A Photocyclization Reaction of 1,1-Dichloro-2,2-bis-(*p*-chlorophenyl)ethylene (DDE)

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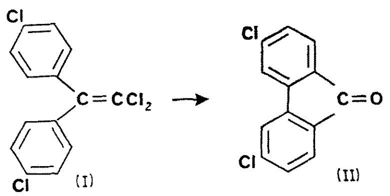
Summary 1,1-Dichloro-2,2-bis-(*p*-chlorophenyl)ethylene (DDE) undergoes photocyclization in methanol in the presence of oxygen to 3,6-dichlorofluorenone.

1,1-DICHLORO-2,2-BIS-(*p*-CHLOROPHENYL)ETHYLENE (DDE) (I) is present in significant quantities in the environment. It is produced by metabolism of 1,1,1-trichloro-2,2-bis-(*p*-chlorophenyl)ethane (DDT) in insects,[1] birds,[2] and mammals[3] and may also arise by photolysis.[4] We report a novel photocyclization reaction of (I) involving the formation of a fluorenone from a substituted diphenylethylene.

The photolysis of (I) (1 g./l.) in methanol was examined in the presence and absence of excess oxygen. Solutions were irradiated for 8 hours by a medium pressure mercury lamp source with a Corex glass filter. The products were investigated by combined v.p.c. and mass spectrometry. Many products identified had resulted from the loss of chlorine from the aromatic rings or ethylene group of (I) by a radical mechanism: hydrogen abstraction from the solvent played a significant part in subsequent reactions of these radicals, and reductively dechlorinated products were identified.[5]

The non-volatile components were complex but a golden-yellow solid was isolated in 10% yield by concentration of the methanolic solution after photolysis. This compound was recrystalized from benzene, m.p. 284° [ν_{max} 1710 (C = O), 1610, 1600 cm.$^{-1}$], molecular formula $C_{13}H_6Cl_2O$ (microanalysis and mass spectrum). The fragmentation pattern showed the molecular ion (*m/e* 248) containing two chlorine atoms and a fragment ion (*m/e* 220) due to expulsion of CO. The assignment of the structure of 3,6-dichlorofluorenone (II) to this product is consistent with the above evidence [fluorenone has ν_{max} 1710(C=O) 1610, 1600 cm.$^{-1}$]. The melting point was lower than that previously recorded for (II).[6] The compound may therefore be somewhat impure and further confirmation of structure was obtained by conversion to an oxime, m.p. 253—254° (lit. 250—252°).[6] The n.m.r. spectrum of the oxime supports the allocated structure: protons at C-1 and C-8 are no longer chemically equivalent in the oxime and gave signals at 7·72 and 8·34 p.p.m. each indicating *o*-coupling (*J* 8 Hz.). Signals at 7·44 (2H) and 8·09 p.p.m. (2H) also appeared in the aromatic region due to the two pairs of equivalent protons (C-2, C-7 and C-4, C-5).



The reaction mixture also contained *p,p'*-dichlorobenzophenone and a small quantity of a dichlorobiphenyl (*m/e* 222). Subsequently the irradiation of *p,p'*-dichlorobenzophenone was carried out under similar conditions. No fluorenone could be isolated from the solution, nor was the solution yellow in colour after photolysis, as is characteristic of fluorenone formation. A small quantity of a dichlorobiphenyl was identified, however, suggesting that this may result directly from photolytic decarbonylation of *p,p'*-dichlorobenzophenone. The cyclization of (I), therefore, does not involve *p,p'*-dichlorobenzophenone and it is possible that the reaction may proceed by way of a C-1 hydroperoxide.

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[1] J. G. Sternburg, E. Vinson, and C. W. Kearns, *J. Econ. Entomol.*, 1954, **46**, 513.
[2] E. I. ElSayed, J. B. Graves, and F. L. Bonner, *J. Agric. Food Chem.*, 1967, **15**, 1014.
[3] E. C. Burns, P. A. Dahm, and D. A. Lindquist, *J. Pharmacol.*, 1957, **121**, 55.
[4] J. Robura, *Chem. and Ind.*, 1963, 1555.
[5] J. R. Plimmer, unpublished.
[6] A. Barker and C. C. Barker, *J. Chem. Soc.*, 1954, 870.