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Reactions of Diazoacetophenones in the Presence of Metal Chelates. V. Reaction of *o*-Methoxy-*α*-diazoacetophenone

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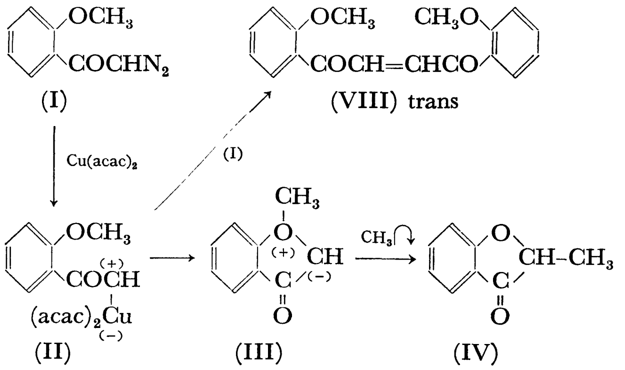
The predominant formation of carbonyl ylides takes place by the intramolecular attack of carbenoid on a carbonyl group in the copper chelate-catalyzed decomposition of *o*-alkoxycarbonyl-α-diazoacetophenones.[1] A similar facilitation might be expected in the formation of oxonium ylide by the intramolecular attack of carbenoid-carbon on ether oxygen at *ortho* position. The copper chelate-catalyzed decomposition of *o*-methoxy-α-diazoacetophenone was carried out, and formation of the oxonium ylide was confirmed.

Decomposition of *o*-methoxy-α-diazoacetophenone (I) was carried out in benzene solution containing a catalytic amount of bis(acetylacetonate)copper. Column chromatography of the reaction mixture on silica gel gave 2-methylcoumaranone (IV, 52%), bis(*o*-methoxybenzoyl)ethylene (VIII, 7%) and a carbene-oligomer (30%).[2] Dibenzoylethylene (VIII), the formal dimer of the carbene intermediate, is considered to be obtained by the reaction of the carbene (II)



Scheme 1.

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1) K. Ueda, T. Ibata, and M. Takebayashi, This Bulletin, **45**, 2279 (1972).

2) The oligomer showed a similar IR spectrum to that described before (M. Takebayashi, T. Ibata, and K. Ueda, This Bulletin, **43**, 1500 (1970)).

with starting diazo compound (I)[3] competing with the formation of IV. Formation of IV might be explained by assuming the intermediacy of an oxonium ylide (III) produced by the intramolecular electrophilic attack of the carbenoid carbon on the ether oxygen atom, followed by methyl migration (Scheme 1).

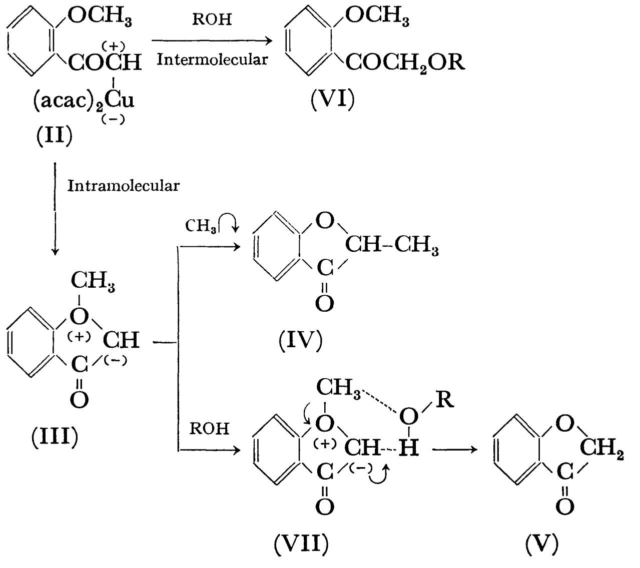
Since the copper chelate-catalyzed decomposition of diazoketones in alcohols gives the corresponding keto-ethers,[4] facility of the oxonium ylide formation was investigated utilizing the competitive reaction between intramolecular formation of the oxonium ylide and the intermolecular reaction with alcohols. The copper-catalyzed decomposition of I was carried out in a mixed solvent of alcohol and benzene in various proportions at 80 °C for 30 min. A soluble part of the reaction mixture in *n*-heptane was analyzed by gas chromatography. Coumaranone (V), 2-methylcoumaranone (IV) and keto-ether (VI) were characterized and determined quantitatively by comparing their retention times with those of authentic samples. Molar ratios of the products are listed in Table 1.

TABLE 1. DECOMPOSITION OF I IN ALCOHOL-BENZENE SOLUTION

Alcohol	wt% of Alc.	Products				
		IV	V	VI	V/IV	VI/IV+V
EtOH	50	10.8	10.9	78.3	1.01	3.61
	10	13.9	12.2	73.9	0.88	3.83
	5	14.7	12.9	72.4	0.88	2.62
	2	18.0	14.1	67.9	0.78	2.12
	1	20.8	16.9	62.3	0.81	1.65
t-BuOH	30	26.4	7.0	66.6	0.24	1.99
	10	36.4	6.9	56.7	0.19	1.31
	2	42.1	5.6	52.2	0.12	1.09
	1	49.3	2.4	48.3	0.05	0.93

With the decrease of alcohol concentration in ethyl alcohol–benzene solution, the yields of VI decreased and those of both VI and V increased. This suggests that the formation of keto-ether (VI) depends upon the concentration of alcohol and competes with the formation of IV and V. Although coumaranone (V) is produced in the acid catalysis[5] of I, a control experiment showed that I did not give V under refluxing in an alcohol–benzene solution in the absence of $Cu(acac)_2$ catalyst. Contribution of alcohol to the formation of V was supported by the fact that V was not obtained in a benzene solution in the presence of $Cu(acac)_2$ without alcohol. Decrease in the value of V/IV with the decrease in alcohol concentration is consistent with the above assumption.

Thus the formation of V might be explained in terms of the intermediacy of oxonium ylide (III) which reacts with alcohols affording coumaranone (V) *via* VII (Scheme 2).



Scheme 2.

Keto-ether (VI) can be obtained by the intermolecular reaction of carbenoid (II) with alcohol competing with the intramolecular formation of the oxonium ylide (III) which gives IV and V by successive reactions. The ratio V/(IV+V) (Table 1) which decreases with decrease in alcohol concentration supports the mechanism shown in Scheme 2.

In the case of *t*-butyl alcohol, similar results were obtained except for the yields of V, which decrease with decrease in alcohol concentration. The ratio VI/IV is one third of that in ethyl alcohol reflecting the reactivity of alcohols toward copper-carbenoid (II).[4]

On the other hand, a product which could be formed through the corresponding oxonium ylide generated by the intermolecular carbenoid reaction was not recognized in a catalytic decomposition of α-diazoacetophenone in anisole in spite of careful inspection of the products.

Experimental

Material. *o*-Methoxy-α-diazoacetophenone (I) was prepared by slow addition of an ethereal solution of *o*-methoxybenzoyl chloride[6] to a large excess (about 3 molar equivalents) of cold ethereal diazomethane.[7] The oily product obtained by the evaporation of ether after drying over $MgSO_4$ was used for the reaction without further purification. IR (neat): 2200 (C=N=N), 1605 (C=O of diazoketone), 1250 (C–O–C), and 755 cm^{-1} (Ph). The elemental analysis of I was satisfactory.

Catalytic Decomposition of I in Benzene. In a flask fitted with a dropping funnel and a reflux condenser connected to a gas burette was placed 0.05 g (0.19 mmol) of $Cu(acac)_2$ dissolved in 50 ml of benzene. To the solution was added dropwise a solution of I (5.8 mmol) in 30 ml of benzene. The evolution of nitrogen was almost quantitative. When it was over, the reaction mixture was separated by silica gel

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[3] W. Kirmse, "Carbene Chemistry", Academic Press, New York and London, (1964) p. 131.

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

[5] a) P. Pfeiffer and E. Ender, *Chem. Ber.*, **84**, 247 (1951). b) H. Krzikalla and B. Eistert, *J. Pract. Chem.*, **143**, 50 (1935). c) A. K. Bose and P. Yates, *J. Amer. Chem. Soc.*, **74**, 4703 (1952).

[6] E. R. Marshall, J. A. Kuck, and R. C. Elderfield, *J. Org. Chem.*, **7**, 444 (1942).

[7] W. E. Bachmann and W. S. Struve, "Organic Reactions", Vol. I, (1942) p. 40.

chromatography. 2-Methylcoumaranone (IV, 0.439 g, 52%) accompanied by bis(*o*-methoxybenzoyl)ethylene (VIII, 0.059 g, 7%) and an oligomer of *o*-methoxybenzoylcarbene (0.253 g, 30%)[2] was obtained. IR (neat) of IV: 1720 (C=O), 1245 (C–O–C), and 755 cm^{-1} (Ph). NMR ($CDCl_3$) of IV: 2.2—3.2 (m, 4H, aromatic proton), 5.65 (q, 1H, methine-H), and 8.61 τ (t, 3H, CH_3). Found: C, 73.12; H, 5.40%. Calcd for $C_9H_8O_2$: C, 72.96; H, 5.44%.

Competitive Reaction of I in Alcohol–Benzene Solution. A solution of I (5.7 mmol) in a mixed solvent (30 ml) of alcohol–benzene was added dropwise to 50 ml of mixed solvent of same composition containing Cu(acac)$_2$ (0.05 g, 0.19 mmol) at 80 °C. After evaporation of solvent under reduced pressure, the reaction mixture was treated with *n*-heptane, and the soluble part in *n*-heptane was analyzed quantitatively by gas chromatography. The product ratios obtained are given in Table 1. Coumaranone (V) was isolated by preparative gas chromatography (and silica gel column chromatography) of the reaction mixture. IR (KBr) of V: 1720 (C=O), 1460 (CH_2), 1190 (C–O–C), and 764 cm^{-1} (Ph). NMR ($CDCl_3$) of V: 2.2—3.1 (m, 4H, aromatic proton) and 5.40 τ (s, 2H, CH_2).