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Reactions of Diazoketones in the Presence of Metal Chelates. II. Reactions with Olefinic Compounds^{*1}

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The reaction of α -diazoacetophenone with olefinic compounds, such as vinyl acetate, *cis*- and *trans*-stilbenes and cyclohexene, has been studied in the presence of bis(acetylacetonato)copper-(II). The reaction gave the corresponding cyclopropane derivatives, the addition products of benzoylcarbene to the double bond of olefinic compounds in good yields, accompanied by *cis*- and *trans*-dibenzoylethylenes, dibenzoylethane or dilactone. Addition of carbene was found to be stereospecific in the cases of *cis*- and *trans*-stilbenes. A mechanism has been advanced in which a ketocarbene-metal chelate complex is included as an intermediate of the reaction.

In a previous paper¹) we reported that the reaction of α -diazoacetophenone (I) with alcohols in the presence of metal chelates, such as bis(acetylacetonato)copper(II) and bis(acetylacetonato)nickel(II), gives the corresponding alkoxyacetophenones(II), and that the tertiary amines such as triethylamine, pyridine and quinoline, suppress the formation of the alkoxyacetophenones (II) and promote that of alkyl phenylacetates (IV) in proportion to the increase in the amount of amines added. The mechanism of the reaction has been explained as follows by assuming the intermediacy of a ketocarbene-metal chelate complex (III).





This paper deals with the reaction of the ketocarbene-metal complex with olefinic compounds. Stork and Ficini²) have studied the copper-catalyzed decomposition of 1-diazo-6-hepten-2-one, and obtained bicyclo[4.1.0]heptanone-2 as an intramolecular cyclo-addition product of olefinic ketocarbene. Thereafter, the intramolecular cycloaddition of olefinic ketocarbenes has been utilized for the formation of strained bicyclo- and tricyclocompounds.^{3,4}) On the other hand, studies of the intermolecular addition of ketocarbenes to carbon-carbon double bonds have recently been reported.^{5,6})

We studied the reaction of α -diazoacetophenone with olefinic compounds in the presence of bis(acetylacetonato)copper(II) in order to gain further insight on the carbenoid mechanism of copper-chelate-catalyzed decomposition of diazoketones.¹)

Results and Discussion

Reaction of α -Diazoacetophenone with Vinyl Acetate. The bis(acetylacetonato)coppercatalyzed decomposition of α -diazoacetophenone (I) was carried out in a large excess of vinyl acetate under a homogeneous condition. Exothermic reaction took place and an evolution of almost theoretical amount of nitrogen was observed. The reaction product was separated into two fractions by vacuum distillation.

By means of elemental analyses and IR and NMR spectra, the lower boiling fraction was confirmed to be a mixture of *cis*- and *trans*-1benzoyl-2-acetoxy-cyclopropanes (V) (1:6), the addition products of benzoylcarbene to vinyl acetate. The NMR spectra of the components are different from each other as shown in Figs. 1 and 2.

3) M. M. Fawzi and C. D. Gutsche, J. Org. Chem., 31, 1390 (1966), and references cited.

4) S. Masamune, J. Am. Chem. Soc., 86, 735 (1964).
5) W. Kirmse, "Carbene Chemistry," Academic

- Press, New York (1964), p. 132.
- 6) D. O. Cowan, M. Couch, K. R. Kopecky and G. S. Hammond, J. Org. Chem., 29, 1922 (1964).

^{*1} Part of this work was presented at the "Symposium of Organic Reaction Mechanism," Toyama, October, 1965.

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

²⁾ G. Stork and J. Ficini, J. Am. Chem. Soc., 83, 4678 (1961).



Fig. 1. NMR spectrum of Va.



Fig. 2. NMR spectrum of Vb.

One component is identified as cis-1-benzoyl-2acetoxy-cyclopropane (Va) and the other as *trans*-isomer (Vb) by the observation of their NMR spectra. The singlet signal of acetoxy proton of Va appears at higher field (8.16τ) than that of Vb (8.05τ) , and the $J_{\rm HaHb}$ coupling constant of Va (9 cps) is larger than that of Vb $(2.3 \text{ cps}).^{*2}$ The

^{*2} The coupling constants were measured by the spin-decoupling method. The *cis*-coupling constant of vicinal protons of cyclopropane ring is generally larger than the *trans*-coupling constant. The *trans*-coupling constant ($J_{\rm HaHb}$) of Vb was observed to be abnormally smaller than usual.⁷) The other coupling constants between protons of Va and Vb will be reported

elsewhere in detail.

^{*3} Decomposition of I in a large excess of vinyl acetate in the presence of catalytic amount of nickelocene was carried out and the same results as shown in the case of Cu(acac)₂ were observed, affording a mixture of Va and Vb in 44% yield.

yield of this isomeric mixture was 58 per cent of the theoretical amount calculated from $I.^{*3}$ The vpc analysis of the lower boiling fraction showed a very small peak at the retention time of 9.5 min, which became larger with the addition of authentic acetophenone. Further investigation of the presence of acetophenone in this fraction was not carried out.

The higher boiling fraction was a mixture of *trans*-1,2-dibenzoylethylene (VIb)⁸⁾ (5% yield) and a trace of 1,2-dibenzoylethane (VII).⁹⁾ The structure of VIb and VII was confirmed by the comparison of the melting points and IR spectra with those of the authentic samples.

 $PhCOCHN_2 + CH_2=CHOCOCH_3$ (I)

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Reaction of a-Diazoacetophenone with Cyclohexene. The reaction of I with cyclohexene in the presence of copper-salts to give 7-benzoylnorcarane (VIII) has been reported by Cowan *et al.*⁶) The decomposition of I in a large excess of cyclohexene at 75°C in the presence of $Cu(acac)_2$ gave a small amount (5%) of VII in addition to the main product VIII (51%). Product VIII was also found to be a mixture of *syn-* and *anti*isomers by elemental analyses, melting point test and IR absorption spectra of their 2,4-dinitrophenylhydrazones, although Cowan *et al.* had reported only one hydrazone of VIII.⁶)



Reaction of a-Diazoacetophenone with Stilbene and Diphenylacetylene. In the cases of the reactions of I with *cis*- and *trans*-stilbenes and

9) Ad. Claus, Ber., 20, 1375 (1887).

diphenylacetylene, the "dropwise addition method" was applied in order to avoid the formation of dimers of benzoylcarbene. In the case of *cis*stilbene, the cyclopropane derivative (IXa) was obtained in 19% yield, accompanied with dilactone $(X)^{10}$ and VII in 3.2 and 2.4% yield, respectively. The structure of X was assigned by the comparison of IR spectrum with that of the authentic sample obtained by the photolysis of I in a benzene solution.¹¹



The structural assignment of IXa was established by the IR and NMR spectra. The NMR spectrum of IXa has quasi-doublet signal of Ha at 6.74τ and quasi-triplet signal of Hb at 6.48τ in 2:1 area ratio as shown in Fig. 3.

This NMR pattern of cyclopropane ring protons agreed with that of calculated AB₂ type having coupling constant of 2.0 cps and chemical shift difference of 6.0 cps.¹²) The coupling constant of cyclopropane ring protons Ha and Hb of IXa, $J_{\rm HaHb}=5$ cps, has a normal value compared with those of usual *trans*-protons in cyclopropane derivatives.⁹)

The reaction of I with *trans*-stilbene gave an adduct (IXb), in 5 per cent yield besides the recovered *trans*-stilbene and X (1.5%).



The structure of IXb was established by means of

- 10) P. Yates and J. J. Clark, Tetrahedron Letters, 1961, 435.
- 11) M. Takebayashi, T. Ibata, H. Kohara and M. Hamaguchi, Sci. Rept., Coll. Gen. Ed. Osaka Univ., 17, 7 (1968).
- 12) K. B. Wiberg and B. J. Nist, "Interpretation of NMR Spectra," W. A. Benjamin, Inc., New York (1962), p. 15.

⁷⁾ F. A. Bovey, "NMR Data Tables for Organic Compounds," Vol. 1, Interscience, New York (1967), p. 3822.

⁸⁾ C. Grundmann and H. Trischmann, Ann., 536, 29 (1938).



Fig. 3. NMR spectrum of IXa.



Fig. 4. NMR spectrum of IXb.

elemental analysis and IR and NMR spectra (Fig. 4).

The sharp melting points of IXa and IXb and their thin-layer chromatograms suggest that they are not contaminated with each other and are chemically pure. The NMR spectrum of IXa has a singlet signal at 3.00τ corresponding to ten protons of two phenyl groups bonding directly to cyclopropane ring. On the other hand, the NMR spectrum of IXb has two singlet signals at 2.78 and 2.87τ attributed to two phenyl groups which are in a different magnetic state, and quasitriplet of one proton at 6.42τ and also quasi-doublet of two protons at 6.74τ of ABB' type. The orthoproton signal of benzoyl group of IXb appears at higher field than that of IXa.

These results indicate that the addition of this carbene complex (III) to stilbene proceeds stereo-specifically.

While the reaction of I with diphenylacetylene in a benzene solution gave no adduct of carbene to carbon-carbon triple bond, small amounts of VII and X (4.5%) were obtained.

Decomposition of α **-Diazoacetophenone in Inert Solvents.** When the catalytic decomposition of I was carried out by the "mixed method" in a benzene solution at 48°C, the adduct of carbene to benzene, *viz.*, a norcaradiene derivative, was not detected. However, *cis-* and *trans-*1,2-dibenzoylethylenes (VIa and VIb), the formal dimers of benzoyl-carbene, were obtained in the yields of 11.3 and 13.6 per cent, respectively.

In a chloroform solution, I also gave VIa and VIb in the yields 13.0 and 0.06 per cent, respectively, contrary to the result of Grundmann and Trischmann⁸) who obtained neither of these products.

In methyl benzoate, 57.0 per cent yield of VIa and 2.9 per cent yield of VIb were obtained by the "mixed method," while only a polymer of benzoylcarbene was produced by the "dropwise addition method."¹³)

Mechanism. From the results mentioned above, the catalytic reaction of α -diazoacetophenone with olefinic compound is also reasonably explained by assuming the copper-carbenoid intermediate (III) as well as the metal-chelate-catalyzed decomposition of I in alcohols.¹) Since no addition products to diphenylacetylene¹⁴) and to benzene were obtained, the reactivity of this carbenoid intermediate seems to be not so large.

The cis- and trans-1,2-dibenzoylethylenes (VI) may be formed by the reaction of I with carbenoid (III) in the case of "mixed method" where no substrate having enough reactivity to the carbenoid is present except I in the reaction system. Grundmann and Trischmann⁸) have reported that the copper-powder-catalyzed decomposition of I in various solvents gives trans-1,2-dibenzoylethylene (VIa). However, the isolation of cis-isomer has not been accomplished yet by the catalytic decomposition of α -diazoketones. The ratio of cisand trans-isomers largely depends upon the nature of the solvents.

On the other hand, dilactone (X) was observed in the reaction of I with cis- and trans-stilbenes and diphenylacetylene, which have no large reactivity toward III. In these cases, the concentration of substrate reacting with III is so small that a part of carbenoid (III) releases benzoylcarbene, which leads to phenylketene (XI) by concerted phenyl migration. The phenylketene reacts with I and finally affords dilactone as reported in the case of photolysis of I.¹¹) The release of benzoylcarbene from carbenoid (III) seems to be rather slow, since the yield of X is small (1.5-4%). This may be supported by the fact that the formation of esters, produced from phenylketene, is accelerated in alcohols by the addition of tertiary amines.1) The formation of 1,2-dibenzoylethane (VII) is explained by the dimerization of relatively stable phenacyl radical, which is formed by the hydrogen abstraction of the carbenoid from the solvents or substrates.

The mechanism of the formation of products obtained is summarized as follows:



Experimental

All melting and boiling points described in this paper were not corrected. The IR spectra were determined in potassium bromide disks for crystals or in liquid film for liquid samples, respectively, on a Hitachi Infrared Spectrophotometer, model EPI-S2. The NMR spectra were recorded at 60 Mc with a Hitachi High Resolution NMR Spectrometer, model R-20, using tetramethylsilane as an internal standard.

Materials. α -Diazoacetophenone was prepared from benzoyl chloride and diazomethane according to the method of Newman and Beal,¹⁵) and recrystallized several times from *n*-hexane, mp 47.5–48.0°C.

Bis(acetylacetonato)copper(II) was prepared according to published directions.¹⁶)

cis-Stilbene was prepared by the decarboxylation¹⁷) of α -phenylcinnamic acid in the presence of copper chromite in a quinoline solution, and purified by distillation, bp 108—110°C/5 mmHg.

trans-Stilbene was obtained by the reduction of benzoin¹⁸⁾ by zinc amalgam and hydrochloric acid, and was recrystallized from 95% ethanol, mp 123.5—124.0°C.

- 17) "Organic Syntheses," Coll. Vol. 4, p. 857 (1963).
- 18) Ibid, Coll. Vol. 3, p. 786 (1955).

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¹³⁾ M. Takebayashi, T. Ibata and K. Ueda, unpublished data.

¹⁴⁾ N. Obata and I. Moritani, This Bulletin, 39, 1975 (1966).

Diphenylacetylene was prepared by the oxidation of

¹⁵⁾ M. S. Newman and P. F. Beal, J. Am. Chem. Soc., 71, 1506 (1949).

¹⁶⁾ H. S. Booth, "Inorganic Syntheses," Vol. 2, McGraw-Hill, New York (1949), p. 14.

benzil dihydrazone using yellow mercuric oxide,¹⁹⁾ mp 60-61°C.

Cyclohexene was obtained by dehydration of cyclohexanol in the presence of catalytic amount of sulfuric acid,²⁰⁾ and dried over calcium chloride and purified by distillation before use.

Vinyl Acetate, Benzene and Chloroform. Commercial products were purified by distillation before use.

vinyl acetate bp 71.5-72.0°C benzene bp 79.5-80.0°C

chloroform bp 61.0-61.2°C

Reaction of *a*-Diazoacetophenone (I) with Vinyl Acetate in the Presence of Cu(acac)₂. A solution of 5.0 g (0.034 mol) of I and 0.1 g $(3.8 \times 10^{-4}$ mol) of Cu(acac)₂ in 150 ml of vinyl acetate was warmed gradually under an atmosphere of nitrogen. The evolution of nitrogen was observed at 48°C, and then the temperature rose to 55-56°C by exothermic reaction. Within 20 min an almost theoretical amount of nitrogen was evolved and the color of the mixture turned to dark-green with the evolution of nitrogen. After leaving the reaction mixture to stand for two hours more at 50°C, unreacted vinyl acetate was removed by distillation under ordinary pressure. The residue was fractionally distilled under reduced pressure and two fractions were obtained; bp 115-125°C/1 mmHg, and bp 160-172°C/1 mmHg.

The lower boiling fraction was further purified by distillation, bp $114-116^{\circ}C/1 \text{ mmHg}$.

Found: C, 70.63; H, 6.09%. Calcd for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92%.

IR (neat); 3050, 1750(ester), 1665(benzoyl), 1450 and 1230 cm⁻¹.

The gas chromatogram^{*4} of this fraction showed two main peaks of retention time 17.5 and 22.5 min in the area ratio of about 1:6. The former indicates *cis*-isomer (Va) and the latter *trans*-isomer (Vb).

The higher boiling fraction crystallized on standing at room temperature. The fractional recrystallization from light petroleum gave two substance. One was 0.24 g (5%) of yellow crystals and the other was a trace of colorless crystals. The yellow compound of melting point 107—109°C was identified as *trans*-1,2dibenzoylethylene (VIb) in good agreement with the IR spectrum and the melting point (mp 110°C) with the authentic sample⁸) prepared by the copper-bronze catalyzed decomposition of I.¹¹ The colorless crystalline compound, mp 147—148°C (from ethanol), was identified as 1,2-dibenzoylethane (VII) in agreement with elemental analysis data with C₁₆H₁₄O₂, and IR (KBr disk); 3025, 2900, 1675, 1590, 1220, 990, 775, 740 and 695 cm⁻¹.

Reaction of I with Cyclohexene in the Presence of Cu(acac)₂. A solution of 5.0 g (0.34 mol) of I in 150 ml of cyclohexene was decomposed at 75°C until nitrogen evolution was complete in the presence of 0.1 g $(3.8 \times 10^{-4} \text{ mol})$ of Cu(acac)₂ by the method described above. The reaction mixture was distilled under reduced pressure after removal of cyclohexene,

20) Ibid., Coll. Vol. 2, p. 14 (1950).

*4 Gas chromatographic measurement was carried out with a Yanagimoto Gas Chromatograph, model GCG-3DH, using a 3 m column packed with Apiezon Grease M. Temp. : 195°C; carrier gas: H₂, 80 cc/min. and 3.5 g of distillates was obtained, bp 124—140°C/ 1 mmHg. The elemental analysis data of this compound agreed with the calculated one for 7-benzoylnorcarane, $C_{14}H_{16}O$, after further distillation. IR (neat); 3050, 3020, 1450, 760, 700 cm⁻¹ (phenyl), 2940 2860, 1420 cm⁻¹ (aliphatic C-H) and 1675 cm⁻¹ (C=O). NMR (in CCl₄); 2.05—2.17 τ , (m), 2H, *o*-H in phenyl group: 2.5—2.75 τ , (m), 3H, *m*- and *p*-H in phenyl group: 7.55—7.70 τ , (m), 1H, methyne-H adjacent to benzoyl group: 7.9—8.4 τ , (broad d), 6H: 8.55—8.80 τ , (broad s), 4H.

The IR and NMR spectra showed no olefinic absorption bands. From these results this compound was identified as VIII. The 2,4-dinitrophenylhydrazone of VIII was derived from 1.0 g of VIII and 1.1 g of 2,4-dinitrophenylhydrazine in the presence of sulfuric acid in aqueous alcoholic solution. The hydrazone obtained was fractionally recrystallized from ethyl acetate and two hydrazones were obtained; one was cubic orange crystals, mp 210–211°C. Found: C, 63.25; H, 5.21; N, 14.87%. Calcd for $C_{20}H_{20}N_4O_4$: C, 63.15; H, 5.30; N, 14.73%. The other was orange needles, mp 188.5–189.0°C (easily soluble in ethyl acetate). Found: C, 63.34; H, 5.16; N, 14.40%.

The distillation residue was further distilled at higher temperature, and 0.20 g (5%) of 1,2-dibenzoylethane was obtained mp 147.0—148.0°C (from ethanol).

Reaction of I with cis-Stilbene in the Presence of Cu(acac)₂ (by Dropwise Addition Method). The 50 ml of benzene solution of 5.0 g (0.034 mol) of I was added drop by drop to the 100 ml of benzene solution of 6.2 g (0.036 mol) of *cis*-stilbene and 0.1 g $(3.8 \times$ 10⁻⁴ mol) of Cu(acac)₂ at 80°C under stirring. After the evolution of nitrogen was observed and the reaction was complete, the reaction mixture was allowed to stand for one hour at 80°C and then overnight at room temperature. The white substance precipitated was separated by filtration, and washed several times by a small amount of benzene. This precipitate did not dissolve in the usual organic solvents at room temperature. It melted at 250-255°C (lit⁶) 290-292°C) but its IR spectrum was completely superimposable with that of dilactone (X) prepared by the photolysis of I in a benzene solution.¹¹) The yield of X was 0.12 g (3.2%). Benzene was removed by distillation from the filtrate and the residue was distilled under reduced pressure. Unreacted cis-stilbene was removed by distillation at 108°C/1 mmHg, 5.0 g (80%). The fraction boiling at 150-170°C/1 mmHg crystallized at room temperature, and was left to recrystallize four times from ethanol and twice from light petroleum, mp 93.0-94.5°C.

Found: C, 88.80; H, 6.15%. Calcd for $C_{22}H_{18}O$: C, 88.56; H, 6.08%. IR (KBr disk); 3050, 1655, 750 and 700 cm⁻¹.

From the distillation residue, 0.10 g (2.4%) of VII was isolated by the distillation at higher temperature and recrystallized from ethanol, mp 147—148°C (lit⁸⁾ 140°C).

Reaction of I with *trans*-Stilbene (by Dropwise Addition Method). The reaction of 3.3 g (0.023 mol) of I and 4.0 g (0.022 mol) of *trans*-stilbene was carried out by the "dropwise addition method" at the reflux temperature of benzene in the presence of 0.1 g of Cu(acac)₂. 0.06 g (1.5%) of X was obtained as an insoluble precipitate. A part of the residue crystallized

¹⁹⁾ Ibid., Coll. Vol. 4, p. 377 (1963).

by the removal of benzene under reduced pressure. The crystals, 2.6 g (65%), were identified as the recovered *trans*-stilbene by comparison of IR spectrum with that of the authentic sample, and by the mixed melting point test, mp 127—128°C. The liquid part crystallized on standing in the refrigerator for several days, and was purified by repeated recrystallization from *n*-hexane, mp 155.5—156.5°C.

Found: C, 88.84; H, 5.95%. Calcd for $C_{22}H_{18}O$: C, 88.56; H, 6.08%.

Reaction of I with Diphenylacetylene. The reaction of I (5.0 g, 0.034 mol) and diphenylacetylene (6.1 g, 0.034 mol) was carried out by the "dropwise addition method" in benzene at 80° C in the presence of Cu(acac)₂ (0.1 g). By a similar treatment of the reaction mixture, 0.2 g (4.5%) of X and a trace of VII (mp 143—145°C) were obtained besides the recovered diphenylacetylene. No other detectable compound was isolated.

Reaction of I in Inert Solvents. The Cu(acac)₂

catalyzed decomposition of I (5.0 g, 0.034 mol) was performed in benzene or chloroform by "mixed method" at 48—80°C. Solvent was removed *in vacuo* from the reaction mixture, and residue was fractionally recrystallized into two compounds from *n*-hexane. One was identified as *trans*-1,2-dibenzoylethylene. The other was identified as *cis*-1,2-dibenzoylethylene by elemental analyses and IR and NMR spectra, white needles from *n*-hexane, mp 135.5—136.5°C (Found: C, 81.43; H, 5.37%).

NMR (in CDCl₃); 2.89τ , (s), 2H, olefinic-H: 2.4— 2.7τ , (m), 6H, *m*- and *p*-H in phenyl: 1.95— 2.25τ , (m), 4H, *o*-H in phenyl.

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