

Note

An unusual impurity 1, 2, 3, 4, 6, 7, 8, 9, 10, 10, 11, 11-dodecachloro-1, 4, 4a, 5a, 6, 9, 9a, 9b-octahydro-1, 4, 6, 9-dimethanodibenzo-furan formation in minor amount during endosulfan synthesis

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An unusual product, 1, 2, 3, 4, 6, 7, 8, 9, 10, 10, 11, 11-dodecachloro-1, 4, 4a, 5a, 6, 9, 9a, 9b-octahydro-1, 4, 6, 9-dimethanodibenzo-furan, as an impurity in minor quantity has been isolated from technical endosulfan and its structure was determined by spectroscopic data (IR, ¹H and ¹³C NMR and Mass) and finally confirmed by synthesis. The route for the formation of this compound is also discussed.

Many technical grade pesticides contain associated minor components. It is essential to identify these minor components for maximizing the quality of commercial pesticides¹⁻⁴. Endosulfan (6, 7, 8, 9, 10, 10-hexachloro-1, 5, 5a, 6, 9, 9a-hexahydro-6, 9-

methano-2, 4, 3-benzodioxathiepin-3-oxide), a mixture of α - and β -isomer **1**, is an organochlorine insecticide, widely being used on a variety of cereals, fruits, vegetables and cotton⁵. The synthesis of endosulfan involves the Diels-Alder reaction of hexachlorocyclopentadiene and *cis*-2-butene-1, 4-diol and followed by the reaction with thionyl chloride.⁶ During the synthesis of endosulfan, the formation of 4, 5, 6, 7, 10, 10-hexachloro-4, 7-endomethylene-4, 7, 8, 9-tetrahydrophthalan (endosulfan ether) **2** and 1, 2, 3, 4, 7, 7-hexachloro-5, 6-bis(chloromethyl)-bicyclo-[2.2.1]-heptene-2 **3** have been well-established⁷.

From the technical endosulfan, we isolated a minor impurity by virtue of its low solubility in most of the common organic solvents and creating a haziness problem while formulating as emulsifying concentrate. The present paper describes the isolation, characterization and proposed a route for formation of this impurity.

The retention time (Rt) of all impurities present in endosulfan technical (95.2%) along with endosulfan isomers (α and β) by gas chromatography are given in the **Table I**. The impurity at Rt 36.95 min was isolated as colourless crystals from endosulfan technical due to its poor solubility. The IR spectrum showed the presence of C=C (1605 cm⁻¹) and C—O str. (1105 cm⁻¹) indicating the presence of oxygen in

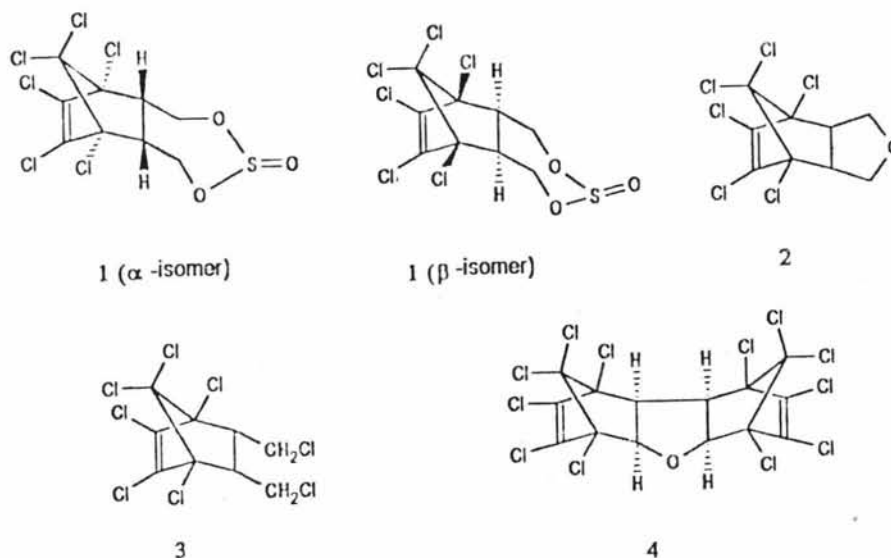
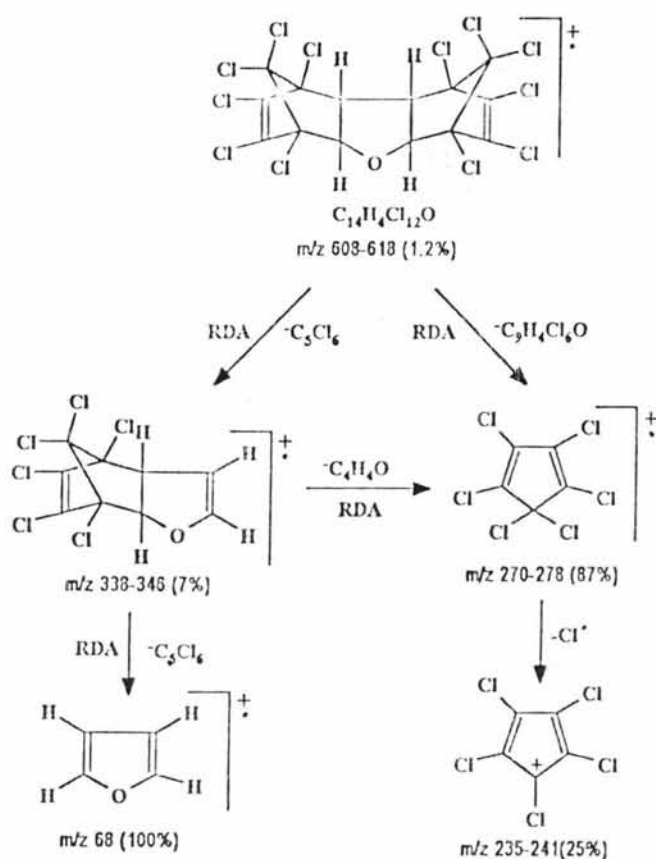


Table I—Gas chromatographic retention time (min) of different impurities in endosulfan technical (95.2%)

Sl. No.	Compd	GC-Rt (min)
1	HCCP	8.09
2	Endo-ether(2)	18.42
3	Unknown	22.89
4	α -Endosulfan (1)	24.2
5	β -Endosulfan (1)	25.73
6	Unknown	29.37
7	Compound (4)	36.95

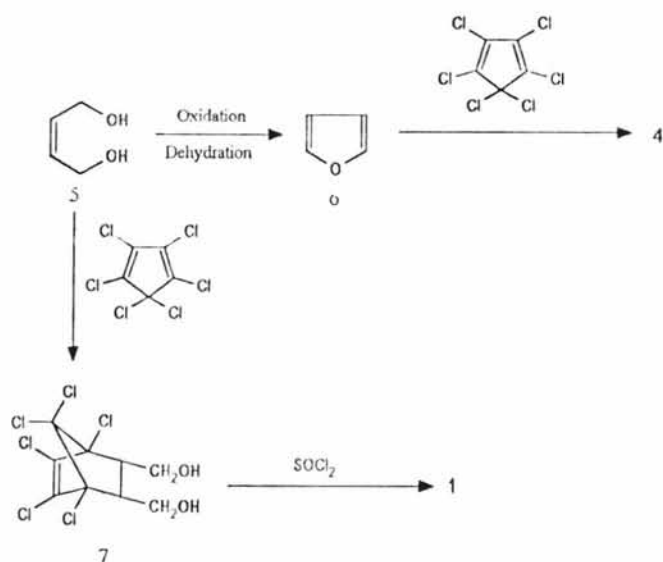
the molecule. The electron impact mass spectrum showed the molecular ion at m/z 608[†] (M^+) and other fragments were at m/z 338[†] [$M-C_5Cl_6$][†], 270[†] [C_5Cl_6][†], 235[†] [C_5Cl_5][†] and 68 [C_4H_4O][†] as base peak (Scheme I). The m/z 68 showed the presence of a furan moiety in the compound. Mass spectrum clearly showed that the compound contains 2 molecules of hexachlorocyclopentadiene (HCCP) and one molecule of furan. Hence, the compound is a Diels-Alder adduct of HCCP (2 mole) and furan (1 mole) and 4 could be the most probable structure where HCCP act only as a diene⁸ and furan as ene. The ¹H NMR spectrum showed two signals at δ 3.52 (d , $J=6.2$ Hz, $2H$) and 4.92 (d , $J=6.2$ Hz, $2H$) and NOESY spectrum showed that the protons at δ 3.52 had interaction with protons at δ 4.92 and hence these protons are *cis* to each other and assigned to 9a, 9b-*H* and 4a, 5a-*H*, respectively. The ¹³C NMR showed 9 signals out of which 5 signals are due to 10 carbon atoms appeared at δ 133.42, 128.97, 101.88, 94.25 and 54.49 and other 4 carbons appeared at δ 80.03, 81.79, 93.96 and 94.54 which indicate the molecule is somewhat symmetrical. Hence, the compound was identified as 1, 2, 3, 4, 6, 7, 8, 9, 10, 10, 11, 11-dodecachloro-1, 4, 4a, 5a, 6, 9, 9a, 9b-octahydro-1, 4, 6, 9-dimethanodibenzofuran (5-oxapentacyclo-[2.2.1.1.0.0]-1, 2, 3, 4, 6, 7, 8, 9, 10, 10, 11, 11-dodecachloropentadeca-2, 7-diene) 4. The assignment of all carbon atoms were made by analogy with ¹³C NMR of endrin and dieldrin⁹ (Experimental). The structure 4 was further confirmed by its synthesis^{10, 11}. The Diels-Alder reaction of HCCP (2 mole) and furan (1 mole) at 135–45°C for 4 hr afforded the diadduct, which was found to be identical with 4 isolated from

[†]The m/z values are calculated using only Cl^{35} isotope

**Scheme I**

endosulfan, in all spectroscopic data (superimposable IR, ¹H and ¹³C NMR and MS) and mp and mmp.

The compound 4 had formed by Diels-Alder reaction of HCCP with furan and probably furan might have been present in *cis*-2-butene-1, 4-diol (BD; 5). Hence, commercial BD samples were screened for the presence of furan and it was found that all samples contain traces of furan [0.01-0.09% (GC area%)] which was confirmed by GC-MS and by comparison with authentic sample of furan by co-injection in GC. In another experiment BD free from furan was treated with HCCP at 160°C for 6 hr under the condition of endosulfan synthesis and found that compound 4 was also formed in the reaction mixture which clearly indicate that furan had formed from BD during the reaction. The formation of furan from BD was further confirmed by heating of BD at 160°C for 6 hr and found that furan had formed in small amount (0.5%). Hence, in the present case furan had formed on heating of BD *via* oxidation followed by subsequent dehydration which underwent Diels-Alder reaction with HCCP to afford 4 along with the 1, 2, 3, 4, 7, 7-hexachloro-5, 6-bis(hydroxymethyl)-bicyclo-[2.2.1]-heptene-2 (endosulfan alcohol; 7) during the



Scheme II

first step of the synthesis of endosulfan and compound 4 has been carried forward to the final step due to its poor solubility as shown in **Scheme II**. The formation of furan from BD is further supported by the fact that oxidation of BD in presence of oxidising agent¹² or catalyst¹³ afforded furan in good yield.

Experimental Section

Melting points were determined in open capillaries and are uncorrected. Gas liquid chromatography was conducted on a Perkin-Elmer GC auto system 1022 model equipped with flame ionization detector (FID) for routine analysis. A glass column (2 m \times 2 mm i.d.) packed with 10% SE-30 on a chromosorb WHP (80-100 mesh) was used. Injector and detector temperature were 250°C and 280°C, respectively and oven temperature programmed from 125°C to 240°C at the rate of 5°C min⁻¹ with an initial temperature for 1 min. Nitrogen was used as carrier gas at a flow rate of 25 ml min⁻¹. GC-MS was recorded by Shimadzu QP-2000 operating at 70 eV equipped with capillary column DB-1 (30 m \times 0.3 mm i.d., film thickness 0.25 μ) and helium was used as carrier gas. Oven temperature was programmed from 40°C to 200°C at the rate of 5°C min⁻¹ with initial temperature for 5 min and injector temperature was 150°C. ¹H (500 MHz) and ¹³C (125 MHz) NMR were recorded by Bruker DRX-500 FT-NMR instrument in CDCl_3 and CCl_4 using tetramethylsilane as an internal standard. IR spectra were recorded in KBr pellet using Perkin-Elmer model 1310 spectrophotometer. The electron impact mass spectra (EIMS) of the purified compounds were obtained at 70 eV on a

JEOL model MS-DX-300 mass spectrometer. Technical grade endosulfan (95.2% purity), hexachlorocyclopentadiene (98%) and *cis*-2-butene-1,4-diol were obtained from E.I.D. Parry (I) Ltd., Technical Pesticide Plant, Mumbai, India. Furan (>98% purity) was purchased from E. Merck, Germany. All solvents used in this study were of analytical grade.

Isolation of 1, 2, 3, 4, 6, 7, 8, 9, 10, 10, 11, 11-dodecachloro-1, 4, 4a, 5a, 6, 9, 9a, 9b-octahydro-1, 4, 6, 9-dimethanodibenzofuran 4 from endosulfan technical. Technical endosulfan (1 kg) was dissolved in 750 mL of acetone and filtered through Whatman No. 1 filter paper. The residue on filter paper was washed thoroughly with acetone and recrystallized from CCl_4 to afford colourless crystals of 1, 2, 3, 4, 6, 7, 8, 9, 10, 10, 11, 11-dodecachloro-1, 4, 4a, 5a, 6, 9, 9a, 9b-octahydro-1, 4, 6, 9-dimethanodibenzofuran (4; 200 mg): m.p. 291-92°C (Lit¹⁰ m.p. 277-81°C) Anal. Found: C, 27.22; H, 0.66. Calc. for $\text{C}_{14}\text{H}_4\text{Cl}_{12}\text{O}$: C, 27.36; H, 0.65%; IR: 1605 (C=C), 1105 cm⁻¹ (C—O); ¹H NMR (CDCl_3): δ 3.52 (d, $J=6.2$ Hz, 2H) and 4.92 (d, $J=6.2$ Hz, 2H); ¹³C-NMR (CCl_4): δ 54.49 (C_{9a} and C_{9b}), 80.03 (C_1 or C_9), 81.79 (C_9 or C_1), 93.96 (C_4 or C_6), 94.54 (C_6 or C_4), 94.25 (C_{4a} and C_{5a}), 101.88 (C_{10} and C_{11}), 129.97 (C_3 and C_7) and 133.42 (C_2 and C_8); EIMS m/z : 608-618 (M^+ , 1.2), 338-346 (7), 270-278 (87), 235-241(25) and 68 (100%).

Synthesis of 1, 2, 3, 4, 6, 7, 8, 9, 10, 10, 11, 11-dodecachloro-1, 4, 4a, 5a, 6, 9, 9a, 9b-octahydro-1, 4, 6, 9-dimethanodibenzofuran 4. Hexachlorocyclopentadiene (10.9 g) was placed into a four necked round bottom flask (250 mL) equipped with stirrer, thermometer and reflux condenser. The ice cold water was circulated through the condenser and temperature of flask was raised to 145°C by keeping it in an oil bath. A mixture of furan (13.6 g) and hexachloropentadiene (10.9 g) was added to the flask over a period of 30 min through pressure equalising separating funnel. The reaction mixture was heated at 135°C to 140°C for 4 hr. The reaction mixture was cooled to room temperature, the solid obtained was filtered and washed thoroughly with CCl_4 and acetone. The solid was recrystallised by CCl_4 to give 1, 2, 3, 4, 6, 7, 8, 9, 10, 10, 11, 11-dodecachloro-1, 4, 4a, 5a, 6, 9, 9a, 9b-octahydro-1, 4, 6, 9-dimethanodibenzofuran (6.7 g), mp 291-92°C, mmp 291-92°C.

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