Conversion of Heptachlor to its Epoxide

by JOGINDER SINGH
Scientific Services Laboratory
Department of Agriculture, Ottawa, Canada

Carlson (1) has shown that one of the isomers of heptachlor epoxide (1,4,5,6,7,8,8-heptachlor-2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-endo methanoindane) with m.p. 157-158°C is very toxic to a wide variety of insects. It was in 1953 when Davidow and Radomski (2) observed that adipose tissue of dogs fed heptachlor (1,4,5,6,7,8,8-heptachlor-3a,4,7,7a-tetrahydro-4,7-endomethanoindene) indicated the presence of metabolically altered derivative of heptachlor. They extracted the derivative from dog fat and found it to be the above isomer of heptachlor epoxide. Their trials to prepare it from heptachlor via halohydrin formation gave another isomer of heptachlor epoxide with m.p. 86-89°C. Synthesis of this isomer from chlordene has been described (3). Carlson's synthesis of the toxic isomer of heptachlor epoxide (m.p. 157-158°C) involves many steps and does not give very high yield.

In this communication a method is described to prepare the isomer of heptachlor epoxide (m.p. 157-160°C) from heptachlor in one step oxidation with yield approximately 60% of the theoretical

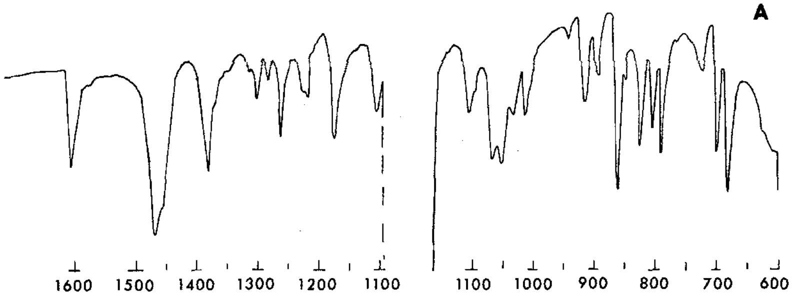
Bulletin of Environmental Contamination & Toxicology,
Vol. 4, No. 2, 1969, published by Springer-Verlag New York Inc.

amount. The oxidation of heptachlor was carried out by using CrO_3 in acetic acid.

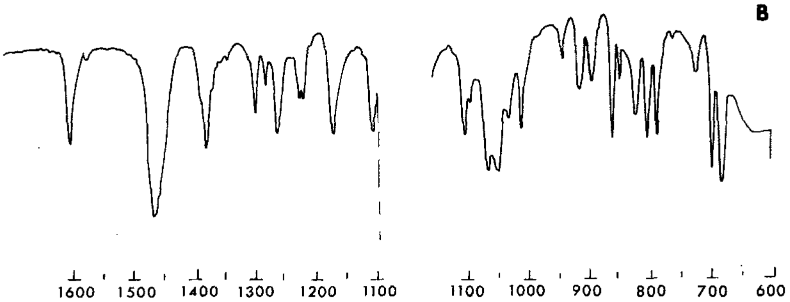
The identity of the prepared derivative with the authentic compound (from Velsicol Chemical Corporation) was established by the following three criteria: (a) no depression in melting point (157-159°C); (b) identical I.R. spectra (Figure 1); (c) identical N.M.R. spectra. The N.M.R. spectra gave one proton doublet of doublets at τ 6.70 with J values of 3 and 8 cps, three proton triplet at τ 6.30 with J value of 3.5 cps and multiplet at τ 5.70.

Figure 1

I.R. SPECTRUM OF HEPTACHLOR EPOXIDE PREPARED FROM HEPTACHLOR



I.R. SPECTRUM OF HEPTACHLOR EPOXIDE PREPARED FROM VELSICOL



CORRECTION - B should read "I.R. spectrum of heptachlor epoxide prepared by Velsicol"

The I.R. was taken in nujol. The spectrum beyond 1600 cm^{-1} does not show any band except that due to nujol at 2865 and 2950 cm^{-1}.

Experimental

Oxidizing Mixture:- Weigh five grams of chromium trioxide (Analar reagent BDH) in 5 ml of distilled water and then add to this 50 ml of glacial acetic acid (Analytical reagent Mallinckrodt).

Pure heptachlor, 200 mg, was taken in an Erlenmeyer (50 ml capacity) with ground glass stopper. To this was added 10 ml of oxidizing mixture and 0.5 ml of concentrated sulfuric acid. The reaction mixture was well shaken and heated in boiling water for 5 - 7 minutes. At this stage the reaction mixture was cooled, diluted with 75 ml of distilled water in a separatory funnel of 150 ml capacity and extracted with 200 ml of Skellysolve F (Pet. ether 30-60°C) in four portions of 50 ml each. The Skellysolve F fraction was then washed twice with distilled water and dried by filtering through a bed of anhydrous sodium sulfate. The Skellysolve F was evaporated and the residue crystallized from aqueous ethanol. The m.p. of the compound was 158-160°C. The yield was 125 mg, i.e. 60% of the theoretical amount.

References

1. Arthur W. Carlson (Velsicol Chem. Corp.), Patent U.S. 3,118,913 C.A. Vol. 60, p 9245h (1966)

2. Bernard Davidow and Jack L. Radomski, J. Pharmacol. Expte. Therapy, 107, p 259 (1953)

3. Arvey Corporation, Patent Brit. 714,869, C.A. Vol. 50, p 402b (1956)