A Convenient Route to Chlorobenzilic Acid

S. S. Tomar, N. K. Roy and S. K. Mukerjee

Division of Agricultural Chemicals, Indian Agricultural Research Institute,
New Delhi-110012, India
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Chlorination of DDT gave unexceptional tetrachloro derivative which was converted into 4,4'-dichlorobenzil in a single step of rearrangement and hydrolysis by heating with p-toluenesulfonic acid or monochloroacetic acid containing a little water. The optimum condition for the conversion of 4,4'-dichlorobenzil to chlorobenzilic acid is also described.

Esters of chlorobenzilic acid, like ethyl and isopropyl 2-hydroxy-2,2-bis(4-chlorophenyl) acetates (VI) commonly known as chlorobenzilate and chloropropylate respectively, are important acaricides having contact action against all stages of red spider mites.

Two methods are known in literature for the preparation of chlorobenzilates. In the first one by Gomberg1), 4,4'-dichlorobenzoin from p-chlorobenzaldehyde is converted to the corresponding benzil which on further rearrangement followed by esterification gives chlorobenzilate. The over all yield is poor and the cost of the starting material is high hence the process is uneconomical. A more useful economical method starting from DDT was developed by Clark and Hilton2) in 1953. DDT (I) on treatment with strong alcoholic KOH is converted into DDA (II) which on chlorination gives the a-chloro acid (III). Substitution of the a-chlorine in (III) by hydroxyl group cannot be done directly. It requires conversion first to the acid chloride (IV) which on hydrolysis with aqueous Na₂CO₃ yields the benzilic acid (V). Subsequent esterification gives the desired product. Although several steps are involved, the yields are good and the process is under commercial exploitation by A. G. Geigy since 1954.

In connection with a general programme of developing acaricides a new and convenient route to chlorobenzilic acid and its esters, developed in this laboratory, is now reported. A convenient starting material for this new route is 1,1-bis (4-chlorophenyl)-1,2,2,2-tetrachloroethane (VII), a cheap photochlorination product³ of DDT. Walton⁴ reported that this unsymmetrical tetrachloro derivative undergoes exothermic rearrangement to the symmetrical isomer (VIII) on heating with catalytic
amounts of anhydrous FeCl₃. It seemed to us that this symmetrical compound (VIII) would be a most convenient intermediate for the benzil (IX) and thence to chlorobenzilic acid (V). This isomerisation reaction was, therefore investigated in detail not only in the presence of anhydrous FeCl₃ but other Lewis acids like anhydrous AlCl₃ and ZnCl₂. The best condition appeared to be heating with small quantity of anhydrous FeCl₃ at 180–230°C under reduced pressure when an 85% conversion was achieved. Other Lewis acids like ZnCl₂ and AlCl₃ did not give clean products. Although the symmetrical tetrachloro compound can be obtained in this way in high yield its hydrolysis to the benzil (IX) proved to be difficult. It is completely unaffected by mild alkali and the use of the stronger alkaline conditions at higher temperatures led to its degradation to p-chlorobenzoic acid. The difficulty seems to be due to the bulky chlorine atoms which makes normal hydrolytic mechanism difficult. The reported hydrolysis of this compound at higher temperature under acidic conditions⁴ (acetic acid in a sealed tube) led us to investigate conditions for carrying out the rearrangement and hydrolysis simultaneously using protonic acids at higher temperatures. Use of a mixture of acetic and sulphuric acid at 160°C gave the benzil (IX) in moderate yield but the product was not very pure. However, when (VII) was fused with p-toluenesulphonic acid containing water (2–3%) at 160°C or a solution of it in monochloroacetic acid was heated at 170°C conversion to the benzil (IX) took place in high yield in a short time. The reaction evidently proceeds through a Sₗ¹ mechanism. The compound (X) also rearranges smoothly to the benzil (IX) under these conditions and is presumably an intermediate in this conversion.

Attempted rearrangement of 4,4′-dichlorobenzil (IX) to be benzilic acid (V) by heating with alcoholic KOH under normal conditions produced p-chlorobenzoic acid as the major product. Use of other solvents like DMSO and dioxan and variations in temperature did not improve the yield. The reaction however proceeded smoothly when a benzene solution of the benzil (IX) was stirred with aqueous methanolic KOH at 40–50°C.

There is some confusion in literature regarding the melting point of chlorobenzilic acid. Montagne⁵ reported a melting point of 101°C but later Clark and Hilton² revised it to 91°C. The product obtained above melts at 114–115°C and is identical in all respects with an authentic sample. It was further characterised by the preparation of methyl and ethyl esters identical in all respects with authentic samples.

**EXPERIMENTAL**

*Conversion of 1,1-bis (4-chlorophenyl)-1,2,2,2-tetrachloroethane (VII) to 4,4-dichlorobenzil (IX)*

_a) Using p-toluenesulphonic acid._ A mixture of 1,1-bis (4-chlorophenyl)-1,2,2,2-tetrachloroethane (VII, 2 g), p-toluenesulphonic acid (30 g) and water (1 ml) was melted and stirred. The resulting homogenous mass was kept at 160–170°C for 45 min, then cooled and diluted with ice water (200 ml). The precipitated...
solid (1.4 g) was filtered and washed with hot water until free from acid. It crystallized from a mixture of ethanol and dioxane as pale yellow needles, mp 202–3°C. (Found Cl, 25.2, C₁₄H₈Cl₂O₂ requires Cl, 24.4%), IR νₘₐₓ cm⁻¹): 1670 (>C=O). Literature⁴) mp 198–99°C. The filtrate, on evaporation gives back p-toluenesulphonic acid contaminated with a little impurity but can be reused in the above manner several times.

b) Using monochloroacetic acid. A solution of 1,1-bis (4-chlorophenyl) 1,2,2,2-tetrachloroethane (VII, 2 g) in monochloroacetic acid (10 g) and water (1 ml) was heated at 170°C for 1 hr, cooled and diluted with ice water (70 ml). The precipitated solid (1.3 g) was almost pure 4,4-dichlor benzil. Recrystallisation gave a sample identical in all respects with the above product.

c) From 2,2,2-trichloro-1,1-di-(4-chlorophenyl)-ethanol (X). A solution of (X) (2 g) in a mixture of monochloroacetic acid (10 g) and water (1 ml) was heated at 150–160°C for 0.5 hr. Dilution of the cooled mixture with ice water gave 4,4'-dichlorobenzil (1.2 g) identical in all respects with samples obtained in (a) and (b).

Rearrangement of the benzil (IX) to 4,4'-dichlorobenzilic acid (V). A solution of 4,4-dichlorobenzil (2 g) in benzene (100 ml) was stirred at 40–50°C with aqueous methanolic KOH (50 ml) (20 mg KOH in 20 ml water diluted with 30 ml methanol) for 0.5 hr when the benzene layer became almost colourless. The mixture was diluted with cold water and aqueous layer was carefully separated. Acidification furnished chlorobenzilic acid (1.8 g) which crystallised from a mixture of petroleum ether and benzene as colourless needles mp 114–15°C, IR νₑₘₚₓ (cm⁻¹): 3515 (OH) and 1710 (>C=O).

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REFERENCES