

## Synthesis and Photorearrangement of 9-Thiabicyclo[3,3,1]nona-3,7-diene-2,6-dione

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9-Thiabicyclo[3,3,1]nona-3,7-diene-2,6-dione (8) has been synthesised. The u.v. spectrum shows anomalous features attributable to intramolecular interactions. The photoelectron spectrum suggests considerable ground state interactions in addition to those in the excited state. Photorearrangement of the dione (8) gives 2-thiabicyclo[3,3,1]nona-3,7-diene-6,9-dione (12).

THE importance of intramolecular charge transfer in controlling the course of photochemical reactions has been emphasised by the recent work of Padwa and Battisti.<sup>1</sup> Irradiation of the ketone (1a) in methanol gave the ester (2a), but irradiation of the ketone (1b) gave not only the ester (2b) but also the ketone (3). The

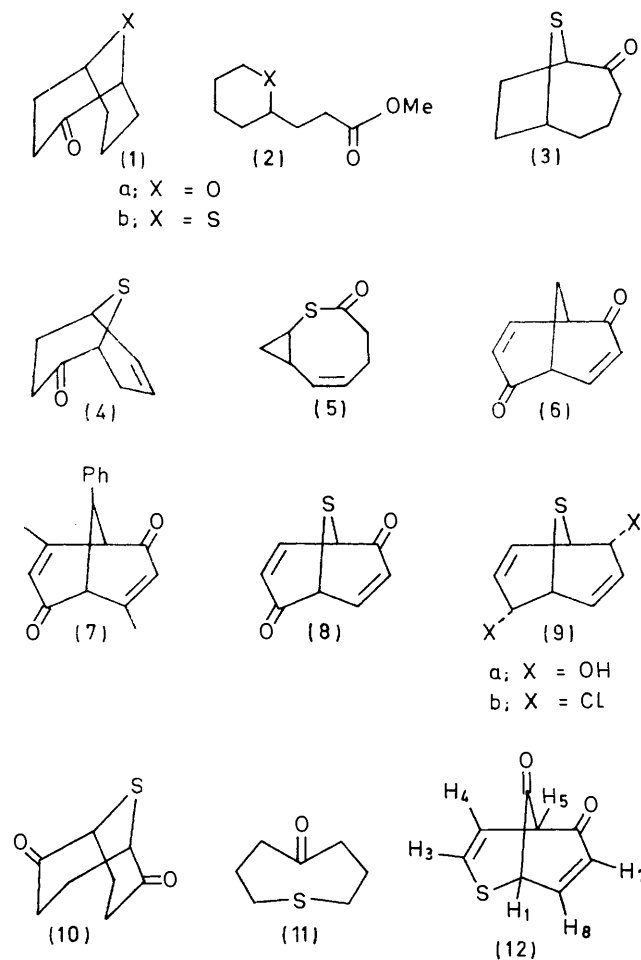
Following our study<sup>2</sup> of the photoreactivity of bicyclo[3,3,1]nona-3,7-diene-2,6-diones in which [1,5] and [1,2] sigmatropic rearrangements were observed with the dione (6) but [1,3] and [1,2] sigmatropic rearrangements with the dione (7), we have examined the photochemistry of the dione (8). The existence of interactions of the sulphur atom with the unsaturated chromophores was likely, but their influence on the course of any photochemical reaction was not clear. We report the synthesis of the dione (8), spectroscopic results which show that an interaction between sulphur and the conjugated chromophores exists not only in the excited state but also in the ground state, and the photorearrangement of the dione (8).

Oxidation of the diol (9a)<sup>3</sup> with manganese dioxide gave 9-thiabicyclo[3,3,1]nona-3,7-diene-2,6-dione (8) in 92% yield. Structure (8) was confirmed by i.r. and n.m.r.

U.v. data of bicyclo[3,3,1]nonadienediones and related compounds, and vertical ionisation potentials

Compound	$\lambda_{\max.}/\text{nm}$	$\epsilon_{\max.}$	I.P./eV
(8) <sup>a</sup>	239	6910	8.5, 9.4, 10.5
	267	2775	
	311	164	
	340	166	
	359	337	
	378	470	
	414	244	
	240	6820	
	262	3380	
	310	273	
(6) <sup>b</sup>	336	240	
	350	371	
	368	458	
(7) <sup>b</sup>	413	344	
	229 <sup>d</sup>	8000	
(10)	349	560	8.73, 9.6, 10.2
	237 <sup>d</sup>	15,700	
	348	758	
	234	468	
	249	340	
	308	252	
	317	233	
	234 <sup>c</sup>	564	
	250	379	
	306	379	

<sup>a</sup> In hexane. <sup>b</sup> In EtOH. <sup>c</sup> In 95% EtOH. <sup>d</sup> From ref. 6.



formation of the ketone (3) was considered<sup>1</sup> to proceed *via* a charge-transfer excited state. Similarly the rearrangement of the unsaturated ketone (4) to the thiolactone (5) was explained by a zwitterionic excited state. In such a charge transfer the sulphur atom can participate more easily than the oxygen atom, and in these examples this is shown both by the u.v. spectra and by the course of the photochemical reactions.

<sup>1</sup> A. Padwa and A. Battisti, *J. Amer. Chem. Soc.*, 1971, **93**, 1303.

spectra, and the mass spectrum, which showed prominent ions at  $m/e$  166 (75%,  $M^+$ ), 138 (base peak,  $M - \text{CO}$ ), and 110 (84%,  $M - 2\text{CO}$ ). The u.v. spectrum is reported in the Table together with the spectra of the diones (6), (7), and (10). By comparison with the other ketones a marked red shift in the  $n \rightarrow \pi^*$  transition of the dione (8) is observed. Such a shift has three possible explanations: (a) a change in energy of the

<sup>2</sup> P. A. Knott and J. M. Mellor, *Tetrahedron Letters*, 1970, 1829.

<sup>3</sup> F. Lautenschlaeger, *J. Org. Chem.*, 1968, **33**, 2627.

$n_{CO}$  orbital, *i.e.* a change of energy of the ground state; (b) a change in energy of the  $\pi_{CO^*}$  orbital, *i.e.* a change of energy of the excited state; or (c) a change in energy of both the  $n_{CO}$  and the  $\pi_{CO^*}$  orbital such that the  $n \rightarrow \pi^*$  transition requires less energy. U.v. spectroscopy alone does not discriminate between the three possibilities. I.r. spectroscopy, which might be expected to reveal ground state interactions as in the case of the transannular interaction in the thia-ketone (11),<sup>4</sup> shows no abnormality ( $\nu_{max}$  1680  $cm^{-1}$ ). However photoelectron spectroscopy does discriminate between the possibilities. In the dione (8) the first ionisation potential (I.P.) associated with the  $n_{CO}$  orbital is depressed and that associated with an  $n_s$  orbital is elevated. These results will be discussed more fully elsewhere but they establish an interaction in the ground state. The red shift observed in the  $n \rightarrow \pi^*$  transition of (8) and of related compounds is not simply due to changes of energy of the excited state. The interaction in the ground state implies effective charge transfer from the sulphur atom to the unsaturated chromophores.

The dione (8) is very photosensitive and photorearrangement is rapid. Analysis of the crude product indicated the formation of a single photoproduct in addition to polymeric material. The photoproduct was purified by column chromatography to give a yellow crystalline solid, which decomposed slowly in air, and was shown by mass spectrometry to be isomeric with the dione (8). The i.r. spectrum showed two carbonyl groups ( $\nu_{max}$  1743 and 1693  $cm^{-1}$ ). The n.m.r. spectrum showed four low-field signals, at  $\tau$  2.90, 3.45, 3.78, and 4.39 and a complex signal at 6.11. Decoupling experiments showed that the signals at  $\tau$  2.90 and 3.45 were coupled ( $J$  10.0 Hz), as were those at 3.78 and 4.39 ( $J$  9.5 Hz). The signals at  $\tau$  2.90 and 4.39 were both coupled to that at 6.11. Only structure (12) accommodates these data (see Experimental section). The observed coupling constants are in agreement with those found in other bicyclo[3,3,1]nona-3,7-diene-2,6-diones.<sup>2,5</sup>

In the course of the photorearrangement, polymeric material was formed, but careful chromatography showed that the dione (12) was the only monomeric photoproduct. The dione (12) is a product of a [1,3] shift, probably proceeding by a concerted sigmatropic rearrangement. The rearrangement is not markedly influenced by solvent, and preliminary studies do not conflict with the view that the photoreaction proceeds *via* the singlet state. The contrast with the photorearrangement of the dione (6) is marked: no products of [1,2] or [1,5] rearrangement are observed. This might be attributed to the instability of the products of such rearrangements, hence leading to polymer, or to the influence of the sulphur atom which controls the direction of reaction in the dione (8). We prefer the latter explanation.

## EXPERIMENTAL

I.r. spectra were measured for solutions in chloroform with a Unicam SP 200 spectrophotometer. N.m.r. spectra were measured for solutions in deuteriochloroform with a Varian HA 100 spectrometer. U.v. spectra were measured for ethanolic solutions unless otherwise stated with a Unicam SP 800 spectrophotometer. Mass spectra were measured with an A.E.I. MS12 spectrometer.

**Materials.**— 2,6-Dichloro-9-thiabicyclo[3,3,1]nona-3,7-diene (9b), m.p. 101–102° (lit.,<sup>3</sup> 101–102°), was prepared as previously described in 18% yield.<sup>3</sup> On exposure to air the white crystalline solid rapidly decomposed. 9-Thiabicyclo[3,3,1]nona-3,7-diene-2,6-diol (9a) was prepared as described previously<sup>3</sup> [by hydrolysis of the dichloride (9b)], m.p. 177.5–178° (lit.,<sup>3</sup> 176–179°), yield 45%.

9-Thiabicyclo[3,3,1]nona-3,7-diene-2,6-dione (8).—The diol (9a) (2.72 g) was dissolved in dry acetone (150 ml) with stirring and freshly prepared active manganese dioxide (15 g) was added. The suspension was stirred in the dark for 72 h, filtered, and evaporated to give the crude dione (8). Purification by chromatography on silica gave feathery yellow crystals of 9-thiabicyclo[3,3,1]nona-3,7-diene-2,6-dione (8) (2.43 g, 92%), m.p. 98.5–99° [from benzene–light petroleum (b.p. 40–60°)] (Found: C, 57.8; H, 3.85; S, 19.6.  $C_8H_6O_2S$  requires C, 57.8; H, 3.65; S, 19.3%).  $\nu_{max}$  3030, 1680, 1622, 1375, 1269, 1246, 1138, 1090, 1015, 980, 970, 962, and 825  $cm^{-1}$ ,  $m/e$  166 ( $M^+$ ), 138 ( $M - 28$ ), and 110 ( $M - 56$ ),  $\tau$  2.92 (2H, q,  $J$  10.7 and 6.8 Hz), 4.15 (2H, d,  $J$  10.7 Hz), and 6.24 (2H, d,  $J$  6.8 Hz).

2-Thiabicyclo[3,3,1]nona-3,7-diene-6,9-dione (12).—The dione (8) (400 mg) was dissolved in dry benzene (200 ml) and was irradiated for 40 min under nitrogen through quartz with a 115 W medium-pressure lamp. Removal of the solvent under reduced pressure gave a yellow-brown solid. Chromatography on silica gel with ether–light petroleum (b.p. 40–60°) as eluant gave, in order, unchanged starting material (166 mg) and a pale yellow photoproduct (96 mg). Elution with chloroform afforded polymeric material. Crystallisation of the photoproduct from benzene–light petroleum (b.p. 40–60°) gave 2-thiabicyclo[3,3,1]nona-3,7-diene-6,9-dione (12), m.p. 87–87.5°,  $\nu_{max}$  3200, 2770, 1743, 1693, 1640, 1613, 1595, 1370, 1360, 1320, 1015, 952, and 904  $cm^{-1}$ ,  $m/e$  166 ( $M^+$ ), 138 ( $M - 28$ ), and 110 ( $M - 56$ ),  $\tau$  2.90 (1H, q,  $J$  10.0 and 5.5 Hz, 8-H), 3.45 (1H, d,  $J$  10.0 Hz, 7-H), 3.78 (1H, d,  $J$  9.5 Hz, 3-H), 4.39 (1H, q,  $J$  9.5 and 6.4 Hz, 4-H), and 6.11 (2H, complex, 1- and 5-H). Analysis of the photoproduct (12) by g.l.c. (10% Apiezon L on Chromosorb W at 180°) showed a single peak. Analysis by t.l.c. with several different solvents showed a single spot.

The photoreaction was studied in various solvents in both quartz and Pyrex systems, with the following results [yields of dione (12), based on recovered starting material, in parentheses]: in benzene through quartz for 40 min (41%); in benzene through Pyrex for 45 min (41%); in methanol through Pyrex for 30 min (56%); in ether through Pyrex for 45 min (56%); and in ether with added acetophenone through Pyrex for 45 min (36%).

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<sup>5</sup> P. A. Knott and J. M. Mellor, unpublished results.

<sup>6</sup> P. A. Knott and J. M. Mellor, *J. Chem. Soc. (C)*, 1971, 670.

<sup>4</sup> N. J. Leonard, T. W. Milligan, and T. L. Brown, *J. Amer. Chem. Soc.*, 1960, **82**, 4075.