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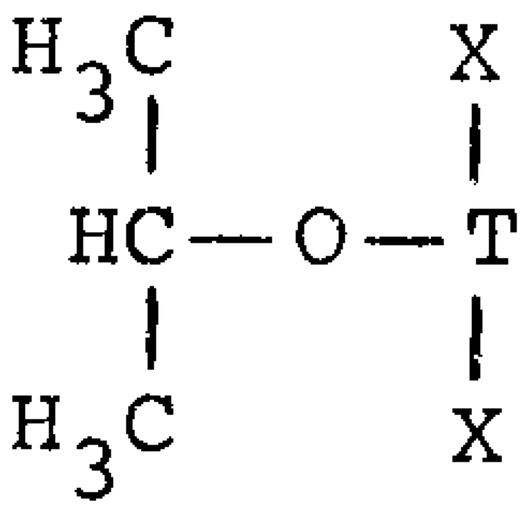
(54) Titre : CHELATES DE TITANE STABLES A BASSE TEMPERATURE
(54) Title: LOW-TEMPERATURE-STABLE TITANIUM CHELATES



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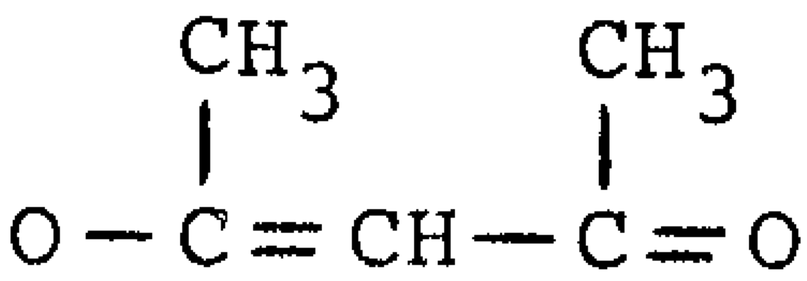

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(57) Abrégé/Abstract:
Titanium chelates of the formula (see formula I) in which X represents (see formula II) and R is selected from the group consisting of ethyl, n-propyl, n-butyl, i-butyl and t-butyl, and mixtures thereof are disclosed. The compounds are prepared by mixing diisopropoxytitanium bis-(acetylacetonate) $(i\text{-PrO})_2TiX_2$ with dialkoxytitanium bis(acetyl-acetonate) $(RO)_2TiX_2$ and allowing the mixture to react at a temperature of from 1 to 100°C above the melting point of the higher melting component of the mixture for 0 to 60 minutes. The compounds are useful as adhesion promoters between inorganic and organic surfaces and printing inks and for coating sheet glass, hollow glassware and glass fibres to improve mechanical and optical properties thereof.

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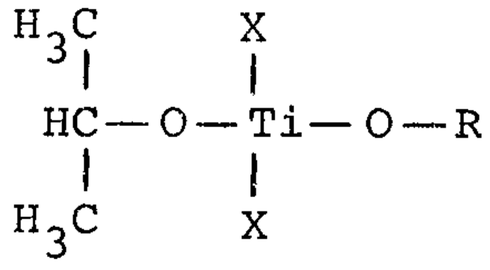
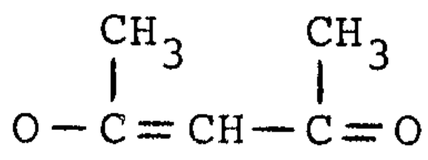
ABSTRACT

Titanium chelates of the formula



in which X represents



and R is selected from the group consisting of ethyl, n-propyl, n-butyl, i-butyl and t-butyl, and mixtures thereof are disclosed. The compounds are prepared by mixing diisopropoxytitanium bis-(acetylacetonate) $(i\text{-PrO})_2TiX_2$ with dialkoxytitanium bis(acetyl-acetonate) $(RO)_2TiX_2$ and allowing the mixture to react at a temperature of from 1 to 100°C above the melting point of the higher melting component of the mixture for 0 to 60 minutes. The compounds are useful as adhesion promoters between inorganic and organic surfaces and printing inks and for coating sheet glass, hollow glassware and glass fibres to improve mechanical and optical properties thereof.

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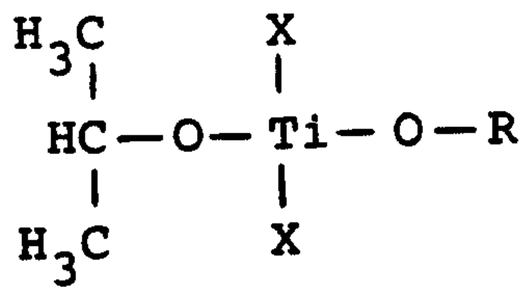
The invention relates to novel titanium chelates, in particular to novel titanium acetylacetone chelates and mixtures thereof and to a method for preparing these compounds.

The preparation of titanium chelates of the formula $(RO)_2TiX_2$, in which X is an acetylacetonate radical and R is a C_{2-4}-alkyl radical either branched or unbranched, is in general carried out by reaction of titanium ortho esters of the formula $Ti(OR)_4$ with two equivalents of the chelating agent acetylacetone with the elimination of two equivalents of the alcohol ROH. The titanium chelates so prepared are usually left in the reaction solution and the alcohol formed in the reaction is not separated off. This was the only known manner to achieve moderate low-temperature stability of these substances. When such acetylacetonate solutions are used in industry, very low flash points due to the alcohol content have to be accepted. Also the effects achieved often vary substantially and are therefore not satisfactory. Moreover, the alcohol present in the solution enters the waste air and/or the waste water and has to be removed therefrom by expensive procedures. The separation by distillation of the alcohols formed in the reaction results in viscous liquids whose setting points are above -18°C or which crystallise spontaneously over a short period of time even at room temperature **and thus become unusable.**

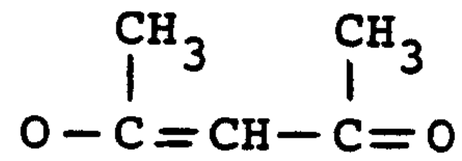
One aspect of the present invention is to develop products which allow easy and low-risk handling and have a reliably good effect, especially in the treatment of surfaces. A further aspect **is to lower the solvent content of the product to reduce the environmental pollution.**

According to one aspect, the invention provides for a process for producing a compound of the formula



comprising contacting $(i\text{-}PrO)_2\text{-}TiX_2$ with $(RO)_2TiX_2$

wherein X is



R is selected from the group consisting of ethyl, n-propyl, n-butyl, n-butyl and t-butyl, and mixtures thereof; the molar ratio of $(i\text{-}PrO)_2\text{-}TiX_2$ to $(RO)_2TiX_2$ is in the range of from 1:0.1 to 1:1.9; said process is carried out at a temperature between 20°C and 100°C above the melting point of the higher melting component of $(i\text{-}PrO)_2\text{-}TiX_2$ or $(RO)_2TiX_2$.

The invention further relates to a process for the preparation of titanium chelates $(i\text{-}PrO)(RO)TiX_2$ and to applications of these titanium chelates for increasing the adhesiveness of printing inks on inorganic and organic surfaces and for coating sheet glass, hollow glassware and glass fibres for improving mechanical and optical properties thereof.

The titanium chelates according to the invention have never been prepared in pure form.

The previously used processes for the preparation of titanium acetylacetonates having different alkoxy radicals on the central atom, such as, for example, mixing the titanium ortho esters $(i\text{-}PrO)_4Ti$ and $(RO)_4Ti$, reacting this mixture with the chelating agent acetylacetone and removing the alcohols formed in

the reaction by distillation or mixing one of the starting chelates $(R'O)_2TiX_2$ with the titanium ortho ester $(R"O)_4Ti$, where R' is R or i-Pr, R" is R or i-Pr, and R' ≠ R", reacting the mixture with the chelating agent and removing the alcohols formed in the reaction by distillation, do not lead to the uniform final products having the stoichiometry predetermined by the ratio of the titanium compounds used. These processes merely lead to non-uniform solutions of mixed titanium chelates having variable compositions and the disadvantageous properties resulting therefrom.

The titanium chelates $(R'O)_2TiX_2$ which are suitable as starting materials for the process according to the invention are prepared separately in a preceding reaction in a manner known per se by mixing the corresponding titanium ortho esters $Ti(OR')_4$ with the chelating agent acetylacetone and distilling off the alcohol R'OH formed in the reaction. The components are then reacted with one another at temperatures between 1°C to 100°C, preferably 1°C to 30°C, above the melting point of the higher melting component, for from about 0 to about 60 minutes, preferably for about 30 minutes.

Spectroscopic and chromatographic analyses clearly show that the starting chelates are no longer present in the reaction products obtained and the compounds according to the invention have been formed:

$$(i\text{-}PrO)_2TiX_2 + (RO)_2TiX_2 \longrightarrow 2\ (i\text{-}PrO)(RO)TiX_2$$

If it is desired that the final product with respect to the alkyl groups R and i-propyl present has a composition which differs from the 1 : 1 ratio, one of the components can be used in the appropriate excess amount in the reaction described above. The molar ratio of components can vary in a broad range, typically from 1:0.1 to 1:1.9. This gives the mixtures of the titanium chelate (i-PrO) (RO)TiX_2 with excess titanium chelate (R'O)TiX_2, which can be also obtained by mixing the mixed titanium chelate (i-PrO)(RO)TiX_2 with further starting chelate $(R'O)_2TiX_2$.

The procedure according to the invention ensures that the reaction product always has the preselected stoichiometric composition. The procedure according to the invention further ensures that the alcohol R'OH formed in the reaction is separated and thus recovered in the pure form. This alcohol can be recycled into the synthesis of the basic titanates $Ti(OR')_4$ and is not lost in a manner polluting the environment.

Example 1

200 g of acetylacetone are added dropwise with cooling to 284 g of titanium tetraisopropoxide. After stirring for a further half an hour, the liberated isopropanol (120 g) is completely distilled off. A setting point of -18°C is measured for the residue diisopropoxytitanium bis(acetylacetonate). In a second reaction vessel, 340 g of titanium tetra-n-butoxide are reacted in the same way with 200 g of acetylacetone, and 148 g of n-butanol are then distilled off. The reaction product di-n-butoxytitanium bis(acetylacetonate), if not immediately processed further, forms crystals having edges several centimetres in length at room

temperature. The residue from the first distillation is mixed with the residue of the last distillation and the mixture is stirred at room temperature for another 30 minutes. The reaction product isopropoxy-n-butoxytitanium bis(acetylacetonate) has a setting point of -42°C.

Example 2

Solvent-free diisopropoxytitanium bis(acetylacetonate) is prepared from 284 g of titanium tetraisopropoxide and 200 g of acetylacetone as described in Example 1. The second reaction vessel is charged with 228 g of titanium tetraethoxide. 200 g of acetylacetone are added dropwise with cooling, and 92 g of ethanol are then distilled off. The remaining diethoxytitanium bis(acetylacetonate) crystallises, if the bottom temperature in the distillation flask towards the end of the distillation is allowed to drop below 35°C and melts again at 44 to 50°C. The residue from the first distillation is added to the residue from the second distillation at 60°C, and the reaction mixture is kept at 60°C for a further 30 minutes. A setting point of -33°C is measured for the reaction product ethoxyisopropoxytitanium bis-(acetylacetonate) which is formed quantitatively.

Example 3 which follows demonstrates the adhesion-increasing effect of the substances according to the invention as additives in nitrocellulose lacquers:

Example 3

A nitrocellulose white lacquer containing 25 percent of nitrocellulose is mixed with 1 percent of isopropoxy-n-butoxy-titanium bis(acetylacetonate). The untreated lacquer is applied

by means of a knife to one half of a degreased polypropylene sheet and the lacquer to which the titanium chelate according to the invention has been added to the other half. The sheet thus treated is dried in air for 5 minutes. Two adhesive strips are then attached horizontally and pulled off in one go, beginning in each case from opposite ends. Comparison of the two sheet halves shows that more than 95 percent of the untreated lacquer was removed from the sheet but only about 50 percent of the lacquer treated according to the invention.

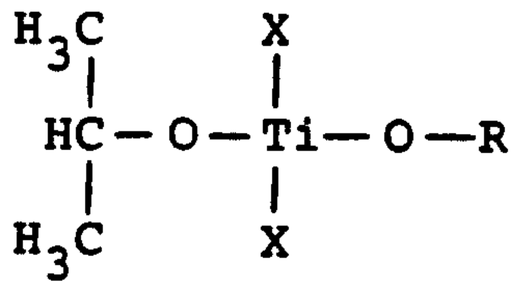
Comparative Example

The comparative example which follows does not form part of the present invention:

284 g of titanium tetraiospropoxide and 340 g of titanium tetra-n-butoxide are mixed. 400 g of acetylacetone are added dropwise, and the alcohol mixture liberated is distilled off. This mixture of isopropanol and n-butanol cannot be separated into the components in a cost-effective manner and has to be disgarded. Furthermore, the composition of the alcohol mixture is dependent on the change in pressure during the distillation and is therefore difficult to reproduce. This also has an effect on the composition of the product, as evidenced by the TiO_2 contents varying between 19.5 and 22.5 percent in several experiments.

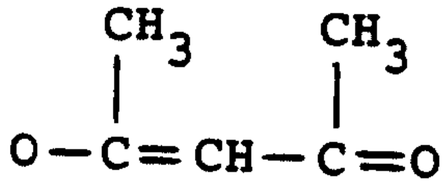
What is claimed is:

1. A process for producing a compound of the formula



comprising contacting $(i\text{-}PrO)_2\text{-}TiX_2$ with $(RO)_2TiX_2$

wherein X is



R is selected from the group consisting of ethyl, n-propyl, n-butyl, n-butyl and t-butyl, and mixtures thereof;

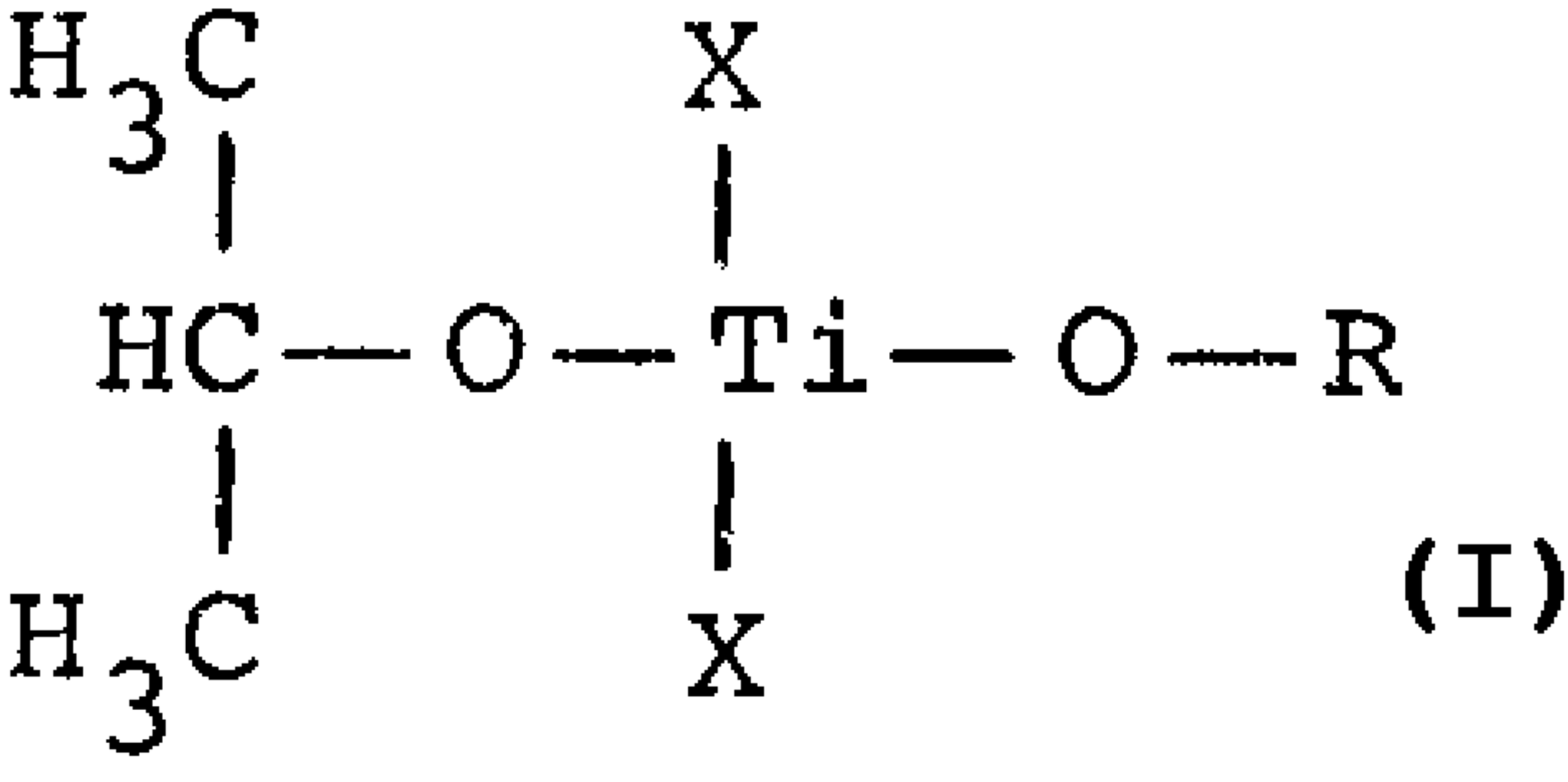
the molar ratio of $(i\text{-}PrO)_2\text{-}TiX_2$ to $(RO)_2TiX_2$ is in the range of from 1:0.1 to 1:1.9;

said process is carried out at a temperature between 20°C and 100°C above the melting point of the higher melting component of $(i\text{-}PrO)_2\text{-}TiX_2$ or $(RO)_2TiX_2$.

2. A process according to claim 1, wherein said process is carried out at a temperature between 1°C and 30°C above the melting point of the higher melting component of $(i\text{-}PrO)_2\text{-}TiX_2$ or $(RO)_2TiX_2$.

3. A process according to claim 1, wherein process is carried out for from about 0 to about 60 minutes.

4. A process according to claim 1, wherein thè molar ratio is 1:1.



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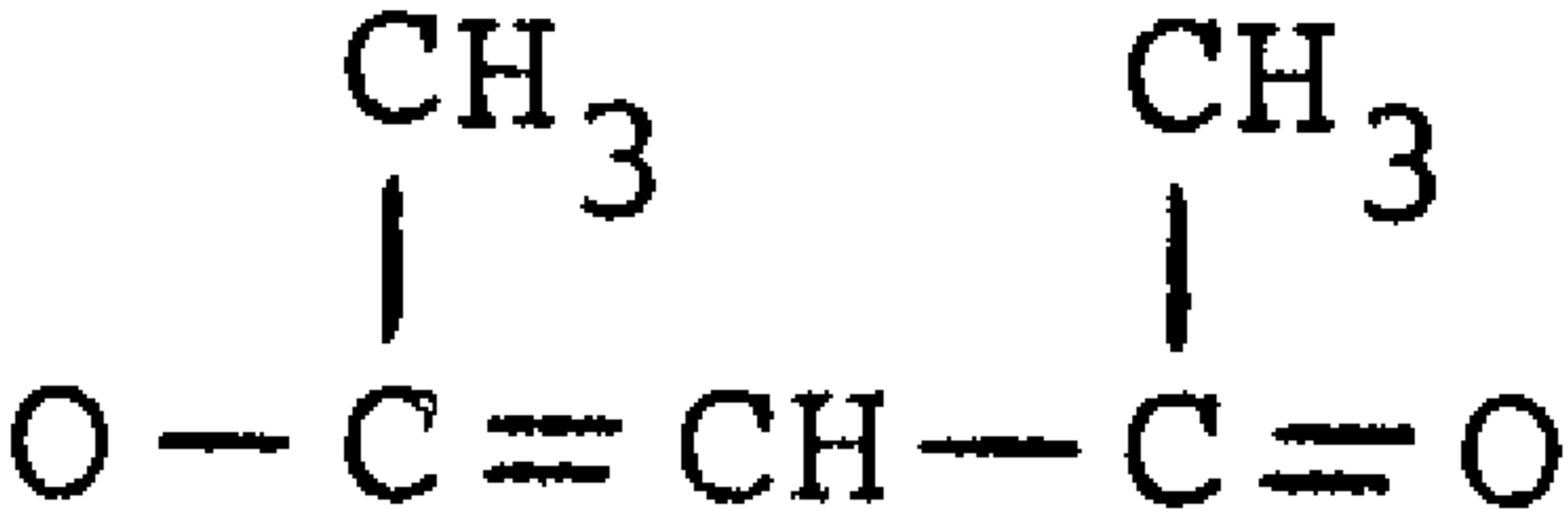

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