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The Catalytic Decomposition of 9-Diazofluorene by Metal Carboxylates

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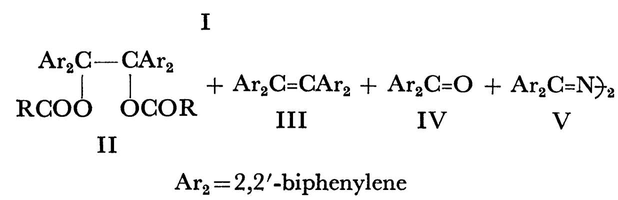
We have found that Cu(II) carboxylates in aq DMF catalyze the decomposition of 9-diazofluorene (I), thus affording fluorenone pinacol diesters (II) in addition to bifluorenylidene (III). The reaction is, therefore, analogous to that of diphenyldiazomethane recorded previously.[1] Though fluorenone pinacol diacetate may alternatively be obtained by treating fluorenone (IV) with zinc and acetyl chloride,[2] the present reaction does furnish a practical, simple method for preparing this class of esters, II.



$$(RCO_2)_2Cu(II) + \underset{I}{Ar_2CN_2} \longrightarrow \underset{II}{\begin{array}{cc} Ar_2C- & CAr_2 \\ | & | \\ RCOO & OCOR \end{array}} + \underset{III}{Ar_2C{=}CAr_2} + \underset{IV}{Ar_2C{=}O} + \underset{V}{\left.Ar_2C{=}N\right)_2}$$

$Ar_2 = 2,2'$-biphenylene

Table 1 summarizes the reactions of I with Cu(II) carboxylates in aq. DMF to give II, III, and IV. Diacetate IIa was identified by means of the spectral and analytical data, and by the thermal decomposition,[3] which afforded IV and fluorenyl acetate (VI) at 170°C. In contrast to Cu(II) carboxylates such as acetate, propionate, and *n*-butyrate, the Cu(II) isobutyrate afforded IId in an inferior yield, whereas the Cu(II) tartrate gave no pinacol diester, II, but mainly III, along with fluorenone azine (V). Such a difference between Cu(II) carboxylates and the chelate salt may be attributed to the mobility of ligands around the central Cu(II) ion toward the newly-attached fluorenylidene moiety. Chelate ligands are tightly bound to the central metal ion and should be less accessible than simple carboxylate anions.

TABLE 1. REACTIONS OF I WITH Cu(II) CARBOXYLATES IN aq DMF

Cu(II) cabroxylate	Reaction		Products (yield in %)[a]			
	temp (°C)	time (hr)	II	III	IV	V
a Acetate	40	18	55	24	15	—
b Propionate	40	19	47	17	18	—
c *n*-Butyrate	40	20	51	16	23	—
d Isobutyrate	40	17	36	36	19	—
e Tartrate	40	6	—	85	—	12

a) Recovery was not considered in calculation of yields.

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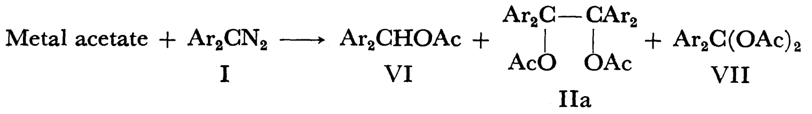
[1] T. Shirafuji, Y. Yamamoto, and H. Nozaki, *Tetrahedron*, **27**, 5353 (1971).

[2] C. Gräbe and H. Stindt, *Ann. Chem.*, **291**, 1 (1896).

[3] For a similar decomposition of benzopinacol diesters, see Ref. 4.

[4] T. Shirafuji, Y. Yamamoto, and H. Nozaki, This Bulletin, **45**, 2574 (1972).



$$\text{Metal acetate} + \underset{\text{I}}{\mathrm{Ar_2CN_2}} \longrightarrow \underset{\text{VI}}{\mathrm{Ar_2CHOAc}} + \underset{\text{IIa}}{\begin{array}{c}\mathrm{Ar_2C{-}CAr_2}\\ |\qquad |\\ \mathrm{AcO\quad OAc}\end{array}} + \underset{\text{VII}}{\mathrm{Ar_2C(OAc)_2}}$$

Ar_2 = 2,2′-biphenylene

Table 2. Oxidation of I with various metal acetates

Metal acetate	Reduction potential in water (eV)[a]	Reaction		Solvent	Products (Yield in %)[b]			
		°C	hr		VI	IIa	VII	IV
Cr(III)$(OAc)_3$	−0.41	60	23	aq DMF	9	—	—	55
Cu(II)$(OAc)_2$	+0.15	40	18	aq DMF	—	55	—	15[c]
Tl(III)$(OAc)_3$	+1.21	25	19	CH_2Cl_2	—	—	42	56
Pb(IV)$(OAc)_4$	+1.69	25	25	CH_2Cl_2	—	—	61	30

a) These data were taken from N. A. Lange, "Handbook of Chemistry" 10th ed. McGraw-Hill (1961), p. 1212.
b) Recovery was not considered in calculation of yields. c) A 24% yield of III was obtained.

Being interested in oxidation reactions brought about by metal ions,[5] we then investigated the decomposition of I by means of various other metal acetates, as is shown in Table 2. The Cr(III) acetate catalyzed the decomposition of I to afford VI in a low yield, while the Tl(III) or Pb(IV) acetate gave fluorenone diacetate (VII) as the major product.[6] This behavior is parallel to that of diphenyldiazomethane with the metal acetates.[1]

Experimental

All the melting points are uncorrected. The NMR spectra were obtained on a 60 MHz instrument (JEOL C-60-H spectrometer) in $CDCl_3$ unless otherwise stated. The chemical shifts are given in ppm from the TMS internal standard, and the abbreviations of s, d, t, q, and m are used with their common meanings.

The mass spectra were obtained on a Hitachi RMU 6L spectrometer. The microanalyses were performed by Mrs. K. Fujimoto.

General Procedure of the Catalytic Decomposition of 9-Diazofluorene (I) with Metal Salts. Under N_2, metal salts were dissolved in aq DMF (1: 1) or methylene chloride so as to give a *ca.* 0.3 M solution; this solution was then kept at an appropriate reaction temperature (25—60 °C) with stirring. To this we then added, drop by drop, a solution (*ca.* 0.5 M) of I in the same solvent. The molar ratio of diazo compound/metal salt was taken to be 1: 1 unless otherwise stated. Heating and stirring were continued until the evolution of N_2 had ceased. The mixture was then worked up as usual. The crude products were separated by glc, recrystallization, or column chromatography, and then identified. The following descriptions will be concerned with cases which are not covered sufficiently by Tables 1 and 2.

Preparation of Fluorenone Pinacol Diesters (II). The diazo compound I was treated with solutions of Cu(II) carboxylates in aq DMF. The chromatography of the reaction mixture on a short silica gel column (benzene elution) gave bifluorenylidene,[7] II, and fluorenone. The spectral

Table 3. Physical properties of II

Compd II R	Mp °C [a]	IR (cm^{-1}) [b]	NMR (δ ppm)
Me[c]	252 (decomp)	1742, 1363, 1291, 1225, 1197, 1073, 1023, 976, 950	7.70—6.67(m, 16H, aromatic), 2.13 (s, 6H, -OAc)
Et[d]	244 (decomp)	1735, 1267, 1210, 1191, 1060, 1008, 990, 931	7.51—6.55 (m, 16H, aromatic),2.45 (q, 4H, -$\underline{CH_2}$Me), 1.10 (t, 6H, -$\underline{CH_3}$)
n-Pr[e]	169 (decomp)	1740, 1248, 1202, 1157, 1070, 1010, 970, 940	7.50—6.65 (m, 16H, aromatic), 2.43 (t, 4H, -$\underline{CH_2}$Et), 1.17 (m, 4H, -$\underline{CH_2}$Me), 0.95 (t, 6H,-$\underline{CH_3}$)
iso-Pr[f]	210—211 (decomp)	1743, 1254, 1210, 1186, 1142, 1109, 1050, 963	7.45—6.65 (m, 16H, aromatic), 2.78 (m, 2H, methines), 1.21 (d, 12H, methyls)

a) Recrystallized from benzene-ethanol (1: 1).
b) KBr disk unless otherwise stated.
c) Found: C, 80.6;H, 4.9%. Calcd for $C_{30}H_{22}O_4$: C, 80.7; H, 5.0%. Mass *m/e* (relative abundance): 344 (70), 328 (40), 180 (100).
d) Found: C, 81.1; H, 5.6%. Calcd for $C_{32}H_{26}O_4$: C, 81.0; H, 5.5%. Mass *m/e* (relative abundance): 344 (7), 328 (4), 180 (4), 29 (100).
e) Found: C, 81.4; H, 5.9%. Calcd for $C_{34}H_{30}O_4$: C, 81.3; H, 6.0%. Mass *m/e* (relative abundance): 344 (60), 328 (30), 180 (21), 43 (100).
f) Found: C, 81.2; H, 5.8%. Calcd for $C_{34}H_{30}O_4$: C, 81.3; H, 6.0%. Mass *m/e* (relative abundance): 344 (26), 328 (26), 180 (21), 43 (100).

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[5] a) T. Shirafuji, Y. Yamamoto, and H. Nozaki, *Tetrahedron Lett.*, **1971**, 4713; b) C. L. Jenkins and J. K. Kochi, *J. Amer. Chem. Soc.*, **94**, 843, 856 (1972).

[6] A. Stojiljković, N. Orbović, S. Sredojević, and M. Lj. Mihailović, *Tetrahedron*. **26**, 1101 (1970).

[7] R. J. S. Jennings and A. Fowler-Williams, *J. Appl. Chem.* (London), **3**, 426 (1953).

and analytical data of II are shown in Table 3.

Reaction of I with Tl(III) Acetate. I (370 mg, 1.94 mmol) was treated with Tl(III) acetate (1530 mg, 4.0 mmol) in methylene chloride (20 ml) at room temperature for 19 hr. After filtration, the reaction mixture was concentrated *in vacuo*. The products were recrystallized from carbon tetrachloride to give fluorenone diacetate (230 mg, 42%); mp 138—140 °C. IR (Nujol): 1740, 1200, 999 cm^{-1}. NMR (CCl_4, 10%): δ 7.80—7.20 (m, 8H, aromatic) and 2.20 (s, 6H, -OAc). Mass spectrum (relative abundance): *m/e* 180 (100), 152 (36), 105 (15), 76 (20), 43 (84).

Found: C, 72.1; H, 5.0%. Calcd for $C_{17}H_{14}O_4$: C, 72.3; H, 5.0%.

The subsequent concentration of the filtrate gave fluorenone (200 mg, 56%).

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