

## SYNTHESIS OF 2-FLUOROPROPENOIC ACID DERIVATIVES

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A method is described for the synthesis of 2-fluoropropenoic acid esters, amides, and nitrile from the corresponding derivatives of 2-fluoro-3-(4-toluenesulfonyloxy)propanoic acid by heating with potassium phthalimide *in vacuo*. The free acid *Ia* and its chloride have also been synthetized. The reactivity of esters and nitrile of acid *Ia* has been verified by the Michael addition of diethyl acetamidomalonate to these compounds.

2-Fluoropropenoic acid (*Ia*), its esters and other derivatives are compounds of prospective application in the synthesis of fluorinated organic compounds, provided that these derivatives are readily available. The reactivity of the compounds is comparable to the reactivity of the corresponding derivatives of propenoic acid; this suggests their possible use, *e.g.* in syntheses of the Michael addition and Diels-Alder reaction type, and also in the chemistry of polymers. Nevertheless, the synthetic applications of 2-fluoropropenoic acid have so far been rather scarce. In this paper an effort has been made to develop a simple and general method of synthesis of these compounds.

The synthesis of acid *Ia* by dehalogenation of 2,3-dibromo-2-fluoropropanoic acid with zinc has been recorded<sup>1</sup>; similarly some of its esters have been obtained<sup>2,3</sup>. These can also be synthetized by the reaction of formaldehyde with the sodium derivative of the corresponding fluoroacetate<sup>4</sup>, formyl fluoroacetate<sup>5</sup>, and ethoxalyl fluoroacetate<sup>5-7</sup> (several efforts to repeat these experiments in our Laboratory were unsuccessful, however). An azeotrope of butyl 2-fluoropropenoate with n-butanol, separable only with difficulties, has been obtained by an analogous procedure from dibutyl fluoromalonate<sup>8</sup>. The dehydrohalogenation of esters *IIa* and *IIb* by dimethylamine<sup>9</sup> afforded methyl 2-fluoropropenoate (*Ib*). Similarly<sup>10</sup> treatment of *IIIc* with potassium carbonate afforded ester *Ic*. 2-Fluoropropenenitrile (*Ie*) is formed by the reaction of 1,2-dicyano-1,2-difluoroethylene with ethylene at high temperatures<sup>11</sup> and also by dehydration (using phosphorus pentoxide) of 2-fluoropropenamide ( *Ig*), obtained by ammonolysis of the corresponding butyl ester<sup>8</sup>. Amide  *Ig* has also been prepared<sup>10</sup> from tosylated amide *IIIg* by treatment with alkaline reagents.

For the synthesis of the monofluoro derivatives of certain aliphatic amino acids large quantities of ester *Ic* were needed. This could not be prepared by the method of Hudlický<sup>3</sup> since the large scale preparation of the intermediate ethyl 2,3-dibromo-2-fluoropropanoate is rather troublesome. We chose therefore a modification of the method<sup>10</sup> consisting in heating 2-fluoro-3-(4-toluenesulfonyloxy)propanoic acid ethyl ester (*IIIc*) with a basic reagent. The most suitable base is potassium phthalimide; its use does not involve the formation of either water or other volatile by-products and the losses occurring during isolation are thus eliminated. On heating the homogenized mixture of ester *IIIc* with three equivalents of potassium phthalimide in the absence of solvent in an evacuated system we obtained a 100% conversion to *Ic*. The product collected at  $-78^{\circ}\text{C}$  was at least 99% pure according to GLC and was used in subsequent operations without redistillation. Since this procedure was simple and easy to perform we used it for the synthesis of a series of acid *Ia* derivatives from stable compounds *IIIb*–*IIIg* as shown in Table I. All products showed without additional purification an at least 99% purity according to GLC, except for amide *Ig* which was contaminated by phthalimide. The described method was used for a large scale preparation of compound *Ic*; more than 290 g of this ester was prepared and treated further in 14 days.



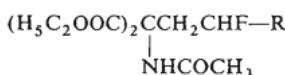
*Ia*, R = COOH  
*Ib*, R = COOCH<sub>3</sub>  
*Ic*, R = COOC<sub>2</sub>H<sub>5</sub>  
*Id*, R = COOC(CH<sub>3</sub>)<sub>3</sub>  
*Ie*, R = CN  
*If*, R = CON(CH<sub>3</sub>)<sub>2</sub>  
*Ig*, R = CONH<sub>2</sub>  
*Ih*, R = COCl



*IIa*, Y = Cl  
*IIb*, Y = Br



*IIIa*, R = COOH  
*IIIb*, R = COOCH<sub>3</sub>  
*IIIc*, R = COOC<sub>2</sub>H<sub>5</sub>  
*IIId*, R = COOC(CH<sub>3</sub>)<sub>3</sub>  
*IIIe*, R = CN  
*IIIf*, R = CON(CH<sub>3</sub>)<sub>2</sub>  
*IIIf*, R = CONH<sub>2</sub>  
*IIIf*, R = COCl



*IVa*, R = COOH  
*IVb*, R = COOC<sub>2</sub>H<sub>5</sub>  
*IVc*, R = COOC(CH<sub>3</sub>)<sub>3</sub>  
*IVd*, R = CN

The reactivity of compounds *Ic*–*Ie* is documented by the Michael addition of diethyl acetamidomalonate to these compounds. Two products of the reaction with ester *Id* were isolated: in addition to the expected product *IVc* a considerable quantity of triethyl ester *IVb* (by reesterification of *IVc* by ethanol, used as a solvent), has been also formed. Addition product *IVc*, which did not crystallize, was converted to acid *IVa* by acidolysis.

Free acid *Ia* was prepared by saponification of ester *Ic* followed by treatment of the resulting sodium salt with 4-toluenesulfonic acid. The reaction of sodium 2-fluoropropenoate with benzoyl chloride afforded 2-fluoropropenoyl chloride (*Ih*).

2-Fluoro-3-(4-toluenesulfonyloxy)propanoic acid (*IIIa*) and a series of its derivatives were prepared from ester *IIIc*. The acidolysis of *IIIc* gave a 90% yield of free acid *IIIa* which was subsequently converted into esters *IIIb* and *IIIc* by treatment with diazomethane and 2-methylpropene, respectively. The treatment of acid *IIIa* with thionyl chloride gave chloride *IIIh*, from which dimethyl amide *IIIf* was prepared. Amide *IIIf* was prepared as described elsewhere<sup>10</sup>. This compound shows an unusual resistance to dehydrating reagents. Many procedures recommended<sup>12-18</sup> for the dehydration of amides were unsuccessful. Finally, the dehydration of amide *IIIf* to nitrile *IIIe* was effected by thionyl chloride in dimethylformamide<sup>19</sup> in a 60% yield and by trifluoroacetic anhydride<sup>20</sup> in an up to 90% yield.

## EXPERIMENTAL

The temperature data are not corrected. The melting points were determined in a capillary in the apparatus of Tottoli (Büchi, Switzerland). Varian Model 3700 Gas Chromatograph was used for the GLC analyses. The NMR spectra were measured in FT Jeol FX-60 NMR Spectrometer (59.797 MHz for <sup>1</sup>H, 15.036 MHz for <sup>13</sup>C, FT mode, CDCl<sub>3</sub>, 25°C, tetramethylsilane as internal standard). The chemical shifts are expressed in the  $\delta$ -scale. They were calculated from the digitally obtained address differences (accuracy  $\pm 0.005$  ppm and  $\pm 0.06$  ppm for <sup>1</sup>H and <sup>13</sup>C, respectively).

TABLE I

Preparation of 2-fluoropropenoic acid derivatives from 4-toluenesulfonates *IIIb*–*IIIf*

Compound	B.P., °C	Yield %	Vacuum used for preparation kPa
<i>Ib</i>	95 <sup>a</sup>	97	1.6
<i>Ic</i>	107–109 <sup>b</sup>	100	1.6
<i>Id</i>	104	85	1.6
<i>Ie</i>	35 <sup>c</sup>	70	5.33
<i>If</i> <sup>d</sup>	55/1.6 kPa	50	1.6
<i>Ig</i>	115–116 <sup>e</sup>	77 <sup>f</sup> ; 50 <sup>g</sup>	9.33 <sup>h</sup>

<sup>a</sup> Ref.<sup>9</sup>, b.p. 95°C; <sup>b</sup> ref.<sup>3</sup>, b.p. 110°C; <sup>c</sup> ref.<sup>8</sup>, b.p. 35–36°C; <sup>d</sup>  $n_D^{20}$  1.4417; <sup>e</sup> melting point (ref.<sup>10</sup>, m.p. 115–116°C); <sup>f</sup> crude yield; <sup>g</sup> yield of twice resublimed product; <sup>h</sup> reaction performed in a sublimator (cf. Experimental).

Ethyl 2-Fluoro-3-(4-toluenesulfonyloxy)propanoate (*IIIc*)

The compound was prepared as described before<sup>10</sup> except that only 1.4 equivalent of 4-toluenesulfonyl chloride was used. After recrystallization from ethanol the m.p. was 57–59°C (ref.<sup>10</sup> 53–54°C). For the conversion into *IVc*, the crude product may be used without purification.

2-Fluoro-3-(4-toluenesulfonyloxy)propanoic Acid (*IIIa*)

A mixture of ester *IIIc* (22.8 g), anhydrous formic acid (350 ml), and 4-toluenesulfonic acid (3 g) was heated 5 h at 100°C, evaporated *in vacuo*, another 350 ml portion of formic acid was added, and the procedure was repeated. After evaporation the residue was diluted with water (200 ml); after shaking for a short while it solidified to a product which was filtered off and washed with water. The yield was 19.3 g (94%) of acid *IIIa*, m.p. 110–111°C. The m.p. did not change after recrystallization from benzene. For  $C_{10}H_{11}FO_5S$  (262.2) calculated: 45.81% C, 4.19% H, 7.25% F, 12.23% S; found: 46.11% C, 4.34% H, 7.36% F, 12.41% S.

Methyl 2-Fluoro-3-(4-toluenesulfonyloxy)propanoate (*IIIb*)

Acid *IIIa* (2.6 g), dissolved in tetrahydrofuran (5 ml) was slowly treated with a solution of diazomethane (1 g) in ether (40 ml). After 30 min of reaction the excess of diazomethane was decomposed by methanolic hydrogen chloride and the mixture evaporated *in vacuo*. The oily ester *IIIb* crystallized after evaporation with a small volume of ether; yield 2.75 g (100%), m.p. 84–86°C. The sample for analysis had a m.p. 85–86°C (methanol). For  $C_{11}H_{13}FO_5S$  (276.3) calculated: 47.82% C, 4.74% H, 6.88% F, 11.61% S; found: 48.07% C, 4.89% H, 6.79% F, 11.31% S.

Tert-Butyl 2-Fluoro-3-(4-toluenesulfonyloxy)propanoate (*IIIc*)

A mixture of acid *IIIa* (2.6 g), dichloromethane (20 ml), 2-methylpropene (10 ml) and concentrated sulfuric acid (0.1 ml) was stirred 24 h in a closed vessel at room temperature. After the vessel had been opened the excess of 2-methylpropene was allowed to evaporate, the solution was extracted with sodium bicarbonate, dried, and evaporated *in vacuo*. The residue was taken to dryness over phosphorus pentoxide and recrystallized from a mixture of ether and light petroleum. Yield 2.4 g (75%) of ester *IIIc*, m.p. 60–62°C. The sample for analysis was crystallized by the same procedure, m.p. 61–62°C. For  $C_{14}H_{19}FO_5S$  (318.4) calculated: 52.81% C, 6.02% H, 5.97% F, 10.07% S; found: 52.94% C, 6.23% H, 6.03% F, 9.88% S.

2-Fluoro-3-(4-toluenesulfonyloxy)propanenitrile (*IIIe*)

A) Amide *IIId* (1.83 g), dissolved in dimethylformamide (15 ml) was treated dropwise with thionyl chloride (1.61 g) at 0°C with stirring. The mixture was set aside for 2 days at room temperature, then poured into an equal volume of water and the oil which had separated was extracted with ethyl acetate. The extract was washed with water until neutral, dried, and evaporated. The yield of nitrile *IIIe* was 1.02 g (60%), m.p. 44–45°C light petroleum. For  $C_{10}H_{10}FNO_3S$  (243.3) calculated: 49.37% C, 4.14% H, 7.81% F, 5.76% N, 13.18% S; found: 49.30% C, 4.16% H, 8.02% F, 5.67% N, 13.11% S.

B) A stirred solution of amide *IIId* (2.6 g) in a mixture of dioxane (10 ml) and pyridine (1.6 ml) was treated dropwise under cooling with ice-cold water 30 min with a solution of trifluoroacetic anhydride (1.6 ml) in dioxane (5 ml). The mixture was stirred 20 h without cooling, then diluted with water (100 ml) and extracted with three 30 ml portions of ether. The extract was washed

with water, dried and evaporated *in vacuo*. The remaining oil was triturated with ether (5 ml); after cooling (at  $+5^{\circ}\text{C}$ , overnight) a small quantity of unreacted amide *IIIg* had separated. The latter was filtered off, the filtrate was evaporated and the same operation was repeated once more; the remaining oil crystallized after inoculation. After drying in a desiccator the yield of nitrile *IIIe* was 2.2 g (90%), m.p.  $40-42^{\circ}\text{C}$ ; this product was identical with the compound prepared as described under *A*).

### 2-Fluoro-3-(4-toluenesulfonyloxy)propanoyl Chloride (*IIIh*)

A mixture of acid *IIIa* (10.0 g) and redistilled thionyl chloride (40 ml) was refluxed with stirring for 2 h, then evaporated *in vacuo*, the residue triturated with ether, repeatedly evaporated, and dried in a desiccator. The crude yield was 10.7 g of an oil which was subsequently used for the preparation of amide *IIIf*. For purification, ether (3 ml) was poured over the crude chloride, the mixture was allowed to stand overnight at  $-15^{\circ}\text{C}$  and the crystals were washed with ice-cold ether; yield 9.2 g (86%), m.p.  $48-48.5^{\circ}\text{C}$ . The crystals were dissolved in dichloromethane (30 ml), a small amount (*c.* 0.5 g) of an insoluble matter was filtered off and the solution was evaporated; the residue was dissolved in ether and again evaporated. The residue crystallized after 3 days *in vacuo* over phosphorus pentoxide; yield 8.5 g (80%) of a not entirely pure compound, m.p.  $60-61^{\circ}\text{C}$ . For  $\text{C}_{10}\text{H}_{10}\text{ClFO}_4\text{S}$  (280.7) calculated: 42.78% C, 3.59% H, 12.63% Cl, 11.42% S; found: 44.25% C, 3.94% H, 12.12% Cl, 11.95% S.

### N,N-Dimethyl-2-fluoro-3-(4-toluenesulfonyloxy)propanamide (*IIIj*)

A stirred solution of dimethylamine (4.4 g) in ether (45 ml) was treated dropwise within 30 min at  $-5^{\circ}\text{C}$  with a solution of crude chloride *IIIh* (from 10 g of acid *IIIa*) in benzene (35 ml). The mixture was stirred for 30 min, subsequently diluted with ether, washed with water, 5% hydrochloric acid, sodium bicarbonate, and water. Drying and evaporation *in vacuo* afforded an oil on which tetrachloromethane was layered; crystals had formed after two days. Yield 9.1 g (82%, calculated in terms of acid *IIIa*), m.p.  $63-66^{\circ}\text{C}$ . The sample for analysis had a m.p.  $64.5-66.5^{\circ}\text{C}$  (benzene-light petroleum). For  $\text{C}_{12}\text{H}_{16}\text{FNO}_4\text{S}$  (289.3) calculated: 49.81% C, 5.57% H, 6.57% F, 4.84% N, 11.08% S; found: 49.92% C, 5.55% H, 6.41% F, 4.82% N, 11.39% S.

### Derivatives of 2-Fluoropropenoic Acid *Ib*-*If*

A homogenized mixture of the appropriate 4-toluenesulfonyl derivative *IIb*-*IIf* with three equivalents of potassium phthalimide was placed in a vacuum flask with a wide flat bottom; the flask was connected to a trap cooled to  $-78^{\circ}\text{C}$ . The apparatus was connected to a pump through another dry ice trap in which moisture condensed, and evacuated to the value given in Table I. The flask with the reaction mixture was slowly heated in an oil bath. The main amount of the derivative of acid *Ia* distilled at  $100-120^{\circ}\text{C}$ ; the reaction was completed by 15 min heating at  $150^{\circ}\text{C}$ . The products, obtained in the yields specified, were always above 99% pure according to GLC and were either used immediately as such for the additional reactions or were stabilized by a trace of hydroquinone and then redistilled before the analysis or the NMR measurement.

**Ethyl 2-fluoropropenoate (Ic).**  $^1\text{H}$  NMR: 1.35 t (3 H,  $J = 7.3$  Hz,  $\text{CH}_3\text{CH}_2$ ); 4.31 q (2 H,  $J = 7.3$  Hz,  $\text{OCH}_2\text{CH}_3$ ); 5.26 dd (1 H,  $^2J_{\text{H,H}} = 3.4$  Hz,  $^3J_{\text{H,Feis}} = 6.8$  Hz); 5.73 dd (1 H,  $^2J_{\text{H,H}} = 3.4$  Hz,  $^3J_{\text{H,Feis}} = 36.6$  Hz).  $^{13}\text{C}$  NMR: 14.2 q ( $\text{CH}_3$ ); 62.0 t ( $\text{OCH}_2$ ); 102.5 t ( $^2J_{\text{C,F}} = 15.6$  Hz,  $\text{C}_{(3)}$ ); 153.6 s ( $^1J_{\text{C,F}} = 263.7$  Hz,  $\text{C}_{(2)}$ ); 160.4 s ( $^2J_{\text{C,F}} = 35.2$  Hz,  $\text{C}_{(1)}$ ).

**Tert-butyl 2-fluoropropenoate (Id).** For  $\text{C}_7\text{H}_{11}\text{FO}_2$  (146.2) calculated: 57.52% C, 7.59% H, 13.00% F; found: 57.68% C, 7.45% H, 13.16% F.

**2-Fluoropropenenitrile (Ie).**  $^1\text{H}$  NMR: 5.27 dd (1 H,  $^3J_{\text{H},\text{Ftrans}} = 23.0$  Hz,  $^2J_{\text{H},\text{H}} = 4.6$  Hz); 5.73 dd (1 H,  $^3J_{\text{H},\text{Feis}} = 8.8$  Hz,  $^2J_{\text{H},\text{H}} = 4.6$  Hz).  $^{13}\text{C}$  NMR: 108.3 t ( $^2J_{\text{C},\text{F}} = 17.6$  Hz, C<sub>(3)</sub>); 110.4 s ( $^2J_{\text{C},\text{F}} = 45.8$  Hz, C<sub>(1)</sub>); 138.0 s ( $^1J_{\text{C},\text{F}} = 252.0$  Hz, C<sub>(2)</sub>).

**N,N-Dimethyl-2-fluoropropenamide (If).** For C<sub>5</sub>H<sub>8</sub>FNO (117.1) calculated: 51.27% C, 6.88% H, 11.96% N, 16.22% F; found: 50.95% C, 6.89% H, 12.10% N, 16.01% F.

### 2-Fluoropropenamide (Ig)

The described procedure<sup>10</sup> was improved when carried out at reduced pressure. The optimum vacuum value lies in the range 9.0–9.5 kPa; if the pressure is further reduced considerable sublimation of the phthalimide takes place. The yield after resublimation was 50%, m.p. 115–116°C.

### 2-Fluoropropenoic Acid (Ia)

Ester Ic (1.8 g) was dissolved in a mixture of ethanol (14 ml) and water (5 ml) and hydrolyzed by stepwise addition of 2M aqueous sodium hydroxide until a positive reaction with phenolphthalein was obtained. After evaporation and drying the sodium salt of acid Ia was obtained in a yield of 1.6 g (94%). Acid Ia was mixed with anhydrous 4-toluenesulfonic acid (7.9 g) in a pre-cooled mortar and the mixture was heated in a sublimator at 80°C and a vacuum of 1.3 kPa. The mixture was pulverized after 30 min and the sublimation process was repeated. Yield, 0.5 g (39%) of acid Ia, m.p. 47–49°C, after resublimation 50–51°C (ref.<sup>1</sup>, m.p. 51.5–52°C).

### 2-Fluoropropenoyl Chloride (Ih)

A stirred mixture of sodium 2-fluoropropenoate (1.6 g) and benzoyl chloride (8 ml), containing hydroquinone (50 mg) was heated in a bath at 160°C. A total of 0.8 g of distillate was collected which yielded after redistillation 0.7 g (47%) of chloride Ih, b.p. 60°C. For C<sub>3</sub>H<sub>2</sub>ClFO (108.5) calculated: 32.68% Cl; found: 32.41% Cl.

### Addition of Diethyl Acetamidomalonate to 2-Fluoropropenoic Acid Derivatives

A) *To ethyl 2-fluoropropenoate (Ic):* The reaction was carried out essentially by the procedure described in literature<sup>3</sup>. Sodium (130 mg) and diethyl acetamidomalonate (13.5 g) were dissolved in warm ethanol (28 ml) with heating; to the partly cooled solution (c. 40°C) ester Ic (7.7 g) was added in one portion with stirring. The mixture was set aside for 3 h at room temperature and then placed for 20 h in the refrigerator. Product IVb was filtered off and washed with cold ethanol. Yield 18.7 g (88%), m.p. 102°C (ref.<sup>3</sup>, yield 58.7%, m.p. 103–104°C after recrystallization). The experiment was repeated several times with batches of ester Ic ranging up to 40 g; the yields varied from 80 to 88%.

B) *To tert-butyl 2-fluoropropenoate (Id):* The solution of diethyl acetamidomalonate (1.0 g) and sodium (10 mg) in ethanol (2.5 ml) was treated with ester Id (0.7 g). After two days of standing at room temperature the mixture was neutralized by 1 drop of methanolic solution of hydrogen chloride, evaporated *in vacuo* and dried in a desiccator. The yield of the resulting oil was 1.7 g. The latter was dissolved in dichloromethane (15 ml), a slow stream of hydrogen chloride was passed through the solution for 1 h at 0°C and the mixture was set aside for 48 h at +5°C. The solvent was evaporated *in vacuo*, the residue was extracted with ethyl acetate, the extract was shaken with a concentrated solution of sodium bicarbonate, and the aqueous phase again washed with a small volume of ethyl acetate. The pooled organic extracts yielded after drying and eva-

poration 0.7 g (45%) of triethyl ester *IVb* formed by partial reesterification; m.p. 98–100°C, without depression when mixed with an authentic sample. The alkaline aqueous solution was acidified by hydrochloric acid, the oil which had separated was extracted with ethyl acetate, dried, and evaporated. The oily residue was dissolved in ether (2 ml); on cooling to –15°C 0.35 g (25%) of the ester-acid *IVa* separated. M.p. 115–117°C, analytical sample 116–117°C (benzene–light petroleum). For  $C_{12}H_{18}FNO_7$  (307.3) calculated: 46.90% C, 5.90% H, 6.18% F, 4.56% N; found: 46.90% C, 5.91% H, 6.24% F, 4.51% N.

C) To 2-fluoropropenenitrile (*Ie*). A 40% solution of benzyltrimethylammonium hydroxide in methanol (0.5 ml) was added to a solution of diethyl acetamidomalonate (2.1 g) in dioxane (14.5 ml); subsequently the mixture was treated with nitrile *Ie* (0.7 g) in dioxane (1.8 ml) at 10°C. The mixture was set aside overnight at room temperature, acidified with hydrochloric acid to pH 1, and concentrated *in vacuo*. The residue was dissolved in ethyl acetate, washed with water, sodium bicarbonate, again with water, dried, and evaporated. The oil crystallized in the desiccator during 4 days; yield 1.9 g (68%). The crude addition product was crystallized from a mixture of ether and light petroleum (30–40°C); the total yield was 1.35 g (48%) of *IVd*, m.p. 64–69°C. The analytical sample showed a m.p. of 73–75° (aqueous ethanol). For  $C_{12}H_{17}FN_2O_5$  (288.3) calculated: 49.99% C, 5.95% H, 6.59% F, 9.72% N; found: 49.91% C, 5.98% H, 6.44% F, 9.60% N.

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*Note added in proof:* The described method has been successfully applied also for the synthesis of 2-fluoro-1-buten-3-one (*Ii*; R = COCH<sub>3</sub>). The desired 4-toluenesulfonate *IIIi* (R = COCH<sub>3</sub>) was prepared from 3-fluoro-4-hydroxy-2-butanone in a 30% yield, m.p. 48–49.5°C (ether–light petroleum); 2,4-dinitrophenylhydrazone of *IIIi*, m.p. 181–121°C (ethanol). Crude *IIIi* gave, on heating with potassium phthalimide, 91% of *Ii*, b.p. 66–69°C. Addition of diethyl acetamidomalonate to *Ii* (refluxing acetonitrile, potassium fluoride with 18-crown-6 as a catalyst) afforded *IVe* (R = COCH<sub>3</sub>) in a 63% yield, m.p. 78–79°C (ether–light petroleum).