784. *Organic Fluorine Compounds. Part XXV.* Further Reaction of Aldehydes with Diethyl Fluoro-oxaloacetate.*

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Under certain conditions, aldehydes and diethyl fluoro-oxaloacetate give substituted 2-fluoroalk-2-enoic acids directly. However, phenylacetaldehyde gives a $\beta\gamma$-unsaturated acid. The product from 2-methyl-3-oxopentanal has been converted into 4-fluoro-2,6-dimethylresorcinol, that from *o*-acetoxybenzaldehyde into 3-fluorocoumarin.

Diethylfluoro-oxaloacetate reacts with primary and secondary amines, the keto-group being replaced by two amino-groups.

The reaction of diethyl sodiofluoro-oxaloacetate with aliphatic aldehydes has recently been described.[1,2] If the condensation is followed by treatment with aqueous alkali, 2-fluoroalk-2-enoic acids are obtained:[3]

$$R{\cdot}CHO + EtO_2C{\cdot}CO{\cdot}CHF{\cdot}CO_2Et \longrightarrow EtO_2C{\cdot}CO_2H + R{\cdot}CH{=}CF{\cdot}CO_2H + EtOH$$

As the product obtained from the sodio-enolate of ethyl fluoroacetate [4] and diethyl oxalate [5] can be used, without isolation, for the condensation, the reaction represents in fact condensation of the aldehydes with a protected form of ethyl fluoroacetate. The direct

* Part XXIV, Bergmann and Shahak, *Chem. and Ind.*, 1961, 591.

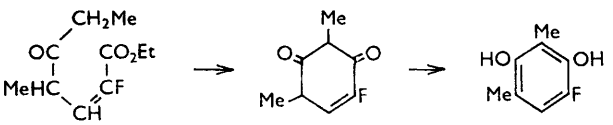
[1] Bergmann and Shahak, *J.*, 1960, 5261.
[2] Gault, Rougé, and Gordon, *Compt. rend.*, 1960, **250**, 1073.
[3] Cf. the preparation of 2-chlorononon-2-enoic acid by Gault and Ritter (*Compt. rend.*, 1948, **226**, 816).
[4] Bergmann and Szinai, *J.*, 1956, 1521.
[5] Bergmann and Shahak, *J.*, 1960, 3225.

condensation of aromatic aldehydes with ethyl fluoroacetate has been described before [6] but the yields were not satisfactory. The method now described proceeds in a single step and gives reasonable yields; the reaction is easy to carry out, and only in the case of formaldehyde are some precautions necessary because of the easy polymerisation of ethyl α-fluoroacrylate.

The following aldehydes have been studied, in addition to heptaldehyde: [1] butyraldehyde, isobutyraldehyde, butyl glyoxylate, 2-methyl-3-oxopentanal, benzaldehyde, *p*-tolualdehyde, *p*-chlorobenzaldehyde, *o*-acetoxybenzaldehyde (the acetoxy-group undergoes hydrolysis), phenylacetaldehyde, and 2- and 3-formylpyridine. The spectra showed that the compounds had the expected structures: whilst α-fluorocrotonic acid and 2-fluoro-4-methylpent-2-enoic acid showed no selective absorption above 210 mμ, introduction of higher alkyl groups into the β-position caused a bathochromic shift: 2-fluorohex-2-enoic acid absorbed at 214 and ethyl 2-fluorononon-2-enoate at 223 mμ. Fluorofumaric acid absorbed at 217 mμ (to be compared with fumaric acid at 210 mμ [7]) and ethyl α-fluoro-2-hydroxycinnamate at 260, 264, and 324 mμ (α-fluorocinnamic acid has been reported [8] to exhibit bands at 226 and 262 mμ). An exception has been observed for the product obtained from phenylacetaldehyde; it absorbs at 292 mμ (ε 450), *i.e.*, at about the same wavelength as styrene [9] (282 mμ, ε 450) and is, therefore, the βγ-unsaturated ester $CHPh{:}CH{\cdot}CHF{\cdot}CO_2Et$. The same phenomenon has been observed in the condensation of phenylacetaldehyde and malonic acid.[10,11]

α-Fluoro-2-hydroxycinnamic acid, formed from *o*-acetoxybenzaldehyde, is cyclised by hydrogen chloride in boiling glacial acetic acid to 3-fluorocoumarin which showed the lactone-carbonyl band at 1724 and the C:C absorption at 1613 cm.$^{-1}$.

A similar cyclisation was observed on condensation of 2-methyl-3-oxopentanal, $Et{\cdot}CO{\cdot}CHMe{\cdot}CHO$, in ethanol. In addition to the normal product, ethyl 2-fluoro-4-methyl-5-oxohept-2-enoate, a product, $C_8H_9FO_2$, was obtained which no longer contained a carbonyl group but showed a strong, broad hydroxyl band and an aromatic ultraviolet spectrum ($\lambda_{max.}$ 278 and 282 mμ). As the hydroxyl groups were phenolic, the product is assumed to be 4-fluoro-2,6-dimethylresorcinol:



Resorcinol absorbs at 274 mμ.[12] The only analogy to this somewhat surprising reaction appears to be the indirect formation of 5-butylresorcinol from diethyl 2-butyl-4-oxopent-2-ene-1,1-dicarboxylate [13] which is a δ-keto-ester like the above compound.[14]

In order to prove finally the structure of the acids and esters obtained, the observation of Gault and Ritter [3] was utilised that β-substituted α-chloroacrylic acids are hydrolysed to the corresponding pyruvic acids: $R{\cdot}CH{:}CCl{\cdot}CO_2H \longrightarrow R{\cdot}CH_2{\cdot}CO{\cdot}CO_2H$. Indeed, boiling alcoholic alkali converted ethyl α-fluorocrotonate into α-oxobutyric acid, and 2-fluorohex-2-enoic into 2-oxohexanoic acid (the two liquid products were identified as known crystalline derivatives).

Diethyl oxaloacetate with aliphatic primary and secondary amines gives adducts which

[6] Bergmann and Schwarcz, *J.*, 1956, 1524.
[7] Ley and Wingchen, *Ber.*, 1934, **67**, 501.
[8] Bergmann and Schwarcz, *J.*, 1956, 1524.
[9] Braude, *Ann. Reports*, 1945, **42**, 105.
[10] Vorlaender and Straack, *Annalen*, 1906, **345**, 244.
[11] Fichter, *J. prakt. Chem.*, 1906, **74**, 297, 339.
[12] Hodgson, *J.*, 1943, 380; cf. Kiss, Molnar, and Sandorfy, *Bull. Soc. chim. France*, 1949, **16**, 275.
[13] Anker and Cook, *J.*, 1945, 311.
[14] Bergmann, Ginsburg, and Pappo, "Organic Reactions," 1959, Vol. X, 254.

have not been characterised and decompose to a self-condensation product of the keto-ester;[15] and with aniline it gives the anil and at higher temperature α-phenylimino-succinanil[16] or ethyl 4-hydroxyquinoline-2-carboxylate.[17] However, diethyl fluoro-oxaloacetate reacts differently with primary or secondary amines: the keto-group is replaced by two substituted nitrogen atoms:

$$EtO_2C{\cdot}CO{\cdot}CHF{\cdot}CO_2Et \longrightarrow EtO_2C{\cdot}C(NRR')_2{\cdot}CHF{\cdot}CO_2Et \ (R = \text{alkyl or aryl, } R' = H \text{ or alkyl})$$

The structure of the products is supported by the following observations: Hydrolysis with acid gives the amine hydrochloride and fluoropyruvic acid (which is formed from fluoro-oxaloacetic acid under acid conditions).[18] Treatment with acetic anhydride affords two mol. of the acetyl derivative of the amine and diethyl α-acetyl-α-fluoro-oxaloacetate; it may be that this acylation takes place at the enamine stage, thus:[19,20]

$$EtO_2C{\cdot}C(NRR')_2{\cdot}CHF{\cdot}CO_2Et \longrightarrow EtO_2C{\cdot}C(NRR'){:}CHF{\cdot}CO_2Et$$
$$EtO_2C{\cdot}C(NRR')(OAc){\cdot}CFAc{\cdot}CO_2Et \longrightarrow EtO_2C{\cdot}CO{\cdot}CFAc{\cdot}CO_2Et + NRR'Ac$$

Experimental

Condensation of Diethyl Oxalofluoroacetate with Aldehydes.—General procedure. (*a*) To a suspension of sodium hydride (2·4 g., 0·1 mole) in xylene (100 ml.), a few drops of anhydrous ethanol, diethyl oxalate (16 g.), and a solution of ethyl fluoroacetate (10·6 g.) in xylene (15 ml.) were added successively at 40—50° with stirring. Within 1 hr. the temperature was raised to 70°, then the ethanol formed was distilled off through a column at 30 mm. (until the b. p. of xylene was reached). A small quantity (10 ml.) of xylene was distilled off, and after 30 min. the aldehyde (0·1 mole), dissolved in xylene (30 ml.), was added. When the (usually exothermic) reaction had subsided, the mixture was refluxed for 15 min. and poured into water (500 ml.). The xylene layer was washed with 5% sodium carbonate solution (100 ml.) and water (100 ml.), dried, and concentrated. When appropriate, the residual ethyl β-alkyl-α-fluoroacrylate was fractionated through a column; when its b. p. was too near that of the other products (diethyl oxalate, diethyl α-fluoro-α-fluoroacetyloxaloacetate [5]), the residue was hydrolysed to the free acid as follows: Ethanol (50 ml.) and then 25% aqueous potassium hydroxide were added so that the temperature did not rise above 50°, and until the liquid remained alkaline for 30 min. Water (20 ml.) was added and the ethanol evaporated *in vacuo*; the aqueous solution was acidified with concentrated hydrochloric acid (30 ml.). Solid acids were filtered off and purified; liquid acids were extracted with benzene (which extracts hardly any oxalic or fluoroacetic acid) and re-esterified azeotropically with anhydrous ethanol and benzene in the presence of a little toluene-*p*-sulphonic acid; the solution of the ester was washed with sodium hydrogen carbonate solution, dried, and distilled.

(*b*) (Cf. Rougé and Gault.[21]) A mixture of sodium ethoxide solution (from 4·6 g., 0·2 g.-atom, of sodium), diethyl oxalate (30 g.), and ethyl fluoroacetate (21·2 g.) was kept at room temperature for 12 hr. in a closed flask and, after addition of the aldehyde (0·2 mole), refluxed for 45 min. The alcohol was distilled off (if necessary, through a column), and the residue taken up in dilute hydrochloric acid and benzene. The benzene solution was washed with 5% sodium carbonate solution, dried, and distilled.

Products. The following were prepared:

2-Fluorohex-2-enoic acid [from butyraldehyde; (*a*) 66%; (*b*) 35%], b. p. 84°/1 mm. (Found: C, 54·6; H, 6·9; F, 14·2. $C_6H_9FO_2$ requires C, 54·5; H, 6·8; F, 14·4%), $\lambda_{max.}$ 214 mμ (ε 4·15) in EtOH.

2-Fluoro-4-methylpent-2-enoic acid (from isobutyraldehyde; 70%), b. p. 80°/1 mm. (Found: C, 54·3; H, 7·0; F, 14·0%). The derived benzylisothiouronium salt melted at 171°; the free

[15] Claisen and Hori, *Ber.*, 1891, **24**, 120; Wislicenus and Beckh, *Annalen*, 1903, **295**, 339.
[16] Wislicenus and Spiro, *Ber.*, 1889, **22**, 3348.
[17] Riegel, *J. Amer. Chem. Soc.*, 1946, **68**, 2685; cf. Halberkann, *Ber.*, 1921, **54**, 3090.
[18] Blank, Mager, and Bergmann, *J.*, 1955, 2190.
[19] Stock, Terrell, and Szmuszkovicz, *J. Amer. Chem. Soc.*, 1954, **76**, 2009.
[20] Benary and his co-workers, *Ber.*, 1909, **42**, 3915; 1917, **50**, 65; 1922, **55**, 3417.
[21] Rougé and Gault, *Compt. rend.*, 1960, **251**, 95.

acid showed no selective absorption above 210 mμ in ethanol. The *ethyl ester* had b. p. 78—80°/35 mm. (Found: F, 12·0. $C_8H_{13}FO_2$ requires F, 11·9%), $\nu_{max.}$ (film) 1724 (CO), 1668 (C:C), 1110 (:CF) cm.$^{-1}$.

4-*Butyl* 1-*ethyl* 2-*fluorofumarate* (from butyl glyoxylate); 75%, b. p. 100—102°/2 mm. (Found: C, 55·2; H, 6·8; F, 8·5. $C_{10}H_{15}FO_4$ requires C, 55·0; H, 6·9; F, 8·7%). Butyl glyoxylate, prepared in analogy to diethyl glyoxylate,[21] from dibutyl tartrate (yield, 71%), had b. p. 70—72°/2·5 mm.

Fluorofumaric acid [23] was obtained from the butyl ethyl ester by hydrolysis with hydrochloric acid in acetic acid. It was insoluble in all organic solvents except alcohols and sublimed (transformation into fluoromaleic anhydride?) without melting. It had $\lambda_{max.}$ 217 mμ (ε 2·68) in EtOH, $\nu_{max.}$ (in KBr) 3448 (OH), 1724 (CO) cm.$^{-1}$ (Found: C, 36·5; H, 2·5; F, 14·0. Calc. for $C_4H_3FO_4$: C, 35·8; H, 2·2; F, 14·2%).

Ethyl 2-*fluoro*-4-*methyl*-5-*oxohept*-2-*enoate* (from 2-methyl-3-oxopentanal; [24] 60%), b. p. 110—111°/2 mm. (Found: C, 59·0; H, 7·4; F, 9·0. $C_{10}H_{15}FO_3$ requires C, 59·4; H, 7·4; F, 9·4%), $\lambda_{max.}$ (in EtOH) 256 mμ (ε 3·71), $\nu_{max.}$ (film) 1754 (CO), 1642 (C:C), 1110 (:CF), 1026 (C–F) cm.$^{-1}$.

When this reaction was carried out in ethanol, only two-thirds of the product consisted of this ester; it was accompanied by a crystalline product which, recrystallized from benzene, melted at 98—99°. Its analysis and spectrum indicated that it was 4-fluoro-2,6-dimethylresorcinol (diazomethane caused methylation) (Found: C, 61·4; H, 5·6; F, 11·8. Calc. for $C_8H_9FO_2$: C, 61·6; H, 5·7; F, 12·2%); it had $\nu_{max.}$ (in KBr) 3300—3400 (broad, OH), 1110 (:CF), 1020 (C–F) cm.$^{-1}$, and $\lambda_{max.}$ (in EtOH) 278 (ε 3·38), 282 mμ (ε 3·40). Further, when ethyl 2-fluoro-4-methyl-5-oxohept-2-enoate (2 g.) was kept at room temperature with a solution from sodium (0·5 g.) in anhydrous ethanol (30 ml.) for 1 hr. and the solution was acidified with hydrochloric acid and evaporated *in vacuo* to dryness, and the residue extracted twice with boiling benzene (50 ml.), concentration of the extract and cooling gave the same resorcinol derivative (1·5 g.), m. p. 98—99°.

Ethyl α-*fluorocinnamate* (from benzaldehyde; 68%), b. p. 120—122°/30 mm. (lit.,[25] 142—143°/20 mm.) (Found: C, 68·0; H, 5·9; F, 9·9. $C_{11}H_{11}FO_2$ requires C, 68·0; H, 5·7; F, 9·8%). Hydrolysis gave α-fluorocinnamic acid, m. p. 157°.[6]

Ethyl α-*fluoro*-4-*methylcinnamate* (from *p*-tolualdehyde; 65%), b. p. 111—113°/3 mm. (Found: C, 69·0; H, 6·0; F, 9·0. $C_{12}H_{13}FO_2$ requires C, 69·3; H, 6·2; F, 9·2%).

Ethyl 4-*chloro*-α-*fluorocinnamate* (from *p*-chlorobenzaldehyde; 74%), b. p. 122—123°/3 mm. (Found: Cl, 15·7; F, 8·0. $C_{11}H_{10}ClFO_2$ requires Cl, 15·5; F, 8·3%).

α-*Fluoro*-2-*hydroxycinnamic acid* (from *o*-acetoxybenzaldehyde,[26] 61%), m. p. 200° (sublimation) (from water) (Found: C, 59·4; H, 3·6; F, 10·1. $C_9H_7FO_3$ requires C, 59·3; H, 3·8; F, 10·4%), $\lambda_{max.}$ (in EtOH) 260 (ε 3·20), 264 (ε 4·20); 324 mμ (ε 3·79), $\nu_{max.}$ (in KBr) 3448 (OH), 1668 (CO), 1613 (C:C), 1130 (:CF), 1053 (C–F) cm.$^{-1}$.

Ethyl 2-*fluoro*-4-*phenylbut*-3-*enoate* (from freshly distilled phenylacetaldehyde; 63%), b. p. 120—121°/1 mm. (Found: F, 9·3. $C_{12}H_{13}FO_2$ requires F, 9·2%), $\lambda_{max.}$ (in EtOH) 292 mμ (ε 2·65), $\nu_{max.}$ (film) 1724 (CO), 1668 (C:C), 1042 (C–F) cm.$^{-1}$.

Ethyl α-*fluoro*-β-2-*pyridylacrylate* (from 2-formylpyridine; 35%), b. p. 118—120°/4 mm. (Found: N, 7·2; F, 9·6. $C_{10}H_{10}FNO_2$ requires N, 7·2; F, 9·4%).

Ethyl α-*fluoro*-β-3-*pyridylacrylate* (from 3-formylpyridine; 40%), b. p. 120—122°/4 mm. (Found: N, 7·3; F, 9·0%).

3-*Fluorocoumarin*.—α-Fluoro-2-hydroxycinnamic acid (3·5 g.) was refluxed for 3 hr. with a mixture of concentrated hydrochloric acid (5 ml.) and acetic acid (15 g.). The solution was evaporated and the residue treated with 5% sodium hydrogen carbonate solution, dried, and recrystallised from benzene. The *product* (0·5 g., 15%) melted at 148° (Found: C, 65·5; H, 3·2; F, 11·5. $C_9H_5FO_2$ requires C, 65·8; H, 3·1; F, 11·6%) and had $\nu_{max.}$ (in KBr) 1724 (lactone), 1613 (C:C), 1460, 1310, 1165, 1100 (C–F), 930, 760 (*ortho*-substituted benzene) cm.$^{-1}$. From the alkaline washings, α-fluoro-2-hydroxycinnamic acid (1·5 g., 43%) was recovered by acidification.

[22] Criegee, *Ber.*, 1931, **64**, 260.
[23] Martius, *Annalen*, 1948, **561**, 217 (no physical constants given); cf. Middleton and Sharkey, *J. Amer. Chem. Soc.*, 1959, **81**, 803.
[24] Claisen and Meyerowitz, *Ber.*, 1889, **22**, 3273.
[25] Sterlin, Yatsenko, and Knunyants, *Khim. Nauka i Prom.*, 1958, **3**, 580, *Chem. Abs.*, 1959, **53**, 4194.
[26] Malkin and Nierenstein, *J. Amer. Chem. Soc.*, 1931, **53**, 239.

Ethyl α-Fluoroacrylate.[2]—To the enolate of diethyl fluoro-oxaloacetate (prepared as above; 0·2 mole), dry paraformaldehyde (6 g.) was added and the mixture refluxed for 10 min. After addition of quinol (1 g.), the product was distilled through a column; the fraction of b. p. 78—95° was redistilled. The ester (11 g., 45%) boiled at 82—84°; it polymerised very easily (Found: C, 51·2; H, 6·3; F, 15·6. Calc. for $C_5H_7FO_2$: C, 50·9; H, 5·9; F, 16·1%).

Ethyl α-Fluorocrotonate.—In this case, because of the low b. p. of the product, tetrahydrofuran or ethanol is used as reaction medium.

(*a*) Ethyl oxalate (32 g.) and ethyl fluoroacetate (1 g.) were added with stirring to a suspension of sodium hydride (4·8 g.) in tetrahydrofuran (100 ml.). When the reaction had been initiated by refluxing, the balance of the fluorinated ester (20·2 g.) was slowly added at 40—45° and the whole heated for 3 hr. at 60°. Then freshly distilled acetaldehyde (9 g.) was added at 0° and the mixture brought slowly to the b. p. at which it was maintained for 1 hr.; then it was poured into water (400 ml.) and extracted with methylene chloride (100 ml.). The organic layer was washed with 5% sodium carbonate solution (100 ml.) and water (100 ml.), dried, and distilled. The *ester* (15 g., 61%) boiled at 134—136° (Found: C, 54·6; H, 7·0; F, 14·1. $C_6H_9FO_2$ requires C, 54·5; H, 6·8; F, 14·4%).

(*b*) Reaction in ethanol gave a 40% yield of ethyl α-fluorocrotonate.

Hydrolysis of the ester gave *α-fluorocrotonic acid* which, sublimed at 80—90°/5 mm. and recrystallised from light petroleum (b. p. 40—60°), had m. p. 111—112° (Found: F, 18·9. $C_4H_5FO_2$ requires F, 18·3%), no selective absorption above 210 mμ (in ethanol), $\nu_{max.}$ (in KBr) 3030—2857 (associated OH), 1668 (CO), 1162 (CF), 1075 (C–F) cm.$^{-1}$.

α-Oxobutyric Acid.—A solution of ethyl α-fluorocrotonate (10·5 g.) and potassium hydroxide (9 g.) in ethanol (70 ml.) was refluxed for 1 hr. Most of the solvent was distilled off *in vacuo* and the residue taken up in water (20 ml.), treated with concentrated hydrochloric acid (20 ml.), and extracted with ether. The acid (6·5 g., 80%) boiled at 84° and melted at 30°. It was identified as the *p*-nitrophenylhydrazone,[27] m. p. 192°.

α-Oxohexanoic Acid.—A solution of 2-fluorohex-2-enoic acid (10·5 g.) and potassium hydroxide (9 g.) in ethanol (80 ml.) was refluxed for 1 hr. and worked up as above. The acid (7·5 g., 80%) boiled at 93—95°/6 mm.; its oxime [28] melted at 140°.

Reactions with Amines.—The amine (0·21 mole) in toluene (50 ml.) was added to a solution of freshly distilled diethyl fluoro-oxaloacetate [5,29] (20·6 g., 0·1 mole) in toluene (50 ml.), with cooling to check the exothermic reaction. The solution was kept for 30 min. at room temperature. If the products proved to be oils, the toluene was removed *in vacuo* at ≯65°. The yellowish oily products could not be distilled, but gave correct analytical figures.

For hydrolysis, the product was heated with concentrated hydrochloric acid (50 ml.), with stirring, until a homogeneous solution resulted, which was diluted with water (100 ml.) and divided into two parts:

(*a*) Addition of 2,4-dinitrophenylhydrazine reagent gave the 2,4-dinitrophenylhydrazone of fluoropyruvic acid.[18] (*b*) The solution was made alkaline with concentrated potassium hydroxide solution, and the amine distilled off into aqueous picric acid. The picrates were compared with authentic specimens. Alternatively, the amines were absorbed in a known quantity of hydrochloric acid, and the excess of the acid was titrated. Thus, it could be shown in every case that 2 moles of amine had reacted with 1 mole of diethyl fluoro-oxaloacetate.

If the condensation products were solid, they were filtered off and recrystallised (see below). The hydrolysis was carried out as for the oily products.

(1) *Piperidine.* The piperidine recovered from the reaction with 0·1 mole of the keto-ester amounted to 0·18 mole (15·5 g.); its picrate had m. p. and mixed m. p. 151—152°.

(2) *Diethylamine.* Recovery 0·16 mole (12 g.); picrate, m. p. and mixed m. p. 155°.

(3) *Butylamine.* Recovery 0·19 mole (13·5 g.); picrate, m. p. 151°, mixed m. p. 149°.

(4) *Methylaniline.* Recovery 0·2 mole (20·5 g.); acetyl derivative, m. p. and mixed m. p. 104°. In this case, the amine was not distilled off, but was extracted from the alkaline solution.

Reaction of the Amine Condensation Products with Acetic Anhydride.—A solution of the oily product in toluene (50 ml.) was refluxed for 3 hr. with acetic anhydride (30 ml.), and the toluene and the acetic acid were removed at 30 mm. In the case of the methylaniline product, the acetyl derivative of the base, m. p. 103°, was filtered off and the remainder distilled; in the

[27] Tschelinzeff and Schmidt, *Ber.*, 1929, **62**, 2210; White, *J.*, 1943, 238.
[28] Barré, *Ann. chim.* 1928, **9**, 253.
[29] Blank, Mager, and Bergmann, *Bull. Res. Council Israel*, 1953, **3**, 101.

other cases, the acetyl derivatives were isolated by fractionation. In all cases, diethyl α-acetyl-α-fluoro-oxaloacetate,[5] b. p. 105—107°/1 mm. (Found: F, 7·6; OEt, 36·0. Calc. for $C_{10}H_{13}FO_6$: F, 7·7; OEt, 36·3%), was isolated. The *acetyl derivatives* obtained (from 0·1 mole of diethyl fluoro-oxaloacetate) were: 1-acetylpiperidine [30] (25 g.), b. p. 79—80°/2 mm. (Found: C, 66·2; H, 10·7; N, 10·6. Calc. for $C_7H_{13}NO$: C, 66·1; H, 10·2; N, 11·0%). *NN*-Diethylacetamide (22 g.), b. p. 80—82°/30 mm. (Found: C, 68·5; H, 12·2; N, 12·9. Calc. for $C_6H_{13}NO$: C, 68·6; H, 12·4; N, 13·3%). *N*-Butylacetamide (22 g.), b. p. 86—88°/30 mm. (Found: C, 68·6; H, 12·4; N, 13·3. Calc. for $C_6H_{13}NO$: C, 68·6; H, 12·4; N, 13·3%).

*Diethyl α-Fluoro-α′α′-*di-(2-*naphthylamino*)*succinate*.—2-Naphthylamine (28·9 g.) was refluxed with diethyl fluoro-oxaloacetate (10·6 g.) in benzene (100 ml.) for 30 min., filtered, and diluted with light petroleum (b. p. 40—60°). The *product* was filtered off and recrystallised from cyclohexane or benzene–light petroleum; it had m. p. 74° (Found: C, 70·3; H, 6·0; F, 4·2; N, 6·1; OEt, 18·5. $C_{28}H_{27}FN_2O_4$ requires C, 70·9; H, 5·7; F, 4·0; N, 5·9; OEt, 18·8%). Hydrolysis with hydrochloric acid gave β-naphthylamine hydrochloride, m. p. 254°, and fluoropyruvic acid, identified as 2,4-dinitrophenylhydrazone; treatment of the amine salt with acetic anhydride gave *N*-acetyl-2-naphthylamine,[31] m. p. 136°.

*Diethyl α′α′-Di-*p-*bromoanilino-α-fluorosuccinate* was obtained analogously, by using *p*-bromoaniline (36 g.). Recrystallised from cyclohexane, it melted at 61—62° (Found: C, 44·8; H, 4·0; F, 3·9; N, 5·1. $C_{20}H_{21}Br_2FN_2O_4$ requires C, 45·1; H, 3·9; F, 3·6; N, 5·3%).

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Jerusalem, Israel. [*Received, January 30th*, 1961.]

[30] Staudinger and Schneider, *Ber.*, 1923, **56**, 704.
[31] Pawlewski, *Ber.*, 1902, **35**, 112.