670. *Organic Fluorine Compounds. Part XXI.* α-Fluorinated Keto-compounds.*

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Alkyl or aryl fluoromethyl ketones are obtained from Grignard reagents and fluoroacetonitrile. 1,3-Difluoroacetone also reacts normally with phenylmagnesium bromide; fluoroacetone gives phenylacetone. Their Reformatzky reactions proceed normally.

Other reactions of these fluoro-ketones and fluorinated β-keto-esters have been studied, amongst them the reaction with keten.

For the preparation of fluoro- and difluoro-acetone, methods have been described [1,2] and were improved by Cherbuliez *et al.*[3] Direct replacement of chlorine by fluorine in α-chloro-ketones has been found possible also in the case of 2-chlorobutan-3-one, which gave a 55% yield of 3-fluorobutan-2-one. The ketals derived from α-chlorinated ketones did not exchange the chlorine for fluorine under the usual operating conditions, though bromoacetaldehyde diethyl acetal gave a 9% yield of fluoroacetaldehyde diethyl acetal.

In view of the somewhat abnormal behaviour of ethyl fluoroacetate [4] and fluoroacetone (see below), it is noteworthy that fluoroacetonitrile behaves normally towards Grignard reagents, giving alkyl or aryl fluoromethyl ketones in 25—80% yield. This seems the more surprising as aliphatic nitriles are often enolised by aliphatic organomagnesium compounds and do not yield ketones with them; [5] fluorine appears thus to depress the tendency to enolisation here as in other cases [6] (see below).

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* Part XX, preceding paper.

[1] Kitano and Fukui, *Kogyo Kagaku Zasshi*, 1956, **59**, 395; *Chem. Abs.*, 1957, **51**, 11,282.

[2] Bergmann and Cohen, *J.*, 1958, 2259.

[3] Cherbuliez, de Picciotto, and Rabinowitz, *Helv. Chim. Acta*, 1960, **43**, 1143.

[4] Mirosevic-Sorgo and Saunders, *Tetrahedron*, 1959, **5**, 38.

[5] Bruylants, *Bull. Classe Sci., Acad. roy. Belg.*, 1922, **8**, 7; Mignonac and Hoffmann, *Compt. rend.*, 1930, **191**, 718.

[6] Blank, Mager, and Bergmann, *J.*, 1955, 2190.

Fuoroacetone and 1,3-difluoroacetone show to a large extent the normal reactivity of ketones, which appears to be only slightly modified by the fluorine atom. Similar observations have been recorded for more highly fluorinated ketones by Simmons and Wiley.[7]

Whilst 1,3-difluoroacetone, under defined conditions, reacts normally with phenylmagnesium bromide, giving 1,3-difluoro-2-phenylpropan-2-ol in 72% yield, fluoroacetone loses its fluorine under these conditions, and phenylacetone is obtained, probably by dehydrohalogenation and rearrangement of the primary product $CH_2F\cdot CPhMe\cdot OH$. Analogous reactions have been observed for chloroacetone [8] and ω-fluoroacetophenone.[9]

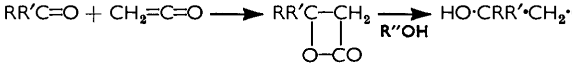
Condensation of fluoroacetone with ethyl cyanoacetate in the presence of ammonium acetate [10] yields, with spontaneous dehydration, ethyl α-cyano-γ-fluoro-β-methylcrotonate; on the other hand, attempts to dehydrate the hydroxy-esters obtained in the Reformatzky reaction of ethyl bromoacetate with fluoroacetone and 1,3-difluoroacetone gave no defined product, a behaviour which recalls that of other α-fluoro-hydroxy-compounds [11] and indicates that the C–OH bond in such compounds is strengthened. An attempt has also been made to condense the two ketones with ethyl chlorofluoroacetate,[12] as the latter compound has been shown to participate in this type of condensation: [13,14] the attempt failed, although acetone reacted smoothly with the chlorofluoro-ester (in the presence of magnesium), giving a 20% yield of ethyl α-fluoro-β-hydroxy-β-methylbutyrate which again could not be dehydrated without complete resinification. Another route to this ester is described in the following paper.

Condensation of 1,3-difluoroacetone with malonic acid in the presence of pyridine and piperidine gave a 40% yield of γ-fluoro-β-fluoromethyl-β-hydroxybutyric acid; in this case, also, the condensation was not accompanied by dehydration.[14a]

Fluoroacetone is attacked by elemental bromine preferentially at the methylene group, as proved by oxidation of the corresponding acid without loss of halogen. Greater reactivity of the methylene than of the methyl group in fluoroacetone is found also in reaction with formaldehyde which will be discussed later.

The influence of two fluorine atoms on the reactivity of the carbonyl group permits condensation of 1,3-difluoroacetone with dimethyl phosphite in the presence of sodium methoxide to give the ester $(CH_2F)_2C(OH)\cdot PO(OMe)_2$; analogously, ethyl γγγ-trifluoroacetoacetate gives the phosphonate $EtO_2C\cdot CH_2\cdot C(CF_3)(OH)\cdot PO(OMe)_2$.

For a more detailed study of fluorinated β-hydroxy-acids the reaction of various fluorinated keto-compounds with keten was studied, zinc chloride being used as catalyst. According to Hagemeyer,[15] the following general reaction was expected:



$$RR'C{=}O + CH_2{=}C{=}O \longrightarrow \underset{O-CO}{RR'C-CH_2} \xrightarrow[R''OH]{} HO\cdot CRR'\cdot CH_2\cdot CO_2R''$$

However, from ethyl γ-fluoroacetoacetate and ethyl γγγ-trifluoroacetoacetate only the enol acetates could be isolated under these conditions, and ethyl acetoacetate itself gave the same result. On the other hand, ethyl α-fluoroacetoacetate gives the expected product

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[7] Simmons and Wiley, *J. Amer. Chem. Soc.*, 1960, **82**, 2288.

[8] Tiffeneau, *Ann. Chim.* (*France*), 1913, **10**, 369.

[9] Bergmann and Kalmus, *J. Amer. Chem. Soc.*, 1954, **76**, 4137; cf. Ando, *Chem. Abs.*, 1960, **54**, 4492.

[10] Cope, Hofmann, Wyckoff, and Hardenbergh, *J. Amer. Chem. Soc.*, 1941, **63**, 3452; Whyte and Cope, *ibid.*, 1943, **65**, 1999; cf. Schnider and Hellerbach, *Helv. Chim. Acta*, 1950, **33**, 1437; Cragoe, Robb, and Sprague, *J. Org. Chem.*, 1950, **15**, 381.

[11] See, for literature, Bergmann, Moses, Neeman, Cohen, Kaluszyner, and Reuter, *J. Amer. Chem. Soc.*, 1957, **79**, 4174.

[12] Cf. McBee, Birmingham Symposium on Fluorine Chemistry, Butterworths, London, p. 44.

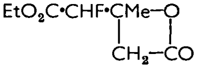
[13] Bergmann, Cohen, and Shahak, *J.*, 1959, 3278.

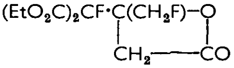
[14] McBee, Pierce, and Christman, *J. Amer. Chem. Soc.*, 1955, **77**, 1581.

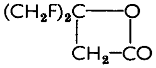
[14a] Cf. Knunjants, Chen, and Gambaryan, *Izvest. Akad. Nauk. S.S.S.R.*, *Otdel. khim. Nauk*, 1960, 686.

[15] Hagemeyer, *Ind. Eng. Chem.*, 1949, **41**, 765; cf. Zaugg, " Organic Reactions," Wiley, New York, 1954, Vol. VIII, p. 305; cf. Knunjants and Cheburker, *Izvest. Akad. Nauk S.S.S.R.*, *Otdel. khim. Nauk*, 1960, 678.

(I). It seems that the difference in behaviour of these compounds can be ascribed to the enolisation-depressing influence of α-fluorine and the enolisation-enhancing influence of γ-fluorine atoms. Enol titrations by Hieber's method [16] indeed led to the following values for the enol content of equilibrium mixtures: ethyl acetoacetate 7·7; ethyl α-fluoroacetoacetate 0·99; ethyl γ-fluoroacetoacetate 18·2; ethyl γγγ-trifluoroacetoacetate 49·0; diethyl malonate 0; diethyl fluoromalonate [17] 0·91%. In accordance with this explanation, a good yield of the β-lactone (II) was obtained from diethyl α-fluoro-α-fluoroacetylmalonate


(I)


(II)


(III)

$CH_2F\cdot CO\cdot CF(CO_2Et)_2$, which has no enolisable hydrogen atom, and from 1,3-difluoroacetone. The compound (III) formed in the latter case was converted by alcoholic potassium hydroxide solution into a mixture of the hydroxy-ester $(CH_2F)_2C(OH)\cdot CH_2\cdot CO_2Et$ and the corresponding hydroxy-acid.

EXPERIMENTAL

The infrared data are for liquid films.

3-*Fluorobutan*-2-*one*.—In an efficient column, 3-chlorobutan-2-one [18] (106·5 g.) was added slowly at 170—180° to a mixture of potassium fluoride (87 g.), ethylene glycol (200 g.) and diethylene glycol (100 g.), so that the product distilled off continuously (70—120°). Fractionation gave 3-*fluorobutan*-2-*one* (49 g., 55%), b. p. 74—76°, $\nu_{max.}$ 1725 (C=O), 1025 and 1100 (C–F) cm.$^{-1}$ (Found: C, 54·0; H, 7·9. C_4H_7FO requires C, 53·4; H, 7·8%), and some (8 g., 7%) starting material. The semicarbazone had m. p. 144°.

Fluoroacetaldehyde Diethyl Acetal.—Analogously, bromoacetaldehyde diethyl acetal (160 g.), potassium fluoride (80 g.), ethylene glycol (100 g.), and diethylene glycol (130 g.) gave a liquid, b. p. 120—140°, which was fractionated. The first fraction (20 g.), b. p. 78—80°, was mainly ethanol; the second (10 g., 9%), b. p. 120—122°, was the desired *acetal* (Found: C, 52·6; H, 9·4. $C_6H_{13}FO_2$ requires C, 52·9; H, 9·6%), $\nu_{max.}$ 1100—1180 (acetal [19]), 1013 (C–F) cm.$^{-1}$.

Reaction of Grignard Reagents with Fluoroacetonitrile.—To a Grignard solution from the alkyl or aryl bromide (0·20 mole) and magnesium (0·20 g.-atom) in ether (250 ml.) fluoroacetonitrile (0·20 mole) in ether (100 ml.) was added at −20° dropwise and with stirring, during 30—45 min. A pasty, ether-insoluble material was formed, so that vigorous mixing was required. After an additional hour's stirring at 0°, the mixture was poured on ice and sulphuric acid, the ethereal layer separated, and the aqueous phase extracted twice with ether. The combined ether extracts were dried (Na_2SO_4) and distilled. No attempt was made to find optimum conditions for the preparation of the ketones, but the following *fluoromethyl ketones* were obtained:

(1) *Butyl*, b. p. 55—56°/30 mm., n_D^{28} 1·4002 (34%) (Found: C, 61·2; H, 9·3; F, 16·0. $C_6H_{11}FO$ requires C, 61·0; H, 9·3; F, 16·1%).

(2) s-Butyl, b. p. 126—128°, n_D^{28} 1·4045 (34%) [2,4-*dinitrophenylhydrazone*, needles, m. p. 99—100° (from methanol) (Found: C, 48·8; H, 5·0; F, 6·3. $C_{12}H_{15}FN_4O_4$ requires C, 48·3; H, 5·0; F, 6·4%)].

(3) *Hexyl*, b. p. 55—60°/0·5 mm., n_D^{26} 1·4122 (24%) (Found: C, 65·7; H, 10·5. $C_8H_{15}FO$ requires C, 65·7; H, 10·3%) (no crystalline dinitrophenylhydrazone).

(4) Cyclopentyl, b. p. 73—74°/30 mm., n_D^{28} 1·4445 (32%) [2,4-*dinitrophenylhydrazone*, orange plates, m. p. 110—113° (from methanol) (Found: C, 52·0; H, 5·4; F, 6·3. $C_{13}H_{15}FN_4O_4$ requires C, 50·3; H, 5·0; F, 6·1%)].

(5) Cyclohexyl, b. p. 45—46°/0·6 mm., n_D^{26} 1·4510 (24%) [2,4-*dinitrophenylhydrazone*, prisms, m. p. 125—127° (from methanol) (Found: C, 52·0; H, 5·4; F, 6·3. $C_{14}H_{17}FN_4O_4$ requires C, 51·9; H, 5·3; F, 5·9%)].

(6) *Dodecyl*, b. p. 110—125°/0·6 mm., m. p. 34—35° [from light petroleum (b. p. 40—60°)]

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[16] Hieber, *Ber.*, 1921, **54**, 902.
[17] Bergmann, Cohen, and Shahak, *J.*, 1959, 3286.
[18] Korschun, *Ber.*, 1905, **38**, 1125.
[19] Young and Tarrant, *J. Amer. Chem. Soc.*, 1948, **71**, 2432.

(54%) (Found: C, 73·1; H, 12·2; F, 8·1. $C_{14}H_{27}FO$ requires C, 73·0; H, 11·8; F, 8·3%) [2,4-*dinitrophenylhydrazone*, needles, m. p. 105—106° (from methanol) (Found: C, 58·8; H, 7·7; F, 4·7. $C_{20}H_{31}FN_4O_4$ requires C, 58·5; H, 7·6; F, 4·7%)].

(7) m-*Tolyl*, b. p. 85—90°/0·9 mm., n_D^{28} 1·5278 (80%) (Found: C, 71·2; H, 6·1; F, 12·2. C_9H_9FO requires C, 71·0; H, 5·9; F, 12·5%) [2,4-*dinitrophenylhydrazone*, orange prisms, m. p. 205—208° (from methanol) (Found: C, 54·3; H, 4·0; F, 6·1. $C_{15}H_{13}FN_4O_4$ requires C, 54·2; H, 3·9; F, 5·7%)].

(8) o-*Methoxyphenyl*, m. p. 88—89° (from methanol) (35%) (Found: C, 64·3; H, 5·7; F, 11·2. $C_9H_9FO_2$ requires C, 64·4; H, 5·4; F, 11·3%) [2,4-*dinitrophenylhydrazone*, dimorphic, orange prisms, m. p. 210—215° (Found: C, 51·5; H, 3·9; F, 5·6. $C_{15}H_{13}FN_4O_5$ requires C, 51·7; H, 3·7; F, 5·5%)].

These ketones had C=O maxima at (1—4) 1727, (5) 1681, (6) 1724, (7) 1700, (8) 1681 cm.$^{-1}$, and C–F absorption at (1) 1042, (2) 1020—1050, (3) 1053, (4) 1053, 1020, (5, 6) 1053, (7) 1031, (8) 1075, 1053, 1025 cm.$^{-1}$.

1,3-*Difluoro*-2-*phenylpropan*-2-*ol*.—At 0°, a solution of 1,3-difluoroacetone [2] (19 g.) in ether (50 ml.) was added to a Grignard solution prepared from magnesium (4·8 g.), bromobenzene (32 g.), and ether (100 ml.). After 15 min., the product was decomposed with ice-cold dilute sulphuric acid and the ethereal layer separated, dried, and distilled. The *alcohol* (25 g., 72%) boiled at 120—125°/24 mm., 82—83°/4 mm. (Found: C, 63·8; H, 5·8; F, 21·6. $C_9H_{10}F_2O$ requires C, 62·9; H, 5·8; F, 22·1%). $\lambda_{max.}$ (in EtOH) 250 mμ (log ε 3·00), $\nu_{max.}$ 3570, 3450, 1110, 1068, 1028, 1018 cm.$^{-1}$.

Reaction of Fluoroacetone with Phenylmagnesium Bromide.—At −10°, fluoroacetone [2] (7·6 g.) was added to a Grignard solution from magnesium (2·4 g.), bromobenzene (15·7 g.), and ether (100 ml.). The product was decomposed with ice and hydrochloric acid, and the ethereal layer washed with sodium hydrogen carbonate solution, dried, and distilled. The product (6·5 g., 48%) boiled at 114—116°/30 mm.; it was free from fluorine and the infrared spectrum showed a very pronounced carbonyl band at 1750 cm.$^{-1}$. By preparation of the 2,4-dinitrophenylhydrazone (m. p. 154°) and comparison with an authentic sample, the compound was identified as phenylacetone.

Ethyl α-Cyano-γ-fluoro-β-methylcrotonate.—A mixture of fluoroacetone (9 g.), ethyl cyanoacetate (11 g.), ammonium acetate (1·5 g.), acetic acid (5 g.), and benzene (30 ml.) was subjected to azeotropic distillation for 5 hr. The resulting solution was washed with water, dried, and distilled. The *ester* produced had b. p. 74—75°/1 mm. (7 g., 34%) (Found: C, 56·1; H, 6·3. $C_8H_{10}FNO_2$ requires C, 56·1; H, 5·9%).

Ethyl γ-Fluoro-β-hydroxy-β-methylbutyrate.—To a stirred mixture of zinc (7·8 g.) and benzene (60 ml.), fluoroacetone (9 g.) and ethyl bromoacetate (16·7 g.) in benzene (30 ml.) were added slowly at 50—60°. Heating was continued for 3 hr. and the mixture cooled and decomposed with ice and hydrochloric acid. Distillation of the benzene layer gave the desired *ester* (6 g., 40%), b. p. 90—95°/29 mm., 92°/25 mm., $\nu_{max.}$ 3500 (OH), 1750 (C=O), 1030 (C–F) cm.$^{-1}$ (Found: C, 51·6; H, 8·1; F, 11·3. $C_7H_{13}FO_3$ requires C, 51·2; H, 7·9; F, 11·6%).

Ethyl γ-Fluoro-β-fluoromethyl-β-hydroxybutyrate.—To a mixture of zinc (14·7 g.) and a little copper powder, a portion (20 ml.) of a solution of ethyl bromoacetate (38 g.) and 1,3-difluoroacetone (21 g.) in benzene (100 ml.) and toluene (50 ml.) was added, and the mixture was heated until the exothermic reaction set in. The rest of the solution was then added within 1 hr. without further heating and the product refluxed for 2 hr. and decomposed with ice and dilute sulphuric acid. The *ester* (15 g., 37%) boiled at 120—130°/40 mm. and, on redistillation, at 112°/30 mm., it had $\nu_{max.}$ 3480 (OH), 1725 (C=O), 1030 (C–F) cm.$^{-1}$ (Found: C, 46·0; H, 6·5; F, 21·4. $C_7H_{12}F_2O_3$ requires C, 46·1; H, 6·6; F, 20·9%).

Ethyl α-Fluoro-β-hydroxy-β-methylbutyrate.—To a suspension of magnesium (8·5 g.), activated with a little iodine, in benzene (30 ml.), a mixture of acetone (17·5 g.), ethyl chlorofluoroacetate [19] (35 g.), and benzene (70 ml.) was added so that the whole boiled gently. The mixture was refluxed for 30 min. more and then decomposed with ice-cold dilute sulphuric acid. Distillation gave the *hydroxy-ester* (8 g., 20%), b. p. 90°/20 mm., that slowly decomposed (Found: C, 50·8; H, 8·3; F, 11·9; OEt, 28·5. $C_7H_{13}FO_3$ requires C, 51·2; H, 7·9; F, 11·6; OEt, 27·4%) and had $\nu_{max.}$ 3230 (hydrogen-bonded OH), 1130 (broad, C–F) cm.$^{-1}$.

γ-Fluoro-β-fluoromethyl-β-hydroxybutyric Acid.—A mixture of 1,3-difluoroacetone (23 g.), malonic acid (25 g.), pyridine (40 g.), and piperidine (1 ml.) was kept at room temperature for 24 hr. and the excess of pyridine then removed *in vacuo*. 63% Hydrobromic acid (30 ml.) was added to the residue and the solution again brought to dryness *in vacuo*. Distillation *in vacuo* gave a viscous liquid which was dissolved in acetone, filtered (from a little pyridine hydrobromide), and distilled again. The *acid* (15 g., 40%) had b. p. 120—125°/0·5 mm., $\nu_{max.}$ 3420 (OH, broad), 1724 (C=O), 1030 (C–F) cm.$^{-1}$ (Found: C, 38·5; H, 5·0. $C_5H_8F_2O_3$ requires C, 38·9; H, 5·2%).

Bromination of Fluoroacetone.—Bromine (80 g.) was added slowly to fluoroacetone (38 g.) in chloroform (150 ml.). After the first drops had been added, the solution had to be heated slightly, until the reaction set in. The remainder was added at 10—20°. The time required was 90 min. The solution was washed with sodium hydrogen carbonate solution and dried. Distillation gave fractions, b. p. 80—110° (60 g.) and 65—85°/17 mm. (25 g.). The first fraction, on redistillation, boiled at 106—110° (35 g., 45%) and was 1-*bromo*-1-*fluoroacetone* (Found: C, 23·4; H, 2·6. C_3H_4BrFO requires C, 23·2; H, 2·6%); it had $\nu_{max.}$ 1740 (C=O), 1180, 1120, 1080, and 1030, (C–F), 665 (C–Br) cm.$^{-1}$. The compound (35 g.) was added to 80% nitric acid (112 ml.) with stirring. When the exothermic reaction subsided, the mixture was heated at 100° for 2 hr. Distillation gave 16 g. (45%) of fluorobromoacetic acid, b. p. 98—99°/29 mm., n_D^{25} 1·4382 (Found: C, 15·3; H, 1·6; Br, 50·3. Calc. for $C_2H_2BrFO_2$: C, 15·3; H, 1·3; Br, 51·0%).

The second fraction boiled, on redistillation, at 82—83°/17 mm. (22 g., 19%) and was a crude dibromofluoroacetone (Found: C, 16·4; H, 1·6; F, 8·6. $C_3H_3Br_2FO$ requires C, 15·4; H, 1·3; F, 8·1%).

Dimethyl 2-*Fluoro*-1-*fluoromethyl*-1-*hydroxyethylphosphonate.*—To a mixture of dimethyl phosphite (40 g.) and 2N-methanolic sodium methoxide (50 ml.), 1,3-difluoroacetone (28·2 g.) was added. After 16 hr., glacial acetic acid (6 g.) was added and the product distilled. The *ester* (13 g., 21%) had b. p. 125—127°/4 mm. (Found: C, 29·1; H, 5·3. $C_5H_{11}PF_2O_4$ requires C, 29·4; H, 5·4%). $\nu_{max.}$ 3480 (OH), 1750 (C=O), 1240 (P=O),[20] 1080 (C–F), 1018 (C–F) cm.$^{-1}$.

Dimethyl 2-*Ethoxycarbonyl*-1-*hydroxy*-1-*trifluoromethylethylphosphonate.*—A mixture of dimethyl phosphite (11 g.) and ethyl γγγ-trifluoroacetoacetate [21] (18·1 g.) was refluxed, and 2N-sodium methoxide (5 ml.) added. The mixture was heated for 1 hr. more at 100° and distilled. The *product* (10 g., 30%) boiled at 116—118°/3 mm. (Found: C, 32·9; H, 5·1. $C_8H_{14}PF_3O_6$ requires C, 32·7; H, 4·8%).

γ-Fluoro-β-fluoromethyl-β-butyrolactone (III).—Keten [22] (~1·5 mol.) was passed into a stirred solution of 1,3-difluoroacetone (40 g.) and freshly fused zinc chloride (1 g.) in anhydrous ether (50 ml.) at 25—30°; then a saturated solution of sodium carbonate (2 g.) in water was added, and the mixture stirred for another hour. The solution was then filtered and distilled. The *lactone* (49 g., 95%) had b. p. 105—107°/16 mm., n_D^{13} 1·4140 $\nu_{max.}$ 1850 (β-lactone), 1030 (C–F) cm.$^{-1}$ (Found: C, 44·5; H, 4·3. $C_5H_6F_2O_2$ requires C, 44·2; H, 4·4%).

Potassium hydroxide (6 g.) in ethanol (20 ml.) was added at 0° to a solution of this lactone (14 g.) in ethanol (50 ml.), and the mixture was left overnight at room temperature; aqueous concentrated hydrochloric acid was then added until the reaction was acid; the solution was filtered and distilled, giving *ethyl γ-fluoro-β-fluoromethyl-β-hydroxybutyrate* (6 g., 32%), b. p. 53—54°/0·8 mm. (Found: C, 46·7; H, 6·7; F, 21·0. $C_7H_{12}F_2O_3$ requires C, 46·2; H, 6·6; F, 20·9%), and *γ-fluoro-β-fluoromethyl-β-hydroxybutyric acid* (6 g., 38%), b. p. 113—115°/0·6 mm. (Found: C, 40·1; H, 5·4; F, 24·4. $C_5H_8F_2O_3$ requires C, 38·9; H, 5·2; F, 24·6%).

Enol Acetate of Ethyl γγγ-Trifluoroacetoacetate.—Keten was passed into a solution of ethyl γγγ-trifluoroacetoacetate [22] (12 g.) and zinc chloride (0·5 g.) in anhydrous ether (50 ml.), as described above. The catalyst was destroyed with sodium carbonate (1 g.) in a little water, and the filtered solution was distilled. The *enol acetate* (10 g., 68%) had b. p. 72—74°/15 mm., n_D^{13} 1·3940, $\nu_{max.}$ 1810 (enol acetate [23]), 1730 (unsaturated ester C=O), 1075 and 1030 (C–F) cm.$^{-1}$ (Found: C, 42·1; H, 4·2. $C_8H_9F_3O_4$ requires C, 42·5; H, 4·0%).

Ethyl β-Acetoxycrotonate.—Keten was passed into a stirred mixture of ethyl acetoacetate (86 g.) and zinc chloride (2 g.) at 30—33°. Working up as above gave *ethyl β-acetoxycrotonate* (48 g., 42%), b. p. 105—107°/20 mm. (lit.,[24] 99°/12 mm.), n_D^{13} 1·4510 (Found: C, 56·3; H, 6·8. Calc. for $C_8H_{12}O_4$: C, 55·8; H, 6·9%).

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[20] Bellamy and Beecher, *J.*, 1952, 475.

[21] McBee, Pierce, Kilbourne, and Wilson, *J. Amer. Chem. Soc.*, 1953, **75**, 3152.

[22] Hanford and Sauer, " Organic Reactions," Wiley, New York, 1946, Vol. III, p. 108.

[23] The frequency is higher than usual (1750—1770 cm.$^{-1}$; see, *e.g.*, Jones and Herling, *J. Org. Chem.*, 1954, **19**, 1252) probably because of the influence of the three neighbouring fluorine atoms.

[24] Michael, *Ber.*, 1905, **38**, 2083.

γγ-Diethoxycarbonyl-γ-fluoro-β-fluoromethyl-β-butyrolactone (II).—Keten was passed into a stirred solution of diethyl α-fluoro-α-fluoroacetylmalonate [17] (18 g.) and zinc chloride (1 g.) in anhydrous ether (50 ml.). The catalyst was destroyed as described above. Fractionation gave some starting material, then the β-lactone (II) (5 g., 24%), b. p. 149—150°/0·5 mm., $\nu_{max.}$ 1870 (β-lactone), 1770 (α-halogenated ester C=O [25]), and in the C–F region 1120, 1060, 1025 cm.$^{-1}$ (Found: C, 48·1; H, 5·6. $C_{11}H_{14}F_2O_6$ requires C, 47·2; H, 5·0%).

γ-Ethoxycarbonyl-γ-fluoro-β-methyl-β-butyrolactone (I).—Keten was passed into a solution of ethyl α-fluoroacetoacetate [13] (14 g.) and zinc chloride (0·5 g.) in chloroform (50 ml.) at 5—10°. A saturated solution of sodium carbonate (5 ml.) was then added, and the mixture was stirred for 1 hr. The chloroform solution was separated, filtered, and distilled. The β-*lactone* (8 g., 45%) had b. p. 108—110°/0·2 mm. (polymerised on prolonged heating), $\nu_{max.}$ 1850 (β-lactone), 1740 (α-halogenated ester C=O [25]), 1090 and 1025 (C–F) cm.$^{-1}$ (Found: C, 50·2; H, 6·0; F, 9·5. $C_8H_{11}FO_4$ requires C, 50·5; H, 5·8; F, 10·0%).

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[*Received, January 3rd,* 1961.]

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[25] Cf. Gillette, *J. Amer. Chem. Soc.*, 1936, **58**, 1143.