Acknowledgment. We wish to thank Dr. Edward Rosenberg for helpful discussions and suggestions.

Registry No.—II, 63059-14-3; II HCl, 51431-51-7; III, 30314-63-7; IV, 22817-10-3; V, 32250-84-3; VI, 63059-15-4; VII, 63059-16-5; 1-phenyl-1-(2-methoxyphenyl)ethene, 24892-80-6; 2-methoxybenzophenone, 2553-04-0.

References and Notes

(1) C. E. Spivak and F. L. Harris, *J. Org. Chem.*, **37**, 2494 (1972).
(2) (a) S. Winstein, *Experientia, Suppl. 2*, 153 (1955); (b) R. Heck, J. Corse, E. Grunwald, and S. Winstein, *J. Am. Chem. Soc.*, **79**, 3278 (1957).
(3) J. Blaake and G. B. Lorentzen, *Acta Chem. Scand., Ser. B*, **28**, 650 (1974).
(4) C. Bernardon and J. Bourdais, *Tetrahedron Lett.*, 4711 (1970).
(5) G. A. R. Kon and R. G. W. Spickett, *J. Chem. Soc.*, 2724 (1949).
(6) G. M. Loudon and D. S. Noyce, *J. Am. Chem. Soc.*, **91**, 1433 (1969).
(7) V. Seidlova, L. Novak, J. O. Jilek, J. Metys, and M. Protiva, *Collect. Czech. Chem. Commun.*, 299 (1971).
(8) H. Kauffmann, *Justus Liebigs Ann. Chem.*, **433**, 237 (1923).
(9) R. G. F. Giles and M. V. Sargent, *J. Chem. Soc., Perkin Trans. 1*, 2447 (1974).
(10) B. M. Benjamin and C. J. Collins, *J. Am. Chem. Soc.*, **78**, 4952 (1956).
(11) L. S. Ciereszko and J. G. Burr, Jr., *J. Am. Chem. Soc.*, **74**, 5431 (1952).
(12) B. M. Benjamin, P. Wilder, Jr., and C. J. Collins, *J. Am. Chem. Soc.*, **83**, 3654 (1961).
(13) V. F. Raaen and C. J. Collins, *J. Am. Chem. Soc.*, **80**, 1409 (1958).
(14) K. Matsumoto, R. Goto, A. Sera, and T. Asano, *Nippon Kagaku Zasshi*, **87**, 1076 (1966).
(15) R. Goto, K. Matsumoto, and A. Sera, *Nippon Kagaku Zasshi*, **87**, 93 (1966).
(16) K. Matsumoto, *Bull. Chem. Soc. Jpn.*, **41**, 1356 (1966).
(17) R. Stoermer and E. Friderici, *Ber.*, **41**, 324 (1908).
(18) R. M. Roberts and M. B. Abdel-Baset, *J. Org. Chem.*, **41**, 1698 (1976).
(19) H. Cassebaum and H. Hofferek, *Chem. Ber.*, **92**, 1643 (1959).

Mass Spectrometry of Alkenyl and Aryl Thiolacetates

Denis L. Foerst and John R. Grunwell*

Department of Chemistry, Miami University, Oxford, Ohio 45056

Received March 15, 1977

The mass spectra of alkenyl and aryl thiol acetates were studied in connection with our investigations of the photochemistry of these compounds.[1,2,3] The three important fragmentation mechanisms involve cleavage of the sulfur carbonyl carbon bond as shown by paths a, b, and c in Schemes I and II. Homolysis of this bond is also the primary photochemical reaction.

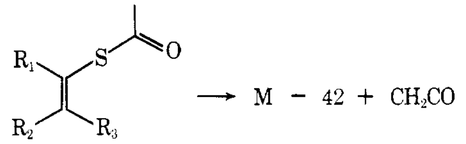
Path a, which involves the simultaneous dissociation of the sulfur–carbonyl carbon bond and the transfer to the sulfur fragment of the α-hydrogen atom, may occur by a four-centered mechanism to form ketene and the vinyl thiol radical cations or by a six-centered mechanism to form ketene and thioaldehyde radical cations (Scheme III).

For alkyl vinyl thioethers, the six-centered hydrogen-atom transfer is highly favored over the four-centered mechanism as ion cyclotron resonance spectroscopy has been used to show that deuterium is transferred from the β carbon of the alkyl side chain to the sulfur fragment to form thioaldehyde radical cations in preference to vinyl thiol radical cations by a 9:1 ratio.[4]

In the mass spectra of four saturated alkyl thioacetates, namely methyl, ethyl, propyl, and isobutyl thiolacetate, we observed no M − 42 ions. In contrast, the seven alkenyl thiolacetates which we studied formed the M − 42 ion in relative abundances ranging from 5 to 100% as shown in Table I.

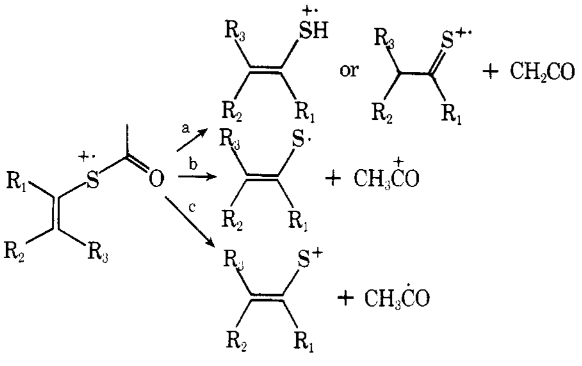
In saturated esters the six-centered hydrogen-atom transfer is structurally precluded, but the four-centered mechanism is possible. Thus, the absence of the M − 42 ions for the saturated alkyl thiolacetates coupled with the ICR work on alkyl vinyl thiol ethers indicates the six-centered mechanism is probably responsible for the formation of the M − 42 ions from the alkenyl thiolacetates.

Table I

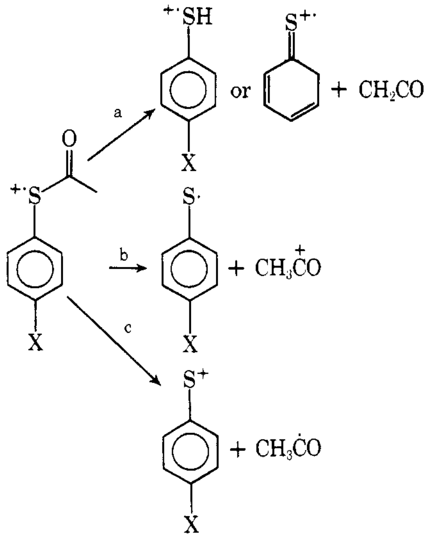


R_1	R_2	R_3	Registry no.	Rel abundance M − 42, %
H	H	H	10340-63-3	5
H	CH_3	CH_3	63059-17-6	70
H	$(CH_3)_3C$	H	63059-18-7	17
H	C_6H_5	H	52214-53-6	78
H	CH_3	H	63059-19-8	10
$(CH_2)_3$		H	16214-69-0	38
$(CH_2)_4$		H	15786-82-0	100

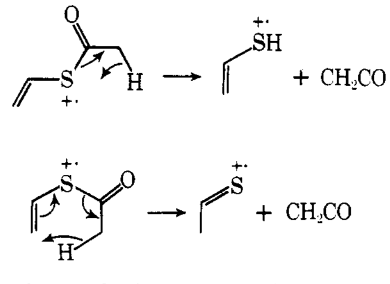
Scheme I



Scheme II

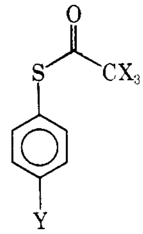


Scheme III

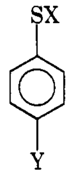


The two cyclic enethiolacetates, cyclopentenyl thiolacetate (**1**) and cyclohexenyl thiolacetate (**2**), display relative abundances of the M − 42 ion of 38 and 100%, respectively. If the transition state for the formation of these M − 42 ions were four centered, then the relative abundances of the ions should be independent of ring size. The observed difference in the relative abundances of the M − 42 ions may reflect the fact that in the transition state for the six-centered mechanism the 5–6 ring junction for **1** is less stable than the 6–6 ring junction for **2**.

Phenyl thiolacetate (**3**) and the 4-methoxy, 4-dimethylamino, 4-chloro, and 4-methyl analogues all lost ketene from the parent ion to form M − 42 ions. Phenyl thiolacetate-d_3 (**4**) and 4-toluene thiolacetate-d_3 (**5**) lose ketene-d_2 from the parent ions to form ions at *m/e* 111 and 125, respectively. As discussed below, these spectra show that deuterium has been transferred from the acetyl group to the benzene ring carbons either by the six-centered mechanism directly or by the thiol intermediate formed by the four-centered mechanism.



3, X = Y = H
4, X = D; Y = H
5, X = D; Y = CH_3
9, X = H; Y = CH_3



6, X = Y = H
7, X = D; Y = H
8, X = H; Y = CH_3

Thiophenol **6** and **3** form the same ions below *m/e* 110, although ions derived directly from *m/e* 110 are more intense for **6** than for **3**.

The cyclopentadiene radical cation appears at *m/e* 66 in the spectra of **6** and **3** and at *m/e* 67 in the spectra of the thiophenol-*s*-d_1 (**7**) and **4**. 4-Toluene thiol (**8**) and 4-toluene thiolacetate (**9**) form analogous, but less intense, ions at *m/e* 80, while **5** forms the deuterated ion at *m/e* 81. These ions arise from loss of CS from the 2,4-cyclohexadienethione radical cations which would be formed in the six-centered fragmentation of the aryl thiolacetates.

The phenyl cation is partially deuterated in the spectra of **7** and **4** and appears at *m/e* 77 and 78. The analogous ion at *m/e* 91 is the most intense ion in the spectrum of **8** and is very intense for **9**. **5** shows large peaks at *m/e* 91 and 92.

Deuterated and nondeuterated thiophene radical cations appear at *m/e* 85/84 in a ratio of 2:1 for both **7** and **4**. This scrambling of deuterium in **7** from sulfur onto the benzene ring before the loss of acetylene[5] and also before other fragmentations[6,7] represents complete randomization and is evidence for the interconversion of the thiophenol and 2,4-cyclohexadiene thione ions. Therefore, interpretation of the loss of ketene for the aryl thiolacetates in terms of whether a four- or six-centered mechanism is operative is precluded.

Photolysis of **3** produces **6**, which was thought to arise from the secondary photolysis of diphenyl disulfide.[8,9] However, **6** could be formed either by abstraction of a hydrogen atom from the acetyl group by the thiyl radical produced from photocleavage of the *S*-acyl bond or by transfer of a hydrogen atom from the acetyl group to the ortho carbon atom prior to photocleavage of the *S*-acyl bond.

In order to test these possibilities of hydrogen-atom transfer from the acetyl group, **4** and **5** were irradiated in cyclohexane for 3 h at 254 nm. Products were isolated by gas chromatography of the photolysis mixture after removal of solvent. The photolysis of **4** produced deuterium-free diphenyl disulfide and deuterium-free **6**. The deuterium label of **7** is not lost under the gas chromatographic isolation procedure employed. Likewise, **5** photolyzed to deuterium-free 4,4′-ditolyl disulfide. Thus, **6** is not formed by hydrogen-atom transfer from the acetyl group.

In summary, the ICR evidence for the transfer of the *β*-hydrogen atom of alkyl vinyl sulfides, the lack of M − 42 ions in the spectra of saturated alkyl thiolacetates, and the difference in intensity of M − 42 ions for **1** and **2** indicate that hydrogen-atom transfer from the acetyl group to the sulfur fragment occurs by a six-centered mechanism for alkenyl thiolacetates. However, the interconversion between cyclohexadienethione and thiophenol radical cations precludes distinguishing between four- and six-centered mechanism for arene thiolacetates. The analogy between the photochemistry and mass spectra of arene thiolacetates is limited to simple cleavage of the *S*-acyl bond and does not extend to the transfer of hydrogen from the acetyl group to the sulfur entity.

Experimental Section

Mass spectra were obtained on a Hitachi-Perkin Elmer RMU-6 spectrometer at 70 eV. Gas chromatography was performed on a Hewlett-Packard Model 700 gas chromatograph equipped with a thermal conductivity detector and a 20 ft × 1/8 in. OV-225 column. Thiol esters were prepared according to literature procedures as listed: methyl thiolacetate,[10] ethyl thiolacetate,[11] propyl thiolacetate,[11] isobutyl thiolacetate,[11] vinyl thiolacetate,[12] isobutenyl thiolacetate,[12] *β*-*tert*-butyl vinyl thiolacetate,[13] cyclopentenyl thiolacetate[16] (**1**), cyclohexenyl thiolacetate[16] (**2**), phenyl thiolacetate[17] (**3**), 4-methoxyphenyl thiolacetate,[17] 4-dimethylaminophenyl thiolacetate,[18] 4-chlorophenyl thiolacetate,[17] 4-toluene thiolacetate[17] (**9**). Structure assignments were confirmed by NMR and IR spectra. Phenyl thiolacetate-d_3 (**4**) and 4-toluene thiolacetate-d_3 (**5**) were prepared from the thiol and acetic-d_3 acid using dicyclohexylcarbodiimide.[11] Photochemistry of the deuterated esters was conducted exactly as previously reported.[2]

Supplementary Material Available: A table of mass spectra data for compounds which are not reported in the literature (1 page). Ordering information is given on any current masthead page.

Registry No.—$CH_3CH_2SCOCH_3$, 625-60-5; $(CH_3)_2CH$-$CH_2SCHOCH_3$, 2432-37-3; 4-Cl-$C_6H_4SCOCH_3$, 21021-60-3; 4-$CH_3OC_6H_4SCOCH_3$, 60787-31-7; $C_6H_5SCOCD_3$, 60860-51-7; 4-$CH_3C_6H_4SCOCD_3$, 60860-52-8.

References and Notes

(1) J. R. Grunwell, *Chem. Commun.*, 1437 (1969).
(2) J. R. Grunwell, N. A. Marron, and S. I. Hanhan, *J. Org. Chem.*, **38**, 1559 (1973).
(3) J. R. Grunwell and D. L. Foerst, *J. Org. Chem.*, in press.
(4) K. B. Tomer and C. Djerassi, *J. Am. Chem. Soc.*, **95**, 5335 (1973).
(5) S. Reinhardt, Abstracts, 158th National Meeting of the American Chemical Society, New York, N.Y., Sept 1969, No. 66.
(6) D. Earnshaw, G. Cook, and G. Duneen, *J. Phys. Chem.*, **68**, 296 (1964).
(7) S. O. Lawesson, J. O. Madsen, G. Schroll, J. H. Bowie, and D. H. Williams, *Acta Chem. Scand.*, **20**, 2325 (1966).
(8) E. L. Loveridge, B. R. Beck, and J. S. Bradshaw, *J. Org. Chem.*, **36**, 221 (1971).
(9) Y. Schaafsma, A. F. Bickel, and E. C. Kooyman, *Tetrahedron*, **10**, 76 (1960).
(10) J. Obermeyer, *Ber.*, **20**, 2920 (1887).
(11) J. R. Grunwell and D. L. Foerst, *Synth. Commun.*, **6**, 453 (1976).
(12) E. I. duPont de Nemours and Co., *Chem. Abstr.*, **41**, 4509e (1947).
(13) H. Boehme, H. Beyzenberger, M. Clement, A. Dick, E. Nuernberg, and W. Schlephack, *Justus Liebigs Ann. Chem.*, **648**, 15 (1961).
(14) H. Behringer, *Justus Liebigs Ann. Chem.*, **546**, 219 (1949).
(15) A. A. Oswald, K. Griesbaum, B. E. Hudson, and J. M. Bregman, *J. Am. Chem. Soc.*, **86**, 2877 (1964).
(16) J. D. Willett, J. R. Grunwell, and G. A. Berchtold, *J. Org. Chem.*, **33**, 2297 (1968).
(17) V. Baliah and K. Ganapathy, *Trans. Faraday Soc.*, **59**, 1784 (1963).
(18) V. Baliah and K. Ganapathy, *J. Indian Chem. Soc.*, **40**, 1 (1963).

Synthesis of Aryl Alkynes. 1.
2-Ethyl-4-methoxyphenylacetylene

Deanna J. Nelson* and Ellen A. Uschak[1]

Organic Chemistry Laboratory, Indiana University of Pennsylvania, Indiana, Pennsylvania 15701

Received February 7, 1977

While many aryl alkenes and alkanes have been synthesized for study as potential synthetic estrogens,[2] no systematic