United States Patent Office

3,189,628

Patented June 15, 1965



3,189,628

# PHOSPHONATED OILS AND PHOSPHONATED ESTERS

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No Drawing. Filed Feb. 27, 1962, Ser. No. 176,157
25 Claims. (Cl. 260—403)
(Granted under Title 35, U.S. Code (1952), sec. 266)

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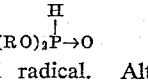
This invention relates to alkyl phosphonate derivatives of alkyl and glyceryl esters of polyunsaturated acids or mixtures containing them, and to a process for their preparation.

The esters of polyunsaturated fatty acids have heretofore behaved as inhibitors and have been essentially unreactive in peroxided initiated synthetic addition reactions, thus limiting free radical reactions conducted in their presence. The inhibitory effect is assumed to be caused by the presence in polyunsaturated fatty acids, such as linoleic and linolenic acids, of highly reactive allylic systems which are converted on reaction with free radical generating sources, to sluggishly reactive radicals. These sluggishly reactive radicals prefer to dimerize rather than to add other species to their double bond systems. The radical-inhibiting effect of glyceryl esters of polyunsaturated fatty acids is also shown by alkyl esters of polyunsaturated fatty acids.

Therefore, the discovery that dialkyl phosphonates can be added in good yield to the double bonds of polyunsaturated fatty acid moieties in alkyl esters and in glyceryl esters is unexpected.

In general, according to the present invention polyphosphonate derivatives of esters of polyunsaturated fatty acids are prepared by the free radical addition of dialkyl phosphonates to alkyl and glyceryl esters of polyunsaturated fatty acids or to mixtures containing them.

The dialkyl phosphonates are compounds of the formula



wherein R is an alkyl radical. Although the alkyl groups, R may be different instead of identical and may contain less than 2 and more than 8 carbon atoms, the invention is exemplified with dialkyl phosphonates in which a straight chain or branched chain alkyl radical contains 2 to 8 carbon atoms, such as ethyl, butyl and 2-ethylhexyl, because of their availability and price.

Similarly, the alkyl esters of a polyunsaturated acid are exemplified with ethyl, butyl and 2-ethylhexyl esters, but many other straight and branched chain alkyl radicals may be the alkyl group in the alkyl ester of the polyunsaturated fatty acid from which the polyphosphonated derivative is prepared.

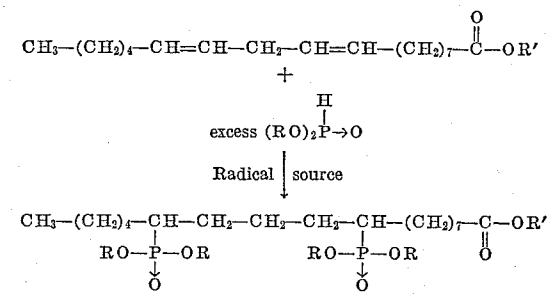
The polyunsaturated fatty acids are typically represented by the diunsaturated acid, linoleic, and the triunsaturated acid, linolenic. Other fatty acids may be selected for use from among the following:

Sorbic
2,4-decadienoic



9,15-octadecadienoic
2,4-dodecadienoic
10,13-nonadecadienoic
11,14-eicosadienoic
17,20-hexacosadienoic
6,10,14-hexadecatrienoic (hiragonic)
7,10,13-hexadecatrienoic
Cis-6, cis-9, cis-12-octadecatrienoic
Cis-9, trans-11, trans-13-octadecatrienoic ($\alpha$-eleostearic)
Trans-9, trans-11, trans-13-octadecatrienoic ($\beta$-eleostearic)
Cis-9, cis-11, trans-13-octadecatrienoic (punicic)
9, 12, 14-octadecatrienoic
Trans-9, trans-12, trans-15-octadecatrienoic (linolenelaidic)
Trans-10, trans-12, trans-14-octadecatrienoic (pseudoeleostearic)
10, 12, 15-octadecatrienoic
5, 8, 11-eicosatrienoic
8, 11, 14-eicosatrienoic
7, 10, 13-docosatrienoic
8, 11, 14-docosatrienoic
4, 8, 11, 14-hexadecatetraenoic
6, 9, 12, 15-hexadecatetraenoic
4, 8, 12, 15-octadecatetraenoic (morotic)
9, 11, 13, 15-octadecatetraenoic ($\alpha$-parinaric)
9, 11, 13, 15-octadecatetraenoic ($\beta$-parinaric)
4, 8, 12, 16-eicosatetraenoic
5,8,11,14-eicosatetraenoic
4,7,10,13-docosatetraenoic
7,10,13,16-docosatetraenoic
8,12,16,19-docosatetraenoic
4,8,12,13,16-docosapentenoic
4,8,12,15,19-docosapentenoic (clupanodonic)
Tetracosapentenoic (scoliodonic)
Hexadosapentenoic (shibic)
4,7,10,13,16,19-docosahexaenoic
4,8,12,15,18,21-tetracosahexaenoic (nisinic)

The addition of a dialkyl phosphonate to a polyunsaturated fatty acid, here exemplified with an alkyl linoleate, is illustrated showing one of the isomeric products:




(wherein R and R′ are alkyl radicals)

In a preferred embodiment of the invention an amount of dialkyl phosphonate in excess of that which will add to the double bonds is combined with the ester of the unsaturated fatty acid. A molar excess of the dialkyl phosphonate is recommended for optimum yields and maximum rates of reaction. Since the excess phosphonate can be recovered by vacuum distillation at the end of the reaction and reused, a general procedure was adopted in most cases using about three moles of dialkyl phosphonate

per double bond in the fatty acid, and the dialkyl phosphonate served both as solvent and reactant. Alternatively, by using lesser quantities of dialkyl phosphonates per double bond it is possible to add the dialkyl phosphonate to a controlled number of available double bonds. The products, phosphonates still containing residual unsaturation, can be epoxidized or otherwise reacted at the double bonds remaining.

Tertiary butyl peresters are preferred initiators for the addition reaction because their decomposition characteristics are suitable for initiating the reaction in the temperature range in which the polyunsaturated esters are activated and prefer to undergo addition of phosphonate rather than to dimerize or react in other undesirable fashion. Tertiary butyl perbenzoate is a preferred initiator because of its relatively low cost and high efficiency. Approximately 5 mole percent of initiator based on unsaturated ester is usually employed. Benzoyl peroxide, di-tertiary butyl peroxide and azobisisobutyronitrile are not as effective initiators as are the peresters.

The reactants and initiator may be combined in various ways to obtain good yields from the addition reaction. In one convenient method, the polyunsaturated ester, dialkyl phosphonate and a portion of the initiator (5–15% of the total amount to be used) are mixed and heated at 90–100° in an inert atmosphere with more-or-less equal incremental additions of initiator at one to two hour intervals for a total reaction period of 20 to 40 hours, depending on the unsaturated ester. Alternatively, (a) the polyunsaturated ester at room temperature and containing the total quantity of initiator is added slowly to the stirred dialkyl phosphonate, heated to reaction mixture and maintained in an inert atmosphere or, (b) the addition is conducted as in (a) except that a portion of the dialkyl phosphonate is used as a diluent and solvent for the polyunsaturated ester, and they are added simultaneously from a dropping funnel to the remainder of the dialkyl phosphonate in the reaction vessel at reaction temperature. By operating as in (a) or (b), a large excess of dialkyl phosphonate is always present with respect to the polyunsaturated fatty ester being added; and, also, there is a uniform concentration of initiator being added at all times to the reaction. By the incremental addition of initiator, it is present in markedly varying amounts. By all three reaction procedures, however, yields are usually high and are about the same. At the conclusion of the reaction, the excess dialkyl phosponate and other volatiles are recovered by vacuum stripping. Infrared examination of the non-volatile residue shows that the dialkyl phosphonate groups have been added to the double bonds present in the unsaturated esters used. Ultimate analysis for phosphorus and determination of residual unsaturation confirm this conclusion.

Under reaction conditions to introduce the maximum of dialkylphosphono groups into the product, the derivative of a linolenate contains three dialkylphosphono groups, the derivative of an arachidonate ester contains four, and esters of fatty acids with greater degrees of unsaturation will add correspondingly more dialkylphosphono groups.

The addition of the dialkylphosphono groups to polyunsaturated fatty acids proceeds in high yields when the fatty acids are contained in natural and synthetic triglycerides. Some typical natural triglycerides to which dialkyl phosphonates add readily are soybean, cottonseed, safflower, corn, sunflower, tung and linseed oils, fish oils, tallow, lard, lard oil and oleo oil. These triglycerides are mixed glyceryl esters of saturated, monounsaturated, and polyunsaturated fatty acids. It is readily apparent that products with a wide range of phosphorus content made be obtained from triglycerides. The glyceryl ester formed from two stearic acids and one linoleic acid could add a maximum of two dialkylphosphono groups. A triglyceride containing ten double bonds (two linolenic and one arachidonic acids) could add as many as ten dialkylphosphono groups. Products with a predetermined average phosphorus content can be prepared by using a mixture of natural or synthetic glycerides having a certain average degree of unsaturation, or by blending the addition products to achieve a similar result. Alternatively, by limiting the reaction time or the quantity of dialkyl phosphonate residual unsaturation can be left in the molecule.

The following examples, corresponding to 13 and 21, respectively, of Table I, are typical illustrations of the preparation of a dialkyl phosphonate addition product.

## EXAMPLE A

Dibutyl phosphonate, 90.7 g. (0.47 m.) and cottonseed oil, 33.0 g. were placed in a 250 ml. round-bottom 3-necked flask equipped with a magnetic stirrer, a nitrogen inlet tube, and thermometer. The contents of the flask were heated to 100° C., with stirring, and 0.3 g. of t-butyl perbenzoate was added. The temperature was maintained between 100° and 110° C., with stirring, in an atmosphere of nitrogen, and additional t-butyl perbenzoate, 0.3 g., was added at 2 hour intervals (i.e. 2, 4, 6, 8, etc., through the 28th hour of reaction time). The total t-butyl perbenzoate (catalyst) used was 4.5 g. At the end of 30 hours the reaction mixture was degassed at 1 mm. or less mercury pressure to remove the excess di-butyl phosphonate and any volatiles. The final product was isolated as the residue from the stripping action of a rotating-brush, falling-film type molecular distillation unit operated up to 150° C. at 10$\mu$ mercury pressure. The yield of product was 58.5 g. (92.7% of theoretical). Phosphorus analysis: calculated, 7.61%; found, 7.44%. (This example corresponds to Example 13 of Table I.)

## EXAMPLE B

Diethyl phosphonate, 46.0 g. (0.33 m.) and lard, 43.2 g. were treated as in Example A, except that 3.5 g. of t-butyl perbenzoate was used as the catalyst and the reaction time was 20 hours. The product isolated exactly as in Example A weighed 53.0 g. (90.4% of theory). Phosphorus analysis: calculated, 5.7%; found, 6.4%. (This example corresponds to Example 21 of Table I.)

Other examples were carried out in a similar manner, the principal variation in procedure being in reaction time, as indicated in the results present in Table I.

The utility of the products of the present invention is related to the number of dialkylphosphono groups added to double bonds of alkyl and glyceryl esters of polyunsaturated fatty acids and not with the particular isomeric configurations of the addition products. For example, the four position isomers of a linoleate (9,12; 10,12; 10,13; and 9,13) contain two dialkylphosphono groups.

*Table I.—Phosphonated triglycerides and phosphonated synthetic esters*

| Example No. | Reactants [a] | Reaction Time, Hrs. | Products | | Iodine No. |
|---|---|---|---|---|---|
| | | | Yield, Percent | Phosphorus, Percent | |
| 1 | Ethyl Linoleate (I No. 163.5) and Diethyl Phosphonate. | 30 | 98 | 9.65–11.75 | 1 |
| 2 | Butyl Linoleate (I No. 142.5) and Di-2-Ethylhexyl Phosphonate. | 30 | 87 | 5.85 | 7 |
| 3 | 2-Ethylhexyl Linoleate (I No. 120) and Di-2-Ethylhexyl Phosphonate. | 30 | 83 | 5.11 | 8 |
| 4 | Ethyl Linolenate (I No. 226) and Diethyl Phosphonate. | 40 | 40 | 8.52 | 42 |
| 5 | Butyl Linolenate (I No. 225) and Diethyl Phosphonate. | 40 | 44 | 6.77 | 54 |
| 6 | 2-Ethylhexyl Linolenate (I No. 174) and Dibutyl Phosphonate. | 40 | 72 | 5.03 | 29 |

See footnote at end of table.

*Table I.—Phosphonated triglycerides and phosphonated synthetic esters*—Continued

| Example No. | Reactants [a] | Reaction Time, Hrs. | Products | | Iodine No. |
|---|---|---|---|---|---|
| | | | Yield, Percent | Phosphorus, Percent | |
| 7 | Butyl Esters of Tall Oil Fatty Acids (I No. 110) and Dibutyl Phosphonate. | 30 | 84 | 7.23 | 4.5 |
| 8 | 2-Ethylhexyl Esters of Tall Oil Fatty Acids and Dibutyl Phosphonate. | 30 | 96 | 6.97 | 25 |
| 9 | Soybean Oil (I No. 144) and Diethyl Phosnate. | 40 | 100 | 9.94 | 5 |
| 10 | Soybean Oil and Di-2-Ethylhexyl Phosphonate. | 30 | 73 | 5.19 | 19 |
| 11 | Butyl Esters of Soybean Oil Fatty Acids (I No. 119) and Dibutyl Phosphonate. | 30 | 58 | 6.54 | 23 |
| 12 | Cottonseed Oil (I No. 118.5) and Diethyl Phosphonate. | 30 | 94 | 10.2 | 6.5 |
| 13 | Cottonseed Oil and Dibutyl Phosphonate. | 30 | 93 | 7.44 | 2.3 |
| 14 | Ethyl Esters of Cottonseed Oil (I No. 105.6) and Di-2-Ethylhexyl Phosphonate. | 30 | 88 | 6.02 | 1.5 |
| 15 | 2-Ethylhexyl Esters of Cottonseed Oil (I No. 82) and Di-2-Ethylhexyl Phosphonate. | 30 | 98 | 6.08 | 1.4 |
| 16 | Safflower Seed Oil (I No. 145) and Diethyl Phosphonate. | 30 | 73 | 10.2 | 2.2 |
| 17 | 2-Ethylhexyl Esters of Safflower Seed Oil (I No. 109) and Dibutyl Phosphonate. | 30 | 96 | 7.73 | 2.2 |
| 18 | Butyl Tallate (I No. 110) and Dibutyl Phosphonate. | 30 | 84 | 7.23 | 4.5 |
| 19 | 2-Ethylhexyl Tallate (I No. 93.4) and Dibutyl Phosphonate. | 40 | 96 | 6.97 | 2.5 |
| 20 | Oleo Oil (I No. 46.5) and Diethyl Phosphonate. | 20 | 86 | 4.75 | 11 |
| 21 | Lard (I No. 65.5) and Diethyl Phosphonate. | 20 | 90 | 6.38 | 2.6 |
| 22 | Lard and Dibutyl Phosphonate. | 24 | 96 | 5.64 | 1.6 |
| 23 | Oleo Oil and Dibutyl Phosphonate. | 24 | 100 | 4.89 | 1.7 |
| 24 | Lard and Di-2-Ethylhexyl Phosphonate. | 24 | 81 | 3.69 | 26 |
| 25 | Oleo Oil and Di-2-Ethylhexyl Phosphonate. | 24 | 96 | 4.01 | 10 |

[a] Three moles of dialkyl phosphonate were used per mole of double bond at a reaction temperature of 90–110°. Tertiary butyl perbenzoate was used as initiator (5 mole percent based on unsaturated compound). At the end of the initiated reaction period all volatiles were stripped under high vacuum (1 mm. or less), and the residual products were analyzed for phosphorus content and iodine number.

When adding the maximum number of dialkylphosphono groups to a linolenate there is the possibility of eight isomers, to an arachidonate, sixteen isomers, etc.

The phosphorus-containing esters are useful as lubricant additives for improving the wear and extreme pressure properties of petroleum and of synthetic diester lubricants. Some of the dialkyl phosphonate addition products are useful plasticizers for polyvinyl chloride resins, especially the addition products derived from alkyl esters of polyunsaturated fatty acids.

As an illustration of the utility of the new phosphorus-containing triglycerides and synthetic esters, Table II shows the improvement in the wear properties of an additive-free paraffin base lubricating oil and of a synthetic diester base fluid lubricant (di-2-ethylhexyl sebacate) when only 5% of phosphorus-containing ester is added. It is evident that many of the new phosphorus-containing products are effective wear additives for paraffin base and synthetic fluids. Especially effective are Examples 11, 12, 13, 20, 24 and 25, although others are moderately effective (Examples 7, 15 and 22).

*Table II.—Improvement in wear properties of paraffin oil and of synthetic diester lubricant by use of 5% of phosphonated triglycerides or phosphonated synthetic esters*

| Phosphonated Product From Table I | Base Fluid | Scar Diameter, mm.[a] |
|---|---|---|
| Control, No Additive | Paraffin Base Oil | 0.63 |
| | Synthetic Fluid | 0.84 |
| Example: | | |
| 7 | Paraffin Base Oil | 0.46 |
| | Synthetic Fluid | 0.52 |
| 15 | Paraffin Base Oil | 0.48 |
| | Synthetic Fluid | 0.47 |
| 11 | Paraffin Base Oil | 0.40 |
| | Synthetic Fluid | 0.48 |
| 17 | Paraffin Base Oil | 0.61 |
| | Synthetic Fluid | 0.50 |
| 12 | Paraffin Base Oil | 0.44 |
| | Synthetic Fluid | 0.43 |
| 13 | Paraffin Base Oil | 0.45 |
| | Synthetic Fluid | 0.50 |
| 20 | Paraffin Base Oil | 0.45 |
| | Synthetic Fluid | 0.45 |
| 21 | Paraffin Base Oil | 0.45 |
| | Synthetic Fluid | 0.45 |
| 22 | Paraffin Base Oil | 0.50 |
| | Synthetic Fluid | 0.48 |
| 23 | Paraffin Base Oil | 0.65 |
| | Synthetic Fluid | 0.50 |
| 24 | Paraffin Base Oil | 0.40 |
| | Synthetic Fluid | 0.46 |
| 25 | Paraffin Base Oil | 0.40 |
| | Synthetic Fluid | 0.47 |

[a] Standard test with Shell-Boerlage four-ball wear tester; 1 hour; 120° C.; applied load 50 kg.; SKF 1/2 inch, grade 25, steel balls.

We claim:

**1.** A compound selected from the group consisting of the addition product of a dialkyl phosphonate to an alkyl ester of a polyunsaturated fatty acid, and the addition product of a dialkyl phosphonate to a glyceryl ester containing at least one polyunsaturated fatty acid moiety.

**2.** A compound selected from the group consisting of the addition product of a dialkyl phosphonate to an alkyl ester of a polyunsaturated fatty acid and mixtures thereof.

**3.** The compound of claim **2** in which the dialkyl phosphonate is diethyl phosphonate and the alkyl ester is ethyl linoleate.

**4.** The compound of claim **2** in which the dialkyl phosphonate is di-2-ethylhexyl phosphonate and the alkyl ester is butyl linoleate.

**5.** The compound of claim **2** in which the dialkyl phosphonate is di-2-ethylhexyl phosphonate and the alkyl ester is 2-ethylhexyl linoleate.

**6.** The compound of claim **2** in which the dialkyl phosphonate is diethyl phosphonate and the alkyl ester is butyl linoleate.

**7.** The compound of claim **2** in which the dialkyl phosphonate is dibutyl phosphonate and the alkyl ester is 2-ethylhexyl linolenate.

**8.** A compound selected from the group consisting of the addition product of a dialkyl phosphonate to a glyceryl ester containing at least one polyunsaturated fatty acid moiety.

**9.** The compound of claim **8** in which the dialkyl phosphonate is diethyl phosphonate and the glyceryl ester is soybean oil.

**10.** The compound of claim **8** in which the dialkyl phosphonate is di-2-ethylhexyl phosphonate and the glyceryl ester is soybean oil.

**11.** The compound of claim **8** in which the dialkyl phosphonate is dibutyl phosphonate and the glyceryl ester is cottonseed oil.

**12.** The compound of claim **8** in which the dialkyl phosphonate is diethyl phosphonate and the glyceryl ester is safflower seed oil.

**13.** The compound of claim **8** in which the dialkyl phosphonate is di-2-ethylhexyl phosphonate and the glyceryl ester is oleo oil.

**14.** The compound of claim **8** in which the dialkyl phosphonate is di-2-ethylhexyl phosphonate and the glyceryl ester is lard.

15. A process for the preparation of a dialkyl phosphonated derivative of an ester of a polyunsaturated fatty acid comprising the free radical addition of a dialkyl phosphonate to at least one double bond in a polyunsaturated fatty acid-containing compound selected from the group consisting of an alkyl ester of a polyunsaturated fatty acid and a glyceryl ester containing at least one polyunsaturated fatty acid moiety.

16. The process of claim 15 in which the alkyl ester is a butyl ester of tall oil fatty acids.

17. The process of claim 15 in which the polyunsaturated fatty acid-containing compound is a 2-ethylhexyl ester of cottonseed oil fatty acids.

18. The process of claim 15 in which the polyunsaturated fatty acid-containing compound is a 2-ethylhexyl ester of safflower seed oil fatty acids.

19. The process of claim 15 in which the glyceryl ester is lard.

20. The process of claim 15 in which the glyceryl ester is safflower seed oil.

21. The process of claim 15 in which the dialkyl phosphonate is dibutyl phosphonate and the polyunsaturated fatty acid-containing compound is the 2-ethylhexyl ester of tall oil fatty acids.

22. The process of claim 15 in which the dialkyl phosphonate is dibutyl phosphonate and the polyunsaturated fatty acid-containing compound is the butyl ester of soybean oil fatty acids.



23. The process of claim 15 in which the dialkyl phosphonate is di-2-ethylhexyl phosphonate and the polyunsaturated fatty acid-containing compound is soybean oil.

24. The process of claim 15 in which the dialkyl phosphonate is diethyl phosphonate and the polyunsaturated fatty acid-containing compound is cottonseed oil.

25. The process of claim 15 in which the dialkyl phosphonate is diethyl phosphonate and the polyunsaturated fatty acid-containing compound is safflower oil.

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