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Reactions of Diazoketones in the Presence of Metal Chelates. I. Reactions in Alcohols[1]

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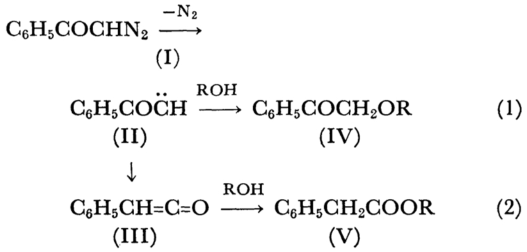
The reaction of diazoacetophenone with alcohols has been studied in the presence of metal chelates. Metal chelates, such as bis(acetylacetonato)copper(II), bis(acetylacetonato)nickel(II), and bis(acetylacetonato)lead(II), were found to be active catalysts for this reaction; they modified the reaction to give alkoxyacetophenones instead of alkyl phenylacetates. When tertiary amines, such as triethylamine, pyridine, and quinoline, were added to the reaction mixture, the formation of alkoxyacetophenones was suppressed and that of alkyl phenylacetates was promoted in proportion to the increase in the amount of amines added. The mechanism of the reaction can reasonably be explained by assuming the intermediacy of a ketocarbene-metal chelate complex.

It has been recognized that the Wolff rearrangement of α-diazoketones, with a loss of nitrogen, to carboxylic acids or their derivatives in protonic solvents is promoted by metal catalysts, such as silver oxide,[2] silver nitrate,[2,3] silver benzoate,[4] cuprous chloride[4] and cuprous acetate.[4] Newman and Beal[4] have observed that a solution of silver benzoate in triethylamine is an effective homogeneous catalyst for the rearrangement in alcohols. Yates,[5] however, has shown that the reaction of α-diazoketones with alcohols in the presence of metallic copper occurs without rearrangement to give α-alkoxyketones.

Recently, we have discovered that bis(acetylacetonato)copper(II) is an active catalyst for the decomposition of diazoacetophenone (I) in alcohols, and that the reaction is modified to give alkoxyacetophenones (IV), instead of alkyl phenylacetates (V),[6] in the same manner as when copper powder was employed as a catalyst.



$$\begin{array}{lll} \underset{\text{(I)}}{C_6H_5COCHN_2} \xrightarrow{-N_2} & & \\ \underset{\text{(II)}}{C_6H_5CO\ddot{C}H} \xrightarrow{ROH} \underset{\text{(IV)}}{C_6H_5COCH_2OR} & & (1) \\ \quad\downarrow & & \\ \underset{\text{(III)}}{C_6H_5CH{=}C{=}O} \xrightarrow{ROH} \underset{\text{(V)}}{C_6H_5CH_2COOR} & & (2) \end{array}$$

The results suggest that the reaction proceeds with the intermediate formation, by means of the interaction of the diazoacetophenone and the copper chelate, of benzoylcarbene (II), which then reacts with alcohols. Nozaki and his co-workers[7] have also independently found a similar effect of bis(acetylacetonato)copper(II) in the reaction of diphenyldiazomethane.

We studied the reactions of diazoacetophenone with alcohols in the presence of various kinds of metal chelates and investigated the effects of amines on the catalytic actions of metal chelates.

Results and Discussion

Catalytic Actions of Metal Chelates. The decomposition of diazoacetophenone in alcohols has been carried out with a small amount of a metal chelate at 50—80°C in an atmosphere of nitrogen. In the first place, the catalytic action of metal acetylacetonates ($M(AcAc)_n$) on the decomposition of diazoacetophenone was investigated in an ethanol solution. The results are shown in Table 1.

Among the metal acetylacetonates employed, $Cu(AcAc)_2$ and $Ni(AcAc)_2$ were found to be the most effective catalysts in the decomposition to give ethoxyacetophenone (Table 1). On the contrary, $Al(AcAc)_3$, $Ba(AcAc)_2$, $Be(AcAc)_2$, $Ca(AcAc)_2$, $Cd(AcAc)_2$, $Co(AcAc)_2$, $Co(AcAc)_3$, $Fe(AcAc)_3$, $Mg(AcAc)_2$, $Mn(AcAc)_2$, $Mn(AcAc)_3$, and $Zn(AcAc)_2$ manifested practically no catalytic influence on the decomposition, even when the reaction mixture was refluxed for thirty hours.

The catalytic action of copper chelates was compared with that of nickel chelates. As is shown

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1) Presented in part at the Symposium of Organic Radical Reactions, October, 1965, and at the Symposium of Organic Reaction Mechanism, Tokyo, October, 1966.

2) L. Wolff, *Ann.*, **394**, 23 (1912).

3) K. Banfolzer, *Helv. Chim. Acta*, **35**, 1577 (1952).

4) M. S. Newman and P. F. Beal, *J. Am. Chem. Soc.*, **72**, 5163 (1950).

5) P. Yates, *ibid.*, **74**, 5376 (1952).

6) T. Ibata, H. Kohara and M. Takebayashi, Abstracts of Papers presented at the Symposium of Organic Radical Reactions (1965), p. 16.

7) H. Nozaki, S. Moriuti, Y. Yamabe and R. Noyori, *Tetrahedron Letters*, **1966**, 59.

TABLE 1. CATALYTIC ACTIONS OF METAL ACETYLACETONATES

$C_6H_5COCHN_2$ 3.4×10^{-2} mol, $M(AcAc)_n$ 3.5×10^{-4} mol, C_2H_5OH 150 cc

$M(AcAc)_n$	React. temp., °C[a]	React. time[b]	Yield of $C_6H_5COCH_2OC_2H_5$ %
None	80	30 hr	0[c]
$Cu(AcAc)_2$	50	30 min	60
$Ni(AcAc)_2$	70	3 hr	80
$Pb(AcAc)_2$	80	20 hr	60
$2Ti(AcAc)_3TiCl_6$	80	30 hr	62

a) Initial temperature of the reaction.
b) Time required until the evolution of nitrogen is over.
c) No reaction took place.

TABLE 2. CATALYTIC ACTIONS OF COPPER CHELATES AND NICKEL CHELATES

$C_6H_5COCHN_2$ 1.7×10^{-2} mol, Metal chelate 1.9×10^{-4} mol, C_2H_5OH 150 cc

Cu catalyst	React.[a] temp., °C	React.[b] time	Yield of $C_6H_5COCH_2OC_2H_5$ %
$Cu(AcAc)_2$	50	50 min	60
$Cu(AcAc)_2$ (1.9×10^{-6} mol)	60		64
$Cu(AcAc)_2$-(II)[c] complex	45	30 min	40
$Cu(CH_3COCHCO_2C_2H_5)_2$	45	60 min	35
$Cu(C_6H_5COCHCOC_6H_5)_2$	63	30 min	66
$Cu(DMG)_2$[e]	60	30 min	45
$[Cu(OAc)_2\cdot H_2O]_2$	45	30 min	70
$CuSO_4\cdot 5H_2O$	30	30 min	70
Cu powder (0.05 g)	60	30 min	60

Ni catalyst	React.[a] temp., °C	React.[b] time	Yield of $C_6H_5COCH_2OC_2H_5$ %
$Ni(AcAc)_2$	70	3 hr	80
$Ni(AcAc)_2$ (1.9×10^{-6} mol)	refl.		No react.
$Ni(AcAc)_2$-(II)[d] complex	80	1 hr	86
$Ni(DMG)_2$[f]	refl.		No react.
$Ni(OAc)_2\cdot 4H_2O$	70	3 hr	90
Ni powder (0.05 g)	refl.	3 hr	80

a) Initial temperature. b) Time required until the evolution of nitrogen is over.
c) A complex formed by the reaction of $Cu(AcAc)_2$ and I.
d) A complex formed by the reaction of $Ni(AcAc)_2$ and I. e) Bis(dimethylglyoximato)copper(II).
f) Bis(dimethylglyoximato)nickel.

in Table 2, the results indicate that the decomposition in the presence of copper chelates occurs more rapidly than that in the presence of nickel chelates, even at lower temperatures, suggesting that the copper chelates are more active catalysts than the corresponding nickel chelates. In the case of $Cu(AcAc)_2$ especially, the decomposition took place with a very small amount of $Cu(AcAc)_2$ (1.9×10^{-6} mol), yielding 64% of ethoxyacetophenone, while no decomposition was observed with the same amount of $Ni(AcAc)_2$. A similar result was recognized in the cases of copper and nickel powder. The catalytic action of metal chelates may be based on the nature of the metals and on the structure of the ligands.

The Reaction of Diazoacetophenone with Alcohols in the Presence of Bis(acetylacetonato)copper(II). Three kinds of alcohols were employed as solvents. The reaction proceeded to give the alkoxyacetophenones corresponding to the alcohols employed; a small amount (<1 mol%) of benzoic acid was also obtained in all cases. When the alkoxyacetophenones produced were left standing in the air for several days, the acetophenones were converted to benzoic acid to some extent. Therefore, the benzoic acid seems to be produced by the partial decomposition of alkoxyacetophenones during the treatment of the reaction products.

If a mixture of alcohol and water was used as the solvent, two kinds of competitive reaction products, alkoxyacetophenone (IV) and α-hydroxyacetophenone (IV′), may be expected:

$$C_6H_5COCHN_2 + ROH \xrightarrow{Cu(AcAc)_2} \underset{(IV)}{C_6H_5COCH_2OR} \tag{3}$$

$$C_6H_5COCHN_2 + H_2O \xrightarrow{Cu(AcAc)_2} \underset{(IV')}{C_6H_5COCH_2OH} \tag{4}$$

As Table 3 shows, however, the reaction gave a single product (IV), excepting the case where a mixture of t-butyl alcohol and water (130 : 20) was used as the solvent, and in every case the yields of alkoxyacetophenones decreased compared with those obtained in non-aqueous alcohols. An especially marked fall in yields was found in the case of aqueous t-butyl alcohol.

Since the values of the acidity constant (pK_a) of the alcohols used are nearly equal (pK_a: CH_3OH 16; C_2H_5OH 18; $(CH_3)_2CHOH$ 18; $(CH_3)_3COH$ 19), the reaction must be controlled by the steric effects of alcohols,

Effect of Amines. It has been reported that the catalytic action of bis(acetylacetonato)copper is suppressed in a pyridine solution.[7] Supposing this to be true in our case also, this fact seems suggest an elucidation of the reaction mechanism. The effect of amines on the catalytic action of

TABLE 3. REACTIONS OF DIAZOACETOPHENONE WITH ALCOHOLS IN THE PRESENCE OF BIS(ACETYLACETONATO)COPPER*

Solvent	Product, mol%**	
CH_3OH	$C_6H_5COCH_2OCH_3$ (bp 122°C/19 mmHg)[5]	(65)
C_2H_5OH	$C_6H_5COCH_2OC_2H_5$ (bp 142°C/29 mmHg)[5]	(60)
$(CH_3)_2CHOH$	$C_6H_5COCH_2OCH(CH_3)_2$ (bp 129°C/17 mmHg)	(60)
$(CH_3)_3COH$	$C_6H_5COCH_2OC(CH_3)_3$ (bp 141°C/22 mmHg)	(36)
$CH_3OH + H_2O$ (100 : 50)	$C_6H_5COCH_2OCH_3$	(45)
$C_2H_5OH + H_2O$ (130 : 20)	$C_6H_5COCH_2OC_2H_5$	(35)
$(CH_3)_2CHOH + H_2O$ (130 : 20)	$C_6H_5COCH_2OCH(CH_3)_2$	(24)
$(CH_3)_3COH + H_2O$ (130 : 20)	$C_6H_5COCH_2OC(CH_3)_3$ $C_6H_5COCH_2OH$	(13) (6)

* Experimental condition: $C_6H_5COCHN_2$ 3.4×10^{-2} mol, $Cu(AcAc)_2$ 3.8×10^{-4} mol, solvent 150 cc.

** The melting points of 2,4-dinitrophenylhydrazones of methoxy-, ethoxy-, isopropoxy- and t-butoxyacetophenone were observed to be of 190—191°C, 148—149°C, 170—171°C and 188—189°C, respectively.

TABLE 4. EFFECT OF THE AMOUNT OF AMINES ON THE CATALYTIC ACTION OF BIS(ACETYLACETONATO)COPPER*

Amine	ROH (R)	Product			
		C_6H_5COOR mol%	$C_6H_5COCH_2OR$ (IV), mol%	$C_6H_5CH_2COOR$ (V), mol%	IV : V
None	C_2H_5	0	60	0	100 : 0
$(C_2H_5)_3N$					
1 cc	C_2H_5	trace	60	trace	100 : 0
10 cc	C_2H_5	6	54	14	79 : 21
15 cc	C_2H_5	8	37	12	75 : 25
Pyridine					
1 cc	C_2H_5	3	35	8	82 : 18
5 cc	C_2H_5	8	12	26	32 : 68
10 cc	C_2H_5	7	6	41	13 : 87
15 cc	C_2H_5	6	5	59	8 : 92
15 cc	$(CH_3)_2CH$	5	4	38	9 : 91
15 cc	$(CH_3)_3C$	0.4	1	30	3 : 97
103 cc**	C_2H_5	12	trace	16	

* Experimental condition: $C_6H_5COCHN_2$ 1.7×10^{-2} mol, $Cu(AcAc)_2$ 1.9×10^{-4} mol, ROH 75 cc

** A side reaction took place between pyridine and the carbene.

TABLE 5. EFFECT OF PYRIDINE ON THE ACTIONS OF METAL CHELATES AND OTHER CATALYSTS*

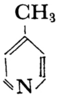
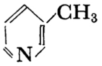
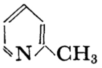
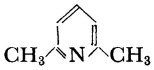
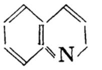
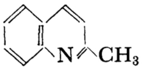
Catalyst	Pyridine	Product			
		$C_6H_5CO_2C_2H_5$ mol%	$C_6H_5COCH_2OC_2H_5$ (IV), mol%	$C_6H_5CH_2CO_2CH_5$ (V), mol%	IV : V
Cu(AcAc)$_2$	None	0	60	0	100 : 0
	15 cc	6	5	59	8 : 92
Cu(DMG)$_2$[a]	None	0	45	0.4	99 : 1
	15 cc	4	3	58	5 : 95
Cu(En)$_2$SO$_4$[b]·2H$_2$O	None	0	67	1	98 : 2
	15 cc	18	18	3	86 : 14
Ni(AcAc)$_2$	None	0	80	0	100 : 0
	15 cc	0	0	0	No react.
[Cu(OAc)$_2$H$_2$O]$_2$ (0.05 g)	None	0	70	0	100 : 0
	15 cc	4	2	60	3 : 97
CuSO$_4$·5H$_2$O (0.05 g)	None	0	69	0	100 : 0
	15 cc	10	4	48	8 : 92
Cu powder (0.05 g)	None	0	59	0	100 : 0
	15 cc	12	7	18	28 : 72

* Experimental condition: $C_6H_5COCHN_2$ 1.7×10^{-2} mol, Metal chelate 0.05 g (1.7—1.9×10^{-4} mol), Pyridine 15 cc (1.8×10^{-1} mol), C_2H_5OH 75 cc

a) Bis(dimethylglyoximato)copper(II).

b) Bis(ethylenediamino)copper(II) sulfate, hardly soluble in ethanol.

TABLE 6. EFFECTS OF AMINES ON THE CATALYTIC ACTION OF BIS(ACETYLACETONATO)COPPER*

Amine	(pK_a)	Product			
		$C_6H_5CO_2C_2H_5$ mol%	$C_6H_5COCH_2OC_2H_5$ (IV), mol%	$C_6H_5CH_2CO_2C_2H_5$ (V), mol%	IV : V
	5.17	6	5	59	8 : 92
	6.02	5	12	46	20 : 80
	5.68	5	4	56	7 : 93
	5.97	1	12	67	15 : 85
	6.75	trace	21	52	29 : 71
	4.80	4	10	44	18 : 82
	5.42	trace	31	41	43 : 57
$C_6H_5N(CH_3)_2$	5.06	1	16	11	59 : 41
$C_6H_5N(C_2H_5)_2$	6.56	trace	51	3	94 : 6
$N(C_2H_5)_3$	10.67	8	37	12	75 : 25

* Experimental condition: $C_6H_5COCHN_2$ 1.7×10^{-2} mol, Cu(AcAc)$_2$ 0.05 g (1.9×10^{-4} mol), Amine 1.8×10^{-1} mol, C_2H_5OH 75 cc

metal chelates was, therefore investigated using various kinds of tertiary amines.

The effect of pyridine was found to be the most remarkable among the amines used. The presence of an excess of pyridine in relation to the amount of copper chelate retards the reaction, but it promotes the rearrangement of ketocarbene (II), giving rise to alkyl phenylacetate (V) (Table 4). Similar effects were observed in the cases of other copper chelates (Table 5).

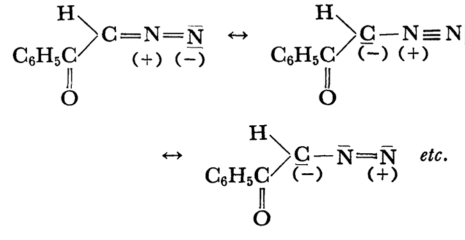
In the case of bis(acetylacetonato)nickel, its catalytic action was suppressed completely in the presence of pyridine, and most of the diazoacetophenone was recovered (Table 5).

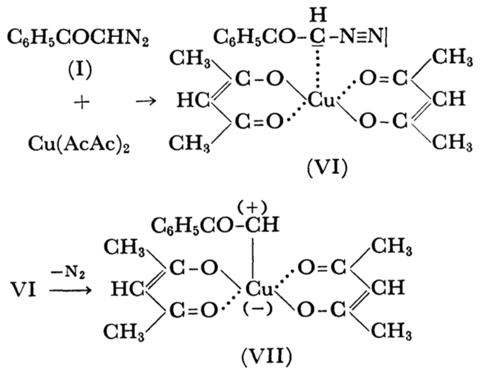
In another experiment, the effects of tertiary amines were compared under the same experimental conditions. The results are listed in Table 6. The ratio of the formation of alkyl phenylacetate (V) to that of alkoxyacetophenone (IV) increased according to the kind of amines, as is shown below:

pyridine, β-picoline$>\alpha$-picoline$>$quinoline$>$ 2,6-lutidine$>\alpha$-quinaldine$>$*N, N*-dimethylaniline$>$trimethylamine$>$*N, N*-diethylaniline.

This order does not accord with that of the basicity of amines,[8] but it indicates that the effects of amines are controlled by the bulkiness of groups attached to the α-carbon atom of the pyridine family or the nitrogen atom of alkyl and aryl amines. The effect of γ-picoline was however, observed to be abnormally smaller than that of pyridine or β-picoline. The results suggest that the nitrogen atoms of amines attack the metal atom of the copper chelate intermediate, as will be described later, to give alkyl phenylacetate (V) through the formation of free ketocarbene (II).

Mechanism. Based on the results presented above, the catalytic decomposition of diazoacetophenone in alcohols may reasonably be explained as follows. Metal chelates such as $Cu(AcAc)_2$, $Cu(C_6H_5COCHCOC_6H_5)_2$ and $Cu(DMG)_2$ have been recognized to have a plane structure of four co-ordinations, while $Ni(AcAc)_2$ is a trimer.[9] α-Diazoacetophenone has the following resonance structure:





$$\xrightarrow[\text{ROH}]{\text{path a}} \underset{\text{(IV)}}{C_6H_5COCH_2OR} + Cu(AcAc)_2 \qquad (6)$$

$$\text{VII} \xrightarrow[\text{Amine}]{\text{path b}} \underset{\text{(II)}}{C_6H_5COCH\colon} \rightarrow \underset{\text{(III)}}{C_6H_5CH{=}C{=}O}$$

$$\xrightarrow{\text{ROH}} \underset{\text{(V)}}{C_6H_5CH_2COOR} \qquad (7)$$

The diazoketone (I) co-ordinates with its α-carbon atom to the metal atom of copper chelates, thus giving an intermediate complex (VI); the complex loses its nitrogen immediately to afford a ketocarbene complex (VII) with a structure analogous to that of pyridine adducts of copper chelates.[10] The bond between the ketocarbene and the copper atom of the complex (VII) is not so strong that the complex may react with alcohols, giving rise to alkoxyacetophenone (IV) in the absence of tertiary amines (path a).

In the presence of tertiary amines such as pyridine and quinoline, the co-ordination of diazoketone to copper chelate would be suppressed to some extent according to the concentration of pyridine (Table 4), resulting in the elevation of the initial reaction temperature. However, the formation of the complexes (VI) and (VII) should proceed in a manner similar to that when the amines are absent, when the concentration of pyridine is not so large. If the formation of VI and VII were suppressed thoroughly by pyridine, no decomposition of the diazoketone would be observed.[11]

When pyridine attacks the complex (VII), free ketocarbene (II) is expelled and the pyridine adduct of copper chelate is formed. The free carbene rearranges to ketene (III) and gives alkyl phenylacetates (V) by reaction with alcohols (path b). However, it is not clear whether pyridine attacks the complex (VII) from the front side of

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[8] Triphenylphosphine and acetonitrile also served to promote the formation of V (IV : V, 92 : 8 and 94 : 6 respectively) in spite of their very small basicity.

[9] G. J. Bullen, R. Mason and P. Pauling, *Nature,* **189**, 291 (1961); *Inorg. Chem.,* **4**, 456 (1965).

[10] D. P. Graddon, *J. Inorg. & Nuclear Chem.,* **14**, 161 (1960); D. P. Graddon and E. C. Watton, *ibid.,* **21**, 49 (1961); D. Hall, S. V. Sheat and T. N. Waters, *Chem. & Ind.,* **1965**, 1423.

[11] When a mixture of benzene and pyridine (1 : 1) was employed as a solvent, the catalytic decomposition of diazoacetophenone did not take place at 80°C.

the linked ketocarbene or from the back side. The effect of tertiary amines will be discussed further in connection with kinetic studies.

Experimental

Materials. α-Diazoacetophenone was prepared from benzoyl chloride and diazomethane according to the method of Newman;[12] mp 47.5—48.0°C.

Metal Chelates. Commercial "Research-Grade" pure metal acetylacetonates $M(AcAc)_n$ were used without further purification. Bis(acetoacetato)copper,[13] bis-(dibenzoylmethano)copper,[14] bis(dimethylglyoximato)-copper,[15] and bis(ethylenediamino)copper sulfate[16] were prepared according to the directions in the literature.

Alcohols. Commercial methanol, ethanol, isopropanol, and *t*-butanol were refluxed with magnesium ribbon[17] or metallic sodium and purified by fractional distillation. Gas chromatography showed no detectable impurities.

Amines. Commercial "Research-Grade" amines were dried over pellets of sodium hydroxide for several days at room temperature and then fractionated under diminished pressure in an atmosphere of nitrogen. No detectable impurities were found by gas chromatography in the amines employed.

General Procedure. *Reactions in the Absence of Amines.* Definite amounts of diazoacetophenone, a metal chelate, and an alcohol were placed in a hard, glass reaction vessel. After it had been flushed with dry nitrogen, the vessel was immersed in a water bath and heated gradually. Soon after nitrogen evolved; the temperature of the reaction mixture rose a further 3—5°C during the reaction. In most cases, the generation of nitrogen was almost quantitative. After the reaction was over, the solvent (alcohol) was distilled off and the reaction products were fractionated under diminished pressure in an atmosphere of nitrogen.

The distillate was confirmed by gas chromatography to be a single product, alkoxyacetophenone (IV). The alkoxyacetophenones obtained in four kinds of alcohols are shown in Table 3. These alkoxyacetophenones were converted to their 2, 4-dinitrophenylhydrazones, and the hydrazones were confirmed by elementary analysis and by the measurement of the infrared absorption spectra. Among them, isopropoxy- and *t*-butoxy-acetophenone seem to be new compounds.

2, 4-Dinitrophenylhydrazone of isopropoxyacetophenone,

Found: C, 56.74%; H, 4.88%; N, 15.50%. Calcd for $C_{17}H_{18}O_5N_4$: C, 56.98%; H, 5.06%; N, 15.64%.

2, 4-Dinitrophenylhydrazone of *t*-butoxyacetophenone:

Found: C, 58.21%; H, 5.20%; N, 15.18%. Calcd for $C_{18}H_{20}O_5N_4$: C, 58.06%, H, 5.41%; N, 15.05%.

The residue was dissolved in benzene, and the solution was extracted by a 5 N aqueous sodium hydroxide solution. When the aqueous extract was acidified with hydrochloric acid, a small amount of benzoic acid was obtained.

Reactions in the Presence of Tertiary Amines. A mixture of diazoacetophenone, bis(acetylacetonato)copper, a tertiary amine, and ethanol was placed in a reaction vessel and heated in a manner similar to that described above. In this case, the generation of nitrogen was also quantitative. The reaction products were treated with 3 N hydrochloric acid in order to remove amines and were then fractionated. The gas chromatogram[18] of the distillate showed three peaks, (A), (B) and (C). The peak (A) accorded with that of ethyl benzoate, (B), with that of ethyl phenylacetate (V), and (C), with that of ethoxyacetophenone (IV). The amounts of the three kinds of products were calculated from the ratio of their peak areas appearing in the gas chromatogram.

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[12] M. S. Newman and P. F. Beal, *J. Am. Chem. Soc.*, **71**, 1506 (1949).

[13] H. S. Booth, "Inorganic Syntheses," Vol. 2, p. 14 (1946).

[14] *Ibid.*, Vol. 2, p. 19 (1946).

[15] J. V. Dubsky and F. Brychta, *Collection trav. chim.*, **I**, 137 (1929); *Chem. Zb.*, **1929**, II 549.

[16] H. S. Booth, "Inorganic Syntheses," Vol. 5, p. 16 (1957).

[17] H. Lund and J. Bjerrum, *Ber.*, **64**, 210 (1931).

[18] A Yanagimoto gas chromatograph 3DH was used. Column: stainless steel tube, 5 mm × 3 m; adsorbent: Apiezon grease M, 80 mesh; temp.: 157°C; carrier gas: H_2, 58 cc/min; retention time: (A) 8.2 min, (B) 11.0 min, (C) 17.4 min.