

## FORMATION AND REACTION OF CARBONYL YLIDES.

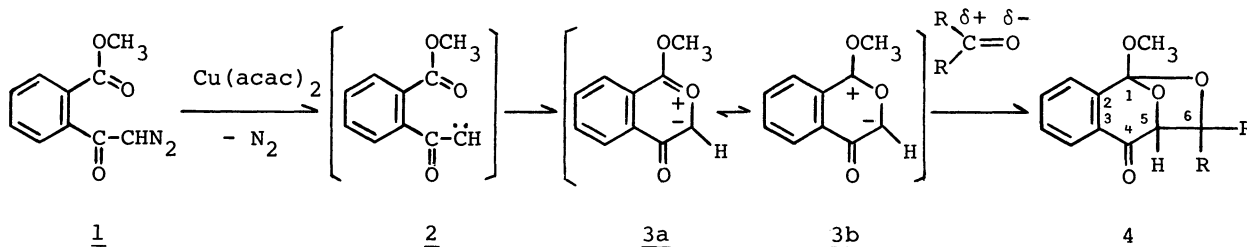
1,3-DIPOLAR CYCLOADDITION OF 1-METHOXY-2-BENZOPYRYLIUM-4-OLATE  
TO CARBONYL COMPOUNDS

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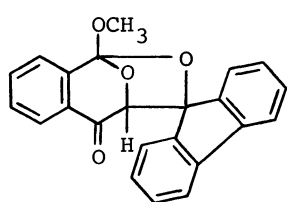
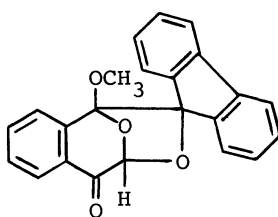
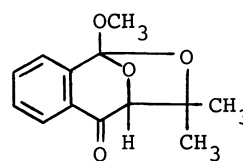
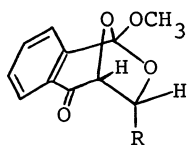
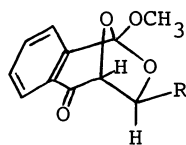
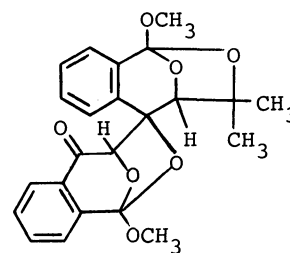
Copper(II) acetylacetonate-catalyzed decomposition of *o*-methoxy-carbonyl- $\alpha$ -diazoacetophenone in benzene in the presence of carbonyl compounds gave 1,3-dipolar cycloadducts of 1-methoxy-2-benzopyrylium-4-olate with carbonyl compounds in high yields.

Chemistry of carbonyl ylide has recently been studied extensively from the synthetic and theoretical interests.<sup>1)</sup> The early work of the 1,3-dipolar cycloaddition of carbonyl ylide with carbonyl compounds was reported by Ullman and Milks in the photolysis of 2,3-diphenylindenone oxide.<sup>2)</sup> Until today only a few examples of the cycloaddition were found in the literature.<sup>3)</sup> In the previous paper of this series, the authors have reported the formation of 1-methoxy-2-benzopyrylium-4-olate (3) as a carbonyl ylide transient species by the intramolecular carbene-carbonyl reaction of ketocarbene (2) generated by the copper chelate-catalyzed decomposition of *o*-methoxy-carbonyl- $\alpha$ -diazoacetophenone (1).<sup>4)</sup> The 2-benzopyrylium-4-olate (3) was found to show strong reactivity toward ethylenic<sup>5)</sup> and acetylenic<sup>6)</sup> dipolarophiles, 1,3-dipolar cycloadducts having been obtained in high yields.



This paper deals with the cycloaddition of the 2-benzopyrylium-4-olate (3) with various ketones and aldehydes. The  $\text{Cu(acac)}_2$ -catalyzed decomposition of *o*-methoxy-

carbonyl- $\alpha$ -diazoacetophenone (1) in benzene at 80 °C in the presence of two molar equivalents of fluorenone proceeded with the vigorous evolution of nitrogen and gave a colorless crystalline product, mp 218-219 °C, in 75% yield. This was characterized to an adduct (5A) of 3 and fluorenone on the basis of its spectral properties and elemental analysis<sup>7)</sup> [IR(KBr) 1700  $\text{cm}^{-1}$ ; NMR( $\text{CDCl}_3$ ) 3.84 (s,  $\text{OCH}_3$ ), 3.83 ppm (s, methine)]. The direction of the cycloaddition was confirmed by a signal of its  $^{13}\text{C}$ -NMR spectrum at 119.1 ppm which was assigned to  $\text{C}_1$ . The other possible isomer 5B may not give a signal of the nonaromatic quaternary carbon in this region. The regioselectivity of the cycloaddition may be explained by the contribution of resonance formula 3b.

5A5B68 endo9 exo7

Acetone also gave a similar adduct (6) in 75% yield [mp 112 °C; IR(KBr) 1705  $\text{cm}^{-1}$ ;  $^1\text{H}$ -NMR( $\text{CDCl}_3$ ) 1.11 and 1.55 (s,  $\text{CH}_3$ ), 3.65 (s,  $\text{OCH}_3$ ), 4.48 ppm (s, methine)] together with 2:1 adduct of 3 and acetone in 12% yield. The structure of the 2:1 adduct is tentatively assigned to 7.<sup>8)</sup>

Decomposition of 1 in the presence of aromatic aldehydes gave two adducts. *p*-Chlorobenzaldehyde gave two products of melting points 135-137 °C and 126-128 °C. Results of elemental analysis and IR spectra showed that these are the isomers with different configuration on  $\text{C}_6$ . The PMR coupling patterns of two methine protons of both adducts indicate that the cycloaddition proceeds in a similar manner with that of fluorenone. The higher melting product has doublet signals of methine protons at 5.08 and 5.53 ppm with coupling constant  $J=6.0$  Hz, the substituent (R) having endo configuration as shown in formula 8. The lower melting adduct has doublet signals of methine

Table 1. Yields, Melting Points and Spectral Data of Cycloadducts of 3 and Aldehydes.<sup>a)</sup>

R	Product	Yield/% <sup>b)</sup>	Mp/°C	IRν/cm <sup>-1</sup>	NMR(ppm)			
					OCH <sub>3</sub>	methine	methine	J/Hz
p-ClC <sub>6</sub> H <sub>4</sub>	<u>8a</u>	42	135.0-137.0	1715	3.73(s)	5.08(d)	5.53(d)	6.0
	<u>9a</u>	43	126.5-127.5	1708	3.72(s)	4.78(d)	4.86(d)	1.3
2,4-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	<u>8b</u>	75	136.5-138.0	1705	3.76(s)	5.38(d)	5.72(d)	5.9
	<u>9b</u>	12	c)		3.77(s)	4.83(d)	5.08(d)	1.8
2,6-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	<u>8c</u>	62	148.0-150.0	1690	3.75(s)	5.42(d)	5.93(d)	5.4
	<u>9c</u>	6	156.0-161.0	1703	3.80(s)	5.27(d)	5.53(d)	2.3
p-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	<u>8d</u>	53	152.0-154.0	1702	3.77(s)	5.17(d)	5.65(d)	6.0
	<u>9d</u>	33	147.5-148.8	1698	3.77(s)	4.92(s)		-
m-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	<u>8e</u>	61	115.0-117.0	1690	3.78(s)	5.23(d)	5.72(d)	5.7
	<u>9e</u>	35	d)		3.78(s)	4.93(s)		-
p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	<u>8f</u>	33	d)		3.53(s) 3.68(s)	5.09(d)	5.53(d)	5.6
	<u>9f</u>	42	116.0-118.5	1705	3.72(s) 3.77(s)	4.78(d)	4.89(d)	1.4
CH <sub>3</sub> CH <sub>2</sub>	<u>8g</u>	23	d)		3.95(s)	4.28(d) <sup>e)</sup>	4.28(dt)	-
	<u>9g</u>	21	d)		3.63(s)	3.75(t) <sup>f)</sup>	4.56(s)	-

a) Reactions were carried out in benzene at 80 °C using 6 mmol of aldehyde and 3 mmol of 1 in the presence of 10 mg of Cu(acac)<sub>2</sub>. b) Isolated yield by silica gel column chromatography. c) Could not be isolated in pure state. d) Decomposed during column chromatography or recrystallization. e) Coupled with adjacent methylene group in J=6.6 Hz. f) Coupled with methylene protons in J=7.5 Hz.

protons at 4.78 and 4.86 ppm with small coupling constant (J=1.3 Hz), suggesting the exo structure (9). Methine protons on C<sub>5</sub> and C<sub>6</sub> of the endo adduct (8a) show its <sup>1</sup>H-NMR signals at lower field than those of exo adduct (9a). This may be attributed to shielding effect due to aryl and carbonyl groups located syn to each methine protons of the exo adduct. Other aldehydes also yielded endo and exo adducts as shown in Table 1.<sup>7)</sup>

High yields of the adducts with fluorenone or 2,6-dichlorobenzaldehyde indicate

that the 1,3-dipolar cycloaddition is not affected by steric repulsion in this system. This may reflect the strong 1,3-dipolar reactivity of the 1-methoxy-2-benzopyrylium-4-olate (3). The regioselectivity to give interesting orthoester derivatives was observed in this reaction. Because of their orthoester structure some of the adducts were unstable and decomposed during silica gel column chromatography. Stability and reactivity of the adducts will be described elsewhere.

#### References

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- 7) All new compounds described here gave satisfactory elemental analyses.
- 8) Spectral properties of 2:1 adduct (7): IR(KBr) 1715  $\text{cm}^{-1}$  (ring C=O); NMR( $\text{CDCl}_3$ ) 1.26 (s,  $\text{CH}_3$ ), 1.51 (s,  $\text{CH}_3$ ), 3.63 (s,  $\text{OCH}_3$ ), 3.71 (s,  $\text{OCH}_3$ ), 4.38 (s, methine-H), 5.26 (s, methine-H), 6.18 (d, aromatic-H), and 6.6-8.1 ppm (m, aromatic-H).

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