CHEMISTRY LETTERS, pp. 1733-1734, 1985.

CARBOXYLATION OF ALCOHOLS WITH CARBON MONOXIDE SUPERSATURATED IN STRONG ACID. FACILE SYNTHESIS OF 2,2-BIS(4-HALOPHENYL)ACETIC,-PROPIONIC, AND RELATED ACIDS

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Using 97% H_2SO_4 supersaturated with carbon monoxide, bis(4-halophenyl)methanols, 1,1-bis(4-halophenyl)ethanols and related alcohols were transformed to the carboxylic acids in 60-95% yields.

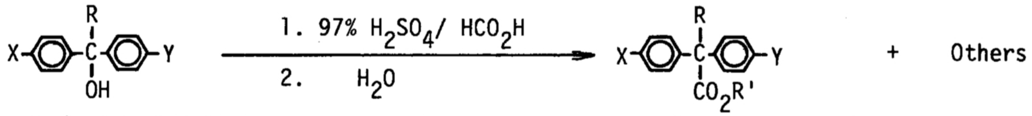
The Koch-Haaf reaction[1)] can not be used for aryl carbinols, because they undergo self-condensation and give complicated products. Particularly, diaryl and triaryl carbinols give highly stable carbenium ions that can hardly react with CO to afford the acyl cations under the ordinary Koch-Haaf reaction conditions.[2)] A synthetic method for 2,2-bis(4-halophenyl)acetic acids, and -propionic acids, and related acids from the corresponding alcohols in 97% H_2SO_4 supersaturated with CO generated in situ from formic acid is now presented.

Reaction of bis(4-halophenyl)methanols, and -ethanols under a few stirring rate conditions are summarized in Table 1. Under the Koch-Haaf conditions in the literature,[1)] bis(4-chlorophenyl)methanol(**1a**) gave mainly bis(4-chlorophenyl)methyl ether obtained by the hydrolysis of bis(4-chlorophenyl)methyl cation (Expt.No.1). The carboxylated product(**2a**) was formed in unsatisfactory yield, since the secondary cation can not sufficiently react with CO under the conditions. Under a similar reaction condition without stirring, **2a** was obtained in a high yield (Expt.No.2). The increase in the yield of **2a** may be produced by the reaction of CO supersaturated in H_2SO_4 with the secondary cation derived from **1a**.[5)] The concentration of supersaturated CO was 0.16-0.38 mol/l, achieved by addition of formic acid to 97% H_2SO_4 without stirring.[6)] Under the same condition as in Expt.No.2, however, 1,1-bis-(4-chlorophenyl)ethanol(**1b**) gave the carboxylated product(**2b**) in a low yield (Expt. No.3). Contrariwise, lengthening of reaction time led to an increase of the yield of **2b** (Expt.No.4). The lower reactivity of **1b** compared with **1a** is produced by the higher stability of the tertiary cation than that of the secondary one.

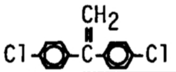
Without stirring, all the bis(4-halophenyl)methanols except bis(4-iodophenyl)-methanol gave bis(4-halophenyl)acetic acids in good yields. Diphenylmethanol, however, did not give the carboxylated product but afforded unidentified products which might arise from the alkylation of aromatic rings and subsequent sulfonation. This stems from the highly reactive property of diphenylmethyl cation in H_2SO_4 solution.[7,8)] Strangely enough, bis(4-iodophenyl)methanol could hardly react with supersaturated CO but gave bis(4-iodophenyl)methyl ether. 1,1-Diphenylethanol, giving stable 1,1-diphenylethyl cation in H_2SO_4 solution,[9)] reacted with supersaturated CO and gave 2,2-diphenylpropionic acid in a good yield. Other 1,1-bis-

(4-halophenyl)ethanols reacted with CO and gave the corresponding propionic acids in yields of 60 to 72%. There are yet no facile synthetic methods for tertiary and secondary 2,2-diarylcarboxylic acids.[10] Thus, the present method is a useful one-pot procedure for such carboxylic acids from readily available alcohols.

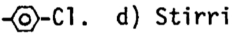
Table 1.



1 (a:R=H,X,Y=Cl;b:R=CH_3,X,Y=Cl) **2** (a:R'=H;b:R'=H)

Expt. No.	Alcohol	Stirring conds.	Time h	Products (yield/%)[a,b,c] **2** (R'=H)	**2** (R'=Ar)	ArOAr		others
1	**1a**	vigorous[d]	1.3	2[e]	22	69	-	5[f]
2	**1a**	no	1.3	92[e]	5	0	-	2[f]
3	**1b**	no	1.3	16[g]	-	-	48	26[h]
4[i]	**1b**	no	10.2	85[g]	-	-	1	11[h]

Alcohol **1**[j] R	X	Y	Stirring conds.	Temp °C	Time h	Yield of **2**[b] %	Mp θ_m/°C
H	F	F	no	15 - 16	2.1	95	141.2 - 142.0
H	F	Br	no	15 - 16	2.1	94	131.0 - 132.0
H	Br	Br	no	14 - 16	2.1	76	186.0 - 187.2
H	I	I	no	14 - 16	2.1	14	196.7 - 197.8
CH_3	H	H	no	14 - 16	10.1	60	173.7 - 174.0
CH_3	F	F	no	20 - 21	10.1	60	145.0 - 145.2
CH_3	F	Cl	no	20 - 21	10.1	72	171.0 - 171.8

a) Reaction conditions: 97% H_2SO_4, 22 ml; HCO_2H, 1 ml; alcohols, 2.5 mmol; react.temp, 15 °C. b) Isolated yields based on alcohols employed. c) Ar = . d) Stirring speed, ≈1000 rpm. e) Mp, 167 - 168 °C (lit.[3], 164 - 166 °C). f) Bis(4-chlorophenyl)methanol. g) Mp, 161 - 162 °C (lit.[4], 160 - 161 °C). h) For the most part, 4,4'-dichlorobenzophenone. i) React.temp, 20 °C. j) HCO_2H, 6 ml.

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(Received April 8, 1985)