

ALIEN PROPERTY CUSTODIAN

PREPARATION OF ORGANIC DIISOCYANATES

Heinrich Rinke, Leverkusen-Schlebusch, 2, and
Karl Taube, Leverkusen-L. G. Werk, Germany;
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The present invention relates to a new process for preparing organic diisocyanates.

Up to the present, organic diisocyanates have been prepared by causing phosgene to react upon diamine dichlorohydrates in the presence of an indifferent organic solvent at an elevated temperature care being taken that the hydrogen chloride evolved is quickly removed from the reaction mixture. The said reaction proceeds relatively slowly as the dichlorohydrates are practically insoluble in organic solvents.

It is the object of our present invention, to do away with these disadvantages and to develop a new process, which allows one to prepare organic diisocyanates in an easy and economical manner.

With this and other objects in view our invention comprises the combination of the following steps:

- (a) we are starting from free diamines,
- (b) these diamines are added into a solution of phosgene in an indifferent solvent at a temperature at which no evolution of hydrogen chloride occurs;
- (c) thereupon the temperature is raised to a point at which hydrogen chloride is split off,

care being taken, that the amount of phosgene during step b is at least 1 mol per each mol of diamine and that during step c the amount of phosgene is at least about 2 mols per each mol of diamine, including that amount of phosgene, which has been consumed during step b. In accordance with a special method of working the amount of phosgene is at least about 2 mols from the very beginning so that the introduction into the reaction mixture of additional phosgene during step c can be dispensed with.

It is believed, that in the course of step b there is formed a chlorohydrate of the aminocarbanic acid chloride of the diamine employed. This intermediate product separates out from the solution and is converted by the additional phosgene during step c into the diisocyanate, hydrogen chloride being split off. As a matter of fact, the chlorohydrate separating out during step b can be isolated from the reaction-mixture prior to the performing of step c.

Our new process can be employed for the preparation of various diisocyanates, for instance of those of the aliphatic or aromatic series. The carbon chains may also contain hetero atoms such as sulphur or oxygen. Suitable indifferent solvents are aromatic hydrocarbons and the alkyl and halogen substitution products such as toluene

or dichlorobenzene. During step b the reaction mixture is preferably kept at a temperature below about 10°C whereas during step c a higher temperature of up to about 200°C is preferred.

In practice we are working at a temperature between about 140—about 170° C. At the end of the reaction a stream of an indifferent gas may be passed through the solution in order to remove excess hydrogen chloride and excess phosgene. This is the more advisable as we prefer to work with an excess of phosgene during step b as well as during step c.

The following examples illustrate the invention without however restricting it thereto the parts being by weight:

Example 1

Into a solution of 120 parts of phosgene in 500 parts of o-dichlorobenzene there is added a solution of 116 parts of hexamethylenediamine in 500 parts of o-dichlorobenzene drop by drop while well cooling and stirring at a temperature of not more than +5°. Immediately the monochlorohydrate of the 1-aminohexamethylene carbanic acid chloride is separated. While stirring quickly the suspension is heated to 150–160°; within 7–8 hours 400 parts of phosgen are added. Hexamethylene diisocyanate is formed by the splitting off of hydrochloric acid. After the evaporating of the o-dichlorobenzene, the hexamethylenediisocyanate is distilled under 10mm at 124°. It is obtained in a yield of more than 80%.

Example 2

Into a solution of 30 parts of phosgene in 110 parts of o-dichlorobenzene there is added a solution of 50 parts of the mixture of undekamethylene- and dodekamethylenediamine (1:1) in 200 parts of o-dichlorobenzene while stirring and cooling. While adding further 240 parts of phosgene the suspension of the chlorohydrate carbanic acid chloride is heated for 4 hours to 150°. The precipitate having been dissolved and the solvent having been distilled off the mixture of the undekamethylene and dodekamethylenediisocyanate is obtained in a yield of more than 90%. $Kp_{10}=168-182^{\circ}$.

Example 3

Into a solution of 60 parts of phosgene in 220 parts of o-dichlorobenzene there is added a solution of 67 parts of 1,3-diaminocyclohexane in 400 parts of o-dichlorobenzene while stirring and cooling. Then the suspension formed is heated to 150–160°, kept at this temperature for 8–9 hours

and meanwhile 300 parts of phosgene are added. After removal of the solvent by distillation hexahydro-m-phenylenediisocyanate of the boiling-point 89° is obtained at 1.8 mm in a good yield.

Example 4

The hot solution of 244 parts of dianisidine in 900 parts of o-dichlorobenzene is added while cooling to a solution of 120 parts of phosgen in 450 parts of o-dichlorobenzene. Then 110° parts of phosgene are added while heating to 150-160°. The still hot solution is treated with animal charcoal, heated and sucked off. The 3,3'-diethoxydiphenyl-4,4'-diisocyanate separates in a crystallized state. (Fp. 121-122°).

Example 5

The solution of 50 parts of 3,3'-diaminodi-

propylether in 260 parts of o-dichlorobenzene is poured into a solution of 50 parts of phosgene in 130 parts of o-dichlorobenzene at a temperature of below 0°. After the heating up to 50° the carbamic acid chloridechlorohydrate which has been precipitated in the cold is dissolved. At 130° after the adding of further phosgene hydrochloric acid is split off, whereupon the 3,3'-diisocyanate-dipropylether, which boils at 102-104° at 2,6mm is formed. The diisocyanate is a waterlight liquor having a sharp smell. Upon adding aniline while heating strongly it forms the 3,3'-bis-(ω -phenylureido)-dipropylether which melts at a temperature of 177-179°.

HEINRICH RINKE.
KARL TAUBE.