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THE ADDITION OF p-CHLOROBENZENETHIOL TO ISODRIN

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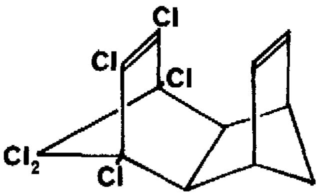
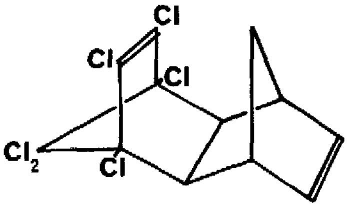
In contrast to the chlorohydrocarbon, isodrin(I), the derived epoxide, endrin, has been used extensively as an insecticide. However, the observation[1] that the isomeric epoxide, dieldrin, is converted microbially into aldrin(II) raises the possibility that isodrin may be introduced into the environment by a similar reduction of endrin. Amongst likely metabolic fates of isodrin is conjugation with thiols such as glutathione. Surprisingly, in contrast to the position with aldrin[2], no such reactions have been reported for isodrin, despite its ideal geometry[3] for the observance of transannular free-radical additions.



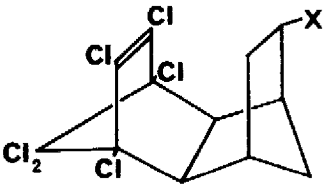
I



II

In order to rectify this situation we have investigated the room temperature addition of p-chlorobenzenethiol to isodrin in cyclohexane solution with free access of oxygen. The sulphide fraction could not be separated into its components by preparative t.l.c. and consequently was oxidised to a mixture of the corresponding sulphoxides by iodobenzene dichloride in pyridine[4]. Subsequent t.l.c. separation gave two isomeric sulphoxides m.p. 195° and 214° which are assigned structures(IIIb) and (IVb) respectively. Particularly notable is the presence of a strong band at 1620 cm^{-1} in the infrared spectrum of (IIIb) diagnostic[3] of the dichloroethylene grouping, which is absent from the spectrum of (IVb). These two sulphoxides were also present as such in the reaction mixture. The major reaction product, m.p. 156°, is the ketone (Va) with ϑ_{max} 1770 (C=O) and 1620 (ClC=CCl) cm^{-1}. Oxidation[4] gave the sulphoxide (Vb), m.p. 196°, which was also isolated directly from the reaction mixture.

The formation of the half-cage sulphide (IVa) and sulphoxide (IVb) is of particular interest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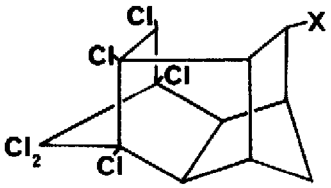
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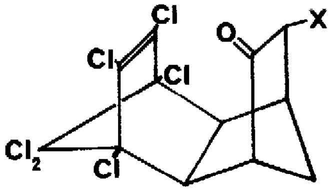
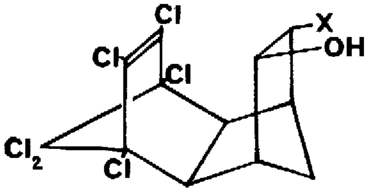
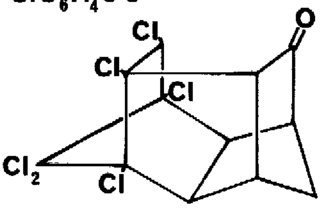

V

(a) X= p-ClC_6H_4S ; (b) X= p-ClC_6H_4SO


VI


VII

since no products of transannular addition were encountered in a recent study[5] of reactions of free-radicals with a similarly disposed diolefin, although such products result[6] from electrophilic addition. The collapse of the intermediary sulphide-hydroperoxide to the ketone (Va) presumably reflects the steric compression of the hydrogen atom of the H-COOH group, as in the aldrin series the corresponding sulphide-hydroperoxide rearranges[2] to the hydroxy-sulphoxide. The identity of the hydroperoxide responsible for oxidation of the sulphides to sulphoxides is not yet known, since we have not observed any of the expected hydroxy-sulphides (VIa,b) derived from isodrin. Oxidation of isodrin also occurs during the reaction as some of the half-cage ketone (VII) is also formed, presumably via rearrangement[2] of endrin.

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REFERENCES

1. F. Matsumara, G. M. Boush and A. Tai, Nature, 1968, 219, 965.
2. C. W. Bird, R. C. Cookson and E. Crundwell, J. Chem. Soc., 1961, 4809.
3. A. A. Oswald and F. Noel, J. Org. Chem., 1961, 26, 3948.
4. G. Barbieri, M. Cinquini, S. Colonna and F. Montanavi, J. Chem. Soc.(C),1968, 659.
5. G. I. Fray, G. R. Geen, D. I. Davies, L. T. Parfitt and M. J. Parrott, J. Chem. Soc., Perkin Trans. I, 1974, 729.
6. R. C. Cookson, J. Hudec and J. Marsden, Chem. & Ind. 1961, 21; D. G. Farnum and J. P. Snyder, Tetrahedron Letters, 1965, 3861.