AMINE INDUCED PHOTODEHALOGENATION OF CYCLODIENE INSECTICIDES

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ABSTRACT:The syn-Cl atom of the geminal bridge of cyclodiene
insecticides and their metabolites, is dechlorinated
stereoselectively by photolysis in the presence of amines.

Specific dehalogenation methods of cyclodiene insecticides and related compounds are important as they provide models for identification of their metabolites formed by biotic and abiotic environmental agencies. Several stereospecific chemical dehalogenating agents for cyclodienes have been reported earlier[1-5] but most photochemical methods are nonspecific and yield mixtures of products. In this paper, we report a stereoselective method of dehalogenation of cyclodiene insecticides induced by amines.

A solution of aldrin $\underline{1}$ (100mg) in triethylamine (25ml) was irradiated for 8hrs with pyrex filtered light from a high pressure Hg lamp (until the reaction was complete by GLC), then diluted with ether (100ml), extracted with dil. HCl to remove Et_3N, dried, and the solvent removed, yielded a mixture of the photoproducts $\underline{2}$ and $\underline{3}$ (ratio 9:1, glc). Isolated by chromatography on silica gel, $\underline{2}$ (70mg) was crystallised from methanol as colourless plates, m.p.92-95° (Found: C,43.53; H,2.9. $C_{12}H_9Cl_5$ requires C,43.95; H,2.7%). MS: m/z 328 (M^+), 262 (M^+-66), 66 ($C_5H_6^+$). PMR ($CDCl_3$) δ :6.42 (2H,s,H_4& H_5), 4.20 (1H,s,H_{11a}), 3.01 (2H,s,H_2& H_7), 2.68 (2H,s, H_3& H_6), 1.28 (2H,d,J=10Hz, H_{12a}& H_{12b}). Structure $\underline{2}$ agrees with these data and appears to have been isolated earlier from a mixture obtained by $NaBH_4$ reduction[6] of $\underline{1}$. Moreover $\underline{2}$ was isomeric with $\underline{3}$ obtained earlier from $\underline{1}$ by treatment with KO_2 and proved to have anti 'H' orientation at the geminal bridge[5]. The H atom at the methano bridge of $\underline{2}$ must therefore have syn orientation.

The relation between the two mono dechlorinated products $\underline{2}$ and $\underline{3}$ was established when both of them could be converted to $\underline{4}$. Thus $\underline{2}$ on treatment with KO_2 in DMSO and $\underline{3}$ when irradiated in Et_3N, gave $\underline{4}$ which crystallised from MeOH as colourless needles, m.p.85-87°(Found: C,49.0; H,3.5. $C_{12}H_{10}Cl_4$ requires C, 48.95; H,3.4%). MS: m/z 294 (M^+). PMR ($CDCl_3$)δ :6.35 (2H,s, H_4& H_5),3.05 (2H,s,H_2& H_7), 2.72 (2H,s,H_3& H_6), 1.8 (2H,d,J=12Hz, H_{11a}& H_{11b}), 1.4 (2H,d,J=12Hz, H_{12a}& H_{12b}).

Thus both $\underline{1}$ and $\underline{3}$ looses only the syn-Cl atom stereoselectively in high yield when photolysed in the presence of Et_3N and other amines.

Dieldrin ($\underline{5}$), on similar photolysis, gave $\underline{6}$ (92%) and $\underline{7}$ (8%) which on crystallisation from MeOH gave $\underline{6}$ as colourless plates, m.p.192-194°(Found: C,41.20; H,2.2. $C_{12}H_9Cl_5O$ requires C, 41.55; H,2.5%). MS: m/z 344 (M^+). Its

NMR spectrum showed a new 1-H singlet at δ 4.18. With KO_2 in DMSO 6 gave 8 which crystallised from MeOH, m.p. 150-53° (Found C,45.81; H,2.9.$C_{12}H_{10}Cl_4O$ requires C,46.15; H,3.2%). MS: m/z 310 (M^+). The NMR of 8 showed a new doublet of 2H at δ 1.88. Photolysis of the known[5] 7 in Et_3N also gave 8.

Endrin (9), on similar photolysis, gave 10 with a trace of 11 (glc) which on crystallisation from MeOH yielded 10 as colourless prisms, m.p.158-60° (Found C,41.70; H,2.2. $C_{12}H_9Cl_5O$ requires C,41.55; H,2.6%). MS: m/z 344 (M^+). Its NMR spectrum showed a new 1-H singlet at δ 4.12. The didechlorinated product 12, obtained from 10 by reaction with KO_2 in DMSO or from the known[5] compound 11 by photolysis in Et_3N, crystallised from MeOH as colourless cubes, m.p.140-43° (Found: C,46.4; H,2.8. $C_{12}H_{10}Cl_4O$ requires C,46.15; H,3.2%). MS: m/z 310 (M^+) and a doublet of 2 protons at δ :1.72 (J=10.5Hz) besides signals due to other protons, agrees with 12.
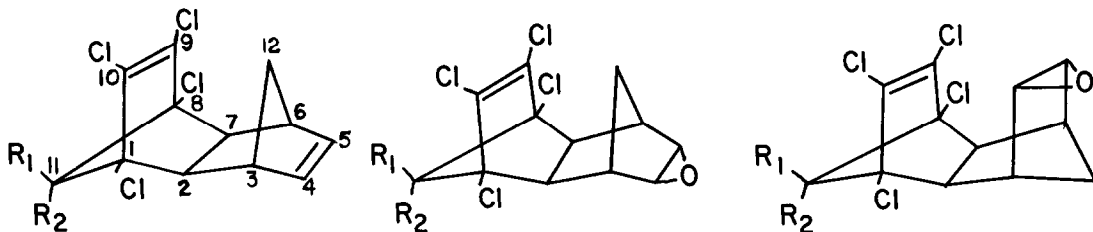
1. $R_1 = R_2 = Cl$ 5. $R_1 = R_2 = Cl$ 9. $R_1 = R_2 = Cl$

2. $R_1 = H, R_2 = Cl$ 6. $R_1 = H, R_2 = Cl$ 10. $R_1 = H, R_2 = Cl$

3. $R_1 = Cl, R_2 = H$ 7. $R_1 = Cl, R_2 = H$ 11. $R_1 = Cl, R_2 = H$

4. $R_1 = R_2 = H$ 8. $R_1 = R_2 = H$ 12. $R_1 = R_2 = H$

Amine induced photodehalogenation of organohalogen insecticides have been observed earlier[7,8] and mechanisms postulating formation of charge transfer complexes have been proposed[9]. Attempts have been made to find practical uses in formulations[10],but this is probably the first example of a stereo-selective photodehalogenation of cyclodiene insecticides induced by amines.

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