ketone IIb and this observation was used as part of the argument against any unusual stability in I. We have studied this reduction and, in contrast to the earlier report, found that IIa[9] was present in the reaction product. The ratio of barbaralane, IIIa, to IIa was dependent on the $LiAlH_4:AlCl_3$ ratio, indicating that rearrangement to the barbaralyl system is probably acid catalyzed. The results are shown in Table II.

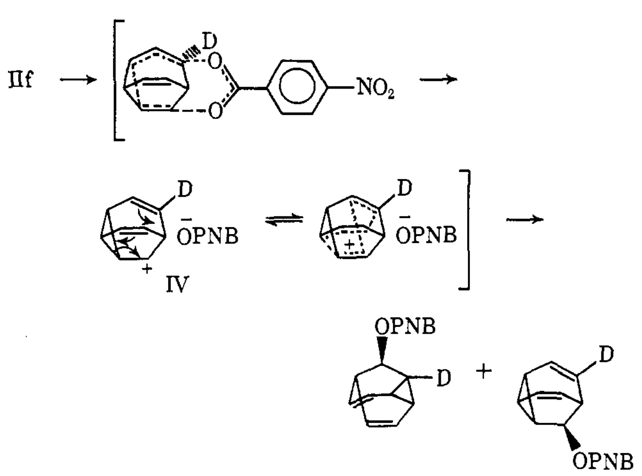
Table II. Reduction of IIb with $LiAlH_4$–$AlCl_3$[a]

	Isolated yields, %			
	Alcohols		Hydrocarbons	
$AlCl_3/LAlH_4$	IIc	IIIb	IIa	IIIa
1.2	30	30	1.5	21.5
0.28	0.5	62	5	6

[a] Reduction was carried to completion (2 hr) at −78° in diethyl ether with a $LiAlH_4$ to ketone ratio of 1.0:0.008 in both cases.

In an attempt to elucidate the mechanism of the solvolytic rearrangement, the solvolysis was repeated with the deuterio-*p*-nitrobenzoate, IIf.[11] Nmr analysis showed that in both the barbaralyl products, IIIb and IIIc, deuterium had been scrambled selectively, within experimental error (±5%), into the 1 and 5 (33% D) and 2, 4, 6, and 8 positions (67% D).[12] No deuterium was found in the 3, 7, or 9 position. This is in accord with the results obtained by Schleyer[6] for the solvolysis of the parent barbaralyl system. In these compounds, the multiplets assigned to H-3 and H-7[13] each consisted of a superimposed doublet (vicinal coupling to one H and one D) and triplet (vicinal coupling to two H's). Careful integration of the relative intensities within these multiplets revealed that the deuterium substitution at positions 2, 4, 6, and 8 in the *p*-nitrobenzoate was asymmetric. Deuterium was found preferentially at the positions *syn* to the *p*-nitrobenzoate group in the ratio 2:1. Within experimental error, the monodeuterio alcohol showed deuterium present equally at positions 2, 4, 6, and 8. These results indicate that in the initially formed barbaralyl cation, the ion pair at least is asymmetric, but that solvent capture is a symmetric process.

Any proposal concerning the mechanism of this rearrangement must be speculative at this time. Schleyer[4,6] has discussed the reasonable alternatives. The mechanism we favor at present for the asymmetric component of the ion pair capture process is[15]



We have chosen this mechanism by consideration of the symmetry properties of cyclopropane ring openings and closures.[16,17] Note that geometric limitations require that all such openings and closures must be disrotatory. The possibilities are: (a) ring opening with involvement of the cationic center (*e.g.*, breaking the 1,2 bond to form I), an allowed two-electron process,[16] but energetically unfavorable; (b) ring opening and closure with involvement of the cationic center and one double bond (*e.g.*, breaking the 1,2 bond and forming the 4,9 bond), a symmetry forbidden four-electron process;[16] (c) ring opening and closure with involvement of the cationic center and both double bonds (*e.g.*, the above mechanism). This is a six-electron process and will be allowed if it involves an even number of negative overlap integrals.[17] This requirement is met in the scheme outlined above, since the transition state involves two negative overlap integrals. This explanation must await further experimental facts for its justification.

---

[9] The structure was confirmed by the nmr spectrum and vpc retention time, which were identical with those of an authentic sample.[10]

[10] J. B. Grutzner and S. Winstein, *J. Amer. Chem. Soc.*, **90**, 6562 (1968).

[11] Obtained from the deuterated alcohol, IId, prepared previously.[10]

[12] Note that positions 1 and 5, 2 and 4, and 6 and 8 cannot be differentiated because of the rapid degenerate Cope rearrangement.[6]

[13] The spectrum is similar to that reported by Doering.[14] The assignment of the more downfield multiplet to H-3 rather than H-7 was based on the chemical shift and line width. The anisotropic deshielding of the *p*-nitrobenzoate group should shift the *syn* proton H-3 downfield of H-7. Further, in all spectra of the alcohols and *p*-nitrobenzoates, both deuterated and undeuterated, the downfield multiplet was slightly, but reproducibly, broader. This is presumably due to a small (<0.3 Hz) coupling with the *anti* hydrogen H-9 *via* a back lobe overlap mechanism. Unpublished observations by Dr. D. Harris of this department on related compounds have confirmed this assignment.

[14] W. von E. Doering, B. M. Ferrier, E. D. Fossel, J. H. Hartenstein, M. Jones, G. Klumpp, R. M. Rubin, and M. Saunders, *Tetrahedron*, **23**, 3943 (1967).

[15] Note that the deuterium scrambling results show that ∼40% of the ion-pair capture process is asymmetric and that the remainder is proceeding *via* symmetrical intermediates (which may include I).

[16] H. E. Zimmerman, *J. Amer. Chem. Soc.*, **88**, 1564, 1566 (1966).

[17] J. J. C. Mulder and L. J. Oosterhoff, *Chem. Commun.*, 305 (1970).

[18] To whom correspondence should be addressed, at the Department of Chemistry, Purdue University, Lafayette, Ind. 47907.

[19] Deceased Nov 23, 1969.

[20] We wish to thank Drs. P. Ahlberg, J. Dirlam, and D. Harris of this department for helpful discussions.

John B. Grutzner,[18] S. Winstein[19,20]
Contribution No. 2590, Department of Chemistry
University of California, Los Angeles, California 90024

Received February 9, 1970

Organocopper Intermediates *via* Decarboxylation of Cuprous Carboxylates

Sir:

Earlier we[1] and several other groups reported that arylcoppers couple with aryl halides to give unsymmetrical biaryls,[2] pyrolyze[3] or oxidize[4] to symmetrical

---

[1] A. Cairncross and W. A. Sheppard, *J. Amer. Chem. Soc.*, **90**, 2186 (1968).

[2] (a) M. Nilsson, *Tetrahedron Lett.*, 679 (1966); (b) M. Nilsson and O. Wennerström, *ibid.*, 3307 (1968); (c) G. M. Whitesides, W. F. Fischer, Jr., J. SanFilippo, Jr., R. W. Bashe, and H. O. House, *J. Amer. Chem. Soc.*, **91**, 4871 (1969); (d) R. J. DePasquale and C. Tamborski, *J. Org. Chem.*, **34**, 1736 (1969).

[3] (a) H. Gilman and J. M. Straley, *Recl. Trav. Chim. Pays-Bas*, **55**, 821 (1936); (b) H. Hashimoto and T. Nakano, *J. Org. Chem.*, **31**, 891

biaryls, and hydrolyze to arenes.[5] The intermediates in the Ullmann reaction[6] and in cuprous oxide–quinoline decarboxylations[7] react similarly. For example, Nilsson found that *o*-nitrobenzoic acid–cuprous oxide–quinoline–iodobenzene gives a low yield (10%) of 2-nitrobiphenyl presumably *via* formation of cuprous *o*-nitrobenzoate, then decarboxylation to *o*-nitrophenylcopper.[7a]

$$\begin{tikzcd}
\mathrm{ArMgX} + \mathrm{CuX} \arrow[drr] & & & \mathrm{Ar{-}Ar'} \\
\mathrm{ArX} + \mathrm{Cu} \arrow[rr, "?"] & & \mathrm{ArCu} \arrow[ur, "\mathrm{Ar'X}"] \arrow[r, "\Delta", "\mathrm{or}\ O_2"'] \arrow[dr, "H^+"] & \mathrm{Ar{-}Ar} \\
\mathrm{ArCO_2H} + \mathrm{Cu_2O} \arrow[r, "?"] & \mathrm{ArCO_2Cu} \arrow[ur, "?"] & & \mathrm{ArH}
\end{tikzcd} \qquad (1)$$

In this communication we describe a general synthesis of cuprous carboxylates, their decarboxylation, and isolation for the first time of the organocopper intermediate.

Cuprous salts of carboxylic acids are quickly formed at 0–25° when the acid is mixed in a nitrogen atmosphere with *m*-(trifluoromethyl)phenylcopper octamer[1,8] solutions. By this method the cuprous salts of $C_6H_5CO_2H$ (99%), *o*-$O_2NC_6H_4CO_2H$ (96%), 2-Cl-6-$O_2NC_6H_3CO_2H$ (99%), 3,5-$(O_2N)_2C_6H_3CO_2H$, $C_6F_5CO_2H$ (94%), *p*-$C_6H_4(CO_2H)_2$ (99%), CH_3CO_2H (99%), CF_3CO_2H (81%), $CClF_2CO_2H$, and $HO_2CCH_2CH{=}CHCH_2CO_2H$ were prepared. Since this reaction is nearly quantitative, the cuprous salts may be conveniently generated *in situ* in decarboxylation solvents such as tetraglyme, tri-*n*-butylamine, or quinoline.

$$8RCO_2H + [m\text{-}(CF_3)C_6H_4Cu]_8 \longrightarrow 8RCO_2Cu + 8C_6H_5CF_3 \qquad (2)$$

Alternatively CH_3CO_2Cu[9] and CF_3CO_2Cu are easily prepared from the acid, Cu_2O, and a little anhydride and CH_3CO_2Cu equilibrates with $C_6F_5CO_2H$, *o*-$O_2NC_6H_4CO_2H$, $CClF_2CO_2H$, and CF_3CO_2H in dioxane forming RCO_2Cu (eq 3).

$$CH_3CO_2H + Cu_2O \rightleftharpoons CH_3CO_2Cu \xrightleftharpoons[CH_3CO_2H]{RCO_2H} RCO_2Cu \qquad (3)$$

Cuprous salts of aryl and indole carboxylic acids thermally decarboxylate. Basic solvents facilitate decarboxylation. For *o*-$O_2NC_6H_4CO_2Cu$ and $C_6F_5CO_2Cu$ the rate increases from dry salt < tetraglyme < nitrobenzene ≪ tri-*n*-butylamine ≪ quinoline. The half-life for $C_6F_5CO_2Cu$ decarboxylation at 107.7° is 62 min in tri-*n*-butylamine and *ca.* 980 min in tetraglyme (4.42 mol of $C_6F_5CO_2Cu$, 16 ml of solvent). Electron-withdrawing nitro, chloro, and fluoro substitutents also facilitate decarboxylation. These are particularly effective in the *ortho* position as in the Ullmann reaction.[6a] Thus cuprous *p*-nitrobenzoate needs *ca.* 50° higher temperature than cuprous *o*-nitrobenzoate for comparable reactivity.

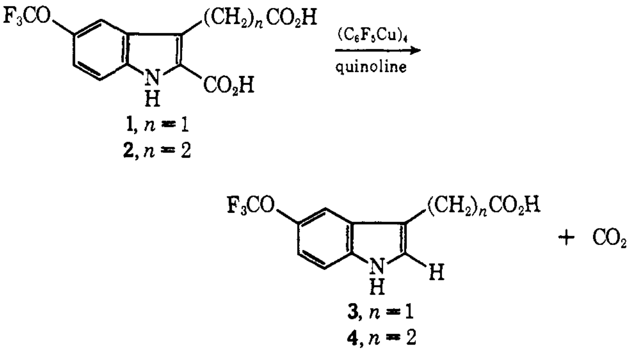
A 50% solution of cuprous pentafluorobenzoate in quinoline decarboxylates at the remarkably low temperature of 60° to give 93% of the theoretical amount of gas (CO_2) and a 72% yield of a brown solid, mp 161–164°, that is identical with an authentic sample of pentafluorophenylcopper–quinoline complex prepared by mixing pentafluorophenylcopper and quinoline and triturating with hexane. To our knowledge, this is the first preparation of an organocopper compound by decarboxylation of a cuprous carboxylate.[10,11]

$$C_6F_5CO_2Cu \xrightarrow[\text{quinoline}]{60^\circ} C_6F_5Cu\text{–quinoline} + CO_2 \qquad (4)$$

Quinoline is the best solvent. After decarboxylation was complete in tri-*n*-butylamine at 107.7°, C_6F_5Cu was not isolated but was trapped by 1-iodo-2-nitrobenzene to give 2,3,4,5,6-pentafluoro-2′-nitrobiphenyl in 27% yield. In tetraglyme at 107.7°, no C_6F_5Cu survived and only decafluorobiphenyl (60%) was isolated.

In confirmation of Nilsson's report,[7a] a solution of equimolar amounts of cuprous *o*-nitrobenzoate and iodobenzene in quinoline decarboxylated readily at 145–165° to give a 50% yield of 2-nitrobiphenyl (39% yield isolated). Most likely *o*-nitrophenylcopper is generated in this reaction. When the same experiment was repeated except that the iodobenzene was added after gas evolution had ceased, no 2-nitrobiphenyl was isolated and thus no *o*-nitrophenylcopper intermediate survived. When iodobenzene is omitted altogether, a 27% yield of 2,2′-dinitrobiphenyl and a 37% yield of nitrobenzene were isolated.

Organocopper compounds are particularly valuable catalysts for the selective decarboxylation of indoledicarboxylic acids. 5-(Trifluoromethoxy)-2-carboxy-3-indolepropionic acid,[12] **2**, gave noncrystallizable products when decarboxylated neat at 250–265° or in quinoline catalyzed by copper powder, copper bronze, or $CuCrO_2$ at 200–230°. However, **1** and **2** were smoothly and selectively decarboxylated in quinoline when 0.1–0.44 equiv of pentafluorophenylcopper tetramer[1,8]



1, $n = 1$
2, $n = 2$

3, $n = 1$
4, $n = 2$

(1966); (c) W. Tochtermann, *Angew. Chem., Int. Ed. Engl.*, **5**, 351 (1966).

[4] (a) R. Reich, *Compt. Rend.*, **177**, 322 (1923); (b) G. M. Whitesides, J. SanFilippo, Jr., C. P. Casey, and E. J. Panek, *J. Amer. Chem. Soc.*, **89**, 5302 (1967).

[5] G. Costa, A. Camus, L. Gatti, and N. Marsich, *J. Organometal. Chem.*, **5**, 568 (1966).

[6] (a) P. E. Fanta, *Chem. Rev.*, **64**, 613 (1964); (b) R. G. R. Bacon and H. A. O. Hill, *Quart. Rev., Chem. Soc.*, 95 (1965); (c) A. H. Lewin and T. Cohen, *Tetrahedron Lett.*, 4531 (1965).

[7] (a) M. Nilsson, *Acta Chem. Scand.*, **20**, 423 (1966); (b) C. Björklund and M. Nilsson, *ibid.*, **22**, 2585 (1968).

[8] A. Cairncross and W. A. Sheppard, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, Abstract ORG 118, and the 4th International Conference on Organometallic Chemistry, Bristol, England, July 1969, Abstract E1.

[9] (a) T. Cohen and A. H. Lewin, *J. Amer. Chem. Soc.*, 88, 4521 (1966); (b) M. Calvin, *ibid.*, **61**, 2230 (1939).

[10] P. Sartori and M. Weidenbruch [*Chem. Ber.*, **100**, 3016 (1967)] prepared and decarboxylated cupric pentafluorobenzoate obtaining 8% decafluorobiphenyl and no pentafluorophenylcopper.

[11] Other metal pentafluorobenzoates have been decarboxylated to the pentafluorophenyl organometallics: (a) Zn, Sartori and Weidenbruch;[10] (b) Cd, M. Schmeisser and M. Weidenbruch, *ibid.*, **100**, 2306 (1967); (c) Hg, J. E. Connett, A. G. Davies, G. B. Deacon, and J. H. S. Green, *Chem. Ind. (London)*, 512 (1965).

[12] These were prepared from *p*-(trifluoromethoxy)aniline by the Japp–Klingman reaction followed by Fischer indole synthesis.

was added. A solution of 43 mmol of **2**, 4.3 equiv of $(C_6F_5Cu)_4$, and 50 ml of quinoline was heated for 2 hr at 213–215° giving a 98% yield of gas and 71.5% yield (81.7% crude) of pure 5-(trifluoromethoxy)-3-indolepropionic acid, **4**: mp 87–87.6°; $\lambda_{\max}^{\mathrm{EtOH}}$ 226, 247, and 286 nm (ϵ 57,000; 9500; 10,700). Similarly **1** decarboxylated easily at 185–205° to give 98% yield of gas and 63.7% yield of pure 5-(trifluoromethoxy)-3-indoleacetic acid, **3**, mp 117–118.5°.

In conclusion, organocopper compounds easily react with carboxylic acids to form cuprous carboxylates. In turn some cuprous carboxylates decarboxylate to give useful organocopper intermediates. *o*-Nitrophenylcopper has not been generated any other way. These two reactions together are the basis of an organocopper-catalyzed decarboxylation.

Allan Cairncross, John R. Roland
Rosetta M. Henderson, William A. Sheppard
Contribution No. 1662, Central Research Department
Experimental Station, E. I. du Pont de Nemours and Company
Wilmington, Delaware 19898

Received December 31, 1969

The Copper–Quinoline Decarboxylation[1]

Sir:

To our knowledge, a mechanism for the loss of carbon dioxide in the widely used copper–quinoline decarboxylation[2] has never been suggested. The reaction is usually performed by heating an aromatic carboxylic acid in quinoline solution with copper powder, although copper salts are sometimes used. We have found that the copper metal procedure is much slower than that involving the cupric[3] or cuprous (acid plus cuprous oxide) salt of the carboxylic acid (180–200°) and that the yields are excellent provided that a nitrogen atmosphere is maintained. Cuprous salts have recently been utilized in studies by Nilsson, who has provided evidence that organocopper compounds are intermediates in the reaction.[4] Our own results confirm this conclusion and, in addition, provide a variety of new observations and a basis for suggesting a mechanism for the loss of carbon dioxide. Pertinent results are as follows. (1) The loss of carbon dioxide is first order in cuprous or cupric carboxylate. (2) Cupric and cuprous salts decarboxylate at nearly the same rate. (3) Either type of salt behaves as a catalyst for the decomposition of excess carboxylic acid and the reactions are pseudo-first-order in the metal ions. (4) Certain chelating agents such as 1,10-phenanthroline and 2,2′-bipyridyl considerably increase the rate of decarboxylation of both types of salt. The latter reagent, which is less effective but far less expensive, increases the rate by a factor of 17 when used in a tenmolar excess. (5) Whereas neither cuprous nor cupric benzoate decarboxylates at a noticeable rate in a solvent such as 1-methylnaphthalene at 200°, and aromatic cupric carboxylates undergo an entirely different type of reaction at higher temperatures in noncomplexing solvents,[5] cupric benzoate does undergo smooth decarboxylation in 1-methylnaphthalene provided that some 2,2′-bipyridyl is present. (6) All substituents on cupric benzoate increase the rate. The salts of the isomeric 2,3-diphenylpropenoic acids and of α-naphthoic acid decarboxylate very much faster than those of benzoic acid, the latter by a factor of 87 at 200°. (7) The cupric salts of the saturated acids adamantane-1-carboxylic acid and dodecanoic acid do not decarboxylate under the same reaction conditions. (8) Decarboxylation products, arenes and substituted arenes, can be obtained in high yield in most cases. However, in the case of the cupric salt of *o*-methoxybenzoic acid, a 5% yield of 2,2′-dimethoxybiphenyl was also isolated and in the case of the cuprous salt of *o*-nitrobenzoic acid (prepared under anhydrous conditions from the anhydride and cuprous oxide) 2,2′-dinitrobiphenyl was obtained in 78% yield. (9) Decarboxylation of the cupric salts of pure *cis*- and *trans*-2,3-diphenylpropenoic acids proceeds with 94 and 99% retention of configuration, respectively. These figures are unchanged when the reaction is performed in the presence of a large excess of 2,2′-bipyridyl and the degree of retention is only slightly different for the corresponding cuprous salts. (10) In the absence of copper salts, the rates of decarboxylation of the acids were either negligible or far slower.

The result that cuprous and cupric salts behave in identical fashion, with regard to both rates and stereochemistry, is rendered understandable by the finding that the esr signal of cupric benzoate disappears in a few minutes under the reaction conditions. It is evident that the quinoline is capable of reducing cupric ion to cuprous ion at a very rapid rate.[6] The destruction of cupric ion before the loss of carbon dioxide, the rate dependence on the concentration of cuprous ion, and the large rate changes caused by the presence of complexing agents for cuprous ion clearly implicate the latter as the active catalyst in this decarboxylation.

The stereochemical results probably rule out mechanisms involving homolytic C–C bond cleavage[7] and allow one involving electrophilic attack of cuprous ion at the carbon atom bearing the carboxyl group only if the subsequent loss of carbon dioxide is much faster than rotation about the resulting C–C single bond. The necessity for unsaturation in the substrate acid, the rate increase with increased polarizability, and the π-complexing ability of cuprous ion[8] suggest the following mechanism in which a π-bonded cuprous ion inductively stabilizes the negative charge which develops as the carbon dioxide is lost.

The replacement of the carboxylate ligand by the "softer" and more electron-accepting (by backbonding)

---

[1] This investigation was supported by Grant No. GP 7262 from the National Science Foundation; taken from the Ph.D. Thesis of Robert A. Schambach, University of Pittsburgh, Pittsburgh, Pa., 1969.

[2] A. F. Shepard, N. R. Winslow, and J. R. Johnson, *J. Amer. Chem. Soc.*, 52, 2083 (1930); P. H. Leake, *Chem. Rev.*, **56**, 27 (1956), and references cited therein; L. F. Fieser and M. Fieser, "Organic Chemistry," 3rd ed, D. C. Heath and Co., Boston, Mass., 1956, p 549.

[3] We thank Mr. Mordecai Treblow and Mr. Edward Slusser for carrying out the rate comparison between the use of the metal and the cupric salt.

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

[5] W. W. Kaeding, H. O. Kerlinger, and G. R. Collins, *J. Org. Chem.*, **30**, 3754 (1965), and references cited therein.

[6] The quinoline appears to be converted mainly to 2-oxygenated quinolines: unpublished observations of F. J. Rattay.

[7] The resulting 1,2-diphenylethenyl radicals undergo rapid stereochemical equilibration: L. A. Singer and N. P. Kong, *J. Amer. Chem. Soc.*, 88, 5213 (1966); J. A. Kampmeier and R. M. Fantazier, *ibid.*, 88, 1959 (1966).

[8] R. N. Keller, *Chem. Rev.*, 28, 229 (1941); M. A. Bennett, *ibid.*, **62**, 611 (1962); R. Jones, *ibid.*, **68**, 785 (1968).