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PHOTO-ISOMERISATION AND PHOTO-DEGRADATION OF DDE

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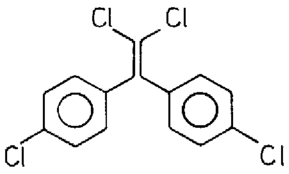
The importance of the photochemical transformation of various pesticides under natural conditions has been referred to in a number of review articles.[1,2] However, in only a few cases the photo-products have actually been identified in natural samples, and then only by sampling in the immediate vicinity of the site of application of the pesticide. No information on the contribution of photo-decomposition to the transformation of a widely distributed pollutant such as DDT (1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane) exists. The numerous degradation products of DDT so far identified in natural samples could all have been formed by metabolism or by ground state reaction. However, Korte *et al.*[3] have shown that DDE (1,1-dichloro-2,2-bis(4-chlorophenyl)-ethene, 1) is photo-isomerised to a product which contains a dichlorophenyl group. The detection of this product in natural samples would serve to establish the importance of the photochemical degradation of DDE (and DDT) in the environment. We have now been able to show that this unique photo-product is in fact a mixture of the E- and Z-isomers of 1-chloro-2-(4-chlorophenyl)-2-(2,4-dichlorophenyl)ethene (2 and 3). We have also investigated a few samples of tobacco and needles from the Swedish pine (*Pinus silvestris*) and have been able to identify (by GC-MS) 2 and 3 in extracts from these samples.

Previous work has shown that 1 is a major product when DDT is photolysed.[4,5] We have, therefore, mainly studied the photo-reactions of 1, but the products discussed in this paper are



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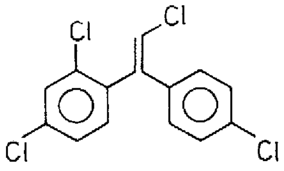

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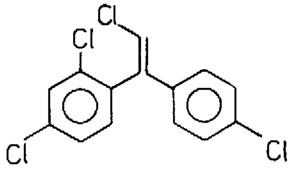

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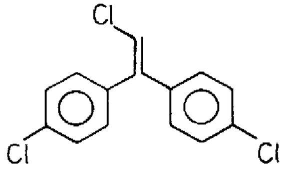

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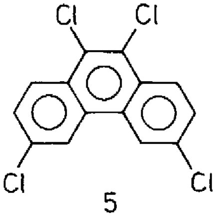

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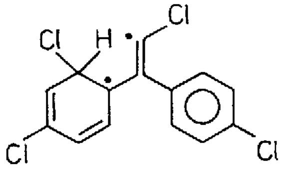

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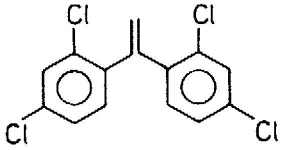

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also obtained by the photolysis of DDT itself. Under natural conditions, DDT is exposed to sunlight both in a relatively inert environment (*i.e.* in the atmosphere and as a water suspension on bare rocks) and while it is in contact with a hydrogen donor (*i.e.* in oil films and in the waxy surface layer of leaves). In order to simulate natural conditions, 1 was dissolved in both inert solvents like perfluoroalkanes and symmetric 1,1,2-trichloro-1,2,2-trifluoroethane, and in a good hydrogen donor solvent like 2-propanol and irradiated with light of a wavelength corresponding to that of the high energy part of sunlight at the earth's surface (≃ 300 nm).[6] In all solvents, 1 underwent efficient photo-isomerisation to a mixture of 2 and 3 (ratio 1:5). Small amounts of the compound 7, resulting from a second chlorine migration, were also formed as shown by the formation of 2,4,2',4'-diphenylketone on oxidation of the reaction product. In the hydrogen donor solvent 2-propanol dehalogenation to DDMU[7] (1-chloro-2,2-bis(4-chlorophenyl)ethene, 4) occurred to the same extent as isomerisation. Small amounts of 3,6,9,10-tetrachlorophenanthrene (5) were also isolated.[7] Trace amounts of tri- and tetrachlorobiphenyls, which have previously been shown to form on gas phase photolysis of DDT,[4] were also detected (GC-MS) after photolysis in perfluoroalkane solution.

The isolation and separation of the compounds 2 and 3 were quite difficult and could be accomplished only by using a novel TLC technique, which involved the use of a tetraalkylammonium salt on silica as the stationary phase.[8] The structures of 2 and 3 were derived from their mass spectra and their transformation to 2,4,4'-trichlorodiphenyl ketone on oxidation. The structures were verified by comparison with authentic samples prepared from 2,4,4'-trichlorodiphenyl ketone by a Wittig reaction.[9]

The problems involved in using mass spectrometry for identification are illustrated by the fact that the MS of 2 and 3 were essentially identical to that of 1. In a structure determination based on mass spectrometry the tetrachlorodibenzofulvene which has previously been claimed to form on photolysis of DDT,[5] could easily be mistaken for the phenanthrene 5. Further studies are therefore desirable to determine if the dibenzofulvene actually is formed.

The mechanism for the transformation of DDT (*via* 1) into 2, 3 and 5 has not yet been studied in detail. Since the isomerisation of 1 to 2 and 3 proceeded in the presence of oxygen, it probably is a singlet reaction. The specificity of the reaction may indicate that it is concerted. However, a diradical intermediate 6, formed by the homolytic cleavage of a C-Cl bond and the capture of a chlorine atom by one of the aromatic rings, could also explain the experimental result, since intramolecular hydrogen abstraction would yield 2 and 3. The radical route is probably preferred as indicated by the fact that coupling with the solvent (hexane[3]) and dehalogenation to 4 compete with isomerisation. The compound 5 was probably formed *via* a stilbene[11] which was photochemically cyclized to a phenanthrene in the usual way. The stilbene could have been formed by the cyclization of the diradical 6 to a cyclopropene, followed by a chlorine shift and rearrangement.

The mechanism for the very slow photochemical formation of biphenyls with a low degree of chlorination from DDT, is unknown but possibly proceeds *via* diphenylketones. It is unlikely that this route contributes appreciably to the world-wide pollution by poly-chlorinated biphenyls, as has been suggested. The importance of the photochemical transformations of DDT in the environment, however, is clearly demonstrated by the identification of 2 and 3 in certain natural samples. Furthermore, the isomerisation of 1 to 2 and 3 is a very efficient photoreaction, which might be of value in estimating, in general, the importance of photochemical transformations under natural conditions.

Acknowledgements

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References and Notes

1. D.A. Watkins, *Chem. Ind.* (1974) 185, and references therein.
2. L. Fishbein, *J. Chromatogr.* 98 (1974) 177.
3. I. Kerner, W. Klein and F. Korte, *Tetrahedron* 28 (1972) 1575.
4. K.W. Moilanen and D.G. Crosby, *Science* 180 (1973) 578.
5. J.R. Plimmer, C.I. Klingebil and B.E. Hummer, *Science* 167 (1970) 67.
6. The irradiation was performed in a Rayonette apparatus at 300 nm. The solutions (1 µM) were kept in Pyrex tubes in a merry-go-round and were removed consecutively after different times of irradiation.
7. Identified by comparison with an authentic sample (m.p., UV, NMR, MS).
8. Å. Bergman, R. Göthe and C.A. Wachtmeister, *J. Chromatogr.*, in press.
9. The Wittig reagent was prepared according to Ref. 10. After reaction at -50° for 3 hr, the reaction mixture was allowed to reach room temperature and the precipitate was removed by filtration. The solvent was evaporated and the products were dissolved in hexane. The starting materials were removed by extraction with conc. sulphuric acid and the desired compounds were isolated by means of preparative TLC (*cf.* Ref. 8). The crystalline isomer, m.p. $95-96^{\circ}$, was tentatively assigned the structure 2 (UV, NMR) and its identity with the crystalline photo-product (m.p. $95-96^{\circ}$) was established by spectral methods and mixed m.p. (UV, NMR, MS). The second isomer could not be crystallized. The identity of the non-crystalline isomer 3, and the second photo-product were established by spectral methods (UV, NMR, MS).
10. D. Seyferth, S.O. Grim and T.O. Read, *J. Amer. Chem. Soc.* 82 (1960) 1511.
11. Traces of the E-isomer of 1,2-dichloro-1,2-bis(4-chlorophenyl)ethene were indicated in the irradiated mixtures (GC, TLC).