Photoreaction of Benzene with 1,2-Dichloroethylenes

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Summary The photoreactions of *cis*- and *trans*-1,2-dichloroethylenes with benzene differ from those of simple ethylenes, giving β-chlorostyrenes as the main products, with smaller proportions of tetrachlorocyclobutanes and bicyclo[3,2,1]- and [3,3,0]-octadiene derivatives.

It has been reported that irradiation of solutions of 1,2-dichloroethylenes in benzene at 254 nm gives the corresponding 1,8-dichloro-octatetraenes.[1] Identification rested on the u.v. spectra of the irradiated solutions, and no products were isolated. Other products absorbing at 250—260 and $<$220 nm were observed but their structures were not elucidated.

We have identified six products formed by the action of 254 nm radiation on a 1 : 4 v/v mixture of *cis*-1,2-dichloroethylene and benzene under nitrogen at 25 °C. Hydrogen chloride is also evolved, and the olefin undergoes a low conversion into the *trans*-isomer. There are three types of product, A, B, and C, which were obtained in the approximate ratio 6 : 1 : 3.† From spectroscopic data of the separated components and comparison with authentic samples, product A was shown to be a mixture of *cis*- and *trans*-β-chlorostyrenes.‡ Product B consisted of the two olefinic dimers (**1**) and (**2**) (*ca.* 1 : 1) which were identified from their mass spectrometric properties, and by dechlorination (Zn–MeOH) to the three isomeric 1,4-dichlorobuta-1,3-dienes which were separated by preparative g.l.c. and had spectroscopic properties identical with those previously reported.[2] The two components (*ca.* 1 : 1 ratio) of product C were both 1 : 1 adducts of the starting materials and their identification as (**3**) and (**4**) rests on the following spectral data and their comparison with related compounds.[3] The mass spectrum of each adduct has *M* 174, 176, and 178 in the ratio 9 : 6 : 1 consistent with the formula $C_8H_8Cl_2$ and in the u.v.

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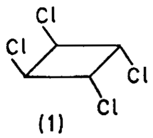
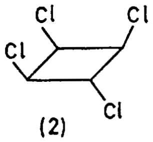
† Irradiation of the solution (500 ml) for 46 h with eight lamps (3·5 Watts output each at 254 nm) gave a brown oil which yielded 3 g of the product mixture (b.p. 50—80° at 0·5 mmHg).

‡ At short irradiation times, the styrenes were formed with a high degree of stereoselectivity from the corresponding *cis*- and *trans*-1,2-dichloroethylenes. Extrapolation of the data to zero time suggested that the reaction was stereospecific in each case; the photostationary state of *cis*- and *trans*-β-chlorostyrenes was 1 : 2.

spectrum neither has significant absorption at >220 nm. The i.r. spectra have absorptions at 3050 (=C–H stretch), 2950 (C–H stretch), and 1615 cm^{-1} (–C=C stretch). The n.m.r. spectrum of adduct (**3**) was assigned by reference to models and the Karplus correlation [τ 4·1—4·4 (4H, ABq, $J_{3,4} = J_{7,8} = 5$ Hz, 3-, 4-, 7-, and 8-H) further split by allylic vicinal coupling; ($J_{1,8} = J_{1,7} = J_{3,5} = J_{4,5} = J_{1,3} = J_{5,7} =$ *ca.* 1 Hz; $J_{2,4} = J_{6,8} = 2·5$ Hz; $J_{2,3} = J_{6,7} \leqslant 1$ Hz), 5·34—5·46br (2H, d, $J_{1,2} = J_{5,6} =$ *ca.*1 Hz, 2- and 6-H), and 6·16—6·26br (2H, s, 1- and 5-H)]. The second adduct (**4**) had n.m.r. resonances at τ 3·9—4·3 (2H, ABq, $J_{6,7} = 5·5$; $J_{5,6} = J_{5,7} = 2$ Hz, 6- and 7-H), 4·1—4·5 (2H, $J_{2,3} = 5·5$; $J_{1,2} = 6·5$ Hz, 2- and 3-H), 4·92—5·08 (1H, $J_{2,4} = J_{3,4} = 2$ Hz; $J_{4,5} = 8·2$ Hz, 4-H), 5·24—5·34 (1H, $J_{1,8} = J_{5,8} = 1·5$; $J_{2,8} =$ *ca.* 1Hz, 8-H), 5·94—6·2 (1H, 5-H), and 6·36—6·56 (1H, $J_{1,4} = J_{1,7} = 2$; $J_{1,6} = J_{1,3} = 1$Hz, 1-H). Neither of these two adducts is considered to be a primary photoproduct but both are suggested to arise from acid-catalysed rearrangement of the 1,4-adduct (**5**),[4] and/or the 1,3-adduct (**6**). The proposed intermediates (**5**) and (**6**) were not detected and the presence of acid scavengers in the irradiation merely changed the ratio of (**3**) to (**4**).



(1)



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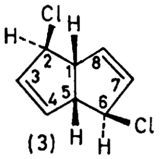

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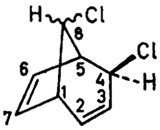

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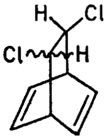

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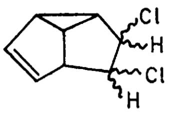

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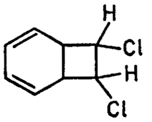

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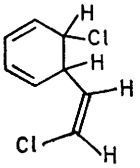

(8)

Attempts to confirm the previously reported[1] formation of 1,8-dichloro-octatetraenes met with only limited success. Certainly irradiation of both *cis*- and *trans*-1,2-dichloroethylenes in benzene leads to the development of a yellow colour and the previously reported absorption spectrum was confirmed, but of the many attempts to detect, trap or isolate the octatetraenes, none succeeded. The compound responsible for the coloration does, however, codistil with 1,8-dichloro-octane but the concentrations obtained were always insufficient for analysis by other spectroscopic methods. Catalytic reduction of the irradiated solution destroys the yellow colour and n-octane is observed among the products. Assuming an ϵ_{max} of *ca.* 5×10^4 mol^{-1} l cm^{-1} for the 1,8-dichloro-octatetraenes, then they are formed in 1/10 the amount of the β-chlorostyrenes. The intermediacy of (**7**) for the β-chlorostyrenes and/or the proposed 1,8-dichloro-octatetraenes has been discounted by its lack of detection even under conditions known to favour 1,2-photocycloaddition,[5] and by the observation that photolysis of *trans*-(**7**) in benzene leads to only slow dissociation to the addends, β-chlorostyrenes, and the yellow product. Formal 1,2-addition of the C–Cl bond of dichloroethylene would lead to a likely precursor (**8**) of both the styrenes and octatetraenes; the involvement of (**8**) in the present reaction is under investigation.

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