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FLUORINE-CONTAINING β-DICARBONYL COMPOUNDS

EFFECT OF NEIGHBORING FLUORINE ATOMS ON THE SPECTRAL PROPERTIES OF β-KETOESTERS, THEIR ENOL ACETATES, AND COPPER CHELATES[1]

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Abstract—The I.R. spectra of ethyl 4,4,4-trifluoroacetoacetate, ethyl 4,4-difluoroacetoacetate and ethyl 4-fluoroacetoacetate, their enol acetates and trifluoroacetates, and their copper chelates are compared with those of ethyl acetoacetate and its corresponding derivatives. The marked influence of neighboring fluorine atoms on the characteristic frequencies associated with such structures is noted. Related data on enol acetates of β-diketones is also presented. The U.V. spectra show only slight changes due to fluorine substitution.

The preparation of the enol acetates and their reduction under catalytic conditions and with complex metal hydrides are described.

INTRODUCTION

THE pronounced effects of electron-withdrawing groups in shifting the position of carbonyl stretching absorption in esters and ketones to higher frequencies has been described by several investigators.[3,4] In particular, the influence of neighboring halogen atoms has been examined in detail.[5,6] Several studies have been reported on the effects on the ester carbonyl frequency of fluorine atoms in close proximity to the carbonyl center.[7–10]

We have now extended this study to γ-fluoro-β-ketoesters, their enol acetates and copper chelates. Related data on fluorine-containing β-diketones have also been obtained.

DISCUSSION AND RESULTS

A. *Preparation of enol acetates of γ-fluoro-β-ketoesters*

Ethyl 4-fluoroacetoacetate[11](II), ethyl 4,4-difluoroacetoacetate,[12] and ethyl 4,4,4-trifluoroacetoacetate[13](III) were prepared by previously described procedures.

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[1] Presented, in part, at the *First International Symposium on Fluorine Chemistry*, Birmingham, England, July 1959.

[2] Abstracted from the Ph.D. thesis of S. M. N., June 1960.

[3] R. S. Rasmussen and R. R. Brattain, *J. Amer. Chem. Soc.* **71**, 1073 (1949).

[4] J. F. Grove and H. A. Willis, *J. Chem. Soc.* 877 (1951).

[5] R. N. Jones, D. A. Ramsay, D. S. Keir and K. Dobriner, *J. Amer. Chem. Soc.* **74**, 80 (1952).

[6] M. L. Josien and R. Calas, *C.R. Acad. Sci., Paris* **240**, 1641 (1955).

[7] D. R. Husted and A. H. Ahlbrecht, *J. Amer. Chem. Soc.* **75**, 1607 (1953).

[8] G. Rappaport, M. Hauptschein, J. F. O'Brien and R. Filler, *J. Amer. Chem. Soc.* **75**, 2695 (1953).

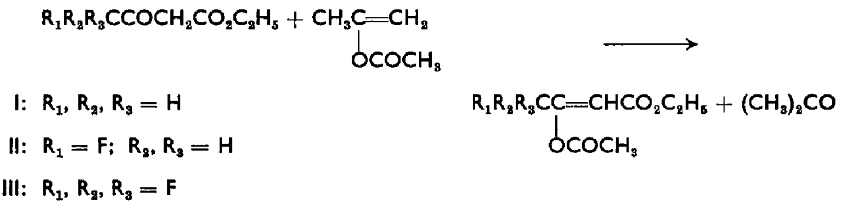
[9] R. Filler, *J. Amer. Chem. Soc.* **76**, 1376 (1954).

[10] E. T. McBee and D. L. Christman, *J. Amer. Chem. Soc.* **77**, 755 (1955).

[11] E. D. Bergmann, S. Cohen and I. Shahak, *J. Chem. Soc.* 3278 (1959).

[12] E. T. McBee, O. R. Pierce, H. W. Kilbourne and E. R. Wilson, *J. Amer. Chem. Soc.* **75**, 3152 (1953).

Ethylacetoacetate (I) and compounds II and III were treated with isopropenyl acetate[14] in the presence of *p*-toluenesulfonic acid to give the corresponding ethyl 3-acetoxycrotonates in 58–70% yields:



$$R_1R_2R_3CCOCH_2CO_2C_2H_5 + \underset{OCOCH_3}{CH_3C{=}CH_2} \longrightarrow \underset{OCOCH_3}{R_1R_2R_3CC{=}CHCO_2C_2H_5} + (CH_3)_2CO$$

I: $R_1, R_2, R_3 = H$

II: $R_1 = F;\ R_2, R_3 = H$

III: $R_1, R_2, R_3 = F$

In analogous fashion the enol acetates of acetylacetone (IV; 45%), 1,1,1-trifluoroacetylacetone[15] (V; 50%) and 1,1,1,5,5,5-hexafluoroacetylacetone[15] (VI; 30%) were obtained in the yields indicated. The enol esters of V and especially of VI were unstable and slowly decomposed on standing at room temperature.

Whereas IV and VI are symmetrical and form only one enol ester, compound V could potentially form two isomers. Indeed, the I.R. spectrum of the product gave evidence of the presence of both isomers, but they could not be readily separated.

For the preparation of enol trifluoroacetates, the copper chelates of I and III[16] were treated with trifluoroacetic anhydride in dioxane. The products, isolated in 40–42% yield, were quite unstable and their identities were inferred from I.R. spectral examination.

B. *Reduction of enol acetates*

The reduction of enol acetates of I and III (compounds VII and VIII) was studied under catalytic conditions and with complex metal hydrides.

In the presence of platinum oxide or palladium on charcoal, both hydrogenation and hydrogenolysis (alkyl-oxygen cleavage) occurred to give the saturated ethyl esters,[17] in 56% and 40% yields, respectively.

When compound VIII was treated with sodium borohydride in 95% ethanol, solvolysis occurred, the carbethoxy group, as expected, remained intact, and compound III was isolated in 50% yield. No products of reduction could be detected.[19]

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[13] F. Swarts, *Bull. Acad. Belg. Cl. Sci.* (5) **12**, 692 (1926). This material was also purchased from Columbia Organic Chemicals Co., Inc., Columbia, South Carolina, and carefully fractionated before use.

[14] R. B. Moffett and D. I. Weisblat, *J. Amer. Chem. Soc.* **74**, 2183 (1952); H. J. Hagemeyer and D. C. Hull, *Industr. Engng. Chem.* (*Industr.*) **41**, 2920 (1949).

[15] Obtained from Columbia Organic Chemicals Co., Columbia, S.C., and used without further purification.

[16] A. L. Henne, M. S. Newman, L. L. Quill and R. A. Staniforth, *J. Amer. Chem. Soc.* **69**, 1819 (1947).

[17] It is of interest that ethyl 4,4,4-trifluorobutyrate, obtained earlier by another method,[18] is more readily prepared by our approach. This is an excellent route to less accessible substituted butyrate esters when the requisite β-ketoesters are available.

[18] E. T. McBee, O. R. Pierce and D. D. Smith, *J. Amer. Chem. Soc.* **76**, 3722 (1954).

[19] In the steroid series, sodium borohydride reduces enol acetates to saturated alcohol functions, i.e. $>C{=}C{-}OAc \rightarrow >CH{-}CHOH{-}$, presumably by reduction of the ketone formed on solvolysis and subsequent tautomerization. Thus, Δ^4-cholesten-3-one enol acetate was converted to cholesterol in 70–85% yield; see e.g., B. Belleau and T. F. Gallagher, *J. Amer. Chem. Soc.* **73**, 4458 (1951) and W. G. Dauben and J. F. Eastham, *J. Amer. Chem. Soc.* **73**, 4463 (1951).

Both VII and VIII were reduced to the corresponding 1,3-diols in poor yield by lithium aluminium hydride.

C. *Infrared studies*

1. *β-Ketoesters.* The I.R. spectra of the fluorine-containing β-ketoesters, measured in carbon tetrachloride, were compared with the spectrum of ethyl acetoacetate. The significant absorption bands are listed in Table 1.

TABLE 1. INFRARED ABSORPTION FREQUENCIES OF β-KETOESTERS IN CM^{-1}
($R = CH_2COOC_2H_5$)

	CH_3COR	FCH_2COR	F_2CHCOR	CF_3COR
OH (free) or O—H—F (?)			3565 (w)	3565 (vw)
O—H—O			3125 (w)	3400 (w–m, broad)
Keto C═O	1715 (s)	1730 (s)	1765 (m)	1775 (w)
Ester C═O	1740 (s)	1745 (s)	1745 (m)	1750 (w–m)
Ester C═O (conjugated)			1720 (vw)	1720 (s)
Ester C═O "Conjugate chelation"	1650 (m)	1660 (s)	1675 (vs)	1680 (vs)
C═C	1635 (m)	1635 (m—s)		
"Free" C—F linkage				1025 (s)
H-bonded C—F				980 (m–s)

Our data for ethyl acetoacetate is in complete agreement with the assignments given by Rasmussen and Brattain.[3] The spectrum of the trifluoro analog (III) is somewhat more detailed. Belford *et al.*[20] reported three well defined carbonyl absorption frequencies for the latter compound, measured as a thin film. The highest frequency, at 1650 cm^{-1}, was assigned to the ester carbonyl group and the next lower frequency (1608 cm^{-1}) to the keto carbonyl stretching vibration. The band at 1545 cm^{-1} was attributed to the hydrogen-bonded chelate form of the ester. These assignments were made by comparison with ethyl acetoacetate by assuming the electron-attracting influence of the CF_3 group on *both* the keto and ester carbonyls to be of similar magnitude. No consideration was given to the proximity of the CF_3 group to the respective carbonyl functions. Moreover, the very marked shift to *lower frequencies* relative to the non-fluorinated analog is in direct contradiction to all existing data on fluorinated esters and ketones.[7–10,21] Joullie *et al.*[22] also reported I.R. data for compound III. Her results (1742 cm^{-1} (m), keto $>$ C═O; 1718 cm^{-1} (m), ester $>$ C═O; 1680 cm^{-1} (vs), ester $>$ C═O, "conjugate chelation") are in general accord with what one would expect from the influence of the CF_3 group, insofar as the shift in direction is concerned. However, these results also do not fully elucidate the salient features of this compound, since the spectrum was not sufficiently resolved.

It will be noted in Table 1 and in Fig. 1 that compound III exhibits weak absorption at 1775 cm^{-1}, which we ascribe to the keto carbonyl flanked by a trifluoromethyl group. This shift of about 60 cm^{-1} to higher frequencies is supported by considerable data for perfluoroalkyl ketones.[21,23,24] That this band is weak is consistent with the

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[20] R. L. Belford, A. E. Martell and M. Calvin, *J. Inorg. Nucl. Chem.* **2**, 11 (1956).

[21] R. N. Haszeldine, *Nature, Lond.* **168**, 1028 (1951).

[22] M. M. Joullie, S. Nasfay and L. Rypstat, *J. Org. Chem.* **21**, 1358 (1956).

[23] J. D. Park, R. E. Noble and J. R. Lacher, *J. Org. Chem.* **23**, 1396 (1958).

[24] D. A. Rausch, L. E. Coleman, Jr. and A. M. Lovelace, *J. Amer. Chem. Soc.* **79**, 4983 (1957),

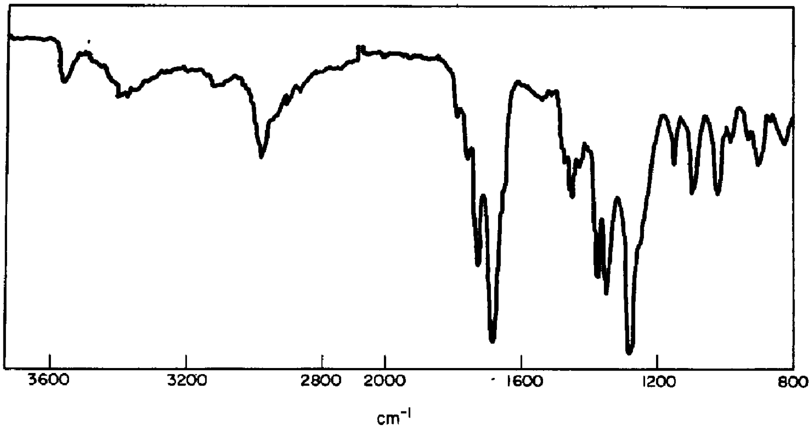


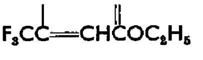
FIG. 1. Infrared absorption spectrum of ethyl 4,4,4-trifluoroacetoacetate in CCl_4.

low keto content (11% pure liquid) of this compound which we have previously determined[25] by proton magnetic resonance spectroscopy. The ester frequency would not be expected to differ appreciably from that of ethyl acetoacetate, since the CF_3 group is sufficiently removed and should not exert any marked influence by an inductive effect. Due to the high enol content of III, this saturated ester carbonyl should exhibit weak absorption. The 1750 cm^{-1} band is thus assigned to this ester carbonyl stretching vibration.

Of much greater significance in this system should be the contribution of the α,β-unsaturated carbonyl moiety of the enol tautomer. There has been ample demonstration that conjugation shifts carbonyl absorption to lower frequencies.[3,9,26,27] Thus, the strong band at 1720 cm^{-1} is attributed to the conjugated ester carbonyl and further support is found by our observation that the structurally similar ethyl 4,4,4-trifluorocrotonate[18] also possesses a strong band near this frequency.

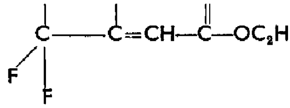
The very strong absorption at 1680 cm^{-1} is undoubtedly due to "conjugate chelation" of the ester carbonyl (A) and supports Joullie's assignment.

The presence of *two* weak absorptions in the —OH stretching region of our spectrum of III was of some concern. We now believe, however, that the broad band near 3400 cm^{-1} is due to the intramolecularly bonded —OH group (A) and the absorption at 3565 cm^{-1} may be assigned to a "free" hydroxyl group which could exhibit weak —OH—F bonding (B).



$$F_3C\overset{O-H-O}{C{=}CH\,C}OC_2H_5$$

A



B

The quasi five-membered ring in B would, of course, be less stable than the six-membered ring in A. Possible evidence for H—F bonding is suggested by the presence

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[25] R. Filler and S. M. Naqvi, *J. Org. Chem.* **26**, 2571 (1961).

[26] H. W. Thompson and P. Torkington, *J. Chem. Soc.* 640 (1945).

[27] R. N. Jones, P. Humphries and K. Dobriner, *J. Amer. Chem. Soc.* **72**, 956 (1950).

of a band at 980 cm^{-1}, in addition to the strong "free" C—F stretching frequency at 1025 cm^{-1}. The former band is in the range assigned to hydrogen-bonded C—F linkages.[28]

The spectrum of ethyl 4,4-difluoroacetoacetate is qualitatively similar to that of III, although the —OH and conjugated ester carbonyl absorptions are very weak. Ethyl 4-fluoroacetoacetate (Fig. 2), on the other hand, closely resembles ethyl acetoacetate. The effect of a single fluorine atom is noticeable for the keto carbonyl, but the magnitude is comparatively small.

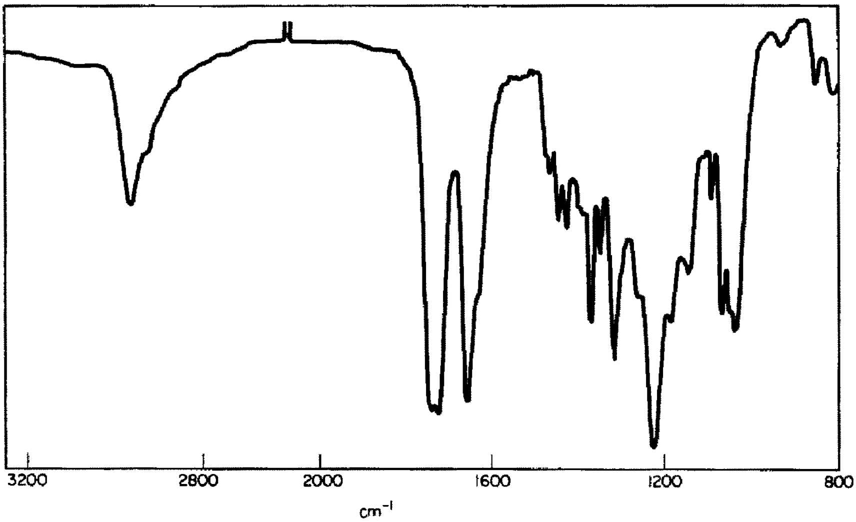

FIG. 2. Infrared absorption spectrum of ethyl-4-fluoroacetoacetate in CCl_4.

Drs. Belford and Martell have suggested that the discrepancies between their data and ours for compound III may be due to their use of the pure liquid rather than a solution of III in CCl_4. To settle this point, we examined this compound as a thin film and observed no significant change in the carbonyl region from that found in CCl_4 solution.

2. *Enol acetates of β-ketoesters.* The enol acetate structure eliminates the possibility of both "conjugate chelation" and hydrogen bonding and creates a stable α,β-unsaturated carbonyl system. This simplifies the spectrum, although a new vinyl ester band appears at the expected higher frequencies.[29] The data for these compounds are summarized in Table 2 and Figs. 3 and 4.

Ethyl 3-acetoxycrotonate exhibits the vinyl ester band at 1760 cm^{-1}, the conjugated ester at 1715 cm^{-1} and $>C{=}C<$ absorption at 1660 cm^{-1}. In ethyl-3-acetoxy-4,4,4-trifluorocrotonate, the electronic field effect of a CF_3 group on the α-carbon of the alcohol portion should independently enhance the vinyl ester frequency by about 25–30 cm^{-1},[8,9] and the strong band at 1795 cm^{-1} is therefore assigned to this ester function. The conjugated ester carbonyl at 1725 cm^{-1} is consistent with that observed for compound III. The anticipated marked shifts due to trifluoromethyl

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[28] E. D. Bergmann, A. Kalmus and S. Pinchas *J. Chem. Soc.* 1519 (1956).

[29] See, e.g., E. J. Hartwell, R. E. Richards and H. W. Thompson, *J. Chem. Soc.* 1436 (1948).

TABLE 2. INFRARED ABSORPTION FREQUENCIES OF ENOL ACETATES OF β-KETOESTERS IN CM^{-1}

	A	B	C	D	E
Vinyl ester C=O	1760 (s)	1795 (s)	1780 (s)	1785 (s)	1790 (s)
Conjugated ester C=O	1715 (s)	1725 (s)	1720 (s)	1715 (m–s)	1737 (m)
C=C	1660 (m)	1675 (w–m)	1678 (m)	1650 (w)	—

A = Ethyl-3-acetoxycrotonate
B = Ethyl-3-acetoxy-4,4,4-trifluorocrotonate
C = Ethyl-3-acetoxy-4-fluorocrotonate
D = Ethyl-3-trifluoroacetoxycrotonate
E = Ethyl-3-trifluoroacetoxy-4,4,4-trifluorocrotonate

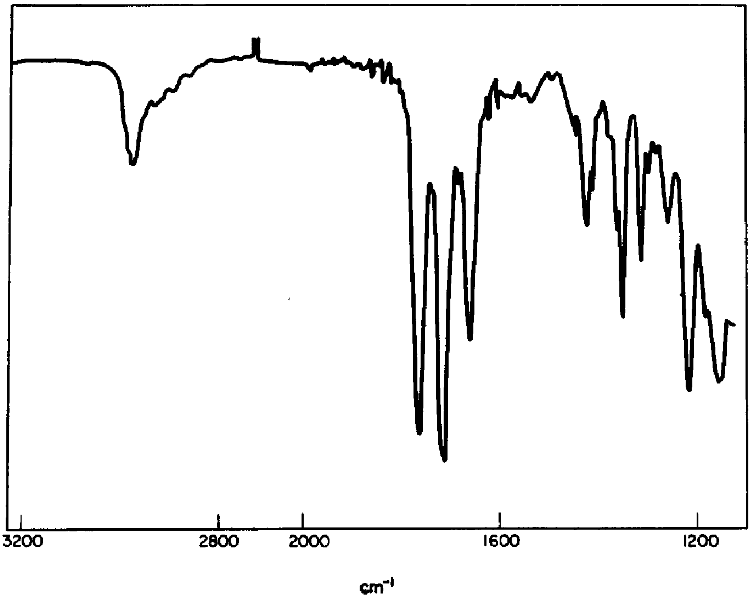
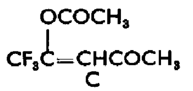


FIG. 3. Infrared absorption spectrum of ethyl 3-acetoxycrotonate in CCl_4.

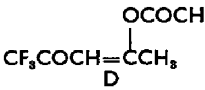
substitution in the acid portion of the enol trifluoroacetate of I and the combined influence of CF_3 substitution in both acid and alcohol portions of ethyl 3-trifluoroacetoxy-4,4,4-trifluorocrotonate, are only partially reflected by the absorptions at 1785 cm^{-1} and 1790 cm^{-1}, respectively.

3. *Enol acetates of β-diketones.* The data for the enol esters of acetylacetone and trifluoroacetylacetone (V) are given in Table 3. The enol acetate of V merits comment. Two structures (C and D) are possible:



$$CF_3\overset{\displaystyle OCOCH_3}{\overset{|}{C}}{=}CHCOCH_3$$

C



$$CF_3COCH{=}\overset{\displaystyle OCOCH_3}{\overset{|}{C}}CH_3$$

D

Previous considerations lead us to attribute the bands at 1798 cm^{-1} and 1709 cm^{-1} to the $CH_3COO\underset{\underset{\displaystyle CF_3}{|}}{C}{=}C<$ grouping and the conjugated keto carbonyl in C, respectively.

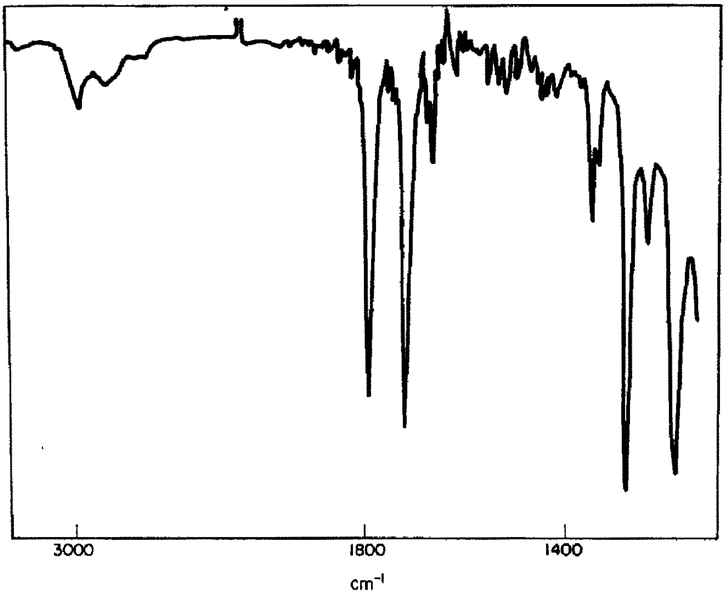
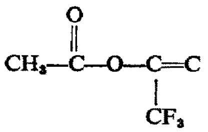
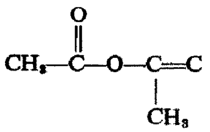
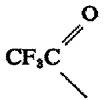


FIG. 4. Infrared absorption spectrum of ethyl 3-acetoxy-4,4,4-trifluoroacetoacetate in CCl_4.

TABLE 3. INFRARED ABSORPTION FREQUENCIES OF ENOL ACETATES OF β-DIKETONES IN CM^{-1}

	Enol acetate of acetylacetone[80]	Enol acetate of trifluoroacetylacetone
Vinyl ester C=O	1762 (s)	1798 (s)  $CH_3-\overset{\overset{O}{\parallel}}{C}-O-\underset{\underset{CF_3}{\vert}}{C}=C$
		1754 (s)  $CH_3-\overset{\overset{O}{\parallel}}{C}-O-\underset{\underset{CH_3}{\vert}}{C}=C$ or  $CF_3C{=}O$
Conjugated keto C=O	1696 (s)	1709 (s)
C=C	1670 (w)	1632 (w)

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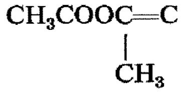
[80] The data for acetylacetone are in excellent agreement with previously published results: R. S. Rasmussen, D. D. Tunnicliff, and R. R. Brattain, *J. Amer. Chem. Soc.* **71**, 1068 (1949).

In the latter assignment, both the trifluoromethyl and acetoxy groups essentially counteract the frequency-decreasing effect of conjugation. The strong absorption at 1754 cm^{-1} is best assigned to the  $\mathrm{CH_3COO}\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{C}}}{=}\mathrm{C} <$ moiety in D. However, it is also possible that this is an unresolved band which includes the keto carbonyl group from the $\mathrm{CF_3COCH{=}C} <$ contribution to D. Although we lack sufficient models for structural correlation, it has been reported[24] that a related compound, $\mathrm{C_3F_7COCH{=}CHCH_3}$, exhibits absorption at 1730 cm^{-1}. We are unable, at present, to make a suitable assignment for the band at 1824 cm^{-1}.

4. *Copper chelates.* The data for the copper chelates of I and III (KBr pellet) are in essential agreement with those previously reported.[20] The double chelated bands (ester and ketonic) at about 100–150 cm^{-1} lower than those of the ligand reflect the enhanced single bond character of the carbonyl groups in the conjugated chelate ring. The shift to higher frequencies for the perturbed (chelated) keto carbonyl in III relative to I emphasizes the electron-attracting influence of the $\mathrm{CF_3}$ group, which leads to a decreased interaction of the metal with the keto carbonyl and consequent decrease in chelate stability and increased double bond character.

D. *Ultraviolet studies*

Calvin *et al.*[20] measured the U.V. spectra of β-diketones and β-ketoesters in chloroform and reported maxima <246 mμ for both compounds I and III. We examined the β-ketoesters in 2,2,4-trimethylpentane as solvent and found the maxima to lie in the range 234–244 mμ, with absorption occurring at shorter wavelengths with increased fluorine substitution (Table 4). This slight but distinct hypsochromic shift is in contrast to the findings of Calvin with β-diketones,[20,31,32] in which trifluoromethyl substitution caused a slight bathochromic shift. The nature of the solvent likely plays a significant role in these divergent observations.

The absorption is due to the presence of the α,β-unsaturated ester chromophore of the enolic forms of the β-ketoesters. Since α,β-unsaturated esters normally absorb near 210 mμ,[33] the bathochromic shift must be associated with the β-hydroxyl group. The relative amount of enolic tautomer, which is stabilized by intramolecular hydrogen-bonding, should be enhanced in the non-polar solvent. The role of the hydroxyl as an

TABLE 4. ULTRAVIOLET SPECTRAL DATA FOR β-KETOESTERS
(solvent: 2,2,4-trimethylpentane)

Compound	λ_{max}(mμ)
$\mathrm{CH_3COCH_2CO_2C_2H_5}$	244
$\mathrm{CH_2FCOCH_2CO_2C_2H_5}$	238
$\mathrm{CHF_2COCH_2CO_2C_2H_5}$	236
$\mathrm{CF_3COCH_2CO_2C_2H_5}$	234
$\mathrm{CH_3C(OAc){=}CHCO_2C_2H_5}$	215
$\mathrm{CF_3C(OAc){=}CHCO_2C_2H_5}$	212

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[31] A. E. Martell, R. L. Belford and M. Calvin, *J. Inorg. Nucl. Chem.* **5**, 170 (1958).

[32] R. L. Belford, A. E. Martell and M. Calvin, *J. Inorg. Nucl. Chem.* **14**, 169 (1960).

[33] J. Cason, N. L. Allinger and G. Sumrell, *J. Org. Chem.* **18**, 850 (1953).

auxochromic group is demonstrated by the shift of the maxima to the 212–215 mμ region after acetylation.

Our observations on the effect of fluorine substitution on the spectra of the copper chelates of β-ketoesters differ from those previously reported[20] only with regard to the principal absorption of the chelate of ethyl acetoacetate. The spectra were measured in ethanol and chloroform and the results are summarized in Table 5. The expected blue shift is noted as one changes to a less polar solvent. Belford *et al.*[20] reported 254 mμ (shoulder 281 mμ) for the chelate of I, in chloroform. Belford and Yeranos have now verified our result for the Cu(II) chelate of I (private communication).

TABLE 5. ULTRAVIOLET SPECTRA OF COPPER (II) CHELATES OF β-KETOESTERS ($RCOCH_2CO_2C_2H_5$)

R (Ligand)	$\lambda_{max}(C_2H_5OH)$	$\lambda_{max}(CHCl_3)$
	mμ	mμ
CH_3	297 (shoulder, 339)	278 (shoulder, 259)
CH_2F	295	277
CHF_2	296	276
CF_3	298	276

EXPERIMENTAL[34]

Ethyl 4,4,4-trifluoroacetoacetate. This compound was prepared from ethyl trifluoroacetate and ethyl acetate according to a previously described procedure;[18] 2,4-dinitrophenylhydrazone, pale yellow needles (ethanol), m.p. 103·5–105°. (Found: N, 15·22, copper chelate, green (ethanol), m.p. 193–194° (lit.[16] 189°). Calc. for $C_{12}H_{11}F_3N_4O_6$: N, 15·38%).

Ethyl 4,4-difluoroacetoacetate. This compound was prepared in 55% yield according to a previously described procedure;[16] 2,4-dinitrophenylhydrazone, yellow crystals, m.p. 90·7–91·7°. (Found; N, 15·99; copper chelate, blue green (ethanol), m.p. 185–187°, (lit.[16] 183–184°). Calc. for $C_{12}H_{12}F_2N_4O_6$: N, 16·18%).

Ethyl 4-fluoroacetoacetate. This compound was prepared by the method of Pattison *et al.*[35] Its proton magnetic resonance spectrum and gas chromatogram revealed the presence of a significant amount of impurity, possibly ethyl acetate.

An alternate procedure described by Bergmann *et al.*,[11] gave the desired product, b.p. 68–70°/6 mm, n_D^{25} 1·4180, in 45% yield, free of impurities; 2,4-dinitrophenylhydrazone, m.p. 91–91·5°; copper chelate, blue green (ethanol), m.p. 175·5–176·5°.

Ethyl acetoacetate. Eastman, White Label, was distilled before use; copper chelate, m.p. 193° decompn. (lit.[20] 193° decom).

Preparation of enol acetates

Ethyl 3-acetoxycrotonate. Fifty g (0·385 mole) ethyl acetoacetate, 115 g (1·15 moles) isopropenyl acetate and 1·5 g *p*-toluenesulfonic acid were refluxed gently. As the reaction proceeded, the acetone produced was removed from the flask by using a modified Dean and Stark apparatus. After completion of the reaction, the mixture was cooled and filtered to remove solid *p*-toluenesulfonic acid, washed with cold water and dried. Isopropenyl acetate was distilled and the product was collected between 95–100°/15 mm, as a colorless liquid, yield 40·4 g (61%), n_D^{25} 1·4406 (lit.[36] b.p. 98°/12 mm).

Ethyl 3-acetoxy-4,4,4-trifluorocrotonate. Forty g (0·216 mole) ethyl 4,4,4-trifluoroacetoacetate, 50 g (0·50 mole) isopropenyl acetate and 1·5 g *p*-toluenesulfonic acid were treated in a manner similar

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[34] All m.p.'s are corrected and b.p.'s uncorrected.

[35] R. R. Fraser, J. E. Millington and F. L. M. Pattison, *J. Amer. Chem. Soc.* **79**, 1959 (1957).

[36] C. E. Dalgliesh, A. W. Johnson and C. Buchanan, *Chemistry of Carbon Compounds* (Edited by E. M. Rodd) Vol. IB, Elsevier, New York, N.Y. p. 877 (1952).

to that described above. The main fraction boiled at 84·5–85·5°/30 mm, n_D^{25} 1·3870, yield 28·2 g (58%). (Found: C, 42·44; H, 4·04; Calc. for $C_8H_9F_3O_4$: C, 42·48; H, 4·01%).

Ethyl 3-*acetoxy*-4-*fluorocrotonate*. Twenty grams (0·135 mole) ethyl 4-fluoroacetoacetate, 76·5 g (0·67 mole) isopropenyl acetate and 1 g *p*-toluenesulfonic acid were treated as above. The product distilled at 55–57°/0·5 mm, n_D^{25} 1·4310, yield 17 g (70%). (Found: C, 50·34; H, 5·94; Calc. for $C_8H_{11}FO_4$: C, 50·52; H, 5·83%).

Ethyl 3-*trifluoroacetoxycrotonate*.[37] Trifluoroacetic anhydride, 16·8 g (0·08 mole) was added slowly to a solution of 14 g (0·04 mole) copper chelate of ethyl acetoacetate, dissolved in 200 ml dioxane, to produce an exothermic reaction. The sides of the flask were scratched and left overnight. Deep blue crystals of copper trifluoroacetate were deposited. The solution was filtered and the solvent removed to give 7 g (40%) of the desired product, distilling at 52–52·5°/5·5 mm, n_D^{25} 1·3748. The liquid turned yellow on standing and gave off a pungent odor. A satisfactory elemental analysis could not be obtained due to the unstable nature of the product.

Ethyl 3-*trifluoroacetoxy*-4,4,4-*trifluorocrotonate*. Trifluoroacetic anhydride and the copper chelate of ethyl 4,4,4-trifluoroacetoacetate were treated as in the previous experiment to give a 42% yield of product, b.p. 57–58°/5·5 mm, n_D^{25} 1·3528. The liquid turned yellow on standing and failed to give a satisfactory elemental analysis.

Enol acetate of acetylacetone. Twenty-five grams (0·25 mole) acetylacetone, 150 g (1·5 moles) isopropenyl acetate and 1 g *p*-toluenesulfonic acid were refluxed and treated as in the previous experiments. The main fraction was collected as a colorless liquid between 78–80°/6·5 mm, n_D^{25} 1·4490. It turned yellow on standing, yield 16 g (45%) (lit.[37] b.p. 79°/11 mm). (Found: C, 58·96; H, 7·13; Calc. for $C_7H_{10}O_3$: C, 59·14; H, 7·09%). 2,4-Dinitrophenylhydrazone, green-red crystals, recrystallized from ethanol, m.p. 181–182° (lit.[38] m.p. 122°). (Found: N, 17·07; Calc. for $C_{13}H_{14}N_4O_6$: N, 17·38%).

Enol acetate of trifluoroacetylacetone. Twenty-five grams (0·16 mole) trifluoroacetylacetone, 100 g (1·0 mole) isopropenyl acetate and 1 g *p*-toluenesulfonic acid were heated under reflux and treated as described previously. The product was collected between 48–50°/6·5 mm, n_D^{25} 1·3880, yield 15·8 g (50%). It was unstable, became yellow on standing, and gave off a pungent odor.

2,4-Dinitrophenylhydrazone, yellow fluffy precipitate, recrystallized from ethanol, mp 153–155°. (Found: N, 15·35; Calc. for $C_{13}H_{11}F_3N_4O_6$: N, 14·89%).

Enol acetate of hexafluoroacetylacetone. Twenty-five grams (0·12 mole) hexafluoroacetylacetone, 72 g (0·72 mole) isopropenyl acetate and 1 g *p*-toluenesulfonic acid were heated under reflux to give 9 g (30%) enol acetate, b.p. 108–110°. The product appeared to be very unstable. Unreacted diketone was also recovered.

Reduction of ethyl 3-*acetoxycrotonate*. Forty grams (0·23 mole) enol acetate in 50 ml glacial acetic acid were reduced in the presence of 1 g PtO_2. The mixture was cooled and filtered, about 50 ml water added, and the mixture extracted with ether. The ether extracts were combined, passed through solid sodium bicarbonate, dried (Na_2SO_4), the solvent removed, and the product, ethyl butyrate, collected between 119–121°, n_D^{25} 1·3890, yield 15 g (56%). The yield was very poor when ethanol was used as solvent.

Forty grams enol acetate, with 1·5 g 10% Pd/C, were reduced in 50 ml glacial acetic acid. Ethyl butyrate was collected between 118–121°, yield 14·3 g (53%). In this case also, the yield was poor when ethanol was used as solvent.

Reduction of ethyl 3-*acetoxy*-4,4,4-*trifluorocrotonate*. Forty grams (0·18 mole) enol acetate were reduced in 50 ml glacial acetic acid in the presence of 2 g PtO_2. The main fraction, ethyl 4,4,4-trifluorobutyrate, distilled between 124–126°, n_D^{25} 1·3499, yield 10·9 g (36%) (lit.[18] b.p. 126·5–127·0°; n_D^{20} 1·3520). Benzylamide, m.p. 98–100° (lit.[39] m.p. 100·5–101°).

Forty grams enol acetate were reduced in 50 ml glacial acetic acid in the presence of 2 g 10% Pd/C to give 12 g (40%) ethyl 4,4,4-trifluorobutyrate.

Reaction of ethyl 3-*acetoxy*-4,4,4-*trifluorocrotonate with sodium borohydride*. Twenty-seven grams (0·12 mole) ester in 50 ml 95% ethanol were cooled to 5°. Sodium borohydride (3·6 g, 0·1 mole) in 30 ml 70% ethanol was added dropwise, the temp being maintained at 5°. The mixture was stirred for 6 hr after all of the sodium borohydride solution had been added. The residual yellow solid was

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[37] This method was suggested by Professor F. Weygand, Technische Hochschule, Munich, Germany.

[38] J. A. Spence and E. F. Degering, *J. Amer. Chem. Soc.* **66**, 1624 (1944).

[39] E. T. McBee, A. E. Kelley and E. Rapkin, *J. Amer. Chem. Soc.* **72**, 5071 (1950).

dissolved in 5% hydrochloric acid, the lower layer was separated and the upper layer extracted with ether and the ether layers combined. The combined fractions were neutralized with sodium bicarbonate, dried and distilled. The main fraction, ethyl 4,4,4-trifluoroacetoacetate, was collected between 44–46°/30 mm, n_D^{25} 1·3738, yield 11 g (50%).

Copper chelate, m.p. 193–194° (ethanol); 2,4-Dinitrophenylhydrazone, m.p. 103–104° (ethanol).

Reduction of ethyl 3-*acetoxycrotonate with lithium aluminium hydride.* Thirty-four grams (0·9 mole) lithium aluminium hydride were dissolved in 250 ml anhydrous ether. The suspension was chilled and 30 g (0·17 mole) ethyl 3-acetoxycrotonate, dissolved in an equal volume of ether, were added dropwise during 48 hr. The mixture was stirred for an additional period of 12 hr. Excess hydride was destroyed with water, the mixture dissolved in 15% sulfuric acid, filtered, and the aqueous layer subjected to continuous extraction with ether for about a week. The ether extract was dried and the solvent removed. A poor yield of 1,3-butanediol, b.p. 205°, was obtained. The I.R. spectrum showed a very intense broad hydroxyl band but no carbonyl absorption.

Reduction of ethyl 3-*acetoxy*-4,4,4-*trifluorocrotonate with lithium aluminium hydride.* Thirty grams (0·13 mole) ethyl 3-acetoxy-4,4,4-trifluorocrotonate in 40 ml ether were added dropwise to a suspension of 15·2 g (0·4 mole) lithium aluminium hydride in 250 ml anhydrous ether. The same procedure as above was followed. The product, which appeared to be 4,4,4-trifluoro-1,3-butanediol, was obtained in poor yield.

Microanalyses were conducted by Micro-Tech Laboratories, Skokie, Illinois. I.R. spectra were obtained on a Perkin-Elmer Model 21 double-beam spectrophotometer using sodium chloride optics and CCl_4 as solvent. KBr pellets were used with the copper chelates. Polystyrene was used to calibrate the instrument. Ultraviolet spectra were measured with a Beckman DK-2 Recording Spectrophotometer.