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CATALYTIC DECOMPOSITION OF DIAZO COMPOUNDS BY METAL SALTS

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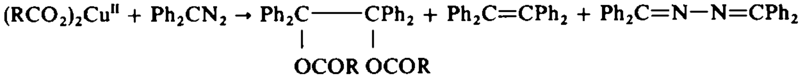
Abstract—Cu^{II} carboxylates dissolved in aq DMF catalyse thermal decomposition of diphenyldiazomethane **1** to afford benzopinacol dicarboxylates **2** in favourable yields. Chelate salts of Cu^{II} carboxylates such as salicylate, glycinate or tartrate accelerate thermolysis of **1** affording not **2** but tetraphenylethylene and beneophenone azine. These products are explained by assuming a copper carbenoid. The decomposition of **1** is catalysed also by various metal acetates (Cr^{III}, Ag^{I}, Hg^{II}, Tl^{III}) affording benzhydryl acetate, benzopinacol diacetate, or benzophenone diacetate, respectively, where the choice of products depends on the reduction potential of each metal ion. Decomposition of phenyldiazomethane or ethyl diazoacetate by metal salts is also described.

MODIFIED carbenes are produced upon decomposition of diazo compounds catalysed by copper or its salts.[1] Thermolysis of diphenyldiazomethane **1** in the presence of bis(acetylacetonato)copper^{II} in benzene gave tetraphenylethylene **3** and benzophenone azine **4**.[2] In continuation of the studies on such copper carbenoids in a homogenous system, we have found that Cu^{II} carboxylates in DMF (or benzene) catalyse the decomposition of **1** to afford benzopinacol dicarboxylates **2** in addition to **3** and **4**. The formation of these products is a novel kind of copper carbenoid reaction and such behaviour of copper salts is in remarkable contrast with that of bis(acetylacetonato)copper^{II}.



$$(RCO_2)_2Cu^{II} + Ph_2CN_2 \rightarrow \underset{OCOR}{Ph_2C}\text{——}\underset{OCOR}{CPh_2} + Ph_2C{=}CPh_2 + Ph_2C{=}N{-}N{=}CPh_2$$

1 **2** **3** **4**

TABLE 1. REACTIONS OF 1 WITH Cu^{II} CARBOXYLATES IN AQUEOUS DMF[a]

Cu^{II} carboxylate	Reaction temp°	hr	Products (Yield in %)[b,c] 2	3	4
a Acetate	25	17	70	nil	nil
b Propionate	25	4	61	nil	nil
c n-Butyrate	30	4	54	nil	nil
d Isobutyrate[d]	40	3	48	nil	nil
e Benzoate	40	7	14	nil	63
f Tartrate	25	5	nil	58	4
g Glycinate	40	10	nil	5	48
h Salicylate	40	10	nil	7	45

[a] The ratio of 1 and Cu^{II} carboxylates was taken so as the molar ratio to be 1:2.

[b] Recovery was not considered in calculation of yields.

[c] Benzophenone was obtained as a minor product (15–30% yields) in each case.

[d] Cu^{II}isobutyrate was prepared by the method similar to the recorded one. Other carboxylates were prepared by the recorded methods. See Ref 3.

Table 1 summarizes the reactions of **1** with Cu^{II} carboxylates in aq DMF to give **2**, **3** and **4**. Diacetate **2**$_a$ was identified by spectral and analytical data, by the highest mass number peak observed at *m/e* 332 which corresponds to tetraphenylethylene and finally by transformation to benzopinacol upon LAH reduction. Cu^{II} carboxylates such as acetate, propionate, n-butyrate and isobutyrate gave **2**$_a$–**2**$_d$ (R = Me, Et, n-Pr and iso-Pr) in favourable yields, although Cu^{II} benzoate afforded **2**$_e$ in a low yield.*[1] The reaction constitutes a unique approach to this novel class of esters, benzopinacol dicarboxylates.†[2] In contrast, Cu^{II} chelate salts such as salicylate, tartrate or glycinate gave no pinacol diesters **2** but a mixture of **3** and **4** only. Especially Cu^{II} tartrate gave **3** in a good yield.‡[3] Such difference between simple Cu^{II} carboxylates and chelate salts would be attributed to mobility of ligands around the central Cu^{II} ion toward the newly attached diphenylcarbene moiety.[5] Chelate ligands are tightly bound to the central metal ion and should be less mobile than simple carboxylate anions.

The origin of **2** is ascribed to a formal one electron oxidation of diphenylcarbene-acetate ion adduct by Cu^{II} ion. The resulting $Ph_2C(OAc)\cdot$ radicals dimerize to **2**, or alternatively are further oxidized to diphenylacetoxycarbonium ions, whose reaction with **1** may constitute another possible route to **2**.[6] Being interesting in such oxidation reaction by metal ions, we then investigated the decomposition of **1** by means of various metal acetates. The results were shown in Table 2. Cr^{III} acetate catalysed the decomposition of **1** to afford benzhydryl acetate **5**, which was in the same oxidation state as diphenylcarbene. Ag^{I} acetate gave **2**$_a$ in the same way as Cu^{II} acetate described above. Hg^{II} acetate gave **2**$_a$ as a major product in ether and, remarkably, benzophenone diacetate **6** as a major product in DMF.[7] The formation of **6** is ascribed to a formal two electron oxidation of diphenylcarbene–acetate ion adduct.§[4] Tl^{III} acetate afforded **6** as a major product. Accordingly, the reduction potential of each metal ion is the principal factor determining the product distribution in the decomposition of **1** catalysed by various metal acetates homogeneously dissolved *in DMF*.

The decomposition of **1** was then examined in the presence of Cu^{II} acetate suspended in benzene or ethanol (0·005 M) instead of a homogeneous solution in DMF or aq DMF. The major product in these systems was again the acetate **2**$_a$ and no other products were obtained. Attempted trapping of diphenylcarbene was carried out in the presence of cyclohexanone morpholine enamine dissolved in benzene with no success in isolating cyclopropane derivative previously recorded.[1,2] Possible explanations on these observations are given in Scheme 1, where postulated carbene complexes **7**$_1$–**7**$_3$ or inverse ylides experience intramolecular acetate transfer affording intermediates **8**$_1$–**8**$_3$.¶[5] These are then converted to the observed products **2**, **5** or **6** according to the various modes of carbon-metal bond fission,[6] which would be determined by the reduction potential of each metal ion. The formation of benzo-

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* Cu^{II} pivalate was attempted to prepare, but this salt was too unstable to be handled.

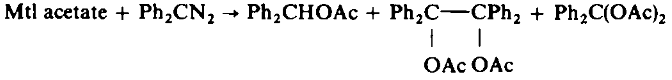
† For the esterification of tertiary alcohol such as t-BuOH, acetone pinacol and acetophenone pinacol, see Ref 4.

‡ This chiral complex may be useful as a homogeneous catalyst for the partial asymmetric synthesis of cyclopropane hydrocarbons (Ref 2). Research is progressing along this line.

§ The reaction of **1** with Pb^{IV} acetate gave **6**. See Ref 8.

¶ A modified carbene complex was assumed in the decomposition of diazoacetophenone with Cu^{II} acetate in ethanol. See Ref 9.

phenone as a by-product is ascribed to the intermediacy of diphenylacetoxycarbonium ion discussed above and/or to direct oxidation of diphenylcarbene with DMSO or contaminated oxygen.



$$\text{Mtl acetate} + Ph_2CN_2 \rightarrow Ph_2CHOAc + \underset{OAc}{Ph_2C}—\underset{OAc}{CPh_2} + Ph_2C(OAc)_2$$

1 **5** $\mathbf{2}_a$ **6**

TABLE 2. OXIDATION OF 1 WITH VARIOUS METAL ACETATES[a]

Metal Acetate	Reduction[b] Potential in water(eV)	Reaction temp°	hr	Solvent	Products (Yield in %)[c]			
					5	$\mathbf{2}_a$	**6**	BzPh
$Cr^{III}(OAc)_3$	−0·41	70	16	DMF	35	nil	nil	30[d]
		50	16	aq DMF	40	nil	nil	27
$Cu^{II}(OAc)_2$	+0·15	25	17	DMF	nil	52	nil	40
		25	14	EtOH	nil	47	nil	40
		80	4	PhH	nil	52	nil	32
Ag^IOAc	+0·799	25	2	DMF	nil	17	nil	20[d]
$Hg^{II}(OAc)_2$	+0·91	25	5	DMF	nil	5	27	50
		25	10	ether	nil	50	3	30
$Tl^{III}(OAc)_3$	+1·21	25	20	DMF	nil	nil	21	50
		25	14	ether	nil	nil	53	trace

[a] The ratio of **1** and metal acetates was taken so as the molar ration to be 1:2.
[b] These data were taken from N. A. Lange, "Handbook of Chemistry" 10th ed. P1212 McGraw-Hill (1961).
[c] Recovery was not considered in calculation of yields.
[d] Benzophenone azine was also obtained (20–25% yields).

Similar decomposition was examined with other diazo compounds such as phenyldiazomethane (1′) or ethyl diazoacetate (1″) in aq DMF. Reaction of **1′** with Cu^{II} or Cr^{III} acetate at room temperature gave a trace amount of benzyl acetate **5′** (3 or 7% yield). Remarkably, the reaction of **1′** with Cu^{II} acetate gave a fair yield (53%) of *trans*-stilbene (3′) in sharp contrast to other systems involving **1′**.[10] Reaction of **1″** with Cu^{II} acetate (aq DMF) at room temperature or with Cr^{III} acetate (aq DMF) at 60–70° afforded ethyl acetoxyacetate (**5″**) in 80 and 60% yield, respectively, as a sole isolable product. These reactions of **1′** or **1″** with Cu^{II} or Cr^{III} acetate gave no product corresponding to $\mathbf{2}_a$ obtained in the reaction of diphenyldiazomethane (**1**). Such difference would be attributed to more effective radical stabilization on doubly phenyl-substituted carbon of the intermediates **8**.

Treatment of these diazo compounds **1** and **1′** with Cu^I cyanide was found to afford diphenylacetonitrile $\mathbf{5}_i$ (49%) and phenylacetonitrile $\mathbf{5}'_i$ (11%), respectively, in aq DMF at room temperature.*[6] The reaction of **1″** gave a complex mixture, which was

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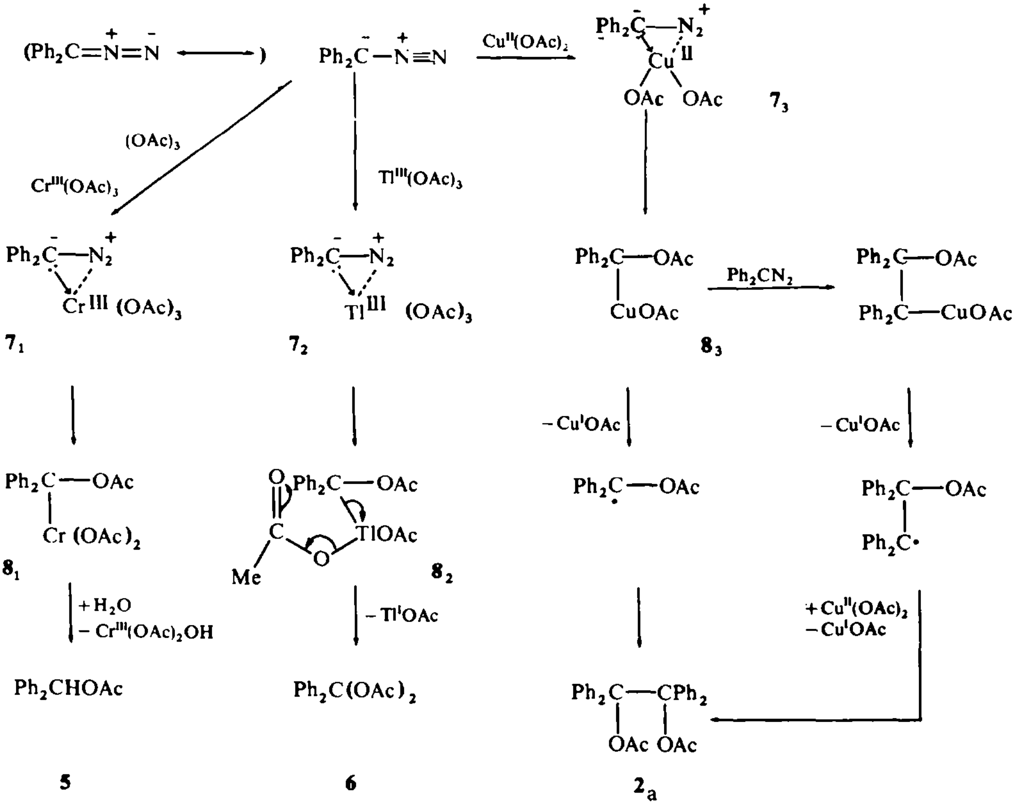
* Benzophenone or benzaldehyde (34 or 33%) was also obtained as well as azine **4** or benzaldehyde azine (trace or 26%).

SCHEME 1



not further investigated. In addition, treatment of **1** with Cu^I cyanide in DMSO gave benzophenone only, whose formation would be ascribed to direct oxidation of diphenylcarbene by DMSO.

EXPERIMENTAL

All m.ps were uncorrected. NMR spectra were obtained on a 60 MHz instrument (JEOL C-60-H spectrometer) and chemical shifts were given in ppm from TMS internal standard. The mass spectra were obtained on Hitachi RMU 6D spectrometer. Microanalyses were performed by Mrs. K. Fujimoto at Prof. Sisido's Laboratory.

General procedure of catalytic decomposition of diazo compounds with metal salts. Under N_2 metal salts were dissolved in aqueous DMF (1 : 1), DMF, DMSO, benzene, ether or ethanol so as to give *ca* 0·3 M soln (or suspension; 0·005 M in benzene) by heating with stirring at 60–70° for 30 min and then the soln was maintained at appropriate reaction temp (20–80°). To this was added dropwise a soln (*ca* 0·5 M) of diazo compounds in the same solvent. The atomic ratio of diazo compound/metal salt was taken to be 1 : 2 unless otherwise stated. Heating and stirring were continued until evolution of N_2 had ceased. The mixture was treated with water and extracted with ether or benzene. The extract was washed with water, dried (Na_2SO_4) and concentrated *in vacuo*. The crude products were separated by GLC, recrystallization or distillation and identified as usual. The following description is concerned with cases which cannot be covered sufficiently by Tables 1 and 2.

Preparation of benzopinacol dicarboxylates (**2**). Diphenyldiazomethane **1**[11] was treated with solns of Cu^{II} carboxylates in aqueous DMF (or benzene). The reaction products were washed with ether. Recrystallization of the resulting crystalline products from benzene–ethanol (1 : 1) or ether gave benzopinacol dicarboxylates 2. The spectral and analytical data were shown in Table 3. In addition, concentration of the filtrate gave benzophenone.

TABLE 3. PHYSICAL PROPERTIES OF BENZOPINACOL DICARBOXYLATES

Compd 2 R	m.p.° (solvent)	IR (cm^{-1})[a]	NMR (δ ppm)[b]
Me[c]	135–140 (dec.) (PhH-EtOH 1 : 1)	1750, 1235, 1222 1202, 1014, 999, 988, 970	7·30–6·93 (*m*, 20 H, aromatic), 2·14 (*s*, 6H, —OAc)
Et[d]	135–140 (dec.) (PhH-ErOH 1 : 1)	1750, 1167, 1150, 1073, 1013, 942, 914,	7·30–6·90 (*m*, 20 H, aromatic), 2·44 (*q*, 4H, —CH_2CH_3), 1·13 (*t*, 6H, —CH_3)
n-Pr[e]	132–135 (dec.)	1750, 1168, 1147, 964,	7·41–7·02 (*m*, 20 H, aromatic), 2·43 0·95 (*t*, 6H, —CH_3)
iso-Pr[f]	145–150 (dec.) (ether)	1745, 1180, 1132, 1108, 1092, 1050, 1039, 992, 958	7·20–6·90 (*m*, 20 H, aromatic), 2·60 (*m*, 2H, —CH<), 1·15 (*d*, 12H, —CH_3)
Ph[g]	149–155 (dec.) (PhH-EtOH 1 : 1)	1728, 1283, 1265, 1250. 1102. 1087. 1067, 1019,	8·17–7·98 (*m*), 7·54–7·12 (*m*)

[a] Neat unless otherwise stated.

[b] Determined in $CDCl_3$ at 24°, 60 MHz unless otherwise stated. NMR signals in singlet are designed as *s*, doublet as *d*, triplet as *t*, quartet as *q* and multiplet as *m*.

[c] Found: C, 80·0; H, 5·7. $C_{30}H_{26}O_4$ requires: C, 80·0; H, 5·8%. MS *m/e* (relative abundance): 332 (16), 182 (44), 105 (100), 77 (67).

[d] Found: C, 80·1; H, 6·1. $C_{32}H_{30}O_4$ requires: C, 80·3; H, 6·3%. MS *m/e* (relative abundance): 332 (3), 182 (40), 105 (100), 77 (65).

[e] Found: C, 80·5; H, 6·6. $C_{34}H_{34}O_4$ requires: C, 80·6; H, 6·8%. MS *m/e* (relative abundance): 332 (2), 182 (36), 105 (100), 77 (64).

[f] Found: C, 80·7; H, 6·8. $C_{34}H_{34}O_4$ requires: C, 80·6; H, 6·8%. MS *m/e* (relative abundance): 332 (3), 182 (52), 105 (100), 77 (65).

[g] Found: C, 83·8; H, 5·3. $C_{40}H_{30}O_4$ requires: C, 83·6; H, 5·3%. MS *m/e* (relative abundance): 332 (12), 182 (37), 105 (100), 77 (66).

Reduction of benzopinacol diacetate with lithium aluminium hydride. Benzopinacol diacetate (50 mg, 0·11 mmole) was treated with LAH (60 mg, 1·60 mmole) in ether (30 ml) under refluxing for 6 hr. The mixture was worked up as usual. The products were washed with MeOH. Recrystallization of the resulting crystalline products from MeOH gave benzopinacol (trace), m.p. 186° (lit.[12] 188–189°). Concentration of the filtrate gave benzhydrol (35 mg, 86%), m.p. 66–68° (lit.[13] 68°).

Reaction of **1** *with* Tl^{III} *acetate.* **1** (500 mg, 2·6 mmole) was treated with Tl^{III} acetate (1970 mg, 5·2 mmole) in ether (20 ml) at room temp for 14 hr. The products were recrystallized from CCl_4 to give benzophenone diacetate (390 mg, 53%), m.p. 118–120° (lit.[8] 121°), which was identical with the authentic sample (IR spectra).

Preparation of phenyldiazomethane (**1′**). Phenyldiazomethane **1′**[14] was prepared as an ether soln by the recorded method and used without isolation.

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