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Confirmation of Residue Identity: Characterisation of Products of the Reaction Between Chromium (II) Solutions and Aldrin

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A procedure has been recommended for confirmation of the identity of several chlorinated cyclodiene insecticides involving the reaction with chromium (II) solutions in an aqueous-polar organic solvent mixture (CHAU 1970a,b, COCHRANE & CHAU 1970, CHAU & COCHRANE 1971). The resulting derivatives, which have similar chromatographic properties to the original compound, are extracted into hexane and injected into the GC, again using electron capture detection mode.

This method of confirmation is considered to be more positive than the injection of the original extract into several columns with differing polarities.

A number of publications (CHAU 1970a,b, COCHRANE & CHAU 1970) have dealt with the identification of these products and, while the question of their identity may not necessarily be of immediate concern to practising residue chemists, some understanding of the reaction that produces them may offer a rational basis for deciding whether or not the method is applicable to other situations. This paper reports that the reaction between chromium (II) solutions and aldrin in aqueous dimethylformamide (DMF) yields three principal products, one of which predominates under the conditions described. Evidence is presented in support of the structural assignments made to these as indicated in Figure 1.

MATERIALS AND METHODS

Instrumentation. Suitably diluted extracts from the reaction mixture were injected into a gas chromatograph with electron capture detection. [Two glass columns each 1.5 m x 4 mm ID were used, one packed with 2% SE-30 on Chromosorb W and another with 1.5% OV-101 on Gas Chrom Q. These were operated at 180°C with a nitrogen carrier gas flow rate of 30 mL/min].

Mass spectral data was obtained using an instrument operating under the following conditions: GC column, OV-1 2% at 200°C, carrier gas He at 20 mL/min, scan rate 3 sec, M/e range 50-415, source mode electron impact.

Proton nmr spectra were obtained in $CDCl_3$ using tetramethylsilane as an internal standard.

Liquid chromatography of the reaction mixture was conducted using a 30 cm x 4 mm ID Micro Pak CH-10 column. Solvent ($CH_3CN:H_2O$, 97:3) was pumped at 1 mL/min and UV detection was at 232 nm.

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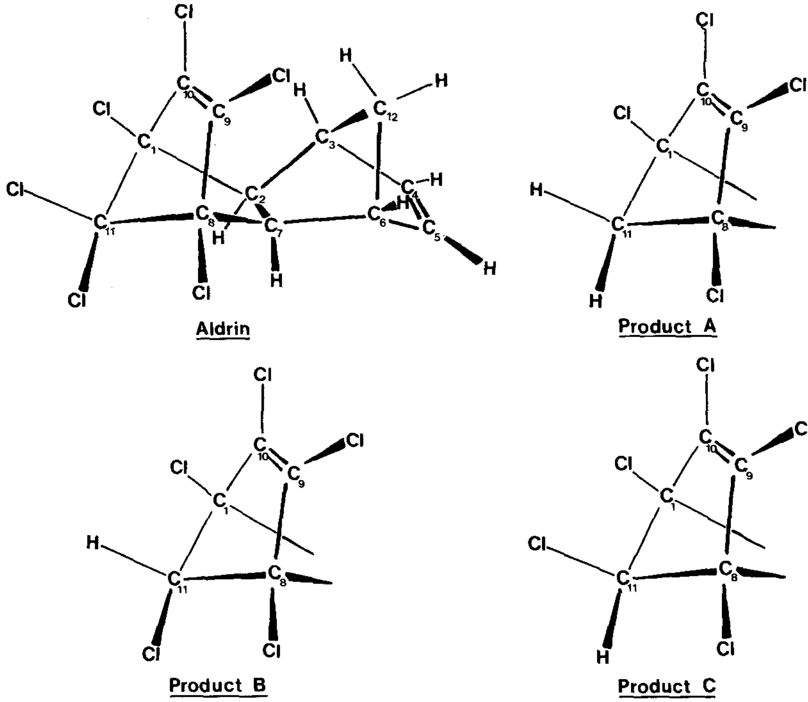

Aldrin

Product A

Product B

Product C

Figure 1. Structures of the products of the Cr(II)-aldrin reaction.

Reagents. Technical grade aldrin was recrystallized from hot ethanol. Its purity was checked against an Applied Science sample (> 90%) by GC.

Chromium (II) reagent - $CrCl_3.6H_2O$ (80 g) was dissolved in 130 mL water to which was added 20 mL of concentrated HCl. The mixture was allowed to stand over amalgamated zinc in a separating funnel fitted with a Bunsen valve, for approximately 12 h to produce a clear deep-blue solution of chromium (II) of approximately 1.2 M. The concentration was estimated using standardised potassium permanganate solution.

Reaction. Aldrin (250 mg) was dissolved in 300 mL DMF and the solution was transferred to a reaction vessel suitable for inert atmosphere reactions. The vessel was placed in a water bath at 70°C and a stream of nitrogen was passed through the solution to de-oxygenate the system. Chromium (II) solution (150 mL) was added and the reaction allowed to proceed for 1.5 h.

Cleanup. The reaction mixture was transferred to a separating funnel where 50 mL of 10% NaCl solution was added. This mixture was then extracted five times with 25 mL portions of hexane. The combined hexane extracts were dried over sodium sulphate and then concentrated using a rotary evaporator.

PRODUCT CHARACTERIZATION

GC of a hexane solution of the product mixture gave a trace consistent with the presence of three components. These all had retention times shorter than that of aldrin [Figure 2].

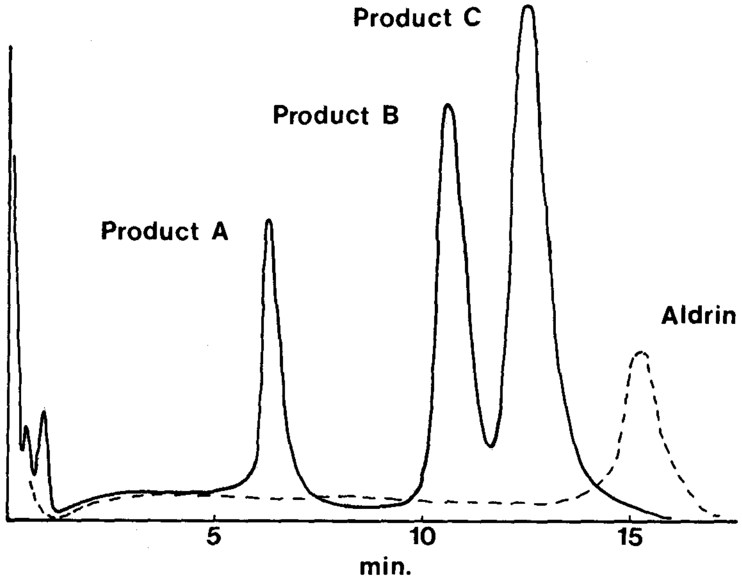

Figure 2. GC trace of the products of the Cr(II)-aldrin reaction

A hexane solution injected into the GC - mass spectrometer showed the earliest eluting component (Product A) had a parent ion of mass number 294 and the second and third components (Products B and C) each had parent ion mass numbers of 328. The distribution of the intensities of the chlorine isotopes in the parent ion of product A was consistent with that expected for four chlorine atoms i.e. a loss of two chlorines from the original six on aldrin. Similarly the intensity distributions for products B and C were each consistent with those expected for five chlorine atoms (Table 1).

TABLE 1a. Normalised intensity distributions of chlorine isotopes in peak of parent ion mass no = 294 (4 x ^{35}Cl, 0 x ^{37}Cl)

Isotope distribution	Expected intensity	Observed intensity for product A
4 x ^{35}Cl, 0 x ^{37}Cl	0.325	0.350
3 x ^{35}Cl, 1 x ^{37}Cl	0.422	0.399
2 x ^{35}CL, 2 x ^{37}Cl	0.205	0.210
1 x ^{35}Cl, 3 x ^{37}Cl	0.044	0.055
0 x ^{35}Cl, 4 x ^{37}Cl	0.004	-*

TABLE 1b. Normalised intensity distributions of chlorine isotopes in peaks of parent ion mass no = 328 (5 x ^{35}Cl, 0 x ^{37}Cl).

Isotope distribution	Expected intensity	Observed intensity Product B	Observed intensity Product C
5 x ^{35}Cl, 0 x ^{37}Cl	0.246	0.250	0.251
4 x ^{35}Cl, 1 x ^{37}Cl	0.398	0.391	0.390
3 x ^{35}Cl, 2 x ^{37}Cl	0.258	0.255	0.254
2 x ^{35}Cl, 3 x ^{37}Cl	0.084	0.084	0.086
1 x ^{35}Cl, 4 x ^{37}Cl	0.014	0.019	0.019
0 x ^{35}Cl, 5 x ^{37}Cl	0.001	-*	-*

* not observed

It was considered impractical to attempt to isolate three closely related species from the product mixture by macro-separation methods, but an attempt was made to separate the components by semi-preparative LC using the conditions described earlier.

Repeated 100 µL injections of a near saturated solution of the mixture in 50:50 CH_3CN/CH_2Cl_2 were made. The three components were then collected manually downstream of the detector and the eluant fractions evaporated at 60°C in a stream of dry filtered air.

Approximately 50 mg of Product C (a crystalline solid, m.p. 95-97°C) was isolated, together with very small quantities of Products A and B.

The stoichiometry of Product C was confirmed by elemental analysis. It was found to be C = 43.88%, H = 3.70%, Cl 53.5% (expected for $C_{12}H_9Cl_5$, C = 43.6%, H = 2.75%, Cl = 53.6%). Thus, both the mass spectral data and the elemental analysis support the assignment of Product C to a compound with the stoichiometry $C_{12}H_9Cl_5$, equivalent to the substitution of one chlorine atom on aldrin by a hydrogen atom.

Evidence in support of the assignment of the structure shown in Figure 1 to Product C i.e. the substitution of a chlorine atom on Carbon 11 by a proton is based on proton nmr data as follows:

A) The nmr spectrum is similar to that of aldrin except for the presence of an additional resonance at δ = 4.38 ppm.

B) This resonance is very sharp and shows no evidence of coupling to other protons as would be the case if this proton were attached to carbons 1 or 8.

C) Furthermore, its downfield shift at 4.38 ppm is consistent with the action of the inductive effect of a chlorine atom still bonded to the same carbon as this proton.

D) Apart from this additional peak the spectrum is as simple as that of aldrin and this is consistent with retention of a plane of symmetry in the molecule, leaving carbons 1, 8; 2, 7; 3, 6 and 10, 9 still equivalent. Substitution of a chlorine atom in any other position would have made all 12 carbon atoms non-equivalent, resulting in a substantially more complex nmr spectrum. Further support for this assignment comes from consideration of the relative reactivity of the chlorine atoms. It has been observed (WILLIAMSON et al. 1968) that mono-dechlorination is more likely to occur at the more reactive gem dichloride site than at other positions.

Acceptance of this assignment, however, still leaves unanswered the question of which of the two non-equivalent chlorine atoms on carbon 11 has been substituted.

The anisotropic influence of the chlorine-substituted double bond (carbons 9, 10) on the proton resonances in its vicinity provides a means by which a tentative choice may be made. Protons in the plane of the double bond experience a downfield shift while those above or below the plane tend to move upfield. The proton on carbon 11 in the structure assigned to Product C (Figure 1) is less under the influence of the paramagnetic effect operating in the region perpendicular to the plane of the double bond and therefore would be expected to appear further downfield than the proton on carbon 11 in the isomer (Product B)

The nmr spectrum of the isolated Product C showed a resonance at 4.38 ppm which was assigned to the proton on carbon 11. The nmr spectrum of the mixture before isolation of Product C showed an additional less intense resonance at 4.27 ppm. The relative positions of these two suggest, therefore, that the position of the proton in Product C is as shown in Figure 1.

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