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revealed the existence of the equilibrium mixture consisting of 1 and 2 in a ratio of 14:86. The same equilibrium mixture was also obtained starting from 2 under the same reaction conditions.

Reaction of the Endo Dibromide 1 with Bromine in the Presence of Radical Inhibitors. To a solution of 40 mg (0.12 mmol) of endo dibromide 1 in 0.5 mL of $CDCl_3$ in a NMR tube was added 16 mg of 2,4,6-tri-*tert*-butylphenol (0.06 mmol) (or 2,4,6-tri-*tert*-butylnitrosobenzene) and followed by addition of 20 mg (0.12 mmol) of bromine. After 10 h no configuration isomerization was observed.

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Reactivity of [(Alkylthio)methylene]ketenes in the Gas Phase and Photoelectron Spectra of Thiophen-3(2*H*)-ones[1]

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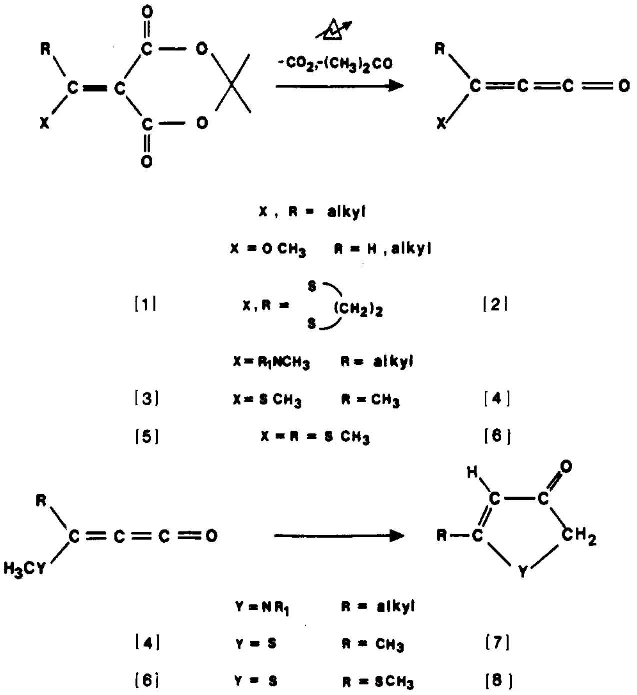
Flash vacuum pyrolysis of substituted Meldrum's acid derivatives is known to give methyleneketenes (alkyl[2] and alkoxy[3,4] compounds) (Scheme I). However, alkylthio[3,5] and alkylamino[6] derivatives further react to the corresponding five-membered heterocycles, and thiophen-3-(2*H*)-ones or pyrrol-3(2*H*)-ones are generally characterized in solution as the reaction products. The only exception concerns the sterically strained bis(alkylthio) Meldrum's acid derivative 1 [isopropylidene (1,3-dithiolan-2-ylidene)malonate], for which the gas-phase characterization of [bis(alkylthio)methylene]ketene 2 could be performed.[4]

As photoelectron spectroscopy (PES) has proved to be a highly efficient tool for the gas-phase characterization of elusive compounds,[7] the PES detection of other [(alkylthio)methylene]ketenes has been attempted and their gas-phase reactivity is described.

Scheme I



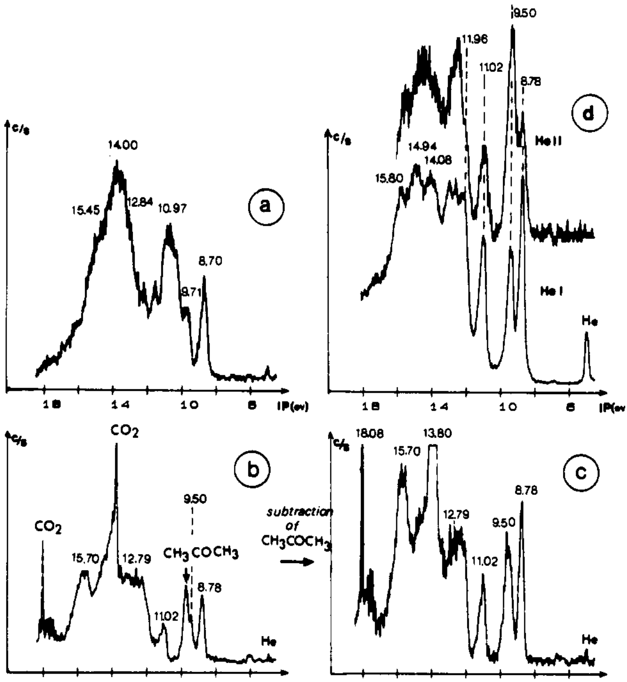


Figure 1. Photoelectron spectra of (a) isopropylidene [1-(methylthio)ethylidene]malonate (3), (b) the pyrolysis of 3 at 893 K, (c) the difference obtained by digitally subtracting acetone from spectrum b, and (d) pure 5-methylthiophen-3(2*H*)-one (7).

The flash vacuum pyrolysis of the alkylthio Meldrum's acid derivatives is monitored "in situ" by photoelectron spectroscopy: the compounds are pyrolyzed in the ionization chamber of the spectrometer (short path pyrolysis: SPP). See ref 8 for a detailed description of the apparatus.

When submitted to SPP, alkylthio compounds 3 and 5 begin to split off acetone and CO_2 at 673 K and the re-

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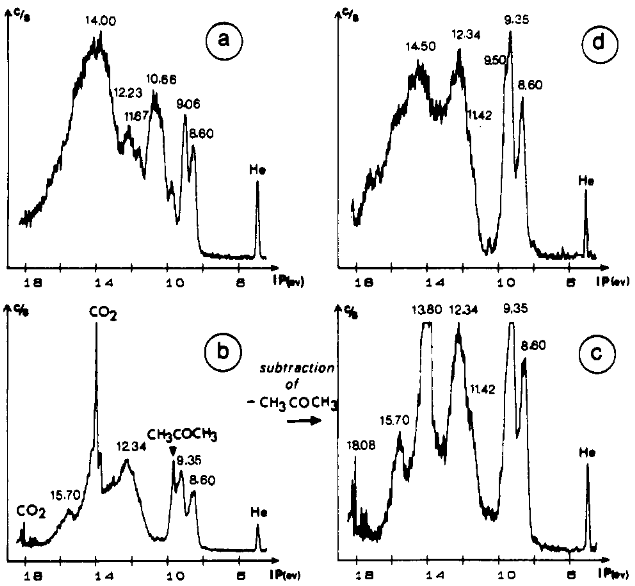


Figure 2. Photoelectron spectra of (a) isopropylidene [bis(methylthio)methylene]malonate (**5**), (b) the pyrolysis of **5** at 793 K, (c) the difference obtained by digitally subtracting acetone from spectrum b, and (d) pure 5-(methylthio)thiophen-3(2*H*)-one (**8**).

action is led to completion at 893 K for **3** and 793 K for **5** (disappearance of the bands corresponding to the starting compounds in Figures 1b and 2b). By digitally subtraction of acetone from these spectra, the difference spectra displayed in Figures 1c and 2c are obtained. The thiophen-3(2*H*)-ones **7** and **8** were independently prepared under the previously reported pyrolysis conditions (843 K for **3** and 813 K for **5**) and their structures confirmed by NMR analysis.[3] The PES spectra of **7** and **8** are presented in Figures 1d and 2d, respectively, and it is observed that they are identical with the difference spectra recorded under SPP conditions (Figures 1c and 2c) in spite of the presence of CO_2 in these latter. It is thus concluded that, even under SPP conditions, the methyleneketenes **4** and **6** are not observed and give rise to the heterocycles **7** and **8**: between 673 and 793 or 893 K, the evolution of the SPP photoelectron spectra is described as the disappearance of the starting compounds with simultaneous formation of the thiophen-3(2*H*)-ones, and the possible presence of the methyleneketenes **4** and **6** is not straightforward.

We have checked that in the gas phase no keto–enol equilibrium was observed (no evolution of the photoelectron spectra even at high temperature). These results indicate that a sole isomer is present in the gas phase.

The identification of this isomer could be inferred from the experimental IPs of the species under study. However, a comparison between calculated and observed IPs does not unambiguously solve this question (Figure 4). Actually, different polarization effects (not included in Koopmans's approximation) are expected for each isomer. Moreover, some discrepancies have been observed for molecules bearing third-row atoms.[9,10]

Thus our analysis relies on the evolution of the spectra with excitation energy 21.21 eV (He I) and 40.81 eV (He II) combined with the localization properties of the wave function inferred from MNDO calculations.[11]

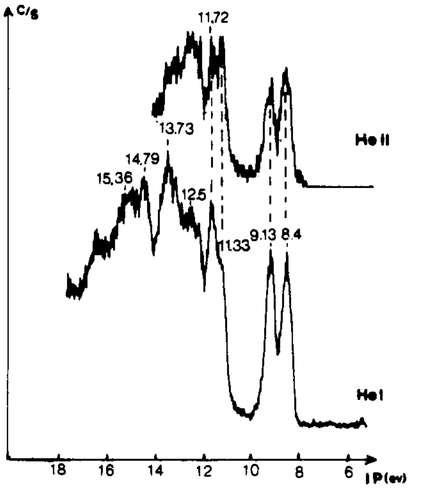
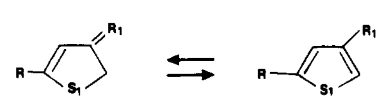


Figure 3. Photoelectron spectrum of 3-methoxythiophene (**13**) (prepared by Williamson etherification of 3-bromothiophene under Cu oxides catalysis[16]).



[7]	$R_1=O$	$R = CH_3$	$R_1=OH$	[10]
[8]	$R_1=O$	$R = SCH_3$	$R_1=OH$	[11]
[9]	$R_1=O$	$R = H$	$R_1=OH$	[12]
		$R = H$	$R_1=OCH_3$	[13]

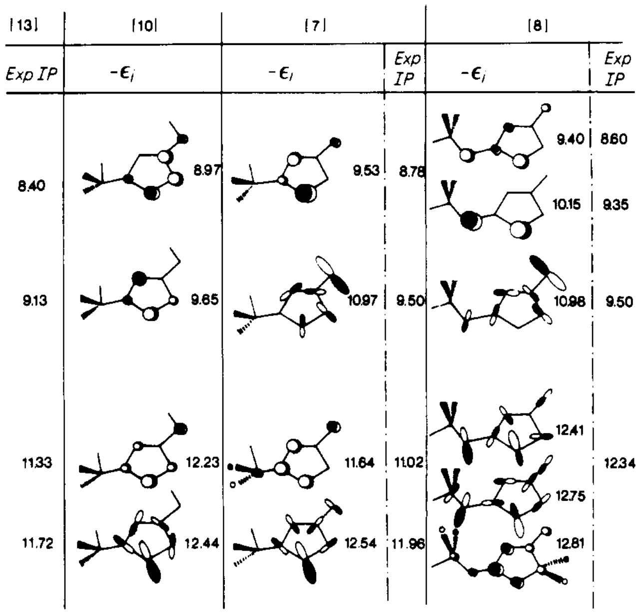


Figure 4. MNDO orbital localizations and eigenvalues of 5-methyl- and 5-(methylthio)thiophen-3(2*H*)-ones (**7** and **8**) and of 5-methyl-3-hydroxythiophene (**10**) with the experimental IP observed for **7**, **8**, and 3-methoxythiophene (**13**).

As a matter of fact, it has been demonstrated that relative band intensities of MOs mainly localized on 3s and 3p AOs of sulfur diminish significantly in the transition from the He I to the He II spectrum. On the contrary, the relative band intensities of MOs with high coefficients at oxygen increase on going from He I to He II spectra.[11]

It follows from the localization properties of the wave functions computed for compounds **7** (keto form) and **10** (enol form) that a different behavior is expected for **7** and **10** on going from He I to He II excitation energy. For the enol compound **10**, the three first π orbitals are described as mixtures of sulfur, oxygen, and carbon AOs (first and

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third ones) or of sulfur and carbon AOs (second one). It is thus expected that for the first and third MOs the relative band intensities will not vary to a large extent on going from HeI to HeII excitation energy, as the decrease due to the contribution of sulfur AOs should be moderated by the increase arising from oxygen AOs. For the band associated with the ionization of the second MO, the important contribution of carbon AOs should temper the expected decrease arising from the participation of the sulfur AO.

These assumptions are in complete agreement with the experimental He I and He II spectra of the model methoxy compound **13** featuring the enol form: for this product, as expected, no dramatic change of the relative band intensities is observed on going from He I to He II excitation energy, except a very slight decrease of the fourth one at 11.72 eV (ionization of a sulfur lone pair) (Figure 3).

On the contrary, for the keto isomer **7**, the decrease of the first band intensity and the invariance of the third one (both associated with π ionizations) may be anticipated. For the second band, attributed to the ionization of the oxygen lone pair, an important intensity increase is forecast. The relative intensity changes observed for the studied compound on going from He I to He II excitation energy are different from the evolution demonstrated for **13** and support our latter expectations in favor of the keto compound **7** (Figure 1): a strong decrease of the first, 8.78-eV band; a weaker decrease of the third, 11.02-eV band; a significant increase of the second, 9.50-eV band (the strong decrease of the fourth, 11.96-eV band, as for the model methoxy isomer **13**, arises from the important contribution of sulfur in a lone pair type MO).

We thus conclude the existence of the keto isomer **7** in the gas phase. The attribution of the spectrum of **8** (for which no He II spectrum could be recorded due to too weak intensity signals) follows from the description of the spectrum of **7** (Figure 2). The alkylthio substitution should bring about a new ionization associated with the antisymmetric combination of the sulfur lone pairs ($n_{S_1} - n_{S_2}$). In agreement with the stabilization expected from the carbonyl lone pair[12] on the experimental IPs (8.2 and 8.8 eV) reported for the 1,1-bis(methylthio)ethylene,[13] the bands associated with the ionizations of the symmetric ($n_{S_1} + n_{S_2}$) and antisymmetric ($n_{S_1} - n_{S_2}$) combinations are thus observed at 8.60 and 9.35 eV, respectively (the first one not very far from the corresponding one of **7** at 8.78 eV). On the other hand, the n_O lone pair ionization should be observed at the same energetic level in **7** and **8**: 9.50 eV. The greater intensity of the 9.35–9.50-eV band of **8** is then accounted for by the attribution of two ionizations arising from the ($n_{S_1} - n_{S_2}$) orbital and from the n_O orbital. Moreover, from the results on the 1,1-bis(methylthio)- and (methylthio)ethylene,[13] it may be anticipated that the ionization related to the ($\pi + n_{S_1} + n_{S_2}$) orbital will be found at a deeper energetic position than for **7** (11.02 eV): indeed for **8** this ionization is hidden in the broad band at 12.34 eV.

The observation of the sole keto isomers of these derivatives of thiophen-3(2*H*)-ones in the gas phase is to be related with the results of their keto–enol equilibrium in solution.

It has been shown that the parent thiophen-3(2*H*)-one (**9**) and its 2,5-dimethyl derivative existed in 75/25 and 90/10 keto/enol mixtures, respectively, in $CHCl_3$ solutions[5,14] and that the percentage of the enol form increased with solvent ability to form hydrogen bonds (100% enol form of **9** in DMSO[14]). On the contrary, compounds **7** and **8** were reported to exist only in the keto form in $CDCl_3$ solutions.[3] We have checked that, for these two latter compounds **7** and **8**, the keto–enol equilibrium was less shifted than for the other previously mentioned thiophen-3(2H)-ones: the keto/enol percentages were found to be 66/34 for **7** and 80/20 for **8** in CD_3COCD_3 and 34/66 and 30/70, respectively, in DMSO-d_6 from NMR spectra. The observation of the keto as the only tautomer for **7** and **8** in $CDCl_3$ bolsters the argument in favor of the identification of the gas-phase species as the keto tautomer since $CDCl_3$, of all the solvents mentioned, is the one most approximating the gas phase (i.e., most lacking in H-bonding ability). It could be pointed out at this stage that, in the MNDO approximation, neglecting correlation effects, the relative energies of the two keto or enol isomers are calculated to be very close (within 1 kcal·mol^{-1}).

In conclusion, compounds **7** and **8** are observed in the keto form both in the gas phase and in $CDCl_3$ solutions.[3] However, the exclusive formation of the cyclic thiophen-3(2*H*)-ones instead of the [(alkylthio)methylene]ketenes from the Meldrum's acid derivatives is a different result from that found in the case of the related methoxy compound: in this latter case, the (methoxymethylene)ketenes were characterized in the gas phase and there was no evidence of furan-3(2*H*)-one formation. Further investigations dealing with these different behaviors are in progress.

Experimental Section

Photoelectron spectra were recorded on an Helectros 0078 photoelectron spectrometer equipped with a 127° cylindrical analyzer and monitored by a microcomputer supplemented with a digital analog converter. The spectra are calibrated on the known ionizations of xenon (12.13 and 13.43 eV) and argon (15.76 and 15.93 eV). The IPs are accurate within 0.02 eV. The short path pyrolysis system has been described elsewhere.[8] The starting Meldrum's acids were synthesized according to the reported methods.[15] The preparations of the thiophen-3(2*H*)-ones[3,5] and 3-methoxythiophene[16] have been described.

Calculations were performed with the AMPAC program[17] on a Vax computer on fully optimized geometries.

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Simple and Convenient Synthesis of *tert*-Butyl Ethers of Fmoc-serine, Fmoc-threonine, and Fmoc-tyrosine

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The protection of the hydroxyl function of serine, threonine, and tyrosine as an acid-labile *tert*-butyl ether is a well-established strategy for the synthesis of polypeptides when using the base-labile 9-fluorenylmethoxycarbonyl (Fmoc) mode of protection for the α-amino

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