

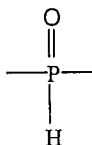
PROCESS FOR THE ALKYLATION OF
PHOSPHORUS-CONTAINING COMPOUNDS

CROSS REFERENCE TO RELATED APPLICATION

This invention claims the benefit of U.S. provisional application Serial No. 60/564,801, filed April 23, 2004, the entire contents of which are incorporated by reference herein.

5 BACKGROUND OF THE INVENTION

This invention relates to processes for alkylating phosphorus-containing compounds. More particularly, this invention relates to processes for alkylating phosphorus-containing compounds possessing at least one phosphorus-hydrogen



10 alkylatable site to provide an alkylated phosphorus-containing product, e.g., a mono- or dialkylphosphinic acid or metal salt thereof, an alkylarylphosphinic acid or metal salt thereof, an alkyl alkylphosphonic acid or metal salt thereof, an alkyl or aryl dialkylphosphinate ester, an alkyl or aryl alkylarylphosphinate ester, an alkyl or arylalkylphosphorous acid or metal salt thereof or a dialkyl or diaryl alkylphosphonate
15 ester.

In order to prepare dialkylphosphinic acid derivatives, a complex synthesis route has been used which includes the hydrolysis of methyldichlorophosphine to provide methylphosphinic acid and the subsequent esterification of this acid to provide an alkyl methylphosphinic ester. The second phosphorus-hydrogen bond can also be alkylated in
20 the presence of a free-radical initiator.

The use of dialkylphosphinic acid derivatives as flame retardants for polyesters (poly(ethylene terephthalate) and poly(butylene terephthalate)) is described in European Patent Publication No. 699,708. These products are synthesized by a complex process using methyldichlorophosphine which is hydrolyzed to methylphosphinic acid; the ester
25 of this acid has been prepared and isolated as intermediate. To prepare dialkylphosphinic acids or derivatives thereof, alkylphosphinic esters can be alkylated by α -olefins at high

temperatures under free-radical catalysis conditions. In the case of the reaction of alkylphosphinic acids under the same conditions, only the disproportionation products, namely, alkylphosphines and alkylphosphonic acids, are obtained while under mild conditions no reaction is observed.

5 U.S. Patent No. 4,632,741 describes a process for preparing mixtures of salts of alkylphosphinic and dialkylphosphinic acids by reacting an olefin with a salt of hypophosphorous acid in the presence of a photoinitiator using UV light. U.S. Patent No. 4,590,014 describes a similar process in which the olefin is reacted with the alkali metal salt of hypophosphorous acid in the presence of a free-radical initiator. However, the
10 predominant product monoalkylphosphinic acid.

U.S. Patent No. 6,300,516 describes a process for preparing dialkylphosphinic acids and/or alkali metal salts thereof by reacting olefins, particularly ethylene, with alkylphosphinic acid or hypophosphorous acid in the presence of azo free-radical
15 initiator. This process is performed in a pressurized reactor with complicated feeding systems which require special safety features. Only high boiling olefins can be reacted with hypophosphorous acid at atmospheric pressure.

The reaction of hypophosphorous acid with isobutene was reported in the literature (S. Deprele and J-L. Montchamp, J. Org Chem. 2001, 66, 6745). The reaction was run in the presence of a stoichiometric amount of triethyl borane as initiator. The
20 yield of monosubstituted isobutylphosphinic acid was only 38%.

SUMMARY OF THE INVENTION

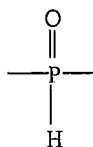
It is an object of the invention to provide a process for the alkylation of phosphorous-containing compounds possessing at least one phosphorus-hydrogen



25 alkylatable site.

It is a particular object of the present invention to provide such a process employing as alkylating agents short chain alkyls which result within a relatively short time in a high yield of the desired alkylated product while avoiding the aforementioned disadvantages associates with the known processes discussed above.

These and other objects of the invention are achieved by the process of alkylation herein which comprises alkylating phosphorous-containing compound possessing at least one phosphorus-hydrogen



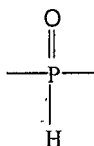
- 5 alkylatable site with reactant which generates alkene and/or cycloalkene alkylating agent *in situ* in the presence of free radical initiator, the alkene and/or cycloalkene alkylating agent alkylating the phosphorus-containing compound to provide alkylated phosphorus-containing product.

Without intending to be bound, it is thought that the reactant which generates
10 alkene or cycloalkene *in situ* under alkylation conditions produces a sufficient concentration of these compounds that will result in alkylation of the at least one phosphorus-hydrogen alkylatable site present in the starting organophosphorous-containing compound and as the alkenes/cycloalkenes are consumed in the alkylation reaction, the equilibrium shifts towards generation of additional alkenes/cycloalkenes.

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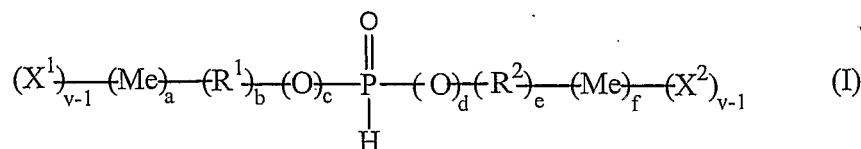
DETAILED DESCRIPTION OF THE INVENTION

The phosphorus-containing compound employed as one of the starting reactants herein must contain at least one phosphorus-hydrogen



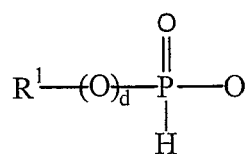
- 20 alkylatable site and can contain more than one such site in which case the alkylated phosphorus-containing product may either be partially or fully alkylated.

In one embodiment of the invention, the phosphorus-containing starting reactant is represented by the general formula (I):

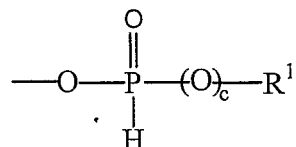


- 25 wherein:

x^1 , where present, is



and x^2 , where present, is



- 5 in which R^1 is H, alkyl of up to 30 carbon atoms, cycloalkyl of from 3 to 12 carbon atoms or aryl of from 6 to 20 carbon atoms; Me is a metal having a valence v of 1, 2, 3 or 4; R^2 is H, alkyl of up to 30 carbon atoms, cycloalkyl of from 3 to 12 carbon atoms or aryl of from 6 to 20 carbon atoms; and,

a, b, c, d, e and f each independently is 0 or 1,

- 10 provided,

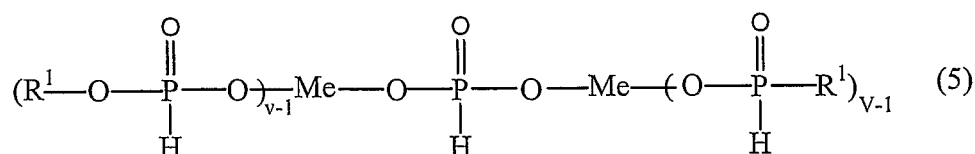
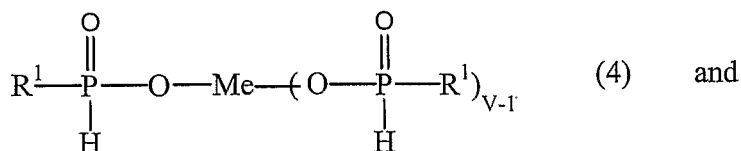
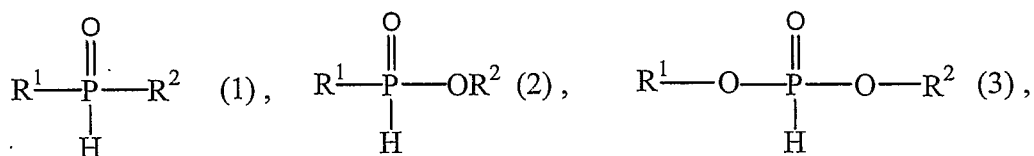
when $a=1, c=1$ and $b=0$,

when $b=1, a=0$ and x^1 is not present,

when $f=1, d=1$ and $e=0$, and

when $e=1, f=0$ and x^2 is not present.

- 15 Particularly useful phosphorus-containing compounds (I) are those of structural formulas (1)-(6):



in which R¹, R², Me and v have the aforesated meanings. In the foregoing structural formulas, R¹ is preferably H, R² is preferably H (except in compounds of structural formula 1 where only R¹ may be H) or alkyl of from 1 to 8 carbon atoms and Me is preferably lithium, sodium, potassium, magnesium, calcium, barium, aluminum, titanium, vanadium, chromium, molybdenum, iron, nickel, cobalt, copper or zinc.

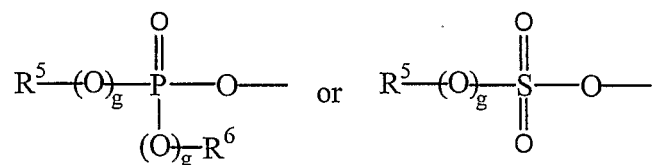
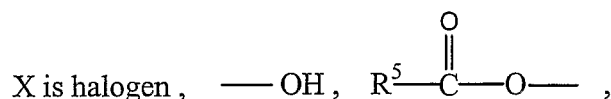
Illustrative of the alkylatable phosphorus-containing starting reactants herein are phosphonic acid (phosphorous acid); hypophosphorous acid; phosphinic acid, phosphinous acid; esters of the foregoing such as phosphonic acid tert-butyl ester, phosphonic acid di-tert-butyl ester, phosphonic acid methyl ester, phosphonic acid phenyl ester, phosphinic acid tert-butyl ester, methylphosphinic acid phenyl ester, benzenephosphinic acid phenyl ester, and the like; and, metal salts of the foregoing such as sodium hypophosphite, calcium hypophosphite, zinc hypophosphite, aluminum hypophosphite, sodium phosphite, calcium phosphite, zinc phosphite, aluminum phosphite, ferric phosphite, sodium benzenephosphinate, sodium methylphosphinate, and the like.

In another embodiment of the invention, the reactant which generates alkene or cycloalkene *in situ* is represented by the general formula



wherein:

R⁴ is alkyl of up to 30 carbon atoms or cycloalkyl of from 3 to 12 carbon atoms;
and,



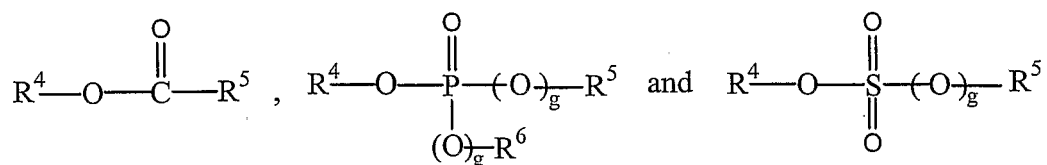
in which R⁵ and R⁶ each independently is H, alkyl of up to 30 carbon atoms, cycloalkyl of from 3 to 12 carbon atoms or aryl of from 6 to 20 carbon atoms and g is 0 or 1.

In reactant (II), R⁴ is preferably branched alkyl since branching more readily provides alkene alkylating agent.

Illustrative of useful halides R^4-X are 2-chloro-2-methylpropane, 2-bromo-2-methylpropane, 2-chloropropane, 2-bromopropane, tert-amyl chloride, tert-amyl bromide, and the like.

Useful alcohols of structure R^4-OH include tert-butyl alcohol, tert-amyl alcohol, isopropyl alcohol, 2-butanol, 2-buten-1-ol and 2-methyl-3-buten-2-ol. Likewise suitable are cyclic alcohols, in particular, 1-methylcyclopentanol, 1-methylcycloheptanol, 1-methylcyclooctanol and 1-methylcyclodecanol.

Useful esters of the structures



include tert-butyl acetate, phosphoric acid tert-butyl ester, phosphonic acid tert-butyl ester, phosphonic acid di-tert-butyl ester, diisobutylphosphinic acid tert-butyl ester, isopropyl tosylate, isopropyl mesylate, and the like.

As free-radical initiators, advantageous use is made of azo compounds.

Preferably, the azo compounds are cationic and/or non-cationic azo compounds.

Preferably, as cationic azo compounds, use is made of 2,2'-azobis(2-amidinopropane) dihydrochloride or 2,2'-azobis(N,N'-dimethyleneisobutyramidine) dihydrochloride. Preferably, as non-cationic azo compounds, use is made of azobis(isobutyronitrile) (AIBN), 4,4'-azobis(4-cyanopentanoic acid) or 2,2'-azobis(2-methylbutyronitrile).

Preferably, as free-radical initiators, use is also made of inorganic peroxide and/or organic peroxide free-radical initiators.

Preferably, as inorganic peroxide free-radical initiators, use is made of hydrogen peroxide, ammonium peroxodisulfate and/or potassium peroxodisulfate.

Preferably, as organic peroxide free-radical initiators, use is made of dibenzoyl peroxide, di-tert-butyl peroxide, tert-butyl peroxybenzoate and/or peracetic acid.

Preferably, UV light initiation alone or in combination with above-mentioned initiators is employed.

Preferably, the reaction is carried out in the presence of carboxylic or mineral acid. Particularly preferably, the carboxylic acid is acetic acid and the mineral acid is sulfuric acid.

Preferably, the reaction is carried out at a temperature of from about 25 to about 130°C. Particularly preferably, the reaction is carried out at a temperature of from about 60°C to about 120°C. Preferably, the reaction is carried out at atmospheric pressure. If generated *in situ*, an alkene tends to evaporate from the reaction vessel prior to reacting with P-H in which case a condenser can be used in order to return the alkene to the reaction vessel. Alternatively, a pressure of about 1-2 atmospheres can be applied in order to prevent evaporation of the alkene.

The present invention also relates in particular to a process in which hypophosphorous acid or sodium hypophosphite is reacted with tert-butyl alcohol or tert-butyl acetate in the presence of azo free-radical initiator or in the presence of a peroxide free-radical initiator to give diisobutyl phosphinic acid and/or sodium salt thereof as main product.

The invention also relates to the use of the dialkylphosphinic acids and/or alkali metal salts thereof obtained by the above-described process for preparing salts of such metals as Mg, Ca, Al, Zn, Fe(II), Fe(III), Cu(II), Zr(IV). These salts find use as flame retardants for thermoplastic polymers such as poly(ethylene terephthalate), poly(butylene terephthalate), polystyrene, polyamide, polyethylene, polypropylene, and the like, and thermoset resins such as epoxy, phenolic or bismaleimide resins, and the like. The dialkylphosphinic acids and/or alkali metal salts thereof obtained by the above-described process are also used as intermediates in the pharmaceutical industry.

The process of the invention is illustrated by the examples which follow.

Example 1

Into a 250 ml three-necked flask equipped with condenser, addition funnel, magnetic stirrer and thermometer were charged 47.79 g (0.362 mol) 50% commercial hypophosphorous acid, 45.94 g (0.395 mol) tert-butyl acetate and 3.2 g AIBN. The reaction mixture was heated to 61°C and stirred for 3 hours. Thereafter, a second portion of 8.7g AIBN in acetic acid solution was gradually added while the temperature of the reaction mixture was slowly raised to 84°C over the course of 11 hours. After addition was complete, ³¹P NMR analysis indicated the formation of 8% di-isobutylphosphinic acid, 63% isobutylphosphinic and 29% hypophosphorus acid. The reaction mixture was either neutralized by aqueous sodium hydroxide solution and then treated with aqueous

aluminum hydroxide or directly reacted with aluminum oxide. The resulting white precipitate was filtered out, washed with water and dried in an oven thus providing 23 g aluminum salt of isobutylphosphinic acid. The mother liquor can, if desired, be recycled and used for preparing another quantity of product.

5 Example 2

Into a 500 ml three-necked flask equipped with condenser, addition funnel, magnetic stirrer and thermometer were charged 65.80 g (0.498 mol) 50% commercial hypophosphorous acid and 79.92 g (1.08 mol) tert-butyl alcohol. The reaction mixture was heated to 70°C and addition of 2.06 g AIBN in 35 g acetic acid solution begun.

- 10 After 6 hours, the addition was complete. The mixture contained 50% isobutylphosphinic acid and 50% hypophosphorus acid as determined by ^{31}P NMR. The mixture was treated with a second portion of 5.5 g AIBN and 5.7 g t-butyl peroxybenzoate in acetic acid while the temperature was gradually increased to 97°C over the course of 10 hours. After addition was complete, the mixture was found to
- 15 contain 75% di-isobutylphosphinic acid, 20% isobutylphosphinic acid and 5% isobutylphosphonic acid. The mixture was dried in a rotavapor under vacuum at 75°C to remove water and solvent and washed with warm water three times. The upper oily phase was separated and dried in a rotavapor under vacuum at 75°C. 57.5 g. The oily material was collected and crystallized at room temperature. The yield based on
- 20 hypophosphorous acid was 65% without recycling the mother liquid. The mother liquid can, if desired, be recycled and used for preparing another quantity of product.

Example 3

- Into a 2L four-necked flask equipped with condenser, addition funnel, mechanical stirrer and thermometer were charged 321.35 g (3.03 mol) sodium hypophosphite
- 25 monohydrate and 637 g acetic acid. After the solution became clear, 149.33 g sulfuric acid was gradually added to the mixture and a slurry was observed. A solution comprised of 458.18 g (6.186 mol) tert-butanol, 107.85 g acetic acid and 18.63 g (0.13 mol) di-tert-butyl peroxide was slowly added at a temperature of from 104 to 110°C over 14.5 hours. Analysis of the mixture by ^{31}P NMR showed it to contain 58 mol % diisobutylphosphinic
- 30 acid and 42 mol % monoisobutylphosphinic acid. There was no measurable amount of hypophosphorus acid as determined by ^{31}P NMR analysis. A portion of the solvent was

then removed. Another solution comprising 98.80 g (1.33 mol) tert-butanol, 5.87 g (0.040 mol) di-tert-butyl peroxide and 23.7 g acetic acid was added to the reaction mixture at a temperature of from 103 to 111°C over 7 hours. ³¹P NMR analysis indicated a mixture of 73% diisobutylphosphinic acid and 25% monoisobutylphosphinic acid with the remainder made up of monoisobutylphosphonate acid and phosphorus acid.

Example 4

The alkylated product mixture obtained in Example 3, *supra*, was filtered and the solvents were stripped out in a rotavapor under vacuum. The liquid mixture was then consecutively washed with 200 mL water, 200 mL 2.7% sodium carbonate three times and 200 mL water twice. The upper layer was separated and dried in a Rotavapor under vacuum. The material crystallized upon standing at room temperature to provide 350 g pure diisobutylphosphinic acid. The yield was 65%.

Example 5

A portion of the above pure diisobutylphosphinic acid (135.01 g, 0.758 mol) was mixed with water and neutralized with dilute aqueous sodium hydroxide solution. The neutralized product was then mixed with a solution of 61.83 g (0.256 mol) AlCl₃ 6H₂O in 2 L water. A large amount of white precipitate was observed. The precipitate was filtered and dried to a constant weight in an oven at 105°C. A white powder, aluminum salt of diisobutylphosphinic acid, of 139.43 g was obtained. The yield was 98.9%.

Example 6

Into a 1L four-necked flask equipped with condenser, addition funnel, mechanical stirrer and thermometer were charged 187.52 g (1.77 mol) sodium hypophosphite monohydrate and 294 g acetic acid. After the solution became clear, 88.18 g sulfuric acid was gradually added thereto and a slurry was observed. A solution comprised of 150.81 g (2.03 mol) tert-butanol, 16.97 g acetic acid and 6.35 g (0.043 mol) di-tert-butyl peroxide was slowly added at a temperature range of from 111 to 118°C over 6 hours. Analysis of the mixture by ³¹P NMR showed the mixture to consist of 13 mol% diisobutylphosphinic acid, 72 mol % monoisobutylphosphinic acid and 13% hypophosphorus acid. Another solution comprising 156.577 g (2.11 mol) tert-butanol, 11.86 g di-tert-butyl peroxide (0.081 mol) and 160.29 g acetic anhydride was then added to the reaction mixture at a temperature of 104 to 111°C over 14.5 hours while 13.71 g

sulfuric acid was added from a second funnel. A mixture of 87.5% diisobutylphosphinic acid, 9.5% monoisobutylphosphinic acid, 1.6% monoisobutylphosphonic acid and 1.4% phosphorus acid was obtained.

Example 7

5 The alkylated product mixture obtained in Example 6, *supra*, was first filtered and then stripped in a Rotavapor at a bath temperature of 100°C. A solution of 302 g was obtained. Part of this solution (233 g, total 1.37 mol P) was neutralized with diluted sodium hydroxide and added to 2.5 L 4% aqueous aluminum chloride (0.435 mol $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$). The resulting white precipitate was filtered and dried in an oven at 75°C
10 overnight. 214 g of white powder, aluminum salts of diisobutylphosphinic acid, monoisobutylphosphinic acid and monoisobutylphosphonic acid, was obtained.

Example 8

 Into a 2L four-necked flask equipped with condenser, addition funnel, mechanical stirrer and thermometer were charged 211.76 g (2.00 mol) sodium hypophosphite
15 monohydrate and 317 g acetic acid. After the solution became clear, 106.97 g sulfuric acid was gradually added to the mixture and a slurry was observed. The mixture was then heated to 120°C. A solution comprised of 243.19 g (2.09 mol) tert-butyl acetate and 7.35 g (0.050 mol) di-tert-butyl peroxide was slowly added at a temperature of 115 to 120°C over 5 hours. Analysis of the mixture by ^{31}P NMR showed the mixture contained
20 11 mol % diisobutylphosphinic acid, 72 mol % monoisobutylphosphinic acid and 17 mol % hypophosphorus acid. A further 20.12 g sulfuric acid was added. Another solution comprising 310.73 g (2.68 mol) tert-butyl acetate and 13.10 g (0.090 mol) di-tert-butyl peroxide was added to the reaction mixture at a temperature of 114 to 120°C over 10 hours. ^{31}P NMR analysis indicated the mixture to contain 88% diisobutylphosphinic acid
25 and 10% monoisobutylphosphinic acid with the remainder made up of monoisobutylphosphonate acid and phosphorus acid.

Example 9

 The alkylated product mixture obtained in Example 8, *supra*, was filtered and the solvents were stripped out in a rotavapor under vacuum. The liquid was mixed with 100
30 mL toluene and consecutively washed by 200 mL water, 150 mL 3.8% sodium carbonate three times and 100 mL water twice respectively. The upper layer was separated and

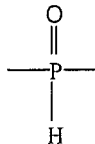
dried at a Rotavapor under vacuum. The layer crystallized upon standing at room temperature to provide 288 g pure diisobutylphosphinic acid. The yield was 81%.

* * *

While the process of the invention has been described with reference to certain
5 embodiments, it will be understood by those skilled in the art that various changes may
be made and equivalents may be substituted for elements thereof without departing from
the scope of the invention. In addition, many modifications may be made to adapt a
particular situation or material to the teachings of the invention without departing from
the essential scope thereof. Therefore, it is intended that the invention not be limited to
10 the particular embodiment disclosed as the best mode contemplated for carrying out the
process of the invention but that the invention will include all embodiments falling within
the scope of the appended claims.

WHAT IS CLAIMED IS:

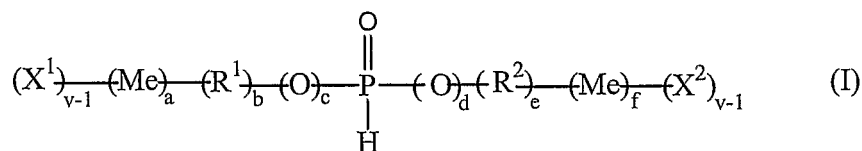
1. A process for alkylating a phosphorus-containing compound to provide an alkylated phosphorus-containing compound which comprises alkylating phosphorus-containing compound possessing at least one phosphorus-hydrogen



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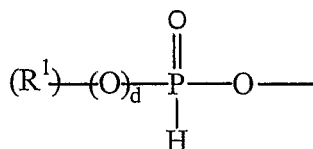
alkylatable site with reactant which generates alkene and/or cycloalkene alkylating agent *in situ* in the presence of initiator, the alkylene and/or cycloalkylene alkylating agent alkylating the phosphorus-containing component to provide alkylated phosphorus-containing product.

10 2. The process of Claim 1 wherein phosphorus-containing compound is represented by general formula (I):



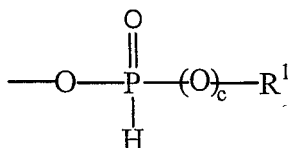
wherein:

x^1 , where present, is



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and x^2 , where present, is



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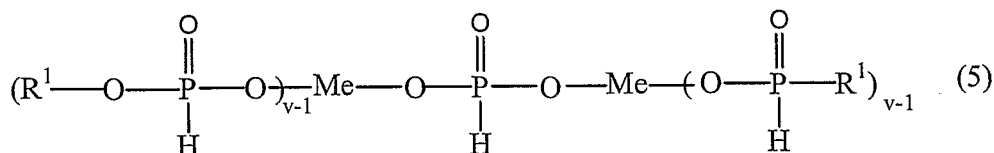
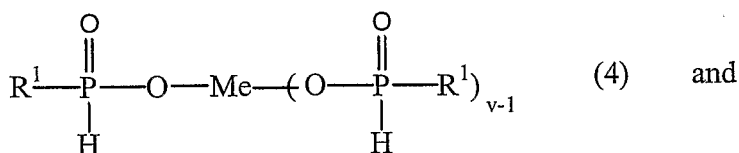
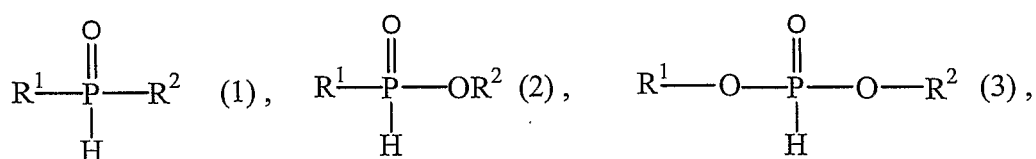
in which R^1 is H, alkyl of up to 30 carbon atoms, cycloalkyl of from 3 to 12 carbon atoms or aryl of from 6 to 20 carbon atoms; Me is a metal having a valence v of 1, 2, 3 or 4; R^2 is H, alkyl of up to 30 carbon atoms, cycloalkyl of from 3 to 12 carbon atoms or aryl of from 6 to 20 carbon atoms; and, a, b, c, d, e and f each independently is 0 or 1, provided,

in which R^1 , R^2 , Me and v have the aforesated meanings.

5. The process of Claim 4 wherein in phosphorus-containing compounds (1)-(6), R^1 is H and Me is lithium, sodium, potassium, magnesium, calcium, barium, aluminum, titanium, vanadium, chromium, molybdenum, iron, cobalt, nickel, copper or zinc.

6. The process of Claim 5 wherein in phosphorus-containing compounds (2) and (3), R^2 is H.

7. The process of Claim 3 wherein phosphorus-containing compound (I) is at least one member selected from the group (1)-(6) consisting of:



in which R^1 , R^2 , Me and v have the aforesated meanings.

8. The process of Claim 7 wherein in phosphorus-containing compounds (1)-(6), R^1 is H and Me is lithium, sodium, potassium, magnesium, calcium, barium, aluminum, titanium, vanadium, chromium, molybdenum, iron, cobalt, nickel, copper or zinc.

9. The process of Claim 8 wherein in phosphorus-containing compounds (2) and (3), R^2 is H.

10. The process of Claim 1 wherein the phosphorus-containing compound is at least one member of the group consisting of phosphonic acid, hypophosphorous acid, phosphinic acid, phosphinous acid, phosphonic acid tert-butyl ester, phosphonic acid di-

tert-butyl ester, phosphonic acid methyl ester, phosphonic acid phenyl ester, phosphinic acid tert-butyl ester, methylphosphinic acid phenyl ester, benzenephosphinic acid phenyl ester, sodium hypophosphite, calcium hypophosphite, zinc hypophosphite, aluminum hypophosphite, sodium phosphite, calcium phosphite, zinc phosphite, aluminum phosphite, ferric phosphite, sodium benzenephosphinate and sodium methylphosphinate.

11. The process of Claim 1 wherein the reactant which generates alkene or cycloalkene *in situ* is at least one member of the group consisting of 2-chloro-2-methylpropane, 2-bromo-2-methylpropane, 2-chloropropane, 2-bromopropane, tert-amyl chloride, tert-amyl bromide, tert-butyl alcohol, tert-amyl alcohol, isopropyl alcohol, 2-butanol, 2-buten-1-ol, 2-methyl-3-buten-2-ol, 1-methylcyclopentanol, 1-methylcycloheptanol, 1-methylcyclooctanol, 1-methylcyclodecanol, tert-butyl acetate, phosphoric acid tert-butyl ester, phosphonic acid tert-butyl ester, phosphonic acid di-tert-butyl ester, diisobutylphosphinic acid tert-butyl ester, isopropyl tosylate and isopropyl mesylate.

12. The process of Claim 10 wherein the reactant which generates alkene or cycloalkene *in situ* is at least one member of the group consisting of 2-chloro-2-methylpropane, 2-bromo-2-methylpropane, 2-chloropropane, 2-bromopropane, tert-amyl chloride, tert-amyl bromide, tert-butyl alcohol, tert-amyl alcohol, isopropyl alcohol, 2-butanol, 2-buten-1-ol, 2-methyl-3-buten-2-ol, 1-methylcyclopentanol, 1-methylcycloheptanol, 1-methylcyclooctanol, 1-methylcyclodecanol, tert-butyl acetate, phosphoric acid tert-butyl ester, phosphonic acid tert-butyl ester, phosphonic acid di-tert-butyl ester, diisobutylphosphinic acid tert-butyl ester, isopropyl tosylate and isopropyl mesylate.

13. The process of Claim 1 wherein the initiator is at least one free radical initiator, UV light or a combination thereof.

14. The process of Claim 13 wherein the free radical initiator is at least one azo compound, inorganic peroxide and/or organic peroxide.

15. The process of Claim 13 wherein the free radical initiator is at least one member selected from the group consisting of 2,2'-azobis(2-amidinopropane) dihydrochloride, 2,2'-azobis(N,N'-dimethyleneisobutyramidine) dihydrochloride, azobis(isobutyronitrile), 4,4'-azobis(4-cyanopentanoic acid), 2,2'-azobis(2-

methylbutyronitrile), hydrogen peroxide, ammonium peroxodisulfate, potassium peroxodisulfate, dibenzoyl peroxide, di-tert-butyl peroxide and peracetic acid.

16. The process of Claim 1 carried out in the presence of carboxylic acid and/or mineral acid.

5 17. The process of Claim 1 wherein the alkylation reaction is carried out at a temperature of from about 25°C to about 130°C and a pressure ranging from about atmospheric up to about 2 atmospheres.

18. The process of Claim 7 wherein phosphorus-containing compound (I) is at least one member selected from the group consisting of (2) and (3), the alkylated reaction
10 product thereafter being converted to the corresponding metal salt.

19. The process of Claim 18 wherein the metal of said metal salt is selected from the group consisting of Mg, Al, Zn, Fe(II), Fe(III), Cu(II) and Zr(IV).

20. The process of Claim 1 wherein:
the phosphorus-containing compound is at least one member of the group
15 consisting of phosphonic acid, hypophosphorous acid, phosphinic acid, phosphinous acid, phosphonic acid tert-butyl ester, phosphonic acid di-tert-butyl ester;

phosphonic acid methyl ester, phosphonic acid phenyl ester, phosphinic acid tert-butyl ester, methylphosphinic acid phenyl ester, benzenephosphinic acid phenyl ester, sodium hypophosphite, calcium hypophosphite, zinc hypophosphite, aluminum
20 hypophosphite, sodium phosphite, calcium phosphite, zinc phosphite, aluminum phosphite, ferric phosphite, sodium benzenephosphinate and sodium methylphosphinate, the reactant which generates alkene or cycloalkene *in situ* is at least one member of the group consisting of 2-chloro-2-methylpropane, 2-bromo-2-methylpropane, 2-chloropropane, 2-bromopropane, tert-amyl chloride, tert-amyl bromide, tert-butyl
25 alcohol, tert-amyl alcohol, isopropyl alcohol, 2-butanol, 2-buten-1-ol, 2-methyl-3-buten-2-ol, 1-methylcyclopentanol, 1-methylcycloheptanol, 1-methylcyclooctanol, 1-methylcyclodecanol, tert-butyl acetate, phosphoric acid tert-butyl ester, phosphonic acid tert-butyl ester, phosphonic acid di-tert-butyl ester, diisobutylphosphinic acid tert-butyl ester, isopropyl tosylate and isopropyl mesylate; and,

30 the initiator is at least one free radical initiator, UV light or a combination thereof.