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Note

Identification of dieldrin derivatives

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Various derivatization reagents have been used for the identification of dieldrin, a chlorinated cyclodiene insecticide[1–5]. However, all of these methods were carried out in test-tubes and the different derivatives were identified by gas chromatography. Recently the derivatization of this insecticide on thin-layer plates and subsequent identification of the derivatives together with the parent compound were reported[6], and it was observed that dieldrin gave two spots due to derivatives; one of them was postulated to be dieldrin ketone but the other could not be identified. The present work shows that both spots are dieldrin ketones.

EXPERIMENTAL

All reagents were of AnalaR grade. The gas chromatographic apparatus and operating conditions were identical with those described previously[7]. Infrared spectra were recorded on a Beckman Acculab-1 instrument. Melting points were determined using micro heating table (Boetius) and were not corrected.

The derivatization of dieldrin was carried out on thin-layer chromatographic (TLC) plates by using zinc chloride–hydrochloric acid reagent as reported earlier[6]. The spots of derivatives at R_F 0.39 and 0.61 were scraped off and collected separately. The scrapings were extracted with *n*-hexane and the extracts were subjected to different tests.

An aliquot of each extract was evaporated to dryness and the melting points of the residues were found to be 155°C (R_F 0.39) and 105°C (R_F 0.61). Each extract was also analysed by gas chromatography and retention times were measured relative to lindane as the internal standard.

RESULTS AND DISCUSSION

Dieldrin on derivatization is known to be converted mainly to dieldrin ketone[2], and hence the predominant spot at R_F 0.39 (Table I) was previously postulated as dieldrin ketone. The data in Table I show that the extract of this spot and also that at R_F 0.61 gave positive responses with reagents such as 3,5-dinitrobenzoic acid and Schiff's reagent that are normally used for locating ketones, and the infrared spectra (KBr) of both extracts exhibited bands to OH (3450 cm^{-1}), C=O (1740 cm^{-1}) and ClC=CCl (1600 cm^{-1}. However, they had different relative retention times (6.8 and 5.9, respectively) and melting points (155 and 105°C, respectively).

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TABLE I
SUMMARY OF THE DIFFERENT TESTS CARRIED OUT ON EXTRACTS OF DIELDRIN DERIVATIVES

R_F value of extract of spot	*Test for ketones*	*Melting point (°C)*	*RRT**	*IR bands (cm^{-1})*
0.39	Positive	155	6.8	C=O (1740) OH (3450) ClC=CCl (1600)
0.61	Positive	105	5.6	C=O (1740) OH (3450) ClC=CCl (1600)

* Retention time relative to lindane.

Wienke and Burke[4] reported that treatment of dieldrin with zinc chloride–hydrochloric acid reagent normally gives a chlorohydrin via epoxide ring opening. Lombardo *et al.*[8] prepared aldrin chlorohydrin (melting point 150–152°C) by zinc chloride–hydrochloric acid method (yield 84%), with IR bands due to OH (3240 cm^{-1}) and ClC=CCl (1595 cm^{-1}). Dieldrin reacts with strong mineral acids to form a number of skeletally rearranged products. Originally Baker and Skerrett[9] used boron trifluoride etherate to produce "dieldrin ketone", which was also formed on using concentrated sulphuric acid[10]. However, all of these reactions yield a multi-component mixture (TLC giving at least three major spots with sulphuric acid and four with boron trifluoride–diethyl ether), although one product from the sulphuric acid reaction was isolated and exhibited IR bands due to C=O (1715 cm^{-1}), ClC =CCl (1602 cm^{-1}) and CH_2 (1368 cm^{-1}). The products from these reactions were collectively designated "dieldrin ketones"[10].

As aldrin chlorohydrin shows IR bands due to OH (3240 cm^{-1}) and ClC=CCl (1595 cm^{-1}) and both of the reaction products obtained in the present study show the presence of a C=O group, it appears that aldrin chlorohydrin formed *in situ* undergoes dehydrochlorination[10], resulting in the formation of two keto compounds. Moreover, the two keto compounds undergo reduction with zinc–hydrochloric acid. resulting in one compound (dieldrin). This indicates that dieldrin on derivatization with zinc chloride–hydrochloric acid on thin-layer plates was converted into two dieldrin ketones.

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