Reaction of Dichloroketen with Diphenylfulvene and Diphenylbenzofulvene

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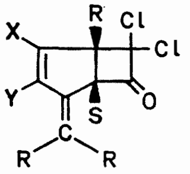
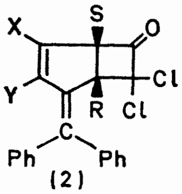
Summary The reactions of dichloroketen with diphenylfulvene and diphenylbenzofulvene afforded 1,2-mono-adducts whose structure and stereochemistry were proved by detailed n.m.r. analysis.

Most of the known cycloaddition reactions of fulvenes result in the formation of either a mono-adduct (using the 1- and 4-positions)[1] or a di-adduct (using the 1-, 2-, 3-, and 4-positions).[2] The formation of a mono-adduct using the 1- and 2-positions of fulvenes is unusual. We know of only two instances where 1,2-mono-adducts have been postulated *e.g.* the additions of benzonitrile oxide[3] and diazomethane[4] to dimethylfulvene. However, the structures of these adducts were not unequivocally defined.

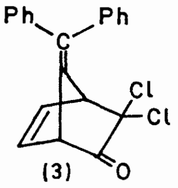
Recently, Kitahara and his co-workers reported[5] that the reaction of dichloroketen with dimethylfulvene yielded a 1 : 1 adduct (**1a**). However, proof of its structure has not yet been reported. Prior to this report, investigations in our laboratories had revealed the formation of a crystalline mono-adduct from the reaction of diphenylfulvene with dichloroketen The structure and stereochemistry of this adduct were proved by n.m.r. and i.r. spectroscopy. The reaction of dichloroketen (generated *in situ*)[6] with diphenylfulvene was conducted by refluxing a hexane solution of dichloracetyl chloride, diphenylfulvene, and triethylamine for 12 h. Filtration and removal of the solvent (after washing with 5% $NaHCO_3$) afforded a colourless crystalline compound in 55% yield, (m.p. 137·5—138°) which could



(1a) R = Me
(1b) R = Ph



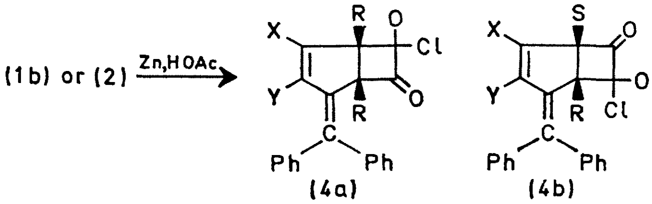
(2)



(3)

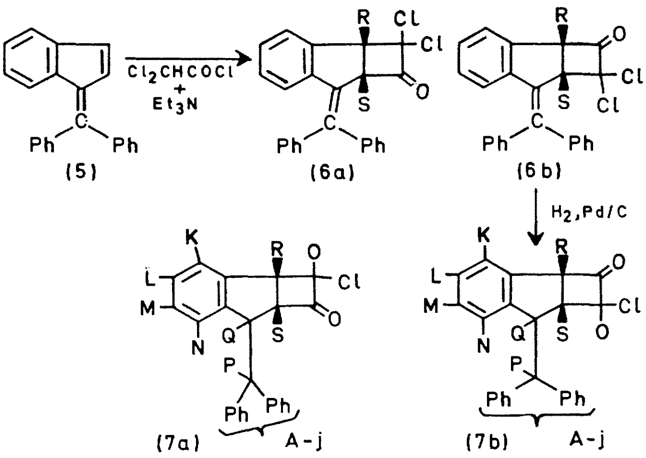
have the structures (**1b**), (**2**) (resulting from a 1,2-cycloaddition), or (**3**) (resulting from a 1,4-cycloaddition), assuming that the initial cycloaddition is *cis*. The product was found to be homogeneous by t.l.c. Its i.r. spectrum showed strong bands at 1810 (C=O), 1610, 1465 (aromatic) and 831, 726, 708, 692 (C–Cl) cm^{-1}. The structure (**3**) was ruled out on the basis of the observed carbonyl absorption at 1810 cm^{-1} which is reasonable for a saturated four-membered ring [structures (**Ib**) and (**2**)] but inconsistent with a saturated five-membered ring.[7] To distinguish between the structures (**1b**) and (**2**) a solution of the adduct in deuteriochloroform was studied by n.m.r. spectroscopy at 100 MHz. The splitting patterns were analysed by construction methods.[8] The proton assignments fit perfectly for the structure (**1b**): δ 7·06—7·50 (m, 10H, Ar*H*), 6·52 (d^2, 1H, J_{YX} 5·7 and J_{YR} – 1·8 Hz, *Y*), 6·02 (d^3, 1H, J_{YX} 5·7, J_{XR} 2·9, J_{XS} 0·9 Hz, *X*), 4·73 (d^2, 1H, J_{RS} 6·6, J_{RX} 0·9 Hz, *S*), 4·2 (d^3, 1H, J_{RS} 6·6, J_{RY} 2·9, J_{RY} – 1·8 Hz, *R*) (d^2 = doublet of doublets; d^3 = doublet doublet of doublets). The structure (**2**) would require a long-range coupling RX of $\pm 2{\cdot}9$ Hz which is too large for this four-bond system. The observed SX coupling of 0·9 Hz was considered reasonable for the four-bond system represented in structure (**1b**). This is also in good agreement with the bond angles ($\phi_1 = 120$, $\phi_3 = 0°$) observed in a Dreiding model of (**1b**) using the Barfield relationship[9] for saturated systems as an approximation (J_{calc} +0·6 Hz). The four-bond RY coupling of −1·8 Hz was in excellent agreement with that calculated from the bond angles (*trans*, $\phi = 30°$) using the Barfield relationship[9] for allylic systems (J_{calc} −1·75 Hz).

To confirm these structural assignments, a methanolic solution of the adduct (**1b**) was treated with zinc dust and acetic acid in order to introduce another proton for n.m.r. studies. Filtration and removal of the solvents under reduced pressure afforded a 57% yield of a colourless crystalline solid m.p. 163·5—164°. Its i.r. spectrum showed strong bands at 1795 (C=O), 1465 (aromatic) and 701, 748 (C–Cl) cm^{-1}. On the basis of elemental and i.r. data, the hydrogenation product could have the structure (**4a**) or (**4b**). As before, the distinction between the structures (**4a**) and (**4b**) was using the n.m.r. spectrum of (**4**). The splitting patterns were analysed by construction methods.[8] The couplings in the ORS system including the long-range OS coupling were consistent with the all-*cis* structure (**4a**): δ 7·08—7·51 (m, 10H, Ar*H*), 6·48 (d^3, 1H, J_{YX} 6·0, J_{YR} 1·5, J_{YX} 0·5 Hz, *Y*), 6·09 (d^3, 1H, J_{XY} 6·0, J_{XR} 2·5, J_{XS} 1·0 Hz, *X*), 5·07 (d^3, 1H, J_{OR} 9·0, J_{OS} 3·0 Hz, *O*), 4·36 (d^3, 1H, J_{SR} 7·0, J_{SO} 3·0, J_{SY} 1·0, J_{SX} 0 Hz, *S*), 4·08 (partly overlapping d^4, 1H, J_{RO} 9·0, J_{RS} 7·0, J_{RX} 2·5, J_{RY} 1·5 Hz, *R*) (d^3 = doublet doublet of doublets; d^4 = doublet doublet doublet of doublets).



(4a) (4b)

Similarly, the addition of dichloroketen to diphenylbenzofulvene[10] (**5**) yielded a 1,2-mono-adduct which could be (**6a**) or (**6b**), on the basis of n.m.r. and i.r. spectroscopy. Catalytic hydrogenation of (**6a**) [or (**6b**)] produced colourless crystals of a compound whose structure was established as (**7a**) by detailed n.m.r. analysis. An unusual feature of the n.m.r. spectrum of (**7a**) was that the PQS sub-spectrum was recognized as a deceptively simple ABX type in which one of the P-energy levels corresponded exactly to one of the Q-energy levels.[8] Thus, the eight-line pattern normally seen in the AB part had collapsed to five lines, one AB *quartet*, and a degenerate singlet. Since the singlet was situated between the A and B shifts of the AB quartet, it illustrated an example of the rare type of deceptive situation where AX and BX couplings have unlike signs (a computed example of such a case is recorded in Figure 28 of ref. 8). This analysis of the OPQRS system was confirmed and refined by computer using the LAOCN-3 program.[8] The correct structure of the original adduct must be (**6a**) and not (**6b**).



(5) (6a) (6b) (7a) (7b)

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