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METHOD FOR THE PRODUCTION OF HIGHER MOLECULAR MERCAPTALS AND MERCAPTOLS

Erik Schirm, Dessau/Anhalt, Germany; vested in the Alien Property Custodian

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It is known that mercaptans with oxo-compounds i. e. with aldehydes and ketones allow of being condensed, by means of hydrogen-halide, to mercaptals or mercaptols respectively. However, those condensation-products were hitherto made and reapplied in technical proportions but in exceptional cases.

Now it has been found that technically valuable higher molecular mercaptals and mercaptols respectively are obtainable for many purposes in condensing mercaptans with no less than 8 C atoms in the molecule and particularly those of the aliphatic series and eventually in the presence of diluents, with oxo-compounds viz. aldehydes, ketones and other compounds containing the carbonyl group or with the ethers ("acetals") or carboxylic acid esters of the oxo-compounds. It was surprising that, as stated within the limits of the present method, the condensation of the oxo-compounds with the higher molecular mercaptans takes an absolutely smooth course. The present procedure therefore constitutes a simple and productive method for the formation of very high molecular and multifarious compounds by the possibility of introducing two higher molecular hydrocarbon residues in a single operation being combined very fastly by means of sulfur atoms into the molecule of oxo-compounds of very different kinds. The thus obtained mercaptals or mercaptols respectively are—which is remarkable—perfectly fast to the reaction of acids and alkalis, apart a few exceptions depending on a peculiar structure of the initial stuffs.

As initial materials for the present invention we may consider any aliphatic mercaptans of a straight or of a ramified chain, further any cycloaliphatic, aromatic, fatty-aromatic, cycloaliphatic-aromatic and cycloaliphatic-fattyaromatic mercaptans and the like such as octyl-, dodecyl-, oleyl-, docosyl-mercaptan, as well as the 2-decahydronaphthyl-, 1-and 2-naphthyl-, 1-menaphthyl, tetrahydro-menaphthyl-mercaptan, the 9-mercaptomethyl-octohydro-anthracene etc. The carbon chain of those mercaptans may also be interrupted one or several times by hetero-atoms or hetero-atom groups such as O,S,NR,CO, SO_2, CO.O, CO.NR, SO_2.NR(R=H or hydrocarbon residue).

For the oxo-compounds serving as second initial component we may, on principle, apply all wellknown oxo-compounds as far as the carbonyl groups contained therein—eventually also several times—are of a sufficient reactivity.

As single or manifold oxo-compounds appliable for the present method there are to be mentioned: formaldehyde and acetaldehyde in their monomeric or polymeric forms, crotonic aldehyde, glyoxal, acetone, palmitone, stearone, mesityl-oxide, acetyl-acetone, cyclo-hexanone, acetophenone, stearo-phenone, benzaldehyde, benzophenone, cinnamic-aldehyde and the like, as well as their ethers and esters such as methylal, ethylal, acetal, ethylidene di-acetate etc. The oxo-compounds may also contain substituents such as nitro groups, further hydrophile groups such as hydroxyl groups, substituted or non-substituted amino groups, quarternary ammonium groups, ether-, carboxyl-, sulfonyl-, sulfonic acid groups and the like or such atoms or atom groups which allow of being easily converted into hydrophile atom groups such as halogen atoms, S, SH, —S.S—. Oxo-compounds of this kind are e. g. aldol, acetonyl-methyl alcohol, glucose, acetic acid ester, levulinic acid, benzoin, phenoxy-acetone, o-benzoyl-benzoic acid, p-tolyl-acetonyl-sulfone, benzaldehyde-m-sulfonic acid, mono- and dichloroacetal, amino-acetal, chloral, mono-chloroacetone, ω-chloro-acetophenone.

The mercaptals and mercaptoles respectively produced according to the present invention of the oxo-compounds and of the higher molecular mercaptans are of a wax-like character especially when the high-molecular cetyl-, octadecyl-, eicosyl, docosyl-, montanyl-mercaptans and the like are applied; in all industries where wax is worked up they will be used with good results.

Moreover the mercaptals and mercaptoles respectively are—either alone or after the introduction of hydrophile atom groups—most suitable as wetting-out-, dispersing-, lathering-, deterging-, dissolving-, softening agents and the like in the washing-means-, textile-, leather-, paper- and similar industries.

The nitro-substituted mercaptals and mercaptoles respectively are further apt e. g. as intermediate products for the manufacture of dyestuffs, means of combating pests and medicaments.

Example 1

1 weight-part of paraformaldehyde is suspended in a solution of 17 weight-parts of cetyl-mercaptan in 34 weight-parts of benzene; then, while stirring at room-temperature, we introduce hydrogen chloride-gas into the mixture until the suspended paraformaldehyde has disappeared and no free mercaptan being any longer detectable in the solution. The benzene is then dis-

tilled off under reduced pressure and thus the formaldehyde-dicetyl-mercaptal is obtained as residue in the form of a wax-like mass.

Example 2

11 weight-parts of mono-chloro-acetal and 21 of n-octyl-mercaptan are mixed, whereupon hydrogen chloride-gas is introduced until the reaction-component is completely converted. The thus obtained chloro-acetaldehyde-dioctyl-mercaptal, in oil-form, is now liberated from the hydrochloric acid by washing with water. The Cl atom present in this compound may be substituted by a SO_3H group, in which case we obtain a product of surface-active properties and soluble in water.

Example 3

Into a mixture of 2 weight-parts of dodecyl-mercaptan, 1 of glucose and 10 of alcohol, an amount of hydrogen chloride-gas is introduced while stirring and cooling until the mercaptan has completely disappeared. Then the reaction-mixture is poured into a large quantity of water, whereupon the amorphously separated reaction-product is filtered off and dried. The thus obtained glucose-didodecyl-mercaptal is applied as an excellent agent to emulsify in water or in aqueous solutions the most heterogeneous organic liquids, fats, oils and waxes otherwise unsoluble in water.

Example 4

3 weight-parts of levulinic acid and 14 of octadecyl-mercaptan are dissolved in 45 weight-parts of ether. To this solution we admix half the volume of concentrated etheric hydrochloric acid; the mixture is then kept for one day at room temperature, whereupon the formed colourless crystal mass is sucked off. The resulting reaction product consisting of di-octadecyl-mercapto-valerianic acid is then re-crystallized from alcohol (melting point 72–74°C). This product allows of being applied as such or in the form of its esters or salts instead of wax.

Example 5

151 weight-parts of m-nitro-benzaldehyde and 573 of octadecyl-mercaptan are dissolved at room-temperature in 900 weight-parts of benzene. While cooling with cold water we introduce, at 20–25° C, an amount of hydrogen chloride-gas until the mixture is solidified to a paste-like mass. After a while we suck off and after drying we obtain appr. 70% of the total amount of the developed m-nitro-benzaldehyde-dioctadecyl - mercaptal in the form of a white powder (melting point 54–55°C). The residue is obtained by evaporating the benzene from the benzene-solution. The reaction-product is obtained in a nearly quantitative yield.

ERIK SCHIRM.