ELSEVIER

Journal of Chromatography A, 685 (1994) 287–293

JOURNAL OF CHROMATOGRAPHY A

Selective thermolysis of the enol forms of acetoacetates during gas chromatography, revealed by combined matrix-isolation Fourier transform infrared and mass spectrometry

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First received 31 May 1994

Abstract

The thermal decompositions of methyl and ethyl acetoacetates have been observed by combined gas chromatography (GC)–mass spectrometry–matrix-isolation Fourier transform infrared spectrometry. Under the conditions employed, keto and enol forms could be separated by GC and, by careful control of interface temperatures, the thermolysis of the individual components could be studied. Each enol acetoacetate form was almost completely converted to a keto-ketene and an alcohol. The keto-acetoacetate forms were only partially decomposed, with reaction products identical to those of the enol forms, indicating that the preferred mechanism of thermal degradation is via the enol-acetoacetate form.

1. Introduction

1.1. Gas chromatography with combined matrix-isolation Fourier transform infrared and mass spectrometry

Recently, work has been performed to evaluate the complementary information obtained from combined matrix-isolation (MI) Fourier transform (FT) infrared (IR) spectrometric and mass spectrometric (MS) examination of peaks eluting from a gas chromatography (GC) column using a Mattson Cryolect GC–MS–MI-FT-IR instrument. The FT-IR spectra are recorded from a portion of the GC eluent trapped in an argon matrix at approximately 11 K on a rotating, gold-coated drum. The mass spectra are recorded in parallel using a VG Trio-1 operating in positive ion electron ionization (EI^+) mode.

During a part of this work, it was noticed that a GC-isolated component, identified as an acetoacetate, had a strong band in the IR spectrum at 2150 cm^{-1}, which was inconsistent with its presumed structure. Similar IR bands appear in several Cryolect matrix-isolation IR reference spectra of acetoacetates, but do not appear in any of the liquid or vapour-phase spectra of acetoacetates.

In this paper we report a study of the GC of methyl and ethyl acetoacetates using the Mattson

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0021-9673/94/$07.00
SSDI 0021-9673(94)00672-5

Cryolect instrument. It was found that, with the conditions employed, the keto and enol forms of the acetoacetates are not rapidly equilibrated and are eluted separately. It was also found that high temperatures in the transfer line connecting the GC column with the matrix spray-on device can induce a selective thermolysis of the enol forms.

1.2. Chromatography of acetoacetates

It has been known for a long time (see, e.g., [1]–[3]) that acetoacetates exist as equilibrium mixtures of the keto (**1**) and enol (**2a** ⇌ **2b** ⇌ **2c**) forms (Fig. 1). The rate of equilibration in the pure state is not very rapid, but traces of H^+ or OH^- catalyse this process. As long ago as 1911, Knorr et al. [4], by careful work at low temperatures, were able to prepare reasonably pure samples of the keto and enol forms of ethyl acetoacetate (**1**, R = Et), and estimated the proportions of keto and enol forms in the equilibrium mixture from refractive index measurements. Recently it has been demonstrated that low-temperature HPLC on silica or modified silica columns can separate the keto and enol forms of both methyl and ethyl acetoacetates, and evidence for a third equilibrium component, possibly the unconjugated enol (**3**, R = Et), was obtained in the latter case [5,6]. The enol form was found to revert to the equilibrium mixture if the eluate was heated to 90°C for 1 min. These HPLC studies showed that the equilibrium constant for ethyl acetoacetate (K = [enol]/[keto]) varies considerably with the medium, e.g. at 25°C from ca. 0.05 in water, through 0.092 in the pure liquid (8% enol), to ca. 1 in hexane and cyclohexane [5]. In the pure liquid at 25°C, methyl acetoacetate (**1**, R = Me) contains about 6% of the enol and is thus slightly less enolized than the ethyl analogue. In the measurement of keto–enol equilibrium constants, HPLC has an advantage over NMR methods, since it can be conveniently applied to more dilute solutions. With unsymmetrical β-dicarbonyl compounds, e.g. **1**, two isomeric *cis*-enols, **2a** and **2c**, are distinguishable in principle, but linewidth measurements in the ^{17}O NMR spectra of some β-diketones suggest that interconversion of these is usually very rapid [7].

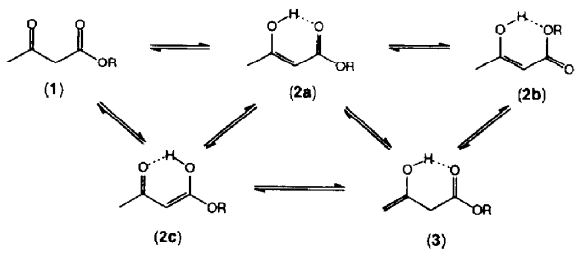

Fig. 1. Keto–enol equilibria in acetoacetates.

Studies of acetoacetates by GC have shown that, in a sufficiently hot injector system, decomposition can occur either intramolecularly [8] or by reaction with traces of water [9]. The term *reaction gas chromatography* has been applied to the use of GC in these conditions [8,10]. When the decomposition yields unstable primary products, they cannot be observed directly by conventional means. The development of MI-FT-IR as a method of examining the components eluted from a GC column provides the opportunity to trap these reactive decomposition products in a low-temperature matrix and identify them by IR spectrometry.

2. Experimental

Methyl and ethyl acetoacetates were 99% pure standards obtained as commercial samples (Aldrich), which were checked for purity by routine techniques. The sample studied here was prepared as a 1:1 mixture of the two acetoacetates as an approximately 0.1% solution in dichloromethane.

The Mattson Cryolect GC–MS–MI-FT-IR instrument [11] was equipped with a CP-SIL-8-CB capillary column (25 m × 0.32 mm I.D., film thickness 0.25 μm). Samples were introduced to the column using split injection (approximately 30:1 split ratio) at 150°C and the following GC temperature program was used for the separation: 50°C (2 min), 10°C/min to 150°C (2 min). Components were eluted using helium as the carrier gas, and the eluate was split three ways

after separation using a simple three-hole ferrule and balanced capillary transfer lines. One stream (20%) passed to a conventional flame ionization detection (FID) system, the second (40%) to the MS transfer line, and the third (40%) to the matrix-deposition system. Here the eluate was diluted with a large excess of argon (approximately 1000:1) and deposited through a fine capillary tip as an argon matrix on a rotating, gold-coated drum at ca. 11 K. The resulting matrix had a helical path on the outer surface of the drum, with the individual components of the sample spatially separated in the matrix. The cryogenic drum could be relocated by a computer-controlled stepper motor to position any part of the matrix in the IR beam. Each component could thus be examined by FT-IR spectrometry. The instrument provides precise control of the temperatures of the injector system, the GC column, the transfer capillaries and the matrix-deposition tip.

3. Results and discussion

Fig. 2 shows a GC–FT-IR chromatogram of a 1:1 mixture of methyl and ethyl acetoacetates obtained with transfer line and deposition tip temperature of 180°C. The chromatogram shows four separated components, denoted *A*–*D*. The major two components (*C* and *D*) can be identified as the keto forms of methyl and ethyl acetoacetates, respectively, and the minor components (*A* and *B*) as the corresponding enols. The reasons for these assignments are as follows. The mass spectra of components *A* and *C* were identical, with a molecular ion at *m/z* 116, in accordance with the formula $C_5H_8O_3$, while components *B* and *D* had a molecular ion at *m/z* 130, indicating the formula $C_6H_{10}O_3$. The MI-FT-IR spectra of components *A*–*D* are shown in Figs. 3–6, respectively. The major components, *C* and *D*, had IR absorptions in the carbonyl (C = O) stretching region at 1724–1755 cm^{-1} (Figs. 5 and 6); whereas the minor components, *A* and *B*, each had weaker carbonyl absorptions (relative to other bands in the spectra) at lower wavenumber (1655–1683 cm^{-1}) and an additional band at 1636–1638 cm^{-1}, which is consistent with a carbonyl group adjacent to an unsaturated carbon–carbon bond (Figs. 3 and 4). The keto forms both exhibit two bands in the carbonyl stretching region, as expected for molecules containing both ketone and ester functionalities, but the possibility of site-effect splitting cannot be excluded (see, e.g., [12]). Each of the enols also showed more than one carbonyl band.

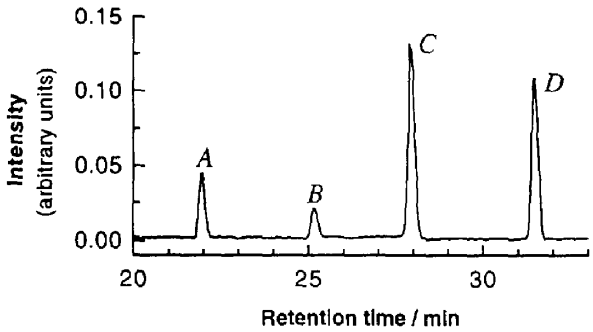

Fig. 2. GC–FT-IR chromatogram of a 1:1 mixture of methyl and ethyl acetoacetates (**1**, R = Me and R = Et), obtained with a GC injector temperature of 150°C and transfer-line temperature of 180°C. The GC conditions were as follows: column CP-SIL-8-CB, 25 m × 0.32 mm I.D., 0.25 μm film thickness; program 50°C (2 min), 10°C/min to 150°C (2 min). Peaks: *A* = methyl acetoacetate enol; *B* = ethyl acetoacetate enol; *C* = methyl acetoacetate keto; *D* = ethyl acetoacetate keto.

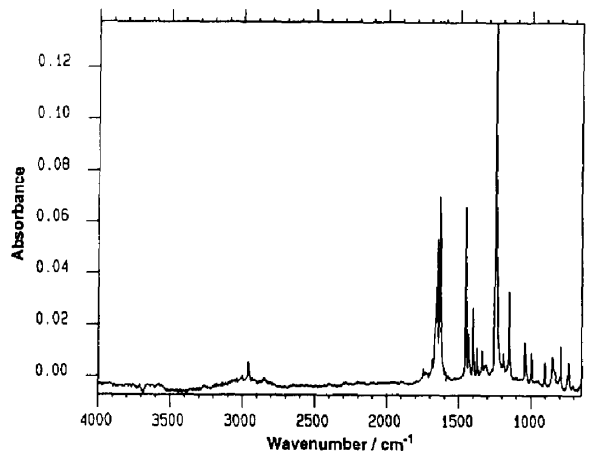

Fig. 3. Argon MI-FT-IR spectrum in the range 4000–650 cm^{-1} obtained from component *A* of Fig. 2 (methyl acetoacetate enol). The GC–matrix-isolation interface transfer-line temperature was 180°C.

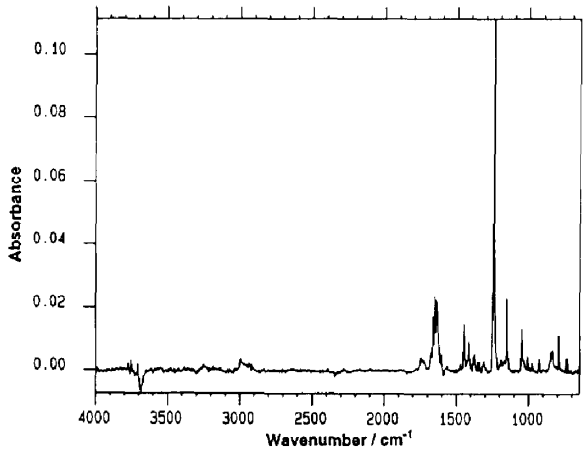

Fig. 4. Argon MI-FT-IR spectrum in the range 4000–650 cm^{-1} obtained from component *B* of Fig. 2 (ethyl acetoacetate enol). The GC–matrix-isolation interface transfer-line temperature was 180°C.

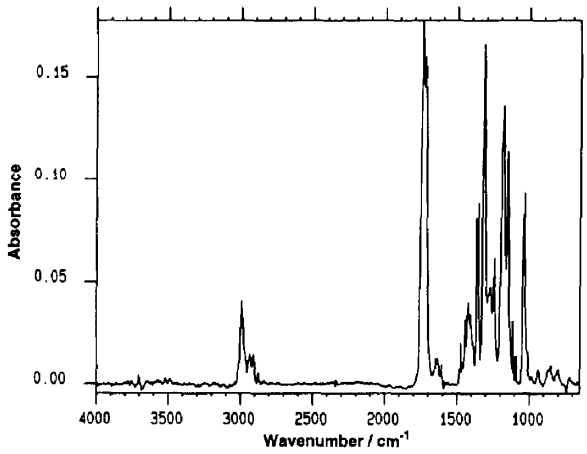

Fig. 6. Argon MI-FT-IR spectrum in the range 4000–650 cm^{-1} obtained from component *D* of Fig. 2 (ethyl acetoacetate keto). The GC–matrix-isolation interface transfer-line temperature was 180°C.

These could be due to the presence of more than one enol isomer in each case (cf. **2a**, **2b**, **2c** and **3**), but could equally reflect matrix site effects. Neither enol had an obvious O–H stretching absorption, but a study of matrix-isolated salicylaldehyde and derivatives by Gebicki and Krantz [13] has shown that sometimes only weak, very broad O–H bands are found for intramolecular hydrogen bonds. It seems that the matrix-isolated enols in our experiments fall into this category.

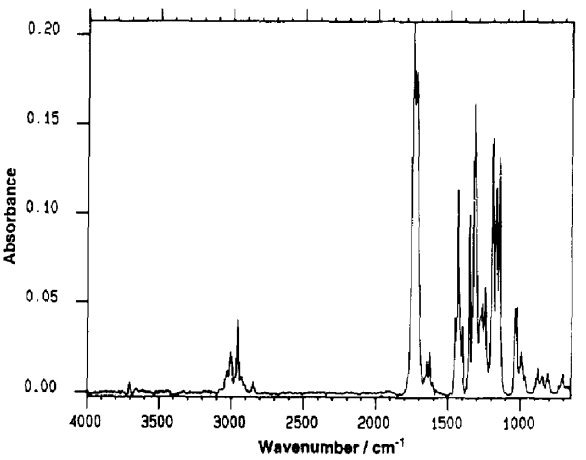

Fig. 5. Argon MI-FT-IR spectrum in the range 4000–650 cm^{-1} obtained from component *C* of Fig. 2 (methyl acetoacetate keto). The GC–matrix-isolation interface transfer-line temperature was 180°C.

The observed solvent effect on keto–enol equilibria (see above) [5] establishes that enols are less polar than the corresponding keto forms. This accords with our observation that the enols are eluted first from the GC column. The measured peak-area ratios (keto:enol) in Fig. 2 are approximately 4:1 for each of the acetoacetates. This is in fair agreement with data reported previously for ethyl acetoacetate at room temperature in dichloromethane [5], but the peak areas in the GC–FT-IR chromatogram —computed from IR intensities— can vary considerably depending on the functional groups present. GC–FID traces, which are probably more reliable as indicators of the relative mol quantities, gave ratios varying between 8.7:1 and 16.4:1. It is likely that these measurements reflect the equilibrium in solution, but the possibility of rapid tautomerization in the GC injector (possibly catalysed by trace acidic impurities) must also be considered. Nevertheless, it is clear from the clean chromatographic peak shapes that such rapid tautomerization did not occur in the GC column during elution, and the dissimilarity of the keto and enol FT-IR spectra indicates that

neither did such tautomerization occur in the transfer line or matrix-deposition tip at 180°C.

When the transfer-line temperature was raised from 180 to 250°C, the resulting FT-IR spectra of the four components showed clear signs of thermally induced decomposition. Each spectrum contained characteristic ketene C = C = O stretching bands at 2133–2143 cm^{-1} (Figs. 7 and 8) (cf., e.g., [14]). The ketenes clearly arise by thermolysis in the transfer line, and the two enols show a much greater degree of decomposition than the keto forms.

The formation of ketenes from the thermolysis of acetoacetates has already been suggested [8], although their direct observation has not previously been achieved. The proposed mechanism of thermolysis involves an enol as the key intermediate, and predicts that a keto-ketene (**4**) and an alcohol are the products (Fig. 9). The advantage of MI-FT-IR is that it allows direct observation of unstable species such as ketenes (**4**). Under this scheme, any ketene found arising from the keto form of acetoacetates probably arises via the corresponding enol. It should be noted, however, that a mechanism can be postulated for the direct transformation to ketenes from the keto form (Fig. 10). The key step is the retro-ene reaction of *trans*-keto form (**5**), which would yield ketene (**6**) and the enol of an ester (**7**). It is likely that this ester enol would tautomerize very rapidly to the normal ester form (**8**).

The validity of the mechanism of Fig. 9 is supported in our experiments by the selective thermolysis of the enols to ketenes. Because the MI-FT-IR spectra of the thermolysed enols un-

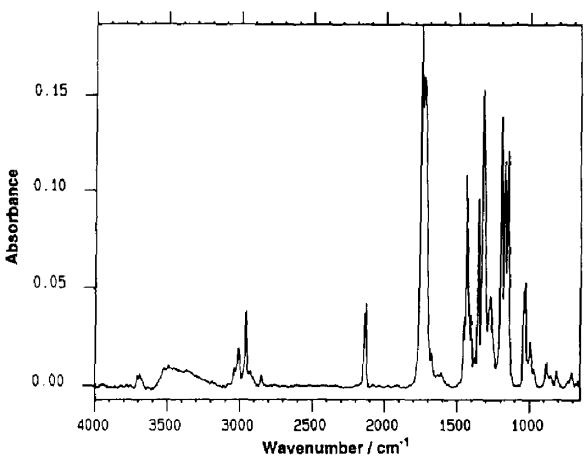

Fig. 8. Argon MI-FT-IR spectrum in the range 4000–650 cm^{-1} obtained from the keto form of methyl acetoacetate (component *C* of Fig. 2) with the GC–matrix-isolation interface transfer-line temperature increased to 250°C. Very similar results were obtained for the keto form of ethyl acetoacetate under these conditions.

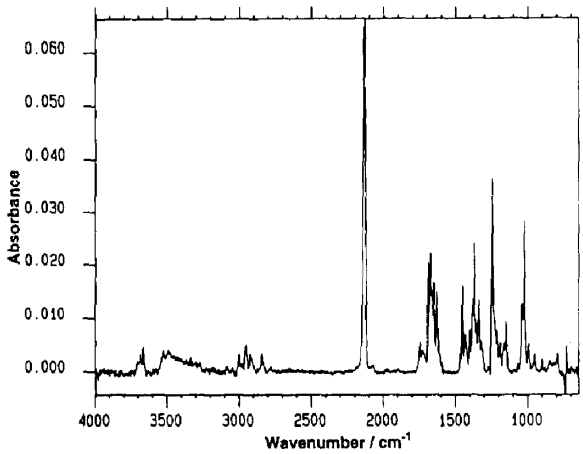

Fig. 7. Argon MI-FT-IR spectrum in the range 4000–650 cm^{-1} obtained from the enol form of methyl acetoacetate (component *A* of Fig. 2) with the GC–matrix-isolation interface transfer-line temperature increased to 250°C. Very similar results were obtained for the enol form of ethyl acetoacetate under these conditions.

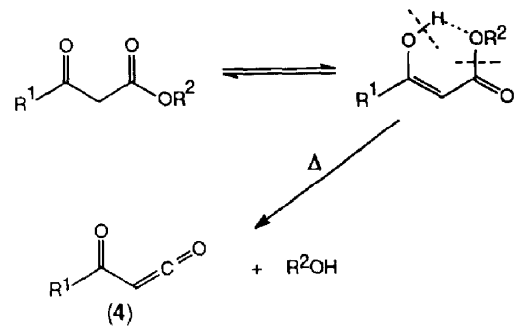

Fig. 9. Thermolytic cleavage pathway for the enol form of acetoacetates.

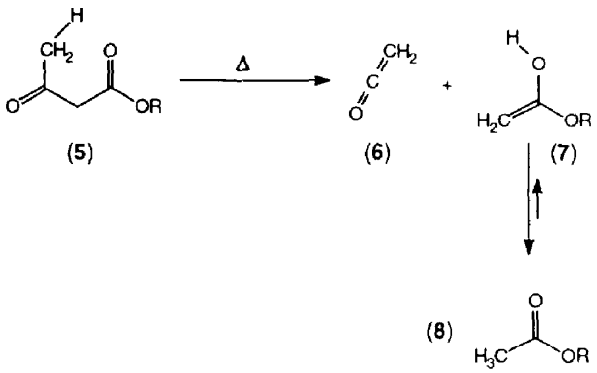

Fig. 10. Possible thermolytic cleavage pathway for the keto form of acetoacetates.

doubtedly arise from mixtures containing unchanged enols and the products, the carbonyl regions of the spectra have numerous absorptions, and it is not immediately possible to confirm that the ketenes formed are indeed keto-ketenes (**4**). It is likewise impossible to determine if only one enol conformer —specifically **2b**— is thermolysed, as predicted by the mechanism, or if the various enols are in rapid equilibrium. The presence of weak, broad O–H stretching bands around 3400 cm^{-1} in the product spectra of the thermolysed keto acetoacetates in our experiments suggests that the observed ketenes do indeed arise via the enols with concomitant alcohol formation, as shown in Fig. 9. It is just possible, however, that acetate enols (**7**) could survive long enough to be trapped in the argon matrices and thus give rise to the observed O–H stretches.

Conclusive evidence for Fig. 9 is finally provided by consideration of the spectrum derived by subtraction of the spectrum in Fig. 3 from that of Fig. 7 (with a suitable scaling factor). This has the effect of revealing the spectra of the thermolysis products only, no longer containing bands due to unreacted acetoacetate. The subtracted spectra from both the enol and keto forms of methyl acetoacetate give rise to identical data (though weaker in the keto case), with the presence of methanol clearly indicated by reference to a library spectrum of pure matrix isolated methanol, as illustrated in Fig. 11.

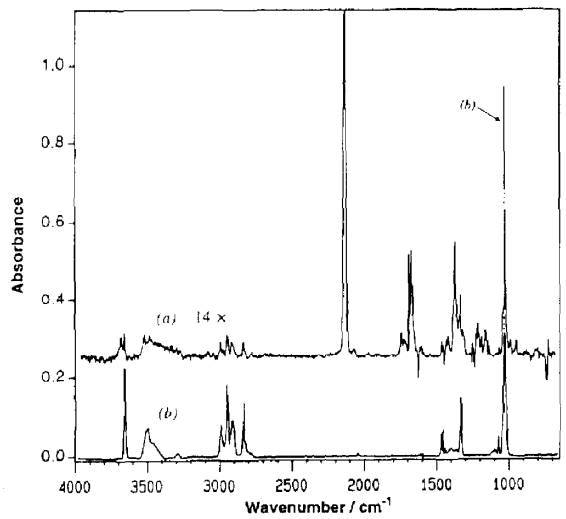

Fig. 11. (a) Argon MI-FT-IR spectrum derived by subtracting the scaled spectrum obtained from the enol of methyl acetoacetate with a transfer-line temperature of 180°C from that obtained with a transfer tube temperature of 250°C. The resulting spectrum contains bands due to the thermolysis products only. (b) Reference MI-FT-IR spectrum of methanol. Note that spectrum (a) has an absorbance-scale expansion of 14 × compared with spectrum (b); and note the overlap of the two spectra at the strong band of methanol at ca. 1020 cm^{-1}.

Likewise, the subtracted spectra obtained from both forms of ethyl acetoacetate are identical, indicating the presence of ethanol. In every case, the remaining bands in the FT-IR spectra are identical, including ketene stretching at 2133–2143 cm^{-1} and carbonyl stretching at 1682–1698 cm^{-1} indicating the formation of keto-ketene (**4**). Band splitting can again be explained in terms of matrix effects.

It should be noted that the analysis of the eluted components by MS did not indicate any differences in spectra between keto and enol forms obtained with both high and low transfer line temperatures. Mixtures of enol decomposition products, the enol itself and, indeed, the keto form would appear to have very similar mass spectra, since the ion fragmentation reactions occurring in the mass spectrometer would include analogues of the thermal fragmentation, or be preceded by thermal decomposition in the ionization source (temperature 250°C).

The foregoing results clearly indicate that the

thermal decomposition of acetoacetates proceeds preferentially via the enol form, as indicated in Fig. 9, with the resulting keto-ketene and alcohol formed. The formation of identical products from the keto acetoacetate indicates that this transformation also progresses via tautomerization to the enol form with subsequent enol degradation.

4. Conclusions

The addition of MI-FT-IR to the available techniques for analysing components eluted from GC columns greatly enhances the ease of identifying the components. In the present study, it was possible to demonstrate the separation of enol and keto forms of both methyl and ethyl acetoacetates.

The MI-FT-IR technique can also give insights into reactions which may occur at various stages of the chromatographic process. At a transferline temperature of 250°C, the enols of methyl and ethyl acetoacetates undergo an efficient thermolysis to yield, in each case, a keto-ketene and an alcohol. This observation gives experimental support to a previously proposed decomposition pathway of acetoacetates. The decompositions were avoided when the temperature in the transfer tube was lowered to 180°C. It is clear that some care must be exercised in choosing temperatures and other parameters in this type of chromatographic study. The inadvertent thermolysis of eluates could lead to anomalous IR spectra being recorded, and indeed this is already found in some of the available reference spectra.

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