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ELUCIDATION OF THERMAL REACTIONS BY VARIABLE TEMPERATURE PHOTOELECTRON SPECTRAL DETECTION OF REACTIVE INTERMEDIATES. THE UV PHOTOELECTRON SPECTRA OF TRANSIENT FULVENEKETENE, FULVENETHIOKETENE, A KETOKETENE, AND THIOBENZPROPIOLACTONE [1]

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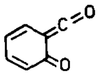
Ketoketene 1, thiobenzpropiolactone 2, ketene 3 and thioketene 4 have been of interest for some time as intermediates in photochemical and thermal organic reactions.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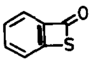
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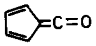
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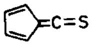
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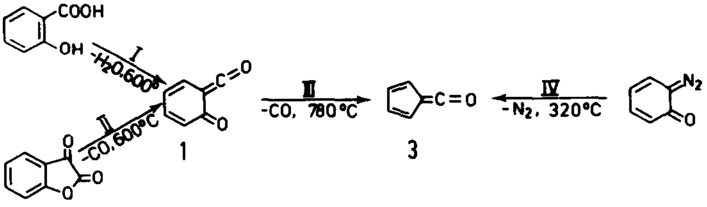
Ketoketene 1 [2-4] and thiobenzpropiolactone 2 [5] were photochemically generated in a solid matrix. Ketene 3 was recorded by pyrolysis mass spectrometry [6] and thioketene 4 both made photochemically in an argon matrix [7], and thermally and identified by trapping experiments [8]. We wish now to record the thermal generation of all four intermediates in variable temperature photoelectron spectral (VTPES) [9] studies of appropriate organic reactions.

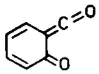
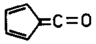
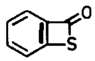
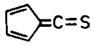
The chemical reactions carried out in the photoelectron spectrometer are summarized in schemes 1 and 2 below.



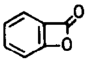
Scheme 1

The intermediates 1 to 4 are identified, firstly by the clearcut observation of the right byproducts (H_2O, CO and N_2, respectively) for each reaction in the product spectra, secondly by the entire agreement of the respective spectra of these intermediates when generated in different reactions (e.g.1 from reactions I and II of scheme 1), thirdly by the interpretation of the changes of spectra when going from HeI to HeII excitation, and finally by the good agreement between the calculated vertical ionization potentials (VIP's) and measured VIP's (Table 1).

Table 1 Measured and Calculated Vertical Ionization Potentials (in eV).

Molecule	Measured	Calculated	Assignment	Band
 1	8.43	8.26	A''(π)	1
	9.38	9.18	A'(n)	2
	10.31	10.35	A''(π)	3
	11.56	11.85	A''(π)	4
 3	8.56	8.57	A_2(π)	1
	9.06	8.70	B_1(π)	2
 2	8.56	8.72	A''(π)	1
	9.94	9.43	A'(σ)	2
		9.96	A''(π)	3
	10.87	11.12	A''(π)	4
	11.76	11.39	A'(σ)	5
 4	8.52	8.25	B_1(π)	1
	8.67	8.66	A_2(π)	2
	11.14	10.91	B_2(π)	3

The theoretical data are based on MNDO [10] optimized structural data and large configuration interaction (PERTCI [11]) calculations using CNDO/S [12] wavefunctions.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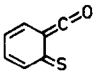
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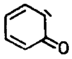
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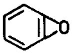
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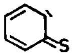
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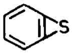
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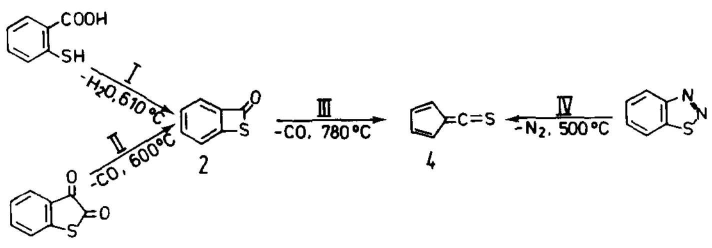

Scheme 2

Reactions I and III of scheme 1 have not been investigated before, just as reactions I to III of scheme 2. Reaction II of scheme 1 was only known to occur photochemically. All the reactions are complete at the temperatures indicated, with the exception of reaction III of scheme 2. In particular, the conversion of intermediates 1 and 2 into 3 and 4, respectively, is novel.

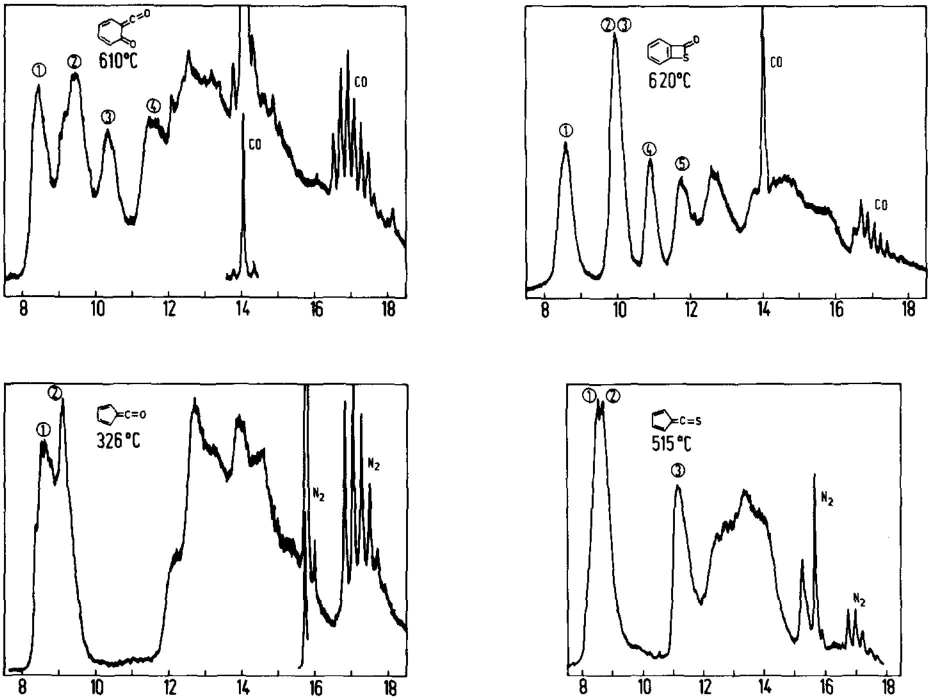

Figure 1: He(I) photoelectron spectra of ketoketene 1, ketene 3, thiobenzpropiolactone 2, and thioketene 4 as obtained in reactions II and IV of schemes 1 and 2, respectively. The ionization potentials (in the abscissa) are in eV.

Possible isomers of 1 (the benzpropiolactone 5), of 2 (the thioketoketene 6), of 3 (the ketocarbene 7 and the benzooxirene 8), and of 4 (the thioketocarbene 9 and the benzothiirene 10) are excluded on the base of the disagreement of their calculated (PERTCI) photoelectron spectra and the observed intermediate spectra (Figure 1).

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