasserstoffgruppe mit 1-12 Kohlenstoffatomen ist.

3. Verbindung nach Anspruch 1, dadurch gekennzeichnet, daß Q Alkyl mit 1-12 Kohlenstoffatomen ist, Z ist OH und X ist Brom.

4. Verbindung nach Anspruch 1, dadurch gekennzeichnet, daß sie ein Novolacharz ist, enthaltend mindestens $\frac{1}{2}$ Gew.-% der durch Y wiedergegebenen Gruppe.

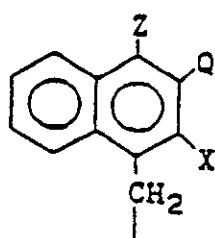
5. Verbindung nach Anspruch 4, dadurch gekennzeichnet, daß die Y-Gruppe eine 2,6-dihalogenierte-4-Hydroxy-3,5-di(C_{1-12} alkyl)benzylgruppe ist.

6. Verbindung nach Anspruch 5, dadurch gekennzeichnet, daß der den 2,6-dihalogenierten-4-Hydroxy-3,5-dimethyl-benzylgruppen zuordbare Halogengehalt von 1-20 Gew.-% beträgt.

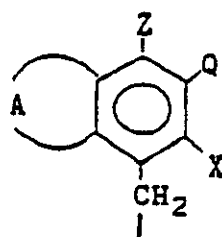
7. Verbindung nach jedem der Ansprüche 1-6, dadurch gekennzeichnet, daß sie ein gehärtetes Epoxyduroplast ist, enthaltend mindestens $\frac{1}{2}$ Gew.-% der Y-Gruppe.

8. Verbindung nach jedem der Ansprüche 1-6, dadurch gekennzeichnet, daß sie ein Aromaten enthaltendes polymeres Harz ist, das mindestens $\frac{1}{2}$ Gew.-% der Y-Gruppe enthält.

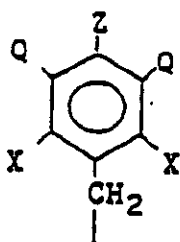
9. Verfahren zum Herstellen der gekuppelten aromatischen Verbindung nach Anspruch 1 durch Inberührungbringen einer aromatischen Verbindung mit einem aromatischen Alkylierungsmittel der Formel (hm)-Y, in der hm Brom, Chlor, OH oder C_{1-4} -Alkoxy ist und Y den Formeln genügt



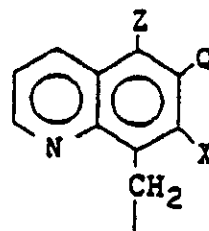
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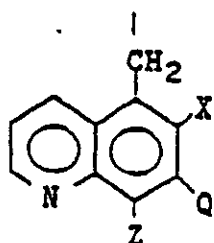
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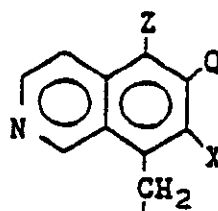
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V,



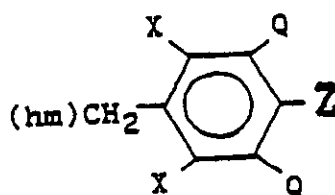
VI oder



VII

in denen Q, X und Z die in Anspruch 1 angegebene Bedeutung haben, unter Bedingungen, die ausreichend sind, um die gekuppelte aromatische Verbindung zu bilden.

10. Verfahren nach Anspruch 9, dadurch gekennzeichnet, daß das Alkylierungsmittel der Formel



genügt, in der (hm) die in Anspruch 9 angegebene Bedeutung hat,

X ist getrennt bei jedem Auftreten eine Halogengruppe, ausgewählt aus der Gruppe bestehend aus Fluor, Chlor und Brom,

Q ist getrennt bei jedem Auftreten Wasserstoff oder C₁₋₁₂-Alkyl oder inert substituiertes Alkyl, jeweils mit höchstens einem sekundären Kohlenstoffatom an den sechsgliedrigen Ring gebunden, und

Z die in Anspruch 9 angegebene Bedeutung hat.

11. Verfahren nach Anspruch 10, dadurch gekennzeichnet, daß das Alkylierungsmittel 4-Brommethyl-3,5-dibrom-2,6-dimethylphenol oder 3,5-Dibrom-4-hydroxymethyl-2,6-dimethylphenol ist.

12. Verfahren nach Anspruch 11, dadurch gekennzeichnet, daß Ar ausgewählt ist aus der Gruppe bestehend aus Alkyl-phenolen und Novolac.

13. Verfahren nach Anspruch 10, dadurch gekennzeichnet, daß Ar ein Hydroxyl enthaltender Aromat ist, und weiterhin dadurch, daß die Veretherung mit Epichlorhydrin ausgeführt wird, um eine endständige Halohydrin-organo-oxy enthaltende Meta-halogen-phenoxy gekuppelte aromatische Verbindung herzustellen.

14. Verfahren nach Anspruch 13, dadurch gekennzeichnet, daß die Epoxidierung der endständigen Halohydrin-organo-oxy-Gruppe ausgeführt wird, um eine Meta-halogen-phenoxy-epoxy gekuppelte aromatische Verbindung herzustellen.

15. Verfahren nach jedem der Ansprüche 9-12, dadurch gekennzeichnet, daß die Reaktion bei erhöhten Temperaturen ausgeführt wird.

16. Verfahren nach jedem der Ansprüche 9-12, dadurch gekennzeichnet, daß die Reaktion bei Temperaturen von 20°C-150°C in Gegenwart eines geeigneten Katalysators ausgeführt wird.

5 17. Verfahren nach jedem der Ansprüche 9-12, dadurch gekennzeichnet, daß die Reaktion bei Temperaturen von 80°C-220°C ausgeführt wird.

18. Verfahren nach jedem der Ansprüche 9-12, dadurch gekennzeichnet, daß die Reaktion in Gegenwart eines inerten organischen Verdünnungsmittels ausgeführt wird.

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