The reaction mixtures were filtered and the precipitated quaternary anilinium perchlorates were washed twice with benzene. Frequently these products were of analytical purity. When necessary, a recrystallization from petroleum ether or acetone was carried out. Details of the microanalyses[52] (C, H, N, Cl, and, in one instance, Br) and of the infrared (KBr) and PMR (CD_3CN) spectra are recorded elsewhere.[2]

In a typical procedure, 50 mL of a benzene solution 0.0401 M in methyl perchlorate and 0.12 M in *N,N*-dimethylaniline was allowed to react at room temperature for 2 weeks. After filtration, the precipitate was washed twice with benzene and dried under vacuum to give 0.462 g (98%) of a white solid, identified as *N,N,N*-trimethylanilinium perchlorate: mp 178–179 °C; IR (KBr) includes 8–10 μ (broad); NMR (CD_3CN) δ 3.54 (s, 9 H), 7.45–7.87 (m, 5 H). Anal. Calcd for $C_9H_{14}NClO_4$: C, 45.82; H, 5.98; N, 5.94; Cl, 15.04. Found: C, 45.65; H, 5.92; N, 5.90; Cl, 14.91.

The percentage yields and melting points (°C) of other isolated products were as follows.

(a) For varying X in $(XC_6H_4NMe_3)^+ClO_4^-$: *p*-OMe, 98, 190.5–191; *p*-Me, 99, 194.5–195.5; *m*-Me, 97, 136–137; *p*-Br, 97, 250 dec; *m*-Cl, 91, 157.5–160; *p*-CN, 93, 162–163.5; *m*-NO_2, 97, 208 dec; *p*-NO_2, 92, 175.5–177.

(b) For varying X in $(XC_6H_4NMe_2Et)^+ClO_4^-$: *p*-Me, 99, 64–66.5; *m*-Me, 97, 103–104.5; H, 97, 90–91; *m*-Cl, 92, 93.2–94.

(c) For varying X in $(XC_6H_4NMe_2\text{-}i\text{-}Pr)^+ClO_4^-$: *m*-Me, 80, 106.5–107.3; *m*-Cl, 60, 103.8–105.

Acknowledgment. We thank the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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(52) Microanalyses were by Spang Microanalytical Laboratory, Ann Arbor, Mich.

Structural Aspects and Low-Temperature Photochemistry of the Monothioacetylacetone System

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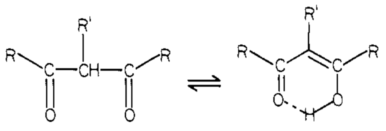
Contribution from the Departments of Chemistry and Pharmacological Sciences, State University of New York, Stony Brook, New York 11794. *Received October 16, 1980*

Abstract: New spectroscopic evidence, which is obtained from low-temperature studies of matrix-isolated monothioacetylacetone (TAA), forces a reformulation of the composition and photochemistry of the system. The infrared spectrum of matrix-isolated TAA, which consists primarily of two substances, A and B, clearly indicates the predominant species (A) to be the chelated thioenol (*Z*)-4-mercaptopent-3-en-2-one (**4**). The minor component B, whose concentration can be substantially increased at cryogenic temperatures by irradiation of TAA with light ($\lambda \sim 350$ nm), exhibits nonchelated S–H, C=C, and C=O stretches in the IR, which correlate with a λ_{max}^{Ar} 279-nm band in the UV spectrum of the system. These spectral data and the fact that B thermally reverts to **4** at ~130 K are uniquely compatible with the assignment of the conformer of **4**, (2-*s-trans*)-(*Z*)-4-mercaptopent-3-en-2-one (**5**), to the minor component. Primary photochemical events in the acetylacetone system (AA) appear to parallel those occurring in TAA.

β-Diketones **1** are known to exist in equilibrium with the corresponding chelated enolic tautomers, **2**. The composition of the system is dependent upon both the pattern of substitution on the carbon framework, and the external environment.[2] For simple alkyl substituents (R = alkyl, R′ = H) the *Z*-chelate **2** is favored in the gas phase and in nonpolar or hydrocarbon solvents. When R′ = alkyl or aralkyl, the proportion of enol is reduced substantially, presumably owing to unfavorable steric interactions.



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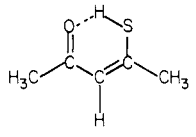
As an analogue of the enolizable *β*-diketones, the monothioacetylacetone system (TAA)[3] is of interest, particularly with respect to the influence of the sulfur atom on kinetic and thermodynamic relations amongst the various rotamers and tautomers that occupy energy minima. However, reports detailing the composition of TAA have been contradictory.[4-10] There is no general agreement as to what extent TAA distributes amongst each chelated *Z*-tautomer **4** and **9**, their conformers or geometrical isomers, or the monothioacetylacetone tautomer, **3**.



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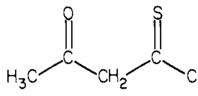

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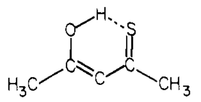

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A current view, promoted by Duus and co-workers,[9,10] is that TAA consists of two chelated forms, **9** and **4**, at room temperature, with the enol dominating by perhaps a factor of 2 or 3.

The argument for the enol **9**–enethiol **4** equilibrium as characterizing the TAA system, with **9** dominating, rests on (a) the

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(1) On leave from the Institute of Applied Radiation Chemistry, Technical University, Lódź, Poland.

(2) Forsen, S.; Nilsson, M. In "The Chemistry of the Carbonyl Group"; Zabicky, J., Ed.; Interscience: New York, 1970.

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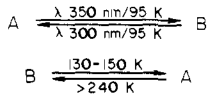
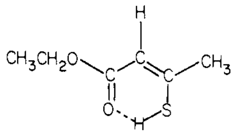
Scheme I



predictions of calculations by Fabian;[7] (b) the difference between comparable coupling constants of **14** and TAA ($J_{CH_3,H} = 1.2$ vs. 0.4 Hz, respectively); (c) the discrepancy between the chemical shift of the low-field proton in TAA (δ 13.53) and the chelated mercapto proton of **14** (δ 7.30). These differences (b and c) have



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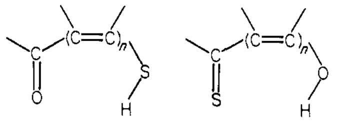
been viewed as signifying only a minor role for **4** in the TAA system. Of the bands which are to be anticipated for a chelated enol such as **9**, only a single band at 1218 cm^{-1} in the IR and one at 1220 cm^{-1} in the Raman (both presumed to be a C═S stretch) were uniquely assigned to the enol **9**. Failure to observe the O–H stretch was assumed to be the consequence of broadening, characteristic of a chelated enol. It was suggested that the "C═C stretch" of **9** coalesced with that of **4**.

Subsequent reports by Carlsen and Duus have explored theoretically the effect of conjugation[10b] and hydrogen bonding[10c] on the enol–enethiol tautomerism. They have also demonstrated[10a] that a photostationary state can be induced between the most stable form of TAA [alleged to be **9** and present exclusively, prior to irradiation, after cooling TAA in 2-methylbutanemethylcyclohexane (MPH) (5:1) to 95 K] and the substance believed to be the enethiol **4** ($\lambda_{\max}^{\mathrm{MPH}}$ 288 nm at 95 K). The maximal absorption of the latter component is slightly shifted from its value of 296 nm in cyclohexane at room temperature. The photoproduct obtained at 95 K and assigned the enethiol structure **4** thermally reverts to the more stable component in the region of 130–150 K. The barrier to B is overcome above 240 K.[10a]

Thus, the current description of the TAA system is formulated in Scheme I, where the major and minor components are designated, without prejudice, as A and B, respectively.

Despite the very excellent experimental work of Duus and co-workers,[8–10a] there are some aspects of their interpretation that are provocative. Duus himself points out, "the degee of enethiolization of thioketones in general is considerably higher than the degree of enolization of ketones,"[9,12e] a fact that reflects the greater bond dissociation energy[11] of a carbonyl C═O (172 kcal mol^{-1}) vs. a thiocarbonyl C═S (129 kcal mol^{-1}).

The enethiol **4** and enol **9** may also regarded as vinylogues of thiolic and thionic acids, respectively. It is the thiolic acid that



$n = 1$, **4** $n = 1$, **9**
$n = 0$, thiolic acid $n = 0$, thionic acid

is the stable form of monothiocarboxylic acids.[12a] Unless a particularly strong hydrogen bond between C═S---H–O was formed[12c,d] or unprecedented stabilization for a hydrogen-bonded chelate occurred in **9**, it would seem that **4** would be the thermodynamically favored chelate.

Table I. Observed Vibrational Frequencies (cm^{-1}) of Argon Matrix-Isolated Monothioacetylacetone (TAA)[a,c]

2926 w	1416 m	859 m
2507 w (broad)	1385 m	801 s
1705 m	1367 m	754 m
1688 w[b]	1361 w[b]	623 w
1628 w	1256 m (broad)	616 w
1577 s (broad)	1221 m	507 w
1508 w	1166 w	438 vw
1472 m	1027 m	361 w
1440 m	994 w	330 w
1432 w	960 w	
1424 m	910 m	

[a] M/R = 500, T = 12 K, 26 mm. [b] Bands of B [2-*s-trans*)-(*Z*)-4-mercaptopent-3-en-2-one (**5**)]. [c] Absorption is predominantly that of A, the chelate (*Z*)-4-mercaptopent-3-en-2-one (**4**).

Table II. Observed Vibrational Frequencies (cm^{-1})[a,b] of Photolysed Monothioacetylacetone (TAA)

2932 w[c]	1382 w	1022 m
2558 w	1361 m	952 m
1705 m[c]	1348 w	801 m[c]
1688 vs	1330 m	612 m
1628 m[c]	1285 w	604 m
1597 w	1263 w	537 w
1577 vs[c]	1209 m	501 w
1560 w	1201 s	486 w
1451 m	1135 m	426 w
1442 w	1104 w	394 w
1432 m[c]	1039 w	350 w

[a] After irradiation of argon matrix-isolated TAA (M/R = 500, T = 12 K, 26 mm) for 30 min, using a 350-nm interference filter. [b] Absorption is predominantly that of **5**. The intensity of bands at 910 and 859 cm^{-1} in Figure 1 as compared with Figure 2 give an indication of the extent of conversion of **4** to **5**. [c] Absorption at these positions is also present in starting material.

The barrier (8–10 kcal mol^{-1})[12b] attributed to the reversion of the less stable chelate (allegedly **4**) to the more stable chelate (presumably **9**) is also somewhat surprising in view of the facts that (1) hydrogen transfer within the analogous acetylacetone (AA) system is exceedingly rapid[13] and probably involves tunneling, and (2) for simple transfers in the thermodynamically favorable direction, proton transfer from sulfur to oxygen is very close to being diffusion controlled.[14]

In view of the controversy surrounding published descriptions of the monothioacetylacetone system, we have undertaken a reinvestigation of TAA, utilizing the matrix-isolation technique (MIT).[15] The ability to sample conformational equilibria in molecular beams by quenching a gaseous sample onto a surface maintained at cryogenic temperatures has enabled us to correlate, unambiguously, room-temperature species in TAA with those involved in the photostationary state at very low temperatures.[16–22] By revealing key functional groups, vibrational spectra of TAA at cryogenic temperatures permit an unambiguous assignment of bands to individual components of the system.

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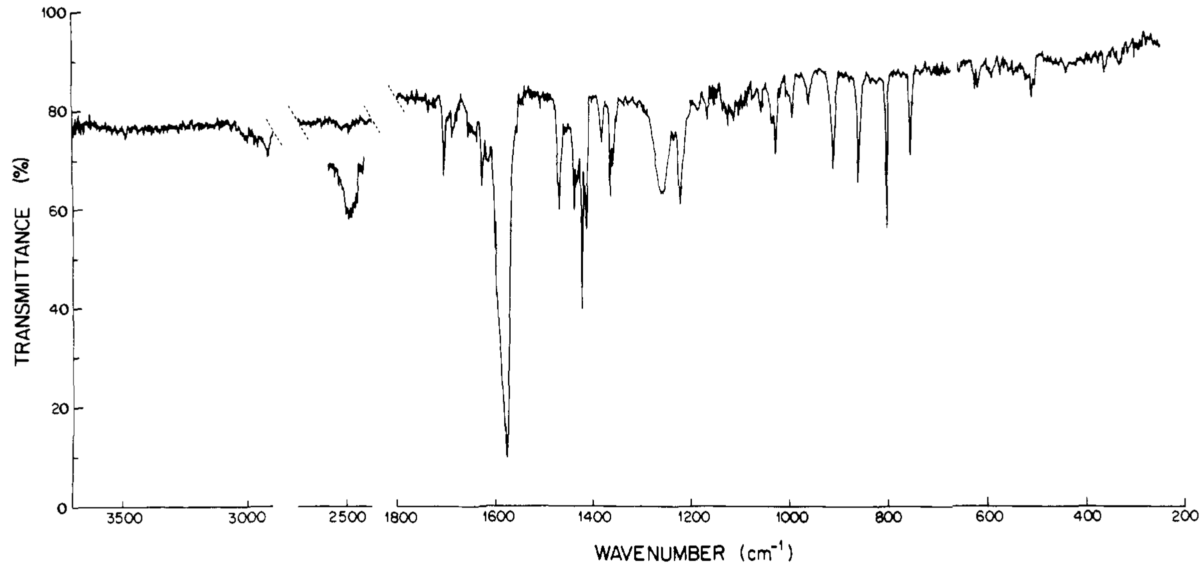

Figure 1. Infrared spectrum of argon matrix-isolated monothioaceytlacetone (TAA), M/R = 500, T = 12 K, 26 mm. Note band at ν_{max} 2507 cm^{-1} with ordinate expanded 5 times.

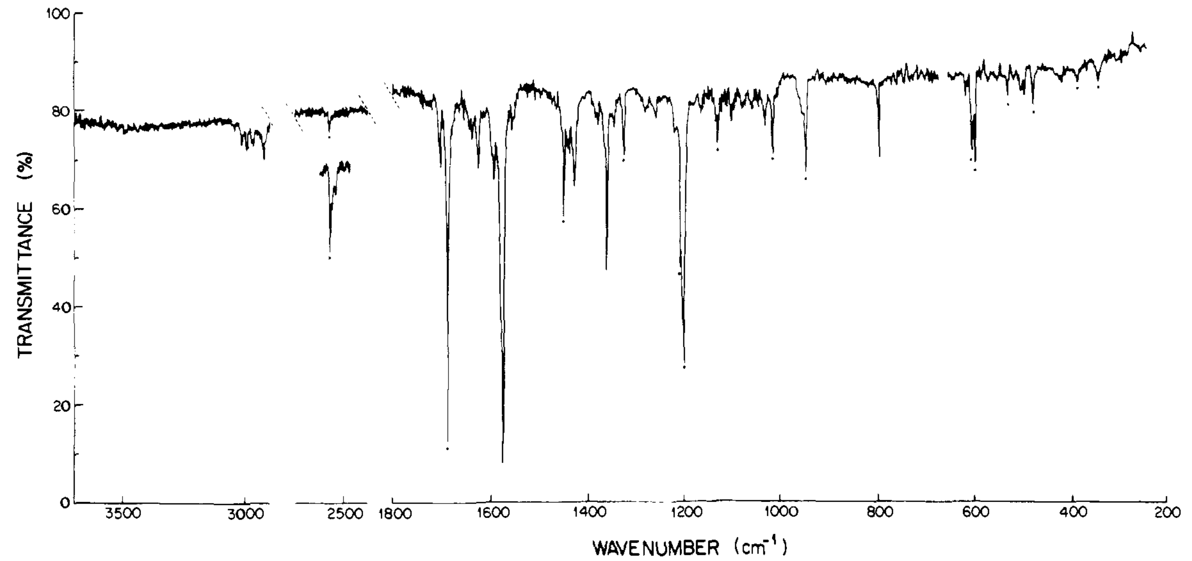

Figure 2. Infrared spectrum of argon matrix-isolated TAA (M/R = 500, T = 12 K, 26 mm) after irradiation for 30 min through a 350-nm interference filter. The spectrum is predominantly that of B. Note band at ν_{max} 2558 cm^{-1} with ordinate expanded 5 times. Dots indicate newly observed bands.

Results and Discussion

A. Structure of A. The spectra of matrix-isolated TAA displayed in Figures 1 and 3a represent room-temperature species that have been trapped at 20 K by quenching a gas-phase sample of TAA in argon "pumped" from a bulb at 298 K.[23] Note that the component B, which absorbs at λ_{max}^{298K} 295 nm in cyclohexane, apparently undergoes a hypsochromic shift of 16 nm when matrix isolated in argon. Duus also reported a shift of λ_{max} for B to 288 nm at 95 K in MPH.[10a]

The IR spectrum of matrix-isolated TAA permits the detection of the feature most diagnostic of the system, namely a very weak, broad absorption centered at 2507 cm^{-1}, in the region characteristic of an S–H stretch (Figure 1). This band is not present in the spectrum of dideuterated [S-^{2}H]TAA (**15**).[6] The signal at 2507 cm^{-1} is broadened and shifted from typical values[24,25] (2590–2550 cm^{-1}) observed for "free" S–H stretches. The intensity of this signal upon irradiation of TAA (vide infra) shows a pattern of growth similar to the UV absorption of λ_{max} 355 nm belonging to the most stable form of TAA. Clearly, the signal at 2507 cm^{-1} is most reasonably ascribed to a chelated S–H stretch that points to the enethiol, (Z)-4-mercaptopent-3-en-2-one (**4**) as the pre-

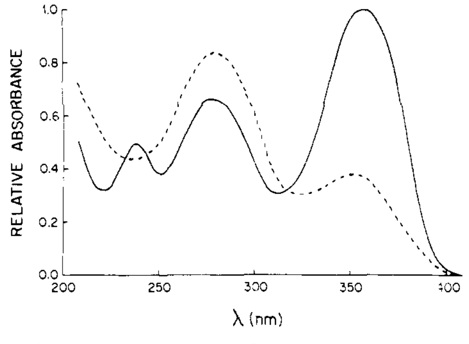

Figure 3. (a) Ultraviolet spectrum of argon matrix-isolated TAA (M/R = 500, T = 12 K, 4 mm, solid curve); (b) ultraviolet spectrum of argon matrix-isolated TAA (M/R = 500, T = 12 K, 4 mm) after irradiation for 30 min through a 350-nm interference filter (dashed spectrum).

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[23] Our matrix-isolated species are necessarily identical with those species Duus has observed[8-10] at room temperature, since quenching of a gaseous sample onto a surface maintained at cryogenic temperatures freezes the high-temperature equilibrium. Felder, P.; Gunthard, Hs. H. *Chem. Phys. Lett.* **1979**, *30*, 347; *Spectrochim. Acta, Part A* **1980**, *36*, 223.

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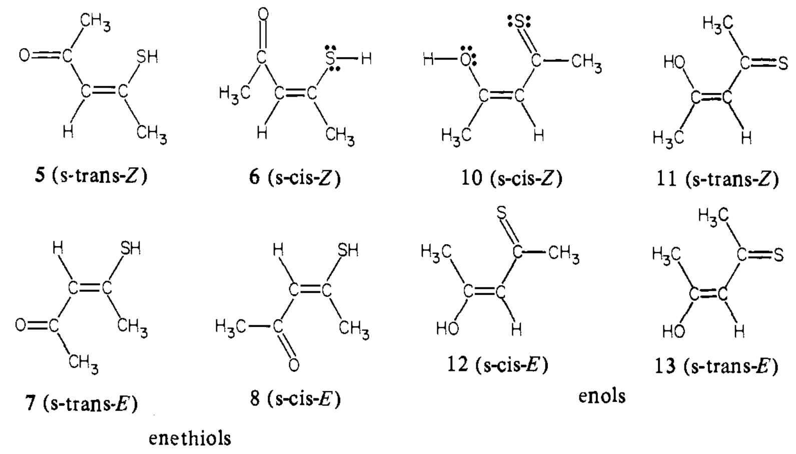
Chart I



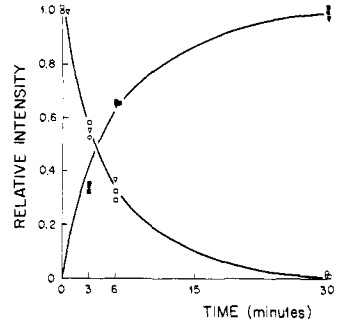


Figure 4. An intensity vs. time plot of selected bands of TAA matrix isolated in argon [(○) 1472 cm^{-1}, (▽) 1256 cm^{-1}, and (□) 859 cm^{-1}] and of product [(●) 1688 cm^{-1}, (▼) 1451 cm^{-1}, and (■) 1330 cm^{-1}] after irradiation at 3, 6, and 30 min, using a 350-nm interference filter.

dominant component (A) of TAA.[26]

All but two of the infrared bands, which are listed in Table I, are related to the thioenol (**4**). Weak signals at 1688 and 1361 cm^{-1} are correlated with the 279-nm band of the minor component B. Irradiation of matrix-isolated TAA at λ 350 nm leads to a steady state dominated by the "279 nm" component (Figure 3b), which reverts to the 355-nm species either upon irradiation with λ 300 nm or thermally above 130 K. This behavior exactly parallels that observed for B in MPH by the Danish workers.[10a] The correspondence between the growth of B and diminution of A upon irradiation at λ 350 nm is clearly evident from intensity vs. time plots of selected infrared bands. The results displayed in Figure 4 are typical.

Whereas absorption from the "C=C" and "C=O" stretches of the enethiol (**4**) overlap at 1577 cm^{-1}, B displays separate and sharp resonances at 1688 and 1577 cm^{-1} that are very reasonable positions for C=O and C=C stretches shifted by conjugation (Figure 2).

The conversion of the thioenol **4** (λ_{max} 355 nm) to B (λ_{max} 279 nm) is accompanied by both a decrease in the intensity of the broad, chelated S–H stretch at 2507 cm^{-1} and the corresponding growth of a considerably sharper band absorbing at 2558 cm^{-1}. Figure 5 reveals the progression from (a) starting material, with the thioenol **4** predominating, to (b) the photolysate (from irradiation at λ 350 nm) dominated by B, and then (c) after irradiation of the photolysate in (b) with light of λ 300 nm, a stage with detectable amounts of both **4** and B is observed. Evidently, the photochemical transformation involves the chelate **4** interconverting with a nonchelated mercaptan.[27]

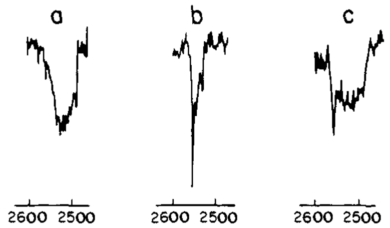
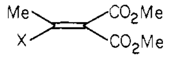


Figure 5. Mercaptan S–H stretch region of the infrared spectrum with ordinate expansion 5 times (a) of argon matrix-isolated TAA as in Figure 1, (b) after irradiation for 30 min as in Figure 2, (c) after irradiation of argon matrix-isolated TAA (M/R = 500, T = 12 K, 30 mm) through 350- (for 20 min) and 300-nm (for 60min) interference filters.

Table III. Comparison of σ_R Values with Activation Parameters for Rotation around Carbon–Carbon Double Bonds



X	$\Delta G^{\ddagger}$, kcal/mol	$\sigma_R{}^X$
NMe$_2$ (16)	<8.9	−0.93
OMe (17)	25.7	−0.52
SMe (18)	>27.5	−0.14

B. Structure of B. A decision regarding the structure of B can be based on B's thermal stability and on the functionality revealed by analysis of the infrared spectrum. The observation of absorption (Figure 2) characteristic of an unchelated ("free") S–H stretch at 2558 cm^{-1} is clearly incompatible with the enolic ensemble of structures **9**–**13**, and the monothioketone **3**. For the conformer **6**, the barrier to internal rotation of the mercapto group leading to the stable chelate **4** would not be expected to differ very much from known barriers for mercaptans, which generally are no greater than 2 kcal mol^{-1}.[28-34] The experimental value of the rotational barrier of thiophenol is lower than 0.8 kcal mol^{-1} [28,29] and is typical.

The structural problem pertaining to **B** can thus be reduced to an assessment of the barriers to rotation about the relevant

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[26] Gray et al. (ref 6) have previously performed a complete analysis of the spectrum of TAA and TAA-d_2 much of which is in accord with our present thinking.

[27] Although we cannot, at present, make an unambiguous assignment, we note the presence of a band at 1858 cm^{-1} in the spectrum of photolyzed TAA-d_2, which is in the region where a S–D stretch would be expected.

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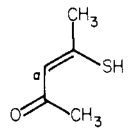
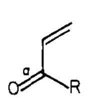
formal single and double bonds in **5**, **7**, and **8** and their compatibility with the conversion of **B** to **A** at 130 K (E_a ~8–10 kcal mol^{-1}).

As regards the *E* species (**7** and **8**), it is well established from the work of Shvo and others[35–43] that the barrier to internal rotation in olefins can be drastically altered from a standard value of ~60–65 kcal mol^{-1} in simple alkyl-substituted olefins[44,45] to significantly lower values in appropriatelysubstituted systems (Table III).[36] However, the rather substantial barrier (>27 kcal mol^{-1}) to internal rotation around the formal double bond in **18** with two electron-withdrawing carbomethoxy groups almost certainly signifies a large barrier for conversion of either **7** or **8** to the chelate **4**.[46] Thus the *E* isomers (**7** and **8**) can be eliminated from further consideration on the grounds that they are not kinetically competent to regenerate the chelate **4** in the range of 130–150 K.

On the other hand, the remaining alternative **5**, which differs from **4** primarily with respect to rotation around the C_2–C_3 bond, is an eminently suitable candidate for B. The estimated barrier (~8–10 kcal mol^{-1}) for the conversion of B → A is only a few kilocalories/mole higher than the barriers to rotation (~5 kcal mol^{-1}) around the central single bond in simple α,β-unsaturated aldehydes or ketones such as acrolein **19** (R = H) and but-3-en-2-one (R = CH_3).[47] The magnitude of the barrier is in accord with expectation for internal rotation around bond a in **5**, since substitution of a β-mercapto substituent for hydrogen would be expected to increase the barrier only modestly above those measured for **19** (R = H, CH_3).[36]

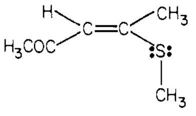


5



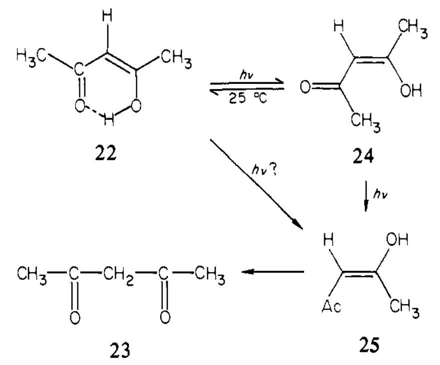
19

The spectral data for B are also comparable to those of 4-(methylthio)pent-3-en-2-one (**20**).[9,48] The infrared spectrum of matrix-isolated **20** displays the key C=C and C=O frequencies with positions and relative intensities that are very similar to the corresponding bands in the spectrum of **B**.[51] Since **20** and B both have λ_{max} ~290 nm,[9,48] all the relevant data bearing on the model 4-(thio)-pent-3-en-2-one system are in agreement with our assignment of **5** to B.

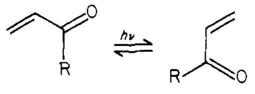


20

Scheme II

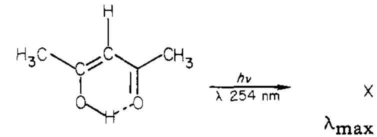


C. Photoinduced Conformational Changes of Matrix-Isolated Molecules. Our proposal of the conformer **5** as the minor component B of TAA, whose concentration can be increased by optical pumping of the matrix-isolated system at λ ~350 nm, is also consistent with results obtained with mixtures of conformers that are irradiated at cryogenic temperatures. Krantz[16,17] and coworkers have established precedents for photoinduced conformational changes, including but-3-en-2-one (**19**, R = CH_3), acrolein (**19**, R = H), and methyl propriolate (**21**), in which each system becomes enriched in a "high-energy" conformer.



19

Relevant to the proposal of the photoconversion of chelate **4** to its s-trans conformer **5** are Fischer and co-workers'[49] flash photolysis experiments with AA at room temperature. AA, which exists predominantly as the chelate **22** in hydrocarbon solvents, was observed to form a short-lived transient (X), absorbing at λ_{max} 250 (ϵ 11 500, hexane). The original spectrum of the system is restored after the flash, with the chelated enol **22** being regenerated in a first-order reaction. The rate constant of reformation of **22** is 0.27 s^{-1} in hexane at room temperature. No substantial conversion to the diketone $(CH_3C{=}O)_2CH_2$ **23** takes place during the flash nor is **23** formed in a secondary thermal reaction. However, under conditions of continuous irradiation of **22** in aliphatic hydrocarbon solvents with λ 254 nm, the diketone **23** is formed and only slowly reverts to the enol **22**.



22

λ_{max} 250
(log ϵ 11 500)

The facts that (1) the phototransient X reverts to chelate **22** on the order of seconds and that (2) unimolecular geometrical isomerization must occur orders of magnitude more slowly[50] exclude *E* isomer **25** from consideration as the phototransient X. X is thus the s-trans conformer **24**.

The infrared spectrum of argon matrix-isolated AA indicates that AA consists predominantly (>95%) of the chelate **22**. A nonchelated form possessing the requisite free O–H (3602 cm^{-1}),

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(35) Shvo, Y.; Taylor, E. C.; Bartulin, J. *Tetrahedron Lett.* **1967**, 3259.

(36) Shvo, Y.; Belsky, I. *Tetrahedron* **1969**, *25*, 4649.

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(40) Dabrowski, J.; Kozerski, L. *J. Chem. Soc. B* **1971**, 345.

(41) Dabrowski, J.; Kozerski, L. *Org. Magn. Reson.* **1972**, *4*, 137.

(42) Dabrowski, J.; Kozerski, L., *Org. Magn. Reson.* **1973**, *5*, 469.

(43) Osman, R.; Zunger, A.; Shvo, Y. *Tetrahedron* **1978**, *34*, 2315.

(44) Benson, S. W.; O'Neal, H. E. "Kinetic Data on Gas Phase Unimolecular Reactions"; NSRDS, NBS21, p 21.

(45) Douglas, J. E.; Rabinovitch, B. S.; Looney, F. S. *J. Chem. Phys.* **1955**, *23*, 315.

(46) Even with allowances for variations in the magnitude of the barrier from phase to phase, the barrier to rotation about the C=C bond may be at least 20–30 kcal mol^{-1} higher than the barrier to the s-cis–s-trans conversion in 4-mercapto-pent-3-en-2-ones.

(47) de Groot, M. S.; Lamb, J. *Proc. R. Soc. London, Ser. A* **1957**, *242*, 36.

(48) Volkov, A. N.; Khuryakova, A. N.; Khudyakova, R. N.; Keoko, V. V.; Trofimov, B. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1978**, 153; they have established that mixtures of (*E*)- and (*Z*)-4-(alkylthio)-but-3-en-2-ones absorb near λ_{max} ~300 nm.

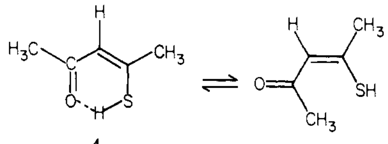
(49) Veierov, D.; Bercovici, T.; Fischer, E.; Mazur, Y.; Yogev, A. *J. Am. Chem. Soc.* **1977**, *99*, 2723.

(50) (a) Eistert, B.; Arndt, F.; Loewe, L.; Ayca, E. *Chem. Ber.* **1951**, *84*, 156; (b) Eistert, B.; Reiss, W. *Ibid.* **1954**, *87*, 108.

C=O (1710 cm^{-1}), and C=C (1621 cm^{-1}) stretches for **24** is obtained as a primary product from **22** by irradiating AA with light λ 300 nm. This nonchelated primary product undergoes further photochemistry to other species possessing carbonyl absorption at 1692 and 1680 cm^{-1}.[51,52] However, we cannot marshal any evidence from our matrix-isolation experiments, indicating the involvement of a β-diketone **23** in the photochemistry of AA. We speculate that the path by which **23** is formed during conventional, continuous photolysis of **22**, as described by Fischer, involves geometrical isomerization of a *Z* to an *E* form (Scheme II). Under flash conditions at 25 °C the conformer **24** rapidly reverts only to chelate **22**, the tautomerization to the diketone **23** being considerably slower. But under continuous photolysis, a steady-state concentration of **24** may be produced which is further converted photochemically to **25**. It is probable [judging from the reported experimental value of $\Delta G^{\ddagger}$ for **17** (Table III) and the stability of the enolic ether analogous to **25**[50]] that the thermal unimolecular geometrical isomerization of **25** is too slow to compete with tautomerization of **25** to the diketone **23**. The latter is photochemically stable under these conditions.

Summary

In summary, the evidence favors the following description for the TAA system. At room temperature the dominant enethiol **4** is in rapid equilibrium (NMR time scale) with its nonchelated conformer **5**. Irradiation of matrix-isolated TAA at λ 350 nm leads to a steady state dominated by **5**, which reverts to the starting chelate either upon irradiation with λ ~300 nm or thermally above 130 K.



4 5

There is no obvious evidence for the chelated enol **9** in either starting material or in the photolysate, although small amounts may be undetectable by our techniques.

Experimental Section

Proton NMR spectra were recorded on a Varian Associates EM 360 or HFT-80 Spectrometer. Infrared spectra of matrix-isolated species were obtained with a Perkin-Elmer Model 180 spectrophotometer in the constant I_0 mode. Ultraviolet spectra were measured with a Varian Associates Techtron spectrometer.

A Displex, closed cycle, two-stage refrigerator, Model CS 202, manufactured by Air Products and Chemicals Inc., was utilized in these studies. Commercial grade helium (grade 6) was employed as the refrigerant.

A cesium iodide plate in contact with a copper block with indium O-rings supported the matrix deposit for infrared spectral studies. The infrared transmitting outer windows were also cesium iodide. Suprasil quartz plates served as windows for photolysis. The temperature of the sample window was monitored with a chromel-gold-0.07 atom-% iron thermocouple.

Photochemical Reactions. Photochemical reactions were carried out with a 1000-W mercury-xenon lamp (Hanovia No. B977B0010) as the light source. Interference filters (Oriel Corp. of America, No. G-572-09, Stamford, Ct) were used as indicated. Samples, which were prepared and isolated by standard procedures,[53] were cooled to 12 K and then irradiated.

The sample was deposited at the rate of 0.4 torr/min. All photochemical experiments, unless otherwise indicated, were carried out at 12 K. Gaseous samples ranged in M/R (matrix host/guest) from 100-1000.

Chemicals. Monothioacetylacetone (TAA) was prepared by the method of Duus and Anthonsen.[9] TAA was purified by gas chromatography, using a column containing 15% SE-30 on 80/100 mesh Chromosorb W (5 ft × 1/4 in.), maintained at 117 °C with a carrier gas flow of 25 mL/min. The peak that had a retention time of 5 min was repassed and used for preparation of the sample. Monothioacetylacetone-d_2 was prepared as described by Gray and co-workers.[6]

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(51) A. Krantz and J. Gebicki, unpublished results.

(52) The primary photoproduct of matrix-isolated **22**, which we tentatively regard as **24**, undergoes further reaction, with light at λ 250 and 300 nm and is most reactive at the lower wavelength end of this range.

(53) Krantz, A.; Laureni, J. *J. Am. Chem. Soc.* **1981**, *103*, 486.

Structure, Reactivity, and Biological Activity of Strained Bicyclic β-Lactams

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Abstract: The antibacterial activities of the structurally simple but highly strained β-lactam compounds **1a**, **2a**, and **3a** are discussed on the basis of their chemical reactivity and the molecular geometry of their crystalline acetonyl esters. The nature of the hydrolysis products of **1a**, **2a**, and **3a** was also determined. It was found that the Δ^2 double bond is essential for biological activity.

Introduction

The synthesis of β-lactam derivatives which are more effective than the existing antibiotics has become a subject of worldwide pharmaceutical and commercial interest. However, in spite of the significance of this class of compounds in chemotherapy, little is known about the fundamental factors contributing to their antibiotic potency.

It has been demonstrated[1] that the penicillins and cephalosporins are able to interfere in the terminal step of the bacterial cell wall biosynthesis. With concomitant cleavage of their labile β-lactam bond, they acylate certain enzymes which direct the cross-linking of linear peptidoglycan strands and thus prevent the buildup of

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‡ Ciba-Geigy.

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