Acknowledgment. Support of this research by the Robert A. Welch Foundation and the National Institute of Arthritis, Metabolism, and Digestive Diseases (PHS Grant AM 15157) is gratefully acknowledged.

Registry No.—**4,** 16178-83-9; **5,** 2230-70-8; **6a,** 3211-27-6; **6b,** 3211-26-5; **7a,** 20826-63-5; **7b,** 20826-64-6; **8,** 5019-82-9; **9,** 53940-53-7; **10,** 53940-54-8; **11,** 53940-55-9; **12,** 53940-56-0; **13a,** 53940-57-1; **13b,** 53940-58-2; **14a,** 53940-59-3; **15a,** 53940-60-6; **15b,** 53940-61-7; 4,4-dimethylcyclohexanone, 4255-62-3; 4-*tert*-butylcyclohexanone, 98-53-3; pyrrolidine, 123-75-1; *N*-(2-methyl-4-*tert*-butylcyclohex-1-enyl)pyrrolidine, 53940-62-8; triethyl phosphonoacetate, 867-13-0; ethyl bromoacetate, 105-36-2; triethyl phosphate, 122-52-1; trimethyl phosphonoacetate, 5927-18-4; trimethyl phosphite, 121-45-9; methyl bromoacetate, 96-32-2; potassium *tert*-butoxide, 865-47-4.

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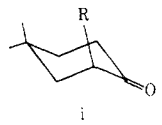

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(4) Even under equilibrating conditions, only the 2,6-diequatorial and 2-axial-6-equatorial isomers of ketone **7** are expected to be present to any significant extent.[5]
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Polyfluoroaryl Carbonyl Chemistry. Benzalacetophenones

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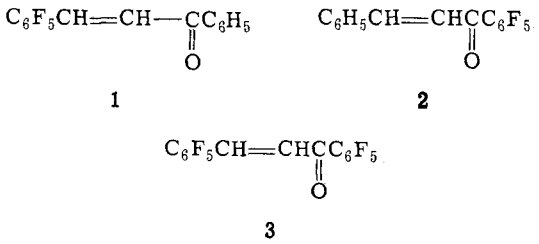
The polyfluorobenzalacetophenones **1, 2,** and **3** have been prepared and the effects of pentafluorophenyl groups on infrared and ultraviolet spectral properties evaluated. When the carbonyl is flanked by C_6F_5, haloform-type cleavage occurs readily in alkaline medium. The subject compounds undergo Michael addition of diethyl malonate with difficulty, but react with C_6H_5MgBr and C_6F_5MgBr to give 1,4-addition products, although in two cases the bimolecular compounds **8** and **9** are formed.

As part of studies on the effects of polyfluoroaryl substitution on the reactivity of neighboring functional groups, we have examined a variety of carbonyl compounds.[2] In this paper we report our observations on the chemistry of polyfluorobenzalacetophenones. The discussion is divided into three parts: preparation, spectral properties, and chemical reactions.

Preparation. Compounds **1, 2,** and **3** were all prepared by the Claisen–Schmidt reaction[3] (eq 1). Pentafluorobenzaldehyde reacted with acetophenone in aqueous ethanolic alkali to give pentafluorobenzalacetophenone (**1**)[4] in 50% yield.

$$ArCHO + Ar'COCH_3 \xrightarrow{OH^-} ArCH{=}CHC(=O)Ar' + H_2O \quad (1)$$

$$Ar = C_6H_5, C_6F_5$$
$$Ar' = C_6H_5, C_6F_5$$



1 **2**

3

2,3,4,5,6-Pentafluoroacetophenone, required for the preparation of benzalpentafluoroacetophenone (**2**) and 2,3-dihydryl-*F*-benzalacetophenone[5] (**3**), was obtained in 56% yield by reaction of bis(pentafluorophenyl)cadmium with acetyl chloride (eq 2). In the subsequent condensation reactions, the concentration of sodium hydroxide was reduced from the usual 6–7% to 1.5% and **2** and **3** were obtained in excellent yield (84–87%). At higher concentrations of alkali, a significant side reaction occurred, which will be discussed later. Compound **3** was prepared previously in 50% yield by a Wittig reaction.[6]

$$2C_6F_5MgBr + CdCl_2 \longrightarrow [(C_6F_5)_2Cd] \xrightarrow{CH_3COCl} C_6F_5COCH_3 \quad (2)$$

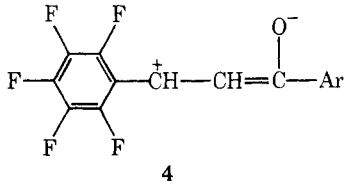
Spectral Properties. Infrared and ultraviolet spectral data for the benzalacetophenones are listed in Table I. The influence of neighboring fluorine atoms on carbonyl stretching frequencies has been reported previously.[7] The effect of the pentafluorophenyl group in shifting the ester carbonyl band to higher frequencies has been described.[2a] This trend is also evident in the present study.

Whereas benzalacetophenone exhibits $\nu_{C=O}$ 1667 cm^{-1}, the pentafluorophenyl group in **1** (ν 1674 cm^{-1}) causes an increase in double-bond character of the carbonyl group by minimizing charge delocalization, e.g., **4.** Although the para fluorine alone would enhance the contribution of **4,** the

Table I
Infrared and Ultraviolet Data for Fluorinated Benzalacetophenones[a]

	$\nu_{C=O}$, cm^{-1}	λ_{max}, nm	ϵ_{max}
$C_6H_5CH{=}CHC(=O)C_6H_5$	1667 (vs)	310	23,400
$C_6F_5CH{=}CHC(=O)C_6H_5$ (1)	1674 (s)	287	25,500
$C_6F_5CH{=}CHC(=O)C_6F_5$ (3)	1689 (s)	287	20,500
	1677 (m)		
$C_6H_5CH{=}CHC(=O)C_6F_5$ (2)	1678 (s)	307	21,600
	1666 (vs)		

[a] Carbon tetrachloride was the solvent for the infrared studies; 95% ethanol was used for the ultraviolet spectra.



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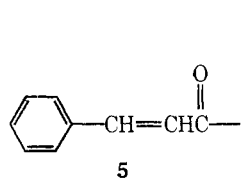
total effect of the C_6F_5 group is to destabilize the positive charge on the benzylic carbon.[8] 2,3-Dihydryl-*F*-benzalacetophenone (3) exhibits two carbonyl bands. The absorption at higher frequency (1689 cm^{-1}) is attributed to the additive effects of two pentafluorophenyl groups, the inductive influence of the C_6F_5 adjacent to >C=O, and destabilization of structure **4**. The lower frequency band (1677 cm^{-1}) probably arises as a result of charge–dipole repulsion between carbonyl oxygen and the ortho fluorines of the neighboring fluoroaryl ring, which forces the ring out of the plane of the >C=O group. Similar considerations would also explain the dual absorption in **2**.

It is evident from the ultraviolet data that the cinnamoyl systems **5** and **6** are the chromophores which absorb in the



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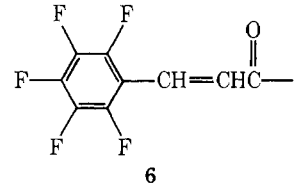

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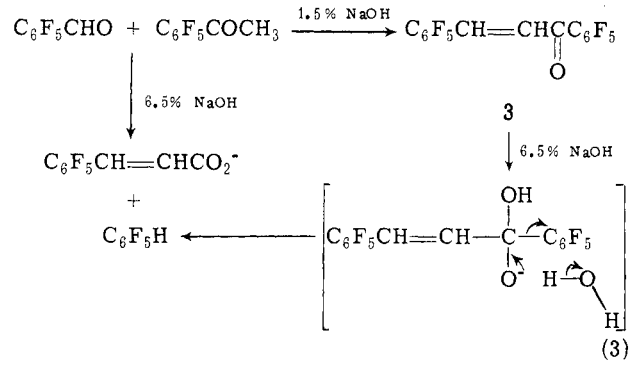
287–310-nm region. The nature of the aryl group attached to carbonyl is of little consequence, in agreement with previous reports[9,10] for benzalacetophenone, but contrary to the claim[11] that the entire molecule is responsible for these absorptions. In **5**, π-electron delocalization makes an important contribution, while the C_6F_5 group, by destabilizing structures, such as **4**, causes a hypsochromic shift. Thus, the ultraviolet and infrared spectra of these compounds are totally consistent.

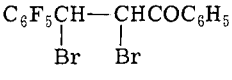
Benzalacetophenones usually exist as the trans isomers.[12] To obtain evidence of the configuration in the fluorinated compounds, proton magnetic resonance spectra were obtained for **2** and **3**. Since all seven protons in **2** exhibit peaks in the same region, interpretation is difficult. However, the spectrum of **3** revealed two doublets located at δ 7.62 and 7.22, J_{HH} = 16 Hz, indicative of a trans configuration.[13] The doublet at δ 7.22 is further split into a triplet, indicating coupling of the benzylidene proton with the ortho fluorines of the adjacent pentafluorophenyl ring.

Reactions. With Alkali. As mentioned earlier, compounds **2** and **3** were prepared in excellent yield when the concentration of alkali was carefully controlled. In an attempt to prepare **3** by using a 6.5% solution of sodium hydroxide in aqueous ethanol, the sole products isolated were 2,3,4,5,6-pentafluoro-*trans*-cinnamic acid[14] and pentafluorobenzene (detected by GC). This observation provides another example of what is now well established,[14,15] that the C_6F_5 group adjacent to carbonyl behaves as a pseudo-halogen which undergoes haloform-type cleavage to pentafluorobenzene in alkaline medium (eq 3). Compound **2** behaves similarly to give cinnamic acid, while benzalacetophenone and **1**, in which the carbonyl is flanked by phenyl, are unreactive under these conditions.



(3)

With Bromine. Addition of bromine to **1** gave the expected dibromide (**7**) in 93% yield, but the subsequent reac-



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tion of **7** with sodium methoxide, followed by acidification, failed to yield the dibenzoylmethane, a reaction which proceeds readily with benzalacetophenone dibromide.[16] The material isolated in low yield was not characterized, other than to establish the presence of weak -C≡C- absorption in the infrared.

With Grignard Reagents. Since conjugate addition of phenylmagnesium bromide to benzalacetophenone to yield β,β-diphenylpropiophenone is a classic reaction,[17] we examined the behavior of the fluorinated chalcones **1–3** with phenylmagnesium bromide and all four chalcones with pentafluorophenylmagnesium bromide. The reactions were conducted by normal addition, with the Grignard reagent in 25% molar excess. The results are summarized in Table II. All of the reactions proceed by 1,4-addition to the α,β-unsaturated carbonyl systems to give saturated ketones. There was no evidence of the presence of tertiary alcohols due to 1,2-addition. However, in two cases, both involving the fluorine-containing Grignard, reaction proceeded beyond the initial 1,4-addition. On the basis of analytical data and infrared spectra, we believe that the products possess structures **8** and **9** (Table II), formed by reaction of 2 mol of the appropriate chalcone per mole of organometallic.

The formation of these bimolecular products from benzalacetophenone and **1** can be explained by the preferential attack on unreacted chalcone by the initially generated carbanion in successful competition with the weakly nucleophilic pentafluorophenylmagnesium bromide (Scheme I). Only when this carbanion is consumed after 1,4-addition to a second molecule of chalcone does the Grignard reagent again attack unreacted starting material to regenerate more of the carbanion. Bimolecular compounds are not observed in corresponding reactions with phenylmagnesium bromide because the phenyl anion is a better nucleophile than the intermediate carbanion. The failure to form biomolecular products by reaction of C_6F_5MgBr with **2** and **3** might be due to low nucleophilicities of the carbanions (vis-a-vis $C_6F_5\delta^-$ $(MgBr)\delta^+$) when flanked by the pentafluorobenzoyl group. In such cases, the anion probably exists primarily in the enolate form.[2b]

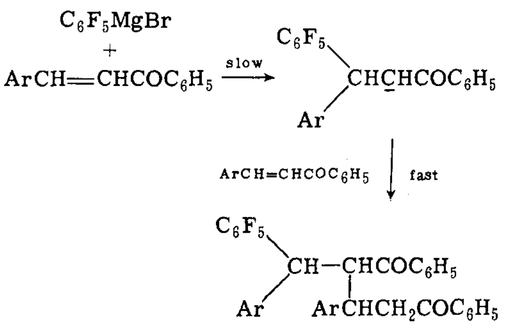
Michael Addition. All three polyfluorinated benzalace-

Table II
Reactions of Benzalacetophenones with Grignard Reagents

Reactants	Product	Yield, %	$\nu_{C=O}$, cm^{-1}
C_6H_5MgBr + $C_6H_5CH{=}CHCOC_6H_5$	$(C_6H_5)_2CHCH_2COC_6H_5$	81	1690
C_6H_5MgBr + $C_6F_5CH{=}CHCOC_6H_5$	see Experimental Section		1685
C_6H_5MgBr + $C_6H_5CH{=}CHCOC_6F_5$	$(C_6H_5)_2CHCH_2COC_6F_5$	83	1720
C_6H_5MgBr + $C_6F_5CH{=}CHCOC_6F_5$	$(C_6H_5)(C_6F_5)CHCH_2COC_6F_5$	60	1720
C_6F_5MgBr + $C_6H_5CH{=}CHCOC_6H_5$	$(C_6H_5)(C_6F_5)CHCHCOC_6H_5$ / $C_6H_5CHCH_2COC_6H_5$ **8**[a]	36	1680, 1690
C_6F_5MgBr + $C_6F_5CH{=}CHCOC_6H_5$	$(C_6F_5)_2CHCHCOC_6H_5$ / $C_6F_5CHCH_2COC_6H_5$ **9**[a]	42	1690
C_6F_5MgBr + $C_6H_5CH{=}CHCOC_6F_5$	$(C_6H_5)(C_6F_5)CHCH_2COC_6F_5$	45	1720
C_6F_5MgBr + $C_6F_5CH{=}CHCOC_6F_5$	$(C_6F_5)_2CHCH_2COC_6F_5$	40	1720

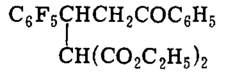
[a] Proposed structure.

Scheme I



8, Ar = C_6H_5
9, Ar = C_6F_5

tophenones failed to undergo the Michael reaction with diethyl malonate under the same experimental conditions in which benzalacetophenone gives the addition product in 90% yield.[18] Neither piperidine nor triethylamine were effective catalysts and the chalcones were recovered almost quantitatively. However, when 1 was mixed with 1 molar equiv of sodium diethyl malonate in ethanol at room temperature, reaction occurred. Although we were unsuccessful in isolating a solid product, we found that the infrared spectrum of the crude material was compatible with the Michael addition product, **10**, since both this material and



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the compound obtained from benzalacetophenone exhibited $\nu_{C=O}$ 1696 cm^{-1}.

Experimental Section

Except where noted, melting points are corrected and were obtained with a total immersion thermometer in an oil bath. Infrared spectra were obtained in carbon tetrachloride on a Perkin-Elmer Model 21 spectrophotometer. Ultraviolet spectra were measured in 95% ethanol using a Cary Model 11 PM spectrophotometer.

With carbon tetrachloride as the solvent, proton magnetic resonance spectra were obtained at 60 MHz on a well-calibrated Varian A-60 spectrometer. The precision of line frequencies was estimated to be ±0.5 Hz. The probe temperature was approximately 25°. The results are reported as δ values.

The elemental analyses were carried out by Micro-Tech Laboratories, Skokie, Ill.

Pentafluorobenzaldehyde was both synthesized[13] and purchased from Imperial Smelting Corp. Ltd., Bristol, England. Bromopentafluorobenzene and pentafluorobenzoyl chloride were obtained from Imperial Smelting Corp., and malonyl dichloride was purchased from Aldrich Chemical Co., Milwaukee, Wis.

Benzalacetophenone. Benzalacetophenone was prepared according to a previously described procedure.[19] After recrystallization from 95% ethanol, the product, mp 55.0–56.0°, was obtained in 58% yield.

Pentafluorobenzalacetophenone (1). A solution of 6.6 g (0.165 mol) of sodium hydroxide in 60 ml of water and 30 ml of 95% ethanol was placed in a 100-ml beaker equipped with a magnetic stirrer. Freshly distilled acetophenone (16.4 g, 0.135 mol) was added, the beaker was surrounded with crushed ice, and the stirrer was started. Pentafluorobenzaldehyde (26.4 g, 0.135 mol) was added at once (temperature rise) and a yellow solid immediately precipitated. The mixture was stirred at 20° for 1 hr, and the solid was filtered off, washed several times with water until all of the base had been removed, and finally washed with cold 95% ethanol. After air drying, the product, mp 144–146°, weighed 20.0 g (50%). It was recrystallized three times from an absolute ethanol–benzene solution (55% alcohol, 45% benzene v/v). After drying in vacuo, the light yellow powder melted at 144.6–145.8° (lit.[4] mp 142–143°); 2,4-dinitrophenylhydrazone, mp 217.8–218.4° (lit.[4] mp 187–189°). Anal. Calcd for $C_{15}H_7F_5O$: C, 60.42; H, 2.37. Found: C, 60.74; H, 2.52. λ_{max} (EtOH) 287 nm (ϵ 25,500); ir 1674 cm^{-1} (s).

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 placed 3.0 g (0.12 mol) 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 over 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 removed by distilla-

tion as stirring was continued until the residue became very viscous. Anhydrous, thiophene-free benzene (45 ml) was added, and 15 ml of liquid was removed by distillation. An additional 45 ml of benzene was added and the reflux condenser replaced. The mixture was refluxed with vigorous stirring for a few minutes, then 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 was complete, the mixture was stirred at room temperature for 18 hr, poured into 150 g of crushed ice containing 75 ml of 25% sulfuric acid, and the resulting two-phase mixture stirred for 5 min. The dark brown benzene layer was separated, and the water layer 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 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 Torr), ^{1}H NMR δ 2.67 (q_5).

2,3,4,5,6-Pentafluorocinnamic Acid. A solution of 0.60 g (0.015 mol) of sodium hydroxide in 5.2 g of water and 4.0 ml of 95% ethanol was placed in a 30-ml beaker equipped with a magnetic stirrer. The solution was stirred and cooled with ice; then 2.5 g (0.012 mol) of 2,3,4,5,6-pentafluoroacetophenone was added at once. This was followed by the immediate addition of 2.36 g (0.012 mol) of pentafluorobenzaldehyde. The mixture quickly turned yellow, then red-brown. In a few minutes, two liquid phases were evident. After an additional 1.5 hr of stirring at 25°, the mixture was left in a refrigerator for 15 hr. No precipitate formed. On acidification of the mixture with dilute hydrochloric acid, the white 2,3,4,5,6-pentafluorocinnamic acid precipitated, mp 146–148°, λ_{max} (EtOH) 260 nm.[13] This material rapidly decomposed on exposure to air.

2,3-Dihydryl-*F*-benzalacetophenone (3). A solution of 0.10 g (0.0025 mol) of sodium hydroxide in 4.2 g of water and 3.2 ml of 95% ethanol was placed in a 30-ml beaker equipped with a magnetic stirrer. The solution was stirred and cooled with ice; then 2.0 g (0.0095 mol) of 2,3,4,5,6-pentafluoroacetophenone was added at once. This was followed by the immediate addition of 1.89 g (0.0096 mol) of pentafluorobenzaldehyde. The mixture rapidly turned yellow, and after a few minutes of stirring, two yellow liquid phases were evident. After nearly 2 hr of stirring at room temperature, a yellow solid formed which was filtered off, washed with water to remove alkali, and air dried. The yellow powder weighed 3.1 g (84%). After a double sublimation the product was in the form of white leaflets, mp 58.4–59.0° (lit.[5] mp 56–57.5°); 2,4-dinitrophenylhydrazone, mp 208.4–209.0°. Anal. Calcd for $C_{15}H_2F_{10}O$: C, 46.41; H, 0.52. Found: C, 46.85; H, 0.73. λ_{max} (EtOH) 287 nm (ϵ 20,500); ir 1689 (s), 1677 cm^{-1} (m); ^{1}H NMR δ 7.62 (d), 7.22 (d), further split into a triplet.

Benzalpentafluoroacetophenone (2). A solution of 0.10 g (0.0025 mol) of sodium hydroxide in 4.2 g of water and 3.2 ml of 95% ethanol was placed in a 30-ml beaker equipped with a magnetic stirrer. The solution was stirred and cooled with ice; then 2.1 g (0.01 mol) of 2,3,4,5,6-pentafluoroacetophenone was added at once. This was followed by the immediate addition of 1.06 g (0.011 mol) of benzaldehyde. A two-phase yellow mixture quickly formed. After a few minutes a solid precipitated, and after 1 hr of stirring at room temperature, the yellow solid was removed by filtration. The solid was washed with water to remove alkali and air dried. The product weighed 2.6 g (87%). Three recrystallizations from 95% ethanol gave white needles, mp 102.2–102.9°; 2,4-dinitrophenylhydrazone, mp 246.8–248.0°. Anal. Calcd for $C_{15}H_7F_5O$: C, 60.42; H, 2.37. Found: C, 60.43; H, 2.51. λ_{max} (EtOH) 307 nm (ϵ 21,600); ir 1678 (m), 1666 cm^{-1} (s).

Pentafluorophenylmagnesium Bromide and Benzalacetophenone. To 1.43 g (0.0585 g-atom) of magnesium turnings just covered with a layer of ether was added at once an approximately 10-ml portion of the solution containing 12 g (0.0488 mol) of bromopentafluorobenzene and 60 ml of ether, while the reaction mixture was being stirred magnetically under a nitrogen atmosphere. After reaction had started and spontaneous refluxing ensued, the remainder of the solution of bromopentafluorobenzene was added dropwise to maintain a gentle reflux. An ice bath was employed to cool the flask whenever the reaction became too vigorous. After addition was complete, the mixture was stirred at room temperature for 2–3 hr, until most of the magnesium had reacted. At this point, the Grignard solution, which was virtually black, was cooled in an ice bath, and a solution containing 8.1 g (0.039 mol) of benzalacetophenone and 81 ml of ether was added dropwise to the solution of Grignard reagent. After addition, the mixture was stirred at room temperature under a nitrogen atmosphere for approximately 18 hr, then decomposed with ice and a saturated solution of ammonium chloride to obtain a clear aqueous phase under the dark organic layer. After the ether layer was separated, the aqueous phase was extracted with ether (3 × 50 ml), and the combined ether layers dried ($MgSO_4$), filtered, and evaporated under reduced pressure. The dark oily residue was kept in a vacuum desiccator overnight. The ir spectrum of this oily residue revealed a strong band at 1685 cm^{-1}, but no band in the hydroxyl region. When the residue was treated with a small amount of alcohol, a solid appeared after a few days. After two recrystallizations from alcohol–benzene, 4.1 g (36%) of white needles, mp 183–184°, was obtained. Anal. Calcd for $C_{36}H_{25}F_5O_2$: C, 73.97; H, 4.31; mol wt, 584. Found: C, 73.86; H, 4.35; mol wt (Rast), 570.

The ir spectrum displayed a partially resolved doublet at 1680 and 1690 cm^{-1}. The above data indicate that this compound is probably 3,5-diphenyl-5-pentafluorophenyl-4-benzoylvalerophenone (8).

Pentafluorophenylmagnesium Bromide and Pentafluorobenzalacetophenone (1). The reaction was carried out according to the procedure described for the reaction between pentafluorophenylmagnesium bromide and benzalacetophenone.

Pentafluorobenzalacetophenone (5.96 g, 0.02 mol) in 40 ml of ether was treated with pentafluorophenylmagnesium bromide, prepared from bromopentafluorobenzene (6.18 g, 0.025 mol) in ether (31 ml) with 0.73 g (0.03 g-atom) of magnesium. The ir spectrum of this crude product did not show any hydroxyl band. The viscous, dark residue, after treatment with decolorizing carbon and alcohol, gave a light-colored solid, mp 152–155°. Recrystallization from alcohol–benzene (4:1) yielded approximately 3 g (42%) of needles, mp 158–159°. Anal. Calcd for $C_{36}H_{15}F_{15}O_2$: C, 56.56; H, 1.97; mol wt, 764. Found: C, 56.25, 56.69; H, 1.87, 2.20; mol wt (Rast), 710. The ir spectrum displayed bands at 1690 (C=O), 1525 and 1505 cm^{-1} (aromatic ring). The data indicated that this compound is probably 3,5,5-tris(pentafluorophenyl)-4-benzoylvalerophenone (9).

Pentafluorophenylmagnesium bromide with Benzalpentafluoroacetophenone (2). This reaction was carried out according to the method described above. The Grignard reagent, prepared from 1.02 g (0.00413 mol) of bromopentafluorobenzene and 0.12 g (0.005 g-atom) of magnesium, was treated with 1 g (0.0033 mol) of benzalpentafluoroacetophenone. The ir spectrum of the crude solid product did not exhibit hydroxyl absorption. After two crystallizations from alcohol, 0.7 g (45%) of product was obtained, mp 63–64.5°. Anal. Calcd for $C_{21}H_8F_{10}O$: C, 54.09; H, 1.73. Found: C, 53.94; H, 1.70. Ir 1720 (C=O), 1525 and 1500 cm^{-1} (aromatic ring), in accord with the structure of 2,2,3 trihydryl-3-phenyl-1,3-*F*-diphenyl-1-propanone.

Pentafluorophenylmagnesium Bromide with 2,3-Dihydryl-*F*-benzalacetophenone (3). The procedure employed for the reaction between pentafluorophenylmagnesium bromide and benzalacetophenone was used. Bromopentafluorobenzene (3.09 g, 0.0125 mol) in 15 ml of ether, 0.364 g (0.015 g-atom) of magnesium, and 3.88 g (0.01 mol) of 2,3-dihydryl-*F*-benzalacetophenone in 20 ml of ether were used. The dark oily product gave no evidence of hydroxyl absorption in the ir spectrum. This material was dissolved in hot absolute ethanol, treated with Norite, and filtered. On cooling, white plates precipitated which were crystallized from absolute ethanol. In this manner, 2.2 g (40% yield) of 2,2,3-trihydryl-1,3,3-*F*-triphenyl-1-propanone was obtained, mp 63.5–64.5°. Anal. Calcd for $C_{21}H_3F_{15}O$: C, 45.34; H, 0.54. Found: C, 45.37; H, 0.77. Ir 1720 (C=O), 1525 and 1500 cm^{-1} (aromatic ring).

Phenylmagnesium Bromide with Benzalacetophenone. This reaction was carried out using 0.365 g (0.015 g-atom) of magnesium, 1.98 g (0.0125 mol) of bromobenzene in 6 ml of ether, and 2.08 g (0.01 mol) of benzalacetophenone in 20 ml of ether, according to the procedure described previously for reaction of pentafluorophenylmagnesium bromide and benzalacetophenone. The oily residue, upon treatment with a small amount of alcohol, gave a white solid. The ir spectrum of this crude product in carbon tetrachloride showed no evidence of a hydroxyl group. After recrystallization from ethanol, 2.3 g (81%) of 1,3,3-triphenyl-1-propanone was obtained, mp 95–96° (lit.[17] mp 96°), ir 1690 cm^{-1} (C=O).

Phenylmagnesium Bromide and Pentafluorobenzalacetophenone (1). Pentafluorobenzalacetophenone (5.96 g, 0.02 mol) was treated with phenylmagnesium bromide, prepared from 0.73 g (0.03 g-atom) of magnesium and 3.93 g (0.025 mol) of bromobenzene, following the usual procedure. From this mixture was ob-

tained a light brown, oily material which after thorough drying in a vacuum desiccator did not reveal the presence of a hydroxyl band in the infrared spectrum. All attempts to isolate a solid product from this oily material were unsuccessful. The ir spectrum of this oil showed strong carbonyl absorption at 1685 cm^{-1}.

Phenylmagnesium Bromide and Benzalpentafluoroacetophenone (2). Benzalpentafluoroacetophenone (2 g, 0.0067 mol) was treated with phenylmagnesium bromide prepared from 0.24 g (0.01 g-atom) of magnesium and 1.31 g (0.0084 mol) of bromobenzene, following the usual procedure. About 2.3 g of crude product, which melted around 110°, was obtained readily. This solid gave no evidence of a hydroxyl group in the ir spectrum. Colorless needles (2.1 g, 83%) were obtained after crystallization from absolute ethanol, mp 116.5–118°. Anal. Calcd for $C_{21}H_{13}F_5O$: C, 67.02; H, 3.48. Found: C, 67.59; H, 3.46. The ir spectrum of this compound, 1-pentafluorophenyl-3,3-diphenyl-1-propanone: 1720 (C=O), 1530 and 1502 cm^{-1} (aromatic ring).

Phenylmagnesium Bromide and 2,3-Dihydryl-*F*-benzalacetophenone (3). 2,3-Dihydryl-*F*-benzalacetophenone (1.25 g, 0.00323 mol) was treated with phenylmagnesium bromide prepared from 1.14 g (0.00403 mol) of bromobenzene and 0.12 g (0.00485 g-atom) of magnesium, following the usual procedure. The ir spectrum of the crude product did not show any hydroxyl band. Colorless needles (0.9 g, 60%) were obtained after two crystallizations from absolute ethanol, mp 63–64.5°. The infrared spectrum and melting point were identical with those of 2,2,3-trihydryl-3-phenyl-1,3-*F*-diphenyl-1-propanone, prepared by reaction of pentafluorophenylmagnesium bromide with benzalpentafluoroacetophenone. There was no depression in mixture melting point of the two products.

Reactions of Benzalacetophenones with Diethyl Malonate and Piperidine. A previously described procedure[17] was followed. An alcoholic solution of ketone, diethyl malonate, and piperidine was refluxed in an oil bath for 3 days. The reaction mixture was cooled and enough water was added to precipitate solid material. The solid was collected by filtration and washed with water, then with cold 95% ethanol, and crystallized from ethanol.

All of the materials used were thoroughly purified before use. Diethyl malonate was distilled under reduced pressure, piperidine was distilled from potassium hydroxide, and alcohol was distilled from magnesium ethoxide.

All compounds isolated were identified by mixture melting points and infrared spectra.

With Benzalacetophenone. Ethyl α-carbethoxy-β-phenyl-γ-benzoylbutyrate (0.94 g, 85%), mp 70–71° (lit.[17] mp 70–71°), was isolated from the reaction of 0.625 g (0.003 mol) of benzalacetophenone, 0.48 g (0.003 mol) of diethyl malonate, and 0.0255 g (0.003 mol) of piperidine in 3 ml of alcohol.

With Pentafluorobenzalacetophenone (1). Pentafluorobenzalacetophenone 0.894 g (0.003 mol), 0.48 g (0.003 mol) of diethyl malonate, 0.0255 g (0.0003 mol) of piperidine, and 3 ml of alcohol were used. About 0.8 g of pentafluorobenzalacetophenone was recovered.

With 2,3-Dihydryl-*F*-benzalacetophenone (3). This ketone (**3**, 0.388 g, 0.001 mol), 0.16 g (0.001 mol) of diethyl malonate, 0.0282 g (0.0003 mol) of piperidine, and 3 ml of alcohol were used. About 0.25 g of purified **3** was recovered.

With Benzalpentafluoroacetophenone (2). Benzalpentafluoroacetophenone (0.894 g, 0.003 mol), 0.48 g (0.003 mol) of diethyl malonate, 0.0255 g (0.0003 mol) of piperidine, and 3 ml of alcohol was used. About 0.7 g of the starting ketone was recovered.

Pentafluorobenzalacetophenone (1) with Sodium Diethyl Malonate. Sodium diethyl malonate was prepared from sodium ethoxide (0.01 mol in 10 ml of alcohol) and diethyl malonate (0.60 g, 0.01 mol) by refluxing the mixture for 3 hr. Then pentafluorobenzalacetophenone (2.98 g, 0.01 mol) was mixed with the sodium diethyl malonate in ethyl alcohol (40 ml) and stirred at room temperature for approximately 24 hr. The orange-colored reaction mixture was acidified with a sufficient amount of acetic acid, and most of ethyl alcohol was removed under vacuum. The resulting syrup was mixed with 150 ml of carbon tetrachloride and 50 ml of *n*-hexane, and filtered to remove insoluble material. A viscous residue was obtained from the filtrate when solvent was removed. All attempts to obtain a solid product from the residue were unsuccessful. The infrared spectrum of this crude product (residue) in carbon tetrachloride showed a band at 1696 cm^{-1}.

Pentafluorobenzalacetophenone (1) with Diethyl Malonate and Triethylamine. Pentafluorobenzalacetophenone (2.98 g, 0.01 mol) was dissolved in a minimum amount of ethyl alcohol (40 ml) and mixed with diethyl malonate (0.01 mol, 1.6 g), triethylamine (0.28 ml, 0.02 mol), and 1 drop of acetic acid. After 24 hr of heating under reflux, 2.5 g of starting material was recovered.

Pentafluorobenzalacetophenone Dibromide (7). Pentafluorobenzalacetophenone (5.0 g, 0.017 mol) was dissolved in 50 ml of carbon tetrachloride and 100 ml of chloroform and the mixture was cooled to 0°. Bromine (2.7 g, 0.017 mol) was added with stirring and, after addition was complete, stirring at 0° was continued for 1 hr. The mixture was then allowed to warm to room temperature over a 1-hr period and the solvent stripped off on a flash evaporator. The white pentafluorobenzalacetophenone dibromide remained, 7.13 g (93%), mp 115–118°.

Reaction of 7 with Sodium Methoxide. Pentafluorobenzalacetophenone dibromide (3.5 g, 0.0074 mol) in 5.0 ml of absolute methanol was heated to reflux with stirring in a three-necked flask fitted with a condenser, a dropping funnel, and a magnetic stirrer. A solution of 0.825 g (0.0153 mol) of sodium methoxide in 6.0 ml of absolute methanol was added over 50 min,[18] a yellow solution being formed. Refluxing was continued for an additional 10 min. The mixture was acidified with 0.2 ml of concentrated hydrochloric acid and refluxed for 5 min. Cold water (5.0 ml) was then added and the mixture was rapidly cooled in ice, forming a yellow solid. This was removed by filtration, washed with water, and recrystallized from methanol to give 0.6 g of a white solid, mp 95–110° after three recrystallizations, ir 2200 cm^{-1} (w, $-C\equiv C-$). The material was not examined further.

Registry No.—**1**, 54081-32-2; **1** 2,4-DNP, 54053-74-6; **2**, 54081-33-3; **2** 2,4-DNP, 54019-70-4; **3**, 32782-50-6; **3** 2,4-DNP, 54003-52-0; **7**, 54003-53-1; **8**, 54003-54-2; **9**, 54003-55-3; benzalacetophenone, 614-47-1; acetophenone, 98-86-2; pentafluorobenzaldehyde, 653-37-2; 2,3,4,5,6-pentafluoroacetophenone, 652-29-9; bromopentafluorobenzene, 344-04-7; 2,3,4,5,6-pentofluorocinnamic acid, 34234-46-3; benzaldehyde, 100-52-7; phenyl bromide, 108-86-1; 2,2,3-trihydryl-3-phenyl-1,3-*F*-diphenyl-1-propanone, 54036-73-6; 2,2,3-trihydryl-1,3,3-*F*-triphenyl-1-propanone, 54003-56-4; 1-pentafluorophenyl-3,3-diphenyl-1-propanone, 54003-57-5; 1,3,3-triphenyl-1-propanone, 606-86-0; diethyl malonate, 105-53-3; piperidine, 110-89-4; sodium diethyl malonate, 996-82-7; triethylamine, 121-44-8; sodium methoxide, 124-41-4.

References and Notes

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