(1.8 to 2.2 g) from ethanol afforded *ca.* 1.0 g of recovered benzil, mp and mmp 92–94°.[5] When conducted on 21.0 g (0.10 mol) of benzil in 50 ml of dioxane and 20 ml of D_2O, the reaction furnished 6.0 g (56%) of distilled benzaldehyde-*formyl-d*.

With 5 ml of D_2O in the cleavage of 10.5 g of benzil, the yield of deuterio aldehyde was only 1.6 g (30%), and a larger amount of still-pot residue (3.5 g) remained. Even with 20 ml of D_2O the yield of aldehyde from 10.5 g of benzil did not exceed 3.2 g (60%). With 10 ml of H_2O containing tritium oxide the reaction afforded 3.0 to 3.25 g (57–62%) of tritium-labeled benzaldehyde. Substitution of tetrahydrofuran or 1,2-dimethoxyethane for 1,4-dioxane as solvent offered no apparent advantage, while use of dimethyl sulfoxide resulted in the formation of deeply colored by-products and very little aldehyde.

Registry No.—Benzaldehyde-*formyl-d*, 3592-47-0; benzil, 134-81-6.

Organocopper Chemistry. The Decarboxylation of a Benzhydryl Carboxylic Acid

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In the course of our synthesis of the highly strained hydrocarbon 4,8-dihydrodibenzo[*cd,gh*]pentalene,[3] we became interested in the decarboxylation reactions of benzhydryl carboxylic acids for which a paucity of examples exist in the literature.[4,5] Recent interpretations of the decarboxylation of aromatic and vinyl carboxylic acids invoke the intermediacy of organocopper species.[6–8] A requirement for the π system was assumed on the basis of a lack of a catalytic effect of copper salts on decarboxylation of aliphatic acids. In contrast to this conclusion, decarboxylation of benzhydryl carboxylic acids exhibits a pronounced dependence on the presence of copper and its salts and on the nature of the copper source. To study this phenomenon for preparative purposes, fluorene-9-carboxylic acid was chosen as a suitable model, and this compound was consequently subjected to a variety of classical and new decarboxylation procedures. A study of these reactions has evolved some new and unusual chemistry attributable to organocopper intermediates.

Heating fluorene-9-carboxylic acid to 290° for several minutes (material sublimes from the reaction mixture) afforded fluorene in 38% yield and 9,9′-bifluorenyl in 12% yield (Scheme I, Table I). The products here and in the following cases were separated by preparative thick layer chromatography on silica gel, and identified by comparison of spectral data and melting points with those of authentic samples. Bifluorenyl was prepared by the reductive coupling of 9-bromofluorene.[9]

SCHEME I

DECARBOXYLATION OF FLUORENE-9-CARBOXYLIC ACID

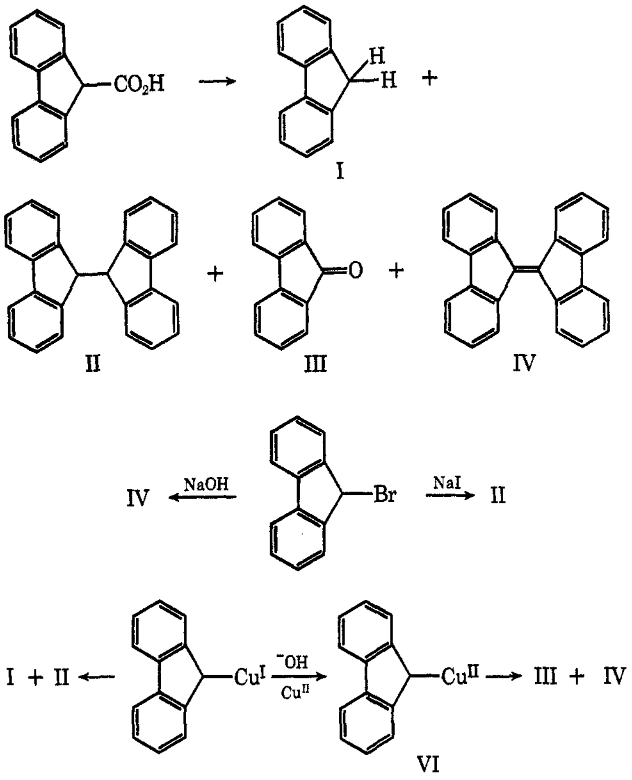

TABLE I

YIELDS OF PRODUCTS OBTAINED ON DECARBOXYLATION OF FLUORENE-9-CARBOXYLIC ACID

Reaction conditions	Yield, % I	 II	 III	 IV
1. Δ 290°	38	12		
2. 0.03 equiv $CuCO_3Cu(OH)_2$ (265°)	48	10	11	3
3. 2.0 equiv $CuCO_3Cu(OH)_2$ (265°)			56	10
4. Cu–quinoline (reflux)	85	6		4
5. Pentafluorophenylcopper quinoline (reflux)	90	Trace		Trace

Heating fluorene-9-carboxylic acid to 265° (material sublimes from the reaction mixture) with 0.03 molar equiv of basic copper carbonate [$CuCO_3Cu(OH)_2$] afforded fluorene (48% yield), 9,9′-bifluorenyl (10% yield), and, unexpectedly, fluorenone (3% yield) and 9,9′-bifluorenylidene (11% yield). Bifluorenylidene was available by base treatment of 9-bromofluorene.[10] Repeating this reaction with 2.0 molar equiv of basic copper carbonate afforded only fluorenone (56% yield) and 9,9′-bifluorenylidene (10% yield). This case represents the first example of a direct oxidative decarboxylation utilizing copper salts catalysis and has clear synthetic utility.[11]

The copper–quinoline decarboxylation[7] is another method which has found wide utility. Employment of copper powder[5] in refluxing quinoline (1 hr) afforded an 85% yield of fluorene, a 6% yield of bifluorenyl, and a 4% yield of bifluorenylidene from fluorenecarboxylic acid. Alternatively, treatment of fluorene-9-carboxylic acid with 0.1 equiv of pentafluorophenylcopper[6] in quinoline for 3 min at 220° followed by addition of a

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[1] Camille and Henry Dreyful Teacher–Scholar.

[2] National Institutes of Health Predoctoral Fellow.

[3] B. M. Trost and P. L. Kinson, *J. Amer. Chem. Soc.*, **92**, 2591 (1970); B. M. Trost, P. L. Kinson, C. A. Maier, and I. C. Paul, *ibid.*, in press.

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[9] Compare J. Thiele and A. Wanscheidt, *Justus Liebigs Ann. Chem.*, **376**, 269 (1910); A. Wanscheidt, *Chem. Ber.*, **59**, 2092 (1926).

[10] R. C. Fuson and H. D. Porter, *J. Amer. Chem. Soc.*, **70**, 895 (1948).

[11] Compare chromic acid procedure [I. M. Hunsberger and E. D. Amstutz, *ibid.*, **71**, 2635 (1949)] and pyridine *N*-oxide procedure [T. Cohen, I. H. Song, and J. H. Fager, *Tetrahedron Lett.*, 237 (1965)].

small amount of water afforded a 90% yield of fluorene accompanied by only traces of 9,9′-bifluorenyl and 9,9′-bifluorenylidene (thin layer comparison). To our knowledge this reaction is the first example of the employment of pentafluorophenylcopper for the decarboxylation of acids other than aromatic and vinyl acids. It is also clearly the reagent of choice.

Table I summarizes the yields of the products obtained in the decarboxylation of fluorene-9-carboxylic acid by the above procedures.

The mechanism of formation of these products, particularly fluorenone and bifluorenylidene, is of considerable interest. Recent investigations[6-8] have shown that aromatic and vinyl carboxylic acids react with a variety of copper salts to afford copper(I) carboxylates. On heating in complexing solvents such as quinoline these materials evolve carbon dioxide with consequent formation of organocopper(I) compounds. These organocoppers, pentafluorophenylcopper, for example, have been isolated in a number of cases. These materials afford the parent hydrocarbon on treatment with acids or water or dimers on heating or oxidation.[12] Analogy of the aryl- and vinylcopper chemistry to our results is apparent. This chemistry thus explains the formation of fluorene and bifluorenyl in the above reactions *via* the intermediacy of 9-fluorenylcopper V (Scheme I). The formation of fluorenone and bifluorenylidene, however, remains unexplained. It is interesting to speculate upon a mechanism for the formation of these products. Organocopper V under the basic conditions could suffer basic oxidation to a copper II fluorenylidene (VI). Such a compound may dimerize to bifluorenylidene or pick up oxygen from the cupric oxide to generate fluorenone.

Experimental Section

Melting points were taken on a Thomas-Hoover melting point apparatus and are corrected. Infrared spectra were determined on a Beckman IR-8 spectrophotometer, and ultraviolet spectra were recorded on Cary Model 11 and Model 15 spectrophotometers. Nmr spectra were determined on a Varian Associates Model A-60A or Model HA-100 spectrometer fitted with a variable temperature probe. Chemical shifts are given in parts per million relative to TMS as an internal standard. Mass spectra were taken on a CEC 103 C or a MS-902 mass spectrometer at an ionizing current of 40 mA and ionizing voltage of 70 V. Chromatographic separations employed silica gel PF-254 (Merck, Darmstadt).

Decarboxylations of Fluorene-9-carboxylic Acid. Method A. Pentafluorophenylcopper.—Under nitrogen, a solution of fluorene-9-carboxylic acid (210 mg, 1.00 mmol) and pentafluorophenylcopper (23 mg, 0.10 mmol) in distilled deaerated quinoline (10 ml) was heated with swirling in a metal bath at 225–230° for 3 min. Rapid bubbling was observed over the first minute. While the reaction mixture was cooling, water (1 ml) was added. The material was taken up in ether (100 ml) and extracted with 20% hydrochloric acid (100 ml), 10% hydrochloric acid (100 ml), water (50 ml), twice with 10% potassium hydroxide (50 ml), and with water (50 ml). The solvent was removed, affording 187 mg (quantitative yield) of a tan solid, mp 90–102° (mp fluorene[13] 116–117°). Acidification of the basic washes, extraction with ether, and removal of solvent afforded only 0.7 mg of a brown oil, indicating that the starting material had been consumed. The neutral material was identified as fluorene by nmr, ir, and thin layer comparison to an authentic sample. Thin layer comparison spots indicated that traces of 9,9′-bifluorenyl and 9,9′-bifluorenylidene were also produced in the reaction, but examination of the nmr indicates that they were produced in less than 3% yield each.

Method B. Copper–Quinoline.—Under nitrogen, fluorene-9-carboxylic acid (200 mg, 0.953 mmol), copper powder [632 mg, 9.96 mmol, Fisher (electrolytic) purified], and distilled deaerated quinoline (3.2 ml) were heated at reflux for 1.1 hr. After cooling, the reaction mixture was taken up in dichloromethane (50 ml), filtered through sintered glass, and extracted twice with 10% aqueous hydrochloric acid. Removal of solvent afforded 191 mg of material. Examination of this material by nmr and thin layer comparison spots indicated that the reaction afforded fluorene, 9,9′-bifluorenyl, and 9,9′-bifluorenylidene in yields of 85, 6, and 4%, respectively.

Method C. Thermal Decarboxylation.—Under nitrogen, fluorene-9-carboxylic acid (50.0 mg, 23.8 mmol) in a sublimation apparatus was heated to 290° for 5 min, subliming material (34 mg) onto the cold finger. This material was examined by nmr and thin layer, and identified on that basis as being mainly comprised of a mixture of fluorene (38% yield), fluorene-9-carboxylic acid (6% yield), and 9,9′-bifluorenyl (12% yield).

Method D. Basic Copper Carbonate (0.03 Molar Equiv).—Fluorene-9-carboxylic acid (61.4 mg, 0.28 mmol) and basic copper carbonate (1.9 mg, 0.0086 mmol) were mixed and heated under nitrogen in a sublimation apparatus to 265° for 5 min. After cooling, the material was removed from the cold finger with dichloromethane and extracted with 5% potassium carbonate solution, and the solvent was removed on a rotary evaporator. The basic aqueous extract was acidified with hydrochloric acid and extracted with dichloromethane, and the solvent was removed on a rotary evaporator, affording 18 mg (30% recovery) of starting material, mp 221–224° (lit.[4] mp 225–228°), confirmed by nmr comparisons. The neutral materials were applied to a preparative thick layer plate, and eluted twice with 3:1 pentane–dichloromethane. The four major bands were removed with chloroform, and identified by comparison of R_f's, melting points, and spectral data with authentic samples of material. The yields (based on starting material consumed) and R_f's of these materials are shown in Table II.

TABLE II

PRODUCTS OF BASIC COPPER CARBONATE DECARBOXYLATION OF FLUORENE-9-CARBOXYLIC ACID

Material	R_f	Yield, mg (%)
Fluorene	0.85	16.3 (48)
Fluorenone	0.21	4.2 (11)
9,9′-Bifluorenyl	0.66	3.5 (10)
9,9′-Bifluorenylidene	0.75	1.0 (3)

Method E. Basic Copper Carbonate (2.0 Molar Equiv).—Fluorene-9-carboxylic acid (50 mg, 0.24 mmol) and basic copper carbonate (106 mg, 0.48 mmol) were mixed and heated to 265° for 5 min under nitrogen in a sublimation apparatus. The material was removed from the cold finger with dichloromethane. The material was applied to a preparative thick layer plate and eluted twice with 3:1 pentane–dichloromethane, affording 24 mg (56% yield) of fluorenone, mp 80–82° (lit.[14] mp 83°), and 4 mg (10% yield) of 9,9′-bifluorenyl, identified by spectral data and thin layer comparison with authentic material.

Preparation of 9,9′-Bifluorenylidene.—Utilizing the method of Fuson and Porter,[10] 9-bromofluorene (1.00 g, 4.09 mmol) generated 391 mg (58% yield) of bifluorenylidene, mp 186.0–187.5° (lit.[10] mp 188–190°) after recrystallization from ethanol–benzene.

Preparation of 9,9′-Bifluorenyl.[9]—9-Bromofluorene (764 mg, 3.1 mmol) was dissolved in 30.5 ml of hot acetone. A solution of 915 mg (6.2 mmol) of sodium iodide in 6.1 ml of acetone was added, and the mixture was refluxed for 5.5 hr. The solution was cooled to 40°, and 4 ml of 10% aqueous sodium thiosulfate and 30 ml of water were added. The resultant crystals were filtered, washed with water, and air dried. The material was recrystallized from 2.5 ml of xylene, filtered, washed with 0.5 ml of xylene, and air dried, affording 357 mg (70% yield) of 9,9′-bifluorenyl: mp 243.5–245.0° (lit.[15] mp 247°); nmr (CCl_4) δ 7.68–6.82 (16 H, m), 4.76 (2 H, s), ir ($CHCl_3$) 1475, 1450 cm^{-1}.

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[13] R. C. Weast, Ed., "Handbook of Chemistry and Physics," 46th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1965, p C-324.

[14] Reference 13, p C-325.

[15] Reference 13, p C-206.

Registry No.—Fluorene-9-carboxylic acid, 1989-33-9.

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The Friedel–Crafts Reaction with 1-Bromo-1-phenyl-2-propanone

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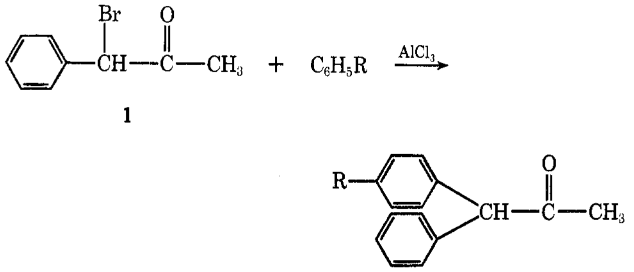
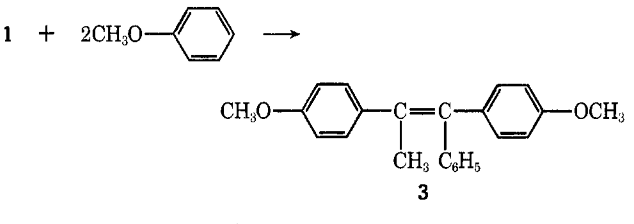
Under Friedel–Crafts reaction conditions, 1-bromo-1-phenyl-2-propanone (**1**) reacts with benzene to give 1,1-diphenyl-2-propanone (**2a**) in good yield.[1] As an extension of this method, Cragoe, *et al.*,[2] reacted **1** with substituted benzene to prepare substituted diphenyl-2-propanones (**2**). However, when they reacted **1** with anisole, they isolated 1,2-bis(*p*-methoxyphenyl)-1-phenylpropene (**3**) in good yield.



1

2a, R = H
b, R = CH3
c, R = Cl



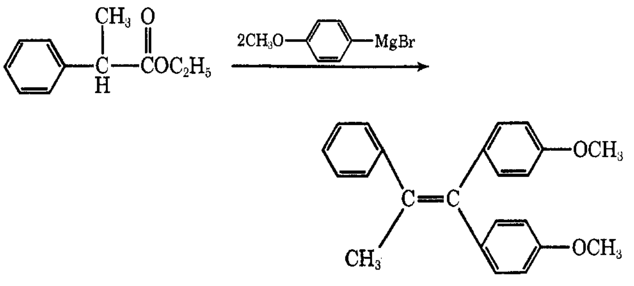
1

3

The structure assignment was based on elemental analysis and infrared data. Similar reaction[3,4] has been reported for acetyl chloride and anisole with aluminum chloride which gave 1,1-bis(*p*-methoxyphenyl)ethylene.

In our synthetic program, we had the occasion to prepare 1,1-bis(*p*-methoxyphenyl)-2-phenylpropene (**4**) by treating ethyl 2-phenylpropionate with *p*-methoxyphenylmagnesium bromide.

The melting point and boiling point of **4** were identical with those of **3** as reported by Cragoe.[2] It seemed unusual that two isomeric compounds should have the same melting point and boiling point. The preparation of **3** was repeated according to the literature procedure.[2]



4

The product was found to be identical in every respect (mixture melting point, ir, uv, nmr, and tlc) with **4**.

It remained to be determined which structure was correct. Ozonolysis of **3** would give 4-methoxyacetophenone and 4-methoxybenzophenone, while ozonolysis of **4** would give acetophenone and 4,4′-dimethoxybenzophenone. Ozonolysis and characterization of the reaction products of 1-bromo-1-phenyl-2-propanone (**1**) with anisole and ethyl 2-phenylpropionate with *p*-methoxyphenylmagnesium bromide confirmed that in both cases the end products are 4,4′-dimethoxybenzophenone and acetophenone, thus proving that **4** is the correct structure.

Ketones are known to rearrange under acidic conditions[5-7] and this may partly explain the formation of **4** from **1** under Friedel–Crafts reaction conditions.

Experimental Section[8]

Ethyl 2-Phenylpropionate.—To a solution of 34 g (0.13 mol) of 2-phenylpropionic acid in 100 ml of ethyl iodide cooled in an ice bath was added 26 g (0.07 mol) of Ag_2O in small portions with stirring. Stirring was continued at room temperature for 2 hr. The AgI was filtered and the filtrate was dried and concentrated. The ester was distilled to give 28.2 g of colorless liquid: bp 112–115° (15 mm); $n^{22}D$ 1.4932; ir 1730 cm^{-1} (ester); nmr δ 7.30 (s, 5, aromatic), 4.10 (q, 2, CH_2 next to CH_3), 3.70 (q, 1, CH), 1.5 (d, 3, CH_3), and 1.17 (t, 3, CH_3).

Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.92; H, 7.79.

1,1-Bis(*p*-methoxyphenyl)-2-phenylpropene. Method A.— To a mixture of *p*-methoxyphenyl Grignard reagent [formed by reacting 41.1 g (0.22 mol) of *p*-bromoanisole and 5.76 g (0.24 g-atom) of Mg in 100 ml of ether] was added slowly 17.8 g (0.1 mol) of ethyl 2-phenylpropionate dissolved in 50 ml of ether. The mixture was refluxed with stirring for 1 hr and then was poured into ice water. The mixture was acidified with concentrated HCl, extracted with ether, and dried. Removal of ether gave a viscous brown residue. The crude product was dissolved in hot hexane to give a pale yellow solution. The hexane was removed under reduced pressure and the residue was distilled to give 25 g of colorless product that solidified immediately, bp 190–195° (0.08 mm). The product was recrystallized from hexane and then from methanol to give 18 g of colorless crystals: mp 93–94.5°; ir 1602 cm^{-1} (C=C conjugated); uv λ_{max} (isooctane) 285 mμ (ϵ 14,736) and 247 (21,530); nmr δ 7.13 (s, 5, aromatic), 7.3 (q, 4, aromatic, J_{AB} = 9 Hz), 6.68 (q, 4, aromatic, J_{AB} = 9 Hz), 3.8 (s, 3, OCH_3), 3.66 (s, 3, OCH_3), and 2.13 (s, 3, CH_3).

Anal. Calcd for $C_{23}H_{22}O_2$: C, 83.60; H, 6.71. Found: C, 83.29; H, 6.63.

Method B[2].—To a stirring solution of 55.5 g (0.41 mol) of 1-phenyl-2-propanone in 250 g of CS_2 was added 67 g (0.42 mol)

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(8) Melting points were determined on a Thomas-Hoover apparatus and are uncorrected. Nuclear magnetic resonance spectra were recorded on a Varian A-60A spectrometer using $CDCl_3$ as solvent and TMS as internal standard. Ultraviolet spectra were obtained on a Cary Model 14 spectrophotometer using spectral grade solvents. Microanalyses were performed by Chemical Analytical Services, University of California, Berkeley, Calif. 94701.