1,1′-Dicinnamoylferrocene (2).—A solution of cinnamoyl chloride (8.25 g, 0.049 mol) and $AlCl_3$ (6.6 g, 0.049 mol) in dry CH_2Cl_2 (75 ml) was added slowly to a solution of ferrocene (4 g, 0.022 mol) in dry CH_2Cl_2 (75 ml). The mixture was stirred for 4 hr at 25° in a N_2 atmosphere, then poured into 300 ml of ice-water. The organic phase was separated and combined with the CH_2Cl_2 extracts of the aqueous phase. The combined organic phases were washed with water, dried with $MgSO_4$, and taken to dryness. The residue was dissolved in a minimum volume of benzene with heating and allowed to crystallize. After removal of crystalline **4** (7.9 g) the solution was reduced to a small volume and chromatographed on neutral alumina. Petroleum ether (bp 20–40°)-diethyl ether (3:2) eluted a small band of ferrocene and a second small band of cinnamoylferrocene. Methylene chloride eluted an additional 0.6 g of **4**. The 8.5 g of crystalline (red needles) product represents an 88% yield, mp 180.5–182° (lit.[2] mp 208–210°), ir 6.01 μ, nmr τ 2.06–3.07 (m, 14 H, vinyl and Ph protons), 5.06, 5.39 (2 t, 8 H, cyclopentadienyl protons).

Anal. Calcd for $C_{28}H_{22}O_2Fe$: C, 75.35; H, 4.97; Fe, 12.51. Found: C, 75.25; H, 5.01; Fe, 12.85.

Due to the discrepancy in melting point, **4** was synthesized from **1** according to the directions of Mashburn, *et al.*,[2] which after repeated recrystallizations from ethanol-water melted at 180.5–182°. Ir and nmr spectra of this compound were also identical with those of **4** synthesized by Friedel-Crafts dicinnamoylation of ferrocene.

3-Phenyl[5]ferrocenophane-1,5-dione (2).—Aqueous 15% NaOH solution (100 ml) was slowly added to a solution of **4** (5 g, 0.011 mol) in 500 ml of 95% ethanol and 150 ml of THF. The mixture was stirred at 25° in a nitrogen atmosphere for 65 hr and diluted with 800 ml of water. The suspension was extracted with $CHCl_3$. The extract was then dried with $MgSO_4$, concentrated, and chromatographed on neutral alumina. Only one band developed, which was eluted with CH_2Cl_2-$CHCl_3$ (1:1). Crystallization from ethanol yielded 3.7 g of yellow feathers (yield 92%), mp >300° (lit.[2-4] mp >300°), ir 6.03 μ (lit.[4] 6.03 μ).

Anal. Calcd for $C_{21}H_{18}O_2Fe$: C, 70.41; H, 5.06; Fe, 15.59. Found: C, 70.18; H, 5.04; Fe, 15.64.

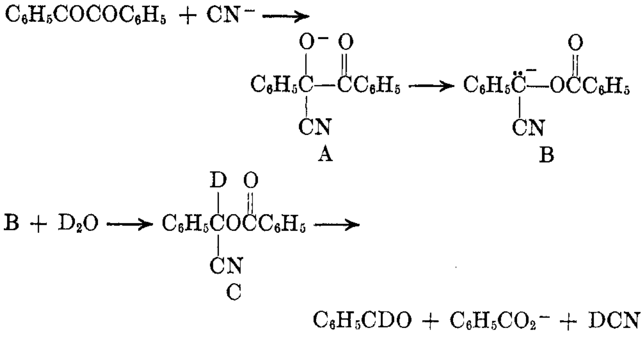
A Convenient Synthesis of Benzaldehyde-*formyl-d* from Benzil[1]

Albert W. Burgstahler, Donald E. Walker, Jr.,
John P. Kuebrich, and Richard L. Schowen*[2]

Department of Chemistry, The University of Kansas, Lawrence, Kansas 66044

Received November 4, 1971

Although various methods[3] are now available for the synthesis of deuterio and tritio aldehydes, practically all of them involve multistep procedures, costly reagents, or extended reaction periods. In seeking a simple, rapid route to benzaldehyde-*formyl-d*, we have found that the facile cleavage of benzil by cyanide ion in the presence of D_2O, occurring apparently through adduct A and its rearrangement products B and C,[4] provides a convenient source of this compound.



When dry potassium cyanide is added at room temperature to 1 equiv of benzil in dioxane containing 10 equiv of D_2O, the yellow α-diketone color gradually disappears. After dilution of the mixture with ordinary water, extraction with ether, and washing of the ether extract, benzaldehyde-*formyl-d* of 98% isotopic purity (by nmr analysis) can be recovered in 55–60% yield by distillation. The remainder of the product consists of an equivalent amount of benzoic acid (separated in the extraction and washing), unchanged benzil, and a mixture of what appears to be α-deuteriobenzoin and its benzoate ester.[4] The benzoin derivatives are evidently formed not by the benzoin condensation but, as shown recently,[4] through trapping of carbanion B by deuteriobenzaldehyde, even though the latter must compete with an appreciable excess of D_2O. (With the use of less than 10 equiv of D_2O more by-products are formed, and the yield of aldehyde is diminished.) When conducted in dioxane-H_2O in the presence of tritium oxide the reaction furnishes benzaldehyde containing benzaldehyde-*formyl-t*.

Although cyanide ion is theoretically required only in catalytic amounts, the reaction is erratic and the yield of aldehyde is lower when less than a full molar equivalent of cyanide is used. In addition, the disappearance of the yellow diketone color occurs much more slowly when less cyanide is used, even when potassium carbonate is added to prevent its loss as DCN. Use of sodium cyanide in place of potassium cyanide is unsatisfactory because of the formation of difficultly soluble salts during the initial stages of the reaction.

Experimental Section

Benzaldehyde-*formyl-d*.—By means of a syringe, 10 ml of D_2O (99.87%, Bio-Rad Laboratories) was added to a magnetically stirred solution of 10.5 g (0.050 mol) of benzil (recrystallized from carbon tetrachloride[5]) in 25 ml of dry 1,4-dioxane under a dry, inert atmosphere (argon or nitrogen) at 20–25°. To the resulting fine suspension of benzil were added, with rapid stirring, at 2-min intervals, four 1-g portions of reagent-grade potassium cyanide (previously dried at 125°). After the second addition of cyanide the mixture became homogeneous, and the yellow color disappeared within 2 min after the last addition. Stirring was continued for 10 min as potassium benzoate gradually precipitated. The mixture was then diluted with 100 ml of distilled water and extracted with two 50-ml portions of ether. The combined ether extracts were washed with 50 ml of 5% sodium carbonate solution, 100 ml of water, and finally with 50 ml of saturated sodium chloride solution. After drying for 2 min over $MgSO_4$ the ether solution was concentrated in a rotary evaporator under aspirator vacuum on a water bath. Distillation of the light yellow residue (5.5 ml) gave, in separate runs, 2.95 to 3.2 g (55–60%) of benzaldehyde-*formyl-d*, bp 84–86° (30 mm). By nmr analysis this contained 0.98 atom of deuterium per molecule. Crystallization of the still-pot residue

---

[1] This research was supported in part by the National Science Foundation and the National Institutes of Health.

[2] Holder of a Research Career Development Award of the National Institute of General Medical Sciences.

[3] *E.g.*, D. Nasipuri, C. K. Gosh, and R. J. L. Martin, *J. Org. Chem.*, **35**, 657 (1970) [citing D. J. Bennett, G. W. Kirby, and V. A. Mess, *Chem. Commun.*, 218 (1967)]; A. I. Meyers, A. Nabeya, H. W. Adickes, and I. R. Politzer, *J. Amer. Chem. Soc.*, **91**, 763 (1969); T. Axenrod, L. Loew, and P. S. Pregosin, *J. Org. Chem.*, **33**, 1274 (1968); J. Cymerman Craig and L. R. Kray, *ibid.*, **33**, 871 (1968); R. A. Olafson and D. M. Zimmerman, *J. Amer. Chem. Soc.*, **89**, 5057 (1967); D. Seebach, B. W. Erickson, and G. Singh, *J. Org. Chem.*, **31**, 4303 (1966); V. E. Althouse, D. M. Feigl, W. A. Sanderson, and H. S. Mosher, *J. Amer. Chem. Soc.*, **88**, 3595 (1966).

[4] For a recent study and references to earlier work, see J. P. Kuebrich and R. L. Schowen, *J. Amer. Chem. Soc.*, **93**, 1220 (1971).

[5] H. T. Clarke and E. E. Dreger, "Organic Syntheses," Collect. Vol. I, 2nd ed, Wiley, New York, N. Y., 1941, p 87.

(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

BARRY M. TROST*[1] AND PHILIP L. KINSON[2]

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

Received September 24, 1971

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

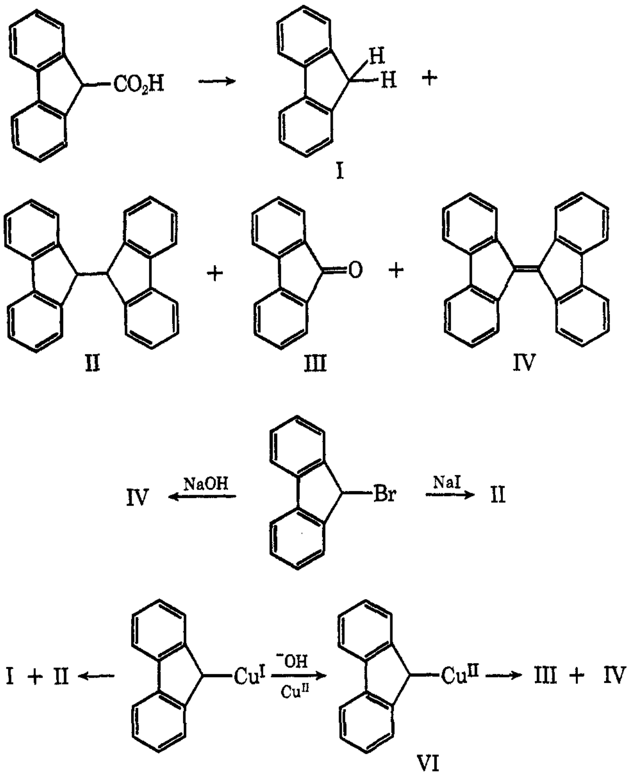


TABLE I

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

---

[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.

[4] P. Friedlander, *Chem. Ber.*, **10**, 536 (1877).

[5] G. Werber and F. Maggio, *Ann. Chim (Rome)*, **50**, 1438 (1960).

[6] A. Cairncross and W. M. Sheppard, *J. Amer. Chem. Soc.*, **92**, 3187 (1970).

[7] T. Cohen and R. A. Schambach, *ibid.*, **92**, 3189 (1970).

[8] M. Nilsson, *Acta Chem. Scand.*, **20**, 423 (1966); C. Bjorklund and M. Nilsson, *ibid.*, **22**, 2585 (1968).

[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)].