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Preparation of Chloroacetaldehyde Cyclic Trimer and Its Depolymerization

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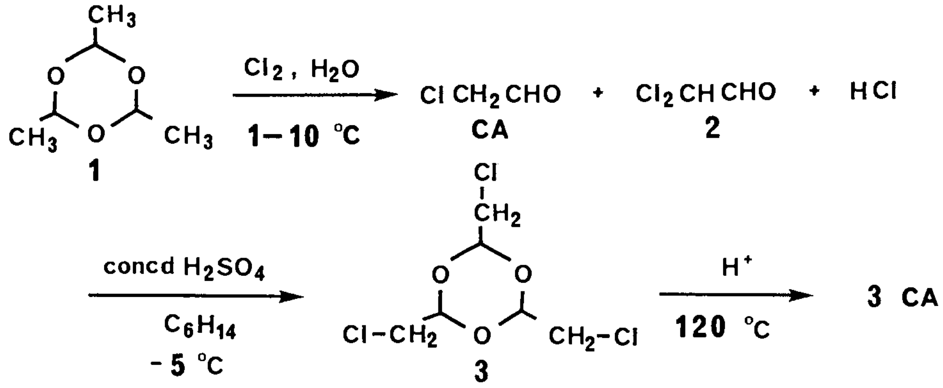
Chlorination of paraldehyde gave chloroacetaldehydes which were treated with concd sulfuric acid to afford cyclic trimer (**3**) of chloroacetaldehyde (CA). Depolymerization of **3** yielded pure CA satisfactory.

Chloroacetaldehyde (CA) is used as one of very useful synthons in organic synthesis,[1)] since it has a very attractive chemical structure containing three functionalities of formyl, chlorine, and active methylene. However, CA is unstable and extremely labile to polymerize and usually stored as an aqueous solution.[2)] The aqueous solution of CA is not suitable for its reactions under anhydrous conditions. It is also difficult to obtain a neat liquid of CA with high purity from the diluted aqueous solution. As can be seen in some aldehydes their cyclic trimers exist stably. Thus CA trimer may be a potential material as a stable precursor of CA itself if it can be depolymerized readily. Natterer already suggested the trimer formation of CA in the literature,[3)] but no detail was reported on the structure, synthetic yield, and characterization of CA trimer.

In this paper we wish to report a practical preparative method of CA cyclic trimer **3** as stable precursor of CA and its depolymerization for obtaining a CA monomer with high purity.



Chlorination of paraldehyde (**1**) with chlorine gas in the presence of catalytic amount of water gave the mixture of CA and dichloroacetaldehyde (**2**). Reaction temperature must be kept below 10 ℃ during chlorination. Degree of chlorination should be in the range of 60-90% of the starting **1** . High degree of chlorination caused significant formation of **2** and chloral.

Before cyclization of CA the chlorinated mixture should be distilled to give highly concd CA solution which contains more than 70wt% of CA. Using this concd CA, cyclization occurred smoothly with concd H_2SO_4 to afford fine crystals of CA trimer **3**. Nitric acid, phosphoric acid, and hydrochloric acid were not effective. In the cyclization reaction it is also important to dilute CA with nonpolar solvent such as hexane or CCl_4 as shown in Table 1.

Table 1. Yield of **3** in Cyclization of CA by the Use of Concd CA [a)]

Solvent	Temp/℃	Time/h	Yield/% [b)]	Solvent	Temp/℃	Time/h	Yield/% [b)]
Hexane	- 5	3.0	51	THF	- 5	5.0	5
Benzene	- 10	1.5	49	Ethanol	- 5	5.0	5
CCl_4	- 10	1.5	53	- [c)]	- 30	4.0	20

a) Concd CA solution which contains CA 75.5-85.7wt% was used.

b) Based on CA in the concd CA. c) Without solvent.

A typical preparative method of CA trimer **3** is as follows : A solution of paraldehyde **1** (10 g) was treated with chlorine gas in the presence of water (0.1 ml) as a catalyst for 6 h at the temperature maintained in the range of 1 to 10 ℃. The reaction mixture was then distilled at 95 ℃ under 150 mmHg to give 6.44 g of crude product which contained 84wt% of chloroacetaldehyde.[4)] The concd CA was then diluted with hexane (20 ml) and cooled to -5 ℃. At the same temperature concd sulfuric acid (3 ml) was added slowly and stirring was continued for 3 h to afford fine crystals of CA trimer. These crystals were then collected by filtration, washed with water and an aqueous sodium hydroxide, and recrystallized from hexane to give colorless needles of CA trimer **3** (2.8 g).[5)]

The CA trimer thus obtained is quite stable under normal conditions. We have found that this pure CA trimer **3** was depolymerized easily to its monomer in the presence of acid catalyst. For example, direct distillation of **3** at 120 ℃ in the presence of a catalytic amount of *p*—toluenesulfonic acid afforded pure monochloroacetaldehyde (CA)[6)] in 80% yield. Other acids such as $SnCl_4$ and $TiCl_4$ were also effective for depolymerization of **3**.

References

1) For example, see : T. Yokozawa, J. Takagi, and T. Endo, J.Polym.Sci.,Polym.Chem.Ed., 27, 291 (1989); W.J. Bailey and L. Zhou, Polym.Prepr.(Am.Chem.Soc.,Div.Polymer Chem.), 29, 410(1988).
2) An aqueous solution which contains 40-45wt% of CA is commercially available.
3) K. Natterer, Monatsh, 3, 461(1882).
4) CA content was determined by GC analysis.
5) The purity was assumed as >99.5% by GC analysis. Mp 87-88 ℃, Molecular weight 233 (GC-MS, $[M-1]^+$), IR 1130 cm^{-1}, ^1H-NMR($CDCl_3$) δ 3.5(6H,d,CH_2); 5.1(3H,t,CH).
6) The purity was assumed as >99.5% by GC analysis. Bp 85-86 ℃, ^1H-NMR ($CDCl_3$) δ 4.1(2H,d, CH_2); 9.6(1H,t,CHO).

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