THE REACTIONS OF ETHYL DIAZOACETATE WITH BIS(ETHYL ACETOACETATO)-COPPER (II) AND BIS(ACETYLACETONATO)COPPER (II)*

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Although the decomposition of diazo compounds under the catalytic action of copper chelates has been studied by many workers⁽¹⁾, the reaction of diazo compounds with copper chelate itself has not been reported except one brief paper read by Takebayashi and Ibata⁽²⁾. They treated diazoacetophenone and p-nitrodiazoacetophenone with bis(acetylacetonato)copper (II), and proposed two alternative cyclopropene structures for each product.

We carried out the reaction of ethyl diazoacetate with bis(ethyl acetoacetato)copper (II) $\underline{1}$ and bis(acetylacetonato)copper (II) $\underline{2}$, and obtained compounds $\underline{3}$ and $\underline{4}$, respectively, as the major products. This type of coupling reaction of carbene is quite unusual and will be described in this communication.

$$(CH_{3}COCHCOR)_{2}Cu$$

$$(CH_$$

 $\frac{2}{2}$, $\frac{4}{4}$: R = CH₃

Ethyl diazoacetate in dioxane was added to a dioxane solution of <u>1</u> at $90-100^{\circ}$ (2:1 molar ratio). The reaction mixture was treated with dil HCl to decompose copper-complex, extracted with ether and distilled <u>in vacuo</u>. Compound <u>3</u> was obtained in 44% yield⁽³⁾, b.p. 163°/3 mmHg. From the forerun ethyl acetoacetate $(17\%)^{(3)}$, diethyl maleate $(45\%)^{(4)}$ and diethyl acetylsuccinate <u>5</u> $(6\%)^{(3)}$

^{*} Part IV of a series on the pyrolysis of organic compounds. Part III: T. Sato and H. Obase, Tetrahedron Letters , 1967, 1633.

Both of the compounds 3 and 4 have not appeared in the literature and the structures were determined from the following evidences⁽⁵⁾.

Compound 3: Found: C, 55.57, H, 7.14; Calcd. for $C_{16}H_{24}O_8$: C, 55.81, H, 6.98. NMR: δ 1.18 (triplet J = 7 c/s) and 1.27 (triplet, J = 7 c/s) for CH_2-CH_3 , δ 2.12 (singlet) and 2.22 (singlet) for CH_3-CO and $CH_3-C(OH)=$ (enol), δ 4.16 (quartet J = 7 c/s) and 4.20 (quartet, J = 7 c/s) for CH_2-CH_3 . IR: 1740 cm⁻¹ for C=O (normal), 1640 cm⁻¹ for C=O (chelated). When 3 was treated with 10% KOH and then with $CH_3OH-H_2SO_4$, it afforded 6. Mass spectrum: m/e 168 (M⁺), m/e 137 (M⁺-OCH₃) and m/e 109 (base peak, M⁺-COOCH₃). NMR: δ 1.99 (singlet) for $CH_3-C=$, δ 3.68 (singlet) for OCH_3 , δ 5.82 (multiplet, J~1 c/s) for -CH= and δ 2.4-3.2 (multiplet) for other protons. IR: 1739 cm⁻¹ for C=O (ester), 1665 cm⁻¹ for C=O (α , β -unsaturated) and 1628 cm⁻¹ for C=C. UV: 234 mµ (CH₃OH).



Compound <u>4</u>: Found: C, 59.19, H, 7.15; Calcd. for $C_{14}H_{20}O_6$: C, 59.15, H, 7.04. IR: 1730 cm⁻¹ for C=O (normal) and 1640 cm⁻¹ for C=O (chelated).

Compound <u>5</u>: Mass spectrum showed a molecular ion peak at m/e 216. NMR spectrum was identical with the published spectrum of diethyl acetylsuccinate⁽⁶⁾ and this compound afforded pyruvic acid upon hydrolysis.

It is assumed that the reactions leading to $\underline{3}$ and $\underline{4}$ would involve the oxidation by cupric ion, the detailed mechanism will be discussed in the future. It should be noted that the reaction of ethyl acetoacetate with ethyl diazoacetate in the presence of anhydrous cupric sulfate afforded only a negligible amount of $\underline{3}$ (<1%).

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REFERENCES

- (1) H. Nozaki, S. Moriuti, H. Takaya and R. Noyori, <u>Tetrahedron Letters</u>, <u>1966</u>, 5239, and references cited therein.
- (2) M. Takebayashi and T. Ibata, Abstracts of papers presented at the 20th meeting of the Chemical Society of Japan, Vol. III, p.94, Tokyo, April, 1967.
- (3) Based on copper chelate.
- (4) Based on ethyl diazoacetate.
- (5) NMR spectra were measured on a Hitachi R-20 spectrometer in CCl₄ solution. Chemical shifts are described in ppm downfield from an internal TMS reference. Mass spectra were taken on a Hitachi RMU-6D mass spectrometer, the electron energy being 70 eV.
- (6) N. S. Bhacca, L. F. Johnson and J. N. Shoolery, <u>High Resolution NMR Spectra of Organic</u> Compounds, Vol. I, Spectrum Number 277. Varian Associates, Palo Alto, Calif. (1962).