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Superoxide-Mediated Monodehalogenation of Cyclodiene Insecticides
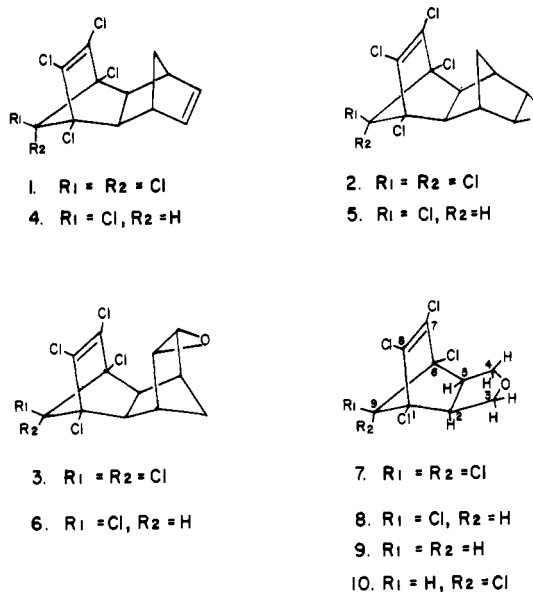
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The reaction of superoxide anion in Me₂SO with cyclodiene insecticides has been studied to examine its dehalogenating effect. Aldrin (1), dieldrin (2), and endrin (3) gave with this reagent only the monohalogenated products 4, 5 and 6, respectively, having *syn*-chloro orientation at the methano bridge C atom. Endosulfan ether (7), although stable photochemically, gave a similar product (8) in high yield. Excess reagent did not cause further dehalogenation even under vigorous conditions.

Superoxide ion (O₂⁻·) is now well-known because of its involvement in biological oxidations, but interest in its organic chemistry has increased very much only in recent years. It is known to have redox properites and is an excellent nucleophilic (basic) reagent alone or in combination with crown ethers (Yoshihiko and Christopher, 1976). These chemical reactions have been reviewed comprehensively (Lee-Ruff, 1977). More recently, this reagent has been shown to cause dehalogenation of organohalogen compounds like CCl₄, CHCl₃, and *p,p′*-DDT with ease in aprotic media (Roberts and Sawyer, 1981). Dureja et al. (1982), on the other hand, observed that this reagent causes facile dehydrohalogenation of the dichlorovinyl side chain of the synthetic pyrethroid permethrin in preference to ester cleavage. In this paper we report a novel stereospecific dechlorination reaction of superoxide ion on some cyclodiene insecticides and related metabolites.

MATERIALS AND METHODS

Chemicals. Aldrin, dieldrin, and endrin were procured from M/s Shell Chemicals (U.K.) and purified before use. Endosulfan was obtained from M/s Excel Industries, Ltd. (India). Endosulfan ether was prepared by the method of Lindquist and Dahm (1957). Photoendosulfan was prepared according to the method of Dureja and Mukerjee (1982). Authentic monodechlorination products 4, 5, and 6 of aldrin, dieldrin, and endrin, respectively, were prepared by treatment of the cyclodiene insecticides with sodium methoxide in methanol and Me₂SO according to the method of Adams and Mackenzie (1969). Potassium superoxide was purchased from Sigma chemicals (Switzerland). Chemical ionization mass spectrometry (CI-MS) was recorded on a Finnegan-3200 spectrometer using methane (0.7–0.9 torr) as the reagent gas at an ionization voltage of 70 eV. ¹H NMR spectra were recorded on a EM-360L spectrometer using Me₄Si as the internal reference. ¹³C NMR spectra were recorded on a Brucker 330-MHz (FT) spectrometer.

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1. R₁ = R₂ = Cl
4. R₁ = Cl, R₂ = H

2. R₁ = R₂ = Cl
5. R₁ = Cl, R₂ = H

3. R₁ = R₂ = Cl
6. R₁ = Cl, R₂ = H

7. R₁ = R₂ = Cl
8. R₁ = Cl, R₂ = H
9. R₁ = R₂ = H
10. R₁ = H, R₂ = Cl

Action of Superoxide Ion on Cyclodiene Insecticides. (i) Aldrin (1) (100 mg) dissolved in dry Me₂SO (10 mL) was stirred with KO₂ (50 mg) for 2 h at 25 °C. The reaction was monitored (TLC) and on completion was terminated by adding cold water (10 mL). The mixture was extracted with hexane. The extract was dried over anhydrous Na₂SO₄ and the solvent distilled off. The product contained a bit of the unreacted material and was purified by column chromatography. It crystallized from hexane–methylene chloride as colorless needles: mp alone or when mixed with an authentic sample of 4 92–94 °C.

(ii) Reaction of KO₂ with dieldrin (2) under the above conditions and chromatographic purification gave 5 as colorless cubes from hexane–chloroform; mp alone or when mixed with an authentic sample 138–140 °C.

(iii) Similar reaction of endrin (3) with KO₂ gave 6 as colorless needles from hexane chloroform: mp alone or when mixed with an authentic sample 182–184 °C.

Action of Superoxide Ion on Endosulfan Ether (7). Endosulfan ether (200 mg) in Me₂SO (10 mL) and KO₂ (200 mg) was stirred at 25 °C for 2 h when the reaction

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Table I. ^{13}C NMR Data of Endosulfan Ether (7) and Monodehalogenated Product (8)

carbon at	endosulfan ether (7)	product (8)
C_3 and C_4	53.76	53.64
C_2 and C_5	66.94	67.45
C_1 and C_6	80.59	80.59
C_7 and C_8	129.89	128.70
C_9	103.77	75.78

appeared to be complete. Water (10 mL) was added to above solution and the mixture extracted with hexane. Purification of reaction product by column chromatography over silica gel gave the product (8) which crystallized from ethanol as colorless cubes: mp 159 °C; MS 306 (M$^+$); NMR (CDCl$_3$) δ 3.22 (m, 2 H), 3.59 (m, 2 H), 4.02 (m, 2 H), 4.33 (s, 1 H); for ^{13}C NMR data, see Table I. Anal. Calcd for C$_9$H$_7$Cl$_5$O: C, 35.07; H, 2.27. Found: C, 34.55; H, 2.80.

Preparation of Metabolite 9 by Pyrolysis of Photo-β-endosulfan. Photo-β-endosulfan (50 mg) in a closed tube was heated in a oil bath (200 °C). The solid melted and rapidly discolored with evolution of gases. The product (9), which sublimed on the cooler parts of the test tube, was collected and crystallized from hexane when it gave colorless plates: mp 188–190 °C; ^{1}H NMR (CDCl$_3$) δ 3.90 (m, 2 H), 3.40 (m, 2 H), 2.2–1.9 (m, 2 H). Anal. Calcd for C$_9$H$_8$Cl$_4$O: C, 39.40; H, 2.90. Found: C, 38.62; H, 2.85.

RESULTS AND DISCUSSION

The dehalogenation reactions of cyclodiene insecticides and related compounds have been subject of numerous investigations. Specific dehalogenation of these compounds with zinc (Soloway et al., 1960), lithium (Bruck et al., 1960) and hydrogen in the presence of catalyst aided by triethylamine (Parsons and Moore, 1966) is known. Adams and Mackenzie (1969) have also found monodehalogenation of these compounds with alkoxides and hydrides taking place specifically at the dichloromethane bridge. Although in most cases the products are single isomers, the conditions employed have been quite vigorous and the yields are not good (ca. 30–40%).

In contrast to the above example, it is now observed that superoxide anion in Me$_2$SO is a very convenient reagent for monodehalogenation of the antichlorine atom of the dichloromethano bridge. In the first three cases examined, viz., aldrin (1), dieldrin (2), and endrin (3), even under the mild conditions employed the yields are much higher than those observed earlier (ca. above 80%). The identity of the products is based on direct comparison with those obtained under conditions of Adams and Mackenzie (1969). In spite of a careful search no other dehalogenation or ring isomerised products were observed.

The specific advantage of superoxide as a dehalogenating agent was examined further by studying its reaction with endosulfan ether (7). Endosulfan ether is very stable and did not undergo any photodehalogenation under conditions in which endosulphan itself gave photoendosulfan (Dureja and Mukerjee, 1982). The reaction of endosulfan ether with superoxide gave 8 as the sole product. Its mass spectrum (M$^+$, 306) and analytical data showed that its formation from 7 involves substitution of one chlorine atom with a hydrogen atom, and this was confirmed by its ^{1}H

NMR spectrum, which showed a new one-proton peak at δ 4.33. A comparison of the ^{13}C NMR signals of endosulfan ether (7) and the new product (8) (Table I) revealed that whereas the peak due to the methano bridge carbon C-9 in 7 resonated at δ 103.7, that due to C-9 in the product (8) appeared at δ 75.78. This large upfield shift indicated that the chlorine atom has been lost from C-9. Except for this, there is hardly any change in the position of signals of other carbon atoms, indicating that the rest of the molecule is unchanged.

The *syn*-chloro orientation of C-9 in 8 is based on its 330-MHz ^{1}H NMR spectrum. A sharp singlet at δ 4.33 for the proton at C-9 shows the absence of coupling of this proton with any other protons in the molecule. In the alternative structure (10) with *anti*-chloro orientation, the long-range coplanar W coupling with endoprotons at C-2 and C-5 with the proton at C-9 would have split this signal as observed in similar *anti*-chloro compounds by Williamson et al. (1968).

Attempts to prepare 9 by further dechlorination of 8 using excess superoxide at higher temperature did not succeed. It was prepared by pyrolysis of photo-β-endosulfan. The structure of compound 9 is based on its ^{1}H NMR spectrum, which showed a new multiplet at δ 1.9–2.2 of two protons due to the methano bridge protons in addition to the peaks present in the ^{1}H NMR spectrum of endosulfan ether (7). Endosulfan itself, however, did not give any dechlorinated product with superoxide but slowly changed to endosulfandiol.

The dehalogenation of simple organohalogens like CCl$_4$, CHCl$_3$, and *p,p'*-DDT by superoxide ion has been assumed to take place by nucleophilic displacement of the Cl$^-$ ion and subsequent changes of the peroxyanion intermediate (Roberts and Sawyer, 1981). In other cases, like dehydrohalogenation of permethrin (Dureja et al., 1982), superoxide acts like a base. To the best of our knowledge the examples described in the present work are the first cases of reductive monodehalogenation (CCl → CH) by this reagent. It is mechanistically similar to the dehalogenations reported by Adams and Mackenzie (1969) with bases like alkoxides and hydrides in aprotic media. The milder conditions required the higher yields obtained with this reagent are indicative of its stronger basic nature.

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