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Reactions of Diazoketones in the Presence of Metal Chelates. III. Reactions with Carbonyl Compounds[*1]

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The reaction of α-diazoacetophenone with carbonyl compounds such as benzaldehyde, acetophenone and *p*-phenylacetophenone, has been studied in the presence of bis(acetylacetonato) copper (II). The reaction gave the corresponding tetrahydrofurans and dioxolanes accompanied by some by-products derived from benzoylcarbene. The mechanism of the reaction has been discussed in terms of an intermediate with a structure of betaine type, produced by the reaction of a ketocarbene-metal chelate complex with carbonyl compounds.

In previous papers,[1),2)] we reported that the reactivity of α-diazoacetophenone (I) toward alcohols could be modified by bis(acetylacetonato)copper (II) to give alkoxyacetophenones, instead of alkyl phenylacetate, and that the reaction with *cis*- and *trans*-stilbenes afforded the stereospecific addition products of benzoylcarbene to the double bond of these olefinic compounds. We also pointed out that the catalyzed reaction of α-diazoacetophenone with acetone gave mainly an enol-ether[3)] when copper powder was employed as a catalyst.[4)] The mechanism of these reactions could be explained by assuming the intermediacy of a ketocarbene-copper chelate complex (II).

This paper deals with the copper chelate-catalyzed reaction of α-diazoacetophenone with aromatic carbonyl compounds such as benzaldehyde, acetophenone and *p*-phenylacetophenone.

[*1] Presented in part at the Symposium of Organic Reaction Mechanism, Yamagata, October, 1968.

1) M. Takebayashi, T. Ibata, H. Kohara and Bu H. Kim, This Bulletin, **40**, 2392 (1967).

2) M. Takebayashi, T. Ibata, H. Kohara and K. Ueda, *ibid.*, **42**, 2938 (1969).

3) M. Takebayashi, T. Ibata and H. Kohara, Symposium of Organic Reaction Mechanism, Tokyo, October, 1966.

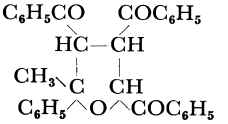
4) M. S. Kharasch, T. Rudy, W. Nudenberg and G. Buchi, *J. Org. Chem.*, **18**, 1030 (1953).

Results and Discussion

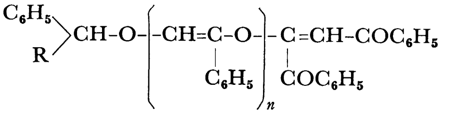
The following two kinds of methods, A and B, were adopted for the copper chelate-catalyzed reaction of α-diazoacetophenone with carbonyl compounds. A. Dropwise addition method: A benzene solution of α-diazoacetophenone was added dropwise to a solution of a carbonyl compound and bis(acetylacetonato) copper (II) (Cu(acac)$_2$) in benzene at 80°C during the course of 2 hr under stirring. B. Mixed method: A mixture of α-diazoacetophenone, Cu (acac)$_2$ and a carbonyl compound was warmed gradually under an atmosphere of nitrogen.

Reaction of α-Diazoacetophenone with Acetophenones. In method A, 2-methyl-2-phenyl-3,4,5-tribenzoyltetrahydrofuran (III, 29%) and an oligomer (IVa, 44%) of benzoylcarbene were obtained as a by-product besides α-hydroxyacetophenone (V, 1%). In method B, however, 2,4-dimethyl-2,4-diphenyl-5-benzoyl-1,3-dioxolane (VIa, 7%) was produced accompanying small amounts of by-products such as V (1.7%), dibenzoylethane (VII, 1%) and a dilactone (VIII, 1%) in addition to III (8.3%) and IVa (10%).

The data of IR and NMR spectra indicate that the three benzoyl groups of III are oriented *trans* to each other, and that IVa is a linear oligomer consisting of 3—4 molecules of benzoylcarbene and one molecule of acetophenone.



(III)



$\begin{matrix}C_6H_5\\ R\end{matrix}\!>\!CH\text{-}O\text{-}\left(\text{-}CH{=}\underset{C_6H_5}{C}\text{-}O\text{-}\right)_n\text{-}\underset{COC_6H_5}{C}{=}CH\text{-}COC_6H_5$

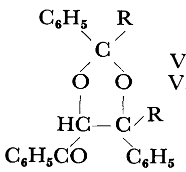
(IV)

n: 1—3 IVa: $R{=}CH_3$, IVb: $R{=}H$

IVc: $R{=}OCH_3$

$C_6H_5COCH_2OH$

(V)



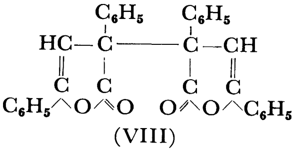
VIa: $R{=}CH_3$

VIb: $R{=}H$

(VI)

$C_6H_5COCH_2CH_2COC_6H_5$

(VII)

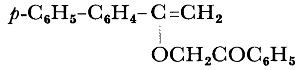


(VIII)

When *p*-phenylacetophenone was employed instead of acetophenone, the reaction (method B) gave *cis*- and *trans*-dibenzoylethylenes (IX, 1.2% and X, 6.2%), formal dimers of benzoylcarbene, and an oligomer (IVa, 12%) with a small amount (—1%) of an enol-ether (XI). However, neither dibenzoylethane, tetrahydrofuran nor dioxolane derivatives were obtained, in contrast to the case of acetophenone.

$C_6H_5COCH{=}CHCOC_6H_5$

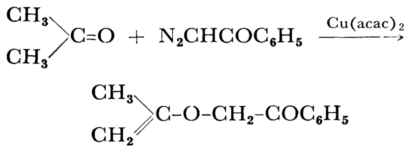
(IX, X)



$p\text{-}C_6H_5\text{-}C_6H_4\text{-}\underset{OCH_2COC_6H_5}{C}{=}CH_2$

(XI)

The formation of enol-ether (XI) is noteworthy though the yield is very low, because such enol-ethers have been scarcely obtained in the reactions with aromatic ketones. Enol-ethers corresponding to XI have been obtained in the reactions with aliphatic and alicyclic ketones such as acetone and cyclohexanone.[3]



$$\begin{matrix}CH_3\\ CH_3\end{matrix}\!>\!C{=}O + N_2CHCOC_6H_5 \xrightarrow{Cu(acac)_2} \begin{matrix}CH_3\\ CH_2\end{matrix}\!\geqslant\!C\text{-}O\text{-}CH_2\text{-}COC_6H_5$$

(35%)

The reaction with substituted acetophenones will be discussed elsewhere in connection with the results obtained above.

Reaction of α-Diazoacetophenone with Benzaldehyde. In method A, the reaction gave *trans*-dibenzoylethylene (X, 4.8%), an oligomer (IVb, 6.7%) and a copolymer (XIII) of benzaldehyde and benzoylcarbene.

In method B, the reaction, contrary to method A, yielded 2,5-diphenyl-4-benzoyl-1,3-dioxolane (VIb, 2.3%), an oligomer (IVb, 9%) and two kinds of copolymers (XII and XIII) of benzaldehyde and benzoylcarbene. IR and NMR spectra showed that XII, major product, and XIII were rich in benzaldehyde- and benzoylcarbene-moieties, respectively. Both copolymers have one benzyl group at one end of polymer chain and one benzoyl group at the other end.

Ried and Omran[5] observed that the thermal reaction of *p*-methyl- and *p*-methoxy-α-diazoacetophenones with substituted benzaldehydes gave dioxoles (XIV) in 25—33% yield. However, no dioxole was detected in our catalytic reaction products. The results suggest that the mechanism of copper chelate-catalyzed reaction between α-diazoacetophenone and benzaldehyde is quite different from that of purely thermal reaction.

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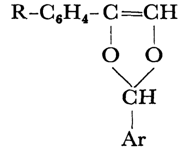
[5] W. Ried and J. Omran, *Ann. Chem.*, **673**, 120 (1964).

TABLE 1. EFFECTS OF THE AMOUNT OF METHYL BENZOATE

Method	$C_6H_5COCHN_2$ (I) (mol)	$C_6H_5COOCH_3$ (ester) (mol)	$\frac{[\text{Ester}]}{[\text{I}]}$	Product (%)		
				IX+X	IVc	VIII
A	0.034	0.17	5	1	89	0
	0.034	0.034	1	51	39	0
	0.034	0.007	1/5	83	12	0.16
	0.034	0	—	82	13	0.43
B	0.068	1.25	18	61	8.8	0



(XIV)

Reaction of α-Diazoacetophenone with Methyl Benzoate. In order to compare the behavior of esters to that of aldehydes and ketones, the reaction was carried out using methyl benzoate.

A large amount (89%) of oligomer (IVc) was produced accompanying a trace (1.1%) of *trans*-dibenzoylethylene (X) in method A, whereas dibenzoylethylenes (IX and X) (*cis*, 2.9% ; *trans*, 58%) were obtained as main products with a small amount (8.8%) of oligomer (IVc) in method B. Neither tetrahydrofurans nor dioxolanes were obtained in both cases.

The effect of the amount of methyl benzoate on the yields of dimers (IX and X) and oligomer (IVc) was studied. The results are summarized in Table 1.

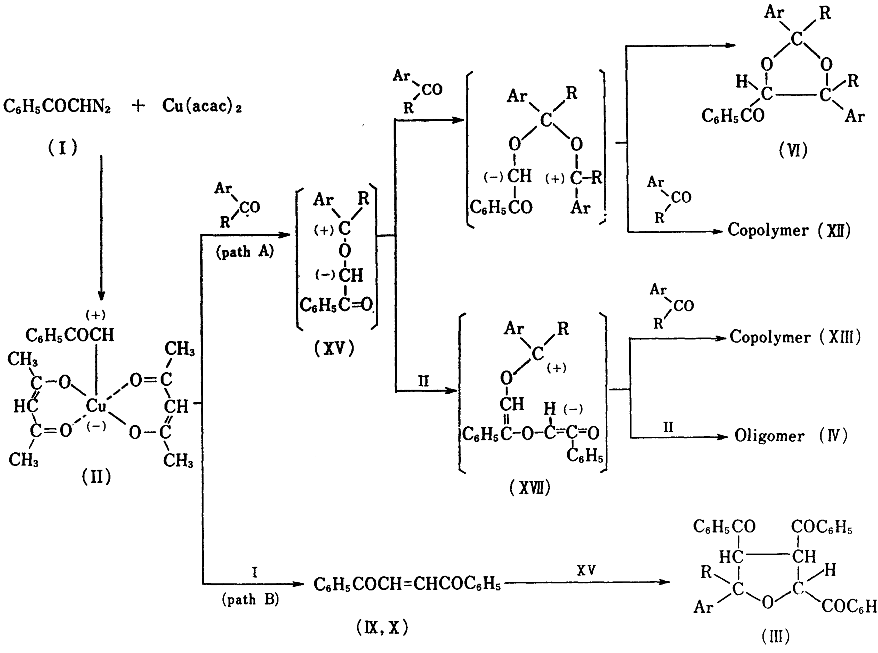
The data listed in Table 1 indicate that the yield of dimers (IX and X) of benzoylcarbene increases with decrease of the amount of methyl benzoate while that of oligomer decreases proportionally, and that dilactone (VIII) is produced when the ratio of the concentration of ester to I is low.

Mechanism

Diazoketone (I) reacts with the copper chelate to afford a ketocarbene-copper chelate complex (II).[1] The complex should react in two ways (path A and path B) according to the reactivity of carbonyl compounds employed.

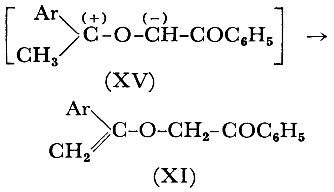
In the case of acetophenone and benzaldehyde, the reaction of path A takes place in preference to that of path B to produce another intermediate (XV) with a structure of betaine type, from which tetrahydrofuran (III), oligomers (IV), dioxolanes (VI) and copolymers (XII and XIII) are derived. In the case of *p*-phenylacetophenone and methyl benzoate, however, the reaction of path B proceeds preferentially to give dimers (IX and X). The mechanism of the formation of these products is summaried in Scheme 1.

The fact that the yield of III increases by the addition of dibenzoylethylene (X) to the reaction mixture supports the reaction path to give III.



Scheme 1

The migration of proton in the intermediate (XV) will give XI.



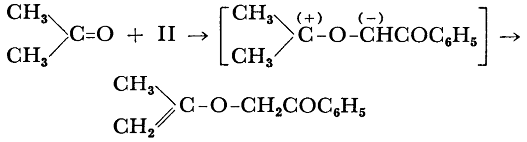
$$\left[\begin{matrix}\mathrm{Ar}\\ \mathrm{CH_3}\end{matrix}\!>\!\overset{(+)}{C}-O-\overset{(-)}{C}H-COC_6H_5\right] \rightarrow$$

(XV)

$$\begin{matrix}\mathrm{Ar}\\ \mathrm{CH_2}\end{matrix}\!\!\geqslant\!C-O-CH_2-COC_6H_5$$

(XI)

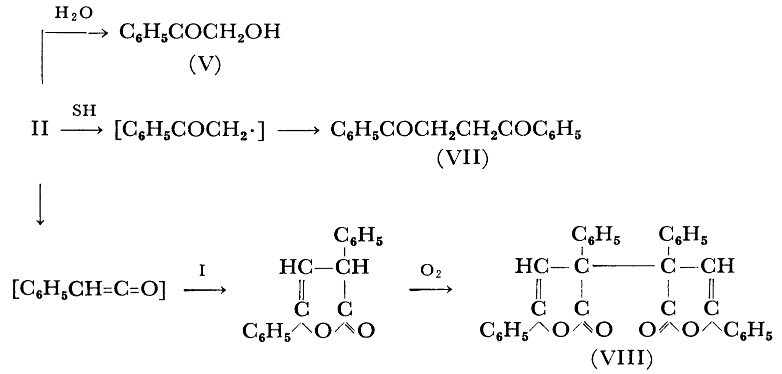
Generally, the proton migration hardly takes place in the intermediate from aromatic carbonyl compounds, since the intermediate (XV) is stabilized due to the resonance effect of aryl group.[6] However, the proton migration is expected to occur easily in the intermediate derived from aliphatic or alicyclic carbonyl compounds.



$$\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{matrix}\!>\!C{=}O + \mathrm{II} \rightarrow \left[\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_3}\end{matrix}\!>\!\overset{(+)}{C}-O-\overset{(-)}{C}HCOC_6H_5\right] \rightarrow \begin{matrix}\mathrm{CH_3}\\ \mathrm{CH_2}\end{matrix}\!\!\geqslant\!C-O-CH_2COC_6H_5$$

Apparently, the enol-ethers are produced by the insertion of benzoylcarbene to the O–H bond of enolated ketones. But this insertion mechanism can hardly explain the fact that the enol-ethers are obtained by the reactions with ketones having less enolic character such as acetone and cyclohexanone, and that no enol-ether is obtained by the reaction with more enolizable acetylacetone under the same conditions. Thus, the mechanism of the formation of enol-ethers can be explained by assuming an intermediate with the structure of betain type.

By-products such as α-hydroxyacetophenone (V), dibenzoylethane (VII) and dilactone (VIII), are derived from complex (II) as shown in Scheme 2. The formation of α-hydroxyacetophenone (V) arises from the reaction of complex (II) with a trace of water, because the yields of (V) vary from 1.7 to 10% according to the amount of water contained in the reaction mixture. If complex (II) abstracts a hydrogen atom from the solvent to give phenacyl radicals, recombination of the radicals takes place and affords dibenzoylethane (VII) as has been recognized in the cases of thermal[7] and copper chelate-catalyzed decomposition[3] of I in various solvents. When free benzoylcarbene is expelled from complex (II), the free carbene rearranges to the phenylketene and gives monolactone by reaction with I ; the monolactone is easily oxidized to afford dilactone (VIII).[8,9]



Scheme 2

Experimental

All melting and boiling points are uncorrected. The IR spectra were measured in potassium bromide disks for crystals and in liquid film for liquid samples, respectively, on a Hitachi Infrared Spectrometer, model EPI-S2. The NMR spectra were recorded at 60 Mc with a Varian Associates model A-60 Spectrometer, using tetramethylsilane as an internal standard. The UV spectra were taken on a Shimadzu Multipurpose Recording Spectrophotometer, model MPS-50L.

Material. *α-Diazoacetophenone* was prepared according to the method of Newman and Beal.[10] mp 47.5—48.0°C (lit,[10] mp 47.8—48.4°C).

Bis(acetylacetonato)copper (II) was prepared according to published directions.[11]

Benzaldehyde and *Acetophenone*. Commercial products were purified by distillation before use.

p-Phenylacetophenone,[12] mp 124.5—125.0°C (lit,[12] mp 121°C).

Reaction of I with Acetophenone (Method A). A solution of 5.0 g (0.034 mol) of I in 50 m*l* of benzene was added drop by drop to a solution of 20.4 g (0.17 mol) of acetophenone and 0.05 g (3.8×10^{-4} mol) of Cu(acac)$_2$ in 100 m*l* of benzene at 80°C under stirring. The color

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[6] See also G. Heublein and P. Hallpap, *Tetrahedron Lett.*, **1968**, 340.

[7] H. Staudinger, *Ann. Chem.*, **356**, 51 (1912).

[8] M. Takebayashi, T. Ibata, H. Kohara and M. Hamaguchi, *Sci. Rep. Osaka Univ.*, **17**, 7 (1968).

[9] P. Yates and T. J. Clark, *Tetrahedron Lett.*, **1961**, 435.

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

[11] H. S. Booth, " Inorganic Syntheses," Vol. 2, McGraw-Hill, Inc., New York, N.Y., p. 14 (1946).

[12] L. M. Long and H. R. Henze, *J. Amer. Chem. Soc.*, **63**, 1939 (1941).

of the reaction mixture turned dark brown with evolution of nitrogen. After the reaction was over, the reaction mixture was fractionated under a reduced pressure. The distillate (A) boiling at 60—90°C/1 mmHg crystallized at room temperature. The fractional recrystallization of A using light petroleum gave a trace of benzoic acid and 0.05 g (1%) of α-hydroxyacetophenone (V), mp 86.0—87.0°C (mp 86.0—87.0°C[13]).

Found: C, 69.99; H, 5.68%. Calcd for $C_8H_8O_2$: C,70.57; H, 5.92%. IR (KBr disk): 3380, 1685, 1405 and 1110 cm^{-1}.

The distillation residue (B) was dissolved in a mixture of benzene and *n*-heptane and allowed to stand for 2 days. A dark red solid (B–1) was isolated from the solution, and red oily substance (B–2) was separated from the filtrate by concentration. Recrystallization of B–1 from benzene-*n*-hexane gave 1.55 g (29%) of 2-methyl-2-phenyl-3,4,5-tribenzoyltetrahydrofuran (III), mp 167.0—168.0°C.

Found: C, 81.18; H, 5.44%. Calcd for $C_{32}H_{26}O_4$: C, 80.99; H, 5.52%. The NMR spectrum is shown in Fig. 1; UV: $\lambda_{\max}^{\text{EtOH}}$ 2683 Å (ε 1770) and 2734 Å (ε 5200). IR: 1685, 1450, 1280, 1245, 1215 and 985 cm^{-1}.

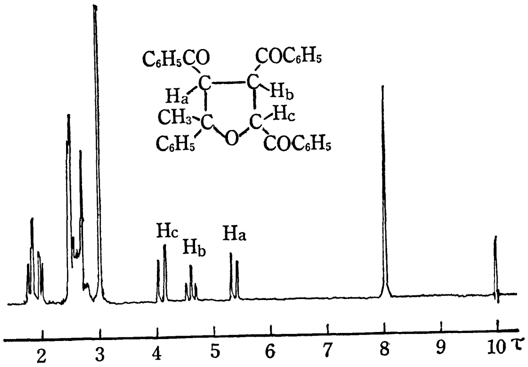

Fig. 1. NMR spectrum of III.

When a benzene solution of oily substance (B–2) was poured into *n*-hexane, a brown solid was obtained. This product did not crystallize from any solvents, but the data of IR and NMR spectra indicated that the product was an oligomer of benzoylcarbene with one molecule of acetophenone (IVa), and that the oligomer has a skeleton of vinyl ether. The yield of oligomer was 1.7 g (44%).

Found: C, 80.75; H, 5.38%. Calcd for $C_{32}H_{26}O_4$ ($C_6H_5COCH_3$+3 C_6H_5COCH:): C, 80.79; H, 5.52%. UV (in dichloromethane): $\lambda_{\max}$ 2480 Å (ε 14200) IR: 1640, 1445 and 1220 cm^{-1}. NMR: 2.65 τ (s, broad). Mol wt (Rast): Found, 490. Calcd for $C_{32}H_{26}O_4$, 474.5.

Reaction of I with Acetophenone (Method B). A solution of 5.0 g (0.034 mol) of I and 0.05 g (3.8× 10^{-4} mol) of Cu(acac)$_2$ in 150 g of acetophenone was warmed gradually under an atmosphere of nitrogen. By distillation of the reaction mixture under a reduced pressure after removal of unreacted acetophenone, a distillate (C) boiling at 60—85°C/0.1 mmHg and a tarry residue (D) were obtained. Fractional recrystallization of C from light petroleum gave a trace of benzoic acid and 0.076 g (1.7%) of α-hydroxyacetophenone (V).*2 Besides, 0.04 g (1%) of dibenzoylethane (VII), mp 147.0—148.0°C (lit,[14]) mp 140°C), was separated from the concentrated mother liquor after one week.

Found: C, 79.11; H, 5.85%. Calcd for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92%. IR: 1687, 1225, 990, 743 and 698 cm^{-1}. The distillation residue D was treated with benzene. A small amount of precipitate was collected by filtration. This precipitate did not dissolve in usual organic solvents. The IR spectrum was completely superimposable with that of dilactone (VIII, 1%) prepared by the photolysis of I in benzene solution.[8,9]

From the benzene layer, 0.39 g (10%) of oligomer (IVa) was separated out by adding *n*-heptane. Moreover, 0.45 g (8.3%) of tetrahydrofuran (III) was obtained from the mother solution after being left to stand for several days at room temperature. Evaporation of the solvent gave a yellow oil. The oil could not be distilled, but the substance was deduced to be 2,4-dimethyl-2,4-diphenyl-5-benzoyl-1,3-dioxolane (VIa, 0.88 g, 7%) by means of IR spectra.

Found: C, 81.85; H, 6.44%. Calcd for $C_{24}H_{22}O_3$: C, 81.42; H, 6.19%.

IR: 1690, 1450, 1370, 1270, 1100, 1060 and 1020 cm^{-1}.

Reaction of I with *p*-Phenylacetophenone (Method B). The reaction of I (5.0 g, 0.034 mol) with *p*-phenylacetophenone (8.24 g, 0.024 mol) was carried out by the mixed method in benzene solution (150 g) in the presence of Cu(acac)$_2$ (0.05 g, 3.8×10^{-4}mol). Unreacted *p*-phenylacetophenone was separated by adding ligroin to the reaction products, and the solvent was removed by distillation. The residue was treated with light petroleum to separate insoluble part (E) from soluble part (F). The insoluble part E was dissolved in cyclohexane at the reflux temperature, and was kept standing overnight at room temperature. 0.48 g (12%) of oligomer (IVa) was separated out from the solution, and 0.1 g (1%) of yellow needles of enol-ether (XI), mp 91.0—92.0°C, precipitated from the filtrate after one week at 10°C.

Found: C, 83.65; H, 5.64%. Calcd for $C_{22}H_{18}O_2$: C, 84.05; H, 5.64%. IR: 1680, 1655, 1295, 1263, 1018 and 960 cm^{-1}.

The bromination of enol-ether (XI) in CCl_4 gave its dibromide, mp 117.0—119.0°C.

Found: C, 57.60; H, 3.53%. Calcd for $C_{22}H_{18}O_2Br_2$: C, 55.84; H, 3.62%. IR: 1685, 1290 and 990 cm^{-1}.

The soluble part F was allowed to stand for several days at room temperature. A yellow solid (F–1) precipitated in preference to solid (F–2). The solid F–1 was recrystallized from light petroleum, and was identified as *trans*-dibenzoylethylene (X) in a good agreement with elemental analyses and IR spectra with the authentic sample; mp 111.0—112.0°C, yield 0.25 g (6.2%).

Found: C, 81.84; H, 5.12%. Calcd for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12%. UV: $\lambda_{\max}^{\text{EtOH}}$ 2608 Å (ε 19700).

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[13] L. Wolff, *Ann. Chem.*, **325**, 143 (1902).

*2 The yield of α-hydroxyacetophenone varied from 1.7 to 10% according to the amount of water contained in the acetophenone employed. When acetophenone was treated with anhydrous magnesium sulfate for one week at room temperature and then distilled, the yield was found to be 1.7%. If the treatment with anhydrous magnesium sulfate was omitted, the yield increased up to 10%.

[14] C. Grundman and H. Trischmann, *Ann. Chem.*, **536**, 29 (1938).

IR: 1655, 1600, 1450, 1325, 1295, 1194 and 1023 cm^{-1}.

The solid F–2 was purified by recrystallization from benzene-*n*-hexane, and was identified as *cis*-dibenzoylethylene (IX) by elemental analyses and UV, IR and NMR spectra; mp 136.0—137.0°C, yield 0.05 g (1.2%).

Found: C, 81.43; H, 4.99%. Calcd for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12%. IR: 1665, 1600, 1450, 1400, 1233 and 1015 cm^{-1}. UV: λ_{max}^{EtOH} 2608 Å (ε 26000).

NMR (12 CDCl$_3$): 2.89 (s, 2H), 2.7—2.5 (m, 6H) and 2.2—2.0 τ (m, 4H).

Reaction of I with Benzaldehyde (method B). The reaction of I (5.0 g, 0.034 mol) with benzaldehyde (150 g, 1.42 mol) was carried out in the presence of Cu(acac)$_2$ (0.05 g, 3.8×10^{-4} mol) by the mixed method. After removal of unreacted benzaldehyde by distillation, the residue was dissolved in hot benzene under heating, and a small amount of ligroin was added to the solution. A white precipitate (G–1) was separated out from the solution. The precipitate G–1 was dissolved again in benzene and poured into *n*-hexane under stirring. When the mixture was let to stand overnight, a white substance precipitated from the solution. The precipitate was collected by filtration, and was confirmed to be copolymer (XII) of benzaldehyde-benzoylcarbene, 4.8 g, mp 127°C. IR: 1690, 1450, 1100 and 710 cm^{-1}. UV (in dichloromethane): λ_{max} 2500 Å. NMR (in CDCl$_3$): 3.3—3.1 (m, 2H), 5.5—4.0 (m, 15H) and 4.0—2.1 τ (m, 85H).

The copolymer (XII) is so stable that no change was observed during the treatment with hot concentrated hydrochloric acid or 10%-sodium hydroxide solution.

To the filtrate was added *n*-heptane under heating and allowed to stand overnight. A black oily substance (G–2) separated out, and then a brown oil (G–3) precipitated by concentrating the filtrate. After evaporation of the solvent, the residue was dissolved in benzene. The benzene solution was let to stand for 3 days to give yellow substance (G–4). The oil G–2 was confirmed to be oligomer of benzoylcarbene with one molecule of benzaldehyde (IVb) by means of IR spectrum; yield 0.29 g (6.7%). IR: 1675, 1600, 1445, 1215 and 1020 cm^{-1}.

The oil G–3 was dissolved in methyl alcohol, and the solution was allowed to stand at room temperature to give a brown precipitate. The IR spectrum indicates that the precipitate is another copolymer of benzaldehyde-benzoylcarbene (XIII) 0.38 g, mp 68—73°C. UV (in dichloromethane): λ_{max} 2500 Å. IR: 1675, 1600, 1450, 1240 and 1100 cm^{-1}.

Recrystallization of the product G–4 from methyl alcohol gave white needles. The crystalline product was identified to be dioxolane (VIb), yield 0.26 g (2.3%); mp 167.0—168.0°C.

Found: C, 80.41; H, 5.49%. Calcd for $C_{22}H_{18}O_3$: C, 79.98; H, 5.49%. The NMR spectrum is shown in Fig. 2. UV: λ_{max}^{EtOH} 2600 A (ε 10400). IR: 1690, 1450, 1410, 1215, 1090, 1052 and 1010 cm^{-1}.

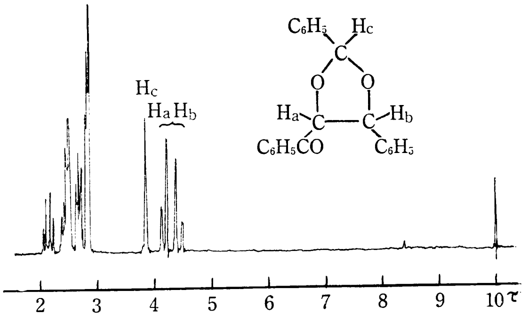

Fig. 2. NMR spectrum of VIb.

Reaction of I with Methyl Benzoate (Method B). The reaction of I (10.0 g, 0.068 mol) with methyl benzoate (150 g, 1.25 mol) in the presence of Cu(acac)$_2$ (0.05 g, 3.8×10^{-4} mol) was carried out by the mixed method. Unreacted methyl benzoate was removed by distillation. No distillate was obtained at 130°C under 0.1 mmHg. The fractional recrystallization of residue gave *cis*-dibenzoylethylene (IX) (0.5 g, 2.9%), *trans*-dibenzoylethylene (X) (4.8 g, 58%) and oligomer of benzoylcarbene with one molecule of methyl benzoate (IVc) (0.65 g, 8.8%).

Found: C, 78.30; H, 5.00%. Calcd for $C_{32}H_{26}O_6$: C, 78.35; H, 5.34%. IR: 1760, 1675, 1220 and 698 cm^{-1}.

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