Tetrahedron Letters No. 13, pp 1097 - 1100.
©Pergamon Press Ltd. 1979. Printed in Great Britain. 0040-4039/79/0322-1097$02.00/0

PHOTOADDITION REACTIONS OF BENZENE AND RELATED COMPOUNDS WITH THIOCHROMONE 1,1-DIOXIDE

Ian W.J. Still* and Toong Sang Leong

Department of Chemistry
University of Toronto
Toronto, Ontario, Canada M5S 1A1

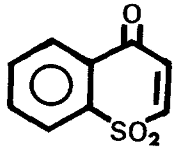
Summary

The photoaddition reactions of benzene and some simple derivatives with thiochromone 1,1-dioxide have been examined in an attempt to correlate the pattern of photochemical behavior with data on ionization potentials.

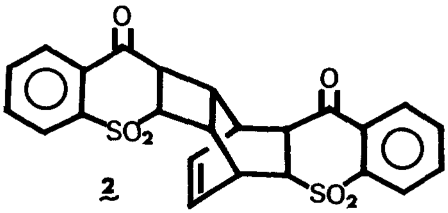
The widespread interest in photochemical addition reactions of aromatic compounds, first aroused by the report of the formation of a stable 2:1 adduct between maleic anhydride and benzene,[1] shows no sign of abating, to judge from the recent literature,[2-5] while a number of reviews of the field have also appeared recently.[6-8] Much attention has been focussed on the general mechanism of the 1,2-addition, especially with electron-deficient alkenes,[9-11] although many examples of the alternative 1,3-[12] and 1,4-addition[6] processes have now been reported. An apparent correlation[13] between the electron donor-acceptor properties of the arene and the alkene (as measured by the difference in ionization potentials) and the degree to which the orbital symmetry "forbidden" 1,2-adducts were formed, led us to investigate the photoaddition reactions of the electron-deficient alkene, thiochromone 1,1-dioxide 1 with benzene and a number of simple derivatives, the results of which we now present.

When a solution of 1 (I.P.=9.93)[14] in degassed benzene was irradiated[15] for 13 hours, some starting material (18%) was recovered after chromatography, along with a white crystalline solid (32%), mp 327-329°; MS (m/e) 466; IR (ν^{KBr}) 1697, 1683, 1320, 1152 cm^{-1}; NMR (δ^{DMSO-d_6}) 2.57-4.83 (8H,m), 6.17 (2H,t,J=4Hz), 7.50-8.17 (8H,m) ppm.[16] These data lead us to formulate the product as the expected 2:1 adduct, 2.[17] Support for the formation of 2 *via* initial 1,2-photoaddition, followed by trapping of the presumed intermediate 3 through a ground-state (Diels-Alder) reaction with excess 1, was provided by repeating the above irradiation in the presence of an equimolar amount of N-phenylmaleimide. The sole product obtained was the mixed (1:1:1) adduct 4[16] (17%), mp >300° dec.; MS (m/e) 445; IR (ν^{KBr}) 1698, 1335, 1151 cm^{-1}; NMR (δ^{DMSO-d_6}) 2.97-4.67 (8H,m), 6.13-6.60 (2H,br s), 6.80-8.30 (9H,m) ppm. In addition, when 1 was irradiated in the presence of cyclohexene (I.P.=9.24)[18] the simple 1:1 adduct 5 was isolated in 26% yield,[19] demonstrating the ability of 1 to undergo the photochemical ($2\pi+2\pi$) reaction, while the dienophilic capability of 1 was readily confirmed by the isolation of the Diels-Alder adduct 6 in 85% yield, by the reaction of 1 with 1,3-cyclohexadiene (2 equivts.) in benzene in the dark at 25°C for 72 h, at a concentration identical to that in the photochemical experiment.

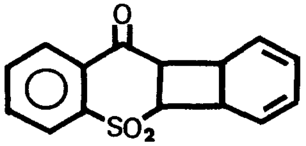
We have also examined the role of sensitizers such as acetophenone or benzophenone on the initial photoaddition, but varying concentrations of the sensitizer had no marked effect beyond a slight reduction in the amount of 2 isolated, thus possibly implicating a



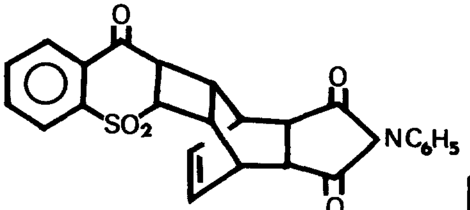
1



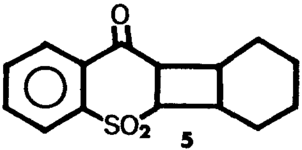
2



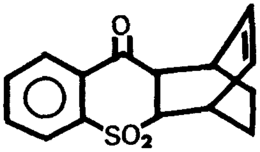
3



4



5



6

singlet excited state. Since all the irradiations were conducted through Pyrex, the excited state involved must either be S_1 (alkene) or a photoexcited charge-transfer complex.[6] When the irradiations were conducted in acetonitrile or methanol, much more complex reaction mixtures resulted although, interestingly, when an equimolar amount of trifluoroacetic acid was added for the irradiation of 1 in benzene, the isolated yield of 2 increased to 42%,[20] while only 7% of the starting material was recovered. For comparison, a number of simple benzene derivatives have also been subjected to irradiation in the presence of 1, and the results are summarized in Table 1.

TABLE 1. Relation of Adduct Formation with Ionization Potential

Arene substituent, X[a]	(Vertical) I.P. of C_6H_5X[b]	Yield of 2:1 adduct (%)[c]	Rec. 1[c]
NMe_2	7.51	0	37
OMe	8.54	0	37[d]
Me	9.13	0	15[e]
Cℓ	9.31	19	27
H	9.40	32	18
CF_3	9.90	4	18[f]

[a] *A number of 1,4-disubstituted benzene derivatives were examined but gave no adduct.*

[b] *A.D. Baker, D.P. May and D.W. Turner, J. Chem. Soc. [B] 22 (1968).*

[c] *These represent isolated yields of the chromatographically pure compounds.*

[d] *1:1-Adducts, arising from 1,3-addition (5%) in the unusual 3,5-addition mode[12,21] and 1,4-addition (3%), were also isolated.*

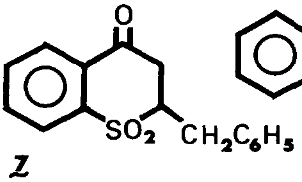
[e] *2-Benzylthiochroman-4-one 1,1-dioxide 7 (2%) and bibenzyl (6%) were also obtained.*

[f] *The 1:1-adduct 9 (2%) and a photodimer[16] (3%) of 1 were also isolated.*

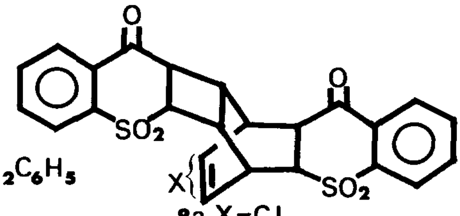
The results in Table 1 fall into two categories - those involving the strongly electron donating class of aromatic substrate (N,N-dimethylaniline, anisole, toluene) and those involving aromatic substrates with I.P.'s closer to that of 1 (benzene, chlorobenzene, α,α,α-trifluorotoluene). In the former group, no 2:1 adduct formation is observed and, indeed, a small amount of 1:1 adduct formation is observed only in the reaction of 1 with anisole. It is possible that the greater degree of charge transfer in the excited state interaction involved in such cases promotes dissociation back to the ground states (i.e., in effect, a quenching process) or leads perhaps to products arising from (ionic) polymerization. For the lower group of arene substrates on the other hand, the extent of 2:1 adduct formation, as expected, correlates well with the ΔI.P. between 1 and the arene. It will be noted that with α,α,α,-trifluorotoluene we obtained a small amount of the 1:1 adduct, assigned one of the isomeric structures 9,[16] on the basis of its nmr spectrum and that of the 2:1 adduct 8b,[16] which reveal the presence of three, or one, vinylic protons respectively. It has been generally observed that yields of the initial 1:1 (1,2-addition) products are small or non-existent, because of ready photodissociation and also because of reasonably efficient trapping by any dienophile present, to give the 2:1 adduct.[8] The isolation of 9 in the present study may reflect a lower efficiency of the Diels-Alder step, because of reduced electron density in the diene component of 9, compared to that in 3, for example.

It is also interesting to note that in the reaction of 1 with toluene a hydrogen abstraction process is competing with the photoaddition, as is evident from the formation of 2-benzylthiochroman-4-one 1,1-dioxide 7,[16] accompanied by bibenzyl. The structure of 7 has been verified from spectral data and by its unambiguous synthesis in three steps from thiochroman-4-one.

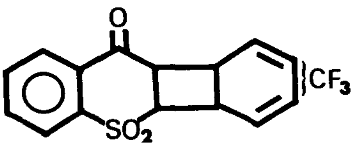
We have also examined the behavior of thiochromone (I.P.=8.68)[14] and the analogous sulfoxide[22] (I.P.=9.24)[14] on irradiation in benzene, for comparison with that of 1. In neither case was any photoadduct observed, although some photodimer (12%) was obtained from the unsaturated sulfide, while deoxygenation[23] of the unsaturated sulfoxide led to the sulfide (21%) as the sole product. In both cases, more than 50% of the starting material was recovered. These results are not unexpected in the light of the above discussion and, furthermore, we have established[14] that the lowest excited singlet (or triplet) state for the sulfide and sulfoxide cases is π,π^* in nature, whereas that for the sulfone 1 is n,π^*. On this basis the apparent inconsistency in the photochemical behavior of these three related compounds is more easily understood.



7



8a X=Cl
8b, X=CF3



9

References and Notes

1. H.J.F. Angus and D. Bryce-Smith, Proc. Chem. Soc. 326 (1959).
2. R.J. Atkins, G.I. Fray, M.G.B.Drew, A. Gilbert and G.N. Taylor, Tetrahedron Lett. 2945 (1978).
3. T. Matsuo and S. Mihara, Bull. Chem. Soc. Japan 50, 1797 (1977).
4. H.-G. Heine and W. Hartmann, Angew. Chem. Internat. Edit. 14, 698 (1975).
5. J.C. Berridge, D. Bryce-Smith, A. Gilbert and T.S. Cantrell, J.C.S. Chem. Commun. 611 (1975).
6. D. Bryce-Smith and A. Gilbert, Tetrahedron 33, 2459 (1977).
7. J.D. Coyle, Chem. Soc. Rev. 3, 329 (1974)
8. D. Bryce-Smith, Pure App. Chem. 34, 193 (1973).
9. M.F. Mirbach, M.J. Mirbach and A. Saus, Tetrahedron Lett. 959 (1977).
10. R.J. Atkins, G.I. Fray, A. Gilbert and M.W. bin Samsudin, Tetrahedron Lett. 3597 (1977).
11. W. Hartmann, H.-G. Heine and L. Schrader, Tetrahedron Lett. 3101 (1974).
12. D. Bryce-Smith, W.M. Dadson, A. Gilbert, B.H. Orger and H.M. Tyrell, Tetrahedron Lett. 1093 (1978), and references therein.
13. D. Bryce-Smith, A. Gilbert, B.H. Orger and H.M. Tyrrell, J.C.S. Chem. Commun. 334 (1974).
14. R.O. Loutfy, I.W.J. Still, M. Thompson and T.S. Leong, Can. J. Chem., in press.
15. All irradiations were conducted in Pyrex, using a 115 watt medium pressure Hg arc, for the same length of time (13 h), at concentrations of 1 of approximately 0.6% (w/v).
16. Satisfactory elemental analyses were obtained for all new compounds reported.
17. The detailed structure, including the stereochemistry, of this adduct will be the subject of a forthcoming publication.
18. J.D. Morrison and A.J.C. Nicholson, J. Chem. Phys. 20, 1021 (1952).
19. This reaction appeared to be essentially complete after 4 h.
20. D. Bryce-Smith, R. Deshpande, A. Gilbert and J. Grzonka, J.C.S. Chem. Commun. 561 (1970).
21. J.A. Ors and R. Srinivasan, J. Org. Chem. 42, 1321 (1977).
22. I.W.J. Still, P.C. Arora and S.N. Sokolowsky, Org. Prep. Proced. Int. 7, 159 (1975).
23. I.W.J. Still, P.C. Arora, M.S. Chauhan, M.-H. Kwan and M.T. Thomas, Can. J. Chem. 54, 455 (1976).

(Received in USA 28 November 1978)