Identification of the Derivatives Employed in the Confirmation of Dieldrin Residues

by ALFRED S. Y. CHAU* and W. P. COCHRANE
Analytical Services Section
Plant Products Division, Canada Department of Agriculture
Ottawa, Ontario, Canada

Although a number of interesting reactions of isodrin, endrin and aldrin have been reported (1,2,3,4,5), the chemistry of the related compound, dieldrin, seems to have been investigated less. This may be due to the unusual stability of the epoxide ring of dieldrin to acids and bases as compared to other epoxides. However, hydrogen bromide in acetic acid (6) and hydrogen bromide in anhydrous dioxane (7), gave, respectively, an acetoxy-bromodihydroaldrin and hydroxy-bromodihydroaldrin. Lewis acids such as BF_3 (8) and mineral acids such as H_2SO_4 (9) and $HClO_4$ (10) were known to rearrange dieldrin presumably to an oxo-dihydroaldrin. The first reaction was the basis for colorimetric determination of dieldrin (8) where the latter was used for the confirmation of dieldrin in agricultural crops (9). Dieldrin also gave a more polar compound when exposed to U.V. light or to sunlight in the field (11,12,13,14).

Recently, Chau and Cochrane (9) reported a chemical derivation method for the confirmation of dieldrin in agricultural sample extracts by reaction of dieldrin with acetic anhydride and catalytic amounts of sulfuric acid; a reaction based in part on the familiar 2,4-dinitrophenylhydrazone colorimetric method (15) for the determination of dieldrin. However, the exact structure of these products from this chemical reaction were uncertain. It seems worthwhile to investigate further the products of this relatively less understood reaction on the macro-scale. This paper delineates the preliminary findings on the structure of reaction products from the acetic anhydride-sulfuric acid reaction with dieldrin.

---

*Present address: Inland Waters Branch, Department of Energy, Mines and Resources, 45 Spencer Street, Ottawa, Ontario, Canada.

Bulletin of Environmental Contamination & Toxicology,
Vol. 5, No. 6, 1971, published by Springer-Verlag New York Inc.

MATERIALS AND METHODS

Reagents

a) Acetic anhydride --- reagent grade, was redistilled twice over anhydrous sodium acetate.
b) Decolorizing charcoal --- Allied chemical and Dye Corp., U.S.A. was used without prior treatment.
c) Analytical grade sulfuric acid, chloroform, and benzene were used without prior purification.
d) Technical dieldrin standard (85% purity) --- City Chemical Corp., U.S.A., was purified before use (see experimental section below).
e) Acetylating reagent --- 0.5 ml conc. sulfuric in 50 ml purified acetic anhydride.

Instruments

IR spectra were recorded on a Beckman IR-7 Spectrophotometer in Nujol mulls and in $CHCl_3$ solution. Melting points were determined on a Fisher-Johns hot stage apparatus and are uncorrected. NMR spectra were determined at 60 Mc/sec on a Varian 60 Mc instrument; chemical shifts are given in τ units relative to tetramethylsilane as an internal standard. Solvent used was deuterochloroform.

Purification of dieldrin (I)

Ten grams of technical dieldrin was dissolved in 50 ml boiling hexane and the solution was passed through a neutral alumina (160 gm.) column, previously prepared from a slurry of alumina and hexane. Elution with 500 ml of hexane-ether (9.5:0.5) solvent mixture and evaporation of solvent under vacuum gave 6.5 gm of white solid. Recrystallization two times from hexane-ether (8:2) at 0°C gave pure dieldrin (as confirmed by TLC, GLC and mixed melting point measurements). This was used for subsequent reactions.

Acetylation of dieldrin (I)

In a 100 ml round bottom flask fitted with a condenser, one gram of dieldrin in 60 ml acetylating reagent was refluxed vigorously using a heating mantle. After one hour of refluxing, the reaction mixture was

concentrated to 25-30 ml by distillation of acetic anhydride. The reaction mixture was cooled to room temperature and poured into a 1 l. separatory funnel containing ice-cooled 50% NaOH solution (100 ml). The mixture was briefly shaken and 20% Na_2CO_3 solution was cautiously added in small portions with agitation until evolution of CO_2 subsided. After dilution with ca. 200 ml of distilled water, the mixture was extracted with chloroform (4 x 100 ml). Concentration of the dried extracts (by anhydrous Na_2SO_4) and purification through a charcoal column gave 0.58g. of solid upon standing overnight. Recrystallization three times from benzene-hexane gave pure II, m.p. 204-205°C.

Calcd. for $C_{16}H_{14}Cl_6O_4$: C,39.6%; H,2.9%; Cl,44.05%

Found: C,39.81%; H,2.73%; Cl,44.34%

The mother liquor was concentrated and passed through ca. 20 gm of charcoal to give 0.32 gm of waxy solid. Crystallizations from benzene-hexane and finally from chloroform gave pure III, m.p. 256-257°C.

Calcd. for $C_{16}H_{14}Cl_6O_4$: C,39.6%; H,2.9%; Cl,44.05%

Found: C,39.61%; H,2.8%; Cl,44.27%

Thin-layer chromatography of the mother liquor of III (silica gel developed in 2 ml acetone and 200 ml hexane) gave a monoacetate, m.p. 214°C, together with some II, III and starting material.

RESULTS AND DISCUSSION

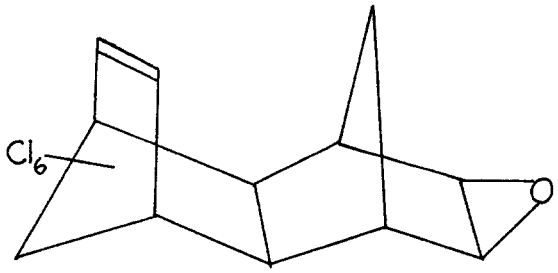
The main products, m.p. 204-205°C, from reaction of dieldrin with acetic anhydride and sulfuric acid displayed a strong IR absorption at 1760cm^{-1} and was devoid of absorptions at 1600cm^{-1} and 1468cm^{-1} attributable respectively to dichloroethylene and methylene moiety of dieldrin. The absorption at 1760cm^{-1} was ascribed to acetate function. This assignment was substantiated by the appearance of strong absorptions at 1238, 1203 and 1070cm^{-1} resulting from asymmetric and symmetric stretching of the c-o-c function. The acetoxyl methyl groups appeared as a strong absorption at 1375cm^{-1}. The epoxide bands at 848 and 830cm^{-1} of dieldrin were absent. These IR data suggested that reaction between chloroethylene and methylene moieties

as well as an epoxide ring opening to form an acetate derivative had taken place. Elemental analysis which agreed with the formula of $C_{16}H_{14}Cl_6O_4$ suggested this compound contained two acetoxyl groups. The NMR spectrum was consistent with these conclusions. A slightly split doublet at 7.92 and 7.95 τ corresponded to the six acetoxyl methyl protons. Multiplets centered at 6.3, 6.8 and 7.25 τ, respectively, arose from four bridge-head protons. A sharp singlet at 5.09 τ was assigned to the migrated hydrogen. The deshielded methine proton and the two protons adjacent to the acetoxyl functions constituted a multiplet centered at 3.5 τ.

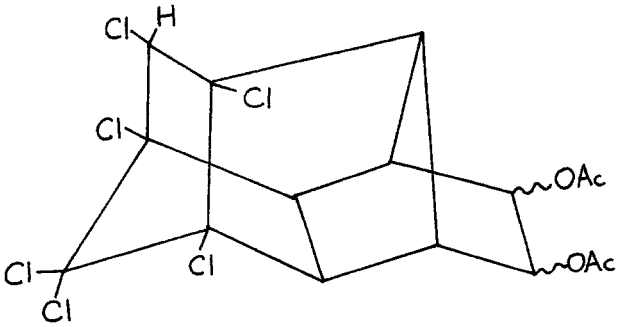
Based on the IR and NMR spectra and elemental analysis, structure II (fig. 1) was assigned to this compound. Attempts to form an acetonide from the diol, m.p. 164°C, after hydrolysis of II, according to Soloway's procedure (1) gave a yellow gum from which no pure products could be isolated. Therefore, the stereochemistry (cis or trans) of dihydroxy, hence diacetoxy, functions at C-6 and C-7 have yet to be determined.

Although both TLC (different supports and solvents) and IR evidence indicated the homogenity of the diacetate II, its chromatogram displayed two peaks when injected into 'old' columns which have been used routinely for injections of plant extracts. If metal instead of glass columns were used, extensive decomposition of this diacetate was observed as evidenced by the increase of the first peak and substantial decrease of the acetate peak. Such decomposition was minimized by using a newly-packed and conditioned glass column. Under this condition, the acetate peak was predominant. Since the first peak had the same retention time as that of the corresponding diol, thermo-conversion of II to the diol was thought to occur on the column.

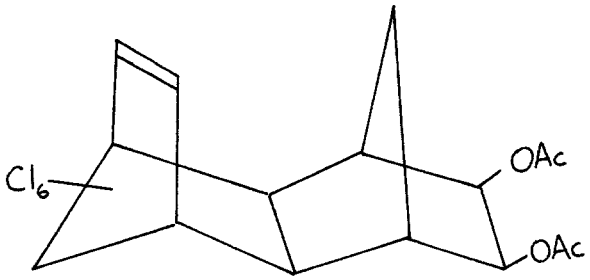
The other product, III, however showed only slight decomposition on 'old' columns. Elemental analysis indicated that it was the isomer of II. Its IR spectrum indicated the presence of ClC=CCl and acetoxy moieties. Upon hydrolysis, it was converted to a diol, m.p. 219-220°C identical in every aspect (IR, TLC, and mixed m.p.) to the cis-diol obtained from alkaline $KMnO_4$ oxidation of aldrin (16). These preliminary investigations indicated that this diacetate had cis-configuration as depicted in III. The third acetate, m.p. 214°C, was shown by elemental analysis to contain only one acetoxy group. The position of this group in the molecule has yet to be determined.



(I)



(II)



(III)

FIGURE 1

In collaboration with Prof. J.W. ApSimon further structural work by double nuclear magnetic resonance spectroscopy is in progress and results will be published at a later date.

Acknowledgment

The author is indebted to Prof. J.W. ApSimon, Carleton University, Ottawa, for NMR spectra, valuable criticisms and suggestions. Thanks are also due to Mr. G. Morris, Scientific Service, Department of Agriculture, Ottawa, for elemental analysis and Mr. H. Won of this Division (present address, Animal Research Institute, Department of Agriculture, Ottawa) for his able technical assistance.

References

1. SOLOWAY, S.B., DAMIANA, A.M., SIMS, J.W., BLUESTONE, H., and LIDOV, R.E., J. Am. Chem. Soc., 82, 5377, (1960).
2. BIRD, C.W., COOKSON, R.C., and CRUNDWELL, E., J. Chem. Soc., 4809, (1961).
3. PHILLIPS, D.D., POLLARD, G.E., and SOLOWAY, S.B., J. Agric. Food Chem., 10, 217, (1962).
4. LIDOV, R.E., BLUESTONE, H., SOLOWAY, S.B. and KEARNS, C.W., Advances in Chemistry Series, 1, 175, (1950), American Chemical Society, New York.
5. DANISH, A.A. and LIDOV, R.E., Analyt. Chem., 22, 702. (1950).
6. O'DONNELL, A.E., JOHNSON, H.W., and WEISS, F.T., J. Agric. Food Chem., 3, 757, (1955).
7. PARSONS, A.M. and MOORE, D.J., J. Chem. Soc., 2026, (1966).
8. SKERRETT, E.J. and BAKER, E.A., Analyst, 84, 376, (1959).
9. CHAU, A.S.Y., and COCHRANE, W.P., J. Assoc. Offic. Agric. Chem., 52, 1220, (1969).
10. CHAU, A.S.Y., WON, H., and WILKINSON, R.J., unpublished results.
11. ROSEN, J.D., SUTHERLAND, D.J., and LIPTON, G.R., Bull. Envir. Cont. Toxic., 1, 133, (1966).
12. ROBINSON, J., RICHARDSON, A., BUSH, B., and ELGAR, K.E., Bull. Envir. Cont. Toxic., 1, 127, (1966).
13. ROBURN, J., Chem. Ind., 1555, (1963).
14. MITCHELL, L.C., J. Assoc. Offic. Anal. Chem., 44, 643, (1961).
15. SKERRETT, E.J., and BAKER, E.A., Analyst, 85, 606, (1960).
16. KORTE, F., and ANET, A., Life Science, 4, 2017, (1965).