JOC Article

Effects of an Electron-Withdrawing Group on Thermal Decomposition of 4-Alkylidene-1-pyrazolines: A Novel Stereoselective Formation of Alkylidenecyclopropane Due to Participation of π-Electrons on the Methylene Carbon in Decomposition

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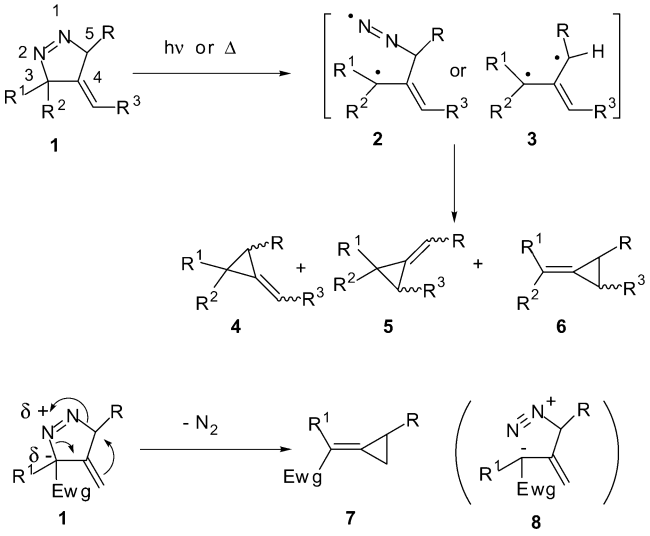
Thermal decomposition of 4-alkylidenepyrazolines **14** bearing a methoxycarbonyl group at C-3, prepared by 1,3-dipolar cycloaddition between allenecarboxylates **12** and diazoalkanes **13**, was carried out. Unlike normal 4-alkylidenepyrazolines, which decompose in stepwise mechanisms at high temperatures, **14** decomposed concertedly at moderately low temperatures (45−110 °C), resulting in selective formation of the two isomeric alkylidenecyclopropanes **7** arising from the bond formation between the *exo*-methylene carbon and the 5-carbon. The selective formation and the configurations of the products are rationalized in terms of the concerted process via the folded conformation of the pyrazolines. Introduction of an electron-withdrawing group at the 3-position of the 4-alkylidenepyrazoline system causes the polarization of the C_3-N_2 bond inducing the properties of intramolecular diazonium salt **8**, in which the π-electrons on the methylene carbon become more nucleophilic and participate in the cleavage of the C_5-N_1 bond. The X-ray crystal structure of the typical normal alkylidenepyrazoline **14a** with only small steric interactions between the substituents was determined to be a nearly planar ring structure.

Introduction

The thermal and photochemical decomposition of 4-alkylidene-1-pyrazolines **1** has been widely studied in detail from mechanistic and theoretical points of view for many years.[1−4] The decomposition of 4-alkylidenepyrazolines **1** has been known to give a mixture of many isomeric alkylidenecyclopropanes **4**, **5**, and **6**, resulting from three modes of cyclization of a diazenyl radical **2** or a trimethylenemethane intermediate **3** (Scheme 1).[5−11]

SCHEME 1



Previously, we found that the 4-arylthio-,[12] 4-arylseleno-,[13] or 4-halopyrazolines **9**,[14] bearing two electron-

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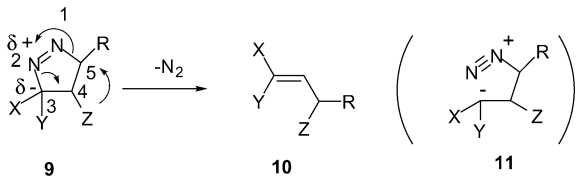
SCHEME 2



withdrawing groups at C-3, underwent decomposition under mild conditions to give 3-heteroatom-substituted propene derivatives **10**, quantitatively, by a concerted mechanism involving migration of the 4-heteroatom substituent Z to C-5 with simultaneous extrusion of nitrogen as shown in Scheme 2. In the reactions of **9**, the polarization of the C_3-N_2 bond due to the electron-withdrawing groups X, Y induces the properties of intramolecular diazonium salts **11**, within which the 4-heteroatom Z at the psuedoequatorial position of the folded envelope structure strongly participates from the backside of nitrogen in the breaking of the C_5-N_1 bond through an episulfonium- or episelenonium-like transition state, resulting in acceleration of the elimination of nitrogen and migration of the 4-heteroatom Z to C-5, giving **10**.

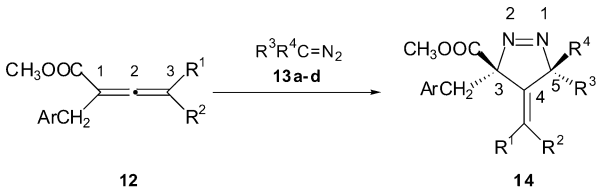
Similarly, introduction of an electron-withdrawing group Ewg at the 3-position of the 4-alkylidenepyrazoline system is expected to cause the polarization of the C_3-N_2 bond inducing the contribution of an intramolecular diazonium salt resonance form **8**, which may allow a similar reaction, that is, the participation of the *exo*-methylene double bond in the breaking of the C_5-N_1 bond and the subsequent bond formation between the methylene carbon and the 5-carbon, resulting in the selective formation of the alkylidenecyclopropane **7** as shown in Scheme 1.

In this paper, we would like to report the first example of a novel reaction of 3-methoxycarbonyl-4-alkylidene-1-pyrazolines to the corresponding alkylidenecyclopropanes, which proceeds in a concerted manner involving no radical intermediate.

Results

Preparation of 4-Alkylidenepyrazolines. The 4-alkylidenepyrazolines bearing a methoxycarbonyl group at C-3 were prepared by the 1,3-dipolar cycloaddition of the corresponding allenic methyl esters **12a**−**g** with diazoalkanes **13** as shown in Scheme 3. The allenes **12a**−**g** were prepared by the reaction of α-substituted acetyl chlorides with α-methoxycarbonyl-*p*-nitrobenzylmethylene(triphenyl)phosphorane in the presence of triethylamine[15] or the reaction of diphenylketene with the phosphorane.[16] The allenes **12** underwent facile, high yield, and totally regiospecific cycloadditions to their C_1-C_2 double bond with diazo compounds **13**. There is a stereochemical

SCHEME 3



12a $R^1=R^2=H$
12b $R^1=Me$; $R^2=H$
12c $R^1=Ph$; $R^2=H$
12d $R^1=p\text{-}MeOC_6H_4$; $R^2=H$
12e $R^1=p\text{-}ClC_6H_4$; $R^2=H$
12f $R^1=p\text{-}NO_2C_6H_4$; $R^2=H$
12g $R^1=R^2=Ph$

Ar = $p\text{-}NO_2C_6H_4$-

14a $R^1=R^2=R^3=R^4=H$
14b $R^1=CH_3$; $R^2=R^3=R^4=H$
14c $R^1=Ph$; $R^2=R^3=R^4=H$
14d $R^1=p\text{-}CH_3OC_6H_4$; $R^2=R^3=R^4=H$
14e $R^1=p\text{-}ClC_6H_4$; $R^2=R^3=R^4=H$
14f $R^1=p\text{-}NO_2C_6H_4$; $R^2=R^3=R^4=H$
14g $R^1=R^2=Ph$; $R^3=R^4=H$
14h(*Z*) $R^1=p\text{-}ClC_6H_4$; $R^2=R^3=H$; $R^4=t\text{-}Bu$
14h(*E*) $R^1=p\text{-}ClC_6H_4$; $R^2=R^4=H$; $R^3=t\text{-}Bu$
14i(*Z*) $R^1=p\text{-}ClC_6H_4$; $R^2=R^3=H$; $R^4=CH_3$
14i(*E*) $R^1=p\text{-}ClC_6H_4$; $R^2=R^4=H$; $R^3=CH_3$
14j $R^1=p\text{-}ClC_6H_4$; $R^2=H$; $R^3=R^4=CH_3$

element in the cycloaddition of **12b**−**f**, except **12a** or **12g**, in that the addition to **12b**−**f** (R^2 = H) can occur from either the side syn to R^1 or anti to it.[11a] In fact, anti addition occurred predominantly.

The structural assignment of these pyrazolines was carried out on the basis of their ^{1}HNMR spectra. The treatment of the allenes **12a**−**g** with excess of diazomethane **13a** gave single isomers of 4-alkylidenepyrazolines **14a**−**g** in quantitative yields. The assignment of anti configuration of these cycloadducts **14b**−**f** is based on the smaller coupling constants (J = 2.0−2.3 Hz) between H^2 and H^3 or H^4 compared to $J_{1,3}$ or $J_{1,4}$ (J = 2.6 Hz) of **14a**. In **14b**, the C-5 protons H^2 and H^3 appeared as doublet of quintets, that is, long-range couplings (J = 2.2 Hz) between the methyl protons on the *exo*-methylene carbon and the C-5 protons (H^3 or H^4) as well as between the olefinic proton (H^2) and the C-5 protons (H^3 or H^4) (J = 2.2 Hz). Large geminal coupling constants (ca. 23 Hz) between the proton H^3 and H^4 were observed in **14a**−**g**. In the case of **14f**, the use of excess of diazomethane resulted in isomerization of **14f** to 2-pyrazolines. The reaction of the allene **12e** with diazoneopentane **13b** gave a mixture of **14h(*Z*)** and **14h(*E*)** in a ratio of 1:2. In the reaction of **12e** with diazoethane **13c**, **14i(*Z*)** and **14i(*E*)** were obtained in a ratio of 2:1. Table 1 shows ^{1}HNMR data for the methylenepyrazolines **14a**−**j**. In **14a**−**g**, the proton H^3 cis to *p*-nitrobenzyl group appeared at ca. 0.5 ppm higher fields than the proton H^4 trans to it. In **14h**−**j**, the alkyl protons (R^3) cis to the benzyl group also appeared at higher fields than R^4 trans to it.

Thermal Decompositions of 5-Unsubstituted 4-Alkylidenepyrazolines 14a−**g.** On heating the 4-methylenepyrazoline **14a** at 80 °C for 16 h, only a single isomer **15** of the methylenecyclopropane was formed in nearly quantitative yield. The "least motion" product **16**, which would have arisen from the bond formation between the C-3 and the C-5 as observed in decomposition of normal pyrazolines, was not formed. Following the reaction by HPLC and NMR revealed that **15** is the

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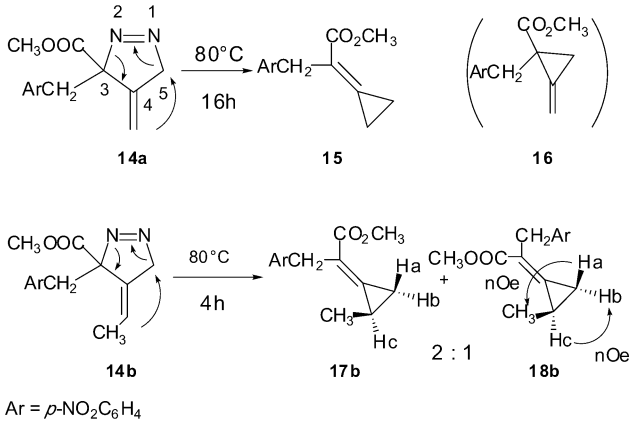
TABLE 1. Chemical Shifts in ppm from TMS and Coupling Constants in ^{1}H NMR Spectra for 4-Alkylidenepyrazolines 14a−j

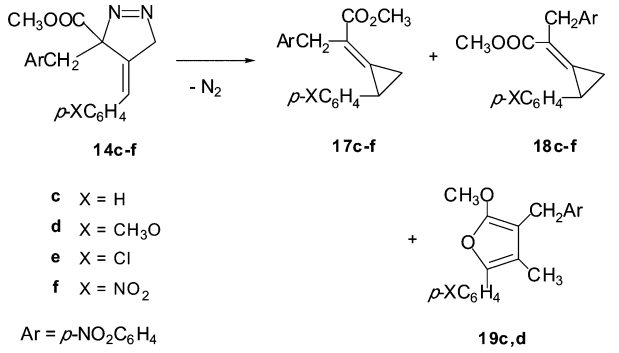
	chemical shifts (ppm)				coupling constants (Hz)				
	H1	H2	H3 (R3)	H4 (R4)	$J_{1,3}$,$J_{1,4}$	$J_{2,3}$	$J_{2,4}$	$J_{3,4}$	notes
14a	5.42	5.37	4.56	5.02	2.6	2.3	2.3	23.1	$J_{1,2} = 0$
14b		5.69	4.26	5.01		2.2	2.2	22.8	$J_{Me,H3}$; $J_{Me,H4} = 2.2$
14c		6.64	4.77	5.33		2.3	2.3	22.8	
14d		6.56	4.75	5.3		2.3	2.3	23.1	
14e		6.59	4.75	5.32		2.3	2.3	23.1	
14f		6.72	4.8	5.39		2.0	2.3	23.1	
14g			4.53	5.05				23.4	
14h(*Z*)		6.71	4.22	(1.12)[a]		2.3			
14h(*E*)		6.87	(0.99)[a]	5.09			2.3		
14i(*Z*)		6.47	4.49	(1.57)[b]		2.3			
14i(*E*)		6.41	(0.96)[b]	5.31			2.3		
14j		6.34	(0.63)[b]	(1.52)[b]					

[a] Chemical shifts of *tert*-butyl protons. [b] Chemical shifts of methyl protons.

SCHEME 4



SCHEME 5



primary product, but not the secondarily formed product from isomerization of **16**.[17] The cyclopropane ring protons of **15** appeared at δ 1.51 and 1.18 as a doublet of doublets. The ^{13}CNMR spectrum of **15** showed two triplets at δ 5.8 and 2.8 (C-2 and C-3) and a singlet at δ 141.1 (C-1) for the cyclopropane ring carbons and a singlet at δ 120.3 for the *exo*-methylene carbon. The formation of **15** resulted from the bond formation between the methylene carbon and the carbon-5 accompanying extrusion of nitrogen (Scheme 4).

The 4-ethylidenepyrazoline **14b**, bearing a methyl group on the *exo*-methylene carbon, decomposed in a similar manner, resulting in quantitative formation of an isomeric mixture of methylenecyclopropanes **17b** and **18b** in a ratio 2:1 (Scheme 4). The configuration of these products was determined on the basis of their ^{1}H NMR spectra assuming that the methyl protons and the cyclopropane ring protons syn to the benzyl group appear at high fields due to the shielding effect of the syn *p*-nitrobenzyl group. Molecular mechanics calculation of **17** and **18** supports such effect of the *p*-nitrobenzyl group. The major product **17b** showed the methyl protons as a doublet at δ 1.09 and the proton on the carbon attached to the methyl group as a multiplet in the range of 1.49−1.60 ppm, while **18b** showed them at δ 1.21 and 1.73−1.86, respectively. Also the protons on the unsubstituted ring carbon of **18b** appeared at higher fields (δ 0.81 (Ha) and 1.34 (Hb)) than those of **17b** (δ 1.15 (Ha) and 1.64 (Hb)). In **18b**, NOE of the signals of methyl protons and Hb (δ 1.34) was observed on the irradiation of the signals of Ha (δ 0.81) and Hc, respectively. The major product **17b** seems to be sterically less stable compared to the minor product **18b** since a benzyl group is bulkier than a methoxycarbonyl group.[18]

The decomposition of the 4-benzylidenepyrazoline **14c**, with a phenyl group on the *exo*-methylene carbon, proceeded much faster than the case of **14a** or **14b**. Heating **14c** at 80 °C for 1 h led to complete decomposition, furnishing the alkylidenecyclopropanes **17c** and **18c** in a ratio of 5:1 along with a trace amount of the furan **19c** (Scheme 5). Again, the sterically less stable **17c** was formed as a major product. Further heating of the reaction mixture resulted in an increase in the furan **19c** with the disappearance of **18c**, but without any change of **17c** (Table 2).

To investigate the substituent effect of the phenyl group on the *exo*-methylene carbon, the thermolysis of para-substituted 4-benzylidenepyrazolines **14d**−**f** was examined (Table 3). Decomposition of **14d**−**f** was completed within 1 h at 80 °C, giving methylenecyclopropanes **17d**−**f** as major products and **18e**,**f** as minor products in very similar ratios (ca. 5:1) as shown in Table 3. The product ratios **17**/**18** seem to be determined by steric factors rather than by electronic factors. However,

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(18) Eliel, E. L. *Angew. Chem*. **1965**, *77*, 784. The conformational free energy $-\Delta G°_X$ of alkyl groups (methyl, 1.5−2.7; ethyl, 1.65−2.25; isopropyl, 1.8−2.5 kcal/mol) in cyclohexane system caused by 1,3-diaxial repulsion betweeen the axial substituent and axial hydrogens is larger than a methoxycarbonyl group (1.1 kcal/mol).

TABLE 2. Thermal Decomposition of the Pyrazoline 14c at 80 °C

	ratio[a] (%)		
reaction time (h)	**17c**	**18c**	**19c**
1	83	15	2
4	83	9	8
12	84	0	16

[a] The ratios were determined by the ^{1}H NMR spectra of the reaction mixture.

TABLE 3. Thermal Decomposition of the Para-Substituted 4-Phenylmethylenepyrazoline 14c−f at 80 °C

entry		X	conditions	ratio[a] **17**/(**18** + **19**)
1	**14c**	H	80 °C, 1 h	5
2	**14d**	CH_3O	80 °C, 0.5 h	5[b]
3	**14e**	Cl	80 °C, 1 h	5
4	**14f**	NO_2	80 °C, 1 h	6

[a] The ratios were determined by the ^{1}H NMR spectra of the reaction mixture. [b] Furan **19d** was formed instead of **18d**.

TABLE 4. Product Ratios in Thermal Decomposition of the Pyrazoline 14d

	conditions		ratio[a] (%)		
entry	*T* (°C)	time (h)	**17d**	**18d**	**19d**
1	80	0.5	84	0	16
2	45	2	85	7	8
3	45	4	85	0	15

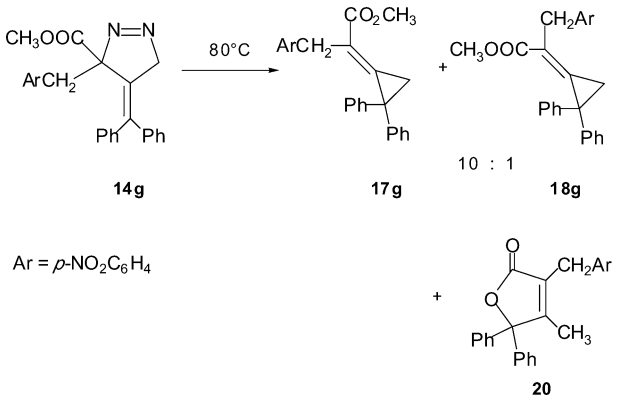
[a] The ratios were determined by the ^{1}H NMR spectra of the reaction mixture.

in the case of **14d**, the furan **19d** instead of **18d** was obtained as a minor product along with the major product **17d** (Table 3, entry 2). The decomposition of the pyrazoline **14d** (X = OMe) was completed within 2 h even at 45 °C to give **18d** and **19d** in a ratio of 1:1 along with the major product **17d** (Table 4, entry 2). On further heating at 45 °C, **18d** was converted to **19d** (Table 4, entry 3), whereas the pyrazolines **14e** (X = Cl) and **14f** (X = NO_2) did not decompose at 45 °C and even further heating at 80 °C **18e**,**f** formed did not convert to **19e**,**f**. These results suggest that an electron-donating group accelerates the decomposition of 4-alkylidenepyrazolines and the conversion of **18** to furans **19**.

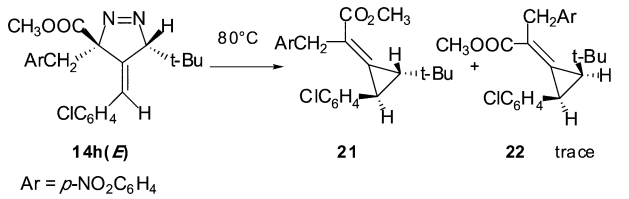
The 4-diphenylmethylenepyrazoline **14g**, bearing two phenyl groups on the *exo*-methylene carbon, gave the methylenecyclopropanes **17g** and **18g** in a ratio of 10:1 along with a trace amount of the lactone **20** (Scheme 6). The minor product **18g** showed the cyclopropane ring protons at 0.43 ppm higher field than the major product **17g**. The lactone **20** showed no methoxy protons but methyl protons at δ 2.04 and also exhibited an absorption of a carbonyl group at 1746 cm^{-1}. Further heating of the reaction mixture resulted in an increase in the lactone **20** with a decrease in **17g** and **18g**.

Decomposition of 5-Substituted 4-Alkylidenepyrazoline. To examine the effect of substituents at C-5, we explored the thermolysis of the 4-alkylidenepyrazolines **14h−j**.

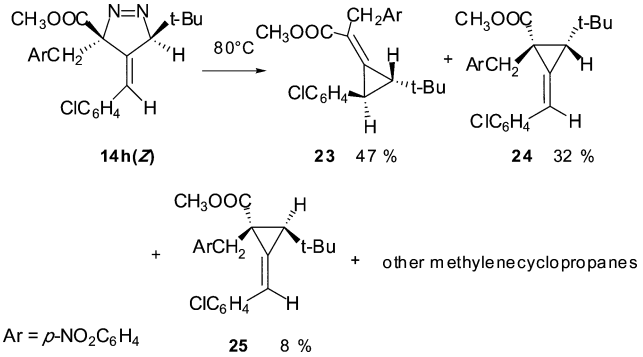
SCHEME 6



SCHEME 7



SCHEME 8

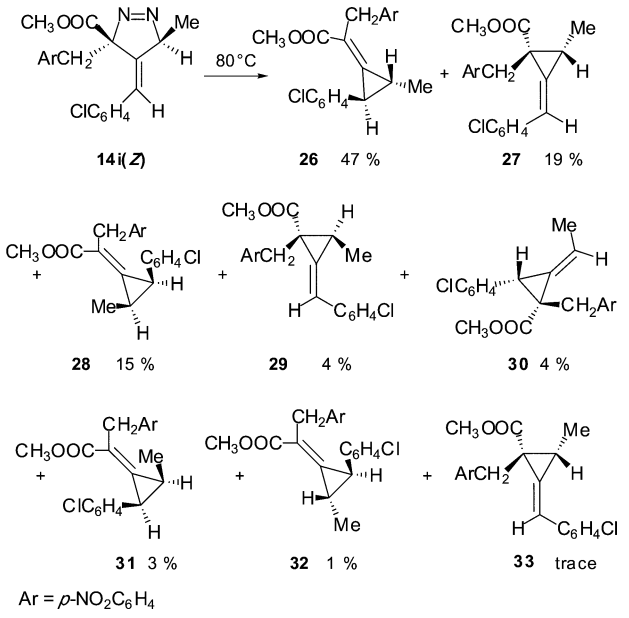


The decomposition of (*E*)-5-*tert*-butylpyrazoline **14h-(*E*)** at 80 °C for 18 h produced the methylenecyclopropane **21** nearly quantitatively along with a trace amount of the isomer **22** (Scheme 7). The NMR spectrum of **21** showed a normal coupling constant (6.3 Hz) between cyclopropane methine protons. On the contrary, **22** showed a large coupling constant (11.7 Hz), indicating cis structure. Benzyl methylene protons of **21** and ester methyl protons of **22** appeared at higher fields compared to those of the corresponding other isomers, indicating the benzyl group syn to chlorophenyl group in **21** and the ester group syn to it in **22**. It is worth noting that only **21** and **22** were formed among four possible isomeric methylenecyclopropanes which are expected from the bond formation between the *exo*-methylene carbon and the C-5; **21** where the *tert*-butyl group is anti to the benzyl group and trans to the chlorophenyl group and **22** where *tert*-butyl group is syn and cis to the both substituents.

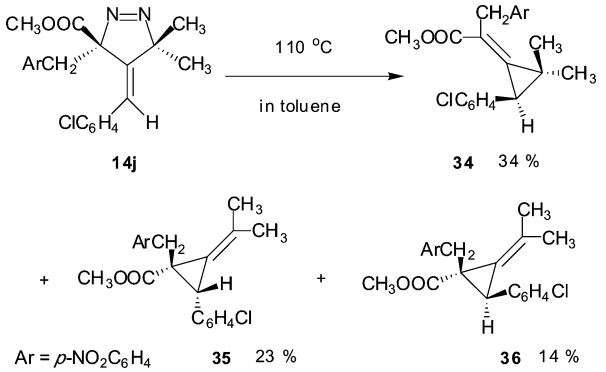
The thermolysis of **14h(*Z*)** required more time for complete decomposition and gave the methylenecyclopropanes **23**, **24**, and **25** along with small amounts of many other isomeric methylenecyclopropanes (Scheme 8).

The 5-methyl-4-*p*-chlorobenzylidenepyrazolines **14i(*E*)** and **14i(*Z*)**, bearing a methyl group at C-5, decomposed

SCHEME 9



SCHEME 10



at 80 °C to give a complex mixture of many isomeric methylenecyclopropanes. Heating 5-methyl-4-methylenepyrazolines **14i(*Z*)** gave the unseparable mixture of at least eight different methylenecyclopropanes, in which main components were **26** (47%), **27** (19%), and **28** (15%) and methylenecyclopropanes **29**, **30**, **31**, **32**, and **33** were also formed as very minor components (Scheme 9). Although **14i(*E*)** could not be isolated in a pure state, a **14i(*E*)**-enriched mixture gave **32** as a main product along with many other methylenecyclopropanes. In **26** and **32**, the coupling constants between ring protons are small (J = 5.9 and 5.6 Hz, respectively), whereas, in **28** and **31**, large coupling constants (J = 10.9 Hz) indicating cis structures.

5,5-Dimethyl-4-*p*-chlorobenzylidenepyrazoline **14j**, bearing two methyl groups at C-5, required the harsh condition of 110 °C for 4 h for decomposition, yielding methylenecyclopropanes **34**, **35**, and **36** in yields of 34, 23, and 14%, respectively (Scheme 10). The methylenecyclopropanes **34** showed two methyl singlets at high fields (δ 0.83 and 1.34). The two methyl protons of **35** and **36** appeared as two doublets with small coupling constants (J = 1.7 and 2.0 Hz, respectively) at low fields, resulting from long-range coupling with the cyclopropane ring protons, which is characteristic for dimethylmethylenecyclopropanes.[4a]

TABLE 5. Activation Parameters at 60 °C for the Thermolysis of 4-Alkylidenepyrazolines 14a−g

14	R^1	R^2	$\Delta G^{\ddagger}_{60°C}$ (kJ mol^{-1})[a]	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})
a	H	H	113.8	118.4	14
b	CH_3	H	112.1	115.6	10
c	Ph	H	102.5	107.5	15
d	*p*-$CH_3OC_6H_4$	H	98.6	103.1	14
e	*p*-ClC_6H_4	H	102.7	109.3	20
f	*p*-$NO_2C_6H_4$	H	104.6	106.9	7
g	Ph	Ph	105.4	132.1	80

[a] Calculated from $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$.

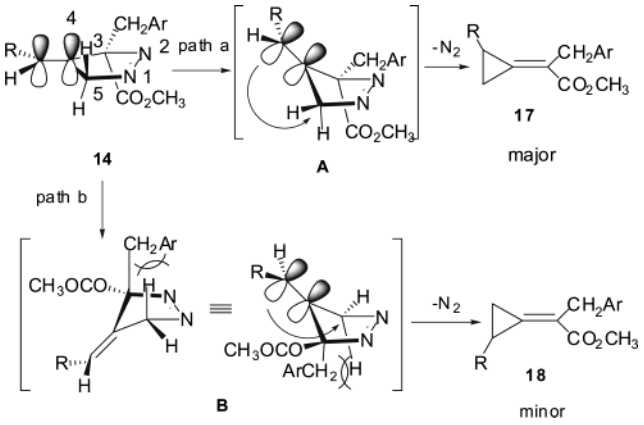
Kinetic Studies of the Decomposition of 4-Alkylidenepyrazolines. To gain insight into the mechanism of the thermolysis of alkylidenepyrazolines, the kinetic studies of the alkylidenepyrazolines **14a−g** in toluene were carried out by following the alkylidenepyrazolines by HPLC. Table 5 lists the activation parameters for the thermolysis. The pyrazoline **14b** (R^1 = Me, R^2 = H) has slightly lower activation free energy ($\Delta G^{\ddagger}$) than **14a** (R^1 = R^2 = H). Introduction of a phenyl group on the methylene carbon decreases $\Delta G^{\ddagger}$ by 10 kJ mol^{-1} compared to the methyl group and increases the rate of the decomposition. The plot of $-\Delta G^{\ddagger}$ for the decomposition of **14c−f** vs substituent constants σ_p^+ yielded a straight line with a negative slope (ρ = −0.62, R^2 = 0.97).

Discussion

Preferential Formation of the Sterically Less Stable Methylenecyclopropanes. Thermolysis of normal 4-alkylidenepyrazolines hitherto reported required a temperature more than 150 °C and proceeded in stepwise mechanisms, giving many isomeric methylenecyclopropanes and diene derivatives. However, the 4-alkylidenepyrazolines bearing an electron-withdrawing group at C-3 described here decomposed at moderately lower temperatures. If the decomposition of the alkylidenepyrazolines examined here proceeds in stepwise mechanisms via the diazenyl radical or the trimethylenemethane intermediates, the alkylidenepyrazolines **14a**, **14g**, **14b−f**,**j**, and **14h**,**i** should give 2, 4, 6, and 12 possible isomeric methylenecyclopropanes, respectively. However, the methylenepyrazoline **14a** gave sole isomer of methylenecyclopropane **15** and **14b−g** or **14h(*E*)** gave only two isomers **17b−g** and **18b−g** or **21** and **22**, arising from the bond formation between the methylene carbon and the 5-carbon with simultaneous extrusion of nitrogen. These methylenepyrazolines did not form any the "least motions" products. The methylenecyclopropane **22**, in which the bulky *tert*-butyl group is cis to the chlorophenyl group, is the most sterically unstable one among the 12 possible ones. Furthermore, in the reaction of **14b−g**, preferential formation of the sterically less stable isomers **17b−g** compared to another isomeric products **18b−g** was observed. These results suggest that a concerted mechanism is involved instead of stepwise mechanisms. On the other hand, **14h(*Z*)**, **14i(*E*)**, and **14i-(*Z*)** gave complex mixtures including many methylenecyclopropane isomers, suggesting that stepwise mechanisms are involved as well as a concerted mechanism.

Concerted Mechanism for Formation of Methylenecyclopropanes. A concerted mechanism should

SCHEME 11

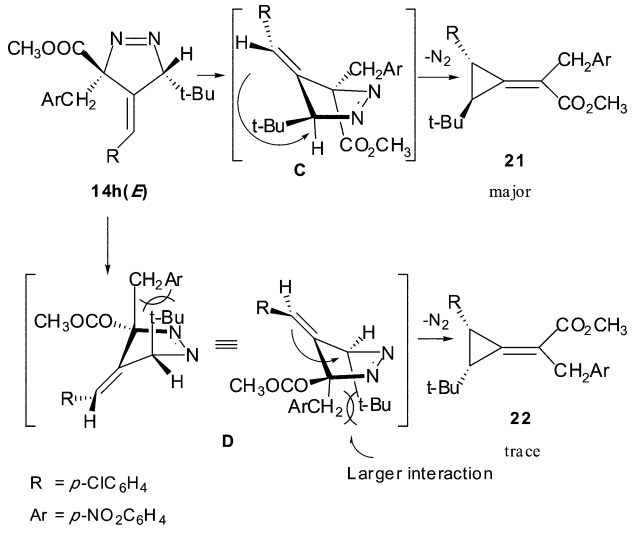


involve the simultaneous extrusion of nitrogen with the bond formation between the methylene carbon and the 5-carbon. The π orbital of the 4-alkylidene substituents should overlap effectively with the breaking C_5-N_1 and C_3-N_2 bonds in order to participate in the simultaneous bond fission. However, the π orbital and the two breaking C−N bonds are nearly orthogonal in the ground state, since the pyrazoline ring of the methylenepyrazoline **14a** proved to be nearly planar by a single-crystal X-ray structure analysis as shown later.

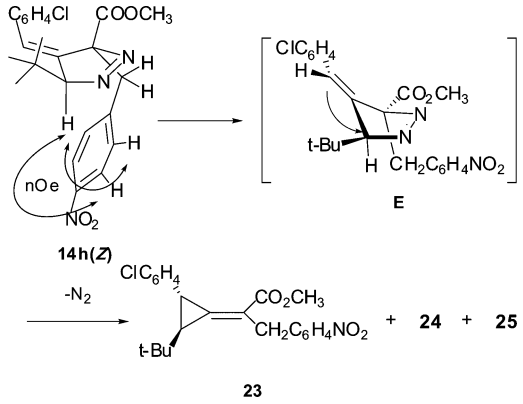
Therefore, on the way to the transition state the pyrazoline ring is required to take an envelope structure such as **A** or **B** (Scheme 11) for the effective overlap between two orbitals, which lowers the energy barrier for nitrogen loss. Furthermore, the π-lobe of the methylene carbon should approach to the 5-carbon from the backside of the C_5-N_1 bond for the concerted bond formation with extrusion of nitrogen. An electron-withdrawing methoxycarbonyl group at C-3 induces the polarization of the C_3-N_2 bond, which enhances the nucleophilicity of the methylene carbon. The negative value of ρ in the kinetic studies indicates a strong nucleophilic participation of the double bond in the C_5-N_1 bond cleavage.

These processes must occur simultaneously. This concerted process is a symmetrically allowed [π2a + σ2a + σ2s] process according to the Woodward−Hoffmann rule. A 1,3-diaxial interaction in the envelope structures should influence stability of their conformations. The conformation **B**, where the larger substituent benzyl group occupies a pseudoaxial position, suffers from a larger 1,3-diaxial repulsion than **A** with the smaller methoxycarbonyl group at that position,[18] so the conformation **A** is more preferable to **B**. Therefore, the path a through conformation **A** takes place preferentially, giving the sterically less stable methylenecyclopropanes **17** as a major product (Scheme 11), which is consistent with the experimental results. Application of the same mechanism to the reaction of **14h(*E*)** gives the major product **21** via conformation **C** with a small 1,3-diaxal repulsion between methoxycarbonyl group and hydrogen and a trace amount of **22** via conformation **D** with a large 1,3-diaxial repulsion between *t*-Bu and $ArCH_2$ groups (Scheme 12). In the products arising from **14h(*E*)**, the stereochemical relationship of *tert*-butyl group to chlorophenyl group is closely related to the configuration around the double bond; trans relationship of the substituents

SCHEME 12



SCHEME 13

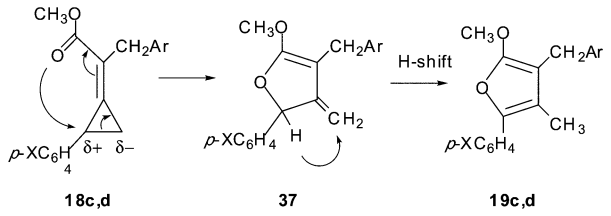


requires *E*-form of the double bond in **21**, while cis relationship requires *Z*-form in **22**. These stereochemical relationships strongly support a concerted process.

Thermolysis of **14h(*Z*)** required more time for completion and gave **23** as a main product along with the "least motions" methylenecyclopropanes **24** and **25** (Scheme 13). The main product **23** seems to be formed in the concerted path via conformation **E**. However, *p*-nitrophenyl group at C-3 in the ground state of **14h(*Z*)** tends to be bent toward 5-cis hydrogen since the 5-hydrogen (δ 4.22) appeared at 0.9 ppm higher field due to the time-averaged orientation of *p*-nitrophenyl ring over it than that (δ 5.09) of **14h(*E*)**. Supporting evidence of their proximity was obtained by NOE difference analysis, which showed significant enhancement of the signals between 5-hydrogen and four aromatic protons of **14h(*Z*)**. The proximity suggests a large 1,3-diaxial interaction between the H-5 and the nitrobenzyl group in the conformation **E**, which is expected to elevate the activation energy for the process via **E** to **23**.

Geminal substitution of two methyl groups on the C-5 interferes with ring folding due to the severe 1,3-diaxial interaction between the methyl group and the benzyl or the methoxycarbonyl group, resulting in an increase in the activation energy for the concerted process. Consequently, 5,5-dimethylpyrazoline **14j** proceeded in a step-

SCHEME 14



wise mechanism to give isomeric mixture of methylenecyclopropanes.

Stepwise Mechanism. An increase in the energy of activation for the concerted process or substitution of radical stabilizing groups at C-3 and C-5 may allow stepwise process. Decompositions of **14h(*Z*)**, **14i(*E*)**, **14i-(*Z*)**, and **14j** seem to proceed partially or completely in a stepwise process. However, their decomposition proceeded at moderately lower temperatures than those required for the decomposition of normal 4-alkylidenepyrazolines without any electron-withdrawing group. In the stepwise mechanism involving a diazenyl radical intermediate as observed in thermal decomposition of normal alkylidenepyrazoline, the one breaking C−N bond should overlap effectively with the 4-alkylidene π orbital to gain stabilization by conjugation with the double bond. Therefore, pyrazoline ring should require to be bent and adopt folded or twisted envelope structures for the overlapping. However, geminal substitution of two alkyl groups in the 5-position interferes with folding due to the steric crowding, which hinders effective stabilization by the conjugation with double bond, resulting in an increase in the activation energy. Therefore, decomposition of the 5,5-dimethylpyrazoline **14j** requires higher temperature for decomposition than the 5-methylpyrazoline **14i**.

Formation of Furans 19c,d. In the reaction at 80 °C for 1 h, **14c** gave a trace of the furan **19c** along with the methylenecyclopropanes **17c** and **18c**. Isomerization of **18c** to **19c** was confirmed by further heating of the reaction mixture (Table 2). However, **14d** at 80 °C gave the furan **19d** but not **18d**, while **14d** at 45 °C for 2 h gave **18d** along with **19d** (Table 4). Isomeric methylenecyclopropanes **17c**,**d** proved to be stable under these conditions by controlled experiments. Above results suggest that the formation of the furans **19c**,**d** resulted from the isomerization of **18c**,**d** but not from **17c**,**d**. The phenyl group on the cyclopropane ring of **18c**,**d** is syn to the methoxycarbonyl group. This isomerization arises from the bond formation between the carbonyl oxygen and the syn C-2 with simultaneous cleavage of the C_2-C_3 bond, giving methylenedihydrofuran **37** followed by hydrogen migration to form **19** as shown in Scheme 14. Fast isomerization of **18d** to **19d**, suggesting that an electron-donating substituent of the phenyl group accelerates the isomerization, indicates that the polarization of the C_2-C_3 bond of **18** is important (Scheme 14).

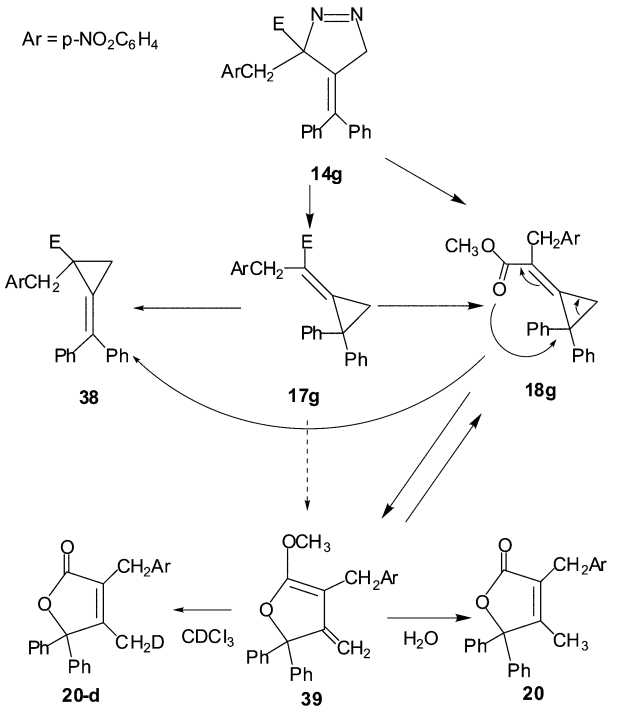
Formation of Lactone 20. A trace amount of the lactone **20** was formed at the early stage of the reaction of **14g**. Further heating of the reaction mixture resulted in an increase in the lactone **20** with decreases in **17g** and **18g** (Table 6). The formation of the lactone can be explained in terms of the isomerization of methylenecyclopropanes **17g** and/or **18g** to the methylenedihydrofuran **39** followed by hydrolysis as shown in Scheme 15.

TABLE 6. Change of Products Rations with Reaction Times in Pyrolysis of 4-Diphenylmethylenepyrazoline 14g in $CDCl_3$ at 80 °C

	ratio[a] (%)					
time (h)	**17g**	**18g**	**39**	**20-*d***	**38**	**18g/39**
2	85	8	4	3		2.3
16	58	14	10	13	4	1.4
40	36	22	16	16	10	1.4
60	27	23	17	19	14	1.4
120	19	20	13	24	24	1.5

[a] The ratios were determined by the ^{1}H NMR spectra of the reaction mixture.

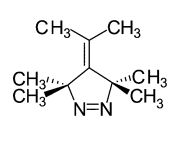
SCHEME 15



In fact, the intermediate **39** was observed in the ^{1}H NMR spectrum of the reaction mixture, which showed the *exo*-methylene protons at δ 4.48 and 4.18, methoxy protons at δ 3.92 and benzyl methylene at δ 3.58 as singlets. Heating the reaction mixture in $CDCl_3$ produced the lactone (**20-*d***) containing a deuterium in methyl group, indicating that the lactone was formed by action of $CDCl_3$ on **39** under this condition. However, in the experiment in $CDCl_3$ including a drop of H_2O, the incorporation of deuterium into the methyl group of **20** was not observed. To look more closely at this isomerization, the absolute $CDCl_3$ solution of pyrazoline **14g** was heated at 80 °C in a sealed tube, and the product ratios were determined by the ^{1}HNMR spectra of the reaction mixture (Table 6). The methylenecyclopropane **17g**, the initial major product, decreased on further heating, whereas the lactone **20-*d*** increased, and **18g** and **39** increased at the early stage and then the increase in **18g** and **39** stopped with decreasing amount of **17g**. The ratios **18g**/**39** remained constant at value of 1.4 during the stationary state, suggesting equilibrium between **18g** and **39** at the temperature. Also, the signals corresponding to the diphenylmethylenecyclopropane **38** (cyclopropane methylene protons; δ 1.75 and 2.34 (ABq, 2 H, J = 9.6 Hz),

the methylene protons of *p*-nitrobenzyl; δ 3.09 and 3.28 (ABq, 2 H, J = 14.5 Hz)) were observed during the reaction and the intensity of **38** gradually increased on heating as shown in Table 6. The formation of **38** presumably arised from the isomerization of the methylenecyclopropanes **17g** and **18g**. These results are summarized in Scheme 15.

X-ray Crystal Structure of 3-Methoxycarbonyl-3-*p*-nitrophenyl-4-methylenepyrazoline 14a. In many 1-pyrazoline derivatives studies, 1-pyrazoline ring adopts an inherent folded envelope structure to avoid the steric hindrance between cis substituents on vicinal carbons.[19] In particular, the structures of 4-methylenepyrazolines having no such hindrance are of interest on the considering the mechanism of the decomposition of the alkylidenepyrazolines **14**, the structures of which have been so far reported on only two derivatives. 4-Isopropylidene-3,3,5,5-tetramethylpyrazoline-1 **40** does not adopt a folded envelope structure but an almost planar one,[20] whereas methylenepyrazoline **41** has a folded structure with the dihedral angle 16°.[21] Both compounds are, however, not suitable to confirm whether **14** adopts inherently a planar or an envelope structure, because the more the ring is folded the greater becomes the steric crash between the methyl groups on C-3 and C-5, suggesting that presence of these methyl groups flattens the ring. Therefore, to confirm the inherent structure of normal alkylidenepyrazolines, we have performed the X-ray crystal analysis of **14a** with small steric interaction between the substituents on C-3 and hydrogens on C-5 as a typical model of normal 4-alkylidenepyrazolines.



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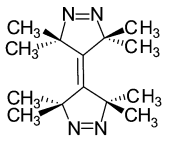
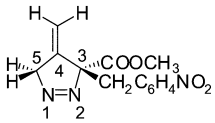


41



14a

The five-membered ring of **14a** proved to be nearly planar; the dihedral angle between the best plane through N_1, N_2, C_3, and C_5 and the plane through C_3, C_4, and C_5 is 4.18(7)°.

Conclusion

Unlike normal 4-alkylidenepyrazolines, which decompose in stepwise mechanisms via diazenyl radical or trimethylenemethane intermediates, the 4-alkylidenepyrazolines bearing an electron-withdrawing group at C-3 decompose in the concerted mechanism and selectively give the two isomeric methylenecyclopropanes resulting from the bond formation between the *exo*-methylene carbon and the 5-carbon. In the formation of two isomeric methylenecyclopropanes, the sterically less stable isomer was formed more than the sterically stable one. Their isomer ratios and configurations are rationalized in terms of the concerted process via the folded conformation of the pyrazolines. The driving force of the present novel reaction should be concluded to be the introduction of an electron-withdrawing group at the 3-position of 4-alkylidenepyrazoline system. The electron-withdrawing group at the 3-position causes the polarization of the C_3-N_2 bond, inducing the properties of internal diazonium salt **8**, which enhances the nucleophilicity of π-electrons on the methylene carbon to participate in the cleavage of the C_5-N_1 bond. The cyclopropanation and the extrusion of nitrogen occur simultaneously. The structure of the typical normal alkylidenepyrazoline **14a** with only small steric interactions between the substituents proved to be nearly planar by a single-crystal X-ray structure analysis.

Experimental Section

Melting points were not corrected. ^{1}H NMR (270.05 MHz) and ^{13}C NMR (60.40 MHz) spectra were recorded in a $CDCl_3$ solution using TMS as an internal standard. Diazomethane, diazoethane, and diazoneopentane were prepared by alkali treatment of *N*-methyl-*N*-nitrosourea,[22] *N*-ethyl-*N*-nitrosourea,[22] and *N*-neopentyl-*N*-nitrosourethane.[23] 2-Diazopropane was prepared by oxidation of acetone hydrazone.[24]

Preparation of Allenic Methyl Esters. Allenes **12a−f** were prepared by the reaction of the corresponding α-substituted acetyl chlorides with (*p*-nitrobenzyl)methoxycarbonylmethylenetriphenylphosphorane in the presence of triethylamine according to the procedure in the literature.[15]

[1-Methoxycarbonyl-2-(*p*-nitrophenyl)ethylidene]triphenylphosphorane. This was prepared from the reaction of methoxycarbonylmethylenetriphenylphosphorane with *p*-nitrobenzyl bromide according to Bestmann and Schultz's method,[25] mp 156−7 °C. The ^{1}H NMR spectrum showed a 1:1.8 mixture of two conformers in $CDCl_3$ solution: ^{1}H NMR ($CDCl_3$) of the major component δ 7.94 (d, J = 8.6 Hz, 2H), 7.57−7.40 (m, 19H), 7.08 (d, J = 8.6 Hz, 2H), 3.47 (d, J = 18.2 Hz, 2H), 3.20 (s, 3H); ^{1}H NMR ($CDCl_3$) of the minor component δ 7.97 (d, J = 8.6 Hz, 2H), 7.57−7.40(m, 19H), 7.08 (d, J = 8.6 Hz, 2H), 3.63 (s, 3H), 3.43 (d, J = 18.8 Hz, 2H). Anal. Calcd for $C_{28}H_{24}NO_4P$: C, 71.63; H, 5.15; N, 2.98. Found: C, 71.26; H, 5.26; N, 3.03.

1-Methoxycarbonyl-1-(*p*-nitrobenzyl)allene (12a). This was obtained in 56% yield from the reaction of the phosphorane with acetyl chloride: colorless needles; mp 79.5−80.0 °C; ^{1}H NMR ($CDCl_3$) δ 8.15 (d, J = 8.9 Hz, 2H), 7.40 (d, J = 8.9 Hz, 2H), 5.17 (t, J = 2.5 Hz, 2H), 3.75 (s, 3H), 3.66 (t, J = 2.5 Hz, 2H); IR (KBr) 1964, 1934, 1709, 1604, 1595, 1517, 1339, 1255 cm^{-1}. Anal. Calcd for $C_{12}H_{11}NO_4$: C, 61.80; H, 4.75; N, 6.01. Found: C, 61.66; H, 4.80; N, 5.94.

1-Methoxycarbonyl-3-methyl-1-(*p*-nitrobenzyl)allene (12b). This was obtained in 65% yield as colorless oil from the reaction of the phosphorane with propionyl chloride: ^{1}H NMR ($CDCl_3$) δ 8.15 (d, J = 8.6 Hz, 2H), 7.39 (d, J = 8.6 Hz, 2H), 5.52 (qt, J = 7.6, 2.3 Hz, 1H), 3.73 (s, 3H), 3.68 and 3.61 (ABq d, J = 15.2, 2.3 Hz, 2H), 1.72 (d, J = 7.6, 3H); IR (KBr) 1957, 1706, 1604, 1517, 1348, 1277, 1218 cm^{-1}. Anal. Calcd for $C_{13}H_{13}NO_4$: C, 63.15; H, 5.30; N, 5.67. Found: C, 63.08; H, 5.32; N, 5.68.

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1-Methoxycarbonyl-1-(*p*-nitrobenzyl)-3-phenylallene (12c). This was obtained in 62% yield from the reaction of the phosphorane with phenylacetyl chloride: colorless oil; ^{1}H NMR ($CDCl_3$) δ 8.12 (d, J = 8.6 Hz, 2H), 7.43 (d, J = 8.6 Hz, 2H), 7.35−7.20 (m, 5H), 6.56 (t, J = 2.3 Hz, 1H), 3.82 and 3.76 (ABq d, J = 15.2, 2.3 Hz, 2H), 3.74 (s, 3H). IR (KBr) 1944, 1706, 1604, 1508, 1341 cm^{-1}. Anal. Calcd for $C_{18}H_{15}NO_4$: C, 69.89; H, 4.89; N, 4.53. Found: C, 69.05; H, 4.94; N, 4.11.

1-Methoxycarbonyl-3-(*p*-methoxyphenyl)-1-(*p*-nitrobenzyl)allene (12d). This was obtained in 44% yield from the reaction of the phosphorane with p-methoxyphenylacetyl chloride: colorless needles; mp 111.5−112 °C; ^{1}H NMR ($CDCl_3$) δ 8.12 (d, J = 8.6 Hz, 2H), 7.43 (d, J = 8.6 Hz, 2H), 7.14 (d, J = 8.6 Hz, 2H), 6.86 (d, J = 8.6 Hz, 2H), 6.52 (t, J = 2.2 Hz, 1H), 3.82 (s, 3H), 3.85 and 3.70 (ABq d, J = 14.6, 2.2 Hz, 2H), 3.74 (s, 3H); IR (KBr) 1940, 1712, 1606, 1518, 1344, 1249 cm^{-1}. Anal. Calcd for $C_{19}H_{17}NO_5$: C, 67.25; H, 5.05; N, 4.13. Found: C, 67.06; H, 5.05; N, 4.10.

3-(*p*-Chlorophenyl)-1-methoxycarbonyl-1-(*p*-nitrobenzyl)allene (12e). This was obtained in 56% yield from the reaction of the phosphorane with *p*-chlorophenylacetyl chloride: colorless needles; mp 97.0−97.6 °C; ^{1}H NMR ($CDCl_3$) δ 8.13 (d, J = 8.6 Hz, 2H), 7.41 (d, J = 8.6 Hz, 2H), 7.29 (d, J = 8.6 Hz, 2H), 7.13 (d, J = 8.6 Hz, 2H), 6.51 (t, J = 2.5 Hz, 1H), 3.78 (br s, 2H), 3.75 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 213.0 (s), 166.1 (s), 146.8 (s), 146.4 (s), 129.8 (s), 129.7 (d), 129.1 (d), 128.8 (s), 128.4 (d), 123.6 (d) 103.2 (s), 98.4 (d), 52.6 (q), 35.4 (t); IR (KBr) 1940, 1714, 1595, 1517, 1345, 1273 cm^{-1}. Anal. Calcd for $C_{18}H_{14}NO_4Cl$: C, 62.88; H, 4.11; N, 4.07. Found: C, 62.73; H, 4.17; N, 4.00.

1-Methoxycarbonyl-1-(*p*-nitrobenzyl)-3-(*p*-nitrophenyl)-allene (12f). This was obtained in 41% yield from the reaction of the phosphorane with *p*-nitrophenylacetyl chloride: colorless needles; mp 133.5−134.0 °C; ^{1}H NMR ($CDCl_3$) δ 8.19 (d, J = 8.6 Hz, 2H), 8.14 (d, J = 8.6 Hz, 2H), 7.42 (d, J = 8.6 Hz, 2H), 7.35 (d, J = 8.6 Hz, 2H), 6.61 (t, J = 2.3 Hz, 1H), 3.82 (d, J = 2.3 Hz, 2H), 3.77 (s, 3H); IR (KBr) 1944, 1704, 1594, 1516, 1348, 1275 cm^{-1}. Anal. Calcd for $C_{18}H_{14}N_2O_6$: C, 61.02; H, 3.98; N, 7.91. Found: C, 60.89; H, 3.93; N, 7.88.

1-Methoxycarbonyl-1-(*p*-nitrobenzyl)-3,3-diphenylallene (12g). This was prepared in 58% yield by refluxing diphenyl ketene with an equimolar of the phosphorane in dry benzene for 4 h: colorless plates; mp 132.5−133.2 °C; ^{1}H NMR ($CDCl_3$) δ 8.06 (d, J = 8.6 Hz, 2H), 7.17−7.36 (m, 12H), 3.85 (s, 2H), 3.78 (s, 3H); IR (KBr) 1942, 1711, 1606, 1598, 1522, 1348, 1255 cm^{-1}. Anal. Calcd for $C_{24}H_{19}NO_4$: C, 74.79; H, 4.97; N, 3.63. Found: C, 75.18; H, 5.11; N, 3.65.

General Procedure for Preparation of Alkylidenepyrazolines 14. An ethereal solution containing 3 mmol of diazo compound was added to the solution of allenes **12** (2 mmol) in dichloromethane at 0 °C. After standing at 0 °C overnight, the solvent was removed, and the product was recrystallized from dichloromethane/ether.

3-Methoxycarbonyl-4-methylene-3-(*p*-nitrobenzyl)-1-pyrazoline (14a). This was obtained quantitatively from the reaction of **12a** with diazomethane: colorless crystals; mp 125.0 °C dec; ^{1}H NMR ($CDCl_3$) δ 8.08 (d, J = 8.6 Hz, 2H), 7.31 (d, J = 8.6 Hz, 2H), 5.42 (t, J = 2.6 Hz, 1H), 5.37 (t, J = 2.3 Hz, 1H), 5.02 and 4.56 (ABq d, J = 23.1, 2.5 Hz, 2H), 3.90 and 3.33 (ABq, J = 13.9 Hz, 2H), 3.75 (s, 3H); IR (KBr) 1734, 1604, 1516, 1349, 1251 cm^{-1}. Anal. Calcd for $C_{13}H_{13}N_3O_4$: C, 56.72; H, 4.76; N, 15.27. Found: C, 56.67; H, 4.77; N, 15.12.

(*Z*)-4-Ethylidene-3-methoxycarbonyl-3-(*p*-nitrobenzyl)-1-pyrazoline (14b). This was obtained quantitatively from the reaction of **12b** with diazomethane: colorless crystals; mp 97.0 °C dec; ^{1}H NMR ($CDCl_3$) δ 8.06 (d, J = 8.6 Hz, 2H), 7.20 (d, J = 8.6 Hz, 2H), 5.69 (qt, J = 7.2, 2.2 Hz, 1H), 5.01 (d quint, J = 22.8, 2.2 Hz, 1H), 4.26 (d quint, J = 22.8, 2.2 Hz, 1H), 3.93 (d, J = 13.9 Hz, 1H), 3.57 (d, J = 13.9 Hz, 1H), 3.78 (s, 3H), 1.80 (dt, J = 7.2, 2.2 Hz, 3H); IR (KBr) 1729, 1606, 1520, 1346, 1253 cm^{-1}. Anal. Calcd for $C_{14}H_{15}N_3O_4$: C, 58.12; H, 5.23; N, 14.53. Found: C, 58.26; H, 5.26; N, 14.42.

(*Z*)-3-Methoxycarbonyl-3-(*p*-nitrobenzyl)-4-benzylidene-1-pyrazoline (14c). This was obtained quantitatively from the reaction of **12c** with diazomethane: colorless crystals; mp 89.2 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.95 (d, J = 8.6 Hz, 2H), 7.48−7.34 (m, 3H), 7.20 (d, J = 6.9 Hz, 2H), 6.89 (d, J = 8.6 Hz, 2H), 6.64 (t, J = 2.3 Hz, 1H), 5.33 and 4.77 (ABq d, J = 22.8, 2.3 Hz, 2H), 4.08 and 3.53 (ABq, J = 14.2 Hz, 2H), 3.77 (s, 3H); IR (KBr) 1736, 1603, 1595, 1514, 1345, 1245 cm^{-1}. Anal. Calcd for $C_{19}H_{17}N_{33}O_4$: C, 64.95; H, 4.88; N, 11.96. Found: C, 64.75; H, 4.88; N, 11.93.

(*Z*)-3-Methoxycarbonyl-4-(*p*-methoxybenzylidene)-3-(*p*-nitrobenzyl)-1-pyrazoline (14d). This was obtained quantitatively from the reaction of **12d** with diazomethane: colorless crystals; mp 69.7 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.95 (d, J = 8.6 Hz, 2H), 7.16 (d, J = 8.6 Hz, 2H), 6.97 (d, J = 8.6 Hz, 2H), 6.89 (d, J = 8.6 Hz, 2H), 6.56 (t, J = 2.3 Hz, 1H), 5.30 and 4.75 (ABq d, J = 23.1, 2.3 Hz, 2H), 4.08 and 3.59 (ABq, J = 14.2 Hz, 2H), 3.87 (s, 3H), 3.77 (s, 3H); IR (KBr) 1740, 1607, 1516, 1343, 1252 cm^{-1}. Anal. Calcd for $C_{20}H_{19}N_3O_5$: C, 62.98; H, 5.02; N, 11.02. Found: C, 62.87; H, 5.06; N, 10.95.

(*Z*)-4-(*p*-Chlorobenzylidene)-3-methoxycarbonyl-3-(*p*-nitrobenzyl)-1-pyrazoline (14e). This was obtained quantitatively from the reaction of **7e** with diazomethane: colorless crystals; mp 89.2 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.97 (d, J = 8.6 Hz, 2H), 7.43 (d, J = 8.6 Hz, 2H), 7.15 (d, J = 8.6 Hz, 2H), 6.91 (d, J = 8.6 Hz, 2H), 6.59 (t, J = 2.3 Hz, 1H), 5.32 and 4.75 (ABq d, J = 23.1, 2.3 Hz, 2H), 4.08 and 3.49 (ABq, J = 14.5 Hz, 2H), 3.77 (s, 3H); IR (KBr) 1743, 1604, 1516, 1348, 1236 cm^{-1}. Anal. Calcd for $C_{19}H_{16}N_3O_4Cl$: C, 59.15; H, 4.18; N, 10.89. Found: C, 59.22; H, 4.28; N, 10.80.

(*Z*)-3-Methoxycarbonyl-3-(*p*-nitrobenzyl)-4-(*p*-nitrobenzylidene)-1-pyrazoline (14f). This was obtained in 55% yield from the reaction of **12f** with 0.9 M amount of diazomethane: yellowish crystals; mp 100.5 °C dec; ^{1}H NMR ($CDCl_3$) δ 8.32 (d, J = 8.6 Hz, 2H), 7.99 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 8.6 Hz, 2H), 6.92 (d, J = 8.2 Hz, 2H), 6.72 (br s, 1H), 5.39 (dd, J = 23.1, 2.3 Hz, 2H), 4.80 (dd, J = 23.1, 2.0 Hz, 2H), 4.11 and 3.44 (ABq, J = 14.5 Hz, 2H), 3.79 (s, 3H); IR (KBr) 1743, 1595, 1516, 1347, 1247 cm^{-1}. Anal. Calcd for $C_{19}H_{16}N_4O_6$: C, 57.57; H, 4.07; N, 14.14. Found: C, 57.22; H, 4.04; N, 13.88.

3-Methoxycarbonyl-3-(*p*-nitrobenzyl)-4-diphenylmethylene-1-pyrazoline (14g). This was obtained quantitatively from the reaction of **12g** with diazomethane; colorless crystals; mp 125.5 °C dec; ^{1}H NMR ($CDCl_3$) δ 8.13 (d, J = 8.6 Hz, 2H), 7.44−7.25 (m, 8H), 7.17−7.13 (m, 2H), 6.94−6.70 (m, 2H), 5.05 and 4.53 (ABq, J = 23.4 Hz, 2H), 3.86 and 3.07 (ABq, J = 14.2 Hz, 2H), 3.78 (s, 3H); IR (KBr) 1741, 1605, 1520, 1491, 1351, 1252 cm^{-1}. Anal. Calcd for $C_{25}H_{21}N_3O_4$: C, 70.25; H, 4.95; N, 9.83. Found: C, 69.87; H, 5.01; N, 9.71.

5-*tert*-Butyl-4-(*p*-chlorobenzylidene)-3-methoxycarbonyl-3-(*p*-nitrobenzyl)-1-pyrazoline (14h). The 1:2 mixture of **14h(*Z*)** and **14h(*E*)** was obtained quantitatively from the reaction of **12e** with diazoneopentane and separated by fractional recrystallization.

(*Z*)-5-*tert*-Butyl-4-(*p*-chlorobenzylidene)-3-methoxycarbonyl-3-(*p*-nitrobenzyl)-1-pyrazoline (14h(*Z*)): colorless crystals; mp 139.5 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.99 (d, J = 8.6 Hz, 2H), 7.42 (d, J = 8.6 Hz, 2H), 7.23 (d, J = 8.6 Hz, 2H), 6.90 (d, J = 8.6 Hz, 2H), 6.71 (d, J = 2.3 Hz, 1H), 4.22 (d, J = 2.3 Hz, 1H), 3.96 and 3.19 (ABq, J = 13.9 Hz, 2H), 3.85 (s, 3H), 1.12 (s, 9H); IR (KBr) 1740, 1672, 1603, 1518, 1348, 1251 cm^{-1}. Anal. Calcd for $C_{23}H_{24}N_3O_4Cl$: C, 62.62; H, 5.47; N, 9.51. Found: C, 62.57; H, 5.43; N, 9.50.

(*Z*)-5-*tert*-Butyl-4-(*p*-chlorobenzylidene)-3-methoxycarbonyl-3-(*p*-nitrobenzyl)-1-pyrazoline (14h(*E*)): colorless crystals; mp 120.3 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.98 (d, J = 8.6 Hz, 2H), 7.41 (d, J = 8.6 Hz, 2H), 7.10 (d, J = 8.6 Hz, 2H), 7.09 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 2.3 Hz, 1H), 5.09 (d, J = 2.3 Hz, 1H), 4.09 and 3.21 (ABq, J = 14.2 Hz, 2H), 3.73 (s, 3H), 0.99 (s, 9H); IR (KBr) 1734, 1604, 1517, 1346, 1236 cm^{-1}. Anal. Calcd for $C_{23}H_{24}N_3O_4Cl$: C, 62.62; H, 5.47; N, 9.51. Found: C, 62.42; H, 5.53; N, 9.38.

4-(*p*-Chlorobenzylidene)-3-methoxycarbonyl-5-methyl-3-(*p*-nitrobenzyl)-1-pyrazoline (14i). A mixture of **14i-(*Z*)** and **14i(*E*)** in a ratio of 2:1 was obtained quantitatively from the reaction of **12e** with diazoethane. The product **14i-(*Z*)** was separated by fractional recrystallization and HPLC. But, **14i(*E*)** could not be separated in a pure state.

(*Z*)-4-(*p*-Chlorobenzylidene)-3-methoxycarbonyl-5-methyl-3-(*p*-nitrobenzyl)-1-pyrazoline 14i(*Z*): colorless crystals; mp 113.4 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.97 (d, J = 8.6 Hz, 2H), 7.42 (d, J = 8.6 Hz, 2H), 7.16 (d, J = 8.6 Hz, 2H), 6.93 (d, J = 8.6 Hz, 2H), 6.47 (d, J = 2.3 Hz, 1H), 4.49 (qd, J = 7.3, 2.3 Hz, 1H), 4.01 and 3.44 (ABq, J = 14.2 Hz, 2H), 3.78 (s, 3H), 1.57 (d, J = 7.3 Hz, 3H); IR (KBr) 1743, 1735, 1606, 1524, 1489, 1351, 1253 cm^{-1}. Anal. Calcd for $C_{20}H_{18}N_3O_4Cl$: C, 60.08; H, 4.54; N, 10.51. Found: C, 60.19; H, 4.61; N, 10.51.

(*E*)-4-(*p*-Chlorobenzylidene)-3-methoxycarbonyl-5-methyl-3-(*p*-nitrobenzyl)-1-pyrazoline 14i(*E*): ^{1}H NMR ($CDCl_3$) δ 7.96 (d, J = 8.9 Hz, 2H), 7.44 (d, J = 8.6 Hz, 2H), 7.43 (d, J = 8.9 Hz, 2H), 6.82 (d, J = 8.6 Hz, 2H), 6.41 (d, J = 2.3 Hz, 1H), 5.31 (qd, J = 7.6, 2.3 Hz, 1H), 4.14 and 3.42 (ABq, J = 14.2 Hz, 2H), 3.83 (s, 3H), 0.96 (d, J = 7.6 Hz, 3H).

(*Z*)-4-(*p*-Chlorobenzylidene)-3-methoxycarbonyl-5,5-dimethyl-3-(*p*-nitrobenzyl)-1-pyrazoline (14j). This was obtained quantitatively from the reaction of **12e** with 2-diazopropane: colorless crystals; mp 140.8 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.97 (d, J = 8.6 Hz, 2H), 7.44 (d, J = 8.6 Hz, 2H), 7.16 (d, J = 8.6 Hz, 2H), 6.86 (d, J = 8.6 Hz, 2H), 6.34 (s, 1H), 4.10 and 3.38 (ABq, J = 13.9 Hz, 2H), 3.85 (s, 3H), 1.52 (s, 3H), 0.63 (s, 3H); IR (KBr) 1731, 1604, 1517, 1346, 1244 cm^{-1}. Anal. Calcd for $C_{21}H_{20}N_3O_4Cl$: C, 60.94; H, 4.87; N, 10.15. Found: C, 60.89; H, 4.88; N, 10.08.

Thermal Decomposition of 14a. The solution of pyrazoline **14a** (2 mmol) in 10 mL of benzene was refluxed for 16 h. The reaction mixture was concentrated under reduced pressure. The ^{1}H NMR spectrum of the residue showed the nearly quantitative formation of methylenecyclopropane **15**. The product was recrystallized from CH_2Cl_2/ether/pentane.

[1-Methoxycarbonyl-2-(*p*-nitrophenyl)ethylidene]cyclopropane (15): colorless needles; mp 74.8−75.0 °C; ^{1}H NMR ($CDCl_3$) δ 8.12 (d, J = 8.6 Hz, 2H), 7.38 (d, J = 8.6 Hz, 2H), 3.86 (br s, 2H), 3.73 (s, 3H), 1.51 (br dd, J = 9.9, 7.9 Hz, 2H), 1.18 (br dd, J = 9.9, 7.9 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 166.9 (s), 147.9 (s), 146.5 (s), 141.1 (s), 129.6 (d), 123.5 (d), 120.3 (s), 51.8 (q), 37.3 (t), 5.8 (t), 2.8 (t); IR (KBr) 1758, 1708,1603, 1596, 1514, 1345 cm^{-1}. Anal. Calcd for $C_{13}H_{13}NO_4$: C, 63.15; H, 5.30; N, 5.67. Found: C, 63.17; H, 5.37; N, 5.71.

Thermal Decomposition of 14b. The solution of pyrazoline **14b** (2 mmol) in 10 mL of benzene was refluxed for 4 h. The reaction mixture was concentrated under reduced pressure. The ^{1}H NMR spectrum of the residue showed a mixture of **17b** and **18b** in a ratio of 2:1. The products was separated by HPLC and recrystallized from CH_2Cl_2/ether/pentane.

(*E*)-1-[1-Methoxycarbonyl-2-(*p*-nitrophenyl)ethylidene]-2-methylcyclopropane (17b): colorless crystals; mp 53.7−53.9 °C; ^{1}H NMR ($CDCl_3$) δ 8.13 (d, J = 8.6 Hz, 2H), 7.38 (d, J = 8.6 Hz, 2H), 3.87 and 3.80 (ABq, J = 15.17 Hz, 2H), 3.72 (s, 3H), 1.64 (t, J = 9.9 Hz, 1H), 1.60−1.49 (m, 1H), 1.25−1.10 (m, 1H), 1.09 (d, J = 5.8 Hz, 3H); IR (KBr) 1753, 1706, 1603, 1594, 1516, 1346 cm^{-1}. Anal. Calcd for $C_{14}H_{15}NO_4$: C, 64.36; H, 5.79; N, 5.36. Found: C, 64.16; H, 5.77; N, 5.36.

(*Z*)-1-[1-Methoxycarbonyl-2-(*p*-nitrophenyl)ethylidene]-2-methylcyclopropane (18b): white powder; mp 50.0−51.0 °C; ^{1}H NMR ($CDCl_3$) δ 8.13 (d, J = 8.6 Hz, 2H), 7.37 (d, J = 8.6 Hz, 2H), 3.83 (s, 2H), 3.74 (s, 3H), 1.86−1.73 (m, 1H), 1.34 (t, J = 10.0 Hz, 1H), 1.21 (d, J = 6.3, 3H), 0.81 (dd, J = 10.0, 6.6 Hz, 1H); NOE of the signals at δ 1.21 and 1.34 was observed on the irradiation of the signals at δ 1.80 or 0.81; IR (KBr) 1750, 1706, 1603, 1595, 1516, 1342, 700 cm^{-1}. Anal. Calcd for $C_{14}H_{15}NO_4$: C, 64.36; H, 5.79; N, 5.36. Found: C, 64.27; H, 5.82; N, 5.37.

Thermal Decomposition of 14c. The solution of pyrazoline **14c** (2 mmol) in 10 mL of benzene was refluxed for 1 h. The reaction mixture was concentrated under reduced pressure. The ^{1}H NMR spectrum of the residue showed a mixture of the methylenecyclopropanes **17c** and **18c** in a ratio of 5:1 and small amount of the furan **19c**. The residue was separated by medium-pressure liquid chromatography (MPLC) and HPLC. **17c** was recrystallized from CH_2Cl_2/ether/pentane. **18c** could not be separated in a pure state.

(*E*)-1-[1-Methoxycarbonyl-2-(*p*-nitrophenyl)ethylidene]-2-phenylcyclopropane (17c): colorless crystals; mp 67.6−68.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.93 (d, J = 8.6 Hz, 2H), 7.26−7.15 (m, 3H), 7.13 (d, J = 8.6 Hz, 2H), 6.92 (dd, J = 7.5, 2.0 Hz, 2H), 3.79 (s, 3H), 3.82 and 3.72 (br ABq, J = 14.8 Hz, 2H), 2.65 (dd, J = 10.2, 6.5 Hz, 1H), 2.12 (tt, J = 10.7,1.4 Hz, 1H), 1.70 (ddt, J = 11.2, 6.5, 1.4 Hz, 1H); NOE of the signals at δ 1.70 was observed on the irradiation of the signals at δ 2.12 and NOE of the signals at δ 2.12 was observed on the irradiation of the signals at δ 2.65; IR (KBr) 1757, 1707, 1601, 1512, 1347 cm^{-1}. Anal. Calcd for $C_{19}H_{17}NO_4$: C, 70.58; H, 5.30; N, 4.33. Found: C, 70.52; H, 5.33; N, 4.35.

(*Z*)-1-[1-Methoxycarbonyl-2-(*p*-nitrophenyl)ethylidene]-2-phenylcyclopropane (18c): ^{1}H NMR ($CDCl_3$) δ 8.16 (d, J = 8.9 Hz, 2H), 7.43 (d, J = 8.9 Hz, 2H), 7.25−7.05 (m, 5H), 3.93 (s, 2H), 3.57 (s, 3H), 2.97 (dd, J = 10.2, 6.3 Hz, 1H), 1.78 (t, J = 10.2 Hz, 1H), 1.36 (dd, J = 10.2, 6.3 Hz, 1H).

2-Methoxy-4-methyl-3-(*p*-nitrobenzyl)-5-phenylfuran (19c): ^{1}H NMR ($CDCl_3$) δ 8.13 (d, J = 8.9 Hz, 2H), 7.52 (dd, J = 8.2, 1.3 Hz, 2H), 7.40−7.32 (m, 4H), 7.20 (t, J = 7.3 Hz, 1H), 3.97 (s, 3H), 3.76 (s, 2H), 2.04 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 156.2 (s), 148.6 (s), 146.4 (s), 139.5 (s), 131.6 (s), 128.9 (d), 128.5 (d), 128.3 (d), 124.6 (d), 123.7 (d), 117.8 (s), 98.3 (s), 58.9 (q), 28.1 (t), 10.4 (q).

Thermal Decomposition of 14d. The solution of pyrazoline **14d** (2 mmol) in 10 mL of benzene was heated at 45 °C for 2 h. The reaction mixture was concentrated under reduced pressure. The NMR spectrum of the residue showed a mixture of methylenecyclopropane **17d**, **18d** and furan **19d** in a ratio of 10:1:1. The methylenecyclopropanes **17d** and **19d** were isolated by MPLC and fractional recrystallization. Since isomerization of **18d** to **19d** occurred on handling, **18d** could not be isolated in a pure state.

(*E*)-1-[1-Methoxycarbonyl-2-(*p*-nitrophenyl)ethylidene]-2-(*p*-methoxyphenyl)cyclopropane (17d): colorless crystals; mp 78.9−79.3 °C; ^{1}H NMR ($CDCl_3$) δ 7.95 (d, J = 8.6 Hz, 2H), 7.15 (d, J = 8.6 Hz, 2H), 6.84 (d, J = 8.6 Hz, 2H), 6.76 (d, J = 8.6 Hz, 2H), 3.83 and 3.73 (br ABq, J = 15.5 Hz, 2H), 3.78 (s, 6H), 2.60 (dd, J = 0.6, 6.6 Hz, 1H), 2.07 (br t, J = 10.7 Hz, 1H), 1.62 (br dd, J = 10.9, 6.6 Hz, 1H); IR (KBr) 1756, 1708, 1605, 1596, 1511, 1347, 1297, 1249 cm^{-1}. Anal. Calcd for $C_{20}H_{19}NO_5$: C, 67.98; H, 5.42; N, 3.96. Found: C, 67.93; H, 5.42; N, 4.01.

^{1}H NMR of **18d**: δ 1.30 (dd, J = 10.2, 6.3 Hz, 1H), 1.75 (t, J = 10.2 Hz, 1H), 2.94 (dd, J = 10.2 Hz, 1H), 3.60 (s, 3 H), 3.92 (br s, 2H). All the other peaks are obscured by those of **17d** and **19d**.

2-Methoxy-4-methyl-3-(*p*-nitrobenzyl)-5-(*p*-methoxyphenyl)furan (19d): orange needles; mp 115.0−117.0 °C; ^{1}H NMR ($CDCl_3$) δ 8.14 (d, J = 8.9 Hz, 2H), 7.45 (d, J = 8.9 Hz, 2H), 7.38 (d, J = 8.9 Hz, 2H), 6.93 (d, J = 8.9 Hz, 2H), 3.95 (s, 3H), 3.83 (s, 3H), 3.76 (s, 2H), 2.00 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 158.04 (s), 155.76 (s), 148.75 (s), 139.68 (s), 128.94 (d), 126.27 (d), 124.51 (s), 123.67 (d), 115.90 (s), 114.03 (d), 98.19 (s), 59.13 (q), 55.30 (q), 28.16 (t), 10.20 (q); IR (KBr) 1642, 1587, 1520, 1508, 1339, 1251 cm^{-1}. Anal. Calcd for $C_{20}H_{19}NO_5$: C, 67.98; H, 5.42; N, 3.96. Found: C, 67.98; H, 5.42; N, 3.96.

Thermal Decomposition of 14e. The solution of pyrazoline **14e** (2 mmol) in 10 mL of benzene was refluxed for 1 h. The reaction mixture was concentrated under reduced pressure. The ^{1}H NMR spectrum of the residue showed a mixture of **17e** and **18e** in a ratio of 5:1. The residue was separated by MPLC and fractional recrystallization.

(*E*)-2-*p*-Chlorophenyl-1-[1-methoxycarbonyl-2-(*p*-nitrophenyl)ethylidene]cyclopropane (17e): colorless needles;

mp 77.2−78.3 °C; ^{1}H NMR ($CDCl_3$) δ 7.98 (d, J = 8.6 Hz, 2H), 7.20 (d, J = 8.6 Hz, 2H), 7.16 (d, J = 8.6 Hz, 2H), 6.85 (d, J = 8.6 Hz, 2H), 3.79 (s, 3H), 3.84 and 3.70 (br ABq, J = 15.2 Hz, 2H), 2.60 (dd, J = 10.1, 6.2 Hz, 1H), 2.13 (br t, J = 10.6 Hz, 1H), 1.65 (br dd, J = 11.2, 6.2 Hz, 1H); NOE of the signals at δ 3.84 and 3.70 as well as at δ 6.85 and 2.13 was observed on the irradiation of the signals at δ 2.60; ^{13}C NMR ($CDCl_3$) δ 166.84 (s), 146.77 (s), 146.43 (s), 143.48 (s), 138.25 (s), 132.13 (s), 129.70 (d), 128.60 (d) 127.16 (d), 123.32 (d), 121.29 (s), 5.09 (q), 36.94 (t), 19.80 (d), 16.80 (t); IR (KBr) 1758, 1708, 1602, 1515, 1490, 1346, 1306 cm^{-1}. Anal. Calcd for $C_{19}H_{16}NO_4Cl$: C, 63.78; H, 4.51; N, 3.92. Found: C, 63.85; H, 4.61; N, 3.97.

(*Z*)-2-*p*-Chlorophenyl-1-[1-methoxycarbonyl-2-(*p*-nitrophenyl)ethylidene]cyclopropane (18e): colorless plates; mp 68 °C; ^{1}H NMR ($CDCl_3$) δ 8.16 (d, J = 8.6 Hz, 2H), 7.42 (d, J = 8.6 Hz, 2H), 7.23 (d, J = 8.6 Hz, 2H), 6.99 (d, J = 8.6 Hz, 2H), 3.93 (s, 2H), 3.59 (s, 3H), 2.93 (dd, J = 10.4, 6.5 Hz, 1H), 1.79 (t, J = 10.4 Hz, 1H), 1.32 (dd, J = 10.5, 6.5 Hz, 1H); NOE of the signals at δ 6.99 and 1.79 was observed on the irradiation of the signals at δ 2.93; IR (KBr) 1764, 1701, 1604, 1596, 1512, 1491 cm^{-1}. Anal. Calcd for $C_{19}H_{16}NO_4Cl$: C, 63.78; H, 4.51; N, 3.92. Found: C, 63.79; H, 4.57; N, 4.05.

Thermal Decomposition of 14f. The solution of pyrazoline **14f** (2 mmol) in 10 mL of benzene was refluxed for 2 h. The reaction mixture was concentrated under reduced pressure. The ^{1}H NMR spectrum of the residue showed a mixture of **17f** and **18f** in a ratio of 6:1. The residue was separated by MPLC and fractional recrystallization.

(*E*)-1-[1-Methoxycarbonyl-2-(*p*-nitrophenyl)ethylidene]-2-*p*-nitrophenylcyclopropane (17f): yellowish crystals; mp 131−132 °C; ^{1}H NMR ($CDCl_3$) δ 8.09 (d, J = 8.6 Hz, 2H), 7.98 (d, J = 8.6 Hz, 2H), 7.17 (d, J = 8.6 Hz, 2H), 7.05 (d, J = 8.6 Hz, 2H), 3.87 and 3.68 (ABq, J = 15.2 Hz, 2H), 3.82 (s, 3H), 2.70 (dd, J = 9.9, 5.9 Hz, 1H), 2.27 (t, J = 10.7 Hz, 1H), 1.77 (dd, J = 11.2, 5.9 Hz, 1H); IR (KBr) 1758, 1702, 1657, 1598, 1513, 1348, 1276 cm^{-1}. Anal. Calcd for $C_{19}H_{16}N_2O_6$: C, 61.96; H, 4.38; N, 7.61. Found: C, 61.69; H, 4.42; N, 7.58.

(*Z*)-1-[1-Methoxycarbonyl-2-(*p*-nitrophenyl)ethylidene]-2-*p*-nitrophenylcyclopropane (18f): ^{1}H NMR ($CDCl_3$) δ 8.18 (d, J = 8.6 Hz, 2H), 8.14 (d, J = 8.6 Hz, 2H), 7.43 (d, J = 8.6 Hz, 2H), 7.18 (d, J = 8.6 Hz, 2H), 3.95 (s, 2H), 3.57 (s, 3H), 3.03 (dd, J = 10.2, 6.3 Hz, 1H), 1.93 (t, J = 10.4 Hz, 1H), 1.44 (dd, J = 10.9, 6.3 Hz, 1H).

Thermal Decomposition of 14g. The solution of pyrazoline **14g** (1 mmol) in 10 mL of benzene was refluxed for 2 h. The reaction mixture was concentrated under reduced pressure. The ^{1}H NMR spectrum of the residue showed a mixture of **17g** and **18g** in a ratio of 10:1 and small amount of **20**. The residue was separated by MPLC and fractional recrystallization. **18g** could not be isolated in a pure state.

(*E*)-1-[1-Methoxycarbonyl-2-(*p*-nitrophenyl]ethylidene]-2,2-diphenylcyclopropane (17g): colorless crystals; mp 107.5−108.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.92 (d, J = 8.6 Hz, 2H), 7.1−7.4 (m, 10H), 6.98 (d, J = 8.6 Hz, 2H), 3.98 (s, 2H), 3.72 (s, 3H), 2.38 (s, 2H); IR (KBr) 1702, 1598, 1519, 1345, 1309 cm^{-1}. Anal. Calcd for $C_{25}H_{21}NO_4$: C, 75.17; H, 5.30; N, 3.51. Found: C, 75.47; H, 5.42; N, 3.35.

(*Z*)-1-[1-Methoxycarbonyl-2-(*p*-nitrophenyl)ethylidene]-2,2-diphenylcyclopropane (18g): ^{1}H NMR ($CDCl_3$) δ 8.14 (d, J = 8.6 Hz, 2H), 7.15−7.40 (m, 12H), 3.94 (s, 2H), 3.67 (s, 3H), 1.95 (s, 2H).

3-Methyl-2-(*p*-nitrobenzyl)-4,4-diphenyl-2-buten-4-olide (20): colorless crystals; mp 133.8−134.2 °C; ^{1}H NMR ($CDCl_3$) δ 8.16 (d, J = 8.6 Hz, 2H), 7.2−7.4 (m, 12H), 3.80 (s, 2H), 2.04 (s, 3H); IR (KBr) 1746, 1706, 1598, 1510, 1345 cm^{-1}. Anal. Calcd for $C_{24}H_{19}NO_4$: C, 74.79; H, 4.97; N, 3.63. Found: C, 74.29; H, 5.11; N, 3.66.

Thermal Decomposition of 14h(*E*). The solution of **14h(*E*)** (0.5 mmol) in 5 mL of benzene was refluxed for 18 h. The reaction mixture was concentrated under reduced pressure. ^{1}H NMR spectrum of reaction mixture showed nearly quantitative formation of **21** and a trace amount of **22**. The methylenecyclopropane **21** was isolated in a 95% yield.

(*E*)-*t*-3-*tert*-Butyl-*r*-2-*p*-chlorophenyl-1-[1-methoxycarbonyl-2-(*p*-nitrophenyl)ethylidene]cyclopropane (21): colorless oil; ^{1}H NMR ($CDCl_3$) δ 8.02 (d, J = 8.6 Hz, 2H), 7.20 (d, J = 8.6 Hz, 2H), 7.18 (d, J = 8.6 Hz, 2H), 6.98 (d, J = 8.6 Hz, 2H), 3.86 and 3.64 (ABq, J = 14.5 Hz, 2H), 3.77 (s, 3H), 3.30 (d, J = 6.3 Hz, 1H), 1.89 (d, J = 6.3 Hz, 1H), 1.00 (s, 9H). Anal. Calcd for $C_{22}H_{24}NO_4Cl$: C, 65.75; H, 46.02; N, 3.49. Found: C, 65.60; H, 5.74; N, 3.30.

(*Z*)-*c*-3-*tert*-butyl-*r*-2-(*p*-chlorophenyl)-1-[1-methoxycarbonyl-2-(*p*-nitrophenyl)ethylidene]cyclopropane (22): ^{1}H NMR ($CDCl_3$) δ 8.02 (d, J = 8.6 Hz, 2H), 7.20 (d, J = 8.6 Hz, 2H), 7.18 (d, J = 8.6 Hz, 2H), 6.98 (d, J = 8.6 Hz, 2H), 3.96 and 3.83 (ABq, J = 14.5 Hz, 2H), 3.60 (s, 3H), 3.12 (d, J = 11.7 Hz, 1H), 2.01 (d, J = 11.7 Hz, 1H), 0.83 (s, 9H).

Thermal Decomposition of 14h(*Z*). The solution of **14h(*Z*)** (0.5 mmol) in 5 mL of benzene was refluxed for 30 h. The reaction mixture was concentrated under reduced pressure. The NMR spectrum of the residue showed a mixture of **23** (47%), **24** (32%), **25** (8%) and many other isomers. These isomeric methylene cyclopropanes could not be separated in a pure state.

(*Z*)-*t*-3-*tert*-butyl-*r*-2-(*p*-chlorophenyl)-1-[1-methoxycarbonyl-2-(*p*-nitrophenyl)ethylidene]cyclopropane (23): ^{1}H NMR ($CDCl_3$) δ 8.16 (d, J = 8.6 Hz, 2H), 7.42 (d, J = 8.6 Hz, 2H), 7.21 (d, J = 8.6 Hz, 2H), 6.95 (d, J = 8.6 Hz, 2H), 3.99 and 3.93 (ABq, J = 14.9 Hz, 2H), 3.54 (s, 3H), 2.75 (d, J = 6.6 Hz, 1H), 1.70 (d, J = 6.6 Hz, 1H), 1.03 (s, 9H).

(*Z*)-*c*-3-*tert*-Butyl-*r*-1-methoxycarbonyl-1-(*p*-nitrobenzyl)-2-(*p*-chlorobenzylidene)cyclopropane (24): ^{1}H NMR ($CDCl_3$) δ 7.97 (d, J = 8.6 Hz, 2H), 7.25 (d, J = 8.6 Hz, 2H), 7.17 (d, J = 8.6 Hz, 2H), 7.16 (d, J = 8.6 Hz, 2H), 6.71 (d, J = 2.3 Hz, 1H), 3.69 (s, 3 H), 3.56 (d, J = 13.5 Hz, 1H), 3.03 (d, J = 13.5 Hz, 1H), 1.55(d, J = 2.3, 1H), 0.96 (s, 9H).

(*Z*)-*t*-3-*tert*-Butyl-*r*-1-(methoxycarbonyl)-1-*p*-nitrobenzyl-2-*p*-chlorobenzylidenecyclopropane (25): ^{1}H NMR ($CDCl_3$) δ 7.97 (d, J = 8.6 Hz, 2H), 7.28 (d, J = 8.6 Hz, 2H), 7.14 (d, J = 8.3 Hz, 2H), 7.02 (d, J = 8.3 Hz, 2H), 6.71 (d, J = 2.6 Hz, 1H), 3.75 (s, 3H), 3.69 (d, J = 16.2 Hz, 1H), 3.23 (d, J = 16.2 Hz, 1H), 2.57 (d, J = 2.6 Hz, 1H), 1.10 (s, 9H).

Thermal Decomposition of 14i(*Z*) and 14i(*E*). The thermolysis of **14i(*Z*)** at 80 °C for 2 h gave a complex mixture of many types of methylenecyclopropanes. The mixture could not be separated in a pure state even by MPLC.

(*Z*)-2-[*trans*-2-(*p*-Chlorophenyl)-3-methylcyclopropylidene]-3-(*p*-nitrophenyl)propionic acid methyl ester (26): ^{1}H NMR ($CDCl_3$) δ 8.17 (d, J = 8.6 Hz, 2H), 7.43 (d, J = 8.6 Hz, 2H), 7.22 (d, J = 8.6 Hz, 2H), 6.95 (d, J = 8.6 Hz, 2H), 3.91 (br s, 2H), 3.57 (s, 3 H), 2.53 (d, J = 5.9 Hz, 1H), 1.61 (quint, J = 6.1 Hz, 1H), 1.23 (d, J = 6.3 Hz, 1H).

(*Z*)-*c*-3-Methyl-*r*-1-methoxycarbonyl-1-(*p*-nitrobenzyl)-2-(*p*-chlorobenzylidene)cyclopropane (27): ^{1}H NMR ($CDCl_3$) δ 7.98 (d, J = 8.6 Hz, 2 H), 7.22 (d, J = 8.6 Hz, 2H), 7.19 (d, J = 8.6 Hz, 2H), 7.11 (d, J = 8.6 Hz, 2H), 6.71 (d, J = 2.3 Hz, 1H), 3.72 (s, 3H), 3.38 (d, J = 14.5 Hz, 1H), 3.24 (d, J = 14.5 Hz, 1H), 1.78 (qd, J = 6.6, 2.3 Hz, 1H), 1.33 (d, J = 6.6 Hz, 3H).

(*E*)-2-[*cis*-2-(*p*-Chlorophenyl)-3-methylcyclopropylidene]-3-(*p*-nitrophenyl)propionic acid methyl ester (28): ^{1}H NMR ($CDCl_3$) δ 8.05 (d, J = 8.9 Hz, 3H), 7.30 (d, J = 8.9 Hz, 2H), 7.24 (d, J = 8.6 Hz, 2H), 6.94 (d, J = 8.6 Hz, 2H), 3.97 (d, J = 14.5 Hz, 1H), 3.79 (s, 3 H), 3.70 (d, J = 14.5 Hz, 1H), 2.56 (d, J = 10.9 Hz, 1H), 2.28 (m, 1H), 0.99 (d, J = 6.6 Hz, 3H).

(*E*)-*t*-3-Methyl-*r*-1-methoxycarbonyl-1-(*p*-nitrobenzyl)-2-(*p*-chlorobenzylidene)cyclopropane (29): ^{1}H NMR ($CDCl_3$) δ 8.07 (d, J = 8.6 Hz, 2H), 7.36 (d, J = 8.6 Hz, 2H), 7.24 (d, J = 8.6 Hz, 2H), 7.14 (d, J = 8.6 Hz, 2H), 6.73 (d, J = 2.3 Hz, 1H), 3.67 (s, 3H), 3.66 (d, J = 16.5 Hz, 1H), 2.86 (d, J = 16.5 Hz, 1H), 2.70 (qd, J = 6.6, 2.3 Hz, 1H), 1.26 (d, J = 6.6 Hz, 3H).

(*E*)-*c*-3-(*p*-Chlorophenyl)-2-(1-ethylidene)-*r*-1-methoxycarbonyl-1-(*p*-nitrophenyl)cyclopropane (30): ^{1}H NMR ($CDCl_3$) δ 8.07 (d, J = 8.6 Hz, 2H), 7.31 (d, J = 8.6 Hz, 2H), 7.23 (d, J = 8.6 Hz, 2H), 7.13 (d, J = 8.6 Hz, 2H), 6.01 (qd, J = 6.6, 2.3 Hz, 1H), 3.67 (s, 3H), 3.59 (t, J = 2.0 Hz, 1H), 3.11 (d, J = 15.2 Hz, 1H), 2.38 (d, J = 15.2 Hz, 1H), 1.95 (dd, J = 6.6, 2.3 Hz, 3H).

(*Z*)-2-[*cis*-2-(*p*-Chlorophenyl)-3-methylcyclopropylidene]-3-(*p*-nitrophenyl)propionic acid methyl ester (31): ^{1}H NMR ($CDCl_3$) δ 8.17 (d, J = 8.6 Hz, 2H), 7.43 (d, J = 8.6 Hz, 2H), 7.23 (d, J = 8.6 Hz, 2H), 7.02 (d, J = 8.6 Hz, 2H), 3.91 (br s, 2H), 3.61 (s, 3H), 3.14 (br d, J = 10.9 Hz, 1H), 1.70 (dq, J = 10.9, 2.3 Hz, 1H), 0.78 (d, J = 6.6 Hz, 3H).

(*E*)-2-[*trans*-2-(*p*-Chlorophenyl)-3-methylcyclopropylidene]-3-(*p*-nitrophenyl)propionic acid methyl ester (32): ^{1}H NMR ($CDCl_3$) δ 7.97 (d, J = 8.6 Hz, 2H), 7.17 (d, J = 8.6 Hz, 2H), 7.18 (d, J = 8.6 Hz, 2H), 6.81 (d, J = 8.6 Hz, 2H), 3.80 (s, 3H), 3.81 (d, J = 14.9 Hz, 1H), 3.69 (d, J = 14.9 Hz, 1H), 2.18 (d, J = 5.6 Hz, 1H), 1.87 (qd, J = 6.3, 5.6 Hz, 1H), 1.36 (d, J = 6.3 Hz, 3H).

(*E*)-*c*-3-Methyl-*r*-1-methoxycarbonyl-1-(*p*-nitrobenzyl)-2-(*p*-chlorobenzylidene)cyclopropane (33): ^{1}H NMR ($CDCl_3$) δ 8.16 (d, J = 8.6 Hz, 2H), 7.43 (d, J = 8.6 Hz, 2H), 7.34 (s, 4H), 6.69 (d, J = 2.3 Hz, 1H), 3.76 (d, J = 14.6 Hz, 1H), 3.64 (s, 3H), 2.70 (d, J = 14.6 Hz, 1H), 2.07 (qd, J = 6.8, 2.3 Hz, 1H), 1.40 (d, J = 6.8 Hz, 3H).

Thermal Decomposition of 14j. The solution of pyrazoline **14j** (1 mmol) in 10 mL of toluene was refluxed for 4 h. The reaction mixture was concentrated under reduced pressure. The ^{1}H NMR spectrum of the residue showed a mixture of **34**, **35**, and **36** in yields of 34, 23, and 14% and with small amounts of other isomers. **34** and **35** were isolated by MPLC and fractional recrystallization.

(*E*)-3-(*p*-Chlorophenyl)-2,2-dimethyl-1-[1-methoxycarbonyl-2-(*p*-nitrophenyl)ethylidene]cyclopropane (34): colorless crystals; mp 87.0−87.5 °C; ^{1}H NMR ($CDCl_3$) δ 8.17 (d, J = 8.6 Hz, 2H), 7.43 (d, J = 8.6 Hz, 2H), 7.24 (d, J = 8.3 Hz, 2H), 6.99 (d, J = 8.3 Hz, 2H), 3.93 and 3.86 (ABq, J = 14.9 Hz, 2H), 3.60 (s, 3H), 2.82 (s, 1H), 1.34 (s, 3H), 0.83 (s, 3H); IR (KBr) 1706, 1603, 1508, 1347, 1303 cm^{-1}. Anal. Calcd for $C_{21}H_{20}NO_4Cl$: C, 65.37; H, 5.23; N, 3.63. Found: C, 65.42; H, 5.22; N, 3.70.

***c*-3-(*p*-Chlorophenyl)-2-isopropylidene-*r*-1-methoxycarbonyl-1-(*p*-nitrobenzyl)cyclopropane (35):** colorless crystals; mp 87.5−88.0 °C; ^{1}H NMR ($CDCl_3$) δ 8.15 (d, J = 8.9 Hz, 2H), 7.42 (d, J = 8.9 Hz, 2H) 7.22 (d, J = 8.6 Hz, 2H), 7.08 (d, J = 8.6 Hz, 2H), 3.78 and 2.88 (ABq, J = 13.6 Hz, 2H), 3.26 (s, 3H), 2.95 (br s, 1H), 1.93 (d, J = 1.7 Hz, 3H), 1.65 (d, J = 2.0 Hz, 3H); IR (KBr) 1713, 1520, 1490 1347, 1222 cm^{-1}. Anal. Calcd for $C_{21}H_{20}NO_4Cl$: C, 65.37; H, 5.23; N, 3.63. Found: C, 65.43; H, 5.23; N, 3.63.

***t*-3-(*p*-Chlorophenyl)-2-isopropylidene-*r*-1-methoxycarbonyl-1-(*p*-nitrobenzyl)cyclopropane (36):** ^{1}H NMR ($CDCl_3$) δ 3.70 (s, 3H), 3.58 (br s, 1H), 2.96 and 2.72 (ABq, J = 14.9 Hz, 2H), 1.92 (d, J = 1.7 Hz, 3H), 1.56 (d, J = 2.0 Hz, 3H). All other signals were obscured by those of other products.

Rate Measurements. Approximately 8 mL of a 2.5 mM toluene solution of 4-alkylidenepyrazoline and stilbene as internal standard was prepared. Sample was immersed in a thermostat. The decrease of 4-alkylidenepyrazoline was monitored by HPLC using 20%H_2O−80%CH_3OH. First-order rate constants were determined by standard least-squares methods. Correlation coefficients were greater than 0.9994 (Table 7).

TABLE 7. Rates for the Thermolysis of 4-Alkylidenepyrazolines 14a−g at Various Temperatures

14	R^1	R^2	T/°C	$10^5 k^a$/s^{-1}
a	H	H	80.0	12.0
			85.0	21.5
			90.0	37.5
b	CH_3	H	77.5	15.8
			80.0	20.8
			82.5	28.3
			85.0	36.8
c	Ph	H	50.0	17.2
			52.5	23.5
			55.0	31.2
			57.5	44.0
d	*p*-$CH_3OC_6H_4$	H	38.0	15.5
			40.0	21.0
			43.0	29.7
			45.0	36.8
e	*p*-ClC_6H_4	H	55.0	29.8
			60.0	55.0
			65.0	100.7
f	*p*-$NO_2C_6H_4$	H	50.0	8.0
			55.0	15.0
			57.5	19.8
			60.0	27.5
g	Ph	Ph	55.0	10.0
			60.0	21.2
			65.0	43.2

[a] The standard deviations in the values of k were less than 5%.

X-ray Crystal Structure Determination of 14a. Crystal data: $C_{13}H_{13}N_3O_4$, FW = 275.26, monoclinic, space group $P2_1/n$, a = 7.3658(5) Å, b = 13.203(1) Å, c = 13.713(2) Å, β = 94.722(6)°, V = 1329.0(2) Å^3, Z = 4, D_c = 1.376 g cm^{-3}, μ (Mo Kα) = 0.104 mm^{-1}, 200 K. Colorless crystals were grown from a benzene solution. Intensity data were measured on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo $K\alpha$ radiation. Of 14 033 reflections collected up to 2θ = 59.9°, 3819 independent reflections were used in calculation. Absorption effects were ignored. The structure was solved by direct methods (SHELXS86)[26] and refined on F^2 by full-matrix least-squares technique (SHELXL97)[27] with anisotropic thermal parameters for non-hydrogen atoms. All hydrogen atoms were placed on geometrically calculated positions and refined isotropically in riding models. The resulting $R1$, R, R_w and GOF values are 0.0556, 0.0940, 0.1549, and 1.084, respectively.

Supporting Information Available: A CIF file of **14a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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