  Bull. Chem. Soc. Jpn., 59, 433—437 (1986)

The Diels-Alder Reactions of 2-Alkyl-5-methoxy-4-(*p*-nitrophenyl)oxazoles with Ethylenic, Acetylenic, and Azo-Type Dienophiles

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(Received July 20, 1985)

The Diels-Alder reactions of 2-methyl- and 2-ethyl-5-methoxy-4-(*p*-nitrophenyl)oxazoles with *N*-methyl-, *N*-ethyl-, and *N*-phenylmaleimides gave endo- and exo-adducts. When the reactions were carried out in an acetonitrile solution containing a small amount of water as an impurity, *N*-substituted 3-hydroxy-2-(*p*-nitrophenyl)-4,5-pyridinecarboximides were obtained via the decomposition of the Diels-Alder adducts, while the methanol was eliminated. The decomposition might be catalyzed by contaminated water at the initial stage of the reaction. The adducts of *N*-phenylmaleimide and *N*-ethylmaleimide were shown to undergo the retro-Diels-Alder reaction on heating at 80°C to give the starting maleimides and oxazole. Diethyl azodicarboxylate and 4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione gave the corresponding single adducts. A reaction with dimethyl acetylenedicarboxylate gave *p*-nitrobenzonitrile (**10**), dimethyl 2-methyl-5-methoxy-3,4-furandicarboxylate (**11**), and tetramethyl 3,5-epoxy-3-methoxy-5-methyl-1,4-cyclohexadiene-1,2,4,5-tetracarboxylate (**12**), although the expected adduct was not isolated. These products were explained on the basis of the Diels-Alder reaction, followed by the retro-Diels-Alder reaction, thus affording **10** and **11**, which gave **12** upon cycloaddition with the second molecule of DMAD.

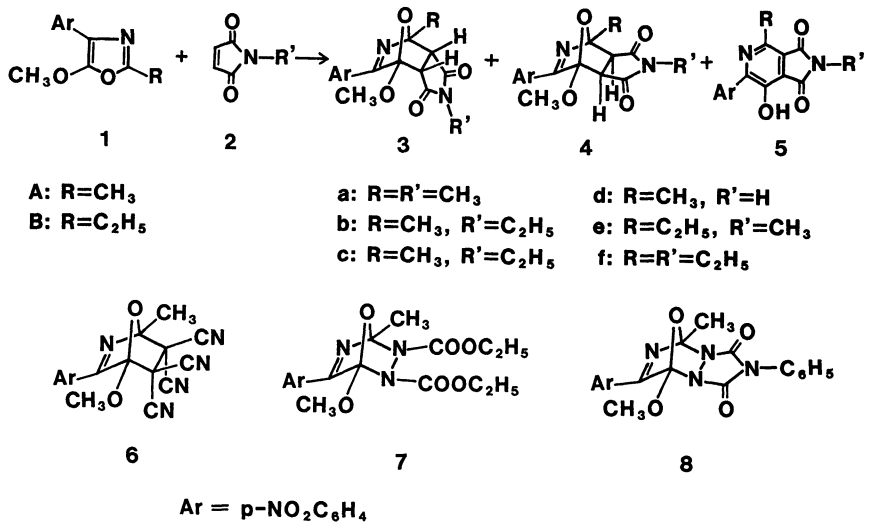
The cycloaddition of the five-membered aromatic heterocycles has been recognized to be one of the most convenient methods of synthesizing six-membered heterocycles.[1] Since the early work of Kondrat'eva,[2] the Diels-Alder reactions of oxazoles with ethylenic dienophiles have been studied extensively in connection with the pathway of synthesizing vitamin B_6.[3] In general, the determination of the stereochemistry of the cycloaddition is important for the mechanistic investigation of the reaction. However, scarcely no stereochemical research into the Diels-Alder reaction of oxazoles has been done because of the instability of the adducts.[4] Recently the present authors have reported a general method of synthesizing oxazoles by the BF_3-catalyzed decomposition of diazo carbonyl compounds in the presence of excess nitriles to give various types of oxazoles.[5] Of the oxazoles obtained, we chose 5-methoxy-2-methyl-4-(*p*-nitrophenyl)oxazole (**1A**) and 2-ethyl-5-methoxy-4-(*p*-nitrophenyl)oxazole (**1B**) as azadiene components of the Diels-Alder reaction for the following reasons: First, a high Diels-Alder reactivity of the oxazoles can be expected because of the electron-releasing effect of the methoxyl group on C-5,[3b,6] second, a high stability of the cycloadducts may possibly be attained by the introduction of the *p*-nitrophenyl group. The retro-Diels-Alder reaction of the adducts was also studied.

Results and Discussion

Reactions with Ethylenic Dienophiles. *N*-Substituted maleimides have been recognized as having high reactivity as dienophiles in the Diels-Alder reactions. The refluxing of an acetonitrile solution of 5-methoxy-2-methyl-4-(*p*-nitrophenyl)oxazole (**1A**) and two molar equivalents of *N*-ethylmaleimide (**2b**) for 50 h gave three products after silica-gel column chromatography of the reaction mixture. The first and successively eluted products were determined to be the expected Diels-Alder adducts on the basis of the analytical and spectral data. The IR spectra of the two products showed absorptions ascribable to the imide carbonyl near 1700 cm^{-1} and to the nitro group at 1535 and 1340 cm^{-1}, and also showed similar absorption patterns in the fingerprint region. The first product (mp 159.0—161.0 °C) has signals of the methyl and methylene protons of the *N*-ethyl group at δ 0.48 (t) and 3.14 (q) respectively in the ^1H NMR spectrum; they are considerably higher (by 0.5—0.7 ppm) than those signals of the second product at δ 1.20 (t) and 3.57 (q). The high field of the *N*-ethyl group of the first product might be attributed to the shielding effect derived from the ring-current anisotropy of the *p*-nitrophenyl group. This indicates that the adduct is the endo-adduct (**3b**). Therefore, the second product may be assigned to the exo-adduct (**4b**). The appearance of methine protons of **3b** in a lower field (δ 3.50 (d) and 3.62 (d)) than those of **4b** at δ 2.96 (d) and 3.07 (d) is also in accord with the above assignment, assuming a deshielding effect of the bridged oxygen in the endo-adduct (**3b**).[7] The X-ray structural analysis of **4b** supported the above determination.[9]

The third product was found to have a molecular formula corresponding to that of the CH_3OH elimination from the adducts, **3b** or **4b**. The ^1H NMR spectrum lacked signals of the methoxyl and methine protons observed in **3b** and **4b** but showed signals of methyl at δ 2.84, *N*-ethyl at δ 1.21 (t) and 3.75 (q), and hydroxyl at δ 7.98, besides the ABq signals of the *p*-nitrophenyl group. The IR spectrum had absorptions of the imide carbonyl group at 1690 cm^{-1}, the hydroxyl group at 3350, and the nitro group at 1505 and 1340 cm^{-1}. These spectroscopic data show that the third product is *N*-ethyl-3-hydroxy-6-methyl-2-(*p*-nitrophenyl)-4,5-pyridinecarboximide (**5b**).

The Diels-Alder adducts between 5-alkoxyoxazoles and ethylenic dienophiles, which have structures like **3b** and **4b**, have already been reported to give 3-



Scheme 1.

Table 1. Product Ratios of the Diels-Alder Reactions of Oxazoles (**1**) with *N*-Substituted Maleimides

Run	R	R'	Solvent	Temp	Time	Product Yield/%		
				°C	h	**3**	**4**	**5**
a-1	CH_3	CH_3	Acetonitrile	80	50	58	32	—
a-2			Acetonitrile[a)]	80	50	32	—	43
a-3			Toluene	100	70	54	29	—
b-1		C_2H_5	Acetonitrile	80	24	58	29	—
b-2			Acetonitrile[a)]	60	100	35	5	50
b-3			Acetonitrile[a)]	80	50	51	3	41
b-4			Acetonitrile[a)]	100	24	41	11	44
b-5			Acetonitrile[a)]	100	6	66	13	20
c-1		C_6H_5	Benzene	40	240	43	17	—
c-2			Benzene	80	50	13	21	—
c-3			Toluene	100	24	6	3	—
d		H	Acetonitrile[a)]	80	100	21	—	21[b)]
e	C_2H_5	CH_3	Acetonitrile	80	50	53	21	—
f		C_2H_5	Acetonitrile	80	50	96	3	—

a) The acetonitrile used in this reaction was stored for months after distillation. b) Unreacted **1A** was recovered in 33% yield.

hydroxypyridine derivatives upon treatment with acid.[3a,3c] The treatment of **3b** and **4b** with *p*-toluenesulfonic acid in a benzene solution readily gave **5b**. The formation of **5b** in the Diels-Alder reaction of **1A** and *N*-ethylmaleimide may also be attributed to the second attack of a protic species such as H_2O, contained in the reaction mixture, on the **3b** and **4b** produced by the cycloaddition. In order to confirm this point, the reaction was examined under various reaction conditions, with differing solvents, reaction temperatures, and reaction times (Runs bl—b5). The results show that the formation of **5b** is greatly affected by the solvent and the reaction time, but only slightly by the reaction temperature. When the reaction was carried out using a freshly distilled solvent, no decomposition to give **5b** was observed. These results suggest that the H_2O present in the solvent might function as a protic species to catalyze the decomposition of **3b** or **4b** formed at the outset. Once the decomposition started, the methanol and **5b** produced might work as catalysts. Quite similar results were obtained in the reaction of **1A** with *N*-methylmaleimide. 2-Ethyl-5-methoxy-4-(*p*-nitrophenyl)-oxazole (**1B**) also showed similar behavior in the reactions with *N*-substituted maleimides.

The preference for the endo-adducts formation in these reactions may be explained by the endo rule.[8] However, a larger endo/exo ratio (96:3) than usual was observed in the reaction of **1B** and *N*-ethylmaleimide (Run f). One of possible explanation is as follows. The CPK-model inspection of the adducts (**3f** and **4f**) indicated that the exo-adduct (**4f**) has a steric repulsion between the C-ethyl group and imide carbonyl. This may indicate that the steric repulsion between these two groups in the transition state to the exo-adduct lowers the rate of the addition and that the *N*-ethyl substitution strengthens this tendency.

On the other hand, *N*-phenylmaleimide (**2c**) gave

Table 2. ^{1}H NMR Data of Cycloadducts and 3-Hydroxypyridines[a)]

Compounds	O-CH_3	C-CH_3	C-CH_2CH_3	*N*-CH_3	*N*-CH_2CH_3	Methine[b)]	*J*
3a	3.61	2.09	—	2.55	—	3.55, 3.67	7.5
4a	3.54	2.01	—	3.04	—	3.04, 3.14	6.3
3b	3.60	2.07	—	—	0.48 (t), 3.14 (q)	3.50, 3.62	7.8
4b	3.54	2.01	—	—	1.20 (t), 3.60 (q)	3.05, 3.15	6.6
3c	3.63	2.14	—	—	—	3.65, 3.78	7.6
4c	3.57	2.07	—	—	—	3.13, 3.25	6.5
3d	3.49	1.91	—	—	—	2.75 (s)	—[c)]
3e	3.62	—	1.22 (t), 2.38 (q)	2.54	—	3.64 (s)	—
4e	3.60	—	1.33 (t), 2.37 (q)	3.09	—	3.12, 3.25	6.0
3f	3.64	—	1.23 (t), 2.46 (m)	—	0.50 (t), 3.14 (q)	3.65 (s)	—
4f	3.52	—	1.20 (t), 2.29 (m)	—	1.29 (t), 3.06 (q)	3.49, 3.66	7.2
5a	—	2.83	—	3.18	—	—	—[d)]
5b	—	2.84	—	—	1.31 (t), 3.75 (q)	—	—[d)]
5c	—	2.91	—	—	—	—	—[d)]
5d	—	2.72	—	—	—	—	—

a) Signals of the aromatic protons were omitted. b) Methine protons showed doublet signals unless otherwise cited. c) A singlet NH signal was at δ=3.27. d) Singlet OH signals of **5a**, **5b**, and **5c** were observed at δ=7.98, 8.03, and 8.18 respectively.

small amounts of both endo- and exo-adducts at 80 °C, and the yields decreased with the increase in the reaction temperature (100 °C). In order to clarify the course of the addition, the proceeding of the reaction between equivalent molar amounts of **1A** and **2c** was traced by monitoring the proton NMR in an NMR tube at 25 and 80 °C in C_6D_6. As a result, the rates of the formation of the endo-adduct were found to be faster than that of the exo-adduct. However, the tracing was interrupted during the course of the reaction because of the crystallization of the adducts in the NMR tube. The reaction of **1A** with *N*-ethylmaleimide (**2b**) exhibited a monotonous increase in the yields of the adducts at 25 °C, without any interruption by the crystallization of the adducts (Fig. 1a). However, at 80 °C the yield of the endo-adduct reached its maximum after 10 h and then decreased gradually, while the yield of the exo-adduct increased constantly, as is shown in Fig. 1b. This indicates that the endo-adduct is converted into the exo-adduct, probably via the retro-Diels-Alder reaction as described below.

The ratio between the adducts (**3**+**4**) and the remaining oxazole (**1A**) depends upon the reaction temperature, showing smaller values at higher temperatures. The ratios were also found to be larger for the reactions of **2b** with **1A** than for the corresponding reactions of **2c**, even though the reaction rates were faster for **2c** than for **2b** at various temperatures. The depressions of the yields of the adducts at higher temperatures may be explained on the assumption that the equilibrium between the Diels-Alder reaction and the retro-Diels-Alder reaction declines to the side of the reactants at higher temperatures.

The reaction of the oxazole (**1A**) and tetracyanoethylene gave a colorless product, which showed an absorption of the ester carbonyl group in its IR spectrum at 1758 cm^{-1}. This indicates that the product is not the expected Diels-Alder adduct (**6**), but the

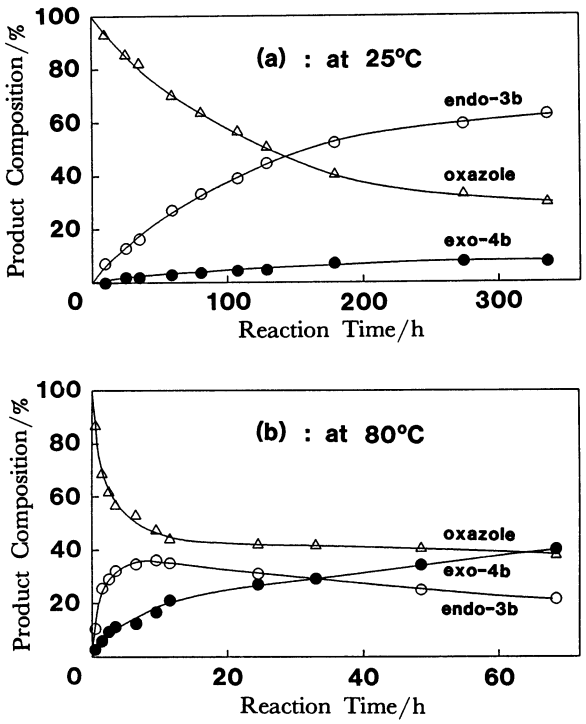
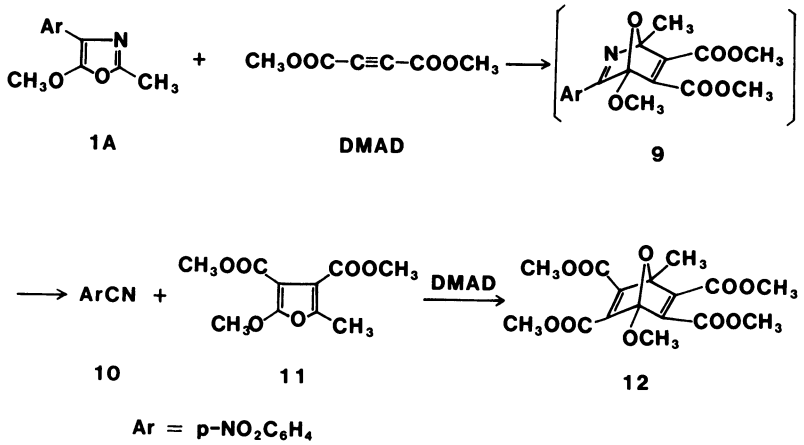


Fig. 1. Changes in the Product Composition during the Reaction of **1A** with **2b** at 25 °C (a) and 80 °C (b).

oxazole-ring-opened product obtained via the step-by-step reaction of **1A** and TCNE.[10] The results of the detailed examination of this reaction will be described elsewhere. Dimethyl fumarate and dimethyl maleate gave no adduct, the reactions with **1A** resulting in the recovery of the starting materials, even under such drastic reaction conditions as at 110 °C for 100 h in toluene.

Reactions with Azo-Type Dienophiles. The azo-type compounds have been reported to have higher Diels-Alder reactivities than the corresponding



Scheme 2.

ethylenic dienophiles.[11] Similar results were observed in the Diels-Alder reaction of oxazoles. That is diethyl azodicarboxylate[12] was found to react readily with the oxazole (**1A**) in a benzene solution at 80 °C within 48 h to give an adduct (**7**) in a fairly good yield (91%). 4-Phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione, which is one of the most reactive dienophiles,[11b] also gave an adduct (**8**) in a high yield. However, azobenzene gave no adduct.

Reaction with Acetylenic Dienophile. As a typical example of acetylenic dienophiles, dimethyl acetylenedicarboxylate was treated with the oxazole (**1A**) in toluene at 110 °C for 50 h. This reaction did not give the expected Diels-Alder adduct (**9**)[12,13] but *p*-nitrobenzonitrile (**10**), dimethyl 2-methoxy-5-methyl-3,4-furandicarboxylate (**11**), and tetramethyl 3,5-epoxy-3-methoxy-5-methyl-1,4-cyclohexadiene-1,2,4,5-tetracarboxylate (**12**) in yields of 86, 20, and 25%, respectively. The reaction may be explained by the retro-Diels-Alder reaction of the adduct (**9**) to give *p*-nitrobenzonitrile and the furan derivative (**11**),[12, 13] followed by the second Diels-Alder reaction of DMAD on the furan (**11**) to produce the adduct (**12**).[13,14] When the reaction was carried out under milder conditions, at 100 °C for 24 h, *p*-nitrobenzonitrile and furandicarboxylate (**11**) were isolated in 30 and 34% yields respectively, along with 61% of the unreacted oxazole (**1A**). Further attempts to isolate the adduct **9** by conducting the reaction at the low temperature of 50 °C were also unsuccessful.

Retro-Diels-Alder Reaction. In order to explain the low yields of the Diels-Alder adducts between the oxazole (**1A**) and *N*-phenylmaleimide, we studied the retro-Diels-Alder reaction of the adducts **3c** and **4c** to reproduce the starting materials. During the recrystallization of the endo-adduct (**3c**), separated by the column chromatograhy of the reaction mixture, yellow crystals of *N*-phenylmaleimide (**2c**) were isolated in a pure state. When the decompositions of **3c** and **4c** were traced by means of NMR spectroscopy in a DMSO solution at 80 °C, the intensities of the signals of **3c** and **4c** decreased, with an accompanying increase in the intensities of the signals of **1A** at δ 2.41 (s, CH_3) and 4.12 (s, OCH_3) and the methine signal of **2c** at δ 7.13. After 200 h, both reaction systems gave mixtures of **1A** (**2c**), **3c**, and **4c** in about a 7:1:2 ratio. In these measurements, the thermal retro-Diels-Alder reactions of **3c** was found to be faster than that of **4c**. This may be explained by the steric repulsion in the endo-adduct. These types of retro-Diels-Alder reactions were also found for the adducts of *N*-methyl- and *N*-ethylmaleimides. However, the rates of the decomposition of these adducts were not so rapid as those of the *N*-phenylmaleimide adducts.

Experimental

The melting points were measured with a Yanagimoto Melting-point Apparatus and are presented without correction. The IR spectra were recorded on a Perkin-Elmer model 983. The ^{1}H NMR spectra were recorded in a $CDCl_3$ solution at 90 MHz on a Varian Spectrometer model EM390, using TMS as the internal standard.

Materials. 2-Alkyl-5-methoxy-4-(*p*-nitrophenyl)oxazoles were prepared by the BF_3-catalyzed decomposition of methyl (*p*-nitrophenyl)diazoacetate in the presence of acetonitrile or propionitrile, as has been described in a previous paper.[15]

5-Methoxy-2-methyl-4-(*p*-nitrophenyl)oxazole (1A): Pale yellow crystals; yield, 75%; mp 122.0—123.0 °C; ^{1}H NMR δ=2.43 (s, CH_3), 4,12 (s, OCH_3), 7.85 and 8.20 (ABq, Ar). Found: C, 56.56, H, 4.29; N, 11.90%. Calcd for $C_{11}H_{10}N_2O_4$: C, 56.41; H, 4.30; N, 11.96%.

2-Ethyl-5-methoxy-4-(*p*-nitrophenyl)oxazole (1B): Pale yellow needles; yield, 84%; mp 96.0—97.0 °C; ^{1}H NMR δ=1.36 (t, CH_3), 2.76 (q, CH_2), 4.13 (s, OCH_3), 7.92 and 8.23 (ABq, Ar). Found: C, 58.26, H, 4.87; N, 11.27%. Calcd for $C_{12}H_{12}N_2O_4$: C, 58.06; H, 4.87; N, 11.29%.

General Procedure of the Diels-Alder Reaction of 1 with Maleimides. A solution of **1** (2.0 mmol) and maleimide (2.5 mmol) in acetonitrile (or toluene) was heated at 60—110 °C for several hours, as shown in Table 1. After the evaporation of the solvent under reduced pressure, the products were separated by silica-gel column chromatography,

Table 3. Melting Points and Analytical Data of the Reaction Products

Compound	Mp θ_m/°C	Found (%)			Calcd (%)			Molecular Formula
		C	H	N	C	H	N	
3a	191—192	55.63	4.30	12.07	55.65	4.38	12.17	$C_{16}H_{15}N_3O_6$
4a	188—189	55.68	4.34	12.02				
3b	159—161	56.94	4.75	11.68	56.82	4.77	11.70	$C_{17}H_{17}N_3O_6$
4b	155—156	56.82	4.77	11.70				
3c	179—180	62.16	4.13	10.20	61.91	4.21	10.32	$C_{21}H_{17}N_3O_6$
4c	173—174	61.71	4.20	10.27				
3d	190—192	54.34	3.93	12.71	54.38	3.96	12.69	$C_{15}H_{13}N_3O_6$
3e	129—130	56.98	4.78	11.53	56.82	4.77	11.70	$C_{17}H_{17}N_3O_6$
4e	177—178	57.00	4.73	11.59				
3f	158—159	58.07	5.12	11.20	57.90	5.13	11.25	$C_{18}H_{19}N_3O_6$
5a	287—289	57.43	3.49	13.35	57.51	3.54	13.41	$C_{15}H_{11}N_3O_5$
5b	197—199	58.78	3.96	12.73	58.71	4.00	12.84	$C_{16}H_{13}N_3O_5$
5c	244—245	64.17	3.42	11.10	64.00	3.49	11.20	$C_{20}H_{13}N_3O_5$
5d	287—289	56.02	3.05	14.30	56.19	3.03	14.04	$C_{14}H_9N_3O_5$
7	116—117	50.26	4.91	13.77	50.00	4.94	13.72	$C_{17}H_{29}N_4O_8$
8	166—167	55.98	3.67	17.16	55.74	3.69	17.11	$C_{19}H_{15}N_5O_6$
11	60—63	52.71	5.29	—	52.63	5.30	—	$C_{10}H_{12}O_6$

using benzene as the eluent.

Reaction of 1A with Diethyl Azodicarboxylate. A benzene solution of **1A** (0.23 g, 1.0 mmol) and diethyl azodicarboxylate (0.17 g, 1.0 mmol) was heated at 80 °C for 48 h. After the usual treatment, an adduct (**7**) was isolated: yield, 0.37 g; 91%; mp 116—117 °C; IR 1751 (ester C=O), 1523, and 1353 cm^{-1} (NO_2); ^1H NMR δ=1.30 (t, CH_3), 1.33 (t, CH_3), 2.46 (s, CH_3), 3.76 (s, OCH_3), 4.29 (q, CH_2), 7.81 and 8.22 (ABq, Ar).

Reaction of 1A with 4-Phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione. A toluene solution of **1A** (0.47 g, 2.0 mmol) and 4-phenyl-1,2,4-triazoline-3,5-dione (0.35 g, 2.0 mmol) was heated at 100 °C for 9 h to give an adduct (**8**; 0.56 g, 69%): Pale yellow crystals; IR(KBr) 1730 (ring C=O), 1515, and 1355 cm^{-1} (NO_2); ^1H NMR δ=2.50 (s, CH_3), 3.73 (s, OCH_3), 7.45 (s, Ph), 7.86 and 8.39 (ABq, Ar).

Reaction of 1A with Dimethyl Acetylenedicarboxylate. A toluene solution of **1A** (0.70 g, 3.0 mmol) and DMAD (0.85 g, 6 mmol) was heated at 120 °C for 50 h. After the evaporation of the toluene under reduced pressure, the reaction products were separated by silica-gel column chromatograhy to isolate three products. The first fraction was assigned to *p*-nitrobenzonitrile (0.38 g, 86%) on the basis of a comparison of the spectral data with those of an authentic sample. The second fraction was characterized dimethyl 5-methoxy-2-methyl-3,4-furandicarboxylate (**11**): Colorless crystals; yield, 0.14 g; 20%; mp 60—63 °C; IR(KBr) 1705 cm^{-1} (ester C=O); ^1H NMR δ=2.38 (s, CH_3), 3.79 (s, OCH_3), 3.83 (s, OCH_3), and 4.06 (s, OCH_3). The third fraction was tetramethyl 3,5-epoxy-3-methoxy-5-methyl-1,4-cyclohexadiene-1,2,4,5-tetracarboxylate (**12**): Colorless oil; yield, 0.28 g; 25%; IR(liquid film) 1710 cm^{-1} (ester C=O); ^1H NMR δ=1.92 (s, 3H, CH_3), 3.61 (s, 3H, OCH_3), 3.80 (s, 6H, OCH_3), and 3.84 (s, 6H, OCH_3).

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