The Reaction of Diazo Ketones in the Presence of Metal Chelates. VIII. The Stereochemistry of the 1,3-Dipolar Cycloaddition of 1-Methoxy-2-benzopyrylium-4-olates to Ethylenic Dipolarophiles

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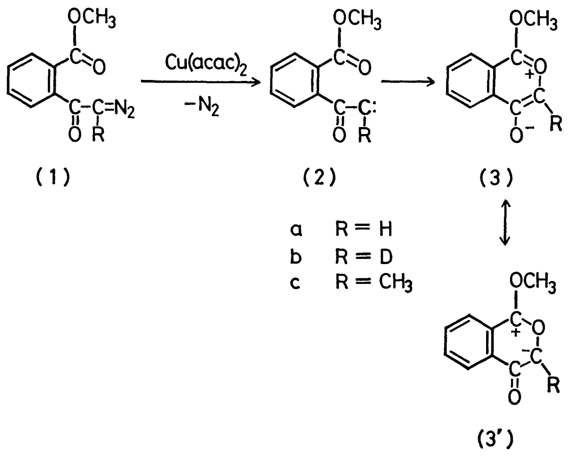
1,3-Dipolar cycloadducts were obtained in the reactions of 1-methoxy-2-benzopyrylium-4-olate (**3a**) with ethylenic dipolarophiles, such as dimethyl fumarate, dimethyl maleate, maleic anhydride, *trans*-1,2-dibenzoylethylene, *N*-substituted maleimides, and acenaphthylene. The configuration of the adducts was determined on the basis of the NMR coupling pattern of the methine protons of the adducts in connection with a deuterium experiment. The previously reported structure of the adduct of **3a** with dimethyl fumarate was corrected according to the experimental results obtained using 3-deuterated **3a**. The stereospecificity of the cycloaddition was confirmed in the reactions of dimethyl fumarate, dimethyl maleate, and *trans*-1,2-dibenzoylethylene; this stereospecificity was explained by the concerted ($_{\pi}2_S + _{\pi}4_S$) mechanism. The *exo*/*endo* ratios of the adducts of *N*-substituted maleimides may be explained by the combination of the steric repulsion and π-π interaction of the phenyl ring of **3** and the substituent on the *N*-atom of maleimides. The cycloadditions of 1-methoxy-3-methyl-2-benzopyrylium-4-olate with *N*-substituted maleimides were also explained in a similar manner.

The 1,3-dipolar cycloaddition of pyridinium-3-olate has recently been studied extensively by Katritzky and his co-workers.1) However, only a few papers are to be found on the reaction of pyrylium-3-olates,2) which is isoelectronic with pyridinium-3-olate. In the previous papers of this series, we reported the transient formation of 1-methoxy-2-benzopyrylium-4-olate (**3a**: R=H) in the copper chelate-catalyzed decomposition of *o*-methoxycarbonyl-α-diazoacetophenone (**1a**: R=H) *via* an intramolecular carbene-carbonyl reaction.3) The 2-benzopyrylium-4-olate was found to react as a 1,3-dipole of a type of carbonyl ylide with electron-deficient olefins3) and acetylenes.4) In this paper, the stereochemistry of the cycloaddition of **3** will be discussed in detail, using various *cis*- and *trans*-ethylenic dipolarophiles, in order to investigate the mechanism of this reaction.

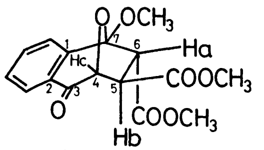


Results and Discussion

The Cu(acac)$_2$ catalyzed decomposition of *o*-methoxycarbonyl-α-diazoacetophenone (**1a**: R=H) in the presence of dimethyl fumarate was reported to give a cycloadduct (**4a**), which was assigned erroneously to 4,7-epoxy-7-methoxy-5-*endo*-6-*exo*-bis(methoxycarbonyl)-1,2-benzocyclohepten-3-one (**4c**).3) The NMR spectrum of the adduct (**4a**) showed signals of three methine protons, at δ 3.50 (dd), 4.00 (d), and 5.00 (d), besides the three singlets of OCH$_3$ and a multiplet of aromatic protons (Table 3). The double-doublet signal at δ 3.50 was readily assigned to Hb by reason of its splitting pattern, attributable to the coupling with the adjacent methine protons, Ha and Hc, on its sides. However, for the assignment of the two doublet at δ 4.00 and 5.00, the above data are not sufficient. In order to assign these signals,4) *o*-methoxycarbonyl-α-diazoacetophenone-α-*d* (**1b**: R=D) was treated similarly in the presence of dimethyl fumarate; a deuterated cycloadduct (**4b**) was thus obtained. The similarity of the structures, **4a** and **4b**, is indicated by the fact that the mixed-melting-point test with **4a** and **4b** does not show any depression (110—111 °C). The IR spectrum of **4b** exhibits a similar pattern almost identical with that of **4a**. In the NMR spectrum of **4b** only two methine protons were observed, δ 4.03 and 3.50, as doublet signals which were coupled each other with J=6.0 Hz. This means that the substitution causes the disappearance of the doublet of **4a** at δ 5.00 and that the double-doublet of **4a** at δ 3.50 is decoupled to form a doublet. Therefore, the signals at 4.00 (d) and 5.00 (d) of **4a** were assigned to Ha and Hc respectively.

The steric relationship between Hb and Hc is determined to be *trans* on the basis of the small value of the coupling constsnt, J_{bc}=1.7 Hz,6) which indicates an *endo* configuration of Hb. Although the coupling constant, J_{ab}(=6.0 Hz), has a medium value of *cis* and *trans* coupling constants, the steric relationship between Ha and Hb is established as *trans* in comparison with the value of J_{ab} (=9.6 Hz) of the adduct (**4d**) of dimethyl maleate, which has a *cis* configuration of Ha and Hb, as is shown below. The geometry of Hb and Hc of **4d** is confirmed to be *trans* (J_{bc}=2.6 Hz); hence, the configuration of Hb is concluded to be *endo*.

On a large-scale experiment on **1a** with dimethyl fumarate, the major adduct (**4a**) was obtained in a 70% yield, along with a minor product, colorless crystals (mp 115—117 °C, 4% yield). The minor



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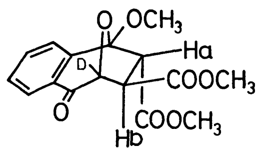

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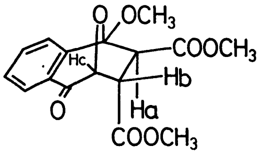

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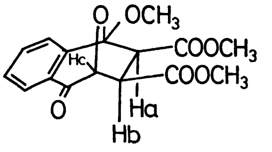


(4d)

product was characterized as the adduct (**4c**) on the basis of its IR and NMR spectra. The similarity of the IR spectra of **4a** and **4c**, expect for a few differences in the finger-print region, indicates that these adducts are structural isomers different in configuration in the two methoxycarbonyl groups. In **4c**, the geometry between Ha and Hb was deduced to be *trans* ($J_{ab}=5.4$ Hz), and that of Hb and Hc, to be *cis* ($J_{bc}=9.0$ Hz). Therefore, the configurations of Hb and Ha are *exo* and *endo* respectively. The fact that the *trans* coupling constants, J_{ab} (6.0 and 5.4 Hz), of **4a** and **4c** are larger than the *trans* coupling constants, J_{bc} (1.7 and 2.6 Hz), of **4a** and **4d** is supported by the inspection of the dihedral angle of a Dreiding Model of the adducts (*trans*-Ha-C-C-Hb, 140°; *trans*-Hb-C-C-Hc, 90°).7)

When the reaction was carried out in the presence of dimethyl maleate, a 1,3-dipolar cycloadduct (**4d**) was obtained in a 51% yield (mp 145—147 °C); this cycloadduct showed different spectral properties and melting point from the adducts, **4a** and **4c**, described above (Tables 1 and 3). The structure of **4d** was confirmed by a comparison of its IR and NMR spectra with those of an authentic sample synthesized by the esterification of the corresponding dicarboxylic acid, which has been obtained by the hydrolysis of the cycloadduct of 2-benzopyrylium-4-olate (**3a**) with maleic anhydride.

The relation with *trans*-1,2-dibenzoylethylene gave two adducts (**5a** and **5c**). The major adduct (**5a**) showed two doublets, at δ 5.32 and 5.03, and a double-doublet at δ 4.68 (Table 3). These signals were assigned to Ha, Hc, and Hb respectively by comparison with the deuterated adduct (**5b**) in a manner similar to that cited above. The relationships between the neighboring methine protons, Ha-Hb and Hb-Hc, are determined to be *trans* on the basis of the coupling constants ($J_{ab}=5.6$, $J_{bc}=1.8$ Hz). The smaller coupling constant J_{ab} (=5.5 Hz) and larger J_{bc} (=8.8 Hz) of the minor adduct (**5c**) show *trans* Ha-Hb and *cis*

TABLE 1. YIELDS, MELTING POINTS, AND ANALYTICAL DATA OF CYCLOADDUCTS OF **3a**

Dipolarophile	Adduct	Yield %	Mp/°C	Found (%)			Calcd (%)			Molecular formula
				C	H	N	C	H	N	
Dimethyl fumarate	**4a**	70	111—112	59.89	5.07	—	60.00	5.04	—	$C_{14}H_{16}O_7$
	4c	4	115—117	59.89	5.19	—				
	4ba)	60	110—111	59.66	4.81	—				
Dimethyl maleate	**4d**b)	51	145—147	60.27	5.11	—				
1,2-Dibenzoylethylene	**5a**	83	151—152	75.89	4.67	—	76.09	4.42	—	$C_{26}H_{18}O_5$
	5c	6	236—239	76.15	4.26	—				
	5ba)	70	151—153	76.28	4.25	—				
Maleic anhydride	**7**	48c)	215—216	57.64	4.06	—	57.54	4.14	—	$C_{14}H_{12}O_7$
N-Phenylmaleimide	**9a**	58	238—239	68.84	4.27	4.18	68.76	4.33	4.01	$C_{20}H_{15}O_5N$
	10a	29	206—207	68.50	4.28	4.00				
N-Ethylmaleimide	**9b**	70	195—197	64.01	5.10	4.77	63.78	5.02	4.65	$C_{16}H_{15}O_5N$
	10b	25	d)							
N-Methylmaleimide	**9c**	61	293—295	62.55	4.64	4.90	62.71	4.56	4.88	$C_{15}H_{13}O_5N$
	10c	33	208—210	62.44	4.52	4.93				
Acenaphthylene	**13**e)	9	210—212	80.20	4.61	—	80.47	4.91	—	$C_{22}H_{16}O_3$
	14	13	178—179	80.54	4.93	—				

a) An α-deuterated diazo ketone (**1b**) was used. b) Isochromandione (**8**) was obtained as a by-product (18%). c) As a by-product, **8** was obtained in a 14% yield. d) An attempt to purify the *endo* adduct (**10b**) was not successful. e) As a by-product, **8** was obtained in a 14% yield.

TABLE 2. YIELDS, MELTING POINTS, AND ANALYTICAL DATA OF CYCLOADDUCTS OF **3c**

Dipolarophile	Adduct	Yield %	Mp/°C	Found (%)			Calcd (%)			Molecular formula
				C	H	N	C	H	N	
N-Phenylmaleimide	**11a**	57	215—217	69.14	4.74	3.66	69.41	4.73	3.86	$C_{21}H_{17}O_5N$
	12a	39	204—206	69.43	4.71	3.72				
N-Ethylmaleimide	**11b**	66	184—186	64.62	5.46	4.22	64.75	5.43	4.44	$C_{17}H_{17}O_5N$
	12b	28	162—163	64.78	5.50	4.35				
N-Methylmaleimide	**11c**	54	229—230	63.56	5.07	4.44	63.78	5.02	4.65	$C_{16}H_{15}O_5N$
	12c	41	191—192	64.03	5.13	4.44				

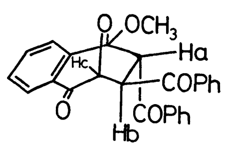
TABLE 3. SPECTRAL PROPERTIES OF CYCLOADDUCTS OF **3** WITH ETHYLENIC DIPOLAROPHILES

Adduct	NMR (δ, $CDCl_3$)									IR (cm^{-1}, KBr) C=O
	Ha	Hb	Hc	J_{ab}	J_{bc}	OCH_3	OCH_3	OCH_3	Others a)	
4a	4.00 (d)	3.50 (dd)	5.00 (d)	6.0 trans	1.7 trans	3.45	3.58	3.80		1710, 1734
4b	4.03 (d)	3.50 (d)	—	6.0 trans	—	3.45	3.60	3.82		1710, 1735
4c	3.43 (d)	4.11 (dd)	5.12 (d)	5.4 trans	9.0 cis	3.44	3.60	3.80		1708, 1737
4d	3.57 (d)	3.15 (dd)	5.46 (d)	9.6 cis	2.6 trans	3.44	3.74	3.80		1717, 1753
5a	5.32 (d)	4.68 (dd)	5.03 (d)	5.6 trans	1.8 trans	3.66				1685, 1700
5b	5.34 (d)	4.70 (d)	—	5.6 trans	—	3.64				1685, 1700
5c	4.80 (d)	5.63 (dd)	5.29 (d)	5.5 trans	8.8 cis	3.33				1675, 1705
7 b)	3.80 (d)	3.67 (dd)	5.98 (d)	9.2 cis	2.3 trans	3.44				1710, 1740
9a	3.43 (s)		5.22 (s)	—	0 trans	3.53				1720
9b	3.30 (s)		5.12 (s)	—	0 trans	3.50			1.21 (t, CH_3) 3.63 (q, CH_2)	1710
9c	3.40 (s)		5.10 (s)	—	0 trans	3.50			3.08 (s, CH_3)	1708
10a	3.93 (d)	4.30 (t)	5.20 (d)	9.0 cis	9.0 cis	3.57				1720
10b	3.82 (d)	4.22 (t)	5.10 (d)	9.0 cis	9.0 cis	3.53			0.27 (t, CH_3) 3.07 (q, CH_2)	1705
10c	3.73 (d)	4.17 (t)	5.14 (d)	9.0 cis	9.0 cis	3.53			2.37 (s, CH_3)	1715
11a	3.20 (d)	3.52 (d)	—	8.0 cis	—	3.53			1.73 (s, CH_3)	1710
11b	3.07 (d)	3.38 (d)	—	8.0 cis	—	3.51			1.67 (s, CH_3) 1.23 (t, CH_3) 3.65 (q, CH_2)	1702
11c	3.12 (d)	3.43 (d)	—	8.0 cis	—	3.53			1.70 (s, CH_3) 3.08 (s, CH_3)	1705
12a	3.75 (d)	4.05 (d)	—	10.0 cis	—	3.58			1.87 (s, CH_3)	1720
12b	3.58 (d)	3.88 (d)	—	10.0 cis	—	3.53			1.80 (s, CH_3) 0.30 (t, CH_3) 3.07 (q, CH_2)	1702
12c	3.62 (d)	3.92 (d)	—	10.0 cis	—	3.55			1.83 (s, CH_3) 2.37 (s, CH_3)	1708
13	4.2 (s)		4.90 (s)	—	0 trans	3.25				1703
14	4.3—5.2			c)	c)	3.53				1708

a) Signals of aromatic protons were omitted. b) The NMR spectrum was measured in a $CDCl_3$-pyridine solution. c) The coupling constant was not determined.

Hb-Hc relationships, which indicate *endo*-Ha and *exo*-Hb configurations.

Reaction with maleic anhydride gave only one adduct in a 48% yield, along with isochroman-1,4-dione (**8**, 14%). The IR spectrum and the results of elemental analysis exhibit that the adduct has a structure (**7**) with two carboxyl groups which were derived from the hydrolysis of the primary adduct (**6**) during the silica-gel-column chromatography. The NMR spectrum of **7** shows doublets at δ 3.80 and 5.98 and a double-doublet at δ 3.67. The coupling constants indicate that the carboxyl groups have the *exo* configuration. The esterification of the adduct (**7**) with diazomethane gave a diester which has the same structure as the adduct (**4d**) obtained by the reaction with dimethyl maleate and the 2-benzopyrylium-4-olate (**3a**). In this case, the absence of an adduct with *endo* carboxyl groups may be attributed to the steric replusion between the anhydride group of the dipolarophile and the carbonyl group of **3a**. The low dipolarophilicity of maleic anhydride caused the by-product formation of lactone (**8**) by the attack



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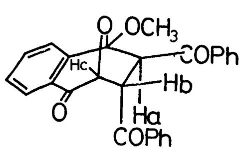

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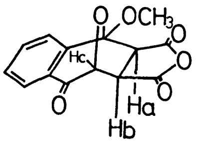

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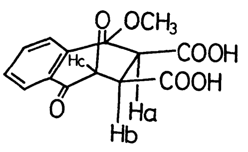

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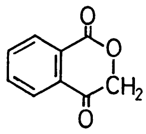


(8)

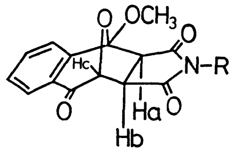
on 2-benzopyrylium-4-olate (**3a**) of water contained in a benzene solution as an impurity.

N-Phenylmaleimide gave two adducts in yields of 58 and 29%. The major adduct (**9a**) was established to be the *exo* isomer on the basis of its NMR spectrum, which showed singlet signals of methine protons at δ 3.43 and 5.22. From the lack of coupling between Hb and Hc, the configuration of Hb was confirmed to be *endo*. In other words, the *exo* configuration of the adduct (**9a**) was established.[8] Therefore, a singlet at δ 3.43 was assigned to both Ha and Hb, which happened to be equivalent to each other, while a singlet at δ 5.22 was assigned to Hc. The minor adduct (**10a**) shows methine-proton signals at δ 3.93 (d), 4.30 (t), and 5.20 (d), which were assigned to Ha, Hb, and Hc respectively. The coupling pattern, especially the doublet signal (J=9.0 Hz) of Hc, indicates the *endo* structure of the adduct (**10a**).[8] The triplet signal of Hb may be attributed to the same value of the coupling constants, J_{ab} and J_{bc} (=9.0 Hz). The *endo* structure (**10a**) of the minor product was also supported by the abnormal high-field shifts (6.27—6.47 ppm) of two ortho-protons of *N*-phenyl group, which were caused by the shielding effect of the condensed benzene ring. A Dreiding-Model inspection of the *endo* adduct indicates the benzene ring and *N*-phenyl group close to one another.

N-Ethyl- and *N*-methylmaleimides also gave *exo* (**9b**, 70%; **9c**, 61%) and *endo* adducts (**10b**, 25%; **10c**, 33%) respectively. A similar pattern of methine signals was observed in the NMR spectrum of the adducts. The high-field shifts of the *N*-ethyl (δ 0.27, CH_3; 3.07, CH_2) and *N*-methyl signals (δ 2.37) of **10b** and **10c** are explained by the shielding effect of the benzene ring, located close to the *N*-alkyl groups.

Similar results were observed in the reaction of *N*-substituted maleimides with 1-methoxy-3-methyl-2-benzopyrylium-4-olate (**3c**, R=CH_3), which was generated by the Cu(acac)$_2$-catalyzed decomposition of 2-methoxycarbonyl-α-diazopropiophenone (**1c**), yielding *exo* (**11**) and *endo* (**12**) adducts (Table 2). The *endo* adducts show the shielding effect by the benzene ring on the PMR shift of the *N*-methyl, *N*-ethyl, and *N*-phenyl groups (Table 3).

When **1a** was decomposed in the presence of acenaphthylene, two adducts (**13** and **14**) were obtained accompanying lactone (**8**, 14%) in yields of 9 and 13% respectively. The NMR spectrum of **13** has a singlet signal of Hc at δ 4.90 and a broad singlet of two methine protons, Ha and Hb, at δ 4.2. The lack of coupling between Hb and Hc establishes the *exo* structure of the adduct (**13**).[8] Although the multiplet signal of the methine protons of **14** is not sufficient for the determination of the configuration of **14**, it may be identified as *endo* by comparison with the spectrum of **13**.



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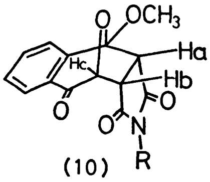

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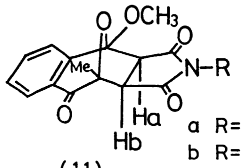
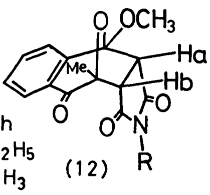


(11)

a R=Ph
b R=C_2H_5
c R=CH_3



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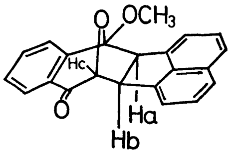

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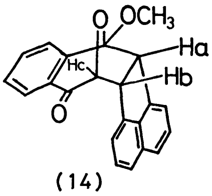
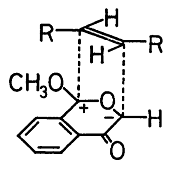


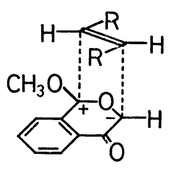
(14)

The stereospecificity of the cycloaddition of the 2-benzopyrylium-4-olate (**3a**) to dimethyl fumarate, dimethyl maleate, and *trans*-1,2-dibenzoylethylene indicates that the cycloaddition proceeds in a $({}_{\pi}2_{s}+{}_{\pi}4_{s})$-type concerted mechanism.[10] In the cycloaddition of *trans* dipolarophiles, such as dimethyl fumarate and *trans*-1,2-dibenzoylethylene, the preferential formation of 5-*endo*-6-*exo* adducts (**4a** and **5a**) to 5-*exo*-6-*endo* adducts (**4c** and **5c**) was explained by the predominance of the transition state (**15a**) over the transition state (**15b**), which contained repulsion between a carbonyl group of dipolarophile and that of 2-benzopyrylium-4-olate. The predominance of the *exo* adducts in the reactions of all the *cis* dipolarophiles except acenaphthylene is explained by the larger stability of the anti-transition state (**16a**) than that of the syn-transition state (**16b**). On the other hand, acenaphthylene showed a reverse tendency to give more *endo* adduct (**14**) than the *exo* isomer (**13**). This might be caused by the π-π interaction[11] between the benzene ring of 2-benzopyrylium-4-olate and the naphthalene moiety of acenaphthylene in the double-layer syn-transition state.[9]

The *endo*/*exo* ratios of the adducts of *N*-substituted maleimides with **3a** and **3c** were found to decrease in the order of *N*-methyl>*N*-phenyl>*N*-ethylmale-



(15a)



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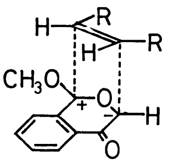
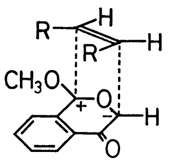
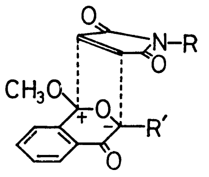


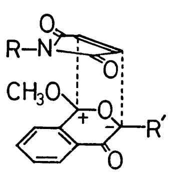
(16a)



(16b)



(17a)



(17b)

TABLE 4. THE *endo*/*exo* RATIOS OF THE ADDUCTS OF MALEIMIDES WITH **3a** AND **3c**

2-Benzopyrylium-4-olate	Maleimide		
	R=Ph	R=C_2H_5	R=CH_3
3a (R′=H)	0.50	0.36	0.54
3c (R′=CH_3)	0.68	0.42	0.76

imide (Table 4). This tendency may be explained by the combination of the steric repulsion and π-π interaction between the benzene ring of 2-pyrylium-4-olate (**3**) and the substituent (R) on the imide nitrogen in the transition state. The steric replusion of *N*-R in the *endo*-transition state (**17b**) may decrease the yield of the *endo* adduct. However, the *endo*/*exo* ratios are not in the order of the bulkiness of the R group. The π-π interaction of the *N*-phenyl group with the benzene ring of **3** may increase the *endo* yield a little more than the expected value because of its bulkiness and may thus give a value in between those of *N*-methyl- and *N*-ethylmaleimides. The large *endo*/*exo* ratios of **3c** adducts (**12**/**11**), in contrast to those of **3a** adducts, may be attributed to the repulsion between the R on the imide-nitrogen and the R′ on the C-3 of **3c** in the *exo* transition state (**17a**), which decreases the yeild of the *exo* adduct slightly (Table 4).

Experimental

All the melting points were measured on a Yanagimoto Melting Point Apparatus and were not corrected. The IR spectra were taken on a Hitachi Spectrometer, model EPI-S2. The ^{1}H-NMR spectra were recorded on a Varian A-60 or EM-360 Spectrometer in a $CDCl_3$ solution; the chemical shifts were described in ppm downfield from TMS as the internal standard (δ scale).

Materials. o-*Methoxycarbonyl-α-diazoacetophenone* (***1a***) was prepared by the procedure described in the previous paper.[3]

o-*Methoxycarbonyl-α-diazoacetophenone-α-*d (***1b***) was synthesized by the reaction of the DCC complex of methyl hydrogen phthalate with deuterated diazomethane, which had itself been prepared by the reaction of *N*-methyl-*N*-nitrosourea with potassium deuteroxide in D_2O.[12] Crude **1b** containing a trace amount of dimethyl phthalate was used without further purification.

o-*Methoxycarbonyl-α-diazopropiophenone* was synthesized by the DCC method using an excess of diazoethane and purified by column chromatography on Al_2O_3 with an activity of 4; viscous liquid, IR (liquid film): 2050 (diazo), 1700 (ester), 1595 cm^{-1} (diazocarbonyl), NMR: 2.57 (s, 3H, CH_3), 3.87 (s, 3H, OCH_3), 7.4—8.1 ppm (aromatic protons).

All the other reagents were purified by recrystallization or distillation before use.

*General Procedure of the Decomposition of **1** in the Presence of Dipolarophiles.* The $Cu(acac)_2$-catalyzed decomposition of **1** was performed according to the procedure described in the previous paper by refluxing a benzene solution of **1** and a 1.2—1.5 molar equivalent of dipolarophile and a catalytic amount of $Cu(acac)_2$ until no more N_2 was evolved.[3] The reaction mixture was separated by silica gel column chromatography, using benzene as the eluent.

*Esterification of Dicarboxylic Acid (**7**).* An ether solution of diazomethane was slowly added to a suspension of 0.10 g of **7** in ether until no more N_2 was evolved. The subsequent evaporation of the ether under reduced pressure yielded 0.11 g of colorless crystals (mp 145—146 °C), later recrystallized from benzene-heptane solution. The IR and NMR spectra were perfectly superimposable on those of **4d** obtained by the reaction of **3a** with dimethyl maleate.

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