BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 1700—1707 (1968)

The Wolff Rearrangement. IV. The Silver-salt Catalyzed Decomposition of α-Diazoacetophenones in Benzene Solution*[1]

Matsuji TAKEBAYASHI and Toshikazu IBATA

Department of Chemistry, College of General Education, Osaka University, Toyonaka, Osaka

(Received January 26, 1968)

The decomposition of α-diazoacetophenone (I) in benzene solution has been studied using a silver benzoate-triethylamine catalyst at 50°C in an atmosphere of nitrogen. The reaction gave 3-benzoyl-4-hydroxy-5-phenylpyrazole (II) and β-phenylpropiophenone (III). In the decomposition of the substituted compounds, such as *p*-methoxy-, *p*-methyl- and *p*-nitro-α-diazoacetophenones, the corresponding substituent products of II and III were also obtained. The formation of II and III is reasonably explained by assuming two kinds of reactions between phenylketene and I.

It has been recognized that the photochemical, thermal, and silver-salt catalyzed decompositions of diazoketones in protic solvents give carboxylic acids and their derivatives (Wolff Rearrangement).(1) Although these products have been interpreted in terms of ketene intermediates,(2) the high reactivity of normal ketenes does not allowed the isolation of them but leads to the carboxylic acids, esters, and amides, respectively, after reacting with water, alcohols, and amines existed in the reaction system.(3)

On the other hand, the decomposition of the diazoketones in aprotic solvents affords the β-lactam(4,5) and 1,2-diazacyaclobutane derivatives(6) in the presence of azomethine and azo compounds respectively.

Recently, one of the authors (T. I.) has made a

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*1 Presented in part at the Symposium of Organic Radical Reactions, Osaka, September, 1964. For the preceding paper in this series, see; *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **88**, 1223 (1967).

1) W. E. Bachmann and W. S. Struve, "Organic Reaction," Vol I, John Wily & Sons Inc., New York (1942), p. 38.

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

3) P. Mayo, "Molecular Rearrangement Part I," Interscience Publishers, New York (1963), p. 528.

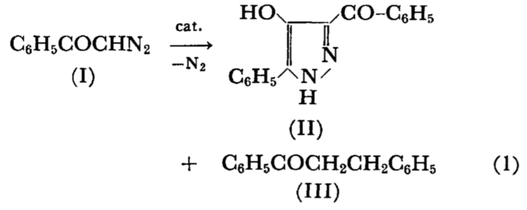
4) H. Staudinger, *Ann.*, **356**, 51 (1912).

5) L. Horner, *Chem. Ber.*, **89**, 2759 (1956).

6) L. Horner, *ibid.*, **89**, 2765 (1956).

kinetic study on the decomposition of substituted α-diazoacetophenones in various kinds of alcohols and in toluene solution,[7] using a solution of silver benzoate in triethylamine as a catalyst,[8] and has found that the substituent effect in alcohols is similar to that in toluene, and also has confirmed that the both reaction mechanisms are alike in the formation of ketene intermediates. In the experiments mentioned above, the evolution of nitrogen was almost quantitative and the corresponding phenylacetic esters were obtained in good yields in alcohols, while the evolution of nitrogen was not quantitative in toluene solution. A possible reason for the decrease in the evolution of nitrogen is given to the reaction between unreacted diazoketone and a ketene intermediate, when reactive substances with ketene are not present in the reaction medium. Therefore the investigation of the reaction products seems to be important. However, only a few studies of the decomposition of diazoketones in aprotic solvents, under the condition leading to rearranged products, have been published;*[2] the photolysis of diazomethyl *t*-butyl ketone and of α-diazoacetophenone (I) in the absence of solvent has been reported by Wiberg,[11] and the thermal decomposition of napthalene-1,2-diazoxide in xylene and that of α-diazoacetophenone (I) in dodecane by Yates.[12,13]

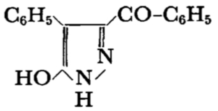
The authors investigated the silver benzoate catalyzed decomposition of α-diazoacetophenones in benzene solution and obtained interesting results differed from those reported by Wiberg and Yates.



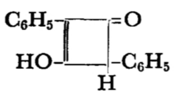
Results

The decomposition of α-diazoacetophenone (I) in benzene solution was carried out in the presence of a 1/10 molar equivalent of silver benzoate, dissolved in a possibly smaller amount of triethylamine, at 50°C in an atmosphere of nitrogen. The reaction mixture turned to dark-brown color accompanied by the evolution of nitrogen gas. The evolution of nitrogen was ceased after about 60—70%*[3] of its theoretical amount was generated (4—5 hr), and no evolution of nitrogen was recognized by further addition of the silver benzoate solution to the reaction mixture. After being left to stand at room temperature overnight, the reaction mixture was extracted several times with a saturated aqueous solution of sodium bicarbonate in succession with a 4 N solution of sodium hydroxide, and was separated in three fractions: (A) acidic fraction (soluble in sodium bicarbonate solution), (B) weak acidic fraction (soluble in sodium hydroxide solution), (C) neutral or basic fraction (soluble in benzene). Fraction (A) gave benzoic acid and a trace of phenylacetic acid. The benzoic acid is thought to be produced from silver benzoate, used as a catalyst, during the reaction or after treatment of reaction mixture, and the phenylacetic acid seems to be formed by the reaction of the phenylketene intermediate with a trace of water contained in the reaction medium.

On the acidification of fraction (B) by a concentrated hydrochloric acid under cooling with ice, followed by recrystallization from ethanol solution, 3-benzoyl-4-hydroxy-5-phenylpyrazole (II)[14] was obtained in the yield of 38%. However, 3-benzoyl-4-phenyl-5-hydroxypyrazole (IV),[14] the isomeric compound of II, and the ketene dimer (V)[15,16] were not detected in this fraction.



(IV)



(V)

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[7] Y. Yukawa, Y. Tsuno and T. Ibata, This Bulletin, **40**, 2613, 2618 (1967).

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

*[2] Some works on the copper powder or copper-salt catalyzed decomposition of diazoketones to give ketocarbene intermediates have been reported.[9,10] In these works, the dimerization of ketocarbenes[9] and the intramolecular or intermolecular cyclo-addition of ketocarbenes to carbon-carbon double bonds[9] have been recoginized.

[9] C. Grundmann and H. Trishmann, *Ann.*, **536**, 29 (1938).

[10] W. Kirmse, "Carbene Chemistry," Academic Press, New York (1964).

[11] K. B. Wiberg and J. W. Hutton, *J. Am. Chem. Soc.*, **76**, 5367 (1954).

[12] P. Yates and E. W. Robb, *ibid.*, **79**, 5760 (1957).

[13] P. Tates and T. J. Clark, *Tetrahedron Letters*, **1961**, 435.

*[3] The yields of nitrogen vary as the concentration of the reaction mixture, making the change of the yields of II and III.

[14] a) P. Yates and B. L. Shapiro, *J. Am. Chem. Soc.*, **81**, 212 (1959).
b) D. G. Farnum and P. Yates, *Chem. & Ind. (London)*, **1960**, 659.
c) D. G. Farnum and P. Yates, *Proc. Chem. Soc.*, **1960**, 224.
d) D. G. Farnum and P. Yates, *J. Am. Chem. Soc.*, **84**, 1399 (1962).
e) D. G. Farnum and P. Yates, *ibid.*, **85**, 2967 (1962).
f) D. G. Farnum and P. Yates, *J. Org. Chem.*, **27**, 2209 (1962).
g) D. G. Farnum and P. Yates, *Tetrahedron Letters*, **1960**, 22.

[15] H. Staudinger, *Ber.*, **44**, 533 (1911).

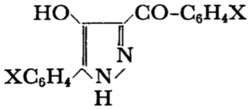
[16] J. E. Baldwin and J. D. Roberts, *J. Am. Chem. Soc.*, **85**, 2444 (1963).

On vacuum distillation of neutral fraction (C) after evaporating the solvent, β-phenylpropiophenone(III)[17-19] was obtained in 13% yield with very small amount of two kinds of compounds containing carbonyl groups. The structure of the ketone (III) was ascertained by the comparison of the IR and NMR spectra with those of authentic β-phenylpropiophenone, and still more ascertained

TABLE 1. THE EFFECT OF THE CONCENTRATION OF THE REACTION MEDIUM ON THE YIELDS OF II AND III

(Run)	(1)	(2)	(3)
$PhCOCHN_2$	5.0 g	10.0 g	15.0 g
PhCOOAg	0.5 g	1.0 g	2.0 g
$(C_2H_5)_3N$	5.0 ml	6.0 ml	20.0 ml
benzene	20 ml	200 ml	1000 ml
reaction temp.	50°C	40°C	40°C
(Products)			
PhCOOH	0.10 g	0.15 g	0.30 g
$PhCH_2COOH$	trace	trace	trace
II	1.70 g (38%)	2.10 g (23%)	0.50 g (3.7%)
III	0.34 g (12%)	0.93 g (13%)	3.05 g (38%)
unknown oil	0.47 g	1.0 g	1.5 g

TABLE 2. PRODUCTS OF THE DECOMPOSITION OF *p*-SUBSTITUTED α-DIAZOACETOPHENONES CATALYZED BY SILVER BENZOATE IN BENZENE[a)]

Substituent			$XC_6H_4COCH_2CH_2C_6H_4X$	
	Mp (°C)	Yield (%)	Mp (°C)	Yield (%)
H	209.5—210.5	38	71.0—72.0	13
p-CH_3	251.0—252.0	26	64.5—65.5	12
p-CH_3O	207.0—208.0	12	84.0—85.0	9.1
p-NO_2	>300[b)]	26		

a) Benzoic acid and a trace of the corresponding *p*-substituted phenylacetic acids were also obtained.
b) The melting point of this compound was not determined precisely because of its high degree.

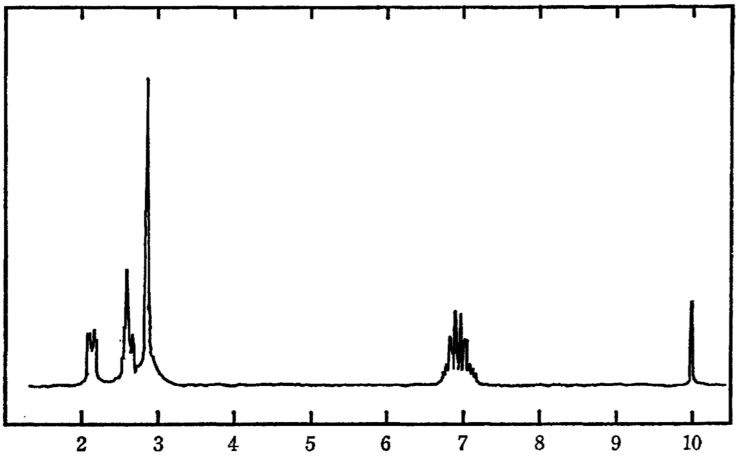


Fig. 1. The NMR spectrum of β-phenylpropiophenone (III).

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17) H. H. Wasserman and N. E. Aubrey, *ibid.*, **77**, 590 (1955).
18) Yu. K. Yur'ev, Z. V. Belyakova and V. P. Volkov, *Zhur. Obshch. Khim.*, **28**, 2372 (1958) (*Chem. Abstr.*, **1959**, 3135e).
19) G. S. Fonken and W. S. Johnson, *J. Am. Chem. Soc.*, **74**, 831 (1952).

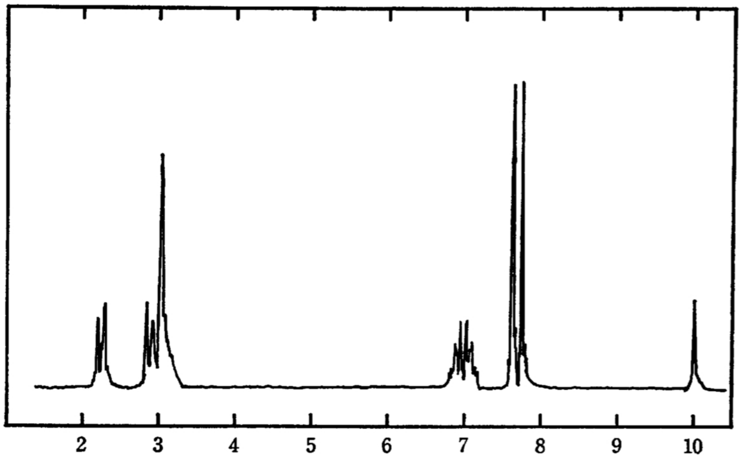
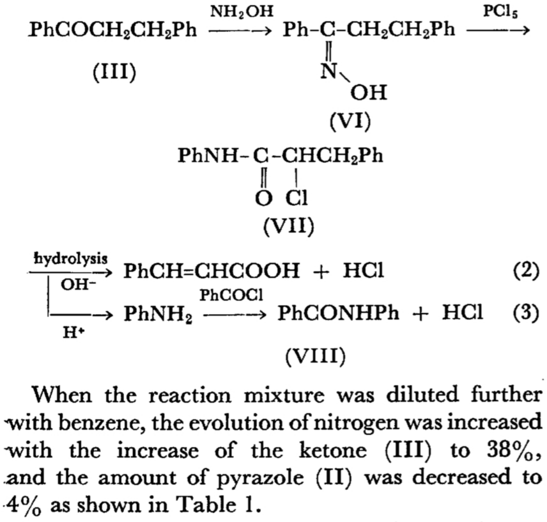


Fig. 2. The NMR spectrum of β-*p*-tolyl-*p*-methylpropiophenone.

by the Beckmann rearrangement of its oxime (VI) to α-chloro-β-phenylpropionanilide (VII) in the presence of phosphorus pentachloride.



$$\underset{\text{(III)}}{PhCOCH_2CH_2Ph} \xrightarrow{NH_2OH} \underset{\text{(VI)}}{Ph\text{-}\underset{\underset{\text{N}\diagdown\text{OH}}{\|}}{C}\text{-}CH_2CH_2Ph} \xrightarrow{PCl_5}$$

$$\underset{\text{(VII)}}{PhNH\text{-}\underset{\underset{O}{\|}}{C}\text{-}\underset{\underset{Cl}{|}}{C}HCH_2Ph}$$

$$\xrightarrow[OH^-]{\text{hydrolysis}} PhCH{=}CHCOOH + HCl \qquad (2)$$

$$\xrightarrow[H^+]{} PhNH_2 \xrightarrow{PhCOCl} \underset{\text{(VIII)}}{PhCONHPh} + HCl \qquad (3)$$

When the reaction mixture was diluted further with benzene, the evolution of nitrogen was increased with the increase of the ketone (III) to 38%, and the amount of pyrazole (II) was decreased to 4% as shown in Table 1.

The catalytic decomposition of *p*-methoxy-, *p*-methyl-, and *p*-nitro-α-diazoacetophenones also gave the corresponding derivatives of pyrazole and β-phenylpropiophenone. The results are listed in Table 2.

These results are quite different from those reported by Wiberg and Yates, and also from those obtained in the copper-salt catalyzed decomposition of α-diazoacetophenone in benzene, yielding 1,2-dibenzoylethylene.[9,20]

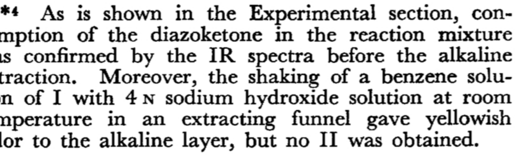
Discussion

Yates and his co-workers have obtained pyrazole derivatives (II) and (IV) besides benzoic acid, acetophenone and 3-benzoyl-5-phenyl pyrazole (IX) in the alkali catalyzed decomposition of α-diazoacetophenone.[14a,e,g] However, the mechanism of the formation of II in the reaction, which was carried out by Yates, will not be similar to that in our silver-salt catalyzed decomposition of α-diazoacetophenone, because both experimental conditions are quite different.[*4]

In the silver-salt catalyzed decomposition, the α-diazoacetophenone is converted, at first, to phenylketene (Eq.(4)) as has been reported previously.[7]

$$\underset{\text{(I)}}{PhCOCHN_2} \xrightarrow[-N_2]{\text{catalyst}} \underset{\text{(X)}}{PhCH{=}C{=}O} \qquad (4)$$

The presence of ketene intermediate (X) is also confirmed by the isolation of a trace of phenylacetic acid, which is produced by the reaction between phenyketene (X) and water. The ketene will then add with its double bond to another molecule of α-diazoacetophenone (I). In general, the addition of diazoketones to the carbon-carbon double bond of unsaturated compounds takes place in two paths (A) and (B):



(5)

(6)

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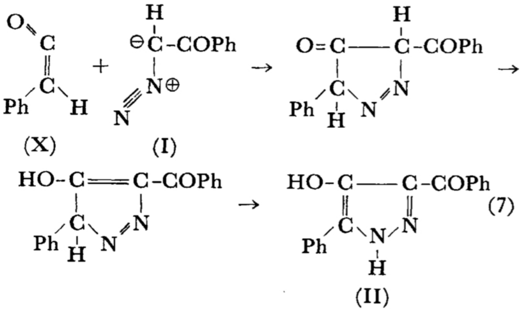
[20] M. Takebayashi, T. Ibata and H. Kohara, unpublished.

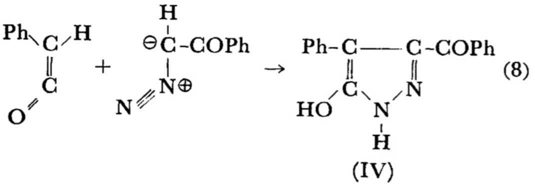
[*4] As is shown in the Experimental section, consumption of the diazoketone in the reaction mixture was confirmed by the IR spectra before the alkaline extraction. Moreover, the shaking of a benzene solution of I with 4 N sodium hydroxide solution at room temperature in an extracting funnel gave yellowish color to the alkaline layer, but no II was obtained.

For example, the formation of 3,4,5-tribenzoyl-2-pyrazoline (XI)[21] by the reaction of *trans*-1,2-dibenzoylethylene with α-diazoacetophenone and that of pyrazoline derivative (XII)[22] by the reaction of ethyl α-isopropylacrylate with diazoacetone have been recognized to proceed according to the path (A). However, the reaction between ketenes and diazoketones to give pyrazole derivatives has not been reported yet.

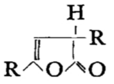
In the present decomposition, the reaction of phenylketene with the diazoketone takes place in a type of 1,3-dipolar cyclo-addition according to the path (A), followed by the enolization and proton shift, to give the product (II) as is shown in Eq. (7).*5

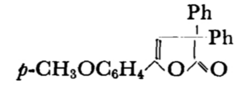


The absence of the isomer (IV) in the reaction products suggests that the direction of addition does not submited to the Eq. (8).



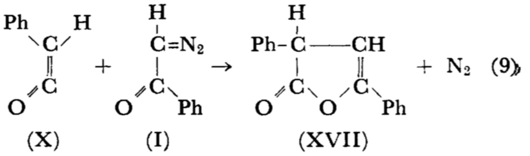
On the other hand, γ-enol-lactones, such as 3,5-di-*t*-butyl-1,2-dihydrofurane-2-one (XIII, R=*t*-Bu),[11] 3,5-diphenyl-1,2-dihydrofurane-2-one (XIII, R=Ph)[13] and 3,3-diphenyl-5-*p*-anisyl-1,2-dihydrofurane-2-one (XIV),[25,26] have been obtained by the photochemical decomposition of diazomethyl-*t*-butylketone, by the thermal decomposition of α-diazoacetophenone, and by the reaction of diazomethyl-*p*-methoxyphenylketone with diphenylketene, respectively.

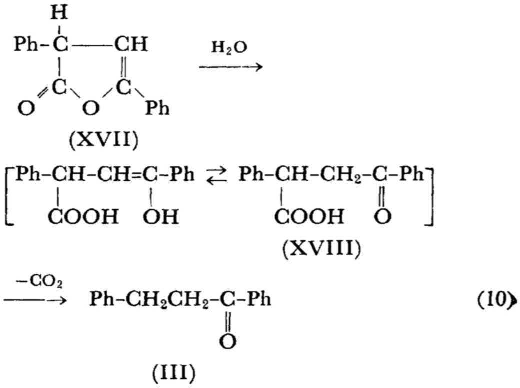

(XIII)


(XIV)

The formation of these compounds is explained by the interaction of a ketene intermediate and another molecule of diazoketone according to the path (B).*6

Then, the formation of β-phenylpropiophenone (III) will be elucidated as follows: The phenylketene (X) adds to unreacted α-diazoacetophenone to give γ-enol-lactone (XVII) according to the path (B). When the enol-lactone (XVII) was hydrolyzed, the α-phenyl-β-benzoylpropionic acid (XVIII) produced will be converted to β-phenylpropiophenone (III) by decarboxylation.





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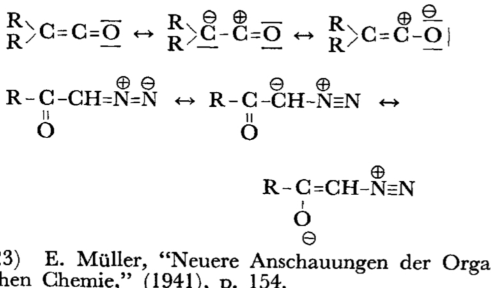
[21] J. Clark and P. Yates, *J. Org. Chem.*, **27**, 286 (1962).

[22] M. S. Muthanna and P. C. Guha, *Chem. Ber.*, **71**, 2665 (1938).

*5 The resonance structures of ketenes[23] and diazoketones[24] are shown as follows, respectively.



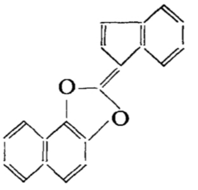
[23] E. Müller, "Neuere Anschauungen der Organischen Chemie," (1941), p. 154.

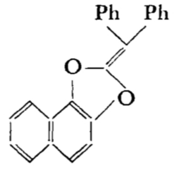
[24] D. J. Cram and G. S. Hammond, "Organic Chemistry," MacGraw-Hill, New York (1959) p. 496.

[25] A. S. Kende, PhD. Thesis, Harvard, 1956.

[26] A. S. Kende, *Chem. & Ind. (London)*, **1956**, 1053.

*6 Besides, the addition of diazoketones to the carbonyl double bond of ketenes also has been reported. For example, the thermal decomposition of *o*-napthoquinonediazide[12] and the reaction of the quinonediazide with diphenylketene[12,27] afford XV and XVI, respectively.


(XV)



(XVI)

[27] W. Ried and R. Rietrich, *Ann.*, **666**, 135 (1963).

If the formation of β-phenylpropiophenone (III) proceeds by the following free radical mechanism, acetophenone and carbon monoxide must be produced during the reaction.

$$\underset{\mathrm{(I)}}{\mathrm{PhCOCHN_2}} \xrightarrow{\mathrm{cat.}} \underset{\mathrm{(XIX)}}{\mathrm{PhCOCH:}} + \mathrm{N_2} \qquad (11)$$

$$\underset{\mathrm{(XIX)}}{\mathrm{PhCOCH:}} + \mathrm{S\text{-}H} \rightarrow \mathrm{PhCOCH_2\cdot} + \mathrm{S\cdot} \qquad (12)$$

$$\mathrm{PhCOCH_2\cdot} + \mathrm{S\text{-}H} \rightarrow \underset{\mathrm{(XX)}}{\mathrm{PhCOCH_3}} + \mathrm{S\cdot} \qquad (13)$$

$$\mathrm{PhCOCH_2\cdot} + \mathrm{PhCH{=}C{=}O} \rightarrow \mathrm{PhCOCH_2\dot{C}HPh} + \mathrm{CO} \qquad (14)$$

$$\mathrm{PhCOCH_2\dot{C}HPh} + \mathrm{S\text{-}H} \rightarrow \underset{\mathrm{(III)}}{\mathrm{PhCOCH_2CH_2Ph}} + \mathrm{S\cdot} \qquad (15)$$

(S-H: benzene, triethylamine, *etc.*)

However, no acetophenone (XX) was obtained, and no peak of carbon monoxide was observed in the gas chromatogram of gaseous products. Moreover, *cis*- and *trans*-1,2-dibenzoylethylene, which should be produced in the reaction of benzoylcarbene (XIX) and diazoacetophenone (I), were not recognized in the reaction products. Therefore, the free radical mechanism is not suitable for the formation of β-phenylpropiophenone (III). The mechanism will be discussed in detail compared with that of photolysis of diazoketone.

Experimental*7

Materials. *The Substituted and Unsubstituted α-Diazoacetophenones* used in this investigation were prepared by the reaction of the corresponding acid chlorides with diazomethane according to the method of Newman and Beal.28) An ether solution of benzoyl chloride was added dropwise to the ether solution of a small excess of diazomethane and an equivalent amount of triethylamine below 0°C with vigorous stirring. After the reaction mixture was allowed to stand overnight at room temperature, the precipitated triethylamine hydrochloride was filtered off. The filtrate was washed with water, saturated sodium bicarbonate, and water successively, and drived over anhydrous magnesium sulfate. The solvent was removed *in vacuo* and yellowish residue was collected. Several recrystallizations from ligroin or benzene gave pale yellow crystals. The melting points of diazoacetophenone were shown below:

unsubstituted: 47.5—48.0, p-$\mathrm{CH_3}$: 52.0—52.8,
p-$\mathrm{CH_3O}$: 87.5—88.5, p-$\mathrm{NO_2}$: 118.0—119.0°C

The diazoacetophenones obtained were stored in a dark place to prevent the decomposition by diffused light.

Benzene and Triethylamine were redistilled over metallic sodium to remove a trace of water dissolved in these materials.

The Silver Benzoate was prepared by the reaction between an equivalent molar amount of silver nitrate and sodium benzoate as has been reported previously.7) The silver benzoate produced was collected on a hot-funnel, washed several times with hot water to remove sodium benzoate and benzoic acid, dried and stored in a dark place.

General Procedure. A solution of silver benzoate (0.5 g, 2.2 mmol) in 5 m*l* of triethylamine was added at a time to the solution of 5.0 g (33 mmol) of α-diazoacetophenone dissolved in 20 m*l* of benzene, which has already been deoxygenated by bubbling of nitrogen gas. The evolution of nitrogen began at once, and the mixture gradually turned to dark-brown. The reaction mixture was maintained at 50°C as long as the gas evolution was continued. After about 60—70% of theoretical amount of nitrogen was evolved, the silver-amine catalyst was added furthermore. However, no nitrogen was generated. The reaction mixture was allowed to stand overnight at room temperature, and the precipitated silver metal was filtered off. The IR spectra of the benzene solution have no characteric absorption band of diazoketone at 2120 $\mathrm{cm^{-1}}$ region. The precipitate was washeds everal times with each 10 m*l* of benzene. The combined benzene solution was further diluted with benzene up to 100 m*l*, and extracted twice with 20 m*l* of a saturated sodium bicarbonate solution. The benzene solution was furthermore extracted several times with 20 m*l* of 4 N sodium hydroxide solution until alkaline layer showed no reddish color. The sodium bicarbonate solution was acidified with 6 N hydrochloric acid. The precipitate produced was extracted with ether. On evaporation of ether, white crystals were obtained yielding 0.10 g. The IR spectra indicate that the crystalline product is a mixture of benzoic acid and a trace of phenylacetic acid. After several recrystallizations from petroleum benzine, the IR spectra and the melting point (122—123°C) were completely consistent with authentic benzoic acid.

The sodium hydroxide solution was acidified with concentrated hydrochloric acid with stirring in the presence of ice. A pale yellow powder was obtained, mp 209.5—210.5°C (from ethanol), yield 1.70 g (38%).

Found: C, 72.82; H; 4.79; N, 10.30%. Calcd for $\mathrm{C_{16}H_{12}N_2O_2}$: C, 72.71; H, 4.58; N, 10.60%.

This compound showed wine-red color in aqueous solution of sodium hydroxide, decolorized alkaline solution of potassium permanganate, and converted an alcoholic solution of ferric chloride to dark-green. The chemical properties and the absorption spectrum data of IR (KBr disk, 3350 (m), 3250 (s), 1625 (s), 910 (s) $\mathrm{cm^{-1}}$) and UV ($\lambda_{max}^{\mathrm{EtOH}}$ 276 mμ, log ε 4.51: 287 mμ, log ε 4.33) were in accord with those of 3-benzoyl-4-hydroxy-5-phenyl pyrazole (II) reported by Yates.14)

The benzene layer was distilled under diminished pressure into two fractions (bp 130°C/1 mmHg, bp 130°C/2 mmHg). The low boiling fraction was found to be a mixture of two components containing carbonyl groups by means of gas chromatography,*8 but their structure

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*7 All melting and boiling points are uncorrected. Infrared spectra were obtained with the Hitachi EPI-S2 model spectrophotometer. The NMR spectra were determined with the Varian Associates model A-60 instrument. Chemical shifts are given in τ units using tetramethylsilane as an internal standard. Gas chromatographic measurement was carried out using a Yanagimoto Gas Chromatograph model GCG-3DH.

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

*8 The experimental conditions are as follows: carrier gas, $\mathrm{H_2}$ 65 m*l*/min at 200°C: 2 meter column packed with Apiezone Grease L; retention time, 46 min and 52 min.

was not determined because of their low yields. The high boiling fraction was crystallized after being left on standing in a refrigerator for several days. Several recrystallizations from petroleum ether (bp 55—60°C) gave white plates, $C_{15}H_{14}O$, 71.0—72.0°C, yield 13%. The IR absorption spectra (KBr, 1680 (s), 1595 (m) cm^{-1}) of this compound (III) showed the presence of carbonyl and phenyl groups. The NMR spectra of (III) in carbon tetrachloride solution showed absorption bands at 2.00—2.70 τ (multiplet, 5H, phenyl-H bonding to carbonyl group), at 2.83 τ (singlet, 5H, phenyl-H bonding to methylene), at 6.95 τ (A_2B_2type of quasi-quartet, 4H, $-CH_2CH_2CO-$). The melting points and the elemental analyses of the oxime (mp 83.0—84.0°C, lit. mp 83.5°C,[17] $C_{15}H_{15}NO$), the 2,4-dinitrophenylhydrozone (mp 179—181°C, lit. 182—183°C,[18] $C_{21}H_{18}N_4O_4$) and the semicarbazone (mp 144—145°C, lit. mp 144.0—144.8°C,[19] $C_{16}H_{17}N_3O$) derived from this compound are consistent with those of β-phenypropiophenone (III)[17-19]

The Beckmann Rearrangement of the Oxime (VI). The oxime (VI) (0.50 g) was treated with 2.0 g of phosphorus pentachloride in 50 m*l* of ether for 10 hr at room temperature. After quenched the reaction mixture with 10 m*l* of water, the ether solution was treated with 10 m*l* of saturated sodium bicarbonate solution, and the ether layer was dried over anhydrous magnesium sulfate. On evaporation of ether, white crystals were obtained, mp 124.5—125.0°C (from petroleum benzine), yield 0.45 g. This product showed positive Beilstein test. IR (KBr): 3240, 1660, 1605, 1550, 1325 cm^{-1}.

Found: C, 69.80; H, 6.18; N, 5.08; Cl, 13.74%. Calcd for $C_{15}H_{14}NOCl$: C, 69.36; H, 5.43; N, 5.39; Cl, 13.65%.

This product corresponds to α-chloro-β-phenylpropion anilide (VII), lit.[29] mp 125°C.

Alkali Catalyzed Hydrolysis of the Amide (VII). This amide (VII) (0.12 g) was hydrolyzed with an aqueous alcoholic solution of potassium hydroxide for 3 hr. After evaporating alcohol *in vacuo*, the reaction mixture was extracted twice with 10 m*l* of ether. On acidification of the alkaline solution, 0.04 g of white crystals were obtained, mp 134.5—135.0°C. The IR spectra of this product were closely agreed with those of authentic cinnamic acid, and the mixed-melting point test showed no depression. The ether layer and the acid layer gave no product besides resinous matter.

Acid Catalyzed Hydrolysis of the Amide (VII). The amide (VII) was hydrolyzed with an ethanol solution of hydrochloric acid (ethanol, 10 m*l*; c.HCl, 5 m*l*; H_2O, 5 m*l*) for 15 hr. The reaction mixture was turned violet *via* pink color. After evaporation of alcohol, 20 m*l* of water was added. The acidic and neutral substances in the reaction mixture were eliminated by the extraction with ether, and then the aqueous acidic solution was made basic with sodium hydroxide. The oily product produced was extracted three times with 20 m*l* of ether, and an excess of benzoyl chloride was added to the ether solution after drying with anhydrous magnesium sulfate. After being left on standing overnight at room temperature, the reaction mixture was washed with sodium bicarbonate solution to remove unreacted benzoyl chloride, and then dried. By evaporation of ether, 0.20 g of white crystals were obtained, mp 162°C (from ethanol and water). The IR spectra and melting point were closely consistent with authentic benzanilide. The IR and NMR spectra of the ketone-(III) were also superimposed completely with those of authentic β-phenylpropiophenone, which prepared by the reduction of benzalacetophenone by zinc powder and acetic acid.[30] The mixed melting point test also showed no depression.

Preparation of β-Phenylpropiophenone (III). An acetic acid (50 m*l*) solution of benzalacetophenone*[9] (10 g, 0.05 mol) was refluxed with 6.5 g (0.10 g atom) of zinc powder for 8 hr. After cooling, unreacted zinc was filtered off, and the solvent was distilled off *in vacuo* giving rise to β-phenylpropiophenone, bp 145°C/3 mmHg, mp 71.0—72.0°C.

Silver Benzoate-Catalyzed Decomposition of *p*-Methyl-α-diazoacetophenone in Benzene Solution. The reaction was carried out using 5.0 g of diazoketone, 0.60 g of silver benzoate, and 4.0 m*l* of triethylamine in 40 m*l* of benzene at 40°C, and the reaction mixture was treated with sodium bicarbonate and sodium hydroxide, successively. From the sodium bicarbonate solution, a small amount of benzoic acid was obtained, while *p*-methylphenylacetic acid was not detected by the measurement of the IR spectra. From the sodium hydroxide solution, 1.20 g (26%) of yellow crystals were obtained, mp 251.0—252.0°C. IR (KBr); 3350, 3260, 1605, 907 cm^{-1}.

Found: C, 73.89; H, 5.55; N, 9.53%. Calcd for $C_{18}H_{16}N_2O_2$: C, 73.95; H, 5.52; N, 9.58%.

These data and chemical properties suggest that the product is 3-*p*-toluyl-4-hydroxy-5-*p*-tolylpyrazole. From the benzene layer, 0.50 g (12%) of white needles were obtained, mp 64.5—65.5°C. IR (KBr), 1680, 1515, 1270, 1180, 800 cm^{-1}. NMR (in CCl_4), 2.25 τ and 2.87 τ (symmetric doublet, 4H, aromatic-H bonding to carbonyl group), 3.04 τ (singlet, 4H, aromatic-H bonding to methylene), 7.00 τ quasi-quartet of A_2B_2type, 4H, $-CH_2CH_2CO-$), 7.64 τ (singlet, 3H, *p*-CH_3) and 7.74 τ (singlet, 3H, *p*-CH_3). The data show that this product is β-*p*-tolyl-*p*-methylpropiophenone.

Silver Benzoate Catalyzed Decomposition of *p*-Methoxy-α-diazoacetophenone. The reaction was carried out using 5.0 g (0.029 mol) of diazoketone, 0.60 (0.0026 mol) of silver benzoate and 5.0 m*l* of triethylamine in 40 m*l* of benzene at 40°C. The reaction mixture was treated as described above. From sodium bicarbonate solution, 0.17 g of an yellow precipitate was obtained. The IR spectra showed that the precipitate was a mixture of benzoic acid and a trace of *p*-methoxyphenylacetic acid with undecided yellow compounds. Recrystallization of the precipitate gave benzoic acid. From the hydroxide solution, pale yellow crystals were obtained on acidification, mp 207.0—208.0°C (from ethanol), yield 0.55 g (12%). IR (KBr), 3350, 3250, 1620, 910 cm^{-1}.

Found: C, 66.61; H, 5.24; N, 8.73%. Calcd for $C_{18}H_{16}N_2O_4$: C, 66.66; H, 4.97; N, 8.64%.

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[29] A. N. Nesmeyanov, V. N. Kost, T. T. Vasil'eva and R. Kh. Freidlina, *Izvest. Akad. Nauk. SSSR., Otdel. Khim. Nauk.* **1958**, 152. (*Chem. Abstr.*, **1958**, 12756a).

[30] N. C. Deno and J. D. Johnson, *J. Org. Chem.*, **17**, 1466 (1952).

*[9] The benzalacetophenone was prepared by the alkali catalyzed reaction of benzaldehyde and acetophenone in ethanol. "Organic Syntheses," Coll. Vol I p. 78, (1948).

These results and the chemical properties show that this product is 3-*p*-anisoyl-4-hydroxy-5-*p*-anisylpyrazole. From the benzene layer, white needles were obtained, mp 84.0—85.0°C, yield 0.86 g (19%). IR (KBr), 1700, 1510, 1250, 1180, 820 cm^{-1}.

Found: C, 75.38; H, 6.73%. Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71%.

From these results, this compound was assigned to β-*p*-anisyl-*p*-methoxypropiophenone. Another fraction of the benzene layer (bp 170°C/1 mmHg) (0.51 g) gave no detectable product.

Silver Benzoate Catalyzed Decomposition of *p*-Nitro-α-diazoacetophenone. The reaction was carried out using 5.0 g (0.029 mol) of diazoketone, 1.2 g (0.0052 mol) of silver benzoate and 5.0 m*l* of triethylamine in 80 m*l* of benzene at 50°C, and the reaction products were treated as described above. From the sodium bicarbonate solution, a small amount of benzoic acid and *p*-nitrophenylacetic acid were obtained. On acidification of the sodium hydroxide solution, 1.2 g (26%) of a yellow precipitate was obtained. This substance could not be purified by recrystallization because of its extremely low solubility in most organic solvents. mp>300°C. IR (KBr), 3350, 1730, 1515, 1350 cm^{-1}.

Found: C, 55.77; H, 3.56%. Calcd for $C_{16}H_{10}N_4O_6$; C, 54.24; H, 2.85%.

Although the analytical data do not agree with the calculated values, the chemical properties and the IR spectra resemble to those of (II). This product is also thought to be a *p*-NO_2-substituted pyrazole derivative of type (II).

The authors wish to express their hearty thanks to Mr. Y. Kawanishi for his experimental aid. This work has been supported in part by a grant-in-aid for Scientific Research from the Ministry of Eductation.