Tetrahedron Letters, Vol. 22, No. 13, pp 1183 - 1186
Printed in Great Britain
0040-4039/81/131183-04\$02.00/0

PHOTODIMERIZATION OF THIOCHROMONE IN AROMATIC SOLVENTS

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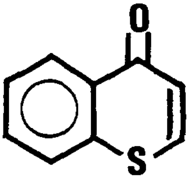
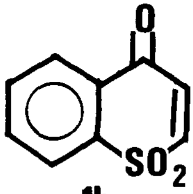
SUMMARY Photolysis of thiochromone **1a** in several aromatic solvents of widely differing ionization potentials leads to the formation of mixtures of all four possible cyclobutane photodimers. In sharp contrast to the photochemical behavior of the analogous sulfone, no evidence for {2+2}, or for substitutive, photoaddition reactions was found.

As part of our continuing interest in the photoaddition reactions of unsaturated compounds with aromatic substrates, we recently reported the results of the irradiation of thiochromone 1,1-dioxide **1b** in benzene and a number of simple non-substituted benzene derivatives. Although {2+2} *ortho*-photoaddition[1] was found to be the normal reaction pathway in aromatic solvents of high ionization potential (I.P.), the photolyses showed a strong dependence on the I.P. of the aromatic substrate, and other types of 1:1 photo-product, such as *meta*-adducts and products of "substitutive" addition of the Ar-H across the carbon-carbon double bond in **1b**, were also observed.[2,3] It was noted at that time[2] that thiochromone **1a** in contrast did not form photoadducts in benzene, but instead underwent photodimerization. The present study addresses the question of whether this striking difference in photochemical behavior between two closely related compounds is due to the difference in I.P. between **1a** and **1b** (8.68 and 9.93 eV, respectively), or to the fact that the lowest excited state for **1a** is π,π^* in nature, whereas that for **1b** has been established[4] as n,π^*.



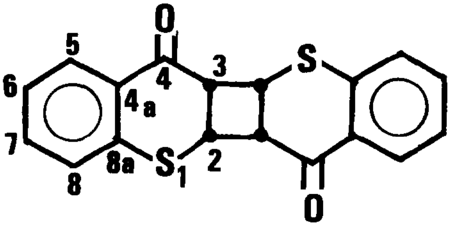
1a



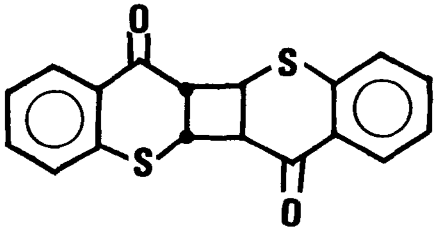
1b

The irradiation[5] of thiochromone in benzene and other aromatic solvents produces mixtures of the cyclobutane {2+2} photodimers **2**-**5** only, in varying amounts (Table 1). The structures of these photodimers have been established by spectroscopic data, some of the main features of which are reported in Table 2, and by elemental analysis.[6,7] All of the dimers show the expected molecular ion in the mass spectrum at m/e = 324. The ^{1}H-NMR data are in accord with the cyclobutane-type dimer formulation for **2**-**5**. ^{13}C-NMR data provide additional strong support for the gross structures of the photodimers.[8] The IR data (Table 2) show an interesting dichotomy in that the carbonyl stretching frequencies for dimers **2** and **3** appear at

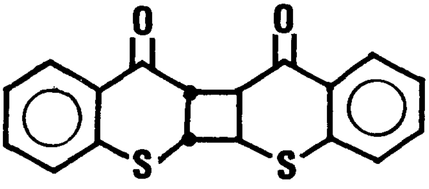
$\sim$1660 cm^{-1}, whereas those for **4** and **5** appear at $\sim$1700 cm^{-1}. We feel that the higher frequencies for **4** and **5** are probably attributable to dipole-dipole repulsion between the two carbonyl groups and that this fact, along with the supporting evidence of their much lower solubilities, higher melting points, lower R_F values on TLC (**2**>**3**>**5**>**4**>>**1**), and relatively higher yields in the more polar aromatic solvents (Table 1) are all consistent with the formulation of **4** and **5** as the more polar head-to-head photodimers and of **2** and **3** as the corresponding head-to-tail pair. Somewhat more tentatively, the *syn* and *anti* relationships, based on the available evidence, are also assigned, as shown in **2**-**5**.[10]



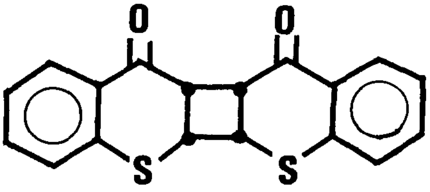
2 (H/T, syn)



3 (H/T, anti)



4 (H/H, anti)



5 (H/H, syn)

$C_6H_5N(CH_3)CH_2CH_2N(CH_3)C_6H_5$

6

The aromatic substrates in Table 1 are listed in descending order of I.P. but no simple correlations emerge between I.P. and the distribution of the photodimers **2**-**5**. Other features of the results in Table 1 merit comment. The relatively efficient recovery of starting material from the acetophenone reaction and the low yields of dimers obtained appear to indicate, in an interesting parallel with the results for **1b**,[2] that photodimerization proceeds *via the singlet state* of **1a**. The irradiation of **1a** in N,N-dimethylaniline gave a 15% yield of the formal (amine) "dehydro-dimer" **6**. It seems likely that in this case electron transfer occurs from the electron-rich arene to thiochromone. Subsequent deprotonation and dimerization of the N-methyl-N-phenylaminomethyl radical, as observed earlier in the γ-radiolysis of

TABLE 1 Results of Photolysis of 1a in Aromatic Solvents.

Arene	(Vertical) I.P. (eV)[a]	Dielectric constant(ε)[b]	Rec. 1a (%)[c]	Photodimers (%)[c]			
				2	3	4	5
1,3-di$(CF_3)C_6H_4$	-	-	36	3	11	33	0
C_6H_5CN	10.02	25.20	29	5	10	24	8
$C_6H_5CF_3$	9.90	9.18[d]	38	5	7	13	5
C_6H_6	9.40	2.28	80	0	0	5	0
$C_6H_5COCH_3$	9.27[e]	17.39	69	0	3	4	4
$C_6H_5CH_3$	9.13	2.38	33	20	5	41	0
$C_6H_5OCH_3$	8.54	4.33	26	8	25	27	0
$C_6H_5N(CH_3)_2$	7.51	4.90[d]	0[f]	0	0	0	0[f]
CH_2Cl_2	11.33[g]	9.08	12	5	23	10	33

[a] Values quoted from A.D. Baker, D.P. May and D.W. Turner, J. Chem. Soc. (B) 22 (1968), unless otherwise stated.

[b] Values, at 20-25°C, quoted from R.L. Schneider, Eastman Organic Chem. Bull. 47 (1), 1 (1975).

[c] These figures represent isolated yields of pure compound in each case.

[d] A.J. Gordon and R.A. Ford, The Chemist's Companion, John Wiley and Sons, New York, N.Y., 1972, p. 2.

[e] H.W. Gibson, Can. J. Chem. 55, 2637 (1977).

[f] A complex mixture of products resulted, from which N,N'-dimethyl-N,N'-diphenyl-1,2-diaminoethane, 6, was isolated in 15% yield; m.p. 44-45°C (hexane), lit.[9] m.p. 47-48°C.

[g] M.J.S. Dewar and S.D. Worley, J. Chem. Phys. 50, 654 (1969).

N,N-dimethylaniline,[11] affords 6. Although the formation of a "dihydro dimer" of 1a would also be expected from this mechanism, no such compound could be isolated from the very complex reaction mixture obtained, possibly due to further photochemical reaction of such a species. The results of the irradiation of 1a in dichloromethane are also shown in Table 1 for comparison. The rather high yield of the normally disfavored H/H *syn* isomer, 5 in this experiment is remarkable. Although it seems likely that an interesting solvent effect is responsible for this result, we can at present offer no reasonable explanation.

The results of this study show that the differences in the photochemical behavior of 1a and 1b towards simple aromatic substrates appear to be attributable more to the differing nature of their lowest excited states (π,π* vs. n,π*) than to the difference in their I.P. values. Other factors, however, such as the I.P. of the aromatic substrate and the dielectric constant of the medium, may also be responsible for interesting variations in the pattern of photochemical behavior.

TABLE 2 Properties of photodimers 2-5.

Dimer	M.p. (°C)	IR [a]	^{1}H-NMR [b,c]	UV [d]
		$\nu_{C=O}$, cm^{-1}	δ	λ_{max},nm(log ε)
2	138-139	1661	3.63(2H,dd,J=8Hz,6Hz) 4.43(2H,dd,J=8Hz,6Hz) 6.98-7.58(6H); 7.73-8.07(2H)	243.5 (4.65); 348 (3.51)
3	180-182	1660	3.60-3.93(2H); 4.07-4.43(2H) 7.07-7.63(6H); 7.97-8.20(2H)	245 (4.59); 337 (3.69)
4	250-1	1700	3.77-4.00(2H); 4.40-4.63(2H) 7.00-7.33(6H); 7.80-8.03(2H)	239.5 (4.54); 335 (3.78)
5	245-6	1701	3.71-4.63(4H); 7.20-7.43(6H); 7.87-8.20(2H)	240 (4.40); 332.5 (3.82)

[a] In $CHCl_3$.

[b] In $CHCl_3$-d_1.

[c] All signals were multiplets, unless stated otherwise.

[d] In methanol.

References and Notes

1. We have adopted the less confusing system of designating photoaddition to benzene as *ortho-*, *meta-*, or *para-* in place of the former, 1,2-, 1,3-, and 1,4-notations; see also D. Bryce-Smith, W.M. Dadson, A. Gilbert, B.H. Orger and H.M. Tyrrell, Tetrahedron Lett. 1093 (1978).
2. I.W.J. Still and T.S. Leong, Tetrahedron Lett. 1097 (1979).
3. I.W.J. Still and T.S. Leong, unpublished results from these laboratories.
4. R.O. Loutfy, I.W.J. Still, M. Thompson and T.S. Leong, Can. J. Chem. 57, 638 (1979).
5. All irradiations were conducted in Pyrex, using a 115-watt, medium pressure Hg arc, for 13h at concentrations of ~0.005 molar.
6. Elemental analysis data consistent with the formula $C_{18}H_{12}O_2S_2$ were obtained within the following limits; C±0.25; H±0.06; S±0.28%.
7. Elemental analyses were obtained by the Scandinavian Microanalytical Laboratory, Box 25, DK-2730 Herlev, Denmark.
8. ^{13}C-NMR ($CHCl_3$-d_1):2, δ192.6(C-4), 138.6(C-8a), 133.7(C-7), 129.8(C-4a), 128.9(C-5), 128.0(C-8), 125.8(C-6), 50.3(C-3), 41.1(C-2).
   3, δ192.7(C-4), 137.9(C-8a), 133.9(C-7), 130.1(C-4a), 129.7(C-5), 128.5(C-8), 126.0(C-6), 49.5(C-3), 43.5(C-2).
   4, δ(DMSO-d_6), 190.9(C-4), 139.8(C-8a), 133.8(C-7), 130.1(C-4a), 128.3(C-5), 127.4(C-8), 125.7(C-6), 47.3(C-3), 44.7(C-2).
   5 proved too insoluble to obtain a good ^{13}C-NMR spectrum.
9. E. Fröhlich, Ber. 40, 762 (1907).
10. The lack of stereospecificity observed here has been noted previously in certain cases involving {2+2} photoadduct formation: R.J. Atkins, G.I. Fray, A. Gilbert, M.W. bin Samsudin, A.J.K. Steward, and G.N. Taylor, J.C.S. Perkin I 3196 (1979).
11. J.M. Fayadh and G.A. Swan, J. Chem. Soc. (C) 1775 (1969).

(Received in USA 28 July 1980)