A Simplified Procedure for the Preparation of 1,2-Dichloro-1-(N,N-dialkylamino)ethenes and 2-Chloro-1,1-bis(dialkylamino)ethenes

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1,2-Dichloro-1-(X,N-dialkylamino)ethenes (3, Alkyl = CH₃ or C₂H₅) are obtained by reaction of dichloroacetylene, prepared in situ from trichloroethylene and lithium dialkylamide in ether with an excess of dichloroacetylene. Further reaction of the compounds 3 with an excess of dialkylamine at 30°C or at reflux gives the chloroketenamines 4. The dialkylamino derivatives can also be obtained by adding trihalo-ethene to a suspension of sodamide in dimethylformamide.

3,β-Dichloroamines (3) and chloroketenamines (4) are potentially useful compounds in organic synthesis. Compounds 4 have been used for the synthesis of ynediamines 5. Earlier published synthetic procedures for the compounds 3 and 4 involved the intermediate isolation of the hazardous dichloroacetylene (2)1 or the use of high pressure in an autoclave.2

We here present simplified procedures, enabling the reactions to be carried out under usual laboratory conditions. The 3,β-dichloroamines 3 were prepared by reaction of a lithium dialkylamide suspension or solution in ether, followed by heating with an excess of dialkylamines. Subsequent anhydrous work-up gave the extremely air- and moisture-sensitive compounds 3 in good yields.

The enamine 3b could be converted smoothly into the chloroketenamin 4b by heating with an excess of diethylamine at 60 to 70°C. Conversion of 3a with dimethylamine, however, appeared to be less successful; reaction for 6 hours in an autoclave yielded only some 30% of the desired product 4a. The use of the more reactive lithium dimethylamide in the presence of an excess of the free amine finally enabled the synthesis of 4a in satisfactory yield. One draw-back of this procedure for 4a is that relatively large amounts of solvents and reagents are required. A more satisfactory, one-pot synthesis for this representative was found when we tried to reproduce the procedure of Viehe et al.3 for the ynediamine bis(dimethylamino)acetylene. These authors first prepared sodamide from sodium and liquid ammonia, using ferric nitrate as a catalyst. The sodamide was isolated and suspended in dimethylformamide, after which trichloroethylene was added. After a 5-hour period of interaction, the solvent was evaporated and the ynediamine could be isolated by “dry” distillation. We found this procedure to be reproducible only when a relatively large amount of ferric nitrate was used as a catalyst. In the case of small quantities (ca. 100 mg, per 1.5 mol of sodium) the results were poor.

Nevertheless, when the reaction mixture was subjected to work-up (evaporation of the dimethylamine followed by addition of ether) after 3 to 4 hours, we could isolate the chloroketeneminal 4a in a good yield. A possible explanation for the difference between our results and those reported is that in our case the particles of sodamide are larger (because of their more slow formation) and hence less reactive than when much catalyst is used.

The 1H-NMR spectra of the 3,β-dichloroamines 3 showed sharp signals for the vinylc and amine-protons, suggesting the presence of one isomer. Previous investigations have shown that the stereochemistry of the addition of secondary amines to acetylenes with electron-withdrawing substituents, e.g. dicyanoacetylen and dicyanacylenedicarboxylate may strongly depend upon the reaction conditions; cis- as well as trans-addition has been observed.4 We have not carried out a separate investigation to determine the configuration of our products.

1,2-Dichloro-1-(X,N-dialkylamino)ethenes 3: General Procedure:

In a 1-1 three-necked, round-bottomed flask, equipped with a mechanical stirrer and a reflux condenser, is placed a solution of trichloroethylene (28 g, 0.20 mol) in dry ether (120 ml). The solution is cooled to 0°C and a suspension of lithium dialkylamide (prepared in a separate flask by addition at – 40°C of n-butyl lithium (0.20 mol) in hexane (140 ml) to a mixture of amine (0.20 mol) and ether (100 ml) is added to the flask over ca. 5 min. During this addition the temperature of the reaction mixture is maintained below – 70°C (occasionally cooling in a bath with liquid nitrogen). Subsequently dialkylamine (0.40 mol) is added and the contents of the flask are warmed to 30°C using a water bath. After stirring the suspension for 30 min at this temperature, it is cooled to 20°C and then subjected to suction filtration (G-2 sintered-glass funnel covered with a thin layer of anhydrous potassium carbonate). The solid on the filter is rinsed well with dry ether. The filtrate is concentrated in vacuo, using a water bath at 25–30°C. Subsequent distillation of the remaining liquid gives:

3a: yield = ca. 20 g (70–75%); b.p. ca. 30°C/15 torr. The 1H-NMR spectrum (10% solution in CDCl₃, TMS as internal standard) shows signals at δ = 2.86 (s, CH₃), and at 5.55 ppm (s, H = – C). The literature5 does not give NMR data.

3b: yield = ca. 25 g (74–80%); b.p. ca. 30°C/0.5 torr (Ref. 1, 79–82°C/18 torr). The 1H-NMR spectrum shows signals at δ = 1.13 (6, CH₃), 2.80 (q, CH₂), and at 5.90 ppm (s, H = – C). The literature6 does not give NMR data.

In view of the sensitivity of the compounds 3 towards oxygen and moisture, the appropriate techniques were applied during their isolation. The compounds should be stored in well-closed bottles at low temperatures.

2-Chloro-1,1-bis(dialkylamino)ethylene 4b:

A mixture of 3b (33.6 g, 0.20 mol) and diethylamine (21.9 g, 0.30 mol) is placed in a 250-ml three-necked, round-bottomed flask, provided with a nitrogen inlet, a mechanical stirrer, a thermometer and a reflux condenser. The mixture is heated under reflux while salt separates from the solution. An additional amount of diethylamine (0.30 mol) is added in three equal portions over 1 h. After 5 to 6 h the mixture is cooled to 20°C and ether (30 ml) is added. Suction filtration through sintered glass, followed by concentration of the filtrate in vacuo and distillation gives the chloroketeneminal 4b. yield = ca. 34 g (60–85%); b.p. ca. 55°C/0.3 torr (Ref. 1, b.p. 58–62°C/0.2 torr; nD 1.4718).

The 1H-NMR spectrum (not reported in literature)5 gives signals at δ = 1.10 (6, CH₃); 2.77–3.22 (m, CH₂), and at 4.45 ppm (s, H = – C).

2-Chloro-1,1-bis(dimethylamino)ethylene 4c:

4: From 1,2-dichloro-1-(dimethylamino)ethylene

In a 500-ml three-necked, round-bottomed flask provided with a nitrogen inlet, a thermometer, a mechanical stirrer and a gas outlet is placed a solution of 3a (28.9 g, 0.20 mol) in dry ether (50 ml). The solution is cooled to – 10°C and a suspension or solution of lithium dimethylamide (0.22 mol) in ether and hexane, prepared as above, is added to the flask over 5 min. Subsequently, liquified diethylamine (18.9 g, 0.40 mol) is added, and the mixture is warmed to 30°C. This temperature is maintained for an additional 6 h. After cooling the contents of
the flask to room temperature the salt mass is filtered through a G-3 sintered-glass funnel and rinsed with dry ether. Concentration of the filtrate in vacuo followed by distillation affords the chloroketenemininal 4a; yield = ca. 21 g (70–75%); b.p. ca. 50 °C/10 torr (Ref. 2, 30–35 °C/0.1 torr); nD²⁰ 1.4807. The ¹H-NMR spectrum (not given in literature) shows signals at δ = 2.50 (s, CH₃), and at 4.24 ppm (s, H⁻C=).

B. From trichloroethene, sodamide and dimethylamine
In a 3-l round-bottomed flask is placed anhydrous liquid ammonia (1 l). After adding ferric nitrate hydrate (100 mg) the flask is swirled manually and sodium (3 g) is introduced in 0.5-g pieces. After the blue color of the dissolved sodium has disappeared and a grey solution has formed, further sodium (43 g) is introduced (total amount 2.0 mol). The flask is swirled occasionally. After all sodium has converted into amide, the flask is placed in a water bath at 40 °C to remove the excess ammonia. The last traces of ammonia are removed by evaporation (water pump). The solid is scratched from the glass wall by means of a curved spatula, after which the flask is again evacuated. During this operation the flask is shaken vigorously in order to break down the lumps of sodamide. The powder is transferred to a 1-l three-necked, round-bottomed flask, provided with a mechanical stirrer, a dropping funnel combined with a gas inlet and a dry-ice condenser filled with acetone and solid carbon dioxide. Anhydrous liquid dimethylamine (240 ml) is placed in the flask and a slow stream of nitrogen is passed through the apparatus. Trichloroethene (39.45 g, 0.30 mol) is added dropwise over 10 min, while stirring at a moderate rate, care being taken that the suspension is not swept into the upper part of the flask. The dropping funnel is then replaced by a combination of a thermometer and a gas inlet. The temperature indicates 6–7 °C just after all trichloroethene has been added. The rate of the reflux from the condenser increases gradually, while the temperature of the mixture drops (ammonia liberated in the initial reaction escapes from the solution, condenses and returns with a temperature of ca. 78 °C). After 1 to 1.5 h the temperature of the mixture has reached a minimum of ca. −11 °C. Stirring is continued for another 2.5 h, then mixture of dry ether and pentane (1:1, 400 ml) is added, the cold finger is removed and the flask is placed in a water bath at 45 °C. A gas outlet is placed on the flask. When the volume of the mixture has decreased to about 350 ml, the solid material is filtered on a sintered-glass funnel and rinsed well with dry ether. Paraffin oil (50 ml) is then added to the brown solution and the solvent is removed by evaporation, using a water bath at 30–35 °C (the bulk of the solvent may first be removed on the rotary evaporator). Subsequently, the product is distilled from the paraffin oil at a pressure lower than 0.5 torr, using a 20 to 30-cm Vigreux column. Product 4a, which is collected in a single receiver cooled at −70 °C, is carefully redistilled through a 40-cm Vigreux column at water-pump pressure; yield = ca. 31 g (68–72%); b.p. ca. 50 °C/10 torr. A small amount of 5 (R = CH₃) (showing a signal at δ = 2.58 ppm in the NMR spectrum) may sometimes be present; repeated distillation will then be necessary.

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(5) Due to the extreme oxygen and moisture sensitivity no reproducible micro-analytical results could be obtained.