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CYCLOBUTYL PHOSPHATE AND PHOSPHONATE ESTERS

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U.S. Cl. 260—958 14 Claims

ABSTRACT OF THE DISCLOSURE

This invention relates to new chemical compounds which are phosphate esters and phosphonate esters having three organic radicals at least one of which is the cyclobutyl radical and the other organic radicals of which are the cyclobutyl radical, the phenyl radical, or the tolyl radical.

These new chemical compounds are useful for thermally stable fire resistant hydraulic fluids, especially for aircraft, either alone or admixed with other additives.

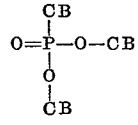
These compounds particularly include the following:

(1) Phosphate esters
- Tricyclobutyl phosphate
- Dicyclobutyl phenyl phosphate
- Monocyclobutyl diphenyl phosphate
- Dicyclobutyl tolyl phosphate
- Monocyclobutyl ditolyl phosphate
- Monocyclobutyl tolyl phenyl phosphate

(2) Phosphonate esters
- Dicyclobutyl cyclobutane phosphonate
- Dicyclobutyl benzene phosphonate
- Diphenyl cyclobutane phosphonate
- Dicyclobutyl toluene phosphonate
- Ditolyl cyclobutane phosphonate
- Monocyclobutyl tolyl benzene phosphonate
- Monocyclobutyl phenyl toluene phosphonate

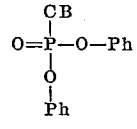
The phosphonate esters particularly include the following:

Dicyclobutyl cyclobutane phosphonate



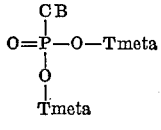
Herein CB stands for the cyclobutyl radical.

Diphenyl cyclobutane phosphonate



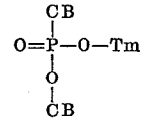
Herein Ph stands for the phenyl radical.

Dimetatolyl cyclobutane phosphonate



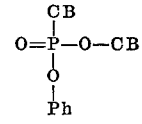
Herein T stands for the tolyl radical and generically designates ortho, meta, and para tolyl and mixtures thereof.

Cyclobutyl metatolyl cyclobutane phosphonate

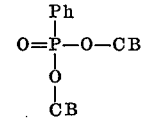


Herein Tm designates the metatolyl radical.

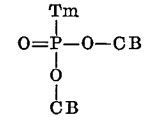
Cyclobutyl phenyl cyclobutane phosphonate



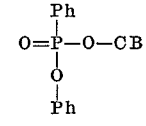
Dicyclobutyl benzene phosphonate



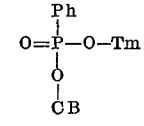
Dicyclobutyl toluene phosphonate



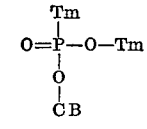
Cyclobutyl phenyl benzene phosphonate



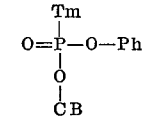
Cyclobutyl metatolyl benzene phosphonate



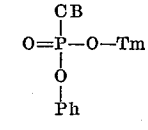
Cyclobutyl tolyl toluene phosphonate



Cyclobutyl phenyl toluene phosphonate



Tolyl phenyl cyclobutane phosphonate



Each of these new foregoing chemical compounds can be made by the same methods used for making the corresponding phosphates and phosphonates where the butyl radical is used instead of the cyclobutyl radical. The methods of making the corresponding phosphates and phosphonates with the butyl radical are known to those skilled in the art, and with the disclosure herein those skilled in the art to which my invention appertains will be able to make and use the new chemical compounds of my invention.

The preparation of the known phosphate esters and phosphonate esters having the butyl radical instead of the cyclobutyl radical of my invention is disclosed in the books entitled "Introduction to Hydraulic Fluids" by Roger E. Hatton, published by Rheinhold Publishing Corporation and "Organo-Phosphorous Compounds" by G. M. Kosolopoff, published by John Wiley and Sons, and numerous other publications and issued patents. The particular relevant disclosure in the book entitled "Introduction to Hydraulic Fluids" appears on pages 190 through 195.

Even though those skilled in the art will be able to prepare and use the new chemical compounds of my invention, there is given below examples of these compounds and their preparation.

EXAMPLE 1

Tricyclobutyl phosphate

3.5 mols of cyclobutyl alcohol are added dropwise with stirring to one mol of phosphorus oxychloride ($POCl_3$) at 25–35° C. The temperature is slowly brought up to about 65° C. and the pressure is slowly reduced to 50 mm./Hg with stirring to remove hydrogen chloride. The mixture is then distilled and tricyclobutyl phosphate is collected boiling at about 160–165° C. at 15 mm./Hg.

EXAMPLE 2

Tricyclobutyl phosphate

To 5 mols of cyclobutanol, three mols of freshly cut metallic sodium are added in small cubes about ¼" with stirring and maintaining the temperature between 25 and 40° C. When reaction is complete as evidenced by cessation of bubbling, one mol of phosphorus oxychloride ($POCl_3$) is added dropwise with stirring while maintaining the temperature at about 25–50° C. The reaction mixture is filtered to remove the precipitated sodium chloride and the filtrate is distilled and tricyclobutyl phosphate is collected boiling at about 160–165° C. at 15 mm./Hg.

EXAMPLE 3

Dicyclobutyl phenyl phosphate

Two mols of cyclobutanol are added dropwise with stirring to one mol of $POCl_3$ at 25–35° C. The temperature is slowly brought up to about 65° C. and the pressure slowly reduced to 50 mm./Hg to remove hydrogen chloride. Without further purification this mixture is added dropwise at 0–5° C. to a saturated solution of one mol of phenol in one mol of sodium hydroxide with good stirring. The mixture is allowed to rise in temperature to 25° C. with continued stirring. The resulting mixture is washed, dried and distilled to separate out the desired water insoluble dicyclobutyl phenyl phosphate. The boiling point of this phosphate is about 165–170° C. at 15 mm./Hg.

EXAMPLE 4

Dicyclobutyl tolyl phosphate

Two mols of cyclobutanol are added dropwise with stirring to one mol of $POCl_3$ at 25–35° C. the temperature is slowly brought up to about 65° C. and the pressure slowly reduced to 50 mm./Hg to remove hydrogen chloride. Without further purification this mixture is added dropwise at 0–5° C. to a saturated solution of one mol of metacresol in one mol of sodium hydroxide with good stirring. The mixture is allowed to rise in temperature to 25° C. with continued stirring. The resulting mixture is washed, dried and distilled to separate out the desired water insoluble dicyclobutyl metatolyl phosphate. The boiling point of this phosphate is about 175–180° C. at 15 mm./Hg.

EXAMPLE 5

Monocyclobutyl diphenyl phosphate

One mol of cyclobutanol is added dropwise with stirring to one mol of $POCl_3$ at 25–35° C. The temperature is slowly brought up to about 65° C. and the pressure slowly reduced to 50 mm./Hg to remove hydrogen chloride. Without further purification this mixture is added dropwise at 0–5° C. to a saturated solution of two mols of phenol in two mols of NaOH with good stirring. The mixture is allowed to rise in temperature to 25° C. with continued stirring. The resulting mixture is washed, dried and distilled to separate out the desired water insoluble monocyclobutyl diphenyl phosphate. The boiling point of this phosphate is about 170–175° C. at 15 mm./Hg.

EXAMPLE 6

Monocyclobutyl paratolyl phosphate

One mol of cyclobutanol is added dropwise with stirring to one mol of $POCl_3$ at 25–35° C. The temperature is slowly brought up to about 65° C. and the pressure slowly reduced to 50 mm./Hg to remove hydrogen chloride. Without further purification this mixture is added dropwise at 0–5° C. to a saturated solution of two mols of paracresol in two mols of NaOH with good stirring. The mixture is allowed to rise in temperature to 25° C. with continued stirring. The resulting mixture is washed, dried and distilled to separate out the desired water insoluble monocyclobutyl paratolyl phosphate. The boiling point of this phosphate is about 180–185° C. at 15 mm./Hg.

EXAMPLE 7

Monocyclobutyl phenyl tolyl phosphate

One mol of cyclobutanol is added dropwise with stirring to one mole of $POCl_3$ at 25–35° C. The temperature is slowly brought up to about 65° C. and the pressure slowly reduced to 50 mm./Hg to remove hydrogen chloride. Without further purification this mixture is added dropwise at 0–5° C. to a saturated solution of one mol of phenol in one mol of sodium hydroxide with good strring. The mixture is allowed to rise in temperature to 25° C. with continued stirring. The mixture is filtered and the filtrate is added dropwise, without further purification, at 0–5° C. to a saturated solution of one mol of metacresol in one mol of NaOH with good stirring. The mixture is allowed to rise in temperature with continued stirring. The resulting mixture is washed, dried and distilled to separate out the desired water insoluble monocyclobutyl phenyl metatolyl phosphate. The boiling point of this phosphate ester is about 175–180° C. at 15 mm./Hg.

EXAMPLE 8

Dicyclobutyl cyclobutane phosphonate

Three mols of cyclobutanol are added dropwise with stirring to one mol of cyclobutane phosphorus oxydichloride $(CH_2)_3CHP(O)Cl_2$, at 25–35° C. The temperature is slowly brought up to about 65° C. and the pressure is slowly reduced to 50 mm./Hg with stirring to remove hydrogen chloride. The mixture is then distilled and dicyclobutyl cyclobutane phosphonate is collected boiling at about 150–155° C. at 15 mm./Hg.

EXAMPLE 9

Diphenyl cyclobutane phosphonate

Three mols of phenol are added dropwise with stirring to one mol of cyclobutane phosphorus oxydichloride at 25–35° C. The temperature is slowly brought up to about 65° C. and the pressure is slowly reduced to 50 mm./Hg with stirring to remove hydrogen chloride. The mixture is then distilled and diphenyl cyclobutane phosphonate is collected boiling at about 155–160° C. at 15 mm./Hg.

EXAMPLE 10

dimetatolyl cyclobutane phosphonate

Three mols of metacresol are added dropwise with stirring to one mol of cyclobutane phosphorus oxydichloride at 25–35° C. The temperature is slowly brought up to about 65° C. and the pressure is slowly reduced to 50

mm./Hg with stirring to remove hydrogen chloride. The mixture is then distilled and dimetatolyl cyclobutane phosphonate is collected boiling at about 155–160° C. at 15 mm./Hg.

EXAMPLE 11

Cyclobutyl metatolyl cyclobutane phosphonate

One mol of cyclobutanol is added dropwise with stirring to one mol of cyclobutane phosphorus oxydichloride at 25–35° C. The temperature is slowly brought up to about 65° C. and the pressure is slowly reduced to 50 mm./Hg with stirring to remove hydrogen chloride. Without further purification this mixture is added dropwise at 0–5° C. to a saturated solution of one mol of metacresol in one mol of sodium hydroxide with good stirring. The mixture is allowed to rise in temperature to 25° C. with continued stirring. The resulting mixture is washed, dried and distilled to separate out the desired water insoluble cyclobutyl metatolyl cyclobutane phosphonate boiling at about 155–160° C. at 15 mm./Hg.

EXAMPLE 12

Cyclobutyl phenyl cyclobutane phosphonate

One mol of cyclobutanol is added dropwise with stirring to one mol of cyclobutane phosphorus oxydichloride at 25–35° C. The temperature is slowly brought up to about 60° C. and the pressure is slowly reduced to 50 mm./Hg with stirring to remove hydrogen chloride. Without further purification this mixture is added dropwise at 0–5° C. to a saturated solution of one mol of phenol in one mol of sodium hydroxide with good stirring. The mixture is allowed to rise in temperature to 25° C. with continued stirring. The resulting mixture is washed, dried and distilled to separate out the desired water insoluble cyclobutyl phenyl cyclobutane phosphonate. The boiling point of this phosphonate is about 155–160° C. at 15 mm./Hg.

EXAMPLE 13

Dicyclobutyl benzene phosphonate

Three mols of cyclobutanol are added dropwise with stirring to one mol of benzene phenyl phosphorus oxydichloride at 25–35° C. The temperature is slowly brought up to about 65° C. and the pressure is slowly reduced to 50 mm./Hg with stirring to remove hydrogen chloride. The mixture is then distilled and dicyclobutyl benzene phosphonate is collected boiling at about 155–160° C. at 15 mm./Hg.

EXAMPLE 14

Dicyclobutyl toluene phosphonate

Three mols of cyclobutanol are added dropwise with stirring to one mol of metatoluene phosphorus oxydichloride at 25–35° C. The temperature is slowly brought up to about 65° C. and the pressure is slowly reduced to 50 mm./Hg with stirring to remove hydrogen chloride. The mixture is then distilled and dicyclobutyl toluene phosphonate is collected boiling at about 160–165° C. at 15 mm./Hg.

EXAMPLE 15

Cyclobutyl phenyl benzene phosphonate

One mol of cyclobutanol is added dropwise with stirring to one mol of benzene phosphorus oxydichloride at 25–35° C. The temperature is slowly brought up to about 65° C. and the pressure is slowly reduced to 50 mm./Hg with stirring to remove hydrogen chloride. Without further purification this mixture is added dropwise at 0–5° C. to a saturated solution of one mol of phenol in one mol of sodium hydroxide with good stirring. The mixture is allowed to rise in temperature to 25° C. with continued stirring. The mixture is washed, dried and distilled and cyclobutyl phenyl benzene phosphonate is collected boiling at about 155–160° C. at 15 mm./Hg.

EXAMPLE 16

Cyclobutyl metatolyl benzene phosphonate

One mol of cyclobutanol is added dropwise with stirring to one mol of benzene phosphorus oxydichloride at 25–35° C. The temperature is slowly brought up to about 65° C. and the pressure is slowly reduced to 50 mm./Hg with stirring to remove hydrogen chloride. Without further purification this mixture is added dropwise at 0–5° C. to a saturated solution of one mol of metacresol in one mol of sodium hydroxide with good stirring. The mixture is allowed to rise in temperature to 25° C. with continued stirring. The mixture is washed, dried and distilled and cyclobutyl metatolyl benzene phosphonate is collected boiling at about 160–165° C. at 15 mm./Hg.

EXAMPLE 17

Cyclobutyl tolyl toluene phosphonate

One mol of cyclobutanol is added dropwise with stirring to one mol of metatoluene phosphorus oxydichloride at 25–35° C. The temperature is slowly brought up to about 65° C. and the pressure is slowly reduced to 50 mm./Hg with stirring to remove hydrogen chloride. Without further purification this mixture is added dropwise at 0–5° C. to a saturated solution of one mol of metacresol in one mol of sodium hydroxide with good stirring. This mixture is allowed to rise in temperature to 25° C. with continued stirring. The mixture is washed, dried and distilled and cyclobutyl tolyl toluene phosphonate is collected boiling at about 165–170° C. at 15 mm./Hg.

EXAMPLE 18

Cyclobutyl phenyl toluene phosphonate

One mol of cyclobutanol is added dropwise with stirring to one mol of metatoluene phosphorus oxydichloride at 25–35° C. The temperature is slowly brought up to about 65° C. and the pressure is slowly reduced to 50 mm./Hg with stirring to remove hydrogen chloride. Without further purification this mixture is added dropwise at 0–5° C. to a saturated solution of one mol of phenol in one mol of sodium hydroxide with good stirring. This mixture is allowed to rise in temperature to 25° C. with continued stirring. The mixture is washed, dried and distilled and cyclobutyl phenyl toluene phosphonate is collected boiling at about 160–165° C. at 15 mm./Hg.

EXAMPLE 19

Tolyl phenyl cyclobutane phosphonate

One mol of metacresol is added dropwise with stirring to one mol of cyclobutane phosphorus oxydichloride at 25–35° C. The temperature is slowly brought up to about 65° C. and the pressure is slowly reduced to 50 mm./Hg with stirring to remove hydrogen chloride. Without further purification this mixture is added dropwise at 0–5° C. to a saturated solution of one mol of phenol in one mol of sodium hydroxide with good stirring. This mixture is allowed to rise in temperature to 25° C. with continued stirring. The mixture is washed, dried and distilled and tolyl phenyl cyclobutane phosphonate is collected boiling at about 160–165° C. at 15 mm./Hg.

The compositions of my invention have high thermal stability apparently due to the presence of the cyclobutyl radical, high fire resistance, good lubricity, especially hydrodynamic lubricity, good boundary lubrication and good anti-wear, have ability to lubricate moving parts, particularly steel on steel, good viscosity and viscosity-temperature properties, and are readily admixed with many additives.

It will be understood that the specific embodiments of my invention described above are intended to illustrate and exemplify my invention and are not necessarily intended as a limitation thereon and that modifications of my invention may be made.

I claim:

1. The phosphate and phosphonate esters represented by the formula $(R_1R_2R_3)O_2O_xPO$ in which x may be one or zero, R_1 is cyclobutyl, and R_2 and R_3 are cyclobutyl, phenyl or tolyl.

2. The chemical compound as defined in claim 1 which is tricyclobutyl phosphate.

3. The chemical compound as defined in claim 1 which is dicyclobutyl cyclobutane phosphonate.

4. The chemical compound as defined in claim 1 which is dicyclobutyl phenyl phosphate.

5. The chemical compound as defined in claim 1 which is dicyclobutyl benzene phosphonate.

6. The chemical compound as defined in claim 1 which is dicyclobutyl tolyl phosphate.

7. The chemical compound as defined in claim 1 which is dicyclobutyl toluene phosphonate.

8. The chemical compound as defined in claim 1 which is monocyclobutyl diphenyl phosphate.

9. The chemical compound as defined in claim 1 which is monocyclobutyl phenyl benzene phosphonate.

10. The chemical compound as defined in claim 1 which is monocyclobutyl ditolyl phosphate.

11. The chemical compound as defined in claim 1 which is monocyclobutyl tolyl toluene phosphonate.

12. The chemical compound as defined in claim 1 which is monocyclobutyl tolyl phenyl phosphate.

13. The chemical compound as defined in claim 1 which is monocyclobutyl tolyl benzene phosphonate.

14. The chemical compound as defined in claim 1 which is monocyclobutyl phenyl toluene phosphonate.

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CHARLES B. PARKER, Primary Examiner

A. H. SUTTO, Assistant Examiner

U.S. Cl. X.R.

260—974, 969, 973; 252—49.8, 78