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SUPEROXIDE-MEDIATED DEHYDROHALOGENATION REACTIONS OF THE PYRETHROID PERMETHRIN AND OTHER CHLORINATED PESTICIDES

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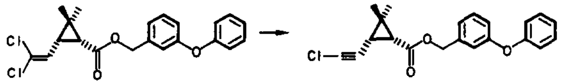
Abstract Superoxide generated in DMF readily converts the dihalovinyl group of permethrin and related compounds to a haloethynyl moiety and yields major products from elimination reactions of DDT, *cis*-chlordane, and 1,2-dibromo-3-chloropropane (DBCP)

Reactions of superoxide ion (O_2^-) are of interest[1,2] because of its nucleophilic[3,4] and oxidative[5,6] characteristics in a variety of systems Superoxide is suggested as a convenient reagent to degrade polychlorohydrocarbons[7] (*e g* DDT and CCl_4) yielding unidentified products We find that elimination reactions of O_2^- with several halogenated pesticides give products known to be important in their metabolic and environmental degradation, thereby providing a potentially useful model system

Reactions of O_2^- were routinely carried out with the pesticide (0 1M) and equimolar KO_2 (Alfa) in DMF by stirring for 1 hr at 20°C. The same products were obtained with added 18-crown-6 or in DMSO Analyses involved recovery on extraction into hexane and GLC-chemical ionization-mass spectrometry (CI-MS) Products were characterized after isolation (TLC) and derivatization, where applicable, by combinations of GLC cochromatography, IR, NMR and CI-MS

cis-Permethrin (1) reacts readily (1 hr, 65% conversion) to yield 2 (95%), characterized as follows CI-MS 355 $[M+1]^+$, 8% rel int , 319 $[M-Cl]^+$, 10, 183, 100 ^1H NMR (C_6D_6), δ 0 6 (s, 3H), 1 28 (d, 1H, *J* = 8 5), 1 35 (s, 3H), 1 45 (d, 1H, *J* = 8 5), 4 89 (ab q, 2H, *J* = 12 6), 6 8-7 2 (m, 9H) ^{13}C-NMR identical to that of authentic material[8] IR 2250 cm^{-1} (C≡C), 1750 (C=O).



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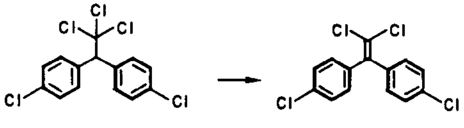
The *trans*-isomer of 1 and the analogous methyl *cis*-2,2-dimethyl-3-(2,2-dibromovinyl)-cyclopropanecarboxylate are also dehydrohalogenated under these conditions The expected ester cleavage reaction[4] of 1 is a minor process yielding the corresponding acid and alcohol (2-4%) The elimination reaction does not involve hydroxide since reaction of 1 with 1N KOH gave only ester cleavage products Compound 2 is also detected in trace amounts upon photolysis (300 nm) of 1 in oxygen-saturated hexane and it is the major product on irradiation of hexane solutions containing 1% triethylamine

DDT (3) on reaction with O_2^- yields DDE (4, 95%), characterized by CI-MS (317 $[M+1]^+$, 100) and by GLC and TLC comparisons with authentic material *cis*-Chlordane (5) is dehydrochlorinated to 6 (90%), identified by CI-MS (335 $[M-35]^+$, 100) and NMR,[9] while heptachlor is converted to an alcohol (335 $[M-OH]^+$, 70, 317 $[M-35]^+$, 38, 217, 100) suggesting a displacement reaction analogous to that accomplished by other bases[9]



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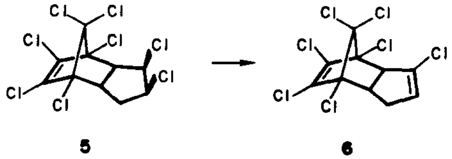

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The soil fumigant DBCP (7) with O_2^- yields a complex mixture including products arising by dehydrohalogenation to 8 (40%) (155 $[M+1]^+$, 100) and 9 (10%) (199 $[M+1]^+$, 100) and by displacement/oxidation to 10 (25%) (153 $[M+1]^+$, 15, 135 $[M+1]^+-H_2O$, 100) Minor products are 3-chloroacrolein (11, ~ 1%) and 2-bromoacrolein (12, < 0 1%) each identified by derivatization with 2,4-dinitrophenylhydrazine (271, 1 Cl $[M+1]^+$, 100, and 315, 1 Br $[M+1]^+$, 100) 2-Bromoacrolein is a potent mutagen in the Ames assay[10] Indeed, the mixture obtained upon KO_2 treatment of 7 exhibited mutagenic activity

$$\underset{\mathbf{7}}{BrCH_2CH(Br)CH_2Cl} \longrightarrow \underset{\mathbf{8}}{CH_2{=}C(Br)CH_2Cl} + \underset{\mathbf{9}}{BrCH_2C(Br){=}CH_2}$$

$$+ \underset{\mathbf{10}}{HOCH_2CH(Br)CHO} + \underset{\mathbf{11}}{OHCCH{=}CHCl} + \underset{\mathbf{12}}{CH_2{=}C(Br)CHO}$$

These results verify the usefulness of O_2^- in syntheses involving elimination reactions under relatively mild conditions and in generating xenobiotic degradation products

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References

1 D T Sawyer and J S Valentine, Acc Chem Res 14, 393 (1981)

2 E Lee-Ruff, Chem Soc Rev 6, 195 (1977)

3 E J Corey, K C Nicolaou, M Shibasaki, Y Machida, and C S Shiner, Tetrahedron Lett , 3183 (1975).

4 J San Filippo, Jr , L J Romano, C -I Chern, and J S Valentine, J Org Chem 41, 586 (1976)

5 Y Moro-oka and C S Foote, J Amer Chem Soc 98, 1510 (1976)

6 J San Filippo, Jr , C -I Chern, and J S Valentine, J Org Chem 41, 1077 (1976)

7 J L Roberts, Jr and D T Sawyer, J Amer Chem Soc 103, 712 (1981)

8 N F Janes, J Chem Soc Perkin I, 1878 (1977), ^{13}C data for 2 provided by N F Janes

9 W P Cochrane, J Assoc Offic Anal Chem 52, 1100 (1969)

10 J D Rosen, Y Segall, and J E Casida, Mutation Res 78, 113 (1980)

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