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INTERMOLECULAR AND INTRAMOLECULAR PHOTOCYCLOADDITION REACTIONS OF FLUOROARENES

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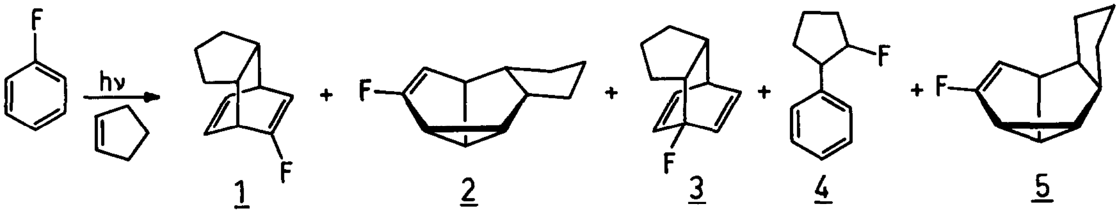
Abstract: The *meta* photocycloaddition of *para*-fluorotoluene to cyclopentene yields 1-methyl-10-fluoro-*endo*- and -*exo*-tetracyclo[6.3.0.0^{2,11}.0^{3,7}]undec-9-ene as major photoproducts, while the intramolecular photoaddition of 5-(*para*-fluorophenyl)pent-1-ene gives exclusively 7-fluorotetracyclo[3.2.1.0^{2,8}.3^{4,8}]undec-6-ene. A reaction pathway via zwitterionic intermediates is proposed.

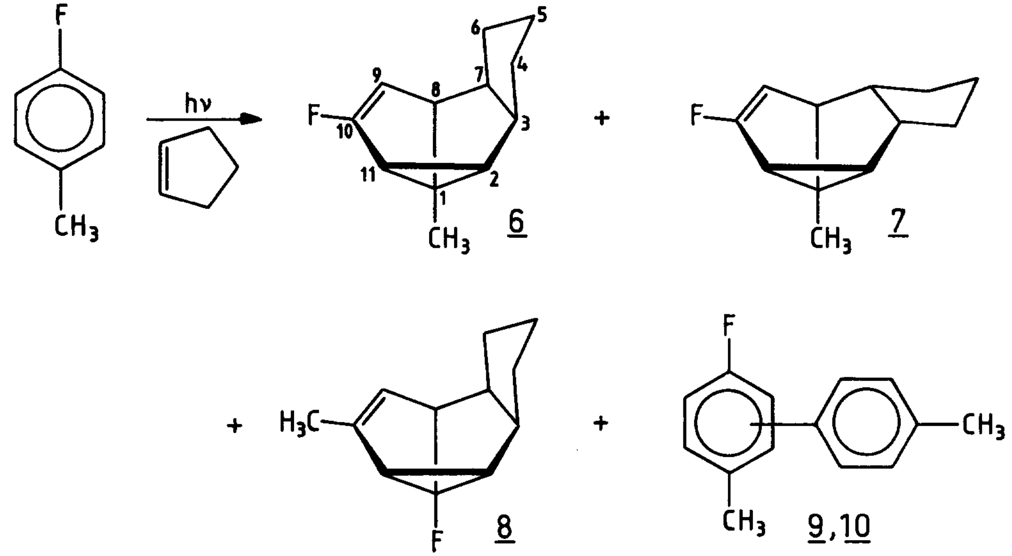
The photochemistry of intermolecular arylhalide/alkene systems is intriguing since with chloro-, bromo-, and iodo-benzenes the principal 1 : 1 photoproducts result from insertion into the carbon-halogen bond, whereas fluorobenzene reacts in a substantially different manner.[1] Our recent interest in the mechanistic aspects of the arene substituent directed *meta* photocycloaddition reactions of anisole and substituted anisoles to cyclopentene and ethyl vinyl ether[2-5] has led us to examine the photochemistry of the *para*-fluorotoluene/cyclopentene and 5-(*para*-fluorophenyl)pent-1-ene systems.

The intermolecular photochemical reaction of fluorobenzene and cyclopentene yields 1 as by far the major product, with 2 - 5 as the other photoproducts in decreasing order of abundance.[1]



In contrast to this photoreaction the predominant mode of cycloaddition in the case of *para*-fluorotoluene/cyclopentene and 5-(*para*-fluorophenyl)pent-1-ene is *meta* cycloaddition. In the case of the intramolecular system, which is the first example of a halogen substituted bichromophore to be reported, the cycloaddition reaction could prove to be of synthetic value.

The irradiation (254 nm) of 1 M *para*-fluorotoluene and 3.5 M cyclopentene in cyclohexane gave photoproducts 6 - 10.

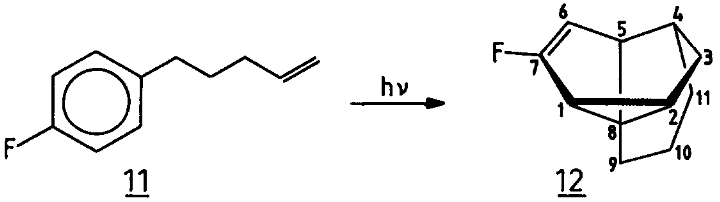


1-Methyl-10-fluoro-*endo*-tetracyclo[6.3.0.0^{2,11}.0^{3,7}]undec-9-ene (6) was by far the major photoproduct (constituting 70 % of the photoproduct mixture by g.c. analysis). The other two cycloadducts detected could not be separated by g.c. or t.l.c. but n.m.r. analysis implies that they were formed in a ratio of 3 : 1. One component was 1-methyl-10-fluoro-*exo*-tetracyclo[6.3.0.0^{2,11}.0^{3,7}]undec-9-ene (7), the other being 1-fluoro-10-methyl-*endo*-tetracyclo[6.3.0.0^{2,11}.0^{3,7}]undec-9-ene (8). The remaining fluorodimethylbiphenyls 9 and 10 were detected by g.c./m.s. and constituted 5 % of the photoproduct mixture.

The structures of 6, 7 and 8 were established on the basis of their ^{1}H and ^{13}C n.m.r. data[6] and comparison with previously reported spectra.[3,5,6,7]

Compound 6: ^{1}H n.m.r. (CDCl$_3$/TMS): 4.66 (H-9; d; $J_{8,9}$ = 2.6); 3.22 (H-7; m; $J_{3,7}$ = 6.7; $J_{6,7}$ = 6.0; $J_{6',7}$ = 4.0; $J_{7,8}$ = 4.2; $J_{7,F}$ = 4.0); 3.00 (H-3; m; $J_{2,3}$ = 5.2; $J_{3,4}$ = 8.3; $J_{3,4'}$ = 5.6; $J_{3,8}$ = 1.5); 2.50 (H-8; m; $J_{8,F}$ = 4.2); 1.51 (H-2; dd; J_{2,CH_3} = 1.9); 1.45 - 1.85 (H-4, H-4', H-5, H-5', H-11; m); 1.23 - 1.33 (H-6, H-6'; m); 1.39 (CH$_3$) (H-4', H-5' and H-6' are *endo*, H-4, H-5 and H-6 are *exo*). ^{13}C n.m.r. (CDCl$_3$/TMS): C-1: 33.2; C-2, C-3 and C-7: 49.4, 36.8 ($J_{X,F}$ = 3.6), 32.3 ($J_{Y,F}$ = 33.0); C-4, C-5 and C-6: 30.0, 29.1, 26.2; C-8: 60.8; C-9: 103.0 ($J_{9,F}$ = 12); C-10: 159.0 ($J_{10,F}$ = 280); C-11: 52.4 ($J_{11,F}$ = 6); CH$_3$: 18.8.

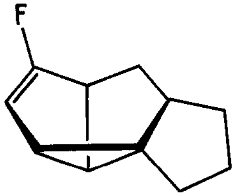
The irradiation (254 nm) of a 1 % solution of 5-(*para*-fluorophenyl)pent-1-ene (11) in cyclohexane gave exclusively 7-fluorotetracyclo[3.2.1.0^{2,8}.3^{4,8}]undec-6-ene (12) in a yield of more than 95 %. This structure was assigned on the basis of ^{1}H and ^{13}C n.m.r. spectroscopy.



Compound 12: ^{1}H n.m.r. (CDCl$_3$/TMS): 4.70 (H-6; dd; $J_{1,6}$ = 1.0; $J_{5,6}$ = 2.7); 2.47 (H-1; dd; $J_{1,2}$ = 9.1); 2.42 (H-4'; m; $J_{3',4'}$ = 1.5); 2.13 (H-5; m; $J_{5,F}$ = 6.4; $J_{3,5}$ = 1.0); 1.78 (H-3 and H-3'; m; $J_{2,3\&3'}$ = 4.5); 0.90 (H-2; dt); 1.0 - 1.6 (H-9, H-9', H-10, H-10', H-11, H-11');

^{13}C n.m.r. (CDCl$_3$/TMS): C-1 and C-5: 54.0, 53.7 ($J_{X,F}$ = 7.0; $J_{Y,F}$ = 30.0); C-2: 24.9; C-3, C-9, C-10 and C-11: 32.2, 31.6, 28.7, 25.0; C-4: 39.4 ($J_{4,F}$ = 31.0); C-6: 99.4 ($J_{6,F}$ = 10.0); C-7: 158.8 ($J_{7,F}$ = 280.0).

In the case of 6-phenylhex-2-ene two other photocycloaddition products were found,[8] but the corresponding adducts 13 and 14 could not be detected in our system.



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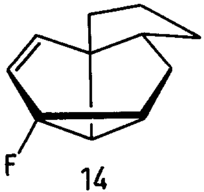

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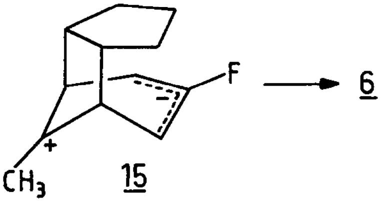
The production of *meta* photoadducts from both the inter- and intramolecular systems reported here is entirely consistent with the Bryce-Smith/Gilbert "ionization potential rule";[9] in this case Δ I.P. = 0.3 eV.[10] It is, however, in stark contrast to the photochemistry previously reported for the fluorobenzene/cyclopentene system[1] (Δ I.P. = 0.13 eV)[10] where *para* photocycloaddition is the predominant mode of reaction.

Of course the Bryce-Smith/Gilbert rule refers to relative quantum yields of *ortho* vs. *meta* photocycloaddition and not to chemical yields. We have, however, observed essentially no time dependence in the product ratios of 1 and 2 and 6 - 8 and *ortho* and *para* cycloadducts are thought to arise from the same excited state of the aromatic compound.[11] Also, our results would be expected on the basis of zwitterionic intermediates[12] 15 and 16: the alkyl substituent stabilises the positive charge whilst the fluoro substituent stabilises the negative charge on the carbon adjacent to that to which it is bonded,[13] and it is at the nodal position of the allylic anion.



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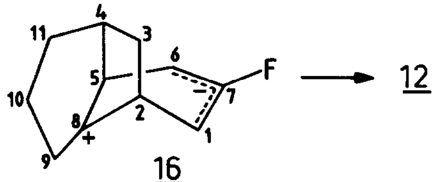

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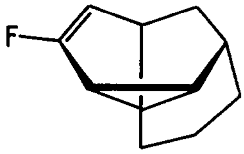
The intermediate 15 is symmetric and the two modes of ring closure are degenerate, both leading to 6. In this intermolecular addition there is also the possibility of *exo* approach of the two molecules and indeed the *exo* isomer 7 has been detected.

The intermediate 16 is asymmetric due to the trimethylene bridging moiety. The intermediate gives rise to the intermolecular adduct 12 by bond formation between C-1 and C-8. The other possible mode of ring closure, between C-6 and C-8, would yield the intramolecular adduct 17. This molecule is very highly strained and its formation has not been observed.



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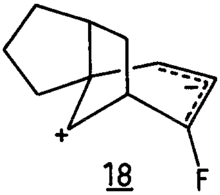
5-Phenylpent-1-ene undergoes intramolecular photocycloaddition at the 1,3 positions of the arene ring (yielding products with structures like 13 and 14) in addition to reaction at the 2,6 positions (yielding one product with a structure such as 12).[14] The ratio of 1,3 to 2,6 addition is 1 : 2. Our *para*-fluoro compound undergoes only 2,6 addition. Examination of intermediate 18 indicates that neither of the charge centres of the zwitterion are stabilised by the arene substituents. Fluorine attached directly to a carbon atom bearing a negative charge can even be destabilising.[13]



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On the basis of such zwitterionic intermediates as 15 and 16 for *meta* photocycloaddition it is entirely consistent that 6, 7 and 12 constitute the majority of the photoproducts from the fluoroarene/ethene systems examined.

Acknowledgement

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