Photoreactions of Halogenobenzenes with Cyclopentene. Insertion into Carbon–Halogen Bonds

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Summary Chloro-, bromo-, and iodo-benzenes photoreact with cyclopentene to give, principally, products derived from insertion into the C–halogen bond, a type of reaction hitherto unknown in this series, but fluorobenzene mainly forms *meta*- and *para*-cycloadducts with only a minor proportion of the *cis*-insertion product

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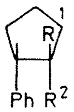
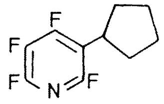


(1) $R^1 = H, R^2 = Cl$
(2) $R^1 = Cl, R^2 = H$
(3) $R^1 = H, R^2 = Br$
(4) $R^1 = H, R^2 = F$



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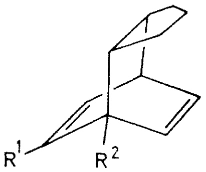
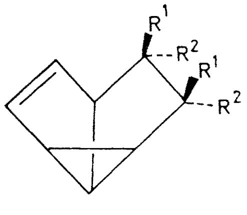
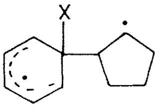


(6) $R^1 = F, R^2 = H$
(7) $R^1 = H, R^2 = F$



(8) $R^1 = H, R^2-R^2 = -[CH_2]_3-$
(9) $R^1-R^1 = -[CH_2]_3-, R^2 = H$



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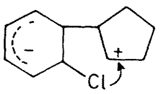

(11)

A RECENT Communication describing novel reactions of halogenopyridines with alkenes[1] prompts us to report that related, but different, reactions occur with halogenobenzenes

Irradiation (254 nm) of an equivolume mixture of chlorobenzene and cyclopentene at 20 °C under air gave a mixture of products, *ca* 60% of which comprised a 1 : 1 mixture of the *cis*- and *trans*- adducts (**1**) and (**2**) respectively The remaining components were 1-phenylcyclopentene [apparently formed thermally from (**1**) and (**2**)] and a mixture of chlorobiphenyls, the latter evidently resulting from reactions of phenyl radicals with chlorobenzene contrast with ref 1, where the corresponding tetrafluoropyridyl radicals are reported not to be formed

Another interesting difference from the results in ref 1 is that whereas cyclopentene and chlorotetrafluoropyridine gave the cyclopentyl derivative (**5**), chlorobenzene and cyclopentene give no significant amount of the corresponding substitution product, cyclopentylbenzene

Under similar conditions, iodobenzene and cyclopentene give 1-phenylcyclopentene [apparently *via* very labile iodo analogues of (**1**) and/or (**2**)], and iodobiphenyls[2] Bromobenzene and cyclopentene surprisingly gave the *cis*-adduct (**3**) as the major product, essentially free from the *trans*-isomer, together with a mixture of bromobiphenyls

Fluorobenzene and cyclopentene photoreact in a substantially different manner to give a thermally very labile mixture of the adducts (**6**), (**8**), (**7**), (**4**), and (**9**) (in order of decreasing abundance) No fluorobiphenyls were detected It is also interesting that '*ortho*'-type adducts analogous to those formed by pentafluoropyridine and ethylene[3] and hexafluorobenzene and cycloalkenes[4,5] were not detected The formation of the *cis*-adduct (**4**) appears to provide the first known example of insertion into a C–F bond

For all four halogenobenzenes, the absence of cyclopentylbenzene from the products appears to rule out the involvement of a diradical species (**10**) analogous to that proposed by Barlow *et al* [1] Further, the formation of the insertion adducts (**1**) and (**2**) by a conventional free-radical chain process propagated by phenyl radicals (which are undoubtedly formed, though not in the case of fluorobenzene) would require the improbable abstraction of chlorine from chlorobenzene by phenylcyclopentyl radicals Since mixtures of chlorobenzene and cyclopentene do not show charge-transfer absorption, we consider that the insertion adducts are likely to arise either by a concerted 4- or 5-centre process involving the S_1 or T_1 halogenobenzene, or *via* chloride transfer within a singlet exciplex species which, for convenience, could be represented as the zwitterion (**11**)

We conclude that, despite certain similarities between the photoreactions of halogenobenzenes and fluorinated pyridines with alkenes,[1,3] substantial qualitative differences exist

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[1] M G Barlow, R N Haszeldine, and J R Langridge, *J C S Chem Comm* , 1979, 608

[2] J McD Blair and D Bryce-Smith, *J Chem Soc* , 1960, 1788

[3] M G Barlow, D E Brown, and R N Haszeldine, *J C S Chem Comm* , 1977, 669 *J C S Perkin I*, 1978, 363

[4] D Bryce-Smith, A Gilbert, and B H Orger, *Chem Comm* , 1969, 800 D Bryce Smith, A Gilbert, B H Orger, and P J Twitchett, *J C S Perkin I*, 1978, 232

[5] B Sket and M Zupan, *J C S Chem Comm* , 1976, 1053, 1977, 365, *Tetrahedron Letters*, 1977, 2811