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META PHOTOCYCLOADDITION OF TRANS-1,2-DICHLOROETHYLENE TO BENZENOID COMPOUNDS: MECHANISTIC CONSIDERATIONS AND PHOTO AND THERMAL LABILITIES OF THE ADDUCTS

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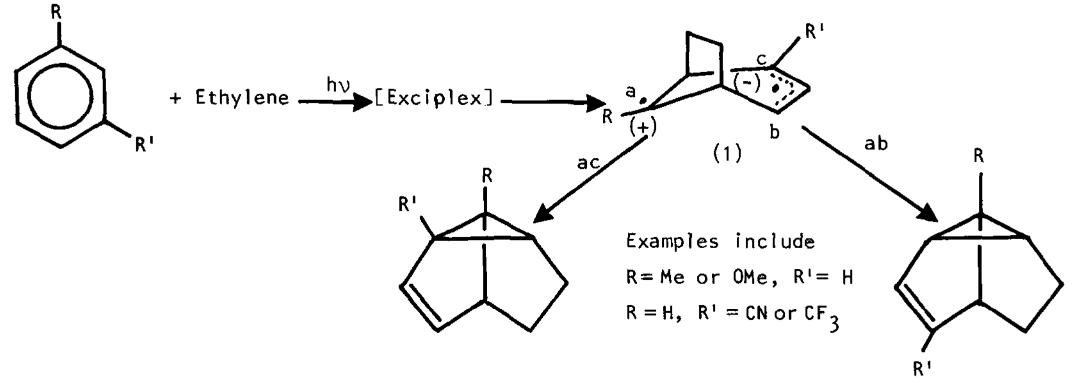
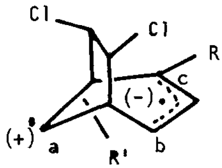
Abstract: The observed specificity of *meta* photocycloaddition of *trans* 1,2-dichloroethylene to benzenoid compounds is deduced to arise from a chlorine atom induced asymmetric distortion of the reaction intermediate: thermal and photochemical isomerisations of the adducts occur by an ethenylcyclopropane-cyclopentene rearrangement and/or 1,3- and 1,5-chlorine shifts.

There is considerable current interest in both the mechanistic[1-3] and synthetic[4] aspects of the *meta* photocycloaddition of ethylenes to benzenoid compounds. Although the involvement of S_1 arene - S_0 ethylene exciplexes has been established for the reactions of dioxoles with benzene and toluene,[1] this feature is still, for the vast majority of systems, more assumed than proven, but the intermediacy of (1) does account for the adduct isomers observed for all reported reactions of substituted benzenes with ethylenes. Closures *ab* and *ac* in (1) yield two adducts frequently in approximately equal yields.[5] This poor selectivity lowers the appeal of the reaction as a synthetic procedure but in marked contrast to other ethylenes, the *meta* photocycloadducts of *trans*-1,2-dichloroethylene (TDCE) and benzene derivatives reflect closure in the intermediate solely to the carbon atom in the delocalised allylic system which has the *endo* C-Cl bond [*i.e.* *ab* closure in (2).][6] The origin of this remarkable and novel effect is now considered along with the thermal and photochemical isomerisations of the dichloro *meta* cycloadducts: study of these processes is of interest here since the mechanism for the ethenyl cyclopropane-cyclopentene rearrangement which interconverts the 2- and 4-substituted *meta* photoadducts[5] may involve the same or a closely similar intermediate to that [*i.e.* (1)] proposed in the photoaddition of ethylenes to benzenes.

We interpret the specificity of the addition of TDCE in the following way. As for all other arene-ethylene systems, a bicyclo[3.2.1] octenyl intermediate is proposed as the immediate adduct precursor. In this species (2) derived from TDCE additions, the chlorine atom *endo* to the allylic moiety may reasonably be assumed to induce an asymmetric distortion of the six-membered ring by steric and repulsive electronic interactions: the latter arises from the n-electrons of the chlorine and the electrons of the allylic system whether this is anionic in character or neutral as in a biradical form of (2). Such distortion results in a more favourable conformation for cyclisation between the *ab* rather than the *ac* positions in the intermediate (2) and evidently this effect is sufficient to promote the former pathway to the apparent exclusion of the latter. This remarkable control over the formation of isomers from the *meta* photocycloaddition of ethylenes to benzenoid compounds should broaden the appeal of the process as a key step in the synthesis of bicyclo[3.3.0] octane derivatives.

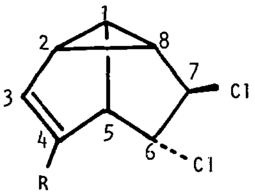
Benzenes which have been reported to undergo addition to TDCE all have strongly perturbing substituents.[6] To assess if this feature is essential for the operation of the Cl-directing effect, the reaction of TDCE with benzene was re-examined. This system has been reported to give a complex mixture of products but <u>meta</u> cycloadducts were not detected.[7] It transpires, however, that the primary photoproducts are extremely thermally labile and highly sensitive to acid surfaces so would not have survived the earlier employed preparative g.l.c. and silica chromatographic conditions. ^{1}H N.m.r. spectroscopic





(2) R = H, R' = CF_3,Cl,F,OH

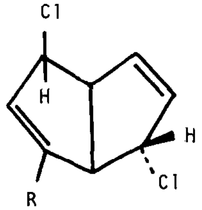
(6) R = CN,R' = H



(3) R = H

(7) R = CN

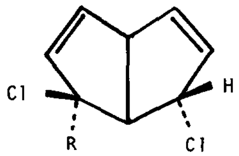
(12) R = CF_3



(4) R = H

(9) R = CN

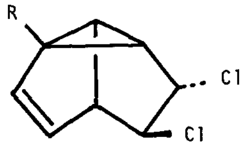
(14) R = CF_3



(5) R = H

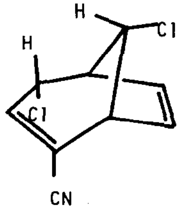
(10) R = CN

(15) R = CF_3



(8) R = CN

(13) R = CF_3



(11)

analysis of the crude product mixture showed the presence of β-chlorostyrenes, ethylene dimers, the ortho cycloadduct and a meta cycloadduct in a respective ratio of 2:1:2:5. Separation of the mixture was achieved by preparative h.p.l.c. and the meta adduct was shown to have the 6-exo,7-endo dichloro structure (3)[8] which is again consistent with the cyclopropane formation being directed by an endo chlorine atom induced asymmetric distortion in the intermediate. Adduct (3) was essentially photostable but both thermally and on passage through a silica column gave a 2:1 mixture of (4) and (5) which respectively reflect 1,3- and 1,5-chlorine shifts: no evidence was obtained for the rearrangement of (3) to the 6-endo,7-exo dichloro meta cycloadduct. In contrast the 9-cyano- and 11-cyano-1-methoxy meta cycloadducts from 3-cyanoanisole and cyclopentene are interconverted by facile thermal and photochemical ethenylcyclopropane-cyclopentene rearrangements.[5] In order to assess the effect of chloro substituents on this interconversion and if the intermediate (6) is a significant species in the process, thermal and photochemical induced reactions of the TDCE-benzonitrile adduct (7) have been studied.

Irradiation (254 nm, 0.1M in cyclohexane or methyl cyanide) of (7) produced a total conversion to three isomers in approximately equal amounts. Two of the isomers were isolated by preparative g.l.c. and shown to be the 2-cyano isomer (8) produced by an ethenylcyclopropane-cyclopentene rearrangement and the 1,3-chlorine shift product (9).[9] The third isomer was, however, thermally labile and readily converted into (9) and from ^{1}H n.m.r. spectroscopic analysis of the crude mixture was deduced to have the 1,5-chlorine shift structure (10).[9] In marked contrast to the photochemical reaction, heating (7) at 234°C in n-tridecane solution produced (9) and a further isomer (respective ratio 2:1) which from n.m.r. spectral investigation was deduced to have the bicyclo[3.2.1]octa-2,6-diene structure (11).[11] Although isomerisations between bicyclo[3.2.1]octa-2,6-dienes and bicyclo[3.3.0]octa-2,6-dienes are known,[12] under the conditions of formation of (9) and (11) neither was the precursor of the other but (11) was also formed from the 2-substituted isomer (8). The formation of (11) from (7) and (8) poses a mechanistic problem but it may be significant that, at least in principle, it may arise via two 1,3-chlorine shifts in the addition intermediate (6) which as noted above may also be involved in the interconversion of meta cycloadducts.

The formation of the 2-cyano isomer (8) photochemically but not thermally from the 4-isomer (7) is consistent with observations reported for other benzonitrile meta cycloadducts and in order to determine the influence of the nitrile substituent on the course of this and the other rearrangement processes, we have studied the thermal and photoreactions of the 4-trifluoromethyl meta cycloadduct (12) from α,α,α-trifluorotoluene and TDCE. As for the cyano adduct (7) irradiation of (12) produced an ethenylcyclopropane-cyclopentene rearrangement and 1,3- and 1,5-chlorine shifts but the isomer ratios differed markedly. Thus (13), (14), and (15) were formed from (12) in a respective ratio of 1:2:6 and the 1,5-chlorine shift product (15), in contrast to (10) from (7), was stable and isolated. The different product yields from the meta adducts (7) and (12) may, however, simply reflect the relative abilities to excite the ethenylcyclopropane and the C-Cl chromophores in the two systems [ε_{max}254 nm (7) = 5400 l mol^{-1}cm^{-1}, ε_{max}254 nm (12) = 220 l mol^{-1}cm^{-1}]. In contrast to (7), heating the trifluoromethyl adduct (12) at 234°C produced the 2-substituted *meta* cycloadduct (13) and this as the major isomer (70%). Further, the two minor isomers (1:1 ratio) were the 1,3- and 1,5-chlorine shift products (14) and (15) and no evidence was obtained for the formation of an isomer analagous to (11).

These results illustrate that the pathways of thermal and photochemical isomerisations of *meta* photocycloadducts are very dependent on the type and position of substituents. At present there is no clear evidence for similar mechanisms for the photoformation of *meta* cycloadducts and their thermal and photochemical interconversions. Chlorine shifts appear to be favoured for the adducts of TDCE but it is somewhat unexpected that the 4-trifluoromethyl isomer (12) is thermally converted to the 2-isomer (13) and this apparently has surprisingly little or no tendency to undergo a thermal 1,5-hydrogen shift. Evidently the $-CF_3$ substituent has a greater stabilising effect as a cyclopropyl than as an ethenyl substituent which is, of course, the reverse of that observed for the -CN group.

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8. ^1H N.m.r. spectrum ($CDCl_3$) of (3) δ values 5.88 (dd + fine splitting, H_3, $J_{3,4}$ = 5.4, $J_{2,3}$ = 2.4, $J_{1,3}$ = 0.5 Hz), 5.40 (m, H_4, $J_{4,5}$= 2.4, $J_{1,4}$ = 0.7 Hz), 4.84 (dd, H_7, $J_{7,8}$ = 6.4 Hz), 4.17 (br.s, H_6), 3.38 (m, H_5, $J_{5,7}$ = 2.4 Hz), 3.12 (br.q, H_1, $J_{1,2}$ = $J_{1,5}$ =$J_{1,8}$ = 7.0 Hz), 2.30 (m, H_8), and 2.09 (m, H_2, $J_{2,8}$ =8.0 Hz) ppm.
9. ^1H n.m.r. spectra ($CDCl_3$) (9): δ values 5.91 (dd, H_4, $J_{4,5}$ = 2.5 Hz), 5.79 (d, H_3, $J_{3,4}$ = 5.6 Hz), 4.30 (dd, H_6, $J_{6,7}$ = 7.9 Hz), 3.83 (d, H_7), 3.67 (t of d, H_5, $J_{5,6}$ = 5.1 Hz), 3.24 (br.t, H_1, $J_{1,5}$ = 6.1, $J_{1,8}$= 7.0 Hz), and 2.67 (d, H_8) ppm; (10): δ values 6.44 (t, H_3, $J_{1,3}$ = 2.4, $J_{3,4}$ = 2.0 Hz), 6.04 (dd, H_6, $J_{6,7}$ = 5.7 Hz), 5.95 (dt, H_7, $J_{7,8}$ = 2.2 Hz), 5.17 (dt, H_4, $J_{1,4}$ = 2.0 Hz), 5.03 (m, H_8), 4.14 (m, H_5, $J_{4,5}$ = 8.5, $J_{1,5}$ = 6.6, $J_{5,7}$ = 2.3, $J_{5,8}$ = 2.4 Hz), and 3.76 (m, H_1) ppm.
10. ^1H n.m.r. spectrum ($CDCl_3$), δ values 6.19 (dd, H_3, $J_{3,4}$ = 5.4, $J_{3,5}$ = 2.6 Hz), 5.80 - 5.96 (3H, m, H_4, H_6, H_7), 5.34 (m, H_8, $J_{7,8}$ = 2.3, $J_{6,8}$= 1.0, $J_{1,8}$ = 2.4 Hz), 4.24 (m, H_5, $J_{5,7}$ = 2.4, $J_{5,6}$ = 2.2 Hz), and 3.74 (dd, H_1, $J_{1,5}$ = 6.5, $J_{1,8}$ = 2.5 Hz), ppm.
11. ^1H n.m.r. spectrum ($CDCl_3$), δ values 6.47 (t, H_3, $J_{3,4}$ = 2.6, $J_{1,3}$ = 2.4, $J_{3,5}$ = 0.4 Hz), 5.85 (br.s, H_6, H_7), 4.91 (m, H_8, $J_{1,8}$ = 0.8 Hz), 4.74 (m, H_4, $J_{1,4}$ = 2.2, $J_{4,5}$ = 1.8 Hz), and 3.95 (m, H_1, H_5, $J_{1,5}$ = 5.6, $J_{1,6}$ = $J_{1,7}$ = $J_{5,6}$ = $J_{5,7}$ = 0.4 Hz), ppm.
12. See for example references in "Hydrocarbon Thermal Isomerisations" by J.J.Gajewski, Academic Press, New York, 1981.

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