

unresolved peaks in the spectrum of the CF_2N fluorines of **2** to the fluorine *trans* to NCl . The downfield shift of the *cis* CF_2N fluorine on going from **2a** to **2b** is consistent with that observed for the related fluorine in **1**. Lee and Orrell¹⁰ have made the same assignment to the CF_2N fluorines of perfluoro-2-methyl-1,2-oxazetidine (spectrum obtained at -74°). The fluorine showing coupling with the CF_3 group (upfield half of AB quartet) was assigned *cis* to NCF_3 , while the downfield fluorine was observed as a broad, structureless absorption.

The assignment of nmr peaks to the CF_2O fluorines is somewhat more difficult. However, it may be argued that the fluorine of this group, which is *cis* to the N-halo group, will experience a greater environmental change and consequently a more pronounced variation in chemical shift as a result of the 1,3-diaxial interaction in conformer a. On this basis, then, the *cis* CF_2O fluorine is assigned to the upfield half of the AB pattern in the spectrum of **1** and to the lower field half in the spectrum of **2**.

A small chemical-shift change was detected for the NF of **1** when the sample was cooled from 24 to -120° . The downfield shift amounted to *ca.* 0.5 ppm ($\phi^* -25.8$ ppm at -120°). The broadness of the signal made the exact measurements of peak position difficult. Since the fraction of conformer **1b** would increase by 0.13 over this temperature range, the change in the NF chemical-shift in going from **1a** to **1b** would represent *ca.* 217 Hz.

Experimental Section

The ^{19}F nmr spectra were obtained with a Varian Model V-4302B spectrometer operating at 56.4 MHz. The spectra were calibrated by the sideband modulation technique using a Hewlett-Packard wide-range oscillator. Chemical shifts and coupling constants represent the average of at least eight measurements. Errors of ± 0.1 ppm and ± 1 Hz, respectively, were estimated.

For both low- and high-temperature studies, the variable-temperature accessory supplied by Varian was used. Temperature measurements were made both before and after recording spectra by means of a copper-constantan thermocouple immersed in a tube filled with a Kel-F oil. The temperature measurements are believed to be accurate to $\pm 1^\circ$.

The chemical-shift differences (Tables II and III) obtained from nmr spectra of CFCl_2 solutions of **1** and **2** were essentially unchanged with the weight per cent of **1** and **2** varied from 25 to 50. However, the chemical-shift values were affected significantly by traces of acetone.

Perfluoro-2-fluoro-1,2-oxazetidine (**1**) and perfluoro-2-chloro-1,2-oxazetidine (**2**) were prepared by fluorination and chlorination, respectively, of perfluoro-1,2-oxazetidine as described previously.¹⁷ Both compounds are low-boiling materials, with boiling points below -30° .

Registry No.—**1**, 21720-81-0; **2**, 21720-80-9.

Acknowledgments.—The authors wish to thank Dr. P. D. Readio for valuable discussions and Dr. J. I. Musher of Yeshiva University for his helpful suggestions. We also appreciate the able assistance of Mr. J. Bienvenue in the preparation of the samples.

(17) R. A. Falk and J. D. Readio, *J. Org. Chem.*, **34**, 4088 (1969).

Polyfluoroaryl β -Dicarbonyl Compounds¹

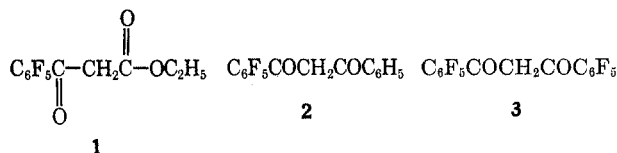
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Ethyl pentafluorobenzoylacetate (**1**) is prepared by oxidation of ethyl 3-hydroxy-3-pentafluorophenylpropionate with Jones reagent, or, better, by reaction of pentafluorobenzoyl chloride (**4**) with diethyl malonate in the presence of magnesium ethoxide. Compound **1** exhibits 54% enolic character as the neat liquid, whereas ethyl benzoylacetate possesses 22% enol. The unsymmetrical 1,3 diketone pentafluorodibenzoylmethane (**2**) is prepared by reaction of the morpholine enamine of acetophenone with (**4**) or from pentafluoroacetophenone and methyl benzoate in the presence of sodium hydride. The symmetrical 1,3 diketone bis(pentafluorobenzoyl)-methane (**3**) has been obtained by three methods, the preferred route being the reaction of **4** with vinyl acetate.

As part of studies aimed at evaluating the effect of pentafluorophenyl substitution on the properties and chemical behavior of neighboring functional groups in organic molecules, we have examined several polyfluoroaryl β -dicarbonyl compounds. In this paper, we report the preparation and some properties of ethyl pentafluorobenzoylacetate (**1**) and the 1,3 diketones pentafluorodibenzoylmethane (**2**) and bis(pentafluorobenzoyl)methane (**3**).



(1) Presented, in part, at the Southeastern Regional Meeting of the American Chemical Society, Louisville, Ky., Oct 1966, and at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1968.

(2) To whom inquiries should be sent.

(3) Abstracted, in part, from the M.S. thesis of V. D. B., Jan 1966, and the Ph.D. thesis of F. N. M., Jan 1967.

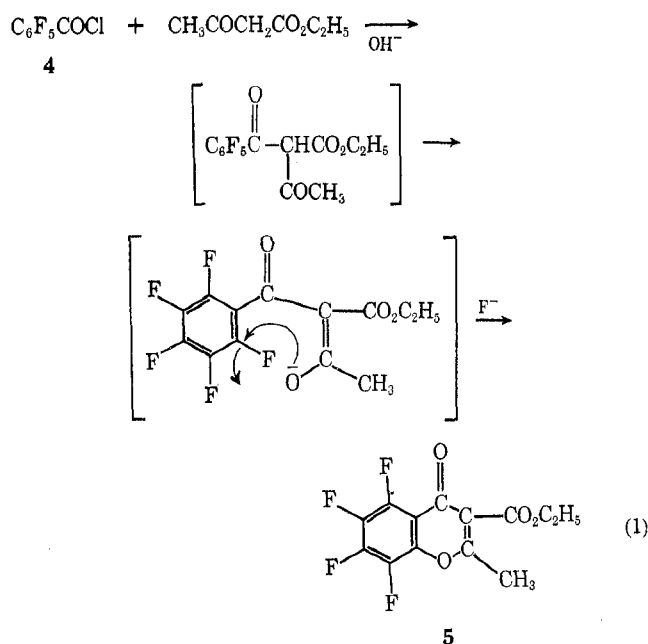
Ethyl Pentafluorobenzoylacetate (1).—In our initial approach to compound **1**, pentafluorobenzoyl chloride (**4**) was treated with ethyl acetoacetate in alkaline medium, according to an established procedure for the preparation of ethyl benzoylacetate.⁴ Instead of the desired β -keto ester, the sole product isolated was a substance whose elemental composition and infrared and proton magnetic resonance spectra were consistent with compound **5**, a substituted chromone (eq 1).

Compound **5** is formed by intramolecular displacement of *ortho* fluorine by the intermediate enolate anion. Such nucleophilic substitution cannot occur on a non-halogenated aromatic ring, and the reaction proceeds by an alternate course, *i.e.*, cleavage of the acetyl group to give the β -keto ester.

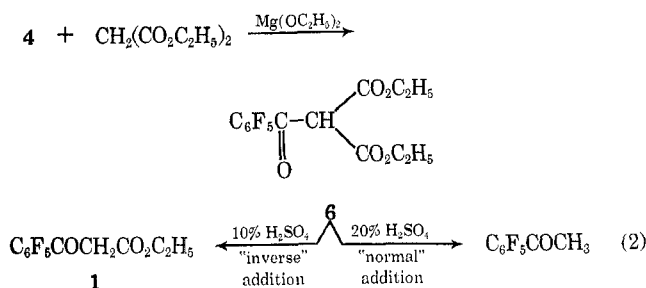
Shortly after completion of this work, our attention was drawn to similar observations by Soviet workers,⁵

(4) J. M. Straley and A. C. Adams, "Organic Syntheses," Coll. Vol. IV, John Wiley & Sons, Inc., New York, N. Y., 1963, p 415.

(5) N. N. Vorozhtsov, Jr., V. A. Barkhash, A. T. Prudchenko, and T. I. Khomenko, *Zh. Obshch. Khim.*, **35**, 1501 (1965).

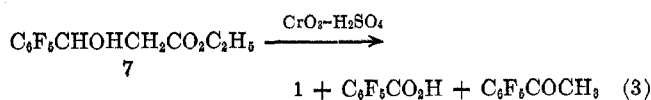


who in subsequent papers⁶ described two methods for the preparation of **1**: (a) reaction of the acid chloride **4** with diethyl malonate in the presence of magnesium ethoxide, and (b) condensation of ethyl pentafluorobenzoate with ethyl acetate, catalyzed by diisopropylaminomagnesium bromide. We have examined method a in some detail and confirm the previous observations. However, we noted that the partial hydrolysis of the intermediate diester **6** is extremely sensitive to the concentration and mode of addition of mineral acid. Thus, when **6** is slowly added to 10% H_2SO_4 (inverse addition) and the product is removed by continuous steam distillation, a 48% yield of **1** is obtained. In contrast, normal addition of 20% H_2SO_4 led to complete hydrolysis and decarboxylation to form pentafluoroacetophenone, also in 48% yield (eq 2).

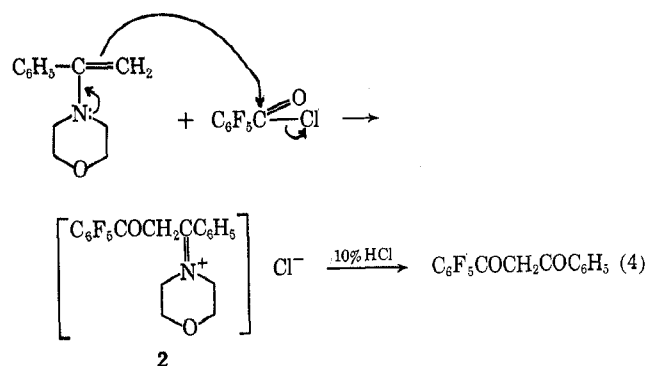


We also prepared compound **1** by a third method, oxidation of ethyl 3-hydroxy-3-pentafluorophenylpropionate (**7**), obtained in 91% yield by the Reformatsky reaction of pentafluorobenzaldehyde with ethyl bromoacetate. Attempts to oxidize **7** to **1** using KMnO_4 , MnO_2 , CrO_3 -pyridine, or dicyclohexylcarbodiimide in dimethyl sulfoxide were all unsuccessful. However, oxidation with Jones reagent proceeded readily, but without selectivity, to give **1** in only 17% yield after a difficult separation from pentafluorobenzoic acid and pentafluoroacetophenone (eq 3).

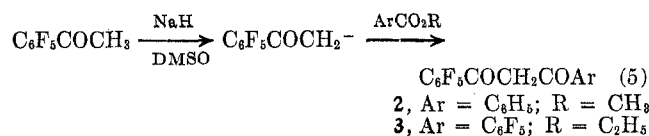
(6) A. T. Prudchenko, V. A. Barkhash, and N. N. Vorozhtsov, Jr., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1798 (1965); see also N. N. Vorozhtsov, Jr., V. A. Barkhash, A. T. Prudchenko, and G. S. Shegoleva, *Zh. Obshch. Khim.*, **35**, 1501 (1965).



Pentafluorodibenzoylmethane (2).—This new unsymmetrical 1,3 diketone was obtained in 25% yield by reaction of the morpholine enamine of acetophenone with the acid chloride **4** (eq 4). A better route to **2**



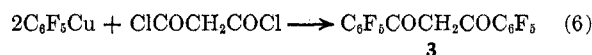
is the reaction of pentafluoroacetophenone with methyl benzoate in the presence of sodium hydride (eq 5),



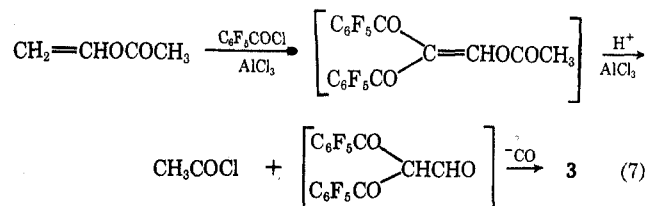
a method described recently by Anselme.⁷ The yield of diketone was 60%.

Bis(pentafluorobenzoyl)methane (3).—This new symmetrical 1,3 diketone could not be obtained by the enamine route, because all attempts to prepare enamines of pentafluoroacetophenone failed. Instead, there was evidence of nucleophilic attack on the fluorinated ring.

However, three methods of preparation of compound **3** were developed: (a) reaction of $\text{C}_6\text{F}_5\text{COCH}_3$ with ethyl pentafluorobenzoate (eq 5) gave a 60% yield; (b) reaction of pentafluorophenylcopper with malonyl dichloride (eq 6) proceeded in a manner analogous to



the preparation of other polyhalo diketones, as described recently by Gilman and coworkers,⁸ and yields in this reaction varied from run to run with a maximum of only 30%; (c) reaction of vinyl acetate with **4** in tetrachloroethane solvent in the presence of anhydrous aluminum chloride gave the desired diketone in 34% yield (eq 7) together with a 20% yield of a by-product,



$\text{C}_6\text{F}_5\text{COCH}_2\text{COCH}_3$ (**8**). Compound **8** probably arises from reaction of vinyl acetate with a mixture of **4** and

(7) J. P. Anselme, *J. Org. Chem.*, **32**, 3716 (1967).

(8) S. S. Dua, A. E. Jukes, and H. Gilman, *J. Organometal. Chem.*, **12**, 24 (1968); *J. Org. Chem.*, submitted for publication.

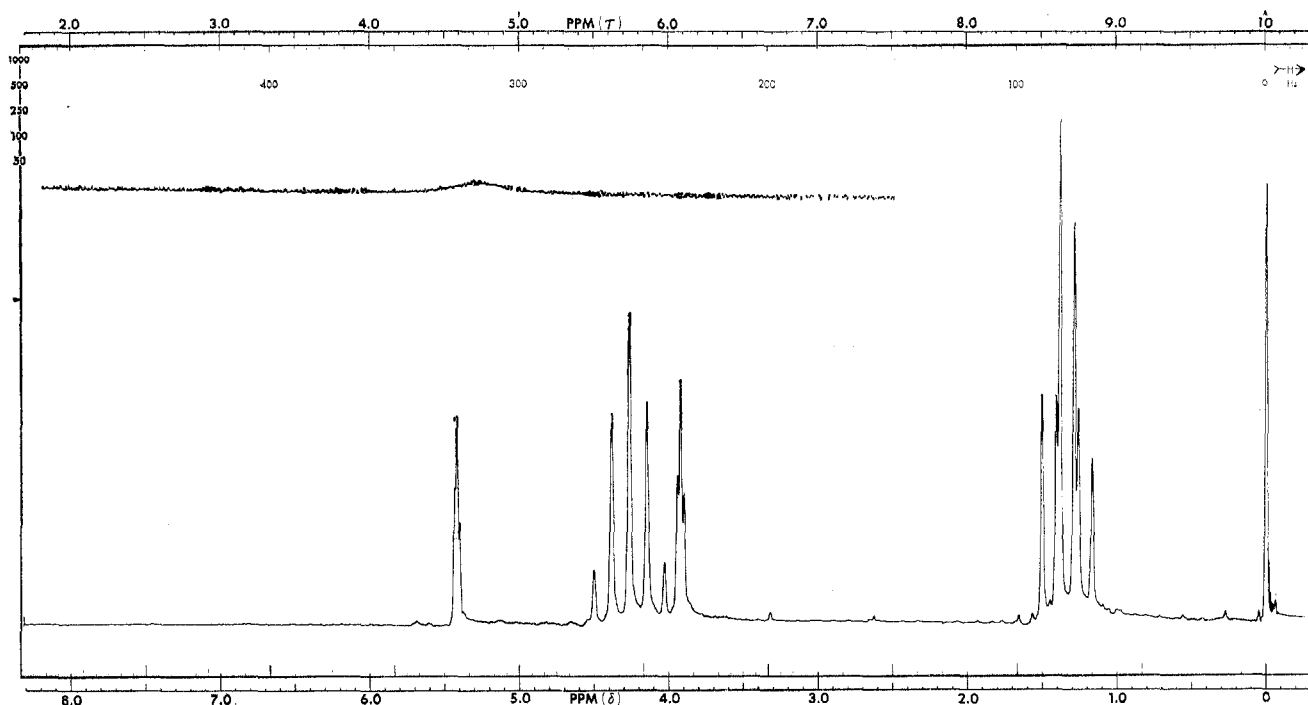
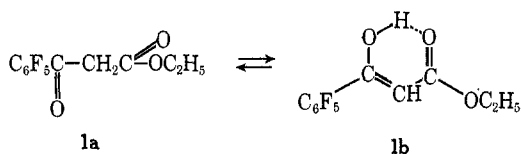


Figure 1.—Proton magnetic resonance spectrum of ethyl pentafluorobenzoylacetate (1) at 60 MHz. Chemical shifts from internal TMS at 37° follow: keto CH₃, 77 Hz ($J = 7$ Hz); enol CH₃, 82 Hz ($J = 7$ Hz); keto CH₂, 235 Hz ($J = 1.3$ Hz); keto + CH₂ (Et group), 255 Hz ($J = 7$ Hz); enol CH, 325 Hz ($J = 1$ Hz); enol OH, 693 Hz.

acetyl chloride (formed either from vinyl acetate and AlCl₃ or as a by-product of the main reaction). Similar behavior with other aroyl chlorides has been observed.⁹ Although the yield of **3** by this latter method is not high, the ready availability of the starting materials makes this the preferred route.

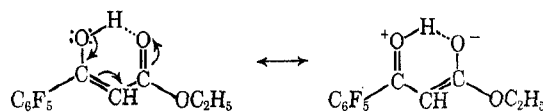
Spectral Properties of the 1,3-Dicarbonyl Compounds and the Keto/Enol Ratio of Ethyl Pentafluorobenzoylacetate.—The infrared spectrum of ethyl pentafluorobenzoylacetate reveals the presence of the intramolecularly hydrogen-bonded enolic structure (**1b**), characterized by strong absorption at 1656 cm⁻¹ (neat liquid), ascribed to “conjugate chelation” of the ester carbonyl group.¹⁰ The presence of a substantial concentration of the keto form (**1a**) is indicated by a band of medium intensity at 1748 cm⁻¹, associated with a “free” ester carbonyl moiety.



In order to establish the position of keto-enol equilibrium, we examined the proton magnetic resonance spectrum of compound **1** (Figure 1). The percentage of enol was determined by comparing the integrated intensity of the vinylic hydrogen in **1b** with that of the keto methylene group or of the methyl groups of **1a** and **1b** combined. Compound **1** possesses 54 ± 1% enol as the neat liquid at room temperature and $K_e = 1.17$. In contrast, the hydrogen analog, ethyl benzoylacetate,

exhibits only 22% enolic character¹¹ under the same conditions, and $K_e = 0.28$.

The internally hydrogen-bonded enolic form is stabilized more in **1b** than in ethyl benzoylacetate because of two factors associated with the increased electron-attracting ability of the C₆F₅ over the C₆H₅ group: (a) enhanced acidity of the enol, leading to a stronger hydrogen bond, and (b) greater resonance stabilization by encouraging charge separation.



We have shown earlier¹² the remarkable influence of neighboring fluorine atoms in altering the keto/enol ratios in β-keto esters. Ethyl 4,4,4-trifluoroacetate exhibits 89% enolic character, whereas ethyl acetate possesses about 8% enol (neat liquids).

The 1,3 diketones **2**, **3**, and **8** exist essentially completely in the mono-enolic form, as determined by titration with sodium methoxide¹³ and by examination of their pmr spectra. However, the infrared spectra of **2** and **3** merit comment. Dibenzoylmethane, which exists completely in the mono-enol form, fails to exhibit normal conjugated carbonyl absorption. Instead, a broad, more intense band in the range 1639–1538 cm⁻¹ is observed.¹⁴ This shift is ascribed to “conjugate

(11) J. L. Burdett and M. T. Rogers, *J. Amer. Chem. Soc.*, **86**, 2105 (1964). Their results were confirmed by us.

(12) R. Filler and S. M. Naqvi, *J. Org. Chem.*, **26**, 2571 (1961); see also ref 11.

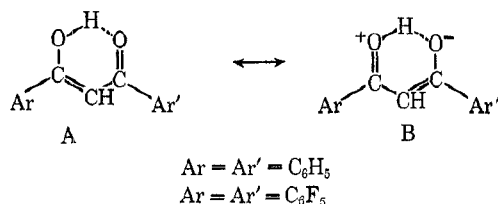
(13) J. S. Fritz, “Acid-Base Titrations in Non-Aqueous Solvents,” G. F. Smith Chemical Co., Columbus, Ohio, 1952, pp 28, 31.

(14) R. S. Rasmussen, D. D. Tunnicliff, and R. R. Brattain, *J. Amer. Chem. Soc.*, **71**, 1068 (1949).

(9) A. Sieglitz and O. Horn, *Chem. Ber.*, **84**, 607 (1951).

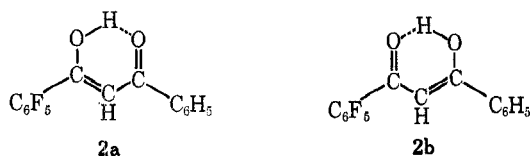
(10) L. J. Bellamy, “The Infrared-red Spectra of Complex Molecules,” 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1958, p 184.

chelation," a resonance effect involving structures A and B.



However, compound **3**, in which both phenyl groups are replaced by C₆F₅, shows a near-normal carbonyl vibration (1677 cm⁻¹), close to that observed in the structurally similar fluorinated benzalacetophenone,¹⁵ C₆F₅CH=CH(C=O)C₆F₅ (1689 cm⁻¹). The strong electron attraction of the pentafluorophenyl group reduces "conjugate chelation" by increasing the double-bond character of the carbonyl group, thus enhancing the contribution of structure A and destabilizing structure B. The spectrum of the unsymmetrical diketone **2** appears to have features common to both dibenzoylmethane and **3**.

The question of the direction of enolization in compound **2** has occupied us for some time. There are three possibilities, **2a**, **2b**, or a rapidly equilibrating mixture of the two forms.



The infrared data are somewhat ambiguous and do not permit a decision between **2a** or **2b**. The ultraviolet spectra [dibenzoylmethane ($\lambda_{\max}^{\text{EtOH}}$ 342 nm), **3** (340), **2** (333)]¹⁶ do not provide useful information, even when compared with data for the corresponding benzalacetophenones,¹⁵ to make a clear choice.

The proton magnetic resonance spectra of the diketones in carbon tetrachloride reveals a sharp triplet at 386 Hz ($J = 1.5$ Hz) for the vinylic proton in **2**, an unresolved multiplet at 386 Hz in **3**, and a singlet at 405 Hz for =CH in dibenzoylmethane. These data suggest a similar environment for this proton in **2** and **3**, =CH-(C=O)C₆F₅.

The sharp vinylic resonance in **2** indicates that the compound probably exists in a single form, unless equilibration occurs more rapidly than the nmr time scale. Finally, comparison with the coupling constants in the model compounds, C₆F₅COCH₃ and C₆F₅C(OCH₃)=CH₂ lead us to the tentative conclusion that **2b** is the correct structure for the mono-enol. This conclusion is based on the following arguments: (1) the coupling constant of the vinylic proton in **2** is similar to that for the methyl protons in C₆F₅COCH₃ ($J = 1.7$ Hz), suggesting that =CH and CH₃ have a similar relationship to the C₆F₅ group, namely, that both are bonded to a carbonyl group, and (2) the vinylic protons in C₆F₅C(OCH₃)=CH₂ are not appreciably coupled ($J < 1.0$ Hz) to the ring fluorine atoms, in support of

(15) The chemistry of fluorinated benzalacetophenones will be the subject of a forthcoming paper.

(16) These intense absorptions are attributed to $n \rightarrow \pi^*$ transitions in the enols: G. S. Hammond, W. G. Borduin, and G. A. Guter, *J. Amer. Chem. Soc.*, **81**, 4682 (1959).

the conclusion that in **2** there is no carbon-carbon double bond in conjugation with the fluorinated ring.

Experimental Section¹⁷

Pentafluorobenzoic Acid.—Pentafluorobromobenzene (39.5 g), dissolved in 100 ml of anhydrous ether was added to 100 ml of *n*-butyllithium in hexane solution and the mixture was cooled to -78° and kept under a nitrogen atmosphere. After addition was complete, the solution was kept at this temperature for 1 hr. Carbon dioxide, dried by passing through H₂SO₄, was passed through the solution at -78° for 20 min and then for an additional 1 hr while the solution was allowed to warm to room temperature. Then 200 ml of 6 *N* HCl was added with vigorous stirring and the organic phase was separated. The aqueous phase was extracted with three 40-ml aliquots of ether and the combined organic extracts were washed with water and dried over MgSO₄. The solvent was stripped off to give a white solid, mp 100–102°, after recrystallization from hexane-benzene (10:1), yield 32 g (93%).

Pentafluorobenzoyl Chloride (4).—Pentafluorobenzoic acid (21.0 g) was mixed with 14 g of thionyl chloride and the mixture was refluxed for 16 hr. Excess reagent was drawn off and the residue was fractionated *in vacuo*. The acid chloride was collected as a slightly yellow oil, bp 35–38° (1.2 mm), yield 18.8 g (81%).

Reaction of Ethyl Acetoacetate with Pentafluorobenzoyl Chloride.—Water (13.3 ml), 6.7 ml of petroleum ether (bp 65–70°), and 5.2 g (0.04 mol) of freshly distilled ethyl acetoacetate were placed in a 100-ml, three-necked, round-bottomed flask, equipped with an efficient stirrer and two dropping funnels. The mixture was cooled to 5° and 1.6 ml of 33% sodium hydroxide solution was added. As the temperature was maintained below 10° and the pH near 11, the mixture was stirred vigorously while 10 g (0.043 mol) of pentafluorobenzoyl chloride and 7.0 ml of 33% sodium hydroxide solution were added dropwise simultaneously from the two funnels. The addition was complete after 1.5 hr and a yellow-white solid formed. The mixture was allowed to warm to room temperature over a 1-hr period. The precipitate was filtered off and washed with petroleum ether. After air drying, the solid weighed 11 g, mp 113–114°.

This white material (5 g) was dissolved in 30 ml of water, and 1.0 g of ammonium chloride was added with stirring. After a few minutes of stirring at room temperature, a white solid began to precipitate. After 45 min, the precipitate was filtered and dried *in vacuo* over Drierite, mp 114–115°. A 1.0-g sample of this compound was heated under reflux with 50 ml of absolute ethanol for 1 hr. The solution was evaporated to dryness, leaving a tacky, yellow solid, which was recrystallized several times by dissolving in ethanol and precipitating with water. After drying, 0.56 g of the chromone **5**, mp 89.8–90.1°, was obtained as white plates: ir (CCl₄) 1678 (s) and 1730 cm⁻¹ (s); pmr δ 4.31 (q, CH₂), 2.47 (s, CH₃), and 1.36 (t, CH₃ of C₂H₅ group).

Anal. Calcd for C₁₈H₈F₄O₄: C, 51.31; H, 2.63. Found: C, 51.75; H, 2.93.

Ethyl Benzoylacetate.—Ethyl benzoylacetate was prepared according to the procedure described in *Organic Syntheses*.⁴ The product distilled at 144–147° (2 mm), yield 23 g (40%).

Ethyl 3-Hydroxy-3-pentafluorophenylpropionate.—Zinc dust (3.5 g, 0.058 g-atom) was placed in a flask under a nitrogen atmosphere, and 13 g (0.066 mol) of pentafluorobenzaldehyde and 9.7 g (0.058 mol) of ethyl bromoacetate were mixed and dissolved in a mixture of 2.5 ml of anhydrous ether and 10 ml of dry benzene. This mixture (3 ml) was added to the zinc and the flask was heated until reaction started. The remaining solution was added dropwise at such a rate as to maintain reflux. After addition was complete, the reaction mixture was refluxed for an additional 2 hr and left at room temperature overnight. The mixture was hydrolyzed with 25 ml of 10% (v/v) H₂SO₄, the aqueous phase was extracted with three 20-ml portions of ether, and the combined extracts were washed with water, sodium carbonate solution, and twice with water and then dried over MgSO₄. The solvents were stripped off and the slightly yellow residual oil crystallized completely upon cooling and scratching to give 15.2 g (91%) of crude product. White crystals, mp 46–

(17) All melting points and boiling points are uncorrected.

48°, were obtained after sublimation, ir (CCl₄) 1718 (s) and 3480 cm⁻¹ (br).

Anal. Calcd for C₁₁H₅F₅O₃: C, 46.48; H, 3.19. Found: C, 46.75; H, 3.53.

Ethyl 3-Keto-3-pentafluorophenylpropionate (1).—Ethyl 3-hydroxy-3-pentafluorophenylpropionate (7.0 g) was dissolved in 200 ml of acetone and treated with 20 ml of Jones reagent (13.4 g of CrO₃, 11.5 ml of concentrated H₂SO₄/50 ml of solution), the temperature not being allowed to exceed 26°. The solution was kept at 24–26° for 1.5 hr and then the excess reagent was destroyed by adding isopropyl alcohol. The resulting dark green mixture was poured into 1500 ml of ice-cooled water and extracted with five 150-ml portions of ether. The ether extracts were washed with water until colorless and then dried over MgSO₄. The solvent was stripped off and the residue was fractionated *in vacuo*. The fraction boiling at 85–105° (1 mm) was refractionated and yielded the desired product, a colorless oil, bp 89–93° (0.9 mm), *n*²⁰_D 1.4594 (lit.⁶ *n*_D 1.4604). The yield was 1.2 g (17%).

When treated at room temperature for 4 hr or at temperatures exceeding 30° for a shorter time with Jones reagent, the hydroxy ester gave as the main product pentafluorobenzoic acid (as determined by melting point and mixture melting point determination with an authentic sample). Oxidation below 12° gave, for varying times from 10 min to 2 hr, only unreacted starting material. Oxidation at 15–20° for 1 hr gave a mixture of product and starting material. Oxidation above 20° gave as a by-product varying amounts of pentafluorobenzoic acid. No combination of time and temperature could be found which gave the keto ester as the only oxidation product. The keto ester was always accompanied by an unidentified by-product, a yellow oil, boiling slightly higher than the keto ester, bp 105–110° (1 mm), *n*²⁰_D 1.4540, and an ir spectrum very similar to that of 1, except for a pronounced OH absorption band. The separation of those two compounds required the product to be refractionated at least two times.

Ethyl 3-Keto-3-pentafluorophenylpropionate (1).⁶—Magnesium (1.7 g, 0.069 g-atom) was covered with 8.9 ml (0.067 mol) of absolute ethanol, a 3-ml portion of 10.7 g (0.067 mol) of freshly distilled diethyl malonate and 0.2 ml of carbon tetrachloride was added, and the reaction mixture was heated until reaction started. The remaining diethyl malonate was added dropwise, and, after slight cooling, 16 ml of anhydrous ether was added and the mixture was refluxed for 3 hr, by which time all of the magnesium had reacted. The solvent was distilled off, 20 ml of dry benzene were added and distilled to remove any excess ethanol, and the remaining syrupy liquid was dissolved in 20 ml of dry ether. Pentafluorobenzoyl chloride (16.0 g, 0.069 mol) dissolved in 10 ml of anhydrous ether was added dropwise and the mixture was heated under reflux for 15 min, cooled, and hydrolyzed by adding 15 ml of water and 8 ml of 20% sulfuric acid. The aqueous phase was extracted with three 15-ml portions of ether and the combined organic phases were washed with water, a dilute solution of sodium bicarbonate, and water, and dried over MgSO₄. The solvent was stripped off to leave a dark yellow, liquid residue. Sulfuric acid (10%, 100 ml) was carefully heated to boiling in a three-necked flask equipped with a dropping funnel and a distillation condenser. The crude diethyl pentafluorobenzoyl malonate was added to the boiling acid in small portions during 3 hr. Simultaneously, water was added to maintain the acid volume, while steam distillate of the product was collected. Caution had to be taken that reactant and product did not accumulate in the reaction vessel, or else hydrolysis and decarboxylation would proceed to the stage of pentafluoroacetophenone. The steam distillate was saturated with ammonium chloride and the oil was extracted with ether; the extracts were washed with water and dried over MgSO₄. The solvent was stripped off and the residue was fractionated *in vacuo*: bp 90–93° (1.2 mm); *n*²⁰_D 1.4590; yield 9.2 g (48%); ir (neat) 3565 (vw), 1748 (s), 1715 (m), 1656 (vs), and 1635 cm⁻¹ (m); pmr, see Figure 1. Derivatives follow: copper chelate, light green crystals, mp 179–181°; 2,4-dinitrophenylhydrazone (from ethanol-water), mp 117–118° (lit.⁶ mp 118°), formed by allowing reactants to stand at room temperature for 3 days. If reactants were heated under reflux for 2 hr, the 2,4-dinitrophenylhydrazone of pentafluoroacetophenone (hydrolysis and decarboxylation), mp 155–157°, was isolated.

When the preparative procedure was modified so that the crude diethyl pentafluorobenzoyl malonate was mixed with 200 ml of 20% sulfuric acid and the product was steam distilled,

the sole substance isolated was pentafluoroacetophenone, bp 43–45° (1.2 mm), *n*²⁰_D 1.4323, yield 48.2%.

Bis(pentafluorobenzoyl)methane (3). *Anselme's Method.*⁷—To a 100-ml, three-necked, round-bottomed flask, equipped with a magnetic stirrer, a condenser to which was attached a drying tube and an addition funnel, attached to a dry nitrogen supply, and a thermometer, was added 1 g of a suspension of sodium hydride (60% in mineral oil). The flask was cooled in an ice bath and 15 ml of dimethyl sulfoxide was added. The cooling bath was removed and the mixture was stirred for 30 min. The temperature was then lowered to 15° and 6.0 g of ethyl pentafluorobenzoate was added while the temperature was kept at 15°. The temperature was allowed to drop to 5° and 3.2 g of pentafluoroacetophenone was added during 30 min. The temperature was then raised to 35° and the mixture was stirred for 24 hr. The dark reaction mixture was poured in a thin stream into 50 g of crushed ice containing 1 ml of 85% phosphoric acid, with stirring. The organic layer was extracted with ether and the ether layer was washed free of sulfur compounds with bromine water. After repeated washings with water, the ether layer was dried and distilled to give a red oil. Chromatography over alumina and elution with benzene and methanol gave 3 (3.5 g, 60%): mp 119–120°; copper chelate, green-blue crystals; mp 192°; uv $\lambda_{\text{max}}^{\text{OH}}$ 340 nm; ir (KBr) 1675 (s) and 1630 cm⁻¹ (w); pmr (CCl₄, 60 MHz, internal TMS) 386 Hz.

Anal. Calcd for C₁₅H₂F₁₀O₂: C, 44.55; H, 0.49. Found: C, 44.49; H, 0.51.

Bis(pentafluorobenzoyl)methane (3). *Vinyl Acetate Method.*—Anhydrous aluminum chloride (5.3 g) was heated with pentafluorobenzoyl chloride (9.22 g) in 20 ml of tetrachloroethane at 45° until the addition compound of AlCl₃ and the acid chloride was formed. Vinyl acetate (3.44 g) was added dropwise at 25° during 30 min. The mixture was heated at 35° for 24 hr and decomposed with ice-cold, dilute hydrochloric acid. The mixture was steam distilled to remove the solvent, the residue was extracted with ether, the ether extract was dried over Na₂SO₄, and the ether was evaporated. On distillation at 80° (1 mm), 2 g (20%) of acetyl pentafluorobenzoylmethane (8) was obtained: ν (CCl₄) 1640 (s) and 1595 cm⁻¹ (br s); nmr δ 2.18 (s, CH₃) and 5.90 (5, *J* = 1.5 Hz vinyl CH). The residue was eluted over alumina with benzene and methanol to give 5.5 g (34%) of 3, mp 119°.

Bis(pentafluorobenzoyl)methane (3). *Pentafluorophenylcopper Method.*—Magnesium (1.25 g) was placed in a dry, three-necked flask under nitrogen, 3 ml of dry ether and 1 ml of bromopentafluorobenzene were added, and the flask was heated until reaction started. The remainder of 12.3 g (0.05 mol) of bromopentafluorobenzene, dissolved in 250 ml of dry ether, was added dropwise. The reaction mixture was refluxed gently for 20 min after addition was complete. Then 5.6 g (0.056 mol) of cuprous chloride was added in small portions during 20 min and the mixture was stirred at room temperature for 2.5 hr. Freshly distilled malonyl dichloride (3.7 g, 0.026 mol) dissolved in 20 ml of dry ether was added dropwise and the reaction mixture was left overnight at room temperature. The mixture was hydrolyzed with 300 ml of ice-cooled 5 N HCl, the aqueous phase was extracted three times with ether, and the combined organic phase was washed with water, dilute sodium bicarbonate solution, and water and dried over MgSO₄. After evaporation of the solvent, a residual yellow oil was obtained, which partly crystallized upon cooling. The product crystallized from 15 ml of ethanol and was further purified by sublimation at 60° (2 mm) to give 2.54 g (31%) of bis(pentafluorobenzoyl)methane, mp 116–118°. There was no melting point depression when this material was admixed with the samples prepared by the other two methods.

2,3,4,5,6-Pentafluoroacetophenone.—In a 250-ml, three-necked, round-bottomed flask fitted with an efficient stirrer, a reflux condenser, and a dropping funnel with a nitrogen inlet tube were put 3.0 g (0.12 g-atom) of magnesium turnings and 30 ml of anhydrous ether (dried over sodium). Bromopentafluorobenzene (30 g, 0.12 mol) in 45 ml of dry ether was added during a 60-min period. After addition was complete, the mixture was stirred at room temperature for 1 hr. The flask was cooled in ice, the dropping funnel was removed, and 11.7 g (0.064 mol) of anhydrous cadmium chloride (dried at 100°) was added over a 5-min period. The funnel was replaced, the ice bath was removed, and the mixture was heated under reflux for 75 min. At this point the Gilman test for the presence of Grignard reagent was negative. The flask and condenser were arranged for

distillation and ether was distilled off as stirring was continued until the residue became very viscous. Anhydrous, thiophene-free benzene (45 ml) was added, and 15 ml of liquid were removed by distillation. An additional 45 ml of benzene was added and the reflux condenser was replaced. The mixture was refluxed with vigorous stirring for a few minutes and cooled to 5°, and a solution of 8.3 g (0.11 mol) of freshly distilled acetyl chloride in 25 ml of dry benzene was added during 2–3 min. After addition, the mixture was stirred at room temperature for 18 hr. It was then poured into 150 g of crushed ice containing 75 ml of 25% (v/v) sulfuric acid, and the resulting two-phase mixture was stirred for 5 min. The dark brown benzene layer was separated, and the water layer was extracted with two 30-ml portions of benzene. The combined benzene layers were washed successively with 45 ml of saturated sodium chloride solution, 45 ml of saturated sodium bicarbonate solution, 45 ml of water, and 25 ml of saturated sodium chloride solution. The benzene layer was dried over anhydrous sodium sulfate and the benzene was removed on a flash evaporator at room temperature. The dark residue was distilled *in vacuo* to give 14.0 g (56%) of 2,3,4,5,6-pentafluoroacetophenone: bp 65–66° (5 mm); pmr δ 2.67 (5, CH₃); 2,4-dinitrophenylhydrazone mp 156–157°.

Dibenzoylmethane.—Dibenzoylmethane, mp 77–78°, was prepared according to the procedure described by Sieglitz and Horn.⁹

Pentafluorodibenzoylmethane (2). Enamine Method.—A mixture of 174 g (2.0 mol) of morpholine, 120 g (1.0 mol) of acetophenone, and 8.6 g (0.05 mol) of *p*-toluenesulfonic acid in 250 ml of toluene was heated under reflux for 72 hr. The water which formed was collected in a Dean–Stark trap and removed from the system. After completion of the reaction, the toluene was removed *in vacuo* and the residue was vacuum distilled to give the enamine in low yield. A large amount of viscous tar remained in the distillation flask.

A mixture of 3.22 g (0.014 mol) of pentafluorobenzoyl chloride and 5.3 g (0.028 mol) of α -(4-morpholino)styrene in 100 ml of dry dioxane was stirred overnight in a dry nitrogen atmosphere, at

room temperature. The reaction mixture was filtered and the residue was washed with ether. The organic layers were combined, mixed with 75 ml of 10% hydrochloric acid, and heated under reflux for 4 hr. The aqueous solution was then diluted with water to a volume of ca. 1 l. and the ether layer was separated and combined with three 100-ml extracts of the aqueous layer. The ethereal solution was dried over Na₂SO₄ and evaporated *in vacuo* to give a red oil which later solidified. Two recrystallizations of the oil from methanol gave 1.1 g (25%) of colorless needles: mp 118°; uv $\lambda_{\text{max}}^{\text{EtOH}}$ 333 nm (log ϵ 4.28) and 246 (3.82); ir (CCl₄) 1645 (s), 1598 (br s), and 1568 cm⁻¹ (br s); pmr (CCl₄) 386 Hz (t, $J = 1.5$ Hz, vinyl CH).

Anal. Calcd for C₁₅H₇F₅O₂: C, 57.34; H, 2.25. Found: C, 57.23; H, 2.35.

Pentafluorodibenzoylmethane (2). Anselme's Method.⁷—This diketone, mp 118°, was prepared in 60% yield from pentafluoroacetophenone and methyl benzoate, according to the procedure described above for bis(pentafluorobenzoyl)methane.

Enol Contents of 1,3 Diketones.—The percentage of enol in the following 1,3 diketones was determined by titration with standard sodium methoxide solution, according to a known procedure.¹³ The results follow: C₆H₅COCH₂COC₆H₅, 100%; C₆F₅COCH₂COC₆H₅ (2), 93%; C₆F₅COCH₂COCH₃ (8), 100%; C₆F₅COCH₂COC₆F₅ (3), 98.8%.

Registry No.—1, 3516-87-8; 2, 23074-28-4; 3, 23074-29-5; 4, 2251-50-5; 5, 4487-61-0; pentafluorobenzoic acid, 602-94-8; ethyl 3-hydroxy-3-pentafluorophenylpropionate, 23115-90-4; 2,4-dinitrophenylhydrazone of pentafluoroacetophenone, 858-82-2; 2,3,4,5,6-pentafluoroacetophenone, 652-29-9.

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Liquid Fluorocarbon from Hexafluoropropene by an Electrical Discharge Process^{1a}

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A mixture of liquid fluorocarbons derived from C₃F₆ was prepared by an electrical discharge process. The gas-phase discharge was initiated at 150–800 Torr in concentric quartz tube reactors at 15–60° using field strengths of 9–13 kV/mm and alternating current at 1.4 or 10 kc/sec. The liquid discharge product contained substantial quantities of linear and branched fluoro alkanes as well as unsaturated (olefinic) fractions. No small-ring components were found. Carbon numbers of the products were shown to be random rather than multiplets of the monomer units. Base-catalyzed reaction of the liquid fluorocarbon with alcohol gave three fractions: (1) unsaturated ethers, (2) nonreactive fluoro alkanes, and (3) small amounts of perfluoroalkyl carboxylic acids. One of the sources of the carboxylic acids could be the stable free radicals shown by epr measurement (10²¹–10¹⁷ spins/cc) to be present in the discharge products. A radical mechanism was suggested in which C₃F₅ was fragmented by the discharge process into reactive radicals which combined with each other and with neutral molecules to form higher molecular weight fractions. The fact that many linear alkanes were found indicated that difluorocarbene (:CF₂) was involved in the chain-extension process. A significant amount of F radical was also postulated to explain the formation of alkanes. Perfluorodienes were suggested as reaction intermediates for the presence of many identified olefinic groups. Halogenation of the discharge product proceeded readily with elemental fluorine, but not with chlorine or bromine trifluoride.

Reports in the literature concerning electrical discharge of gaseous fluorocarbons^{2–5} have described only the discharge at low pressure. The present investiga-

tion was made at higher pressures and the electrical conditions were milder than those of previous workers. The products obtained with hexafluoropropene were predominantly liquids. Instrumental and chemical analyses indicated that the liquid product (herein called liquid fluorocarbon) contained perfluoro alkanes as well as unsaturated fractions.²

Results and Discussion

Hexafluoropropene was converted into a mixture of gaseous (3–10%) and liquid fluorocarbons in quantita-

(1) (a) Presented in part at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968. (b) To whom inquiries should be addressed: 102 Maclean Circle, Princeton, N. J. 08540.

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