

FORMATION OF CARBONYL YLIDE BY THE INTRAMOLECULAR CARBENIC REACTION.

DISROTATORY RING CLOSURE OF CARBONYL YLIDE TO EPOXIDE

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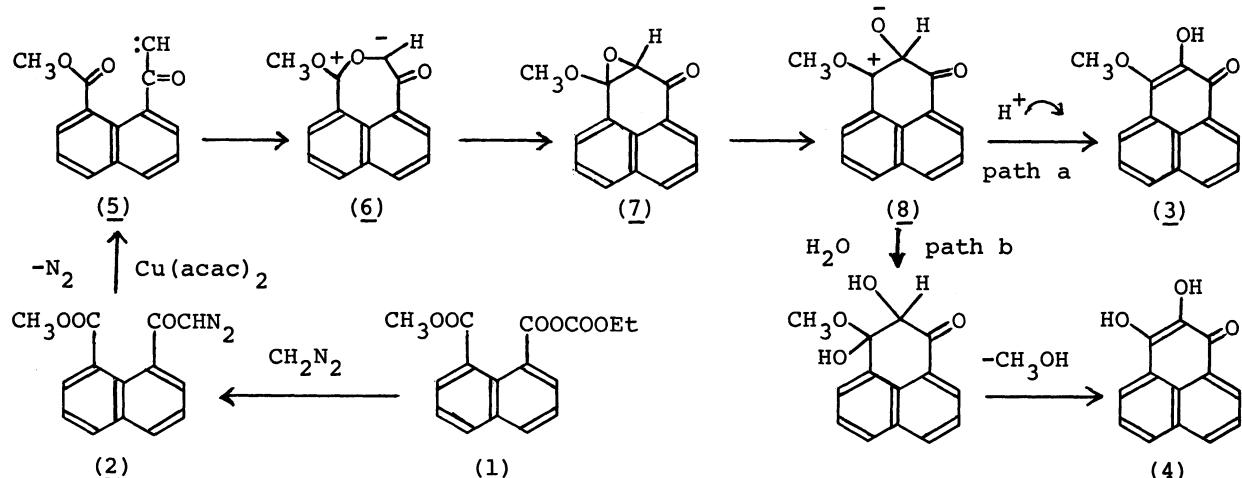
Copper acetylacetonate catalyzed decomposition of 8-methoxycarbonyl-1- α -diazoacetyl naphthalene in benzene solution gave 2-hydroxy-3-methoxyphenalenone and 2,3-dihydroxyphenalenone via thermally forbidden disrotatory ring closure of intermediate carbonyl ylide to epoxide and successive cleavage of the epoxide.

Intramolecular carbene-carbonyl reaction has been known as one of the most effective method of the generation of carbonyl ylides.^{1,2,3} For example, 1-methoxybenzo[c]-pyrylium-4-oxide formed by the copper chelate-catalyzed decomposition of o-methoxycarbonyl- α -diazoacetophenone gave 1,3-dipolar cycloadducts with electron-deficient olefins and acetylenes.¹ We studied the decomposition of 8-methoxycarbonyl-1- α -diazoacetyl naphthalene (2) in order to investigate the structural effect on the reactivity of carbonyl ylide. The diazoketone (2) was prepared by the reaction of mixed anhydride (1), which was prepared by the reaction of sodium 8-methoxycarbonyl-1-naphthoate and ethyl chloroformate, with excess of diazomethane in THF at 0°C for one week;⁴ mp 144-146°C, yellow needles, ir(KBr): 2150 (diazoketone), 1715 (ester C=O), and 1590 cm^{-1} (diazoketone C=O).

Diazoketone (2) was decomposed by adding in small portions into a benzene sloution of catalytic amount of $\text{Cu}(\text{acac})_2$ at 80°C under stirring. Whole over the reaction nitrogen gas evolved and the color of the reaction mixture turned to dark-red. Column chromatography of the reaction mixture after removal of benzene gave two red crystalline products in yields of 75% and 20%. Major product, mp 150-151°C, was identified as 2-hydroxy-3-methoxyphenalen-1-one (3) by the following spectral data;⁵ ir(KBr): 3330 (OH), 1635, 1620, 1580, and 1560 cm^{-1} , nmr(CDCl_3): 1.3-2.6 (m, 6H, Ar-H), 3.10 (broad s, 1H, OH, exchangeable with D_2O), and 5.74 τ (s, 3H, OCH_3). Minor

product, mp 232-234°C, was characterized as 2,3-dihydroxyphenalen-1-one (4) as follows; ir(KBr);⁵ 3350 (OH), 1650, 1625, 1590, and 1575 cm⁻¹, nmr(CDCl₃-pyridine); 3.37 τ (br s, OH, exchangeable with D₂O). Positive FeCl₃ test for 3 and 4 and the facts that the methylation of 4 with equivalent amount of diazomethane affords 3 and that the treatment of 3 with hot concentrated hydrochloric acid gives 4 also support these structures.

The formation of phenalenones (3) and (4) may reasonably be explained by the following mechanism. Intermediate carbonyl ylide (6) generated by the intramolecular attack of carbenic carbon on adjacent carbonyl oxygen of ester group cyclized to give epoxide (7). The thermally forbidden disrotatory ring closure of carbonyl ylide to epoxide^{7,8} may be made allowed in this case by the release of strain of the carbonyl ylide (6). The ease of the ring closure of 6 might suppress the formation of its 1,3-dipolar cycloadduct with excess dimethyl fumarate in contrast to the behavior of benzo[c]pyrylium-4-oxide.¹



The C-O bond fission of epoxide (7) gives betaine intermediate (8) which undergoes either proton transfer to give 3 (path a) or addition of water followed by the elimination of methanol to give 4 (path b). Formation of 3 and 4 in the m-chloroperbenzoic acid oxidation of 3-methoxyphenalenone in CH₂Cl₂ (at r.t.) also supports above mechanism.

References and note

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- 5 The ir spectra reported for these compounds⁶ are slightly different from ours; (3): 3311, 1610 cm⁻¹ and (4): 3325, 1655, 1628, 1578 cm⁻¹.
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(Received December 22, 1975)