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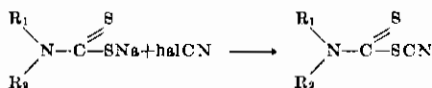
ALIEN PROPERTY CUSTODIAN

PROCESS FOR MANUFACTURE OF SENEVOLS

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Alien Property Custodian

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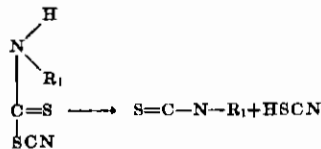
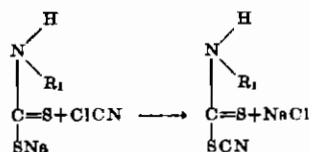
When a halogenide of cyanogen is caused to react upon a dithiocarbamate, a symmetrical monosulphide of thiuram is obtained at the room temperature. It is furthermore known that when the reaction is effected at a sufficiently low temperature, practically in the neighborhood of 0° centigrade, there is observed an intermediate compound according to the following reaction:



in which R₁ and R₂ are any organic radicals. Such compounds may be considered as mixed anhydrides of a dithiocarbamic acid and cyanic or thiocyanic acid. They can be condensed with a second molecule of a dithiocarbamate to lead to monosulphides of thiuram.

I have found that, when a dithiocarbamate derived from a primary amine is used as starting material, the reaction follows another way.

There is readily conjectured the formation of the mixed anhydride by action of a molecule of cyanogen halogenide upon a molecule of dithiocarbamate. But such anhydride is certainly less stable than those responding to the above indicated formula, for it immediately disintegrates by splitting into the corresponding senevol and sulphocyanhydric acid. The reactions proceed according to the following scheme:



It will, therefore, be sufficient to introduce an halogenide of cyanogen into a solution of a dithiocarbamate derived from a primary amine, until disappearance of the totality of the latter, in order to obtain senevols.

In the course of the introduction of halogenide of cyanogen there occurs a turbidness and the senevol sought for progressively separates at the same time as there is observed the presence of

sulphocyanhydric acid in increasing quantity. This reaction of production results in quantitative yields and in products of very good quality.

The following examples are given for the purpose of illustration, but not of limitation, in order to show how the invention may readily be carried into practical effect.

EXAMPLE I.—Production of phenylsenevol

93 grams of aniline are transformed into phenyldithiocarbamate according to any of the known processes by mixing aniline, water, carbon sulphide and the alkaline agent. The solution is filtered, whereafter chloride of cyanogen is introduced. The aqueous liquid becomes turbid, then phenylsenevol is progressively separated, while the formation of sulphocyanide is observed in the aqueous liquid. When all dithiocarbamate has disappeared (drop-tests with perchloride of iron), the further introduction of chloride of cyanogen is stopped and the oil decanted and distilled. After one single distillation there are obtained 120 grams of phenyl-senevol in pretty nearly pure state.

EXAMPLE II.—Production of O-tolylsenevol

By replacing aniline used in the preceding Example with 107 grams of O.toluidine and by operating as per above there are obtained 140 grams of O.tolylsenevol.

EXAMPLE III.—Production of α-naphtylsenevol

By replacing aniline used in the Example I with 143 grams of α-naphtylamine there are obtained 150 grams of α-naphtylsenevol in crystalline state. By one single crystallisation in alcohol there are obtained the fine characteristic needles of P. F.=57° Centigrade.

EXAMPLE IV.—Production of β-naphtylsenevol

When chloride of cyanogen is introduced into a solution of β-naphtyldithiocarbamate there is obtained β-naphtylsenevol in gray flakes which, when recrystallized in alcohol, had the P. F. 61° centigrade.

In all of the previous Examples the introduction of halogenide of cyanogen is stopped whenever it is observed that, by drop-test with ferric chloride, all brown colouring due to dithiocarbamate has disappeared to leave but the characteristic red colouring due to ferric sulphocyanide.

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