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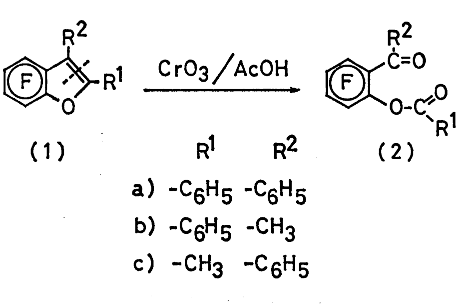
ortho-Disubstituted *F*-Benzenes. IV. The Formation of 2-Acyl-*F*-phenyl Carboxylates from (*F*-Benzo)furans by the Oxidative Cleavage of the Furan-ring

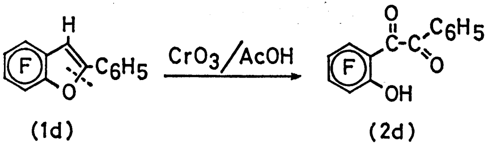
Yoshinari Inukai,† Takaaki Sonoda, and Hiroshi Kobayashi*
Research Institute of Industrial Science, Kyushu University 86, Kasuga 816

(Received May 6, 1981)

Synopsis. 2,3-Diphenyl-, 2-phenyl-3-methyl-, and 2-methyl-3-phenyl(*F*-benzo)furans were oxidized with chromium trioxide in acetic acid to yield 2-benzoyl-*F*-phenyl benzoate, 2-acetyl-*F*-phenyl benzoate, and 2-benzoyl-*F*-phenyl acetate respectively, while 2-phenyl(*F*-benzo)furan was least susceptible to the same reagent, affording 1-(2-hydroxy-*F*-phenyl)-2-phenylethanedione in a poor yield. The spectral data of the products were compatible with the structure of *ortho*-disubstituted *F*-benzene.

In connection with the studies of the *ortho*-disubstituted *F*-benzenes,[1,2] we have examined the oxidative cleavage of the side-ring of (*F*-benzo)furans (**1**), which were previously described.[3] In a manner similar to that of unfluorinated analogues,[4] the (*F*-benzo)furans (**1**) were oxidatively cleaved between the 2- and 3-positions of the furan ring with chromium trioxide to give *ortho*-disubstituted *F*-benzenes. 2,3-Diphenyl-, 2-phenyl-3-methyl-, and 2-methyl-3-phenyl-(*F*-benzo)furans (**1a**—**c**) yielded 2-benzoyl-*F*-phenyl benzoate (**2a**), 2-acetyl-*F*-phenyl benzoate (**2b**), and 2-benzoyl-*F*-phenyl acetate (**2c**) respectively. The *F*-phenyl ester groups remained intact; they were not hydrolyzed in acid-reaction media. 2-Phenyl(*F*-benzo)furan (**1d**), however, behaved in a different manner upon oxidation with the same reagent. The (*F*-benzo)furan (**1d**) was cleaved at the C–O bond under similar reaction conditions to give 1-(2-hydroxy-*F*-phenyl)-2-phenylethanedione (**2d**) in a poor yield. In the meantime, approximately one-third of the starting compound was recovered unchanged. Although a considerable amount of benzoic acid was isolated from the resulting mixture, no trace was found relating to the *F*-benzo moiety, which would be present in the form of *F*-salicylic acid or salicylaldehyde.





(1d) (2d)

The cleavage of the furan-ring structure was proved by the disappearance of the UV band characteristic of the benzofuran moiety.[5] The ^{19}F-NMR signal of the fluorine atom at the 3-position in Compound (**2b**) was assigned by means of the long-range coupling between the fluorine and the three hydrogens on the vicinal-acetyl group. The fluorine atoms at the 3- and 6-positions in Compounds (**2a**) and (**2c**) were assigned on the basis of the fluorine chemical shifts obtained in Compound (**2b**). Those of Compound (**2d**) were tentatively assigned according to the spin-spin coupling pattern exhibited in its ^{19}F-NMR spectrum.

Experimental

General Procedure. A solution of chromium trioxide (2.9 mmol) in water (2 ml) was added to a mixture of a (*F*-benzo)furan derivative (**1a**—**c**) (1.2 mmol) and acetic acid (60 ml). The mixture was refluxed for 9 h, cooled, concentrated to a quarter of the original volume, and poured into ether. The ethereal solution was washed with water, dried over sodium sulfate, and evaporated *in vacuo*. The residue was chromatographed on a silica-gel column. The fraction eluted with hexane–dichloromethane gave a 2-acyl-*F*-phenyl carboxylate (**2a**—**c**). No fraction of the starting compound remained unchanged in the reaction mixture. The ^{1}H- and ^{19}F-NMR shifts were measured against TMS and *F*-benzene respectively as internal references.[6]

*2-Benzoyl-*F*-phenyl Benzoate (2a)*: Yield: 61%. Recrystallization from hexane gave colorless needles, mp 53—54 °C. IR (KBr): 1750 and 1670 cm^{-1} (C=O). ^{1}H-NMR (CDCl$_3$): $\delta=7.0$—8.1 (m, arom.). ^{19}F-NMR (CHCl$_3$): $\delta=5.0$ (ddd, 1F, F^4), 10.5 (ddd, 1F, F^5), 13.5 (ddd, 1F, F^6), and 22.3 (ddd, 1F, F^3), $J_{4-6}=1.9$, $J_{3-5}=2.9$, $J_{3-6}=10.2$, $J_{5-6}=20.4$, and $J_{3-4}=23.4$ Hz). UV (EtOH); λ_{max} (log ε); 202 (4.50) and 238 nm (4.26). Found: C, 64.09; H, 3.06%; M$^+$, 374. Calcd for C$_{20}$H$_{10}$O$_3$F$_4$: C, 64.18; H, 2.69%; M, 374.

*2-Acetyl-*F*-phenyl Benzoate (2b)*: Yield: 48%. Colorless oil. IR (neat): 1760 and 1640 cm^{-1} (C=O). ^{1}H-NMR (CCl$_4$): $\delta=2.45$ (d, $J=3$ Hz, 3H, CH$_3$) and 7.2—8.2 (m, 5H, arom.). ^{19}F-NMR (CCl$_4$): $\delta=4.0$ (ddd, 1F, F^4), 10.4 (ddd, 1F, F^5), 11.3 (ddd, 1F, F^6), and 21.0 (dddq, 1F, F^3), ($J_{4-6}=1.0$, $J_{3-\text{H}}=3.4$, $J_{3-5}=3.9$, $J_{3-6}=9.7$, $J_{5-6}=J_{4-5}=20.4$, and $J_{3-4}=23.4$ Hz). UV (EtOH): λ_{max} (log ε); 205 (3.10), 233 (4.27), and 277 nm (3.44). Found: C, 57.84; H, 2.67%; M$^+$, 312. Calcd for C$_{15}$H$_8$O$_3$F$_4$: C, 57.70; H, 2.58%; M, 312.

*2-Benzoyl-*F*-phenyl Acetate (2c)*: Yield; 81%. Colorless oil. IR (neat): 1790 and 1690 cm^{-1} (C–O). ^{1}H-NMR (CCl$_4$): $\delta=2.0$ (s, 3H, CH$_3$) and 7.2—7.8 (m, 5H, arom.). ^{19}F-NMR (CCl$_4$): $\delta=8.3$ (ddd, 1F, F^4), 8.9 (ddd, 1F, F^5), 14.4 (ddd, 1F, F^6), and 24.1 (ddd, 1F, F^3), $J_{4-6}=1.5$, $J_{3-5}=2.4$, $J_{3-6}=10.2$, $J_{5-6}=J_{4-5}=20.4$, and $J_{3-4}=23.4$ Hz). UV (EtOH): λ_{max} (log ε); 206 (4.19) and 255 nm (4.15). Found: C, 57.65; H, 2.70%; M$^+$, 280. Calcd for C$_{15}$H$_8$O$_3$F$_4$: C, 57.70; H, 2.58%; M, 280.

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† Present address: Government Industrial Research Institute in Kyushu, Shukumachi, Tosu, Saga 841.

*Oxidation of 2-Phenyl(*F*-benzo)furan (**1d**).* After they had been worked-up in a similar manner, the reaction products from the (*F*-benzo)furan (**1d**) were chromatographed on a silica-gel column. The fraction eluted with hexane–dichloromethane gave 1-(2-hydroxy-*F*-phenyl)-2-phenylethanedione (**2d**), in a 3.7% yield. Mp 99—100 °C. IR (KBr): 3500 (OH), 1740 and 1660 cm^{-1} (C=O). ^{1}H-NMR ($CDCl_3$): δ=7.4—8.2 (m, 5H, arom.) and 11.4—11.8 (br.s, 1H, OH). ^{19}F-NMR ($CDCl_3$): $\delta=-6.1$ (br.dd, 1F, F^4), 1.2 (ddd, 1F, F^6), 21.4 (ddd, 1F, F^5) and 28.7 (m, 1F, F^3), ($J_{3-4}=24.5$, $J_{3-5}=8.5$, $J_{3-6}=10.0$, $J_{4-5}=20.0$, $J_{4-6}=3.5$, and $J_{5-6}=20.5$ Hz). Found: *m/e*, 298.0275. Calcd for $C_{14}H_6O_3F_4$: 298.0296. A phenol test with iron(III) chloride in methanol gave red purple coloration. The starting substance (**1d**) (33%) and benzoic acid (13%) were isolated from the hexane- and the dichloromethane fractions respectively.

References

1) Part III: Y. Inukai, Y. Oono, T. Sonoda, and H. Kobayashi *Bull. Chem. Soc. Jpn.*, **54**, 3447 (1981).

2) According to the revised nomenclature of highly fluorinated organic compounds by J. A. Yound, *J. Chem. Document.*, **14**, 98 (1974) and *J. Fluorine Chem.*, **6**, 571 (1975).

3) Y. Inukai, T. Sonoda, and H. Kobayashi, *Bull. Chem. Soc. Jpn.*, **52**, 2657 (1979).

4) A. Wacek and F. Zeisler, *Monatsch. Chem.*, **83**, 5 (1952).

5) Note 9 in Ref. 3 and the literature cited therein.

6) ^{19}F-NMR chemical shifts are given as positive values downfield from the reference signal.