

# Reaction of Vinylcarbenoids with Benzaldehydes: Formation of Vinylcarbonyl Ylides Followed by Ring Closure to Oxiranes and Dihydrofurans

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Received March 6, 2001

Rh<sub>2</sub>(OAc)<sub>4</sub>-catalyzed reaction of vinyl diazo compound **1a** in the presence of *p*-methoxybenz- **2a**, mesit- **2b**, and *p*-chlorobenzaldehyde **2c** gave a mixture of isomeric vinyloxiranes **3a–c** and **4a–c**, and sterically unstable (*E*)-dihydrofurans **5a–c**, but not stable (*Z*)-dihydrofurans **6**. However, the reactions with *p*-nitro- **2d** and 2,4-dinitrobenzaldehyde **2e** gave (*Z*)-dihydrofurans **6d,e** along with **3d, 4d**, and **5d,e**. The reaction in the presence of maleic anhydride and dimethyl fumarate gave single 1,3-dipolar cycloadducts **11** and **13**, respectively, indicating that a single conformer, the sterically unstable *endo*-aryl-*endo*-cyanostyryl carbonyl ylide **14** (**15**), is initially formed in the reaction of **1** with **2**. It was concluded that the *endo*-vinyl-*exo*-aryl vinylcarbonyl ylides **17a–c** arising from **2a–c** undergo disrotatory cyclization to exclusively produce **5**, whereas the ylides **17d,e** arising from **2d,e** undergo partly symmetry-forbidden conrotatory cyclization to sterically stable *trans*-diaryldihydrofurans **6d,e** as well as the symmetry-allowed process to **5d,e**.

## Introduction

The formation and reaction of carbonyl ylides continue to be a subject of considerable interest and intensive investigation.<sup>1</sup> Thermal or photochemical ring opening of oxiranes<sup>2,8</sup> or Δ<sup>3</sup>-1,3,4-oxadiazoline<sup>3</sup> and addition of a

carbene/carbenoid onto the oxygen atom of a carbonyl group<sup>4–7</sup> have been known as traditional methods of

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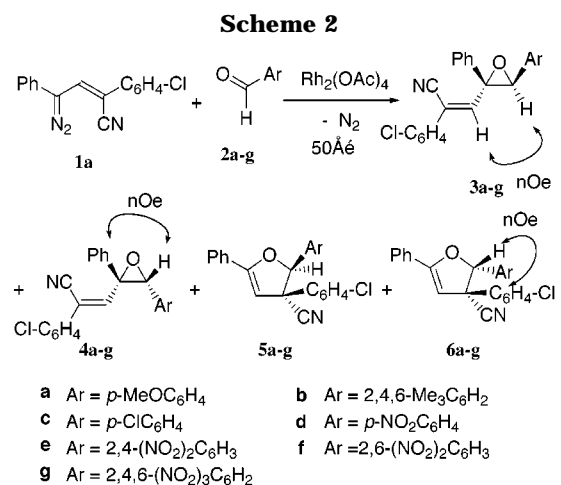
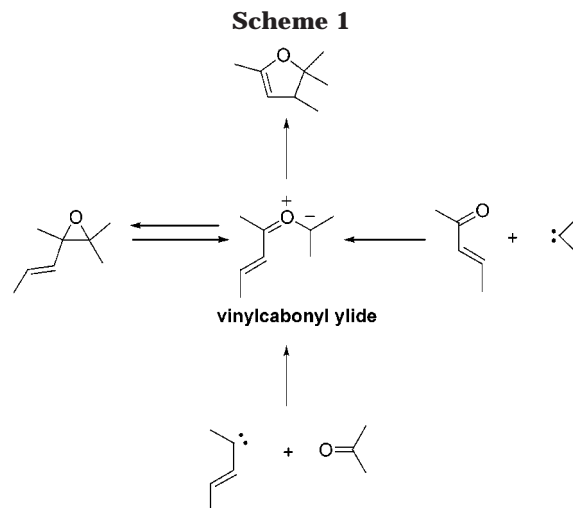
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generation of carbonyl ylides. Recently, intermolecular<sup>4</sup> or intramolecular reaction<sup>5–7</sup> of carbenes and metallo-carbenoids with carbonyl compounds have been widely studied, and intermolecular or intramolecular 1,3-dipolar cycloaddition of the resultant carbonyl ylides have been utilized as a synthetic method of a oxygenated five-membered heterocycle or a complex polycyclic oxygen heterocycle.<sup>4–7</sup> Despite enormous studies of carbonyl ylides, some studies on vinylcarbonyl ylides via thermal ring opening of vinyloxiranes have been reported.<sup>8–13</sup> The thermal ring opening of oxiranes to carbonyl ylides requires high temperature, whereas the generation of carbonyl ylides via the carbenoid–carbonyl reaction can be performed under very mild conditions. A few examples of the generation of vinylcarbonyl ylides, which cyclized to dihydrofurans, from the reaction of carbenes with  $\alpha,\beta$ -unsaturated ketones have been reported.<sup>14</sup> Vinylcarbonyl ylides can undergo electrocyclic ring closures to oxiranes as a  $4\pi$  electronic component and also to dihydrofurans as a  $6\pi$  electronic component.

Here we report the first example of the generation and reactions of vinylcarbonyl ylides from the reaction of the vinyl carbenoids with some substituted benzaldehydes.<sup>15</sup>

## Results

**Rh<sub>2</sub>(OAc)<sub>4</sub>-Catalyzed Decomposition of 2-(*p*-Chlorophenyl)-4-diazo-4-phenyl-*cis*-2-butenenitrile (1a) in the Presence of Substituted Benzaldehydes.** A benzene solution of **1a** (1 mmol) was added dropwise over 1 h to a substituted benzaldehyde **2** (5 mmol) and a catalytic amount of Rh<sub>2</sub>(OAc)<sub>4</sub> in benzene at 50 °C under an argon atmosphere. The reaction



**Table 1. Product Ratios of the Reactions of the Vinyldiazo Compound 1a with Various Substituted Benzaldehydes at 50 °C<sup>a</sup>**

run	substituted benzaldehyde	Ar	ratio (%)			
			3	4	5	6
1	<b>2a</b>	<i>p</i> -CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub>	37	29	34	0
2	<b>2b</b>	2,4,6-(CH <sub>3</sub> ) <sub>3</sub> -C <sub>6</sub> H <sub>2</sub>	29	64	7	0
3	<b>2c</b>	<i>p</i> -Cl-C <sub>6</sub> H <sub>4</sub>	22	58	20	0
4	<b>2d</b>	<i>p</i> -NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	13	21	61	5
5	<b>2e</b>	2,4-(NO <sub>2</sub> ) <sub>2</sub> -C <sub>6</sub> H <sub>3</sub>	0	0	38	62
6	<b>2f</b>	2,6-(NO <sub>2</sub> ) <sub>2</sub> -C <sub>6</sub> H <sub>3</sub>	0	0	0	0
7	<b>2g</b>	2,4,6-(NO <sub>2</sub> ) <sub>3</sub> -C <sub>6</sub> H <sub>2</sub>	0	0	0	0

<sup>a</sup> The ratios were determined by the <sup>1</sup>H NMR spectra of the reaction mixtures.

mixtures were separated by column chromatography to give (*Z*)- and (*E*)-vinyloxiranes (**3** and **4**) and dihydrofurans (**5** and **6**) (Scheme 2 and Table 1). The reaction with *p*-methoxybenz- **2a**, mesit- **2b**, and *p*-chlorobenzaldehyde **2c** furnished sterically unstable *cis*-diaryldihydrofurans **5a–c**, but not stable *trans*-diaryldihydrofurans **6a–c**, along with the oxiranes **3a–c** and **4a–c** in ratios shown in Table 1 (runs 1–3). A small amount of *trans*-diaryldihydrofurans **6d** were also obtained along with other products in the reaction of *p*-nitrobenzaldehyde **2d** (run 4). However, the reaction with **2e** did not afford any oxiranes but *cis*-diaryldihydrofuran **5e** and *trans*-diaryldihydrofuran **6e** in a ratio of 2:3 (run 5). 2,6-Dinitro- **2f** and 2,4,6-trinitrobenzaldehyde **2g** bearing two nitro groups at *ortho*-positions did not react with the carbenoid (runs 6 and 7).

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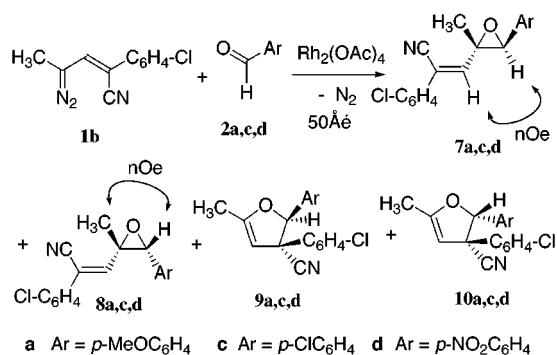
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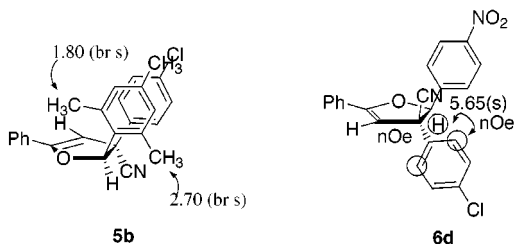
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Scheme 3



It is worth noting that electron-donating substituents of benzaldehydes increased the relative yields of (*Z*)-vinylloxiranes **3**, whereas electron-withdrawing substituents increased the sum of the yields of **4** and dihydrofurans and more electronegative groups favored formation of dihydrofurans.

IR spectra of all products showed the absence of carbonyl groups. The structures of these products were determined on the basis of <sup>1</sup>H and <sup>13</sup>C NMR. For example, the oxirane carbons in **3c** and **4c** were observed at δ 65.6 (d), 66.6 (s) and at δ 67.6 (d), 65.3 (s), respectively, and the dihydrofuran carbons of **5c** were observed at δ 160.1 (s), 97.7 (d), 90.8 (d), and 55.7 (s). The proton signals of phenyl and aryl groups on the oxirane ring of **3** appeared at ca. 0.2 ppm higher fields compared to those of **4**, indicating vicinal *cis*-aryl groups in **3** and *trans*-aryl groups in **4**. Further supports for their structures were obtained from the NOE difference analysis of **3** and **4**. The proton signals of 4-phenyl and 5-aryl groups of dihydrofurans **5a–e** appeared at higher fields, indicating vicinal *cis*-aryl groups. Restriction of rotation of the mesityl substituent was observed in the product **5b** with mesitaldehyde. Two *ortho*-methyl protons of **5b** appeared nonequivalent at δ 2.70 and 1.80 as broad singlets. Elevation of the temperature to 50 °C caused the two broad singlets to collapse to a sharp singlet. Structures of **6d** and **6e** were determined by the NOE difference analysis and appearance of 2-H protons of **6d** and **6e** at ca. 0.7 ppm higher fields than the corresponding protons of **5d** and **5e**.



#### Reaction of 2-(*p*-Chlorophenyl)-4-diazo-*cis*-2-pentenitrile (**1b**) with Substituted Benzaldehydes.

Reactions of **1b** with substituted benzaldehydes **2** (Scheme 3) under the same condition as described above gave a mixture of (*E*)-vinylloxiranes **7**, (*Z*)-vinylloxiranes **8**, and very small amounts of *cis*-diaryldihydrofurans **9** in ratios shown in Table 2. Electron-withdrawing substituents of benzaldehydes increased the relative yields of (*Z*)-vinylloxiranes **8**. The reaction with *p*-nitrobenzaldehyde **2d** predominantly gave **8d**. Structures of these products were determined on the basis of NMR spectra in a similar

Table 2. Product Ratios of the Reactions of the Vinylidazo Compound **1b** with Substituted Benzaldehydes at 50 °C<sup>a</sup>

run	substituted benzaldehyde	Ar	ratio (%)			
			7	8	9	10
1	<b>2a</b>	<i>p</i> -CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub>	50	50	0	0
2	<b>2c</b>	<i>p</i> -Cl-C <sub>6</sub> H <sub>4</sub>	16	82	2	0
3	<b>2d</b>	<i>p</i> -NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	1	98	1	0

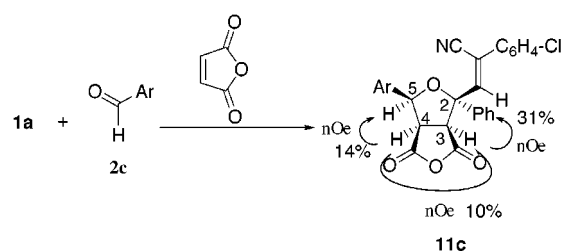
<sup>a</sup> The ratios were determined by the <sup>1</sup>H NMR spectra of the reaction mixtures.

Table 3. Products Ratios in the Reactions of the Vinylidazo Compound **1a,b** in the Presence of 5 Molar Equiv of Substituted Benzaldehydes and Maleic Anhydride in Benzene at 50 °C<sup>a</sup>

run	1	subst benz-aldehydes	Ar	ratio (%)				
				3(7)	4(8)	5(9)	6(10)	11 or 12
1	<b>1a</b>	<b>2a</b>	<i>p</i> -CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub>	0	2	22	0	76
2	<b>1a</b>	<b>2c</b>	<i>p</i> -Cl-C <sub>6</sub> H <sub>4</sub>	8	8	8	0	76
3	<b>1a</b>	<b>2d</b>	<i>p</i> -NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	11	18	51	4	16
4	<b>1a</b>	<b>2e</b>	2,4-(NO <sub>2</sub> ) <sub>2</sub> -C <sub>6</sub> H <sub>3</sub>	0	0	39	61	0
5	<b>1b</b>	<b>2a</b>	<i>p</i> -Cl-C <sub>6</sub> H <sub>4</sub>	0	12	0	0	88
6	<b>1b</b>	<b>2d</b>	<i>p</i> -NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	0	23	0	0	77

<sup>a</sup> The ratios were determined by the <sup>1</sup>H NMR spectra of the reaction mixtures.

Scheme 4



way as described above. The methyl singlet of **7** appeared at ca. 0.45 ppm higher field than that of **8** due to the shielding effect of the phenyl group *cis* to it.

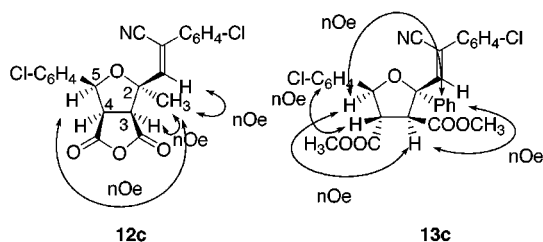
**Reaction of 1 with Substituted Benzaldehydes in the Presence of Dipolarophiles.** We attempted to trap the carbonyl ylide intermediates using reactive dipolarophiles. The Rh<sub>2</sub>(OAc)<sub>4</sub>-catalyzed decompositions of the vinylidazo compounds **1a,b** in the presence of 5 molar equiv of substituted benzaldehydes and dipolarophiles at various temperatures were carried out and gave 1,3-dipolar cycloadducts along with small amounts of **3**, **4**, and **5** (and also with **6d** in the case of **2d**).

The Rh<sub>2</sub>(OAc)<sub>4</sub>-catalyzed reaction of **1a** with *p*-chlorobenzaldehyde in the presence of maleic anhydride at 50 °C produced the single cycloadduct **11c** (isolated yield 71%) along with small amounts of **3c**, **4c**, and **5c** (Table 3). Careful inspection of the NMR spectrum of the reaction mixture showed the absence of any other isomeric cycloadducts. The structure of **11c**, in which the *p*-chlorophenyl and the cyanostyryl group are *syn* to the cyclic anhydride ring, was determined on the basis of large coupling constants (*J* = 8.3 Hz) among three protons (3-H, 4-H, and 5-H) on the tetrahydrofuran ring and NOE difference studies as shown in Scheme 4. On irradiation of the proton (3-H) at δ 4.53 (d), distinctive enhancement of the signals of the *ortho* protons (31%) of 2-phenyl group and 4-H on tetrahydrofuran ring (10%) at δ 3.81 (t) was observed. The irradiation of the signal at δ 3.81 (t) caused distinctive enhancement of the doublets at δ 4.53 (10%) and 5.28 (14%).



The  $\text{Rh}_2(\text{OAc})_4$ -catalyzed reaction of **1b** with **2c** in the presence of maleic anhydride also gave the single cycloadduct **12c** (isolated yield 68%) along with small amounts of **7c**, **8c**, and **9c**. The NMR spectrum of **12c** was very similar to that of **11c**; large coupling constants ( $J = 8.3$  Hz) among three THF ring protons and the irradiation of the methyl protons of **12c** caused distinctive enhancement of the signals of 3-H, 5-H, and the vinylic proton.

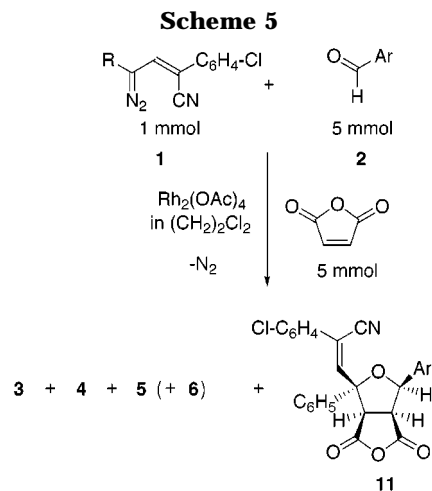
The  $\text{Rh}_2(\text{OAc})_4$ -catalyzed decomposition of **1a** in the presence of 5 molar equiv of *p*-chlorobenzaldehyde and dimethyl fumarate gave sole cycloadduct **13c** along with **3c**, **4c**, and **5c**. The structure of **13c** was determined on the basis of the NOE difference analysis. Irradiation of the tetrahydrofuran ring proton at  $\delta$  4.31 (d) and the doublet of doublets at  $\delta$  3.80 caused distinctive enhancement of the signals of the *ortho* protons of the 5-phenyl group and *ortho* protons of the 2-*p*-chlorophenyl group, respectively, while irradiation of the proton at  $\delta$  5.07 (d) caused distinctive enhancement of the proton at  $\delta$  4.31 (dd) and the *ortho* protons of the 2-*p*-chlorophenyl and 5-phenyl groups. These results are consistent with the structural assignment shown.



The reactions of **1a** with several substituted benzaldehydes **2** in the presence of maleic anhydride were carried out in benzene at 50 °C in order to study substituent effects of benzaldehydes on the ratios of intermolecular 1,3-dipolar cycloaddition to intramolecular cyclization of vinylcarbonyl ylides. The product ratios of the cycloadduct **11** increased with the electron-donating ability of substituents and decreased with increase in the number of nitro groups on benzaldehydes, suggesting that an electron-donating group enhances the rates of 1,3-dipolar cycloaddition compared to intramolecular cyclization. The vinylcarbonyl ylide arising from **2e** did not produce any cycloadduct **11e**, but **5e** and **6e** (Table 3, run 4). The vinylcarbonyl ylide arising from **1b** ( $R = \text{Me}$ ) showed a tendency to form much more intermolecular products **12** than **1a** ( $R = \text{Ph}$ ) as shown in Table 3, indicating that the vinyl carbonyl ylide from **1b** is more reactive toward maleic anhydride.

We examined temperature dependency of the product ratios of cycloadduct **11c**. The reactions of **1a** with **2c** in the presence of maleic anhydride in dichloroethane were carried out at various temperatures. The yield of **11c** increased with lowered temperature. The cycloadduct **11c**, a bimolecular product, was formed quantitatively at 0 °C, whereas the relative yield of **11c** decreased with elevation of the reaction temperature as shown in Table 4.

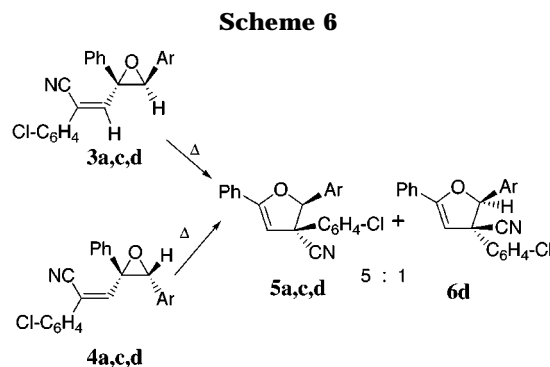
**Thermal Isomerization of Vinyloxiranes to Dihydrofurans.** The hitherto known facts of the thermal conversion of vinyl oxiranes to dihydrofurans via vinyl carbonyl ylides<sup>8-13</sup> prompted us to study the thermal isomerization of vinyloxiranes **3** and **4**. On heating to over 100 °C in tetrachloroethane, vinyloxiranes **3a,c** and **4a,c** isomerized to (*E*)-dihydrofurans **5a,c**, quantitatively



**Table 4. Products Ratios in the Reactions of Vinyldiazo Compound 1a with *p*-Chlorobenzaldehyde 2c in the Presence of Maleic Anhydride in Dichloroethane at Various Temperatures<sup>a</sup>**

temp (°C)	product ratios (%)			
	3c	4c	5c	11c
0	0	0	0	100
40	4	5	6	84
50	8	8	8	76
60	10	10	12	68
80	10	17	17	56

<sup>a</sup> The ratios were determined by the <sup>1</sup>H NMR spectra of the reaction mixtures.



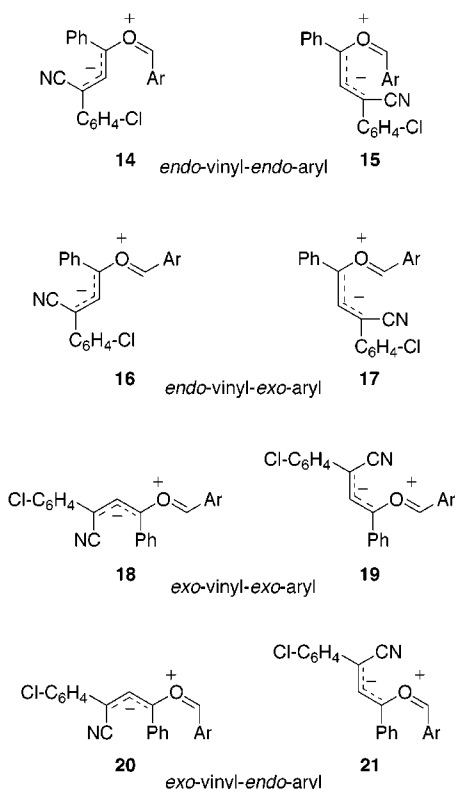
**Table 5. Half-Life Periods of the Thermal Isomerization of 3c and 4c to 5c in Tetrachloroethane**

temp (°C)	$t_{1/2}$ (min)	
	3c	4c
108.5	24.4	163.0
113.2	15.8	98.2

(Scheme 6). During thermal isomerization, a mutual isomerization between **3a,c** and **4a,c** was not observed by HPLC. The rates for the thermal isomerization of **3c** and **4c** in tetrachloroethane at 108.5 and 113.2 °C were measured using HPLC. The rate for isomerization of **3c** was 6–7 times faster than that for **4c** (Table 5). Heating of **3d** and **4d** in refluxing toluene gave *cis*-diaryldihydrofuran **5d** and *trans*-diaryldihydrofuran **6d** in a ratio of 9:1, which is very similar to the case of the carbenoid–**2d** reaction.

We attempted to trap carbonyl ylide intermediates during the thermal isomerization to the dihydrofuran using maleic anhydride. However, oxiranes **3** and **4** in the presence of 5 molar equiv of maleic anhydride in

Scheme 7



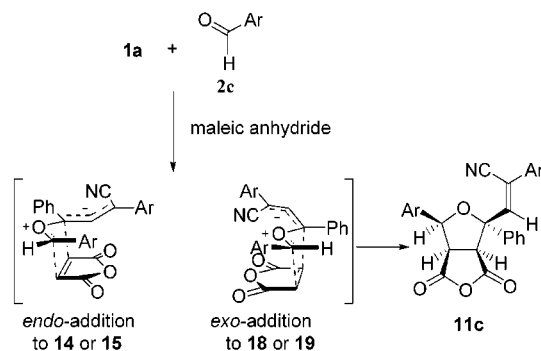
refluxing toluene yielded only dihydrofurans. Even with heating at 110 °C for 6 h in maleic anhydride, the dihydrofuran **5** was predominantly formed without formation of any cycloadducts between the carbonyl ylides and maleic anhydride.

### Discussion

**Mechanism of Reaction of Vinylcarbenoids with Aldehydes.** In general, the reaction of carbenoids with aldehydes has been known to proceed via carbonyl ylides, which are known as a 1,3-dipole.<sup>16</sup> So the present reactions also seem to be a multistep reaction involving vinylcarbonyl ylides as intermediates. Possible conformations of vinylcarbonyl ylides formed are **14**–**21**, which are classified into four categories by the difference of configuration of an aryl and a cyanostyryl group (Scheme 7).

If these cyclizations proceed according to Woodward–Hoffmann rules,<sup>17</sup> the precursors of oxiranes **3** and **4** and dihydrofurans **5** should be the vinylcarbonyl ylides **18** or **19** (*exo*-vinyl-*exo*-aryl), **16** or **17** (*endo*-vinyl-*exo*-aryl), and **17**, respectively. Apparently sterically hindered conformers **14** or **15** (*endo*-vinyl-*endo*-aryl) and **20** or **21** (*exo*-vinyl-*endo*-aryl), in which both bulky substituents are located at *endo*-positions, seem to be unstable ones and to be difficult to form. Therefore, we attempted to trap carbonyl ylide intermediates using maleic anhydride, resulting in the formation of the single cycloadduct **11** among all possible diastereomeric cycloadducts. The cycloadducts **11** would be formed by *endo*-addition of maleic anhydride to the ylide **14** (**15**) or *exo*-addition to the ylide **18** (**19**) (Scheme 8). Predominant formation of

Scheme 8



**11** suggests that the initially formed vinyl carbonyl ylide would be either **14** (**15**) or **18** (**19**).

On the other hand, heating **3a,c** and **4a,c** in tetrachloroethane over 100 °C resulted in quantitative isomerization to the *cis*-dihydrofuran **5a,c**. Furthermore, the rate of isomerization of **3c** was 6–7 times faster than that of **4c**. However, on heating the oxiranes in maleic anhydride, any trapping adducts of intermediate carbonyl ylide were not observed. Although the carbonyl ylides **14** (**15**) and **18** (**19**) could be generated from conrotatory ring opening of **3**, the ring opening to the *endo*-aryl ylides **14** (**15**) is extremely difficult because of the steric repulsion between both of the *endo*-substituents of **14** (or **15**). It implies that the vinylcarbonyl ylides **18** (**19**) generated from thermal ring opening of the vinylloxiranes are different from the initially formed ones in the carbenic reaction, which must be very reactive toward maleic anhydride. The stable *exo*-aryl ylides **18** (**19**) from **3** isomerize to **16** (**17**) via C–O bond rotation followed by fast disrotatory cyclization to **5** (Scheme 10). During the thermal isomerization the intermediates vinylcarbonyl ylides **16** (**17**) and **18** (**19**) are less reactive toward maleic anhydride and convert to the products without capturing maleic anhydride. It is well-known that sterically stable *endo*-vinylcarbonyl ylides such as **17** undergo disrotatory cyclization to give sterically unstable *cis*-dihydrofurans such as **5**.<sup>8–13</sup>

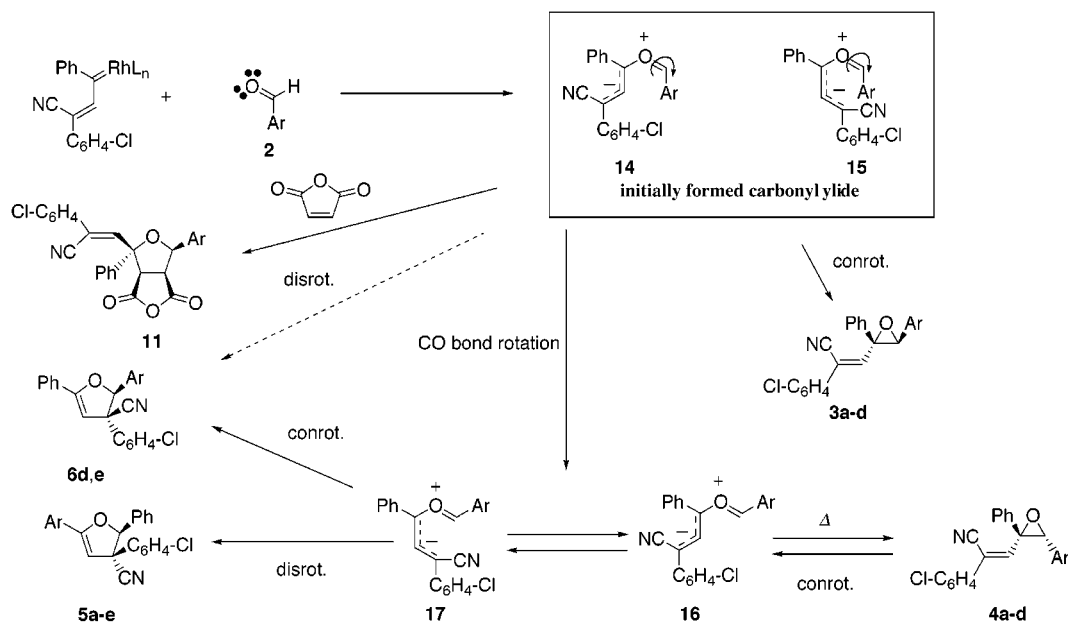
Thus, it is concluded that the vinyl carbenoid reacts with benzaldehydes to initially form the *endo*-vinyl-*endo*-aryl ylides **14** (**15**), which undergoes conrotatory ring closure as a 4 $\pi$  electron system to (*Z*)-oxirane **3** or competitive rotation around C–O bond, giving more stable carbonyl ylides **16** (**17**). Conrotatory cyclization of the *endo*-vinylcarbonyl ylide **16** to oxirane **4** can compete with disrotatory ring closure to **5** (Scheme 9).<sup>8a</sup> In the presence of maleic anhydride, the initially formed *endo*-vinyl-*endo*-aryl ylide **14** (**15**) is effectively captured by maleic anhydride to give the 1,3-dipolar cycloadduct **11** before conversion to (*Z*)-oxirane **3** or isomerization to **16** (**17**). At elevated temperature the intramolecular conrotatory ring closure and rotation around the ArCH–O bond of **14** (**15**) can compete with the bimolecular 1,3-dipolar cycloaddition with maleic anhydride as shown in Table 4.

**Mechanism of Thermal Isomerizations of Vinyl-oxiranes **3** and **4** to Dihydrofurans **5** and **6**.** Thermal conrotatory ring opening of (*E*)-oxiranes **4** leads to stable *endo*-vinyl-*exo*-aryl ylides **16** (**17**) bearing only one substituent at an *endo* position. The *endo*-vinyl ylide **17** undergoes disrotatory ring closure to (*E*)-dihydrofuran **5** with vicinal *cis*-diaryl groups. Conrotatory ring opening

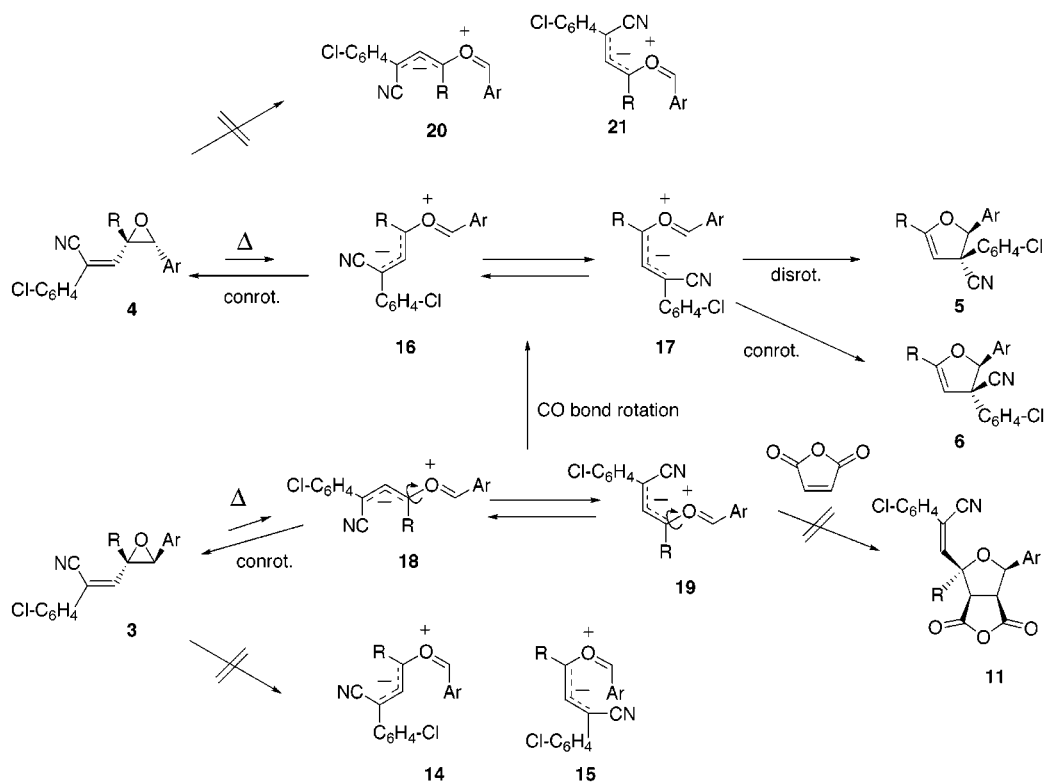
(16) Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 565.

(17) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781.

Scheme 9



Scheme 10

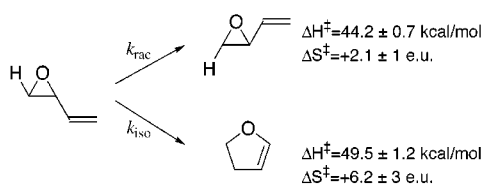


of (*Z*)-oxirane **3** gives predominantly *exo*-vinyl-*exo*-aryl ylide **18** (**19**) bearing one substituent at the *endo*-position, which is more stable than *endo*-vinyl-*endo*-aryl **14** (**15**) bearing two substituents at *endo*-positions. The ylide **18** (**19**) undergoes rotation around RC–O bond to give **16** (**17**) and then cyclization to **5** as shown in Scheme 10.

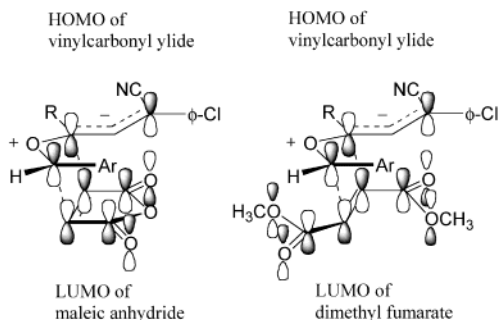
On the other hand, the sterically stable *trans*-diaryldihydrofurans **6d** and **6e** were obtained along with (*E*)-dihydrofurans **5d,e** only in the reactions of **1a** with *p*-nitrobenzaldehyde **2d** and 2,4-dinitrobenzaldehyde **2e** (runs 4 and 5 in Table 1). Formation of **6** can be interpreted by two possible pathways. One is symmetry-allowed disrotatory ring closure of the initially formed

ylide **15**, and the alternative one is symmetry-forbidden conrotatory ring closure of more stable ylide **17**. The fact that **6d** and **5d** were formed in a similar ratio not only in the reaction of vinylcarbenoids with **2d** but also in the thermal isomerization of **3d** or **4d** suggests that **6d** and **5d** were formed from the same intermediate in both reactions. However, the generation of the most unstable carbonyl ylides **14** (**15**) from ring opening of **3d** is not plausible. So the symmetry-forbidden conrotatory ring closure process of **17** should be concluded to be the more likely pathway for formation of **6**. Unlike azomethine ylides, carbonyl ylides, having more “ $\pi$ -diradical character”, allow a symmetry-forbidden process to a stable

Scheme 11



Scheme 12



isomeric product in some cases due to configuration interaction.<sup>2a,18,19</sup>

During thermal isomerization of **3** and **4** to **5**, there was no observation of mutual isomerization between **3** and **4**. Crawford et al. studied thermal isomerization in the gas phase of the parent vinyloxirane and calculated  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  for racemization of vinyloxirane and its isomerization to dihydrofuran as shown in Scheme 11.<sup>10a</sup> Although  $\Delta H^\ddagger$  for racemization of the vinyloxirane is smaller than that of isomerization to the dihydrofuran,  $\Delta S^\ddagger$  for racemization is smaller than that for isomerization to the dihydrofuran. This suggests that cyclization of the vinylcarbonyl ylide to dihydrofuran becomes more favorable than cyclization to vinyloxirane with increasing temperature. Under the high-temperature condition accompanying ring opening of these vinyloxiranes **3** and **4**, the rate for cyclization of the carbonyl ylides **16** (**17**) to **5** might be faster than that for cyclization to the oxiranes **4**.

**Formation of Single Cycloadducts of Vinylcarbonyl Ylides with Dipolarophiles.** Predominant formation of *endo*-addition products of maleic anhydride and dimethyl fumarate to ylide **14** is explained by stabilization of the transition state due to preferred secondary orbital overlap between the vinyl moiety of ylide's HOMO and the carbonyl moiety of the maleic anhydride's or dimethyl fumarate's LUMO as shown in Scheme 11. Thus, the formation of single cycloadduct **11**, **12**, or **13** adds strong support for the initial formation of the *endo*-vinyl-*endo*-aryl carbonyl ylide **14** (**15**) in the reaction with benzaldehydes.

## Conclusions

The vinylcarbenoids derived from  $\text{Rh}_2(\text{OAc})_4$ -catalyzed decomposition of the vinyl diazo compounds **1a** and **1b** attack the carbonyl oxygen atom of benzaldehydes **2** to initially form the *endo*-vinyl-*endo*-aryl vinylcarbonyl ylides **14** (**15**). The ylides **14** undergoes conrotatory cyclization to the oxirane **3** and competitive rotation around the C–O bond to isomerize to the ylides **16** followed by conrotatory cyclization to oxiranes **4** and

conrotatory cyclization to dihydrofurans **5**. The initially formed vinylcarbonyl ylides **14** are efficiently captured by maleic anhydride to give only a single cycloadduct **11** (**12**) through the transition state stabilized by secondary orbital overlap between the vinyl moiety of the ylide's HOMO and the carbonyl moiety of the maleic anhydride's LUMO. The vinylcarbonyl ylides **16** and **18** arising from thermal ring opening of **3** or **4** are inert to maleic anhydride. The ylides **17a–c** arising from the reaction of the carbenoids with **2a–c** or pyrolysis of **3a–c** and **4a–c** undergo disrotatory cyclization to exclusively form the sterically unfavorable *cis*-diaryldihydrofurans **5**, whereas the ylides **17d,e** undergo partly a symmetry-forbidden conrotatory cyclization to the sterically stable *trans*-diaryldihydrofurans **6d,e** and a symmetry-allowed process to **5d,e**.

## Experimental Section

<sup>1</sup>H NMR (270.05 MHz) and <sup>13</sup>C NMR (60.40 MHz) spectra were recorded on a JEOL EX-270 instrument in a CDCl<sub>3</sub> solution using TMS as an internal standard. IR spectra were recorded on a JASCO FT-IR-300E. All melting points were measured with a Yanagimoto melting point apparatus and were not corrected. Phenyl diazomethane<sup>20</sup> and an ethereal solution of diazoethane<sup>21</sup> were prepared by a procedure described in *Organic Synthesis*.

**Preparation of *trans*- and *cis*-3-Chloro-2-(*p*-chlorophenyl)propenenitrile.** A mixture of *p*-chlorobenzyl cyanide (75.7 g, 0.5 mol) and ethyl formate (37.0 g, 0.5 mol) was added dropwise to a stirred solution of sodium hydride (12.0 g, 0.5 mol) in 300 mL of anhydrous ethylene glycol dimethyl ether in an ice bath. After addition was completed, the reaction mixture was gradually warmed to 60 °C and stirred for 2 h. The precipitated sodium salt of 3-hydroxy-2-(*p*-chlorophenyl)propenenitrile was isolated by filtration, dissolved in water, and then acidified by addition of 0.5 N HCl solution. The precipitated 3-hydroxy-2-(*p*-chlorophenyl)propenenitrile was filtered and recrystallized from ether. *trans*- and *cis*-3-Chloro-2-(*p*-chlorophenyl)propenenitrile was prepared from 3-hydroxy-2-(*p*-chlorophenyl)propenenitrile according to Cariou's procedure.<sup>22</sup> Phosphorus pentachloride (29.0 g) was carefully added to 3-hydroxy-2-(*p*-chlorophenyl)propenenitrile (25.0 g) and pyridine (11.0 g) in 250 mL of benzene and refluxed for 5 h. The reaction mixture was poured into 200 g of crushed ice and extracted with 200 mL of ether. The ethereal solution was washed with 200 mL of water, aqueous NaHCO<sub>3</sub>, and then with water. After drying over anhydrous MgSO<sub>4</sub>, the solvent was removed under reduced pressure, and the residue was distilled (170–180 °C/1 mmHg). The distillate was a mixture of *trans*- and *cis*-3-chloro-2-(*p*-chlorophenyl)propenenitrile. *trans*-3-Chloro-2-(*p*-chlorophenyl)propenenitrile: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.49–7.41 (m, 4H), 7.17 (s, 1H). *cis*-3-Chloro-2-(*p*-chlorophenyl)propenenitrile: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.67–7.61 (m, 4H), 7.22 (s, 1H).

**Preparation of 2-(*p*-Chlorophenyl)-4-diazo-4-phenyl-*cis*-2-butenenitrile (**1a**).** To a stirred solution of phenyl diazomethane (5.21 g, 0.044 mol) and triethylamine (6.07 g, 0.06 mol) in 10 mL of dry CH<sub>2</sub>Cl<sub>2</sub> in an ice bath was added all at once the solution of *trans*- and *cis*-3-chloro-2-(*p*-chlorophenyl)propenenitrile (7.92 g, 0.04 mol) in 10 mL of CH<sub>2</sub>Cl<sub>2</sub>. After stirring for 4 h, the reaction mixture was washed with 100 mL of water, and the separated CH<sub>2</sub>Cl<sub>2</sub> layer was dried over anhydrous MgSO<sub>4</sub>. The crude 2-(*p*-chlorophenyl)-4-diazo-4-phenyl-*cis*-2-butenenitrile **1a** was purified by column chromatography on silica gel using benzene as an eluent and

(20) Creary, X. *Organic Syntheses*; Wiley: New York, 1990; Collect. Vol. VII, p 438.

(21) Diazoethane was prepared by a procedure similar to the synthetic method of diazomethane described in: *Organic Syntheses*; Wiley: New York, 1943; Collect. Vol. II, p 165.

(22) Cariou, M. *Bull. Soc. Chim. Fr.* **1969**, 217.

(18) Epiotis, N. D. *J. Am. Chem. Soc.* **1973**, *95*, 1200.

(19) Hayes, E. F.; Siu, A. K. Q. *J. Am. Chem. Soc.* **1971**, *93*, 2090.



recrystallized from  $\text{CH}_2\text{Cl}_2/\text{ether}$ : dark red needles; mp 93.0 °C (decomp);  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.57–7.30 (m, 3H), 7.48 (d, 2H,  $J = 8.6$  Hz), 7.38 (d, 2H,  $J = 8.6$  Hz), 7.18–7.15 (m, 2H), 7.07 (s, 1H); IR (KBr) 2204, 2052, 1597, 1575, 1562, 1496, 1318, 1253, 1101, 825, 746, 688  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{16}\text{H}_{10}\text{ClN}_3$ : C, 68.70; H, 3.60; N, 15.02; Found: C, 68.86; H, 3.78; N, 15.02.

**Preparation of 2-(*p*-Chlorophenyl)-4-diazo-*cis*-2-pentenenitrile (1b).** To the stirred ethereal solution of diazoethane (0.044 mol) and triethylamine (6.07 g, 0.06 mol) in an ice bath was added dropwise the solution of *trans*- and *cis*-3-chloro-2-(*p*-chlorophenyl)-propenenitrile (7.92 g, 0.04 mol) in 10 mL of  $\text{CH}_2\text{Cl}_2$ . After stirring for 2 h, the reaction mixture was washed with 100 mL of water, and the separated  $\text{CH}_2\text{Cl}_2$  layer was dried over anhydrous  $\text{MgSO}_4$ . The crude 2-(*p*-chlorophenyl)-4-diazo-*cis*-2-pentenenitrile **1b** was purified by column chromatography on silica gel using benzene as an eluent and recrystallized from  $\text{CH}_2\text{Cl}_2/\text{ether}$ : orange powders; mp 92.6 °C (decomposition);  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.40–7.30 (m, 4H), 6.89 (s, 1H), 2.36 (s, 3H); IR (KBr) 3043, 2201, 2059, 1574, 1494, 1372, 1283, 1205, 1098, 826  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{11}\text{H}_8\text{ClN}_3$ : C, 60.70; H, 3.70; N, 19.31. Found: C, 60.87; H, 4.06; N, 19.20.

**General Procedure for Reaction of 1a, 1b with Substituted Benzaldehydes.** A substituted benzaldehyde (5 mmol) and a catalytic amount of  $\text{Rh}_2(\text{OAc})_4$  was dissolved in 10 mL of dry benzene. The solution of **1a** (1 mmol) in 4 mL of dry benzene was added over 1 h to the above stirring solution at 50 °C in an argon atmosphere. Stirring was continued until the evolution of nitrogen ceased. The reaction mixture was purified by column chromatography on silica gel using benzene as an eluent, giving (*Z*)-vinyloxirane **3**, (*E*)-vinyloxirane **4**, (*E*)-dihydrofuran **5**, and (*Z*)-dihydrofuran **6** as crystals. These products were recrystallized from  $\text{CH}_2\text{Cl}_2/\text{ether}$ .

**Reaction of 1a with *p*-Anisaldehyde (2a).** **3,4-Epoxy-1-(*p*-chlorophenyl)-*trans*-4-(*p*-methoxyphenyl)-3-phenyl-(*Z*)-butenenitrile (3a):** 26% yield; white cubes; mp 145.2–145.5 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.53 (d, 2H,  $J = 8.6$  Hz), 7.39 (d, 2H,  $J = 8.6$  Hz), 7.36–7.34 (m, 2H), 7.24–7.23 (m, 3H), 7.11 (s, 1H), 7.10 (d, 2H,  $J = 8.9$  Hz), 6.70 (d, 2H,  $J = 8.9$  Hz), 4.66 (s, 1H), 3.72 (s, 3H); IR (KBr) 3062, 3016, 2227, 1612, 1518, 1495, 1254, 1176, 1095, 1032, 1014, 893, 829, 700  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{24}\text{H}_{18}\text{ClNO}_2$ : C, 74.32; H, 4.68; N, 3.61. Found: C, 73.99; H, 4.80; N, 3.60.

**3,4-Epoxy-1-(*p*-chlorophenyl)-*cis*-4-(*p*-methoxyphenyl)-3-phenyl-(*Z*)-butenenitrile (4a):** 25% yield; pale yellow oil;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.54–7.51 (m, 2H), 7.45–7.37 (m, 3H), 7.32 (s, 4H), 7.28 (d, 2H,  $J = 8.6$  Hz), 6.87 (d, 2H,  $J = 8.6$  Hz), 6.85 (s, 1H), 4.29 (s, 1H), 3.79 (s, 3H); IR (KBr) 3060, 2964, 2225, 1613, 1515, 1493, 1251, 1174, 1096, 1032, 1013, 827, 698  $\text{cm}^{-1}$ ; HRMS calcd for  $\text{C}_{24}\text{H}_{18}\text{O}_2\text{NCl}$ : 387.1026; found: 387.1028.

**3-(*p*-Chlorophenyl)-*trans*-2-(*p*-methoxyphenyl)-5-phenyl-2,3-dihydro-3-furancarboxitrile (5a):** 36% yield; colorless cubes; mp 137.2–137.8 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.77–7.74 (m, 2H), 7.47–7.45 (m, 3H), 7.11 (d, 2H,  $J = 8.6$  Hz), 7.04 (d, 2H,  $J = 8.6$  Hz), 6.99 (d, 2H,  $J = 8.9$  Hz), 6.67 (d, 2H,  $J = 8.9$  Hz), 6.16 (s, 1H), 5.70 (s, 1H), 3.73 (s, 3H); IR (KBr) 3052, 2960, 2237, 1637, 1614, 1516, 1491, 1281, 1252, 1016, 829, 750  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{24}\text{H}_{18}\text{ClNO}_2$ : C, 74.32; H, 4.68; N, 3.61. Found: C, 74.37; H, 4.81; N, 3.69.

**Reaction of 1a with Mesityldehyde (2b).** **3,4-Epoxy-1-(*p*-chlorophenyl)-*trans*-4-mesityl-3-phenyl-(*Z*)-butenenitrile (3b):** 7% yield; white needles; mp 131.7–132.5 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.59 (d, 2H,  $J = 8.6$  Hz), 7.42 (d, 2H,  $J = 8.6$  Hz), 7.37 (s, 1H), 7.22–7.16 (m, 5H), 6.65 (s, 2H), 4.61 (s, 1H), 2.31 (br s, 6H), 2.16 (s, 3H); IR (KBr) 2224, 1610, 1491, 1447, 1405, 1096, 1013  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{26}\text{H}_{22}\text{ClNO}$ : C, 78.09; H, 5.54; N, 3.50. Found: C, 77.57; H, 5.65; N, 3.52.

**3,4-Epoxy-1-(*p*-chlorophenyl)-*cis*-4-mesityl-3-phenyl-(*Z*)-butenenitrile (4b):** 18% yield; colorless cubes; mp 113.7–114.3 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.62–7.58 (m, 2H), 7.46–7.43 (m, 3H), 7.27 (d, 2H,  $J = 8.6$  Hz), 7.14 (d, 2H,  $J = 8.6$  Hz), 6.84 (s, 2H), 6.66 (s, 1H), 4.27 (s, 1H), 2.43 (br s, 6H), 2.26 (s, 3H); IR (KBr) 2224, 1609, 1450, 1404, 1095, 1011  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{26}\text{H}_{22}\text{ClNO}$ : C, 78.09; H, 5.54; N, 3.50. Found: C, 78.03; H, 5.69; N, 3.56.

**3-(*p*-Chlorophenyl)-*trans*-2-mesityl-5-phenyl-2,3-dihydro-3-furancarboxitrile (5b):** 14% yield; white needles; mp 166.1–166.4 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.74–7.71 (m, 2H), 7.46–7.43 (m, 3H), 7.08 (br s, 4H), 6.77 (s, 1H), 6.67 (br s, 2H), 5.82 (s, 1H), 2.70 (br s, 3H), 2.19 (s, 3H), 1.80 (br s, 3H); IR (KBr) 3107, 2922, 2231, 1784, 1647, 1612, 1491, 1282, 1093, 1014, 822, 752  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{26}\text{H}_{22}\text{ClNO}$ : C, 78.09; H, 5.54; N, 3.50. Found: C, 78.03; H, 5.67; N, 3.55.

**Reaction of 1a with *p*-Chlorobenzaldehyde (2c).** **3,4-Epoxy-1-(*p*-chlorophenyl)-*trans*-4-(*p*-chlorophenyl)-3-phenyl-(*Z*)-butenenitrile (3c):** 15% yield; white needles; mp 115.2–116.0 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.54 (d, 2H,  $J = 8.9$  Hz), 7.40 (d, 2H,  $J = 8.9$  Hz), 7.36–7.32 (m, 2H), 7.28–7.22 (m, 3H), 7.15 (s, 4H), 7.11 (s, 1H), 4.70 (s, 1H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  142.61 (d), 136.15 (s), 133.92 (s), 133.37 (s), 132.17 (s), 130.64 (d), 129.33 (d), 128.66 (d), 128.48 (d), 128.12 (d), 128.10 (d), 127.59 (d), 127.31 (d), 116.28 (d), 115.84 (t), 66.61 (s), 65.57 (d); IR (KBr) 2225, 1893, 1595, 1446, 1418, 1333, 1098, 987, 868  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{23}\text{H}_{15}\text{Cl}_2\text{NO}$ : C, 70.42; H, 3.85; N, 3.57. Found: C, 70.35; H, 3.99; N, 3.57.

**3,4-Epoxy-1-(*p*-chlorophenyl)-*cis*-4-(*p*-chlorophenyl)-3-phenyl-(*Z*)-butenenitrile (4c):** 42% yield; colorless cubes; mp 159.0–160.5 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.54–7.51 (m, 2H), 7.48–7.39 (m, 3H), 7.37–7.29 (m, 4H), 7.32 (br s, 4H), 6.83 (s, 1H), 4.32 (s, 1H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  138.41 (d), 136.82 (s), 136.14 (s), 134.36 (s), 132.47 (s), 130.79 (s), 129.29 (d), 128.89 (d), 128.82 (d), 128.42 (d), 128.26 (d), 127.06 (d), 125.93 (d), 120.03 (s), 115.51 (d), 67.62 (d), 65.32 (s); IR (KBr) 2224, 1614, 1445, 1326, 1303, 1094, 963, 823  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{23}\text{H}_{15}\text{Cl}_2\text{NO}$ : C, 70.42; H, 3.85; N, 3.57. Found: C, 70.35; H, 3.90; N, 3.55.

***trans*-2,3-Di-(*p*-chlorophenyl)-5-phenyl-2,3-dihydro-3-furancarboxitrile (5c):** 27% yield; colorless cubes; mp 139.9–141.0 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.77–7.73 (m, 2H), 7.49–7.46 (m, 3H), 7.15–7.08 (m, 8H), 6.18 (s, 1H), 5.71 (s, 1H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  160.07 (s), 134.59 (s), 134.53 (s), 132.54 (s), 132.26 (s), 130.45 (d), 128.76 (d), 128.58 (d), 128.37 (d), 127.66 (d), 125.92 (d), 120.89 (d), 97.68 (d), 90.75 (d), 55.65 (s); IR (KBr) 2235, 1635, 1575, 1449, 1403, 1327, 1231, 1030, 982, 876  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{23}\text{H}_{15}\text{Cl}_2\text{NO}$ : C, 70.42; H, 3.85; N, 3.57. Found: C, 70.30; H, 3.98; N, 3.62.

**Reaction of 1a with *p*-Nitrobenzaldehyde (2d).** **3,4-Epoxy-1-(*p*-chlorophenyl)-*trans*-4-(*p*-nitrophenyl)-3-phenyl-(*Z*)-butenenitrile (3d):** 11% yield; white needles; mp 160.5–161.2 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  8.04 (d, 2H,  $J = 8.9$  Hz), 7.56 (d, 2H,  $J = 8.9$  Hz), 7.43 (d, 2H,  $J = 8.6$  Hz), 7.41 (d, 2H,  $J = 8.6$  Hz), 7.36–7.33 (m, 2H), 7.25–7.23 (m, 3H), 7.13 (s, 1H), 4.84 (s, 1H); IR (KBr) 3043, 2225, 1606, 1531, 1495, 1348, 1099, 1014, 827, 700  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{23}\text{H}_{15}\text{ClN}_2\text{O}_3$ : C, 68.58; H, 3.75; N, 6.95. Found: C, 68.23; H, 3.85; N, 6.91.

**3,4-Epoxy-1-(*p*-chlorophenyl)-*cis*-4-(*p*-nitrophenyl)-3-phenyl-(*Z*)-butenenitrile (4d):** 13% yield; white needles; mp 145.3–145.8 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  8.22 (d, 2H,  $J = 8.6$  Hz), 7.57 (d, 2H,  $J = 8.9$  Hz), 7.55–7.51 (m, 2H), 7.50–7.42 (m, 3H), 7.33 (ABq, 4H,  $J = 9.2$  Hz), 6.84 (s, 1H), 4.45 (s, 1H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  147.86 (s), 141.18 (s), 137.29 (d), 136.49 (s), 136.23 (s), 130.30 (s), 129.42 (d), 129.16 (s), 129.04 (d), 127.94 (d), 127.02 (d), 125.94 (d), 123.39 (d), 120.31 (t), 115.43 (d), 67.26 (d), 65.96 (s); IR (KBr) 3060, 2233, 1603, 1522, 1493, 1348, 1095, 1012, 827, 700  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{23}\text{H}_{15}\text{ClN}_2\text{O}_3$ : C, 68.58; H, 3.75; N, 6.95. Found: C, 68.41; H, 3.90; N, 6.94.

**3-(*p*-Chlorophenyl)-*trans*-2-(*p*-nitrophenyl)-5-phenyl-2,3-dihydro-3-furancarboxitrile (5d):** 39% yield; colorless cubes; mp 182.2–182.6 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  8.04 (d, 2H,  $J = 8.6$  Hz), 7.78–7.75 (m, 2H), 7.52–7.48 (m, 3H), 7.35 (d, 2H,  $J = 8.6$  Hz), 7.12 (d, 2H,  $J = 8.9$  Hz), 7.07 (d, 2H,  $J = 8.9$  Hz), 6.30 (s, 1H), 5.74 (s, 1H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  160.00 (s), 147.78 (s), 141.26 (s), 134.94 (s), 131.70 (s), 130.67 (d), 128.84 (d), 128.81 (d), 128.54 (d), 128.02 (s), 127.13 (d), 125.94 (d), 123.35 (d), 120.46 (d), 97.87 (d), 90.04 (d), 55.78 (s); IR (KBr) 3122, 3082, 2252, 1643, 1604, 1525, 1491, 1348, 1282, 1012, 746, 737  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{23}\text{H}_{15}\text{ClN}_2\text{O}_3$ : C, 68.58; H, 3.75; N, 6.95. Found: C, 68.36; H, 3.91; N, 6.90.

**3-(*p*-Chlorophenyl)-*cis*-2-(*p*-nitrophenyl)-5-phenyl-2,3-dihydro-3-furancarboxitrile (6d):** 5% yield; colorless cubes;



mp 191.9–192.1 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  8.30 (d, 2H,  $J = 8.9$  Hz), 7.76–7.72 (m, 2H), 7.51–7.47 (m, 9H), 5.65 (s, 1H), 5.62 (s, 1H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  160.59 (s), 148.56 (s), 141.99 (s), 136.15 (s), 135.36 (s), 130.66 (d), 129.63 (d), 128.79 (d), 128.21 (s), 127.91 (s), 127.33 (d), 125.99 (d), 123.96 (d), 117.65 (d), 97.02 (d), 92.82 (d), 59.09 (s); IR (KBr) 3105, 3070, 2229, 1647, 1606, 1523, 1491, 1348, 1059, 1012, 742, 725  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{23}\text{H}_{15}\text{ClN}_2\text{O}_3$ : C, 68.58; H, 3.75; N, 6.95. Found: C, 68.25; H, 3.70; N, 6.98.

**Reaction of 1a with 2,4-Dinitrobenzaldehyde (2e).** **3-(*p*-Chlorophenyl)-*trans*-2-(2,4-dinitrophenyl)-5-phenyl-2,3-dihydro-3-furancarboxitrile (5e):** 20% yield; colorless cubes; mp 182.4–182.9 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  8.74 (d, 1H,  $J = 2.3$  Hz), 8.32 (dd, 1H,  $J = 2.3, 8.9$  Hz), 7.76 (d, 1H,  $J = 8.9$  Hz), 7.76–7.74 (m, 2H), 7.52–7.49 (m, 3H), 7.17 (d, 2H,  $J = 8.6$  Hz), 7.15 (s, 1H), 7.07 (d, 2H,  $J = 8.6$  Hz), 5.57 (s, 1H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  159.49 (s), 147.68 (s), 146.39 (s), 139.21 (s), 135.21 (s), 132.30 (d), 130.90 (d), 130.52 (d), 129.11 (d), 128.99 (d), 128.66 (d), 127.69 (s), 127.44 (d), 125.96 (d), 120.43 (s), 120.24 (d), 96.89 (d), 85.99 (d), 56.75 (s); IR (KBr) 3111, 2243, 1655, 1608, 1537, 1493, 1350, 1063, 1020, 831, 735  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{23}\text{H}_{14}\text{ClN}_3\text{O}_5$ : C, 61.69; H, 3.15; N, 9.38. Found: C, 61.29; H, 3.22; N, 9.24.

**3-(*p*-Chlorophenyl)-*cis*-2-(2,4-dinitrophenyl)-5-phenyl-2,3-dihydro-3-furancarboxitrile (6e):** 32% yield; white needles; mp 168.9–169.7 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  9.06 (d, 2H,  $J = 2.3$  Hz), 8.56 (dd, 1H,  $J = 2.3, 8.6$  Hz), 7.91 (d, 1H,  $J = 8.6$  Hz), 7.77–7.74 (m, 2H), 7.56 (d, 2H,  $J = 8.6$  Hz), 7.53–7.47 (m, 3H), 7.44 (d, 2H,  $J = 8.6$  Hz), 6.42 (s, 1H), 5.63 (s, 1H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  158.45 (s), 148.18 (s), 147.14 (s), 139.87 (s), 137.00 (s), 135.10 (s), 130.93 (d), 129.47 (d), 129.39 (d), 129.04 (d), 128.28 (d), 127.40 (s), 127.33 (d), 125.94 (d), 120.80 (s), 117.32 (s), 98.87 (d), 87.86 (d), 59.13 (s); IR (KBr) 3109, 2247, 1649, 1608, 1537, 1493, 1350, 1032, 833, 733  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{23}\text{H}_{14}\text{ClN}_3\text{O}_5$ : C, 61.69; H, 3.15; N, 9.38. Found: C, 61.77; H, 3.39; N, 9.21.

**Reaction of 2-(*p*-Chlorophenyl)-4-diazo-*cis*-2-pentene-nitrile (1b) with *p*-Anisaldehyde (2a).** The solution of **1b** (0.218 g, 1 mmol) in 4 mL of dry benzene was added over 1 h to the stirring solution of *p*-anisaldehyde (0.681 g, 5 mmol) and a catalytic amount of  $\text{Rh}_2(\text{OAc})_4$  in 10 mL of dry benzene at 50 °C in an argon atmosphere. Stirring was continued until the evolution of nitrogen ceased. Unreacted *p*-anisaldehyde was removed from the reaction mixture under reduced pressure. The reaction mixture was purified by column chromatography on silica gel. Elution with benzene gave (*Z*)-vinylloxirane **7a** and (*E*)-vinylloxirane **8a**.

**3,4-Epoxy-1-(*p*-chlorophenyl)-*trans*-4-(*p*-methoxyphenyl)-3-methyl-(*Z*)-butenenitrile (7a):** 37% yield; pale yellow oil;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.52 (d, 2H,  $J = 8.6$  Hz), 7.35 (d, 2H,  $J = 8.9$  Hz), 7.39 (d, 2H,  $J = 8.6$  Hz), 6.96 (s, 1H), 6.61 (d, 2H,  $J = 8.9$  Hz), 4.25 (s, 1H), 3.82 (s, 3H), 1.38 (s, 3H); IR (KBr) 2962, 2933, 2837, 2222, 1616, 1515, 1493, 1250, 1173, 1096, 1034, 829  $\text{cm}^{-1}$ ; HRMS calcd for  $\text{C}_{19}\text{H}_{16}\text{O}_2\text{NCl}$  325.0870, found 325.0863.

**3,4-Epoxy-1-(*p*-chlorophenyl)-*cis*-4-(*p*-methoxyphenyl)-3-methyl-(*Z*)-butenenitrile (8a):** 36% yield; pale yellow oil;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.27 (ABq, 4H,  $J = 8.6$  Hz), 7.21 (d, 2H,  $J = 8.9$  Hz), 6.83 (d, 2H,  $J = 8.9$  Hz), 6.61 (s, 1H), 4.13 (s, 1H), 3.76 (s, 3H), 1.81 (s, 3H); IR (KBr) 2965, 2931, 2837, 2223, 1613, 1516, 1493, 1251, 1173, 1096, 1034, 829  $\text{cm}^{-1}$ ; HRMS calcd for  $\text{C}_{19}\text{H}_{16}\text{O}_2\text{NCl}$  325.0870, found 325.0868.

**Reaction 1b with *p*-Chlorobenzaldehyde (2c).** The solution of **1b** (0.218 g, 1 mmol) in 4 mL of dry benzene was added over 1 h to the stirring solution of *p*-chlorobenzaldehyde (0.702 g, 5 mmol) and a catalytic amount of  $\text{Rh}_2(\text{OAc})_4$  in 10 mL of dry benzene at 50 °C in an argon atmosphere. Stirring was continued until the evolution of nitrogen ceased. Unreacted *p*-chlorobenzaldehyde was removed from the reaction mixture under reduced pressure. NMR spectrum of the reaction mixture showed (*Z*)-vinylloxirane **7c**, (*E*)-vinylloxirane **8c**, and (*E*)-dihydrofuran **9c** in a ratio of 16:82:2. The reaction mixture was purified by column chromatography on silica gel. Elution with benzene gave **7c** and **8c**. These products were recrystallized from  $\text{CH}_2\text{Cl}_2$ /ether. (*E*)-Dihydrofuran (**9c**) could not be isolated.

**3,4-Epoxy-1-(*p*-chlorophenyl)-*trans*-4-(*p*-chlorophenyl)-3-methyl-(*Z*)-butenenitrile (7c):** 14% yield; white needles; mp 112.0–112.9 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.53 (d, 2H,  $J = 8.6$  Hz), 7.42 (d, 2H,  $J = 8.6$  Hz), 7.39 (s, 4H), 6.97 (s, 1H), 4.28 (s, 1H), 1.36 (s, 3H); IR (KBr) 3043, 2225, 1606, 1531, 1495, 1348, 1099, 1014, 827, 700  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{18}\text{H}_{13}\text{Cl}_2\text{NO}$ : C, 65.47; H, 3.97; N, 4.24. Found: C, 65.51; H, 4.01; N, 4.20.

**3,4-Epoxy-1-(*p*-chlorophenyl)-*cis*-4-(*p*-chlorophenyl)-3-methyl-(*Z*)-butenenitrile (8c):** 54% yield; colorless cubes; mp 110.0–110.9 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.32 (d, 2H,  $J = 8.6$  Hz), 7.25 (d, 2H,  $J = 8.6$  Hz), 7.26 (s, 4H), 6.59 (s, 1H), 4.15 (s, 1H), 1.82 (s, 3H); IR (KBr) 2980, 2227, 1600, 1493, 1405, 1375, 1332, 1092, 1053, 1013, 834, 824  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{18}\text{H}_{13}\text{Cl}_2\text{NO}$ : C, 65.47; H, 3.97; N, 4.24. Found: C, 65.53; H, 4.05; N, 4.24.

***trans*-2,3-Di-(*p*-chlorophenyl)-5-methyl-2,3-dihydro-3-furancarboxitrile (9c):**  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.13 (d, 2H,  $J = 8.6$  Hz), 7.10 (d, 2H,  $J = 8.6$  Hz), 7.01–6.59 (m, 4H), 6.00 (s, 1H), 5.03 (s, 1H), 2.15 (s, 3H).

**Reaction of 2-(*p*-Chlorophenyl)-4-diazo-*cis*-2-pentene-nitrile (1b) with *p*-Nitrobenzaldehyde (2d).** The reaction was carried out in a procedure described above. (*E*)-vinylloxirane (**8d**) was recrystallized from  $\text{CH}_2\text{Cl}_2$ /ether.

**3,4-Epoxy-1-(*p*-chlorophenyl)-*cis*-4-(*p*-nitrophenyl)-3-methyl-(*Z*)-butenenitrile (8d):** 65% yield; colorless cubes; mp 125.3–126.2 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  8.17 (d, 2H,  $J = 8.9$  Hz), 7.50 (d, 2H,  $J = 8.9$  Hz), 7.32 (d, 2H,  $J = 8.9$  Hz), 7.23 (d, 2H,  $J = 8.9$  Hz), 6.63 (s, 1H), 4.27 (s, 1H), 1.86 (s, 3H); IR (KBr) 3108, 2222, 1603, 1516, 1493, 1346, 1101, 1012, 849, 831, 706  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{18}\text{H}_{13}\text{ClN}_2\text{O}_3$ : C, 63.44; H, 3.85; N, 8.22. Found: C, 63.32; H, 3.94; N, 8.20.

**Reaction of 1a with *p*-Chlorobenzaldehyde (2c) in the Presence of Maleic Anhydride.** *p*-Chlorobenzaldehyde (0.702 g, 5 mmol), maleic anhydride (0.490 g, 5 mmol), and a catalytic amount of  $\text{Rh}_2(\text{OAc})_4$  was dissolved in 10 mL of dry dichloroethane. The solution of **1a** (0.280 g, 1 mmol) in 4 mL of dry dichloroethane was added over 1 h to the above stirring solution at 0 °C in an argon atmosphere. Stirring was continued until the evolution of nitrogen ceased. Unreacted *p*-chlorobenzaldehyde and maleic anhydride were removed from the reaction mixture under reduced pressure. The residue was crystallized from  $\text{CH}_2\text{Cl}_2$  to give 2-*c*-chlorophenyl-5-*c*-[ $\beta$ -cyano-*p*-chlorostyryl]-5-*t*-phenyl-tetrahydro-3*r*,4*c*-furanedicarboxylic anhydride **11c**: 71% yield; colorless cubes; mp 239.5–239.9 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.62–7.58 (m, 2H), 7.54–7.35 (m, 11H), 7.03 (s, 1H), 5.28 (d, 1H,  $J = 8.3$  Hz), 4.53 (d, 1H,  $J = 8.3$  Hz), 3.81 (t, 1H,  $J = 8.3$  Hz); IR (KBr) 3434, 3062, 2225, 1861, 1786, 1597, 1493, 1215, 1088, 1041, 953, 918, 825  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{27}\text{H}_{17}\text{Cl}_2\text{NO}_4$ : C, 66.14; H, 3.49; N, 2.86. Found: C, 66.04; H, 3.56; N, 2.72.

**Reaction of 1b with *p*-Chlorobenzaldehyde in the Presence of Maleic Anhydride.** A solution of **1b** (0.218 g, 1 mmol) in 4 mL of dry dichloroethane was added over 1 h to a stirred solution of *p*-chlorobenzaldehyde (0.702 g, 5 mmol), maleic anhydride (0.490 g, 5 mmol), and a catalytic amount of  $\text{Rh}_2(\text{OAc})_4$  in 10 mL of dry dichloroethane at 0 °C in an argon atmosphere. Stirring was continued until the evolution of nitrogen ceased. Unreacted *p*-chlorobenzaldehyde and maleic anhydride were removed from the reaction mixture under reduced pressure. The residue was crystallized from  $\text{CH}_2\text{Cl}_2$  to give 2-*c*-chlorophenyl-5-*c*-[ $\beta$ -cyano-*p*-chlorostyryl]-5-*t*-methyl-tetrahydro-3*r*,4*c*-furanedicarboxylic anhydride **12c**: 68% yield; colorless cubes; mp 210.2–211.0 °C;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.58 (d, 2H,  $J = 8.6$  Hz), 7.43 (d, 2H,  $J = 8.6$  Hz), 7.40 (s, 4H), 7.03 (s, 1H), 5.57 (d, 1H,  $J = 8.3$  Hz), 3.99 (t, 1H,  $J = 8.3$  Hz), 3.90 (d, 1H,  $J = 8.3$  Hz), 1.18 (s, 3H); IR (KBr) 3064, 2225, 1865, 1784, 1595, 1495, 1203, 1093, 935, 910, 827  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{22}\text{H}_{15}\text{Cl}_2\text{NO}_4$ : C, 61.70; H, 3.53; N, 3.27. Found: C, 61.81; H, 3.59; N, 3.37.

**Reaction of 1a with *p*-Chlorobenzaldehyde (2c) in the Presence of Dimethyl Fumarate.** The reaction was carried out in a procedure described above. NMR spectrum of the reaction mixture showed **3a**, **4a**, **5a**, and cycloadduct **13c** in a ratio of 17:24:11:48. The reaction mixture was purified by column chromatography on silica gel using benzene as an eluent, giving dimethyl 2-*t*-*p*-chlorophenyl-5-*t*-[ $\beta$ -cyano-*p*-chloro-

styryl]-5*c*-phenyl-tetrahydro-3*r*:4*t*-furandicarboxylate **13c** re-crystallized from CH<sub>2</sub>Cl<sub>2</sub>: 39% yield; colorless cubes; mp 124.0–124.9 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.70–7.66 (m, 2H), 7.63 (d, 2H, *J* = 8.6 Hz), 7.48–7.40 (m, 3H), 7.41 (d, 2H, *J* = 8.6 Hz), 7.39 (d, 2H, *J* = 8.6 Hz), 7.36 (d, 2H, *J* = 8.6 Hz), 6.78 (s, 1H), 5.07 (d, 1H, *J* = 9.2 Hz), 4.31 (d, 1H, *J* = 7.6 Hz), 3.80

(dd, 1H, *J* = 7.6, 9.2 Hz), 3.76 (s, 3H), 3.59 (s, 3H); IR (KBr) 2954, 2222, 1744, 1730, 1492, 1438, 1258, 1245, 1169, 1049, 1012, 826, 706 cm<sup>-1</sup>. Anal. Calcd for C<sub>29</sub>H<sub>23</sub>Cl<sub>2</sub>NO<sub>5</sub>: C, 64.94; H, 4.32; N, 2.61. Found: C, 64.734; H, 4.37; N, 2.58.

JO015618L