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POLYFLUORINATED AROMATIC ESTERS PREPARATION AND CARBONYL STRETCHING FREQUENCIES

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As part of studies currently in progress on the chemistry of highly fluorinated aromatic compounds, we have prepared a number of esters and have examined their infrared spectra with reference to the influence of pentafluorophenyl substitution on the carbonyl frequency. The role of perfluoroalkyl groups in shifting the ester carbonyl band to higher frequencies has been discussed previously (1-4).

In this note we report the preparation and infrared spectral data for phenyl benzoates in which a pentafluorophenyl group is located in the acid and (or) phenolic portions of the ester, as well as data for several other esters containing the C_6F_5 group. The results are summarized in Table I.

TABLE I arbonyl frequencies of pentafluorophenyl est	
Compound	$\nu_{\rm C-0} (\rm cm^{-1})$
$\begin{array}{c} C_6H_5CO_2C_6H_5\\ C_6F_5CO_2C_6H_5\\ C_6F_5CO_2C_6F_5\\ C_6F_5CO_2C_6F_5\\ C_6F_5CO_2CH_2CH_3\\ C_6F_5CO_2CH_2CH_3\\ C_6F_5CO_2CH_2CF_3\\ CF_3CO_2C_6F_5 \end{array}$	174017701765178017411760, 17651787

The data may be rationalized in terms of both the inductive and mesomeric effects. If we consider the canonical structures a-d, we see that, when R = alkyl, electron release causes the relative contribution of structure d to be much more significant than when $R = C_6H_5$, thereby enhancing the single-bond character of the C=O group (lower frequency). Thus, methyl benzoate exhibits carbonyl absorption at 1.724 cm^{-1} (5), whereas in phenyl benzoate the band shifts to 1 740 cm⁻¹. Comparison of ethyl pentafluorobenzoate with phenyl pentafluorobenzoate provides a second example.

When the phenyl group is replaced by the C_6F_5 group in the acid portion of the ester, Canadian Journal of Chemistry. Volume 44 (1966)



the strong electron-attracting inductive effect serves to diminish the contributions of structures b, c, and d, thus enhancing the double-bond character of the carbonyl group relative to that of the C₆H₅-substituted ester. However, the mesomeric effect operates in the opposite direction and increases contributions of type c, as indicated in structure I (and its ortho analogues).



In other recent experiments, we have demonstrated that the inductive effect is considerably stronger than the mesomeric effect in the C_6F_5 group. Therefore, the observed increase in the carbonyl stretching frequency is to be expected. When $R = C_6F_5$, structure *d* is strongly destabilized by the inductive effect. This is substantiated by the pronounced shift to higher frequency of pentafluorophenyl benzoate (1 765 cm⁻¹) compared with phenyl benzoate (1 740 cm⁻¹). Pentafluorophenyl pentafluorobenzoate, the first stable, completely fluorinated ester, reflects the influence of the C_6F_5 group at both ends of the molecule (1 780 cm⁻¹), but the effect is somewhat less than additive.

EXPERIMENTAL

Infrared Spectra

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All compounds were measured as 5% solutions in carbon tetrachloride. The spectra were obtained on two instruments, a Beckman IR-8 grating spectrometer and a Perkin–Elmer 21 double-beam spectrometer equipped with sodium chloride optics.

Phenyl Pentafluorobenzoate

Pentafluorobenzoyl chloride (4.58 g) and phenol (1.88 g) were heated under reflux for 1.5 h in a 25 ml flask, with occasional shaking. After the flask was cooled, its contents were dissolved in ether, washed successively with water, 5% sodium carbonate solution, and again with water, and dried over anhydrous sodium sulfate; then the ether was removed. The residue was crystallized from hot methanol to give 1.4 g (24.6%) of ester, m.p. 66-67°.

Anal. Calcd. for C13H5O2F5: C, 54.13; H, 1.73. Found: C, 54.01; H, 1.95.

Pentafluorophenyl Benzoate¹

Pentafluorophenol (3.68 g) and benzoyl chloride (2.8 g) were heated under reflux for 1.5 h. The contents of the flask were dissolved in ether and worked up as described above to give 1.0 g (17.5%) of ester, m.p. 73.0-73.5°.

Anal. Calcd. for C₁₃H₅O₂F₅: C, 54.13; H, 1.73. Found: C, 54.01; H, 1.87.

Pentafluorophenyl Pentafluorobenzoate

A mixture of 10.57 g of pentafluorobenzoyl chloride and 7.86 g of pentafluorophenol was heated under reflux for 3 days to give 16.0 g (99%) of pentafluorophenyl pentafluorobenzoate, b.p. 67–69° at 10^{-5} mm, m.p. $36.5-37.5^{\circ}$.

Anal. Calcd. for $C_{13}O_2F_{10}$: C, 41.30; F, 50.25; mol. wt. 378. Found: C, 41.34; F, 50.31; mol. wt. (osmometry in benzene) 371, 374.

¹Birchall and Haszeldine (6) reported m.p. 74–75° and $\nu_{C=0}$ (mull) 1 773 cm⁻¹.

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Ethyl Pentafluorobenzoate

Pentafluorobenzoyl chloride (8.0 g, 0.035 mole) was added during 30 min to 1.7 g (0.037 mole) of absolute ethanol in a three-necked flask fitted with a dropping funnel, a reflux condenser, and a magnetic stirrer. The mixture was heated under reflux during the addition, and heating was continued for an additional 3 h at 70-80°. The solution was cooled, poured into 3 ml of water, and then washed with two 3 ml portions of a saturated sodium bicarbonate solution and two 3 ml portions of water. After the solution was dried over anhydrous sodium sulfate, distillation gave 4.5 g (54%) of ethyl pentafluorobenzoate, b.p. 93-94° at 10 mm.

Trifluoroethyl Pentafluorobenzoate

To a mixture of 5.0 g (0.022 mole) of pentafluorobenzoyl chloride and 2.2 g (0.022 mole) of trifluoroethanol was added, in small portions, 1.0 g of powdered anhydrous aluminium chloride. The mixture was heated under reflux overnight, cooled, poured into 6 N hydrochloric acid, and extracted with ether. The ether extracts were combined, washed with a 2% solution of sodium bicarbonate until neutral to litmus, and then washed with water. After the solution was dried over anhydrous sodium sulfate, the ether was removed and the product distilled to give 5.0 g (78%) of trifluoroethyl pentafluorobenzoate, b.p. 184-186° at 750 mm, 52-54° at 13 mm.

Anal. Calcd. for C₉H₂O₂F₈: C, 36.75; H, 0.69. Found: C, 37.45; H, 0.87.

Pentafluorophenyl Trifluoroacetate

Pentafluorophenol and trifluoroacetyl chloride reacted at -28° (carbon tetrachloride - dry ice) during 2.5 h. After the mixture was warmed to room temperature, it was dissolved in ether and washed thoroughly with water. The ether layer was dried over anhydrous sodium sulfate. Distillation gave two main fractions, b.p. 65-86° at 10 mm and 85-100° at 10 mm, both of which exhibited a single peak in the carbonyl region at 1787 cm⁻¹.

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SYNTHESIS AND CHROMATOGRAPHIC PROPERTIES OF N-ALKYL-L-ASPARAGINES¹

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Biochemical and physiological studies in this laboratory required a series of N-alkyl-Lasparagines. Unlike the N-alkyl-DL-asparagines, which are readily synthesized (1-4), the L-antipodes, in spite of recent interest in their potential role in biological systems (5–7), are scarcely documented. To our knowledge, only the syntheses of N-ethyl-L-asparagine (6) and N-phenyl-L-asparagine (8) have been reported. We therefore investigated a

¹The abbreviations are derived in accordance with the rules proposed by the commission on the nomenclature of biological chemistry, J. Am. Chem. Soc., 82, 5575 (1960).

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