CHEMISTRY LETTERS, pp. 1267-1270, 1976. Published by the Chemical Society of Japan

REACTION OF DIAZOKETONES IN THE PRESENCE OF METAL CHELATES. REACTION WITH β-DIKETONES

Toshikazu IBATA,* Masashi HAMAGUCHI, and Hideo NISHIGAKI
Department of Chemistry, College of General Education,
Osaka University, Toyonaka, Osaka 560

Copper chelate catalyzed decomposition of substituted α-diazoacetophenones and ethyl diazoacetate in the presence of dibenzoylmethane and benzoylacetone gave two types of products; one was that of formal insertion product of ketocarbene into C-H bond, and the other was into C-CO bond of β-diketone. These products were explained by the cyclopropanation of ketocarbene with C=C double bond of enol form of β-diketone followed by ring opening and proton shift.

A recent paper of Paulissen and his coworkers[1] on the rhodium(II) salt catalyzed reaction of ethyl diazoacetate with acetylacetone prompted us to report our finding on the title reaction.[2] They explained the formation of ethyl 3,5-dimethyl-2-furancarboxylate by cyclization of the intermediate enol-ether which was formed by the insertion of the ethoxycarbonylcarbene into the O-H bind of enolic acetylacetone. As part of the continuing study of the reaction of carbenes generated by the $Cu(acac)_2$ catalyzed decomposition of diazo compounds with carbonyl compounds,[3,4] we carried out the reaction of ketocarbene with β-diketones such as dibenzoylmethane and benzoylacetone, and obtained the results different from those of Paulissen.

A benzene solution of α-diazoacetophenone (1a: X=H) was added dropwise to a benzene solution of dibenzoylmethane (2 molar amount) containing a catalytic amount of $Cu(acac)_2$ at 80°C. The reaction mixture was separated on silica gel column chromatography, and 2-benzoyl-1,4-diphenyl-1,4-butanedione (3a) and enol-ester (5) were obtained in 27% and 40% yields along with trans-1,2-dibenzoylethylene and recovered dibenzoylmethane. Triketone (3a) was characterized by analytical[5] and spectral data. Its NMR spectrum shows a triplet signal at 3.90 τ and a doublet at 6.23 τ, with a coupling constant J=6.4 Hz, besides multiplet signal of aromatic protons. These data suggested the presence of $>CH-CH_2-$ group in 3a which was characterized as the formal insertion product of benzoylcarbene into the central C-H bond of dibenzoylmethane. Further support to this structure was given by the comparison of its IR and NMR spectra with those authentic sample prepared by the reaction of potassium dibenzoylmethanate with phenacyl bromide according to the modified method of Weygand.[6] The enol-ester (5), mp 99-100°C, was identified by the following spectral data [NMR; 6.16 (d, CH_2), 3.65 (t, CH, J=6.3 Hz), 1.6-2.9 τ(m, 15H); IR(KBr): 1730 (ester C=O), 1680 cm^{-1} (C=O)] Its hydrolysis products 1,2-dibenzoylethane and benzoic acid also support the structure 5.

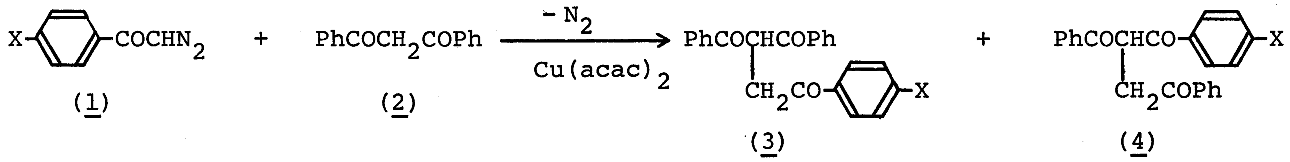


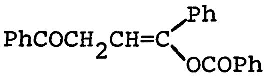
Table 1. Yields, Melting Points, and NMR Data of the Reaction Products (3) and (4)

	X	(3) yield(%)	(3) mp(°C)	(3) NMR(τ, $CDCl_3$) -CH<	(3) NMR(τ, $CDCl_3$) $-CH_2-$	(4) yield(%)	(4) mp(°C)	(4) NMR(τ, $CDCl_3$) -CH<	(4) NMR(τ, $CDCl_3$) $-CH_2-$
a	H	27	99-100	3.90(t)	6.23(d)	—	—	—	—
b	Br	37	105-107	3.89(t)	6.15(d)	30	80-83	3.95(t)	6.22(dd)
c	NO_2	38	169-170	3.33(t)	6.02(d)	24	180-183	3.88(t)	6.23(d)
d	CH_3	20	117-120	3.93(t)	6.30(d)	14	130-132	3.60(t)	6.07(d)

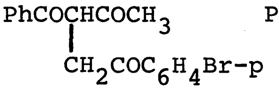
On the other hand, reaction of substituted α-diazoacetophenones with dibenzoylmethane gave two types of triketones (3) and (4) (see Table 1 run b-d), which were assigned to formal insertion products of the ketocarbene into the central C-H and C-CO of β-diketone. For example, in the reaction of p-bromo-α-diazoacetophenone and dibenzoylmethane two crystalline products of melting points 105-107°C and 80-83°C were obtained in 37% and 30% yields, respectively (run b). Both products showed similar IR spectra.[7] High melting product showed a triplet signal of methine at 3.89 τ and a doublet signal of methylene at 6.15 τ which correspond to the symmetrical structure (3b). On the other hand, low melting product has a triplet methine signal at 3.95 τ and a double doublet signal of methylene at 6.22 τ which indicates the presence of asymmetric center.[8] These results supported the structure (4b) which was confirmed by the comparison of its IR spectrum with that of authentic sample prepared by the reaction of sodium p-bromodibenzoylmethane with phenacyl bromide.

Similar results were obtained in the reaction of α-diazoacetophenones with 1-phenyl-1,3-butanedione. Diazoacetophenone afforded a product having a double doublet methylene signal which indicates the existence of asymmetric center [53%, mp 90-93°C, IR(KBr); 1715, 1670 cm^{-1}, NMR; 7.77 (s, CH_3), 6.32 (dd, CH_2), 4.72 (t, CH, J=6.3 Hz), 1.8-2.6 τ (m, Ar)].[10] p-Bromodiazoacetophenone gave two products [(6): 45%, mp 99-100°C, IR(KBr); 1713, 1685 cm^{-1}, NMR; 7.80 (s, CH_3), 6.38 (dd, CH_2), 4.73 (t, CH, J=6.4 Hz), 1.7-2.5 τ (m, Ar). (7): 27%, mp 82-84°C, IR(KBr); 1715, 1671 cm^{-1}, NMR; 7.80 (s, CH_3), 6.30 (d, CH_2), 4.77 (t, CH, J=6.4 Hz), 1.7-2.8 τ (m, Ar).

In these cases, neither the insertion product of carbene into O-H bond of enol form of β-diketones nor furan derivative was obtained different from the results of Paulissen [1] and Kharasch.[9] These differences may not be attributed to the nature of the ketocarbene but to the character of the substrate β-diketone, because a reaction of ethoxycarbonylcarbene with dibenzoylmethane also exhibited a similar result affording formal insertion products [10] into the C-H and C-CO bond [(8): 26%, mp 85-86°C, IR(KBr); 1771 (ester C=O), 1680 cm^{-1} (C=O), NMR; 8.80 (t, CH_3, J=6.6 Hz), 5.88 (q, CH_2, J=6.6 Hz), 6.92 (d, CH_2, J=6.4 Hz), 4.20 (t, CH, J=6.4 Hz), 1.7-2.8 τ (m, Ar). (9): 40%, mp 65-66°C, IR(KBr); 1778 (ester C=O), 1679 cm^{-1} (C=O), NMR; 8.87 (t, CH_3, J=6.8 Hz), 5.90 (q, CH_2, J=6.8 Hz), 6.25 (d, CH_2, J=6.6 Hz), 4.93 (t, CH, J=6.6 Hz), 1.8-2.8 τ (m, Ar)].

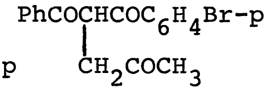


(5)



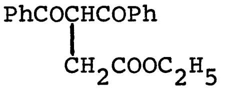
$\begin{array}{l} \mathrm{PhCOCHCOCH_3} \\ \qquad | \\ \quad \mathrm{CH_2COC_6H_4Br\text{-}p} \end{array}$

(6)



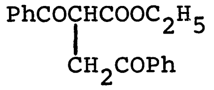
$\begin{array}{l} \mathrm{PhCOCHCOC_6H_4Br\text{-}p} \\ \qquad | \\ \quad \mathrm{CH_2COCH_3} \end{array}$

(7)



$\begin{array}{l} \mathrm{PhCOCHCOPh} \\ \qquad | \\ \quad \mathrm{CH_2COOC_2H_5} \end{array}$

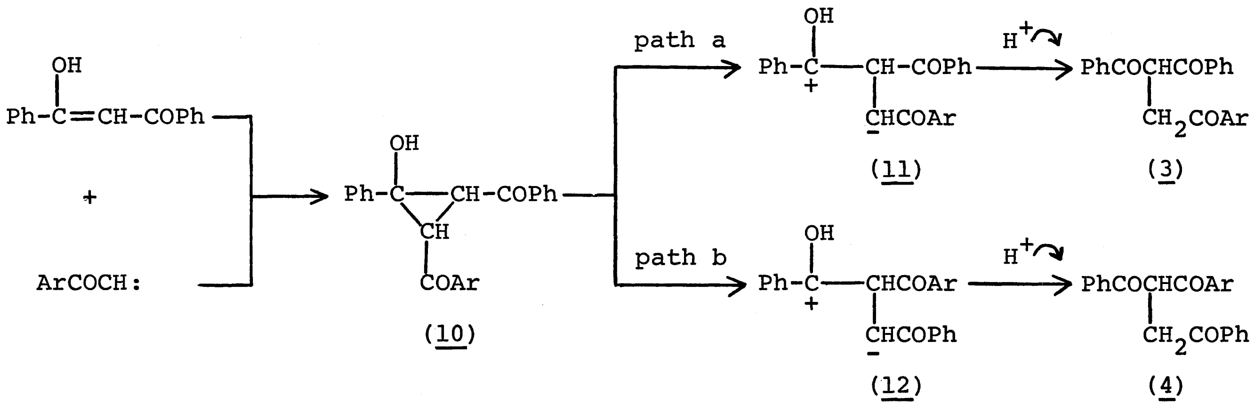
(8)



$\begin{array}{l} \mathrm{PhCOCHCOOC_2H_5} \\ \qquad | \\ \quad \mathrm{CH_2COPh} \end{array}$

(9)

Formation of 3 and 4 may tentatively be explained by the following scheme. A possible intermediate may be the hydroxycyclopropane (10) produced by the cyclopropanation of ketocarbene which was generated by the $Cu(acac)_2$ catalyzed decomposition of diazoacetophenone to the C=C double bond of enol form of β-diketone. Cleavage of cyclopropane ring of 10 may proceed in two manners, path (a) and path (b), yielding betaines (11) and (12) respectively, which give triketones (3) and (4) by successive proton shift. Similar reaction had been observed by Nozaki and his coworkers in the reaction of cyclohexanone with methoxycarbonylnitrene having isoelectronic structure with ketocarbene.[11] In their case, nitrene reacted with C=C double bond of enol form of cyclohexanone to give 1-hydroxy-7-azanorcarane derivative which gave 2-ethoxy-4,5-



tetramethyleneoxazole by subsequent cleavage of a C-N bond of aziridine ring. In general, ring cleavage of a cyclopropane bearing OR[12] or NR_2[13] groups proceeds under acid catalysis. The ease of ring cleavage of cyclopropane derivatives (10) observed in this work seems to be attributed to the presence of OH and/or acyl groups attached on cyclopropane ring. Detailed mechanistic studies on this reaction are now in progress.

References and Notes

1 R.Paulissen, E.Hayez, A.J.Hubert, and P.Teyssie, Tetrahedron Lett., 607 (1974).

2 Presented in part at the 32nd Annual Meeting of Chemical Society of Japan, Tokyo, April 1975.

3 M.Takebayashi, T.Ibata, K.Ueda, and T.Ohashi, Bull.Chem.Soc.Jpn., 43, 1500 (1970).

4 K.Ueda, T.Ibata, and M.Takebayashi, Bull.Chem.Soc.Jpn., 45, 2779 (1972).

5 All new compounds reported herein showed satisfactory elemental analyses.

6 C.Weygand, Ber., 61, 687 (1928).

7 IR of 3b; 1695 and 1675 cm^{-1}. IR of 4b; 1692 and 1675 cm^{-1}.

8 F.Kaplan and J.D.Roberts, J.Am.Chem.Soc., 83, 4666 (1961).

9 M.S.Kharasch, T.Rudy, W.Nudenberg, and G.Büchi, J.Org.Chem., 18, 1030 (1953). They reported the formation of enol-ethers in the reaction of ethyl diazoacetate with monoketones such as acetone and cyclohexanone.

10 The products were confirmed in comparison with the authentic samples.

11 T.Hiyama, H.Taguchi, S.Fujita, and H.Nozaki, Bull.Chem.Soc.Jpn., 45, 1863 (1972).

12 E.Wenkert, R.A.Muller, E.J.Reardon,Jr., S.S.Sathe, D.J.Scharf, and G.Tosi, J.Am. Chem.Soc., 92, 7428 (1970).

13 H.Bieräugel, J.M.Akkerman, J.C.Armande, and U.K.Pandit, Tetrahedron Lett., 2817 (1974).

* To whom correspondence should be addressed.

(Received August 23, 1976)