

Note

Zinc metal assisted hydro-de-halogenation of DDT into DDEthane under sonic conditions

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An efficient method for the hydro-de-halogenation of DDT to 1,1-bis(*p*-chlorophenyl)ethane (DDEthane) exclusively by a simple reaction using commercial zinc dust, is reported. The rate of the reaction is enhanced by irradiating at 35 KHz in a sonic bath at 25°C.

During 1940's DDT having highest intrinsic insecticidal activity was introduced. It was mainly used in agriculture and to control spread of vectorance human diseases, especially malaria. DDT and its two primary environmental degradation products 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane (DDD) and 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethene (DDE) are persistent compounds through long range atmospheric transport have become global pollutants. On the other hand, a number of reports have appeared in recent years on the reductive dehalogenation of DDT into DDD and DDE, among them are zero-valent iron in presence of Triton X-114,¹ electrolytic,² in electron capture mass spectroscopy,³ photochemically⁴ and by matrix enhanced reaction during gas chromatographic analysis.⁵ Zinc/HCl⁶ has been found to give *p*, *p'*-dichlorostilbene along with DDD and DDE.

In continuation of our work on metal-ammonium salt reductions,^{7,8} we present the results of an investigation of a novel reaction of DDT with zinc metal in the presence of ammonium salts under aprotic conditions (Table I) and under other conditions (Table II) to give DDEthane (Scheme I). The results given in Table I clearly indicate that the reaction is possible

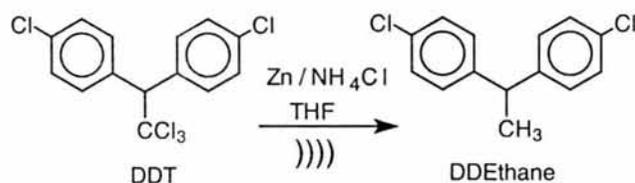


Table I—Hydro-de-halogenation of DDT into DDEthane by zinc dust in the presence of ammonium salts in THF at reflux

Entry	Zn + Ammonium salt	Time (hr) at reflux	Yield (%) of DDEthane
1	Zinc alone	24	—
2	NH ₄ Cl	24	95
3	NH ₄ NO ₃	24	—
4	(NH ₄) ₂ (COO) ₂	24	—
5	NH ₄ OCOH	24	—
6	(NH ₄) ₂ SO ₄	24	—
7	NH ₄ OCOCH ₃	24	—

with zinc in the presence of ammonium chloride to give DDEthane and the reaction takes 24 hr for completion. From Table I, it is clear that zinc metal alone is non-reactive (entry-1) and only ammonium chloride (entry-2) participates in the reaction. However, under the influence of ultrasound at 35 KHz the reaction is appreciably faster (Table II, entry-4) and the hydro-de-halogenation of DDT into DDEthane under other conditions is also noteworthy (Table II). During the course of the reaction, DDD and 2,2-bis(*p*-chlorophenyl)-1-monochloroethane (DDM) were also detected. DDEthane and DDM have been isolated and identified for the first time under these reaction conditions.

In a typical experiment, 1mmole of DDT, 3 mg atom of zinc dust and acetic anhydride (10 mL) were sonicated in a bath working at 35 KHz at 25°C. After completion of the reaction (4 hr), the reaction mixture was taken into ether, washed with saturated sodium bicarbonate and water and then solvent removed to get the crude product (90%), which on separation by silica gel chromatography (1:200) using pet.ether (40-60°) followed by 5% acetone- pet. ether gave DDEthane (50%), DDM (30%) and DDD (20%).

While DDD showed a doublet at δ 4.5 for 1H, α to Cl atoms another doublet at δ 6.27 for a benzylic proton and a multiplet between δ 7.2 to 7.4 for 8 aromatic protons in its ¹H NMR spectrum, DDEthane showed ABA'B' double doublet due to aromatic protons at δ 7.1 and 7.3, a quartet due to benzylic proton at δ 4.1 and a doublet at δ 3.6 for a methyl group. DDM, on the other hand showed a doublet at δ 3.95 for two protons α to Cl and a triplet at δ 4.25 for a benzylic

Table II—Hydro-de-halogenation of DDT with zinc dust under different reaction conditions

Entry	Reaction condition	Reaction time (hr)		Yield (%)	Ratio of the product ^a (DDD: DDM: DDEthane)
		at reflux	at 35 KHz in a sonic bath		
1	(CH ₃ CO) ₂ O	8.00	4.00	90	20:30:50 ^b
2	CH ₃ COOH	9.00	5.00	99	0:5:95
3	HCOOH	24.00	9.00	90	15:20:65
4	THF/NH ₄ Cl	24.00	2.00	95	0:5:95

a) ratios obtained by ¹H NMR spectral analysis.

b) by chromatographic separation and identification of products.

proton apart from the signals due to aromatic protons in its ¹H NMR spectrum.

From the above studies it is clear that, stepwise removal of alkyl halogens from DDT molecule takes place to give DDEthane and *p,p'*-dichlorostilbene formed earlier⁶ by the reaction of DDT and Zn/HCl could not be detected under these conditions.

Experimental Section

All compounds were characterised by ¹H NMR spectral analysis. All the reactions were studied at reflux and at 25°C using JULABO, USR-3 GERMAN make sonic bath working at 35 KHz.

Hydro-de-halogenation of DDT by Zn in the presence of NH₄Cl. A mixture of DDT (100mg, 0.284 mmoles), commercial zinc dust(200mg, 3.76 mg atom), dry THF (5 mL) and ammonium chloride (300mg, 5.64 mmoles) was sonicated at 35 KHz in a sonic bath while maintaining the temperature at 25°C. The progress of the reaction was monitored by TLC [petroleum ether (40-60°) : acetone (95:5)]. At the end of the reaction (2 hr), the mixture was filtered and extracted with ether (2 × 10mL), dried over anhydrous

sodium sulphate and solvent evaporated to get the crude product (67.5 mg, 95%). DDM and DDEthane thus formed were separated by silica gel chromatography using 5% acetone: pet. ether (40-60°), and characterised by ¹H NMR spectral analysis.

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