The Facile Degradation of p,p'-DDT *via* p,p'-DDD Using Chromous Chloride as Reducing Agent

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Introduction

The need to confirm the identity of organochlorine residues and metabolites has recently produced a number of analytical methods (1). Chemical modification followed by electron capture gas chromatography (EC-GLC) is a generally useful approach for their confirmation (1). During recent investigations on the applicability of chromous chloride as a reducing reagent for the confirmation of heptachlor via dechlorination, a preliminary screening of the DDT group of insecticides was performed. Initial results indicated that p,p'-DDT (1,1-bis(p-chlorophenyl)-2,2,2-trichloroethane) is rapidly converted to p,p'-DDD (1,1-bis(p-chlorophenyl)-2,2-dichloroethane) which is subsequently reduced to a number of other degradation products. The recent attention given to the conversion of p,p'-DDT to p,p'-DDD in biological systems (2-6) and the possible mechanism of dechlorination occurring under reducing conditions (7-10) prompted further investigation of the degradation products from the chromous chloride reaction. This paper reports the facile conversion of p,p'-DDT and p,p'-DDD to predominantly DCS (trans-p,p'-dichlorostilbene) with DDNU (1,1-bis(p-chlorophenyl)-ethylene), DDMU (1,1-bis(p-chlorophenyl)-2-chloroethylene) and DBP (p,p'-dichlorobenzophenone) as secondary products under acidic conditions using chromous chloride as the reducing agent.

Materials and Method

Reagents

Hexane, petroleum ether, acetone and thiophene-free benzene were redistilled in an all-glass system using a fractionation column. Analytical grade ether, aqueous chromous chloride ($CrCl_2$) solution (Fisher Scientific Company) and neutral alumina (Woelm activity grade 1) were used without prior treatment.

Instruments

Gas chromatograph-Aerograph Hy-Fi Model 600-D with a tritium foil electron-capture detector. GLC parameters were identical to those reported previously (11).

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Derivatization Techniques

(a) Residue scale - In a 15 ml glass stoppered graduated tube, 20 µl of a standard p,p'-DDT solution (0.1 mg/ml) was evaporated just to dryness with nitrogen. While a gentle stream of nitrogen was flowing into the tube, 1 ml acetone and 0.5 ml $CrCl_2$ solution were added. The tube was tightly stoppered and secured with a spring-loaded clamp. The tube was heated for 2-3 hours at 55-60°C. The cooled contents were diluted with 5 ml distilled water and 5 ml hexane and the mixture shaken. The upper organic layer was then analyzed by EC-GLC.

(b) Preparative scale - Under a nitrogen atmosphere, 125 ml $CrCl_2$ solution was added to 2 gm p,p'-DDT in a 250 ml acetone solution in a glass stoppered flask and the mixture maintained at 55-60°C overnight. The reaction mixture was then concentrated under vacuum to one third the original volume. Approximately 200 ml distilled water was added and the aqueous solution extracted with 6 x 50 ml portions of ether. The combined ether extracts were dried over anhydrous Na_2SO_4. Slow evaporation of the solvent gave a crystalline product identified as DCS (peak 4, Figure 1). Recrystallization from hot chloroform afforded colorless plates, m.p. 177-8°C. Further crystals were obtained by tituration of the mother liquor with 1:1 ether-hexane solvent mixture. A total yield of 45-55% of this product was obtained from the reaction mixture.

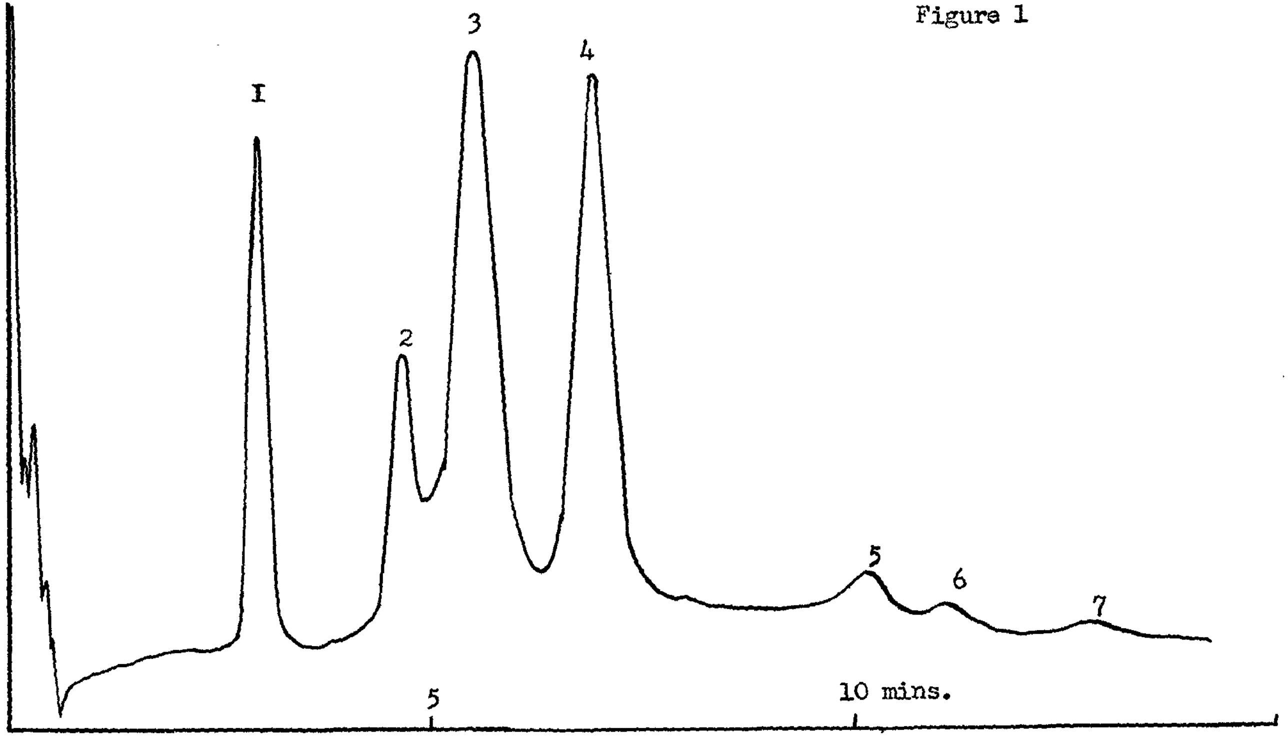
The combined mother liquors were evaporated and chromatographed on a neutral alumina column. The petroleum ether (b.p. 30-60°C) eluates, in 20 ml portions, were monitored by EC-GLC. Two fractions were obtained. Fraction 1 corresponded to peak 1 with traces of peak 3 product, and fraction 2 contained peak 1 and 3 products in approximately equal quantity. Fractional crystallization of both fractions from petroleum ether gave pure peak 1 product, m.p. 88-89°C, identified as DDNU (peak 1, Figure 1). The residue from the combined mother liquors was rechromatographed on the alumina column. Repeated crystallizations of the petroleum ether eluates gave the pure peak 3 product, m.p. 67-68°C, identified as DDMU (peak 3, Figure 1).

Further elution of the column with benzene gave the remaining DCS and peak 2 product in about 1:5 ratio. Evaporation of the eluate gave a yellow gum which upon crystallization at 0°C from an ether-hexane mixture afforded DCS. The mother liquor was repeatedly recrystallized from benzene-hexane at 0°C to yield DBP, m.p. 149-150°C (peak 2, Figure 1).

Results and Conclusions

Reaction of p,p'-DDT with aqueous chromous chloride solution (pH 3.7) on the residue scale proceeded rapidly to produce initially p,p'-DDD together with minor responses for peaks 1 and 3. Continued reaction, although at a slower rate, finally resulted in a chromatogram exhibiting six peaks with traces of starting material (Figure 1).

Figure 1



Chromatogram of p,p'-DDT after $CrCl_2$ reaction.

The chromatogram indicated that three major products (peaks 1, 3 and 4) and three minor components (peaks 2, 5 and 6) were obtained from the reaction. On the preparative scale, DCS (peak 4) was isolated in 45-55% yield. DDNU, DBP and DDMU (peaks 1, 2 and 3, respectively) together comprised approximately 35-45% of isolated products. Approximately 5% of the reaction mixture was composed of unreacted p,p'-DDT, p,p'-DDD and o,p'-DDT. The identity of o,p'-DDT was confirmed by NaOMe conversion to the corresponding dehydrochlorinated product, o,p'-DDE, the retention time of which was compared with an authentic sample. Although o,p'-DDT was not detected in the p,p'-DDT starting material which was analytically pure, it is thought the conversion of p,p'-DDT to o,p'-DDT unlikely. More probable is the ease of detection of any o,p'-DDT impurity with consumption of the more reactive p,p'-DDT isomer.

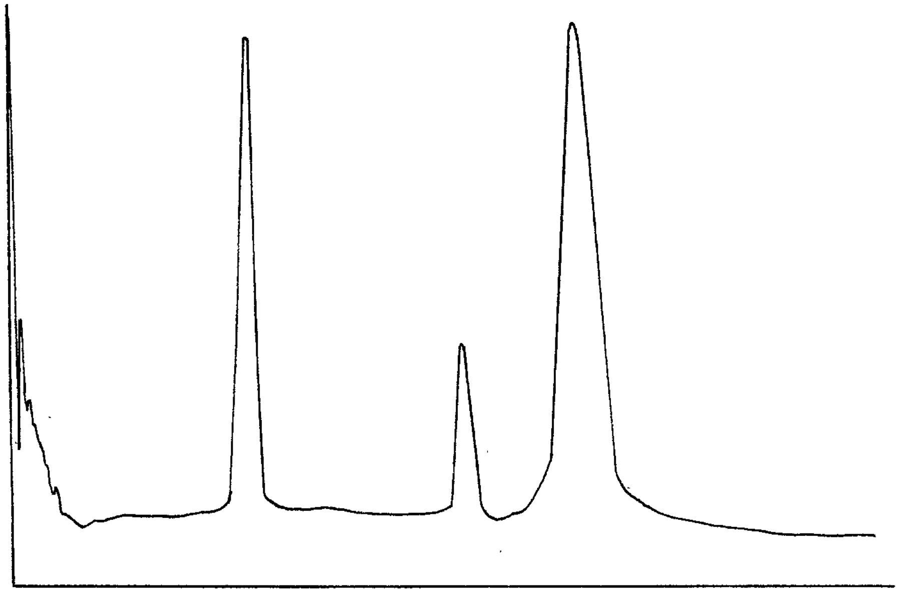
Identification of the isolated products (Table 1) was carried out by mixed melting points and IR spectral analysis (12). In the case of DCS and DDNU both N.M.R. (13, 14) and U.V. spectra (15) comparisons were utilized. DDMU was verified by preparation of an authentic sample by dehydrochlorination of p,p'-DDD according to Cohen <u>et</u> <u>al</u>. (16) All products had satisfactory elemental analysis. Although DDMU gave the highest peak response (peak 3, Figure 1), it was DCS (peak 4, Figure 1) which was obtained in highest yield. This anomaly can be attributed to the difference in EC sensitivity of these two products.

On standing, standard solutions of DCS were rapidly converted in sunlight presumably to the <u>cis</u>-isomer (15). Whether the new peak that appeared in the chromatogram from the photoisomerization of DCS is, in fact, the <u>cis</u>-isomer or a further rearranged product has still to be determined. It was noted that the major conversion product, i.e. DCS, had the same retention time as p,p'-DDE, while DDNU and also the presumed <u>cis</u>-isomer of DCS both had a similar retention time to heptachlor on the column used. Of interest was the absence of any detectable amounts of p,p'-DDE which in a separate experiment was found to be unreactive under the reducing conditions used for p,p'-DDT conversion.

Since p,p'-DDD was observed as the initial product during the $CrCl_2$ reaction, it was deemed worthwhile to submit this compound to a similar reaction. On the residue scale, p,p'-DDD was slowly converted to DCS. With increasing reaction time a peak of equal height due to DDNU appeared. The final chromatogram displayed predominantly three peaks (Figure 2). These peaks were identified after their isolation as described for the reaction with p,p'-DDT as DDNU, DDMU and DCS (major product).

Therefore, under chromous chloride reducing conditions, p,p'-DDT is rapidly monodechlorinated to p,p'-DDD which is further rearranged at a slower rate to DCS. DDMU can arise by dehydrochlorination of p,p'-DDD but the formation of DDNU presupposes the existence of DDMS (1,1-bis(p-chlorophenyl)-2-chloroethane) as a labile intermediate. Reduction of p,p'-DDT using other reducing

Figure 2



Chromatogram of p,p'-DDD after $CrCl_2$ treatment

TABLE 1

Relative Retention Times of p,p'-DDT and Its Reaction Products by Electron Capture Gas Chromatography

Reaction product (Figure 1)	Retention time (Aldrin = 1)	m.p. of isolated products, °C	Assignments
Peak 1	0.82	88-89	DDNU
Peak 2	1.29	149-150	DBP
Peak 3	1.51	67-68	DDMU
Peak 4	1.92	177-178	DCS
Peak 5	2.80	*	p,p'-DDD
Peak 6	3.02	*	o,p'-DDT
Peak 7	3.50	*	p,p'-DDT

* Characterized by comparative TLC and GLC retention times with authentic samples.

agents has been reported, i.e. treatment of p,p'-DDT or p,p'-DDD by Zn/HCl (17) or Zn/HOAc (18) both gave DCS as one of the products. However, no formation of DDNU or DDMU was observed; instead, substituted ethanes were obtained. Recently DCS was isolated and identified as a constituent of mainstream cigarette smoke which was obtained from tobacco products containing p,p'-DDT or p,p'-DDD (15).

The exact route of degradation and the possible interconversion of these p,p'-DDT derivatives by chromous chloride is under investigation. The results together with the mode of degradation of the o,p'-isomers will be reported later.

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References

1. McCULLY, K.A. World Review of Pest Control 8, 59 (1969)
2. PETERSON, J.E. and ROBISON, W.H. Toxicol. Appl. Pharmacol. 6, 321 (1964)
3. KLEIN, A.K., LANG, E.P., DATTA, P.R., WATTS, J.O. and CHEN, J.T. J. Ass. Offic. Anal. Chem. 47, 1129 (1964)
4. McCULLY, K.A., McKINLEY, W.P. and PHILLIPS, W.E.J. J. Ass. Offic. Anal. Chem. 51, 1050 (1968)
5. BARKER, P.S. and MORRISON, F.O. Can. J. Zool. 43, 652 (1965)
6. BRAUNBERG, R.C. J. Agr. Food Chem. 16, 451 (1968)
7. CASTRO, C.E. J. Amer. Chem. Soc. 86, 2310 (1964)
8. OTT, D.E. and GUNTHER, F.A. Residue Reviews, 10, 70 (1965)
9. MISKUS, R.P., BLAIR, D.P. and CASIDA, J.E. J. Agr. Food Chem. 13, 481 (1965)
10. ROWLANDS, D.G. J. Stored Prod. Res. 4, 183 (1968)
11. CHAU, A.S.Y. and COCHRANE, W.P. J. Ass. Offic. Anal. Chem. 52, 1092 (1969)
12. ABOU-DONIA, M.B. and MENZEL, D.B. J. Ass. Offic. Anal. Chem. 51, 1247 (1968)
13. GÜSTEN, H. and SALZWEDEL, M. Tetrahedron, 23, 173 (1967)
14. YUKAWA, Y., TSUNO, Y. and YAMADA, H. Mem. Inst. Sci. and Ind. Res., Osaka Univ., 23, 79 (1966)
15. HOFFMANN, D. and RATHKAMP, G. Beiträge zur Tabakforschung, 4, 201 (1968)
16. COHEN, S., KALUSZYNER, A. and MECHOULAM, R. J. Amer. Chem. Soc. 79, 5979 (1957)
17. FORREST, J., STEPHENSON, O. and WATERS, W.A. J. Chem. Soc. 333 (1946)
18. GAROFANO, T., ARCOLEO, A. and NATOLI, M.C. Atti Accad. Sci. Lettere Arti Palermo, Pt I, 24, 235 (1965)