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Formation and Reaction of Carbonyl Ylides. 1,3-Dipolar Cycloaddition of 2-Benzopyrylium-4-olates with Carbonyl Compounds

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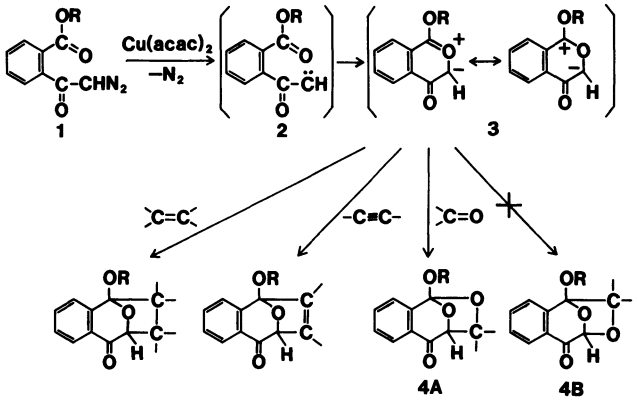
Cyclic orthoester type 1,3-dipolar cycloadducts of 1-methoxy-2-benzopyrylium-4-olate with carbonyl compounds were obtained in high yields in the copper(II) acetylacetonate-catalyzed decomposition of *o*-methoxycarbonyl-α-diazoacetophenone in the presence of carbonyl compounds such as substituted benzaldehydes, acetaldehyde, propionaldehyde, isobutyraldehyde, pivalaldehyde, acetone, methyl ethyl ketone, methyl isopropyl ketone, 1,3-dichloroacetone, substituted acetophenones, benzoyl cyanides, cyclopentanone, cyclohexanone, 1-indanone, 9-fluorenone, anthrone, and anthraquinone. However, methyl *t*-butyl ketone, benzophenone, and xthanthone gave no adduct. Aldehydes and asymmetric ketones gave endo- and exo-adducts. The regiochemistry and stereochemistry of the adducts of aldehydes were determined on the basis of their coupling constants of methine protons. The reactions of *p*-methoxyphenyl *o*-diazoacetylbenzoate also gave similar 1,3-dipolar adducts. When carbonyl compounds of medium reactivity were used as a substrate, 2:1-adduct was obtained together with the 1:1-adduct. The formation of the 2:1-adduct was attributed to the competitive reaction of the corrsponding benzopyrylium-4-olate intermediate toward the carbonyl compounds and 1:1-adduct. The regiospecificity of the 1:1-cycloaddition was explained according to the frontier orbitals calculated by STO-3G method.

The initial 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-epoxy-2,3-diphenyl-1-indenone.[1] However, only a few examples of the cycloaddition were reported in the literature.[2] The present authors have found the novel formation of carbonyl ylides of the type of 2-benzopyrylium-4-olate (**3**) by the intramolecular carbene–carbonyl reaction[3] and studied its 1,3-dipolar cycloaddition with acetylenic[4] and ethylenic compounds.[5] As an extension of this 1,3-dipolar cycloaddition, the authors have preliminarily reported the 1,3-dipolar cycloaddition of 1-methoxy-2-benzopyrylium-4-olate (**3a**:R=OCH_3) with benzaldehydes, propionaldehyde, acetophenones and fluorenone.[6] This paper deals with the application of the cycloaddition of (**3**) with various kinds of carbonyl compounds to understand the scope and limitation of the reaction for the synthesis of cyclic orthoesters. The regiochemistry and stereochemistry was also studied.



Results and Discussion

Reactions with Aldehydes. The $Cu(acac)_2$-catalyzed decomposition of *o*-methoxycarbonyl-α-diazoacetophenone (**1a**: R=OCH_3) in the presence of two molar equivalents of aromatic aldehydes gave each pair of isomeric adducts. For example, *p*-chlorobenzaldehyde gave two products of melting points at 135—137°C and 126—128°C. Results of elemental analysis and IR spectra showed that these are the isomeric adducts of **3a** and *p*-chlorobenzaldehyde having the same regiochemistry but different in configuration. The ^1H NMR coupling patterns of two methine protons of both adducts indicate that the cycloadducts have structures of orthoester as shown in formula **4A**. The higher melting product has doublet signals of methine protons at δ 5.08 and 5.53 with coupling constant J=6.0 Hz, which indicates the cis stereochemistry of two methine protons. Therefore, the substituent (**R′**) has *endo*-configuration as shown in formula **5**. The lower melting adduct has doublet siganls of methine protons at δ 4.78 and 4.86 with small coupling constant (J=1.3 Hz), which suggests the *exo*-structure (**6**) with trans configuration of two methine protons. The methine protons on C_5 (**Ha**) and C_6 (**Hb**) of the exo-adduct (**6c**) show its ^1H NMR signals at

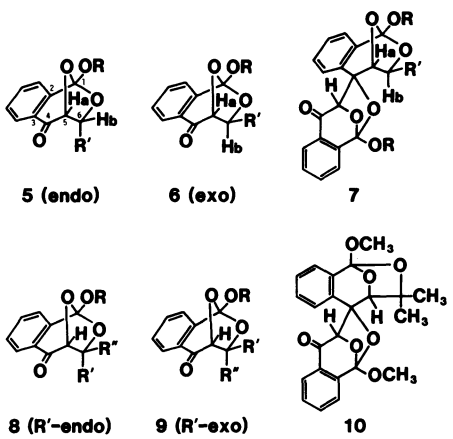


Table 1. Yields, IR, and NMR data of the cycloadducts of **3** with aldehydes

Run	R	R′	Adduct	Yield %	IR/cm^{-1}	NMR/ppm OCH$_3$[a]	Ha	Hb	Jab	Others[b]
Reactions with Aromatic Aldehydes										
a	CH_3	*p*-$CH_3OC_6H_4$	**5a**	33	c)	3.53,3.68	5.53(d)	5.09(d)	5.6	
			6a	42	1705	3.72,3.77	4.89(d)	4.78(d)	1.4	
b		C_6H_5	**5b**	38	1706	3.75	5.57(d)	5.27(d)	5.8	
			6b	44	1691	3.75	4.91(d)	4.81(d)	1.4	
c		*p*-ClC_6H_4	**5c**	42	1715	3.73,	5.53(d)	5.08(d)	6.0	
			6c	43	1708	3.72	4.86(d)	4.78(d)	1.3	
d		2,4-$Cl_2C_6H_3$	**5d**	75	1705	3.76	5.72(d)	5.38(d)	5.9	
			6d	12	c)	3.77	5.08(d)	4.83(d)	1.8	
e		2,6-$Cl_2C_6H_3$	**5e**	62	1690	3.75	5.93(d)	5.42(d)	5.4	
			6e	6	1703	3.80	5.53(d)	5.27(d)	2.3	
f		*p*-$NO_2C_6H_4$	**5f**	53	1702	3.77	5.65(d)	5.17(d)	6.0	
			6f	33	1698	3.77	4.92(s) 2H		—	
g		*m*-$NO_2C_6H_4$	**5g**	61	1690	3.78	5.72(d)	5.23(d)	5.7	
			6g	35	c)	3.78	4.93(s) 2H		—	
h	*p*-$CH_3OC_6H_4$	*p*-$CH_3OC_6H_4$	**5h**	35[d]	1705	3.68,3.80	5.27(d)	4.98(d)	5.6	
			6h	21	1711	3.69,3.79	4.70(d)	4.63(d)	1.3	
i		C_6H_5	**5i**	52[d]	1710	3.77	5.30(d)	5.01(d)	5.8	
			6i	43	1705	3.82	4.77(d)	4.69(d)	2.7	
j		*p*-$NO_2C_6H_4$	**5j**	47	1700	3.81	5.39(d)	5.11(d)	5.9	
			6j	45	1701	3.84	4.86(d)	4.71(d)	1.2	
Reactions with Aliphatic Aldehydes										
k	CH_3	CH_3	**5k**	39	1702	3.63	4.84(d)	4.54(dq)	5.5	1.05(d, CH_3)[f]
			6k	25	1710	3.68	4.52(d)	4.06(dq)	1.1	1.50(d, CH_3)[g]
l		CH_3CH_2	**5l**	e)	c)	3.95	4.86(d)	4.28(dt)	5.5	h)
			6l	e)	c)	3.63	4.56(s)	3.75(t)	—	i)
m		$(CH_3)_2CH$	**5m**	30	1708	3.63	4.90(d)	3.95(dd)	5.3	j)
			6m	47	1705	3.66	4.64(d)	3.41(dd)	1.3	k)
n		$(CH_3)_3C$	**5n**	11	1708	3.62	4.84(d)	4.13(d)	4.9	0.82(s, CH_3)
			6n	57	1710	3.43	4.64(d)	3.43(d)	1.8	1.04(s, CH_3)

a) Singlet signals. b) Signals of aromatic protons were omitted. c) The IR spectrum was not measured. d) The 2:1-adduct was obtained. e) Decomposed during column chromatography. f) J=6.5 Hz. g) J=6.5 Hz. h) δ=1.29 (dq, CH_2, J=6.9 and 7.2 Hz), 0.96 (t, CH_3, J=7.2 Hz). i) δ=1.76 (dq, CH_2, J=7.7 and 7.5 Hz), 1.07 (t, CH_3, J=7.5 Hz). j) δ=1.26 (d sep, CH, J=6.0 and 10.4 Hz), 0.90, 0.96 (d, CH_3, J=6.0 Hz). k) δ=1.95 (d sep, CH, J=6.5 and 10.4 Hz), 0.99, 1.06 (d, CH_3, J=6.5 Hz).

higher field than those of endo-adduct (**5c**). This may be attributed to shielding effect due to aryl (**R′**) and carbonyl groups located *syn* to each methine proton in the exo-adduct.

The assignment of the signals of methine protons (**Ha** and **Hb**) of the adducts (**5c** and **6c**) was determined on the basis of chemical shifts comparing with those of the adducts of aliphatic aldehydes. For example, endo-adduct of acetaldehyde has a doublet signal at δ 4.84 and a double quartet at δ 4.54 which were characterized to **Ha** and **Hb**, respectively. The exo-adduct also shows similar coupling pattern of methine protons (Table 1, Run k). The adducts of propionaldehyde and isobutyraldehyde were also identified similarly. In all of these adducts **Ha** showed a signal at lower field than that of **Hb**. The same tendency was observed in the adducts of aromatic aldehydes, and signals at δ 5.53 and 5.08 of the endo-adduct (**5c**) of *p*-chlorobenzaldehyde were assigned to **Ha** and **Hb**, respectively.

Other substituted benzaldehydes also gave similar results (Table 1, Run a—g). No adduct of the different regiochemistry as is shown by **4B** was obtained despite the detail inspection of the reaction mixture by column chromatography. The electron-attracting substituents on benzaldehyde such as *p*-NO_2 group tend to increase the yields of adducts in comparison with electron-releasing substituents (*p*-CH_3O). This means that the aldehydes with electron-attracting groups have high reactivity in this reaction system. However, these substituents do not show obvious effect on the stereoselectivity of the cycloaddition. Pivalaldehyde gave both endo- (**5n**) and exo-adduct (**6n**) in 11 and 57% respectively, reflecting the bulkyness of *t*-butyl group.

1-Methoxyphenyl *o*-diazoacetylbenzoate (**1b**:R=*p*-$CH_3OC_6H_4$) also gave similar results in the reaction with benzaldehydes. When *p*-anisaldehyde was used as a substrate, a 2:1-adduct (**7h**:R=R′=*p*-$CH_3OC_6H_4$) of **3b** and the aldehyde was obtained together with usual endo- and exo-1:1-adducts in the yields of 25, 35, and 21%, respectively. The 2:1-adduct has two singlet signals of methoxyl group at δ 3.47 (6H) and 3.73 (3H) and two doublets (δ 4.04, 4.65, J=1.5 Hz) and one singlet (δ 5.26) of methine protons besides multiplet signals of aromatic protons. The signals of the methine protons indicate the presence of two adjacent and one isolated methine protons. The coupling pattern of two dou-

TABLE 2. YIELDS, IR, AND NMR DATA OF THE CYCLOADDUCTS OF **3** WITH KETONES

Run	R	R′	R″	Adduct	Yield %	IR/cm^{-1}	NMR/ppm OCH$_3$[a]	NMR/ppm Ha[a]	NMR/ppm Others[b]
Reactions with Aliphatic Ketones									
a	CH_3	CH_3	CH_3	**8a**	75[c]	1707	3.67	4.88	1.11, 1.55(s, CH_3)
b			CH_3CH_2	**8b**	38	1705	3.65	4.50	1.05 (s, CH_3)[d]
				9b	20	1707	3.65	4.50	1.53 (s, CH_3)[e]
c			$(CH_3)_2CH$	**8c**	35	1710	3.67	4.63	0.95 (s, CH_3), f)
				9c	15	1700	3.67	4.53	1.44 (s, CH_3), g)
d		$ClCH_2$	$ClCH_2$	**8d**	96	1709	3.68	4.87	h)
Reactions with Aromatic Ketones									
e	CH_3	CH_3	*p*-$CH_3OC_6H_4$	**8e**	7	1709	3.55, 3.82	5.14	1.31 (s CH_3)
				9e	6	1707	3.50, 3.77	4.78	1.85 (s, CH_3)
f			C_6H_5	**8f**	15	1707	3.53	5.18	1.31 (s, CH_3)
				9f	18	1708	3.80	4.83	1.90 (s, CH_3)
g			*p*-$NO_2C_6H_4$	**8g**	29	1705	3.53	5.15	1.32 (s, CH_3)
				9g	46	1707	3.80	4.90	1.91 (s, CH_3)
h		CN	*p*-$CH_3OC_6H_4$	**8h**	64	1709	3.70, 3.85	5.25	
				9h	3	i)	3.64, 3.80	5.18	
i			*p*-$NO_2C_6H_4$	**8i**	86	1708	3.91	5.27	
				9i	7	i)	3.69	5.18	
j	*p*-$CH_3OC_6H_4$	CH_3	*p*-$CH_3OC_6H_4$	**8j**	—[c]				
				9j	4	1706	3.67, 3.81	4.69	1.32 (s, CH_3)
k			C_6H_5	**8k**	8[c]	i)	3.76	4.98	1.30 (s, CH_3)
				9k	13	1709	3.76	4.73	1.34 (s, CH_3)
l			*p*-$NO_2C_6H_4$	**8l**	54[c]	1710	3.80	5.00	1.33 (s, CH_3)
				9l	29	1708	3.83	4.81	1.37 (s, CH_3)

a) Singlet signal. b) Signals of aromatic protons were omitted. c) The 2:1-adduct was obtained. d) δ=1.04 (t, CH_3, J=7.3 Hz), 1.86 and 1.90 (q, CH_2, J=7.3 Hz). e) δ=0.88 (t, CH_3, J=6.7 Hz), 1.37 and 1.39 (q, CH_2, J=6.7 Hz). f) δ=1.01 (d, CH_3, J=6.8 Hz), 1.12 (d, CH_3, J=6.8 Hz), 2.19 (sep, CH, J=6.8 Hz). g) δ=0.90 (d, CH_3), 1.45 (sep, CH). h) δ=3.30 (d, CH_3, J=12.0 Hz), 3.56 (d, 1H, J=12.0 Hz), 3.87 (d, 1H, J=11.7 Hz), 4.12 (d, 1H, J=11.7 Hz). i) The IR spectrum was not measured.

TABLE 3. YIELDS, IR AND NMR DATA OF THE CYCLOADDUCTS (**8** AND **9**) OF **3** WITH CYCLIC KETONES

R	Ketone	Adduct	Yield %	IR	NMR/ppm OCH$_3$	NMR/ppm Ha	NMR/ppm Others[a]
CH_3	Cyclopentanone	**8m**	78	1706	3.63	4.61	1.2—2.3 (m, 8H, CH_2)
	Cyclohexanone	**8n**	87	1707	3.98	4.56	1.2—2.0 (m, 10H, CH_2)
	1-Indanone	**8o**	1.3[b]	1706	3.73	4.71	1.7—2.3 and 2.8—3.1 (m, 4H, CH_2)
		9o	6.8[c]	1701	3.62	5.01	1.6—2.3 and 2.8—3.1 (m, 4H, CH_2)
	9-Fluorenone	**8p**	75	1705	3.91	4.92	
	Anthraquinone	**8q**	17	1703	4.03	5.82	
	Anthrone	**8r**	21	1710	4.10	4.71	3.91 and 4.03 (d, CH, J=17.4 Hz)
p-$CH_3OC_6H_4$	9-Fluorenone	**8s**	53	1710	3.76	4.73	

a) Signals of aromatic protons were omitted. b) Isomer having phenyl moiety in endo. c) Isomer having phenyl moiety in exo.

blets is quite similar to that of exo-1:1-adduct (**6h**). Therefore, it is suggested that in the 2:1-adduct the *p*-methoxyphenyl group of the aldehyde origin has *exo* configuration, and that the 2:1-adduct is formed by the secondary cycloaddition of **3b** on exo-1:1-adduct (**6h**).

Reaction with Ketones. The decomposition of **1a** in acetone gave a similar adduct (**8a**) in 75% yield together with a 2:1-adduct (**10**: 12%) of **3a** and acetone. The adduct (**8a**) showed two singlet signals in its NMR spectrum at δ 1.55 and 1.11 which corresponded to the signals of the exo- (**6k**:δ 1.50) and endo-adduct (**5k**: δ 1.05) of acetaldehyde. Therefore, signals at δ 1.55 and 1.11 of **8a** were assigned to exo- and endo-methyl groups, respectively. Similar assignment was applied to the characterization of other methyl ketone adducts.

The NMR spectrum of the 2:1-adduct is quite similar to that of **8a** (Table 2). The spectroscopic data of the 2:1-adduct and the behavior of **3a** in the cycloaddition to carbonyl group noted above indicate that the 2:1-adduct is the secondary reaction product obtained by the cycloaddition of **3a** toward the carbonyl group of 1:1-adduct (**8a**), and is indicated by the structural formula **10**. The stereochemistry of the 2:1-adduct is not determined yet. Each of methyl ethyl ketone, methyl isopropyl ketone, substituted acetophenones and substituted benzoyl cyanides gave a pair of adducts different in the stereochemistry at C_6 (Table 2).

However, methyl *t*-butyl ketone and benzophenone did not give any adduct because of their low reactivity attributable to the steric hindrance or aromatic stabi-

lization. Cyclic ketones such as cyclopentanone, cyclohexanone, 1-indanone, 9-fluorenone, anthraquinone, and anthrone gave adducts of type **4A** (Table 3). Except 1-indanone, cyclic ketones gave single adducts because they were symmetric. 1-Indanone afforded two adducts in 1.3 and 6.8% yields which were identified as **Ph**-endo- and **Ph**-exo-adducts respectively on the basis of NMR data. The **Ph**-endo-adduct shows a signal of an aromatic proton of indanone moiety at δ 6.24 which may caused by the shielding effect of benzene ring of **3a** moiety. In the cyclic ketones used, aliphatic ketones were shown to have reactivities higher than those of aromatic ketones such as indanone, anthraquinone, and anthrone which were resonance stabilized. The exception was fluorenone, which gave an adduct in good yield in the reaction with **3a**. The adduct was confirmed to have the same structure with **4A** as the adducts of aldehydes and other ketones described above on the basis of ^{13}C NMR spectrum which showed a signal of nonaromatic quartanary carbon (C_1) at quite low field (δ 119.1). Another type of regioisomer (**4B**) may not give a signal of quarternary carbon in this region.

When the dipolarophilicity of the carbonyl compound was not so high, 2:1-adducts of the benzopyrylium-4-olates (**3**) with the dipolarophiles were also obtained along with 1:1-adducts as described above in the reaction with acetone. The details of the 2:1-adducts will be published elsewhere.

Frontier Orbital Explanation of the Regiospecificity and Reactivity of the Cycloaddition. The stereo-

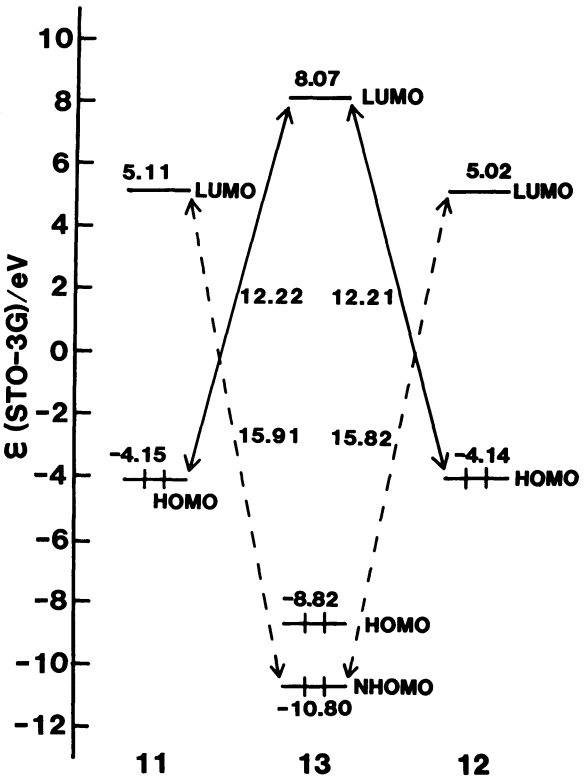


Fig. 1. HOMO and LUMO energy levels of carbonyl ylides (**11**, **12**) and acetone (**13**).

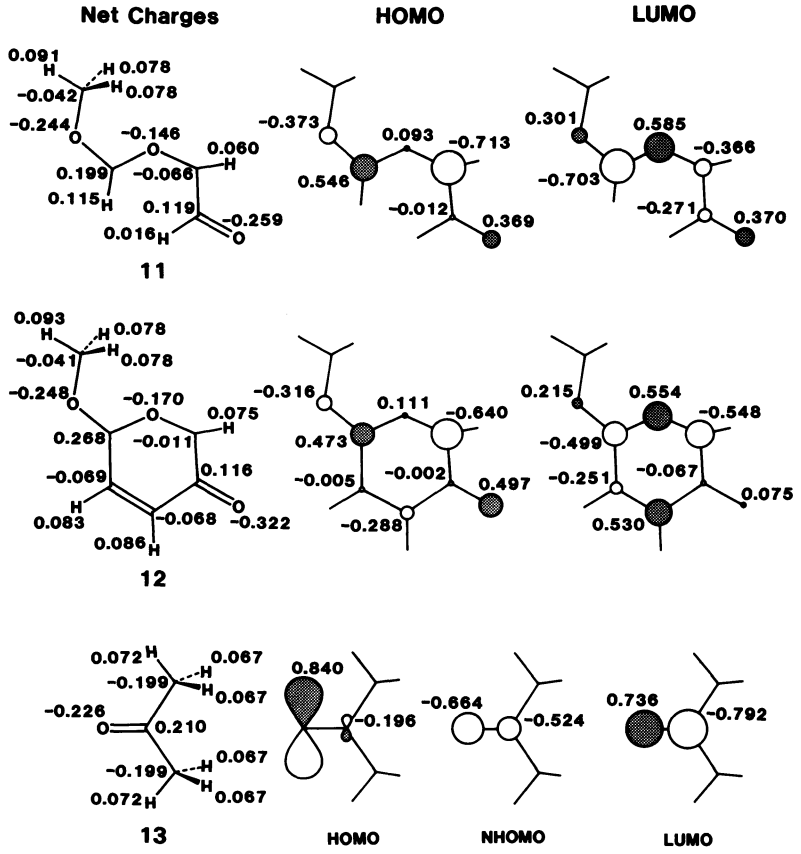


Fig. 2. Orbital coefficients of HOMO and LUMO of carbonyl ylide (**11**, **12**) and acetone (**13**).

specificity observed in the 1,3-dipolar cycloaddition of 2-benzopyrylium-4-olate (**3**) with cis- and trans-ethylenic dipolarophiles indicates that the reaction proceeds in the concerted process.[5] The regioselectivity and reactivity of the 1,3-dipolar cycloaddition has been explained by second-order perturbation expression.[7] Orbital energies and atomic orbital coefficients of carbonyl ylides and acetone were calculated by STO-3G level.[8] Instead of the complex carbonyl ylide like 1-methoxy-2-benzopyrylium-4-olate (**3a**) which has an electron-releasing methoxyl group on a carbonyl ylide carbon and an electron-attracting carbonyl group on another side, we chose 1-methoxy-3-formyl-carbonyl ylide (**11**) and 6-methoxypyrylium-3-olate (**12**) as model compounds. Energy levels of the two model carbonyl ylides (**11** and **12**) calculated are quite similar in their frontier orbitals. Frontier orbital energy levels of **11**, **12**, and acetone indicate that the cycloaddition is controled by the interaction of carbonyl ylide HOMO with carbonyl compound LUMO (Fig. 1).[9]

Atomic orbital coefficients of the frontier orbitals of carbonyl ylides (**11** and **12**) and acetone are shown in Fig. 2. The preferred orientation of the cycloaddition is that in which the atoms having larger terminal atomic coefficients of the interacting frontier orbitals are bonded. Therefore, oxygen atom of carbonyl compound bonded to carbon atom of carbonyl ylide attached by an electron-releasing group (OCH_3), to give an orthoester type adduct (**4A**), because these atoms have larger coefficients in carbonyl compound LUMO and carbonyl ylide HOMO, respectively. Dipole-dipole interaction between the carbonyl ylides, (methoxymethyleneoxonio)formylmethanide (**11**) and 6-methoxypyrylium-3-olate (**12**), and acetone shown in electron-density formula (Fig. 2) also supports the regiospecificity of the cycloaddition cited above.

Strong electron-attracting groups exert considerable

Table 4. Melting points and analitical data of adducts

Adduct	Mp (θ_m/°C)	Found(%)			Calcd(%)			Molecular Formula
		C	H	N	C	H	N	
6a	116.0—118.5	69.01	5.17	—	69.22	5.16	—	$C_{18}H_{16}O_5$
5b	87.5— 89.5	72.22	5.06	—	72.33	5.00	—	$C_{17}H_{14}O_4$
6b	110.0—110.8	72.41	5.00	—				
6c	126.5—127.5	64.41	4.14	—	64.47	4.14	—	$C_{17}H_{13}O_4Cl$
5d	136.5—138.0	58.08	3.45	—	58.14	3.44	—	$C_{17}H_{12}O_4Cl_2$
5e	148.0—150.0	57.87	3.28	—				
6e	158.0—161.0	58.08	3.44	—				
5f	152.0—154.0	62.29	4.04	4.42	62.39	4.00	4.28	$C_{17}H_{13}O_6N$
6f	147.5—148.8	62.35	4.00	4.27				
5g	115.0—117.0	62.36	4.01	4.40				
5h	118.0—119.5	71.48	5.02	—	71.28	4.98	—	$C_{24}H_{20}O_6$
5i	194.0—194.7	74.00	4.91	—	73.79	4.85	—	$C_{23}H_{18}O_5$
6i	163.0—165.0	73.85	4.89	—				
5j	236.7—239.0	65.91	4.16	3.37	65.87	4.09	3.34	$C_{23}H_{17}O_7N$
6j	199.8—201.0	65.81	4.10	3.37				
5k	78.0— 79.0	65.31	5.49	—	65.45	5.49	—	$C_{12}H_{12}O_4$
6k	76.5— 77.3	65.36	5.69	—				
5m	Liquid	67.79	6.60	—	67.73	6.50	—	$C_{14}H_{16}O_4$
6m	Liquid	67.52	6.52					
8a	117.0—112.3	66.65	6.07	—	66.66	6.02	—	$C_{13}H_{14}O_4$
8b	91.0— 94.0	67.90	6.50	—	67.73	6.50	—	$C_{14}H_{16}O_4$
9b	94.5— 95.8	67.73	6.40	—				
8c	Liquid	68.75	6.83	—	68.69	6.92	—	$C_{15}H_{18}O_4$
9c	78.5— 79.5	68.59	6.93	—				
8d	78.3— 79.5	51.57	4.03	—	51.51	3.99	—	$C_{13}H_{12}O_4Cl_2$
8e	103.0—103.5	69.66	5.56	—	69.93	5.56	—	$C_{19}H_{18}O_5$
9e	126.0—128.0	69.86	5.59	—				
8f	175.0—176.5	73.02	5.53	—	72.96	5.44	—	$C_{18}H_{16}O_4$
9f	112.0—112.6	72.51	5.47	—				
8g	208.5—209.0	63.63	4.43	4.10	63.34	4.43	4.10	$C_{18}H_{15}O_6N$
9g	120.0—122.3	63.57	4.40	4.09				
8h	171.5—173.0	67.65	4.51	4.17	67.65	4.48	4.15	$C_{19}H_{15}O_5N$
8i	169.4—171.4	61.60	3.00	7.89	61.37	3.43	7.95	$C_{18}H_{12}O_6N_2$
9j	210.0—212.0	72.06	5.40	—	71.76	5.30	—	$C_{25}H_{22}O_6$
9k	202.5—203.7	74.11	5.25	—	74.21	5.19	—	$C_{24}H_{20}O_5$
8m	Liquid	69.87	6.64	—	70.06	6.61	—	$C_{16}H_{18}O_4$
8n	Liquid	68.75	6.19	—	69.22	6.20	—	$C_{15}H_{16}O_4$
8o	143.0—143.5	73.74	5.32	—	74.01	5.23	—	$C_{19}H_{16}O_4$
9o	123.0—124.0	73.96	5.24	—				
8p	218.0—219.0	77.33	4.56	—	77.51	4.53	—	$C_{23}H_{16}O_4$
8q	208.5—210.5	74.89	4.34	—	74.99	4.20	—	$C_{24}H_{16}O_5$

lowering effect on the LUMO of the carbonyl compounds, resulting in a small energy separation between the carbonyl ylide HOMO and carbonyl compound LUMO. This explains the high reactivity of carbonyl compounds having electron-attracting substituents such as *p*-nitroacetophenone, *p*-nitrobenzoyl cyanide and 1,3-dichloroacetone.

Experimental

All melting points were measured on a Yanagimoto Melting Point Apparatus and were not corrected. The IR spectra were taken on a Hitachi Spectrometer, model 260-10 and Perkin Elmer, model 983 in KBr mull. The ^{1}H NMR spectra were recorded on a Varian EM-390 Spectrometer in a $CDCl_3$ solution using TMS as an internal standard; ^{13}C NMR spectra were recorded on a Bruker AM-360. The chemical shifts were described in ppm downfield from TMS.

Materials. *o*-Methoxycarbonyl-α-diazoacetophenone (**1a**) was prepared by the procedure described in the previous paper.[4,5] *p*-Methoxyphenyl *o*-diazoacetylbenzoate (**1b**) was synthesized in 84% yield by the reaction of excess diazomethane with corresponding acid chloride: mp 67.5—68.8 °C; IR (KBr) 3080 (CH), 2100 (diazo), 1730 (ester C=O), and 1610 cm^{-1} (diazoketone C=O); NMR ($CDCl_3$) δ=3.79 (s, OCH_3), 5.60 (s, CH), 6.88, 7.14 (ABq, arom), and 7.52—7.95 (m, arom). Found. C, 64.83; H, 4.07; N, 9.42%. Calcd for $C_{16}H_{12}O_4N_2$: C, 64.86; H, 4.08; N, 9.45%.

Aldehydes and ketones used were purified just before use by distillation or recrystallization of the commercial reagents.

General Procedure of the Decomposition of 1 in the Presence of Carbonyl Compounds. The Cu(acac)$_2$-catalyzed decomposition of **1** was carried out according to the procedure described in the previous paper:[4,5] a benzene solution of **1** was added drop by drop into a benzene solution of 2—10 molar equivalents of carbonyl compounds and catalytic amount of Cu(acac)$_2$ under reflux of benzene at 80 °C. The reaction mixture was heated until no more N_2 was evolved (about one hour) and then separated by silica-gel column chromatography using benzene as the eluent.

The 2:1-adduct (**7h**) between **3b** and *p*-anisaldehyde: mp 245.5—247.0 °C; IR (KBr) 1711 cm^{-1} (C=O); NMR ($CDCl_3$) δ=3.47 (s, OCH_3), 3.73 (s, OCH_3), 4.04 (d, CH, *J*=1.5 Hz), 4.65 (d, CH, *J*=1.5 Hz), 5.25 (s, CH), and 6.20—8.00 (m, 16H, Ar). Found: C, 71.85; H, 4.88%. Calcd for $C_{40}H_{32}O_{10}$: C, 71.42; H, 4.79%.

The 2:1-adduct (**10**) between **3a** and acetone: mp 184.2—185.0 °C; IR(KBr) 1714 cm^{-1} (C=O); NMR ($CDCl_3$) δ=1.26 (s, CH_3), 1.51 (s, CH_3), 3.63 (s, OCH_3), 3.71 (s, OCH_3), 4.38 (s, CH), 5.26 (s, CH), and 6.19 (d, 1H, arom, *J*=8.1 Hz), 6.80—7.93 (m, 7H, arom). Found: C, 67.71; H, 5.47%. Calcd for $C_{23}H_{22}O_7$: C, 67.31; H, 5.40%.

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8) Details on the MO calculation will be published elsewhere.

9) As the HOMO orbital of acetone has no π-component, the interaction of its NHOMO orbital was taken into account.