

Fluoroalkyl Thieno- and Benzo-fused γ -Lactones

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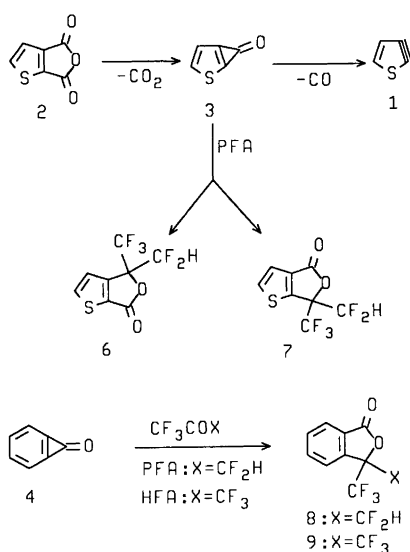
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The four aryl-fused perfluoroalkyl γ -lactones **6–9** have been prepared by the directed *ortho*-lithiation of the *N,N*-diethylamide **10** and the oxazolines **15** and **20** followed by reaction with either pentafluoroacetone or hexafluoroacetone. The two thiophene lactones **6** and **7** gave their corresponding hydroxy acids **18** and **14**, while the benzene lactone **8** lost the elements of CF_2 on saponification to give a new γ -lactone **24** and its corresponding hydroxy acid **25**. This acid closed spontaneously to **24** as did, even more rapidly, the hydroxy acid **28** of lactone **9**.

Dedicated to Professor Salo Gronowitz on the occasion of his 65th birthday.

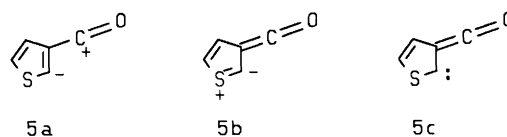
While 2,3-didehydrothiophene (**1**) remains the best confirmed example of a five-membered hetaryne,² the many previous unjustified claims for the generation of these elusive intermediates³ prompted us to probe for the presence of other species during the generation of **1** by the flash vacuum thermolysis (FVT) of the cyclic anhydride **2**.⁴ Polyfluoro carbonyl compounds such as



Scheme 1.

pentafluoroacetone (PFA) and hexafluoroacetone (HFA) are useful for this purpose⁵ yielding aryl-fused γ -lactones

[†] The caveat in Ref. 5 that species referred to as cyclic aryl-fused cyclopropanones may, in fact, be open structures has proved to be warranted in the thiophene series by more recent trapping⁶ and matrix isolation⁷ experiments which show that **3** is best represented as a ring-opened thenoyl species with dipolar (**5a**, **5b**) and/or α -thioetenecarbene (**5c**) character (Scheme 2). Labeling studies indicate that benzocyclopropanone is best represented as the usual cyclic structure (**4**), however.⁸

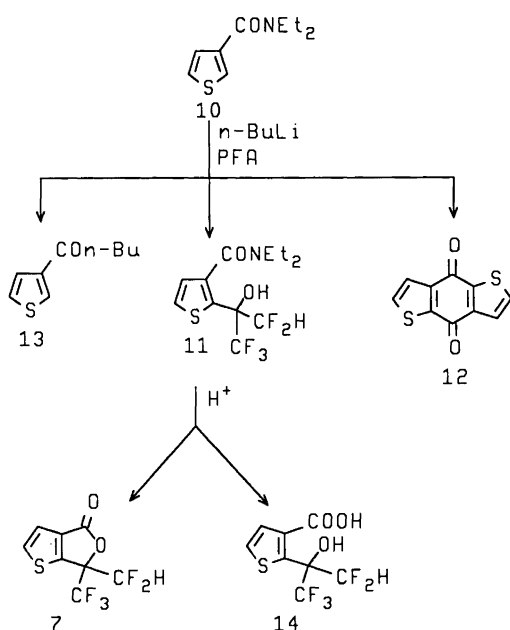


Scheme 2.

by trapping reactive intermediates with the composition, if not necessarily the structure,[†] of aryl-fused cyclopropanones **3** or **4** (Scheme 1). Since, in principle, two γ -lactones, **6** and **7**, might form during the FVT of **2** in the presence of PFA, independent syntheses of both of these isomers were undertaken as described in this paper. In addition, the preparation of the two benzene analogs with $\text{X} = \text{CF}_2\text{H}$ (**8**) and CF_3 (**9**) is reported along with a comparison of their chemical and spectral properties.

Results

The syntheses of these compounds is based on the well-known ability of certain substituents to direct metalation to an *ortho* position of an aromatic ring.⁹ For 3-substituted thiophenes, reaction at the 2-position is strongly favored by the combined directing effect of the substituent and the sulfur atom.¹⁰ Because of the superior *ortho*-directing ability of tertiary amide groups,¹¹ the *N,N*-diethylcarboxamide derivative (**10**)¹² of 3-thenoic acid was metalated with *n*-BuLi/TMEDA followed by treatment with PFA to give a mixture of three products which were separated by preparative TLC (Scheme 3). In addition to the expected hydroxy amide **11**, two additional products were obtained, the known¹³ anthraquinone analog **12**, previously observed upon metalation of the *N,N*-dimethyl analog of **10**,¹¹ and *n*-butyl-3-thienyl ketone (**13**), apparently formed by nucleophilic acyl substitution of the amide moiety. Acid hydrolysis of **11** gave a mixture of the lactone **7** and its corresponding acid **14** whose spectral and chromatographic properties

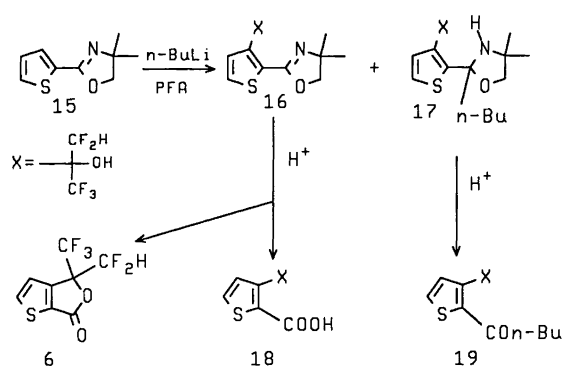


Scheme 3.

proved to be identical with the compounds isolated from the FVT of **2** with PFA.⁵

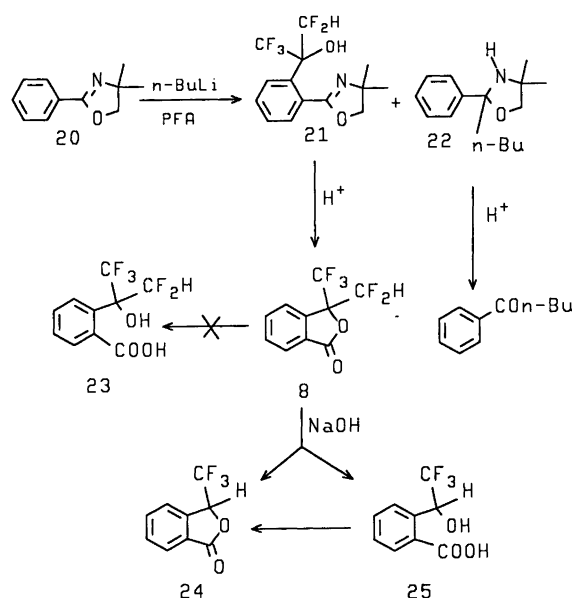
Synthesis of the isomeric lactone **6** by this methodology requires 3-metalation of a 2-substituted thiophene in competition with sulfur-directed 5-metalation. Since the regiochemical outcome is known to be unfavorable with a carboxamide directing group,¹⁰ the 2-oxazolinythiophene **15** was used because of its reported preference for 3-lithiation with the proper selection of solvent.¹⁴ Metalation of **15** with *n*-BuLi in ether at -78° followed by reaction with PFA gave a mixture of three products which were separated by preparative TLC (Scheme 4). The major products were the expected hydroxy oxazoline **16** and its BuLi addition product **17**, as a mixture of diastereomers. The minor product was not identified. Acid hydrolysis of **16** gave a mixture of the desired lactone **6** and its corresponding acid **18**, while the adduct **17** gave the thienyl ketone **19**.

The benzene analog **8** was prepared from the phenyloxazoline **20** in a similar way by metalation with *n*-BuLi followed by treatment with PFA (Scheme 5). The resulting mixture of the expected hydroxy oxazoline **21** and the BuLi addition product **22** of the starting material **20** was hydrolyzed with acid to give valerophenone and the desired γ -lactone **8**. None of the corresponding acid **23** was obtained, even upon an attempted saponification of **8** which instead gave a mixture of a new γ -lactone **24** and its corresponding hydroxy acid **25**. The structure of these products follows from their ¹H NMR spectra where the characteristic CF₂H triplets [*J* = 56 Hz] at δ 6.1–6.2 are replaced by quartets with *J* = 7.5 Hz at δ 5.62 and 6.96, respectively, consistent with the presence of a CHCF₃ group.¹⁵ The acid **25** reverted to the lactone **24** spontaneously at room temperature.

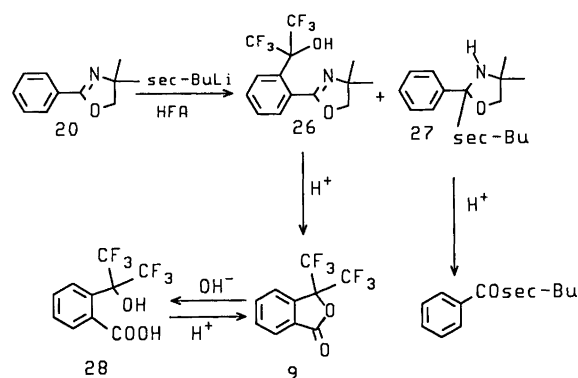


Scheme 4.

The final γ -lactone **9** also was prepared from the phenyloxazoline **20**, but the more hindered *sec*-BuLi was used in the metalation step which reduced the amount of addition by the lithium reagent to the oxazoline group from 27% to 9% (Scheme 6). After reaction with HFA



Scheme 5.

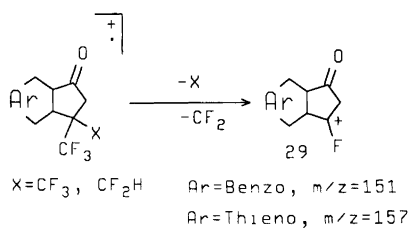


Scheme 6.

the resulting mixture of the hydroxy oxazoline **26** and the addition product **27** was hydrolyzed with acid to give the desired lactone **9** and *sec*-butyl phenyl ketone. Once again, none of the corresponding acid **28** was obtained. Saponification of **9** gave a clear solution of, presumably, the salt of the acid **28**, but upon acidification only the original lactone **9** was recovered.

Discussion

The synthesized γ -lactones are easily recognized by their characteristic infrared carbonyl frequencies¹⁶ above 1800 cm^{-1} and the mass spectral base peak at $m/z = 157$ or 151 , corresponding to the stabilized cation **29** generated by loss of CF_2 and either CF_2H or CF_3 from the molecular ion (Scheme 7).



Scheme 7.

Two aspects of the chemistry of the γ -lactones warrant comment, their differing tendency to ring-open to the corresponding hydroxy acids and the unusual conversion of **8** into **24**. While lactones **6**, **7** and **24** apparently open easily to give the corresponding stable hydroxy acids **14**, **18** and **25**, respectively, lactones **8** and **9** appear strongly to prefer the cyclic structures. In comparing the thiophene with the benzene-fused lactones, this difference can be understood in terms of the greater distance between *ortho* substituents in the former ring system¹⁷ introducing additional strain into the lactone rings which therefore open more readily. This explanation cannot account for the differences among the three benzo-fused lactones, however. In this case the greater tendency of lactones **8** and **9** to remain closed compared with **24** may be due to the absence of a *gem*-dialkyl effect in the latter.¹⁸

The mechanism of the reaction of **8** to **24** most likely involves the base-catalyzed concerted α -elimination of difluorocarbene.¹⁹ The absence of a similar reaction with the thiophene analogs **6** and **7** is also probably related to their relative ease of ring-opening compared with the benzo-fused lactone **8**. The resulting anionic carboxylates would resist the attack of a second anionic species as required for α -elimination.

Experimental

General. Melting points were measured on a Thomas-Hoover apparatus and are corrected. Analyses were performed by M-H-W laboratories of Garden City, Michigan. MS analyses were obtained on a Finnigan 1015

SL instrument at 70 eV. Selected peaks are reported as m/z (rel. int.) including all (except isotope peaks) with $m/z > 100$ and rel. int. > 10 . NMR spectra were obtained on JEOL JNM-MH-100 instrument and are reported in ppm downfield from Me_4Si at $\delta = 0$. Observed couplings J are reported in Hz, and CDCl_3 is the solvent unless otherwise noted. IR spectra were measured on Beckman 33 or Perkin Elmer 237 instruments as liquid films or KBr pellets. Preparative plates were made from TLC-grade silica gel and extracts were dried with anhydrous MgSO_4 .

N,N-Diethyl-2-(1,1,1,3,3-pentafluoro-2-hydroxypropan-2-yl)thiophene-3-carboxamide (**11**). To a solution of 3.8 ml of 1.6 M *n*-butyllithium (6 mmol) in hexane and 0.75 g (6 mmol) tetramethylethylenediamine in 20 ml of anhydrous ether at -78°C which had been stirred for 25 min, was slowly added 0.915 g (5 mmol) of *N,N*-diethylthiophene-3-carboxamide **10** in 10 ml of anhydrous ether. After an additional 1.5 h at -78°C 1.389 g (10 mmol) of PFA was introduced through a gas inlet tube and the mixture was stirred at -78°C for 7 h and at room temperature for 12 h. Addition of 20 ml of water, extraction with ether, and back-washing with 20 ml of 10% HCl gave aqueous and organic fractions. Upon neutralization and work-up the former gave 504 mg (55%) of recovered *N,N*-diethylthiophene-3-carboxamide by NMR comparison with an authentic sample. The organic fraction was dried, and concentrated to give 727 mg of a yellow oil which gave bands A, B, and C on preparative TLC using CH_2Cl_2 as the eluent.

Band A, R_f 0.89, 3.8 mg (3.6%) was identified as 3-(*n*-pentanoyl)thiophene (**13**): $^1\text{H NMR}$: δ 7.64 (d, 1 H, $J = 3.5$ Hz), 7.54 (d, 1 H, $J = 5$ Hz), 7.08 (dd, 1 H, $J = 3.5$ and 5 Hz), 2.88 (t, 2 H, $J = 8$ Hz), 1.84–0.80 (m, 7 H); IR: 3100, 2955, 2920, 2860, 1670 cm^{-1} ; MS: 168 (3, *M*), 153 (2), 139 (5), 126 (22), 110 (100).

Band B, R_f 0.70, 30 mg (5.3%) proved to be the quinone **12** by IR and TLC R_f value comparisons with those of an authentic sample.²⁰

Band C, R_f 0.55, was isolated as a yellow oil, 101.1 mg (13.6%) identified as the hydroxy carboxamide (**11**): $^1\text{H NMR}$: δ 7.38 (d, 1 H, $J = 5$ Hz), 6.98 (d, 1 H, $J = 5$ Hz), 6.04 (t, 1 H, $J = 56$ Hz), 3.54 and 3.38 (overlapping quartets, total 4 H, $J = 8$ Hz), 1.20 (two overlapping triplets, 6 H); IR: 3500–3050, 1600 cm^{-1} ; MS: 331 (17, *M*), 330 (17), 280 (100), 262 (9), 259 (56), 219 (10), 211 (14), 208 (42), 191 (43), 189 (13), 182 (40), 157 (24), 110 (48).

With *sec*-butyllithium instead of *n*-butyllithium, 21.7% of **11** and 1.7% of **12** were obtained.

6-Difluoromethyl-6-trifluoromethylthieno[2,3-*c*]furan-4(6H)-one (**7**). A mixture of 87 mg of **11** and 15 ml of 20% sulfuric acid was heated at reflux for 2 h, cooled and extracted with 30 ml of CH_2Cl_2 which, upon evaporation, left a residue which was dissolved in 15 ml of 10% NaOH and extracted with 30 ml of CH_2Cl_2 . The CH_2Cl_2 layer was dried and evaporated to give a yellow oil which was purified by TLC to give 45 mg (62%) of the lactone **7**: R_f

0.86 in CHCl_3 ; $^1\text{H NMR}$: δ 7.62 (d, 1 H, $J = 5$ Hz), 7.30 (d, 1 H, $J = 5$ Hz), 6.22 (t, 1 H, $J = 56$ Hz); IR: 3120, 1815 cm^{-1} ; MS: 258 (17, *M*), 239 (1), 207 (78), 189 (88), 157 (100), 129 (11), 110 (16).

The aqueous layer was acidified with 10% HCl and extracted with CH_2Cl_2 . The organic extract was dried and evaporated to give 13 mg (19.1%) of the hydroxy acid **14** as a white solid identical with that prepared by hydrolysis of lactone **7** as described below.

2-(1,1,1,3,3-Pentafluoro-2-hydroxypropan-2-yl)-3-thenoic acid (14). A mixture of the lactone **7** (30 mg) and 10 ml 25% NaOH was heated to reflux for 1 h, cooled, acidified with 6 M HCl and extracted with CH_2Cl_2 . Drying and evaporation of the organic extract left 32 mg (95%) of a light yellow solid which was sublimed to give white crystals, m.p. 134–135°C; Anal. $\text{C}_8\text{H}_5\text{F}_5\text{O}_3\text{S}$: C, H, S. $^1\text{H NMR}$: δ 7.61 (d, 1 H, $J = 5$ Hz), 7.41 (d, 1 H, $J = 5$ Hz), 6.60 (exch., br s, 2 H), 6.12 (t, 1 H, $J = 56$ Hz); IR: 3500–2800, 1675 cm^{-1} ; MS: 276 (2, *M*), 259 (1), 258 (1), 257 (1), 225 (55), 207 (100), 189 (34), 161 (18), 157 (97), 133 (14), 129 (9), 111 (29), 110 (15).

3-(1,1,1,3,3-Pentafluoro-2-hydroxypropan-2-yl)-2-(4,4-dimethyl-2-oxazolin-2-ylthiophene (16). To a stirred solution of 0.905 g (5 mmol) of 4,4-dimethyl-2-(2-thienyl)-2-oxazoline **15**¹⁴ in 20 ml of anhydrous ether were slowly added 3.8 ml (6 mmol) of *n*-butyllithium in hexane at -78°C . Stirring was continued for 15 min at -78°C and 30 min at 0°C after which time 1.18 g (8 mmol) of PFA were introduced through a gas inlet tube. After an additional hour at 0°C the mixture was allowed to warm to room temperature, poured into water and extracted with 3×30 ml of ether. The ether extracts were washed, dried, evaporated and the residue was separated into three bands (R_f 0.76, 0.38 and 0.17) by preparative TLC with CH_2Cl_2 as the eluent. The first was 44 mg (4%) of unchanged **15**, and the second 77 mg of an unidentified gummy material.

The third band contained two components which were separated by preparative TLC with benzene–carbon tetrachloride (4:1) into the hydroxy oxazoline **16**, R_f 0.56, 774.6 mg (47%); $^1\text{H NMR}$: δ 7.49 (d, 1 H, $J = 5$ Hz), 7.38 (d, 1 H, $J = 5$ Hz), 6.07 (t, 1 H, $J = 56$ Hz), 4.13 (s, 2 H), 1.37 (s, 6 H); IR: 3200–2200, 2985, 1655 cm^{-1} ; MS: 329 (3, *M*), 314 (14), 310 (2), 278 (100), 260 (10), 207 (21), 206 (12), 157 (19), 130 (26), 110 (11) and the *n*-butyllithium addition products **17** (diastereoisomers), 186.1 mg (9.6%), R_f 0.35, $^1\text{H NMR}$: δ 7.18 (d, 1 H, $J = 5$ Hz), 7.10 (d, 1 H, $J = 5$ Hz), 6.00 and 5.86 (two sets of triplets, $J = 56$ Hz, 1 H), 3.68 and 3.88 (two sets of doublets, 2 H, $J = 8$ Hz), 3.0 (br s), 1.8–2.4 (m, 2 H), 0.7–1.4 (m, 7 H), 1.3 (s, 6 H); IR: 3300, 3120, 2980, 2940, 2880, 1655 (w) cm^{-1} ; MS: 387 (0.8, *M*), 364 (2), 362 (4), 355 (1), 354 (2), 329 (100), 313 (2), 298 (4), 277 (2), 258 (4), 257 (4), 155 (7), 110 (4).

*3-(1,1,1,3,3-Pentafluoro-2-hydroxypropan-2-yl)-2-(*n*-pentanoyl)thiophene (19)*. A mixture of **17** (121 mg) and

15 ml of 6 M HCl was heated at reflux for 6 h, cooled and extracted with CH_2Cl_2 which was dried and evaporated to give 92 mg (93%) of the liquid ketone **19**: $^1\text{H NMR}$: δ 9.38 (d, exch. 1 H, $J = 5$ Hz), 7.65 (d, 1 H, $J = 5$ Hz), 7.49 (d, 1 H, $J = 5$ Hz), 6.02 (t, 1 H, $J = 56$ Hz), 3.04 (t, 2 H, $J = 8$ Hz), 1.76 (quintet, 2 H, $J = 8$ Hz), 1.40 (sextet, 2 H, $J = 8$ Hz), 0.94 (t, 3 H, $J = 7.5$ Hz); IR: 3120, 2940, 1655 cm^{-1} ; MS: 316 (18, *M*), 298 (4), 297 (4), 296 (3), 292 (4), 273 (36), 264 (14), 258 (100), 210 (25), 204 (12), 190 (18), 134 (11), 110 (35).

3-(1,1,1,3,3-Pentafluoro-2-hydroxypropan-2-yl)-2-thenoic acid (18) and its lactone (6). A mixture of 650 mg of the hydroxy oxazoline **16** and 20 ml of 6 M HCl was heated under reflux for 16 h, cooled and extracted with CH_2Cl_2 . The organic layer was stirred with 20 ml of 5% NaOH, dried, and evaporated to give 265 mg (52%) of the liquid lactone **6** which was purified by TLC. $^1\text{H NMR}$: δ 8.01 (d, 1 H, $J = 5$ Hz), 7.24 (d, 1 H, $J = 5$ Hz), 6.22 (t, 1 H, $J = 56$ Hz); IR: 3120, 1815 cm^{-1} ; MS: 258 (12, *M*), 211 (11), 207 (56), 189 (4), 161 (13), 157 (100), 129 (13), 111 (11), 110 (27).

The NaOH layer was acidified with 3 M HCl, extracted with CH_2Cl_2 , dried and evaporated and the residue sublimed to give 202 mg (37%), of **18** as white crystals, m.p. 99–101°C; Anal. $\text{C}_8\text{H}_5\text{F}_5\text{O}_3\text{S}$: C, H, S. $^1\text{H NMR}$: 8.00 (exch. br s, 2 H), δ 7.67 (d, 1 H, $J = 5$ Hz), 7.46 (d, 1 H, $J = 5$ Hz), 6.07 (t, 1 H, $J = 56$ Hz); IR: 3500–2200, 1675 cm^{-1} ; MS: 276 (2, *M*), 259 (2), 258 (1), 257 (1), 225 (60), 207 (100), 189 (24), 157 (88), 133 (10), 111 (52), 110 (15).

1-Difluoromethyl-2-trifluoromethyl-2-benzofuran-3(1H)-one (8). To a stirred solution of 1.312 g (7.5 mmol) of the phenyloxazoline **20**²¹ in 25 ml of anhydrous ether were slowly added 9 mmol of *n*-butyllithium in hexane at -78°C under nitrogen. After 15 min at -78°C and 30 min at 0°C , 1.77 g (12 mmol) of PFA were introduced through a gas inlet tube and the mixture was stirred for an additional hour at 0°C and 5 h at room temperature after which time it was poured into water. The ether extract of the resulting mixture was back-washed with water, dried and evaporated to give 1.802 g of a residue which was separated into two bands by preparative TLC with CH_2Cl_2 . The second band was identified as starting material **20**, 616 mg (47% recovery) while the first was separated into two new bands by further preparative TLC using benzene as the eluent. The first was identified as valerophenone (40 mg) by comparison of its NMR and IR with reported data,²² while the second (881 mg), according to NMR and IR spectroscopy still contained a mixture of **21** and **22**. This mixture was therefore hydrolyzed under reflux for 10 h with 40 ml of 6 M HCl. The CH_2Cl_2 extract of the cooled reaction mixture was stirred with 20 ml of 5% NaOH and the layers were separated. No residue was obtained from extraction, drying and evaporation of the acidified aqueous layer. Drying and evaporation of the organic layer gave a liquid

which was separated into two bands by preparative TLC using CH_2Cl_2 as the eluent. The second was identified as valerophenone, 68 mg (16.8% based on reacted **20**) and the first as the lactone **8** (680 mg, 63.4% based on reacted **20**). ^1H NMR (CCl_4): δ 7.50–8.00 (m, 4 H), 6.24 (t, 1 H, $J = 54$ Hz); IR: 3100, 2940, 1820 cm^{-1} ; MS: 252 (8, *M*), 233 (4), 201 (76), 155 (12), 151 (100), 127 (27), 123 (36), 107 (10), 104 (27).

2-(1,1,1,3,3-Pentafluoro-2-hydroxypropan-2-yl)benzoic acid 25 and its lactone 24. A mixture of 100 mg of the lactone **8** and 10 ml of 2 M NaOH (or 25% NaOH) was heated under reflux for 15 min (or 1 h), cooled and extracted with CH_2Cl_2 . Only a trace of an unidentified residue was obtained from the organic layer. The CH_2Cl_2 extract of the acidified aqueous layer was dried and evaporated to leave a residue (89 mg) which was separated by preparative TLC with CH_2Cl_2 into two bands present in ample amount for characterization. The band with $R_f = 0.80$ was the lactone **24**, 23 mg (28.8%). ^1H NMR: δ 7.52–7.98 (m, 4 H), 5.62 (q, 1 H, $J = 7.5$ Hz); IR: 3100, 2970, 1800 cm^{-1} ; MS: 202 (5, *M*), 183 (0.2), 133 (100), 105 (31).

The band with $R_f = 0.06$ was the hydroxy acid **25** (41 mg, 47%) which slowly reverted to the lactone **24** at room temperature. ^1H NMR (acetone- d_6): δ 7.36–8.02 (m, 4 H), 6.60 (exch., br s, 2 H), 6.46 (q, 1 H, $J = 7.5$ Hz); IR: 3450, 3600–2400, 1700, 1590, 1500, 1460, 1410, 1350, 1310, 1250, 1185, 1120, 1050, 925, 885, 860, 800, 745, 705 cm^{-1} ; MS: 203 (4, *M* – OH), 202 (1, *M* – H_2O), 201 (5, *M* – F), 183 (19), 133 (100), 132 (10), 105 (50), 104 (29).

1,1-Bis(trifluoromethyl)-2-benzofuran-3(1H)-one (9). To a solution of 1.312 g (7.5 mmol) of **20** in 25 ml of anhydrous ether were slowly added 6.9 ml of 1.3 M *sec*-BuLi (9 mmol) in cyclohexane at -78°C with stirring under nitrogen. After 15 min at -78°C and 30 min at 0°C , 1.99 g (12 mmol) of HFA were introduced through a gas inlet tube and the mixture was stirred at 0°C for 2 h, and then at room temperature for 5 h after which it was poured into water. The ether extracts of the resulting mixture were washed with water, dried and evaporated to give 2.29 g of a yellow oil which was hydrolyzed with 20 ml of 6 M HCl at reflux for 12 h. The CH_2Cl_2 extracts of the cooled reaction mixture were stirred with 20 ml of 2 M NaOH and the layers separated. The acidified aqueous layer was extracted with CH_2Cl_2 , which, after drying and evaporation gave 49.3 mg of benzoic acid (equivalent to 5.5% recovery of unchanged **20**), identified by NMR and IR comparisons with an authentic sample.

The dried organic layer was evaporated to give 1.08 g of a yellow oil which was separated by preparative TLC with benzene into two bands present in sufficient amount for characterization. The major compound, $R_f = 0.76$, 740.7 mg (36.6%) was the lactone **9**. ^1H NMR: δ 7.64–8.04 (m); IR: 3090, 1830 cm^{-1} ; MS: 270 (6, *M*), 251 (3), 201 (59), 151 (100), 123 (32), 104 (22).

The second sample, $R_f = 0.53$, was identified as *sec*-butyl

phenyl ketone 111.6 mg (9.2%). ^1H NMR: δ 7.98–7.78 (m, 2 H), 7.44–7.24 (m, 3 H), 3.33 (sextet, 1 H), 1.62 (d of quintets, 2 H, $J = 8, 14$ Hz), 1.15 (d, 3 H, $J = 7$ Hz), 0.88 (t, 3 H, $J = 8$ Hz); IR: 3080, 2980, 2940, 2880, 1690 cm^{-1} .

Attempted hydrolysis of the lactone 9. A mixture of 50 mg of the lactone **9** and 10 ml of 2 M NaOH heated at reflux became homogeneous after 10 min. After an additional 5 min the reaction mixture was acidified with 6 M HCl and extracted with CH_2Cl_2 . The dried and evaporated organic layer gave 36 mg of a liquid which was identified as the recovered lactone **9**.

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