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ALIEN PROPERTY CUSTODIAN

INTERMEDIATES FOR DYESTUFFS

Willem Mees, Mortsel, near Antwerp, Belgium;
vested in the Alien Property Custodian

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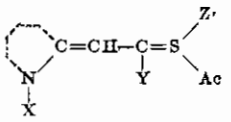
This invention relates to the preparation of intermediates for dyestuffs, constituted most probably according to the following formula:



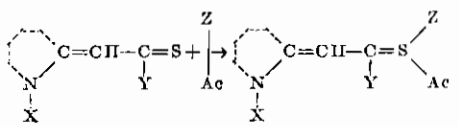
wherein:

is some nitrogen containing ring nucleus, such as for instance thiazole, selenazole, or the like, which may be further substituted by alkyl, phenyl or phenylene or other polynuclear rings, while Z and X represent alkyl or a substituted alkyl such as for instance aralkyl, Y represents alkyl, a substituted alkyl such as for instance an aralkyl or phenyl, and Ac represents any acid radical, such as for instance halogen, alkyl sulphate, toluenesulphonate or the like.

According to the invention, now these compounds can easily be prepared by reacting the thioketones (described in an application filed of even date herewith by Polydoor de Smet and myself, as joint inventors), under the influence of heat, with an ester of the general structure Z—Ac, wherein Z and Ac have the meaning given above. In this reaction the ester is simply fixed to the thioketone.

The condensation can also be carried out in the presence of a solvent for the thioketone such as for instance toluene or benzene, and is preferably effected by heating the components under a reflux condenser.

The reaction is believed to take place according to the following equation:



wherein the symbols used have the meaning given above.

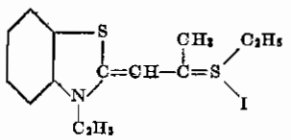
My invention is however not defined by this equation, nor limited by it; it is essentially characterised by the new method of preparation and by the specific compounds obtainable thereby.

These intermediates are fit for use in the preparation of symmetrical and asymmetrical carbocyanines, which are substituted at the central carbon atom of the methine chain.

To this end, the new compounds are heated in the presence of an acid binding agent with 2-alkyl substituted quaternary salts. The dyestuff condensation proceeds under the formation of a mercaptan of the general formula HS—Z and an acid of the formula HAc.

Example 1

In the preparation of the intermediate product characterised by the following probable formula:

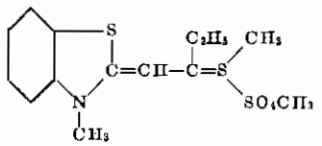


23 gr. N-ethyl-benzthiazolidene-methyl-methyl-thioketone and 18 gr. ethyliodide are heated 1 hour under the reflux condenser in a boiling water bath. The mixture is shaken repeatedly whereupon it solidifies. After cooling it is washed with dry ether. The yield is 29 gr. (73% of the calculated amount). After recrystallization from ethylalcohol small grey-brown needles are obtained, which melt at 228° to 230° C under decomposition.

Determination of S: 16.04% (calculated 16.36%).

Example 2

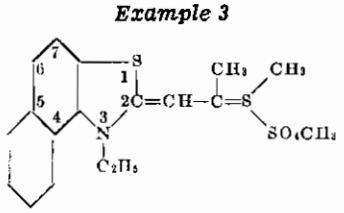
The preparation of the intermediate product characterised by the following probable formula:



To 23 gr. N-methylbenzthiazolidene-methyl-ethyl-thioketone suspended in 100 cc. dry benzene are added 14 gr. dimethyl-sulphate and the mixture is shaken several times and heated 1 hour under the reflux condenser in a boiling water bath. After cooling, the mass is filtered by suction, washed with acetone and dried. The yield is 33 gr. (93% of the theoretical). After recrystallization from a mixture of alcohol and acetone small brown-yellow needles are obtained which melt at 190° C.

Determination of S: 26.66% (calculated 26.59%).

Example 3

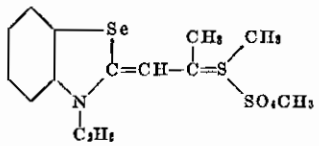


To 28 gr. N-ethyl-4-5-benzo-benzthiazolidene-methyl-methyl-thioketone suspended in 150 cc. dry benzene are added 14 gr. dimethylsulphate and the mixture is heated under repeated shaking 1 hour under the reflux condenser in a boiling water bath. After cooling, the mass is filtered by suction and washed with a little acetone. The yield is 28 gr. (66% of the calculated amount).

After recrystallization from alcohol small, light yellow, silky needles are obtained, which melt at 213–214° C.

Determination of S:23.35% (calculated 23.3%)

Example 4

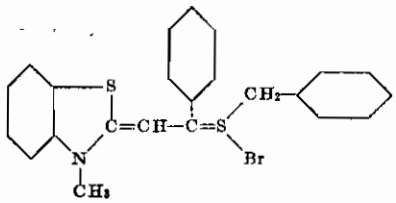


To 28 gr. N-ethyl-benzselenazolidene-methyl-methylthioketone dissolved in 100 cm. benzene are added 14 gr. dimethylsulphate and the mixture is heated under repeated shaking 1 hour under the reflux condenser in a boiling water bath. After cooling the precipitate is filtered by suction and washed with a little acetone.

The yield is 31 gr. (77% of the calculated amount).

After recrystallization from alcohol small, light yellow needles are obtained. Melting point at 174°.

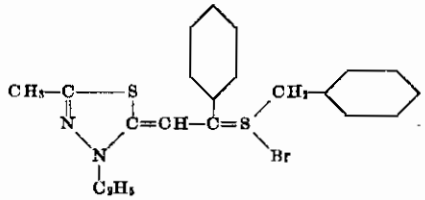
Example 5



56 gr. finely divided (N-methyl-benzthiazolidene-methyl) phenylthioketone and 35 gr. benzylbromide are thoroughly mixed and heated during one hour at 110° C. The solid mass is purified by washing with acetone. Recrystallization from a mixture of acetone and methylalcohol gives yellow crystals, melting by decomposition from 155° to 176° C.

Determination of S: 14.35% (calculated amount: 14.1%).

Example 6



52 gr. finely divided (N-ethyl-5-methyl-thiodiazolidene-methyl)-phenylthioketone and 35 gr. benzylbromide are strongly mixed and heated for one hour at 110° C. The crude product is washed with acetone, and after recrystallization from a mixture of acetone and methylalcohol are formed yellowish crystals, melting by decomposition from 135° to 155° C.

Determination of S: 14.80% (calculated amount: 14.75%).

Various changes may be made in the details disclosed in the foregoing specification without departing from the invention or sacrificing the advantages thereof.

WILLEM MEES.