Confirmation of Residue Identity: Characterisation of the Products of the Reaction Between Vanadium (II) Solutions and Endrin

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A number of papers have reported the use of chromium (II) solutions to form derivatives of chlorinated cyclodiene insecticides to assist in the confirmation of residue identity. (CHAU 1970 a, b, CHAU and COCHRANE 1971). CHAU (1970c) and CHAU et al. (1971) have investigated the reaction between endrin and chromous chloride in aqueous acetone and has assigned structures to the products as indicated in Fig. 1. According to the author, endrin (Fig. 1(a)) is first transformed into the intermediate hexachloropentacyclic ketone (Fig. 1(b)) and then to a dechlorinated product.

The first step in this reaction is one that can also be carried out using concentrated sulphuric acid (CHAU 1970c) and appears to be an acid-catalysed isomerisation. The second step, involving the substitution of Cl by H, requires a reducing agent and this role is filled by the chromium (II) reagent.

There are several other metal ion reducing systems which might also effect this transformation, two such being the V(II)/- V(III) and the Ti(III)/Ti(IV) couple. The present paper reports the results of an investigation of the reaction between vanadium (II) solutions and endrin in aqueous DMF (dimethylformamide). DMF was considered preferable to acetone for several reasons (a) Its lower volatility permits reactions to be carried out at temperatures above ambient without reflux; (b) It is more widely recommended for organic synthesis where reactions between ionic and nonpolar species are attempted; (c) Its greater base strength would tend to enhance the reduction potential of the V(II)/- V(III) couple.

MATERIALS AND METHODS

Endrin: 120 mL of a 20% emulsifiable concentrate was extracted three times with hexane, then back-washed with 2x200 mL of 10% Na_2SO_4 solution, followed by 3x300 mL of distilled H_2O. After drying over anhydrous sodium sulphate, the solvent was removed and the residue recrystallized several times from distilled hexane. The melting point and chromatographic behaviour of this product was compared with that of a 99% pure endrin sample (Applied Science Laboratories) to confirm its purity.
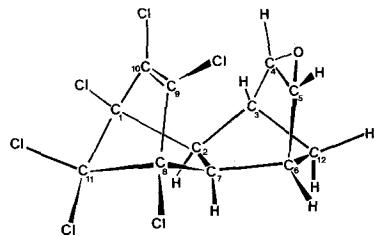
(a) Endrin
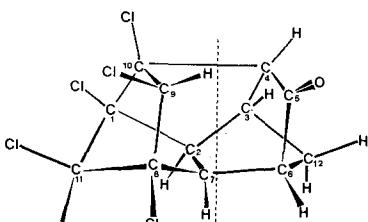
(b) Hexachloropentacyclic Ketone
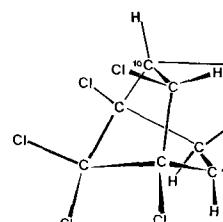
(c)
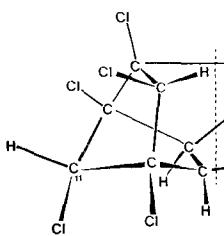
(d)
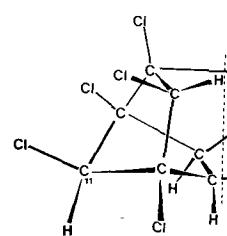
(e)

Figure 1. Structures of the products
of the V(II)-endrin reaction.

Vanadium (II) reagent: a 20% solution of vanadyl sulphate
(BDH, L.R. grade) was dissolved in 2M sulphuric acid. Approximately
200 mL was allowed to remain in contact with amalgamated zinc
(150g) for at least 4 hours under a envelope of N_2 gas after which
time the blue solution changed through green to deep violet. The
concentration of V(II) in the resulting solution (normally 0.6-
0.7M) was estimated by titration with standardised Fe (III)
solution using phenosafranine indicator.

Solvents: Ethyl acetate, chloroform, DMF and hexane were all redistilled.

Instrumentation: Gas chromatograph: Column OV-210 6%/SE-30 4% mixed or OV-17 %, 1.5m x 3mm ID (glass), isothermal at 220°C; arrier gas N_2 at 45 mL/min; detection, [63]Ni electron capture.

GCMS: Kratos MS-25, mass range 14-432, scan rate 1 second/decade; source mode, electron impact; gas chromatographic conditions, capilliary column OV-1 50m x 0.3mm ID, isothermal at 200°C; data system, Nova 4x computer with 64K bytes of 400 ms MOS memory.

NMR: Bruker HX-90 Fourier transform mode, ^{13}C-Nucleus at 22.63 MHz; internal reference, tetramethylsilane; solvent, deuterated chloroform.

Reaction Conditions: Endrin (0.5g) was dissolved in 450 mL of DMF to which 125mL of water was added. This mixture was transferred to a vessel suitable for inert atmosphere reactions where it was degassed with N_2 for 30 mins. Vanadium (II) reagent (100mL) was added via a pressure equalising funnel while an envelope of N_2 was maintained in the vessel. The reaction was allowed to proceed under N_2 typically for either 3 hr at 30°C or 12 hr at 70°C. The reaction mixture was then added to 1 litre of saturated aqueous Na_2SO_4 solution and this was extracted three times with 250 mL portions of ethyl acetate. The combined extracts were back washed with 3 x 250 mL of water and dried over anhydrous Na_2SO_4 for two hours. For those reactions carried out at 30°C and for 3 hr., the dominant product was isolated as follows: after filtration, the extracts were evaporated to dryness on a rotary evaporator, and the solid residue obtained was recrystallised from boiling chloroform and the filtrate with ice-cold hexane. A product which melted with decomposition over the range 275-285°C was obtained. GC, and GCMS studies were on the dried ethyl acetate extracts. Figure 2 shows typical GC traces of the reaction mixtures at 70°C (2(a)), at 30°C (2(b)) and the unreacted endrin solution (2(c)).

PRODUCT CHARACTERISATION

The traces in Fig. 2 are consistent with the presence of four principal components A,B,C, and D. At the lower temperature, the main product is C whilst at the higher temperature A,B, and D predominate.

Component C, which can be isolated in crystallisable amounts, was characterised as follows:

The GC elution behaviour was compared to that of the hexachloropentacyclic ketone (Fig 1(b)) (prepared according to the methods described by CHAU et al, 1971 and SOLOWAY et al, 1960), on two columns - a mixed column OV-210/SE-30, and on OV-17, and was found to be identical in both cases.
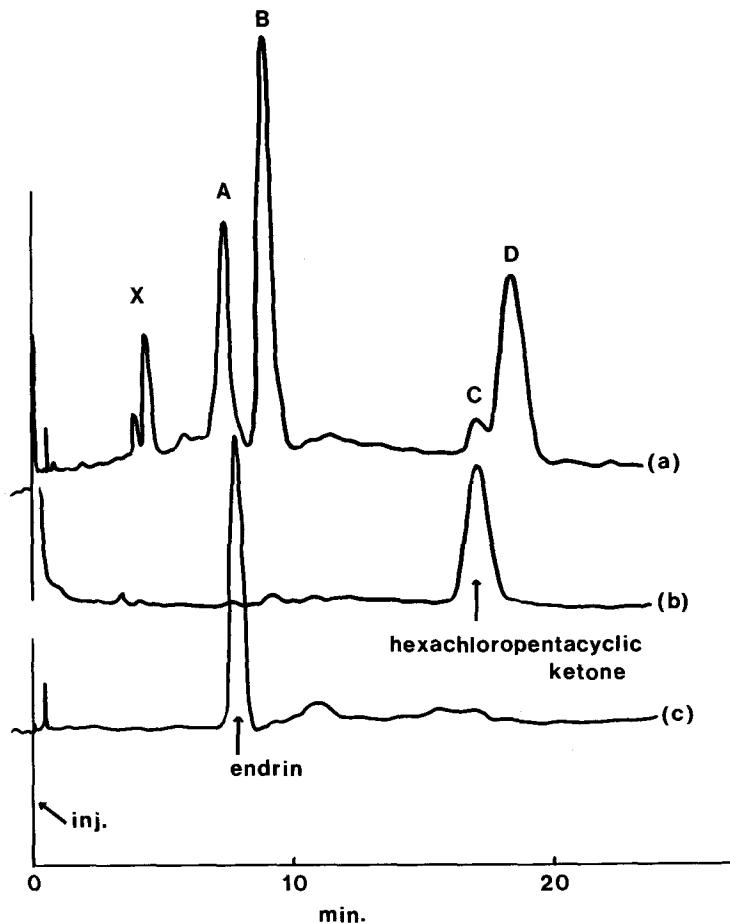
Figure 2. GC trace of the products
of VII-endrin reactions

Elemental analysis yielded the following results C=37.4%, H=2.2%, Cl=56.1%, with that expected for the pentacyclic ketone C=37.8%, H=2.1%, Cl=55.9%.

The pattern of infrared absorptions obtained for both component C and for the hexachloropentacyclic ketone prepared by the literature methods were found to be identical, each showing a characteristic strong absorption at $1750cm^{-1}$ and lacking one at $1600cm^{-1}$ which is a characteristic feature of the dichlororethylene group of endrin itself.

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The Carbon-13 N.M.R. spectrum of component C showed the same features as that of the compound prepared according to the method of Chau. Analysis of the spectra showed twelve unique carbon atoms including seven strong hydrogen substituted carbon resonances indicating loss of the symmetry of the parent molecule, endrin. A single peak appeared well downfield at $\delta=206.0$ ppm relative to TMS and this is considered to be diagnostic of a carbon atom in a carbonyl group.

The mass spectrum of component C together with those of A, B and D were obtained from the dried ethyl acetate extract (Fig. 3). The mass spectrum of C was identical to that for the hexachloro-pentacyclic ketone prepared by the other methods with a parent ion mass number of 378. ($6xCl^{35}$, $0xCl^{37}$)

Components, A,B and D were not isolated and information as to their identity was obtained from GC and GCMS data only.

The GCMS data (Fig. 3) indicates that three distinct pentachloro-species are produced each having a parent ion mass
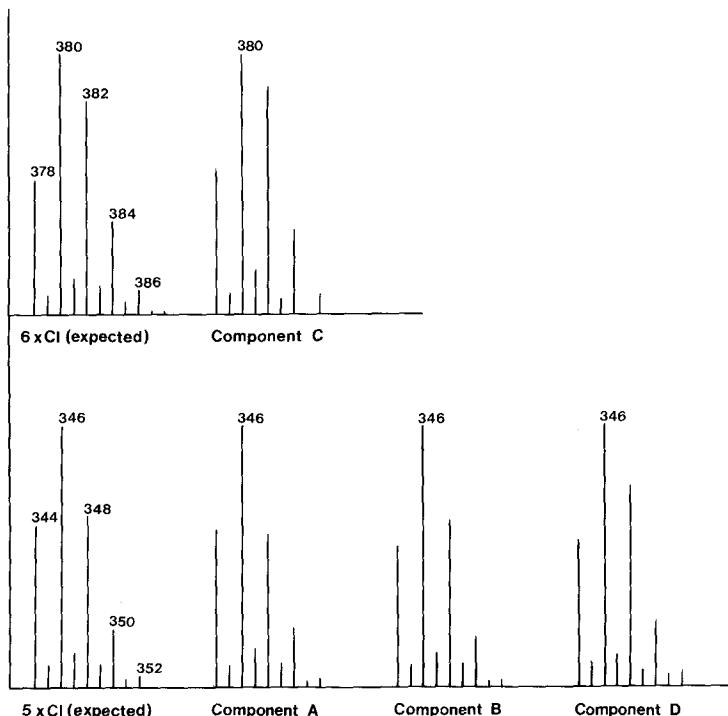

Figure 3. Intensity distributions of chlorine isotope m/e values for parent ions of products A,B,C and D.

number of 344, (5xCl³⁵, 0xCl³⁷) corresponding to the loss of one chlorine atom from endrin. Their proposed structures are shown in Fig. 1.

The GC retention times and the mass spectra of component D and the pentachloropentacyclic ketone prepared according to Chau, were found to be the same, which would allow the assignment to it of the structure in Fig. 1(e) (CHAU and WILKINSON, 1972).

Further support for assignment of these structures to components A,B and D was obtained as a result of an experiment to study the reaction of the hexachloropentacyclic ketone itself with vanadium (II) under the same conditions used for endrin (as described in 2.3 and 2.4). It was found that a GC trace of the product solution comprised four peaks, three with an identical rentention time to those of A,B and D and one corresponding to the remaining unreacted hexachloropentacyclic ketone.

DISCUSSION AND CONCLUSIONS

Under mild conditions, the V(II) reagent converts endrin almost exclusively to the hexachloropentacyclic ketone (Fig. 1(b)). Reaction under more forcing conditions (70°C/12h) results in the gradual disappearance of this compound and the emergence of the pentachloropentacyclic ketone (Component D) together with two other compounds (A,B) which, according to the GCMS data, have the same molecular weight as D, and these have been tentatively assigned the structures 1(c) and 1(d).

It would appear then, that V(II) acts as a combination of Lewis acid (to catalyse the conversion of endrin to the hexachloropentacyclic ketone) and reducing agent, which reductively dechlorinates this ketone.

The loss of more than one chlorine occurs with some difficulty, using this reagent, and 4-chloro species (Fig. 2, Peaks X) appear only after prolonged reaction time at elevated temperature.

By contrast, it was found that Cr(II) solutions in DMF react in a similar way but readily yield a mixture of compounds ranging from 5-chlorine to 2-chlorine species, and this is consistent with one's expectation that Cr(II) solutions would act as a more powerful reducing agent.

As a potential confirmation procedure, the use of V(II) solutions offers the advantage that, under mild conditions, endrin is converted into fewer derivative species which retain greater electron-capturing properties; and this would be of value in the not unusual situation where sensitivity is a consideration.

It should also be added that preparation and manipulation of vanadium (II) reagents presents no greater difficulties than for those of chromium (II).

ACKNOWLEDGEMENTS

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