SHORT COMMUNICATIONS

A Betaine Intermediate in the Copper Chelate Catalyzed Decomposition of *o*-Methoxycarbonyl-*α*-diazoacetophenone

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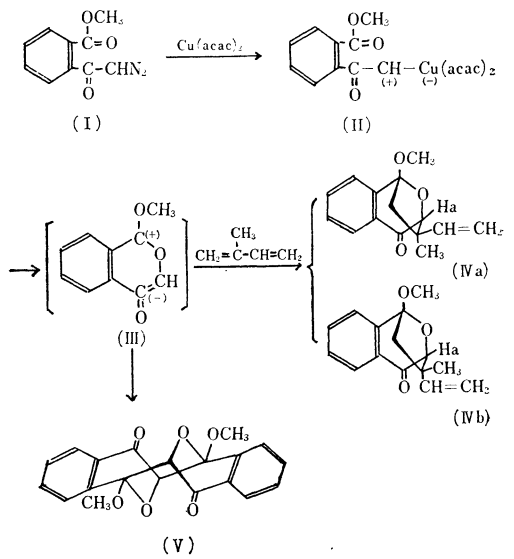
In a previous paper,[1] we showed that the copper chelate catalyzed reaction of α-diazoacetophenone with aromatic compounds such as benzaldehyde and acetophenone gave the corresponding tetrahydrofurans and dioxolanes, and that the mechanism of the reaction could be explained by assuming betaine intermediate, produced by the reaction of a ketocarbene-copper chelate complex with carbonyl compounds. This paper deals with a new type of betaine intermediate.

The copper chelate catalyzed decomposition of *o*-methoxycarbonyl-α-diazoacetophenone[2] (I, 0.0098 mol) was carried out in benzene at 80°C in the presence of conjugated dienes (0.367 mol). In the presence of isoprene, the reaction gave two stereoisomeric products (IVa and IVb) in yields of 43 and 34%, respectively. IR of IVa: 2900, 1700, 1635, 1290, 1050 and 765 cm^{-1}. NMR of IVa (in $CDCl_3$): 1.9—2.8(m, 4H), 4.7—5.8 (m, 3H), 6.55(s, 3H), 6.6—9.2(m, 5H) and 8.13 τ (s, 1H). IR of IVb: The same as above. NMR of IVb (in $CDCl_3$): 1.9—2.8(m, 4H), 4.7—5.8 (m, 3H), 6.55(s, 3H), 6.6—9.2(m, 5H) and 8.27 τ(s, 1H). The Ha of IVa is deshielded by 0.14 ppm in comparison with that of IVb, owing to π-electrons of the ethylenic linkage (Scheme 1). The results indicate that the isoprene employed reacts with a new type of betaine intermediate (III), produced from a ketocarbene-copper chelate complex (II), by 1,2-addition to give IVa and IVb. 1,3-Cyclooctadiene also reacted with III to give 1,2-addition products.



Scheme 1

When the reaction was carried out without conjugated dienes, a dimer (V), mp 233—235°C, of III was obtained in 30% yield. NMR of V (in $CDCl_3$): 1.8—2.7(m, 8H), 5.08(s, 1H), 5.62 (s, 1H), 6.30(s, 3H) and 6.54 τ(s, 3H).

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[1] M. Takebayashi, T. Ibata and K. Ueda, This Bulletin, **43**, 1500 (1970).

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