# Stability and Stereochemistry in the Decomposition of Pentasubstituted 1-Pyrazolines Controlled by Interactions between Bulky Vicinal Substituents

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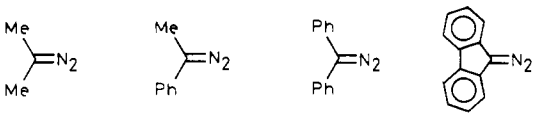
1,2-Diacyl-1-chloroethylenes were reacted with several disubstituted diazomethanes to give the pyrazolines and the cyclopropanes. The thermal decomposition of the isolated pyrazolines was carried out. The thermal stability of the pyrazolines increases with the variation of the substituents at C-5 in the order biphenylylene < Ph, Ph < Ph, Me < Me, Me, while pyrazolines bearing bulky vicinal substituents at C-3, C-4, and C-5 in the cis configuration are substantially more stable than other isomers. This abnormal stability is explained by the reasonable expectation that bulky C-4 substituents partly inhibit conformations of the conjugated substituents at C-3 or C-5 favorable for the decomposition, which increases the activation energy. Although most of the thermal transformations of the pyrazolines to the cyclopropanes retain the stereochemistry of the starting materials, some pyrazolines bearing bulky vicinal cis groups gave mixtures of stereoisomeric cyclopropanes. The mechanism for the thermolysis of these pyrazolines is explained on the basis of stereochemical distribution of decomposition products by (90,90) trimethylene intermediates.

## Introduction

Thermal decomposition of 1-pyrazolines, which has been known to give olefins and cyclopropanes, has been of interest from both synthetic and mechanistic points of view.[1-3] An explanation is required of how formation of the particular products (olefin and cyclopropane) is determined. It is likely that the formation of the olefins is determined by conformational factors.[4] However, the mechanism of cyclopropane formation is a complex problem because it must explain why some reactions giving cyclopropanes are highly stereospecific, others only partly so, and yet others not at all and some pyrazolines give olefins or cyclopropanes depending on the polarity of solvent used.[5] And so, many mechanisms have been proposed. Crawford et al. attributed the single inversion process observed in 3,5-dimethyl-1-pyrazoline to conrotatory ring closure of an intermediary planar "$\pi$-cyclopropane" diradical.[6] Allred et al. accounted for the double inversion process in 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH) by postulating that the $\alpha$-carbon atoms in it are forced to "recoil" into inverted configuration by the departing nitrogen atoms.[7] On the other hand, Roth and Martin suggested that decomposition of DBH proceeded by stepwise cleavage via diazenyl radical,[8] an idea that also explains some of pyrazolines.[9] Bergman et al. suggested from the thermal decomposition of optically active pyrazolines that the thermal decomposition of the pyrazoline proceeded by a "snapshot" mechanism,[10] where nitrogen was extruded in a nonlinear fashion.[11] Jean and Hiberty proposed competitive stepwise reaction paths from theoretical calculation, one via a trans and the other via a gauche diradical.[12]

We carried out the thermal decomposition of 3,3,4,5,5-pentasubstituted pyrazolines that were obtained by 1,3-dipolar cycloaddition of disubstituted diazomethanes (**1**, **2**, **3** and **4**) with 1-chloro-1,2-diacylethylene derivatives in order to obtain further information for pyrazoline decomposition. We report here directing effects of a chlorine substituent on regioselectivity in the 1,3-dipolar cycloaddition of diazoalkanes and steric interactions between vicinal bulky substituents governing the thermal stability of the 1-pyrazolines. We also consider the mechanism of decomposition of these pyrazolines.




1 2 3 4

## Results

**Reaction of Disubstituted Diazomethanes (1, 2, 3, and 4) with 1-Chloro-1,2-diacylethylenes (5, 6, 18, and 19).** Dimethyl chlorofumarate (**5**) rapidly reacted with 2-diazopropane (**1**) at 0 °C to give a pyrazoline in a high yield. An NMR spectrum of the product exhibits a methine singlet at $\delta$ 3.41, indicating that its structure is *trans*-3,4-bis(methoxycarbonyl)-3-chloro-5,5-dimethyl-1-pyrazoline (**7**), but not *trans*-3,4-bis(methoxycarbonyl)-4-chloro-5,5-dimethyl-1-pyrazoline. Reaction of dimethyl chloromaleate (**6**) with **1** at 0 °C gave the *cis*-pyrazoline **8** in high yield. Careful inspection of both NMR spectra of the reaction mixtures of **1** with **5** and **6** showed no existence of **8** and **7**, respectively. Reaction of chlorofumarate **5** with 1-phenyldiazoethane (**2**) gave the pyrazoline **9Z** and the chlorocyclopropane **10E** in yields of 63% and 25%, respectively, whereas chloromaleate **6** gave the two isomeric pyrazolines **11Z** and **11E** in yields of 57% and 26%, respectively. The pyrazolines **9Z**, **11Z**, and **11E** were

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(2) Machezie, K. Formation and Fragmentation of Cyclic Azo Compounds. In *The Chemistry of the Hydrazo, Azo and Azoxy Groups*, Part 1; Patai, S., Ed.; Wiley: New York, 1975; p 239.
(3) Engel, P. S. *Chem. Rev.* **1980**, *80*, 99.
(4) (a) McGreer, D. E.; Wu, W. S. *Can. J. Chem.* **1967**, *45*, 461. (b) McGreer, D. E.; Mckinly, J. W. *Ibid.* **1971**, *49*, 105. (c) McGreer, D. E.; Masters, I. M. E.; Liu, M. T. H. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1791.
(5) (a) Hamaguchi, M.; Nagai, T. *J. Chem. Soc., Chem. Commun.* **1987**, 1299. (b) Begley, M. T.; Dean, F. M.; Houghton, L. E.; Park, B. K. *Ibid.* **1978**, 461.
(6) Crawford, R. J.; Mishra, A. *J. Am. Chem. Soc.* **1966**, *88*, 3963.
(7) (a) Allred, E. L.; Smith, R. L. *J. Am. Chem. Soc.* **1967**, *89*, 7133. (b) Allred, E. L.; Smith, R. L. *Ibid.* **1969**, *91*, 6766.
(8) (a) Roth, W. R.; Martin, M. *Justus Liebigs Ann. Chem.* **1967**, *702*, 1. (b) Roth, W. R.; Martin, M. *Tetrahedron Lett.* **1967**, 4695.
(9) (a) Condit, P. B.; Bergman, R. G. *J. Chem. Soc., Chem. Commun.* **1971**, 4. (b) White, D. H.; Condit, P. B.; Bergman, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 1348. (c) White, D. H.; Condit, P. B.; Bergman, R. B. *Ibid.* **1972**, *94*, 7931.
(10) Clarke, T. C.; Wendling, L. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 2740.
(11) Inagaki, S.; Fukui, K. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 824.
(12) (a) Jean, Y.; Hiberty, P. C. *Bull. Soc. Chim. Belg.* **1976**, *85*, 1005. (b) Hiberty, P. C.; Jean, Y. *J. Am. Chem. Soc.* **1979**, *101*, 2538.

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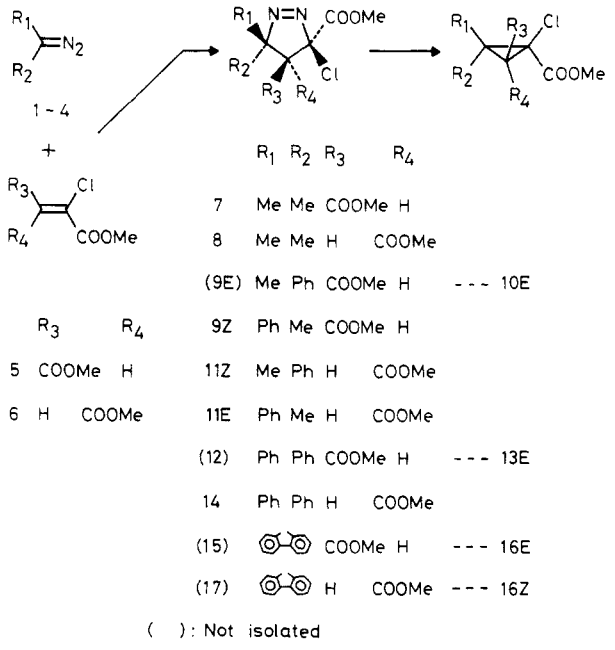
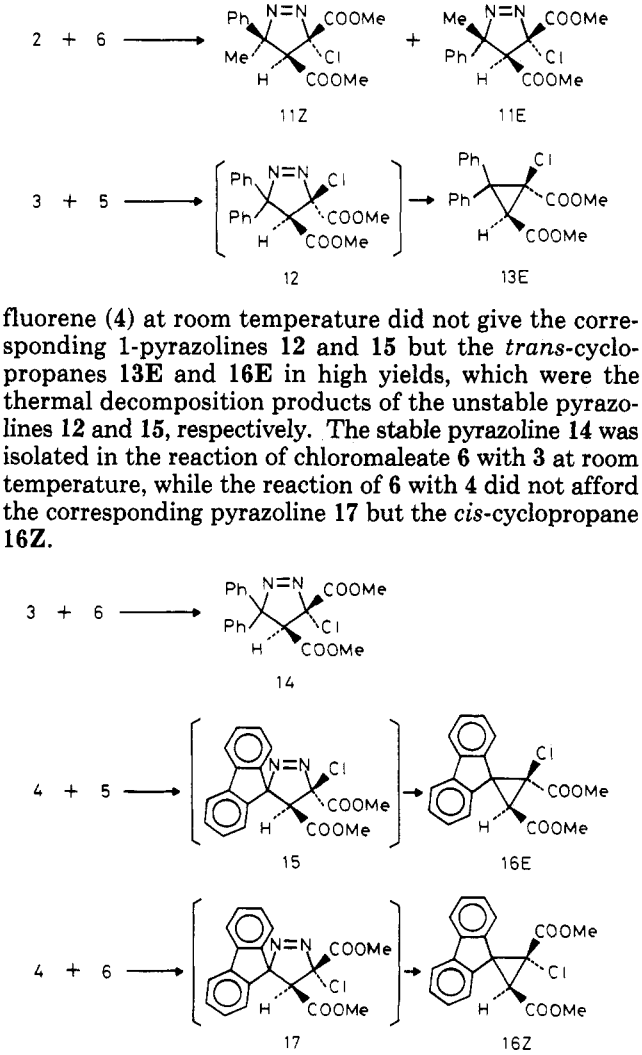
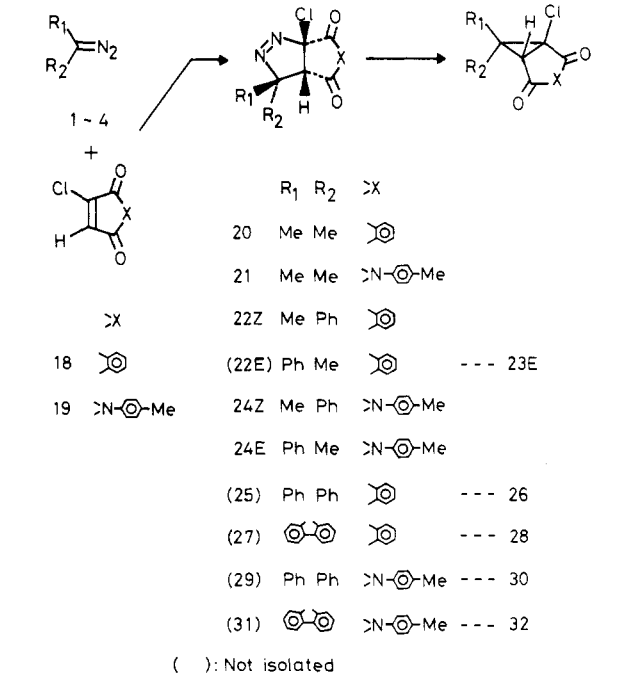
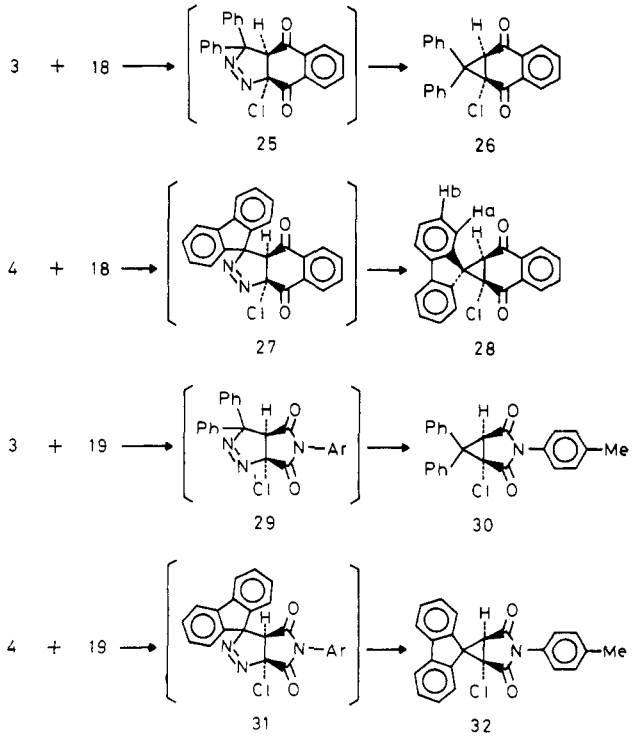



stable at room temperature. The reaction of chlorofumarate **5** with diphenyldiazomethane (**3**) and 9-diazofluorene (**4**) at room temperature did not give the corresponding 1-pyrazolines **12** and **15** but the *trans*-cyclopropanes **13E** and **16E** in high yields, which were the thermal decomposition products of the unstable pyrazolines **12** and **15**, respectively. The stable pyrazoline **14** was isolated in the reaction of chloromaleate **6** with **3** at room temperature, while the reaction of **6** with **4** did not afford the corresponding pyrazoline **17** but the *cis*-cyclopropane **16Z**.

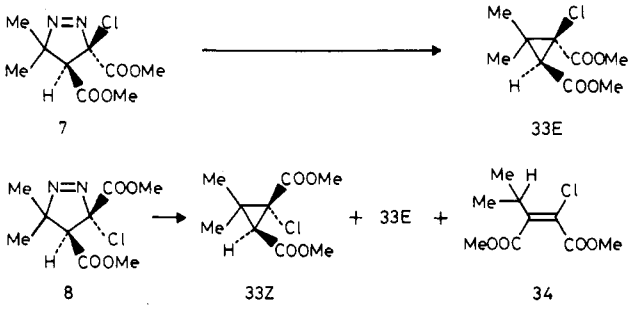



Next, 2-diazopropane (**1**) was reacted with chloronaphthoquinone (**18**) and *N*-tolylchloromaleimide (**19**) to give the pyrazolines **20** and **21** in high yields, respectively. The reaction of **18** with 1-phenyldiazoethane (**2**) gave the corresponding 1-pyrazoline **22Z** and the cyclopropane **23E** in 44% and 34% yields, respectively, whereas the chloromaleimide **19** with **2** gave the stable pyrazolines **24Z** and **24E** in yields of 37% and 48%, respectively. The reaction of **18** and **19** with diphenyldiazomethane (**3**) and 9-diazofluorene (**4**) did not yield stable pyrazolines but the cyclopropanes **26**, **28**, **30**, and **32**, respectively.

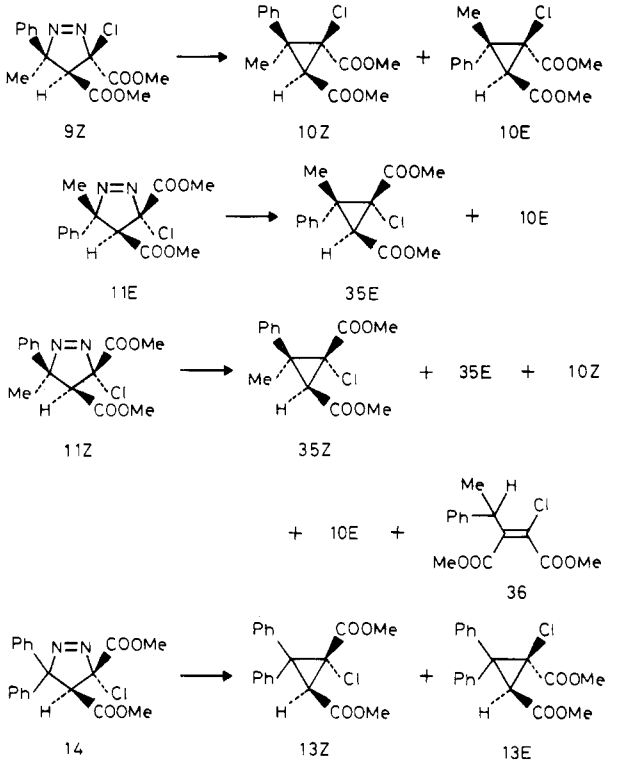


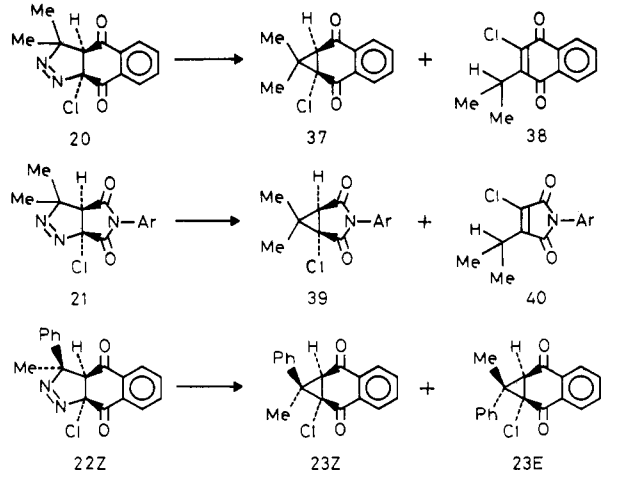

**Thermal Decomposition of Pyrazolines.** The thermal decomposition of the pyrazoline **7** in refluxing toluene gave a single cyclopropane (**33E**), while **8** gave two isomeric cyclopropanes **33Z** and **33E** along with a small amount of the olefin **34**. The pyrazoline **9Z** in refluxing benzene gave the cyclopropanes **10Z** and **10E** in yields of 72% and 21%, respectively. The pyrazoline **11E** in refluxing toluene gave



**35E** and **10E** in yields of 93% and 7%, respectively, and **11Z** gave four isomeric cyclopropanes **10Z**, **10E**, **35Z**, and **35E** and the olefin **36** in yields of 15%, 6%, 16%, 50%, and 4%, respectively. Decomposition of the pyrazoline

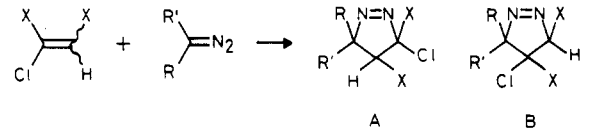


**14** in refluxing benzene gave the cyclopropanes **13E** and **13Z** in yields of 56% and 44%, respectively. In the case of **20** and **21**, the cyclopropanes **37** (81%) and **39** (54%) were obtained along with the olefins **38** (15%) and **40** (43%), respectively. The pyrazoline **22Z** decomposed in

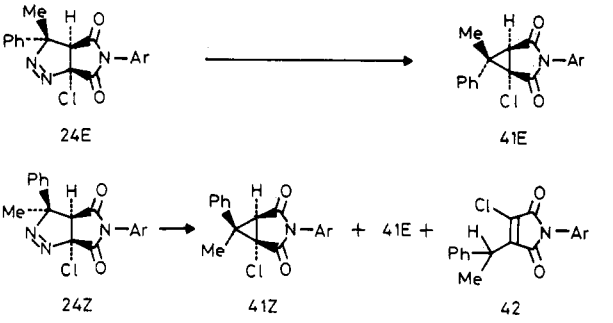


refluxing benzene to give the cyclopropane **23Z** with a small amount of **23E**. The pyrazoline **24Z** in refluxing

**Scheme I**



benzene gave the cyclopropanes **41Z** and **41E** and the olefin **42** in yields of 48%, 41%, and 11%, respectively, while **24E** gave a single cyclopropane (**41E**).



The structures of isolated pyrazolines and cyclopropanes were assigned on the basis of their NMR spectra. Ester methyl protons of the pyrazolines **9Z** ($\delta$ 3.27), **11Z** ($\delta$ 3.02), and **14** ($\delta$ 3.09) and the cyclopropanes **10E** ($\delta$ 3.40) and **13E** ($\delta$ 3.47) appeared at high fields due to the shielding effect of cis phenyl groups. The methine proton of **10Z** ($\delta$ 2.95) appeared at higher field owing to the shielding effect of the cis methyl group[13] than that of **10E** ($\delta$ 3.36) and methyl protons of **10E** ($\delta$ 1.75) appeared at lower field due to the deshielding effect of cis chlorine[14] than those of **10Z** ($\delta$ 1.46). Ortho protons of endo phenyl substituents of the pyrazoline **22Z** ($\delta$ 6.57–6.75) and the cyclopropanes **23Z** ($\delta$ 6.77–7.07), **26** ($\delta$ 6.77–6.93), and **28** ($\delta$ 6.17) and also endo methyl protons of **23E** ($\delta$ 1.45) and **37** ($\delta$ 1.17) appeared at high fields due to the shielding effect of the benzenoid ring of naphthoquinone unit.[15] Ortho protons of *N*-tolyl groups in **24Z** ($\delta$ 6.60), **30** ($\delta$ 6.19), and **41Z** ($\delta$ 6.13) bearing an endo phenyl group appeared at high fields due to the shielding effect of the endo phenyl group.

## Discussion

**Orientation in the Cycloaddition of Diazoalkanes with 1-Chloro-1,2-diacylethylenes.** We know the directing effect of chlorine substituent for 1,3-dipolar cycloaddition of disubstituted diazomethanes with 1-chloro-1,2-diacylethylene derivatives from investigation of the regiochemistry of the products. It is obvious from the structures of all isolated pyrazolines that the cycloaddition occurs in orientation A but not in B (Scheme I).

However, the reactions of diphenyldiazomethane (**3**) and 9-diazofluorene (**4**) did not give stable pyrazolines but cyclopropanes (**13E**, **16Z**, **16E**, **26**, **28**, **30**, and **32**), except the reaction of **3** with the chloromaleate **6** giving the pyrazoline **14**. Precursors of the obtained cyclopropanes proved to be 3-chloropyrazoline derivatives, which were formed in the A orientation cycloaddition, on the basis of

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(14) (a) Bothner-By, A. A.; Colin, C. N. *J. Am. Chem. Soc.* **1958**, *80*, 1728. (b) Bothner-By, A. A.; Pople, J. A. Diamagnetic Anisotropy of Electron Groups. In *Annual Review of Physical Chemistry*; Annual Reviews, INC.: Palo Alto, CA, 1965; Vol. 16, p 43. (c) Closs, G. L.; Closs, L. E. *J. Am. Chem. Soc.* **1960**, *82*, 5723.

(15) (a) Dean, F. M.; Jones, P. G.; Morton, R. B.; Sidisunthorn, P. S. *J. Chem. Soc.* **1963**, 5336. (b) Jones, G. W.; Kerur, D. R.; Yamazaki, T.; Shechter, H.; Woolhouse, A. D.; Halton, B. *J. Org. Chem.* **1974**, *39*, 492.

**Table I. Ratios of Diastereomers in 3-Chloro-3,4-diacyl-5-methyl-5-phenyl-1-pyrazolines Formed in Cycloaddition of 1-Phenyldiazoethane with 1-Chloro-1,2-diacyethylenes**

| pyrazolines | yield of diasteroisomers (%) | |
|---|---|---|
| | *E* form[a] | *Z* form[a] |
| 9 | (25)[b] | 63 |
| 11 | 26 | 57 |
| 22 | (34)[b] | 44 |
| 24 | 48 | 37 |

[a] *E* form refers to pyrazolines bearing an acyl group at C-4 and a phenyl group at C-5 in trans configuration. *Z* form refers to those in cis configuration. [b] Yields of the corresponding cyclopropanes.

the following results. It has been known that a 1-pyrazoline bearing a proton at C-3 attached to a carbonyl group, easily isomerizes to a carbonyl-conjugated 2-pyrazoline.[16] If 4-chloropyrazoline with 5-hydrogen (B) was formed, it might isomerize to 2-pyrazoline before decomposition to cyclopropanes, whereas 3-chloropyrazoline with 4-hydrogen (A) cannot undergo such isomerization. Although the reactions were carried out in the presence of an excess of triethylamine as an isomerization catalyst, 2-pyrazolines were not formed,[17] indicating that the precursors of the cyclopropanes were 3-chloropyrazolines (A). The above consideration revealed that in the orientation of cycloaddition of diazoalkanes with 1-chloro-1,2-diacylethylene derivatives, a chlorine group has the same directing effect as that of a phenyl or a methyl group.[18]

On the other hand, the reactions of 1-phenyldiazoethane (**2**) gave two diastereomeric adducts (*E* form and *Z* form) with the same regiochemistry. The preferential formation of the *E* form is expected from a consideration that 1,3-dipolar cycloaddition is sensitive to steric effect. However, *Z* form adducts (**9**, **11**, and **22**) bearing a 4-carbonyl group and a 5-phenyl group in cis configuration were preferentially formed in the reaction of **2** with **5**, **6**, and **18** as shown in Table I. A similar phenomenon was observed in the reaction of methyl diazoacetate with ethyl cinnamate.[19] These should be explained by attractive interaction between a phenyl group and a carbonyl group in the transition state of cycloaddition.

**Thermal Stability of Pyrazolines.** Reaction of 2-diazopropane (**1**) with 1-chloro-1,2-diacylethylenes **5**, **6**, **18**, and **19** gave the stable pyrazolines **7**, **8**, **20**, and **21**. On the contrary, the reaction of 9-diazofluorene (**4**) did not afford stable pyrazolines but the corresponding cyclopropanes. The reaction of 1-phenyldiazoethane (**2**) with chloromaleate **6** and chloromaleimide **19** gave the stable (*E*)- and (*Z*)-pyrazolines (**11E**, **11Z**, **24E**, and **24Z**, respectively), while the reaction with chlorofumarate **5** and chloronaphthoquinone **18** gave the (*Z*)-pyrazolines (**9Z** and **22Z**, respectively) and the (*E*)-cyclopropanes (**10E** and **23E**, respectively). No existence of thermal decomposition products of the isolated (*Z*)-pyrazolines (**9Z** and **22Z**) in the reaction mixture indicates that these (*Z*)-pyrazolines were stable under the reaction condition and that the

**Table II. Extent of Decomposition of Pyrazolines after Heating at 60 °C for 1 h**

| pyrazolines | substituent C-3 | C-4 | C-5 | percent reaction[a] |
|---|---|---|---|---|
| 7 | Cl | COOMe | Me | 24 |
| | COOMe | H | Me | |
| 8 | COOMe | COOMe | Me | 0 |
| | Cl | H | Me | |
| 9*Z* | Cl | COOMe | Ph | 41 |
| | COOMe | H | Me | |
| 11*E* | COOMe | COOMe | Me | 12 |
| | Cl | H | Ph | |
| 11*Z* | COOMe | COOMe | Ph | 0 |
| | Cl | H | Me | |
| 14 | COOMe | COOMe | Ph | 8 |
| | Cl | H | Ph | |
| 20 | CO-C=C-CO | | Me | 83 |
| | Cl | H | Me | |
| 21 | CO-N-CO | | Me | 43 |
| | Cl | H | Me | |
| 22*Z* | CO-C=C-CO | | Ph | 96 |
| | Cl | H | Me | |
| 24*E* | CO-N-CO | | Me | 78 |
| | Cl | H | Ph | |
| 24*Z* | CO-N-CO | | Ph | 4 |
| | Cl | H | Me | |

[a] After heating a solution of pyrazoline (0.50 mmol) in benzene (5 mL) at 60 °C for 1 h, solvent was removed under reduced pressure. Decomposition ratios of pyrazolines were determined by NMR spectra.

primarily formed (*E*)-pyrazolines (**9E** and **22E**) were too unstable to be isolated and decomposed stereospecifically to give (*E*)-cyclopropanes retaining the stereochemistry. The stable pyrazoline **14** was also obtained from the reaction of diphenyldiazomethane (**3**) with chloromaleate **6**. The results described above mean that the thermal stability of pyrazolines decreases with the variation of the substituents at C-5 in the order Me, Me > Ph, Me > Ph, Ph > biphenylylene. It seems likely that the high stability of **9Z** and **22Z**, compared with **9E** and **22E**, is ascribed to the two bulky cis groups[28] (a carbonyl and a phenyl group) at C-4 and C-5. Furthermore, in order to investigate the effects of substituents at C-3, C-4, and C-5 on the thermal stability of pyrazolines, we examined extent of decomposition of the pyrazolines after 1 h of heating at 60 °C. The results are presented in Table II. The thermostability of (*Z*)-pyrazolines bearing bulky vicinal cis groups was also observed in **8** and **11Z**. Comparisons between **8** and **7**, **11Z** and **11E**, and also **24Z** and **24E** reveal that bulky vicinal substituents at C-3, C-4, and C-5 in a cis configuration increase the thermal stability, which is closely related to elevation of the activation energy for decomposition. Table II also indicates that the bicyclic pyrazolines **20** and **21** are more decomposable than the monocyclic pyrazolines **7** and **8**. The observed decelerating effect of bulky vicinal cis groups is explained as follows. A conjugated group such as a methoxycarbonyl or a phenyl group at C-3 or C-5 may reduce the activation energy for decomposition by resonating with the breaking C–N bonds, while the bulky

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**Table III. Ratio of Inversion Cyclopropane to Retention Cyclopropane in the Thermal Transformation of Pyrazolines to Cyclopropanes**

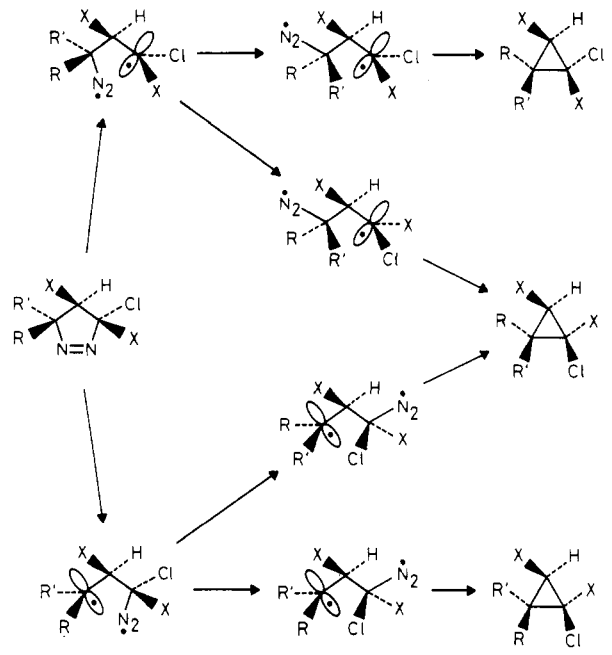
| pyrazolines | substituents C-3 | C-4 | C-5 | inversion/retention ($i/r$)[a] C-3 | C-5 |
|---|---|---|---|---|---|
| **7** | Cl | COOMe | Me | 0 | |
| | COOMe | H | Me | | |
| **8** | COOMe | COOMe | Me | 0.12 | |
| | Cl | H | Me | | |
| **9E**[b] | Cl | COOMe | Me | 0 | 0 |
| | COOMe | H | Ph | | |
| **9Z** | Cl | COOMe | Ph | 0 | 0.23 |
| | COOMe | H | Me | | |
| **11E** | COOMe | COOMe | Me | 0.08 | 0 |
| | Cl | H | Ph | | |
| **11Z** | COOMe | COOMe | Ph | 1.31 | 3.50 |
| | Cl | H | Me | | |
| **14** | COOMe | COOMe | Ph | 1.27 | |
| | Cl | H | Ph | | |
| **22Z** | CO–C=C–CO | | Ph | | 0.09 |
| | Cl | H | Me | | |
| **24Z** | CO–N–CO | | Ph | | 1.03 |
| | Cl | H | Me | | |

[a] The values were obtained from the thermal decomposition of pyrazolines in refluxing toluene. [b] **10E** was not isolated, giving only cyclopropane **11E** (see text).

methoxycarbonyl group at C-4 could partly inhibit conformations of the cis-conjugated substituent at C-3 or C-5 favorable for their effective resonance with the breaking C–N bonds, resulting in an increase in the activation energy.

**Thermal Decomposition of Pyrazoline. Formation of Cyclopropanes.** Although most transformations of the pyrazolines to the cyclopropanes proceeded with retention of the stereochemistry of the starting materials, some pyrazolines (**8**, **9Z**, **11Z**, **11E**, **14**, **22Z**, and **24Z**) gave mixtures of stereoisomeric cyclopropanes. In order to clarify what kind of pyrazolines convert to cyclopropanes, stereospecifically or nonstereospecifically, we consider the relationship between the stereochemistry of four isomeric 3,4-bis(methoxycarbonyl)-3-chloro-5-methyl-5-phenylpyrazolines (**9E**, **9Z**, **11E**, and **11Z**) and the ratio of cyclopropane isomers obtained. Unstable **9E** bearing trans-3,4-$(COOMe)_2$ and 5-Ph trans to 4-COOMe gave stereospecifically a single cyclopropane (**10E**), while **9Z** bearing trans-3,4-$(COOMe)_2$ and 5-Ph cis to 4-COOMe and **11E** bearing cis-3,4-$(COOMe)_2$ and 5-Ph trans to 4-COOMe gave the cyclopropanes **10Z** and **35E** as major products, respectively, along with **10E** as a minor product. Obviously the minor product **10E** was formed by inverstion at C-5 in **9Z** and inversion at C-3 in **11E**. Furthermore, **11Z** bearing three bulky groups in cis configuration afforded **35E** (inversion at C-5), **10Z** (inversion at C-3), and **10E** (inversion at both of C-3 and C-5) as well as a small amount of **35Z**, which retained the stereochemistry of the starting material (Table III). Thus pyrazolines with two bulky vicinal cis groups resulted in inversion at C-3 or C-5 bearing the bulky cis substituent. It seems likely that a steric repulsion between the bulky vicinal groups in the cyclopropane formation is concerned with the inversion process.

**Scheme II**

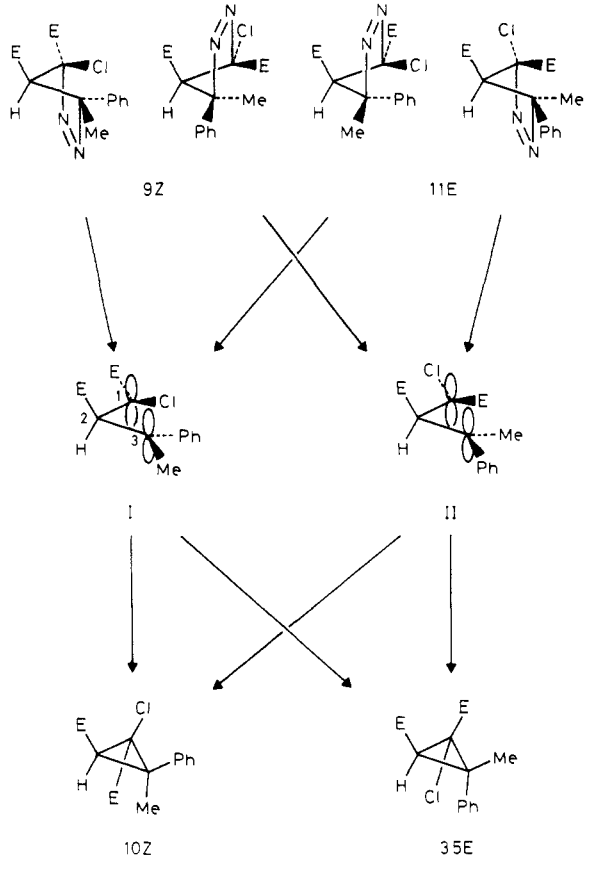


Before we consider a specific mechanism that might be able to account for the present results, let us consider (i) a diazenyl diradical intermediate[8,9,12] and (ii) a (0,0) trimethylene intermediate for cyclopropane formation,[6,21,22] which have been proposed. If decomposition proceeds with sequential C–N bond cleavage, a carbon-centered radical formed first by C–N bond cleavage can in principle attack the diazenyl radical from the back or after rotation of radical center about the radical C–C bond it can attack leading to single or to double inversion of stereochemistry (Scheme II), which conflicts with the present observation. Planar (0,0) trimethylene formed by simultaneous C–N bond cleavage might collapse to cyclopropane with disrotatory or conrotatory ring closure, both of which occur in two alternative directions. Disrotatory ring closure results in retention products that are mainly formed in the present case. Extrusion of nitrogen from "envelope" configuration of **9Z** and **11E** can lead to (0,0) trimethylene I or II, which may undergo disrotatory ring closure in two directions to give **10Z** and **35E** as shown in Scheme III. The direction of ring closure of the intermediates could be determined by eclipsing steric repulsions between bulky vicinal substituents, a methoxycarbonyl group at C-2, and a methoxycarbonyl group at C-1 or a phenyl group at C-3. Considering the fact that **9Z** and **11E** gave different products (**10Z** and **35E**, respectively), transformations of **9Z** and **11E** do not proceed via a common intermediate: **9Z** should specifically give I (or II) leading to **10Z** and **11E** should specifically give II (or I) leading to **35E**. The direction of ring closure in a path from I (or II) to **10Z** should be determined by an eclipsing steric repulsion between the methoxycarbonyl groups at C-1 and at C-2 rather than that between the methoxycarbonyl group at C-2 and the phenyl group at C-3, whereas a path from II (or I) to **35E** should be governed by the steric repulsion between the methoxycarbonyl group at C-2 and the phenyl group at C-3. Thus, the assumption of planar (0,0) trimethylene inter-

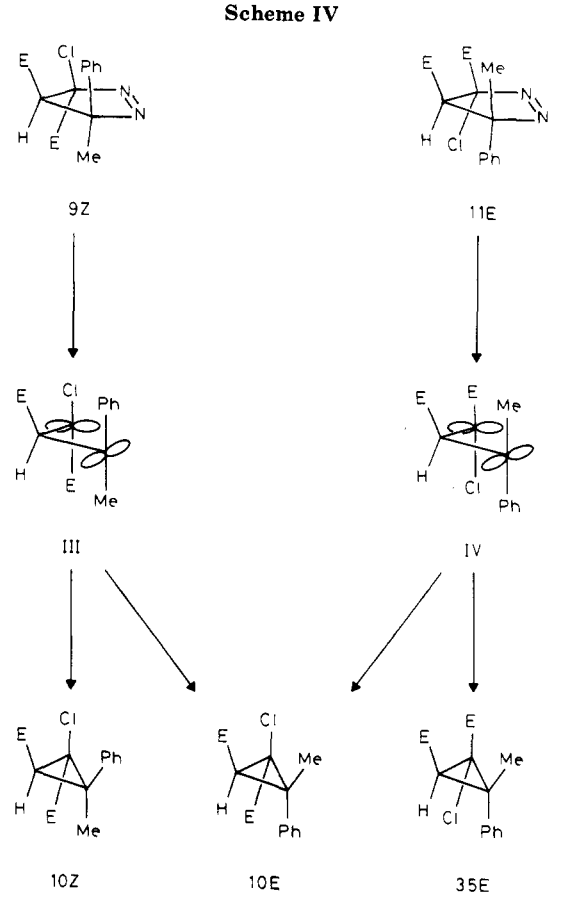
(21) (a) Hoffmann, R. *J. Am. Chem. Soc.* **1968**, *90*, 1475. (b) Schneider, M.; Mossiger, G. *Tetrahedron Lett.* **1974**, 3081. (c) Schneider, M.; Strohacker, H. *Tetrahedron* **1976**, *32*, 619.

(22) (a) Crawford, R. J.; Cameron, D. M. *Can. J. Chem.* **1967**, *45*, 619. (b) Crawford, R. J.; Erickson, G. L. *J. Am. Chem. Soc.* **1967**, *89*, 3907. (c) Al-Sader, B. H.; Crawford, R. J. *Can. J. Chem.* **1968**, *46*, 3301.

**Scheme III**



**Scheme IV**



mediate bears conflicts that dominant steric interactions are reverse in the ring closure of I and II, and although minor products from **11E** and **9Z** should be **10Z** and **35E**, respectively, their minor product was **10E**. Similar consideration of planar (0,0) trimethylene intermediates from **11Z** and **9E** leads to more unreasonable conflicts.

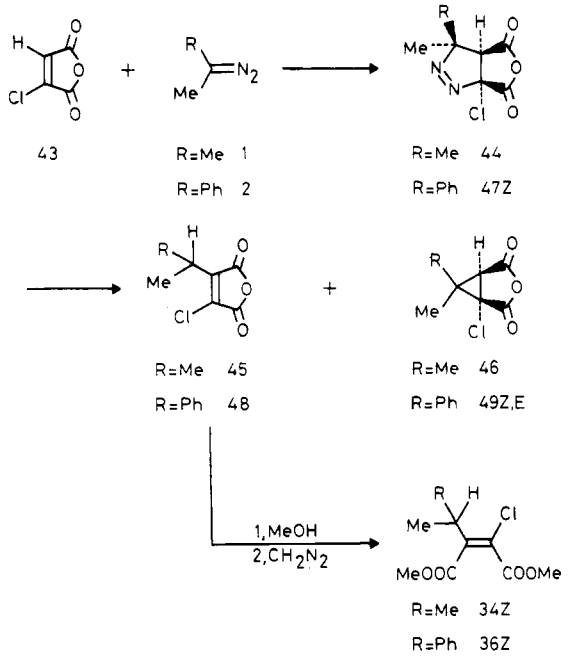
Here let us consider (90,90) trimethylene[23] as a third intermediate for cyclopropane formation. The fact that most pyrazolines, even if bearing bulky vicinal cis substituents, tend to afford cyclopropanes with retention can be explained by (90,90) trimethylene intermediate such as III or IV as shown in Scheme IV. A simple extrusion of nitrogen from a nearly coplanar pyrazolines[24] leads to (90,90) trimethylenes retaining stereochemistry of the starting pyrazoline, which can collapse to a cyclopropane with retention. Rotation of a terminal methylene about radical C–C bond before ring closure leads to a cyclopropane with inversion at the rotated methylene carbon. Therefore, the relative rate of ring closure vs rotation determines stereochemistry of products. Steric repulsion between bulky vicinal cis substituents in the (90,90) trimethylene will cause the rate enhancement of rotation, while bulky vicinal trans groups will cause the rotational barrier to be higher, reducing the rate of rotation. The rate of ring closure of the (90,90) trimethylene bearing bulky vicinal cis groups is expected to be slow because a bulky group at C-2 may depress the conformations of bulky C-1 or C-3 cis substituents favorable for the ring closure. Ultimately, in the (90,90) trimethylene with bulky vicinal cis substituents, the rotational rate increases to a value comparable with the rate of ring closure, resulting in formation of inversion products as well as retention products. Therefore, it is expected that the bulkier the cis substituents at vicinal positions the (90,90) trimethylene bears, the more inversion products are formed. The observed ratios of inversion to retention products ($i/r$), as shown in Table III, increased in the series **7**, **9E** < **8**, **11E**, **22Z** < **9Z** < **11Z**, **14**, **24Z**. These observed trends are consistent with the expectation described above. The value of $i/r$ at C-3 for **11Z** and **14**, which bears three bulky cis groups at C-3, C-4, and C-5, is about 16 times greater than that for **11E** bearing two bulky cis groups at C-3 and C-4. The value of $i/r$ at C-5 for **11Z** is about 15 times greater than that for **9Z** bearing two bulky cis groups at C-4 and C-5. These results indicate that the steric repulsion between the bulky vicinal cis groups in the intermediate from **11Z** and **14** is substantially greater than the steric repulsion in the intermediates from **11E** and **9Z**. It is most likely that the large steric repulsion between bulky vicinal cis substituents in **11Z** and **14** is caused by another bulky cis substituent at C-3 or C-5. The small value of $i/r$ for the bicyclopyrazolines (**22Z** (0.09) and **24Z** (1.03)), when compared with that of **11Z** (3.50), indicates that the steric repulsion between the condensed ring substituent at C-3 and C-4 and the cis phenyl group at C-5 is remarkably smaller than the corresponding interaction for **11Z**.

It has been proposed that thermal $_{\sigma}2_s + _{\sigma}2_s$ extrusion of nitrogen from "envelope" configuration of the parent 1-pyrazoline leading to the (0,0) trimethylene intermediate is a symmetry-allowed process, whereas nitrogen extrusion from a nearly planar pyrazoline leading to the (90,90) trimethylene intermediates is a symmetry-forbidden pro-

(23) (a) Dreibelbis, R. L.; Khatri, H. N.; Walborsky, H. M. *J. Org. Chem.* **1975**, *40*, 2074. (b) Howe, N. E.; Yankee, E. W.; Cram, D. J. *J. Am. Chem. Soc.* **1973**, *95*, 4230. (c) Horsely, J. A.; Jean, Y.; Moser, C.; Salem, L.; Stevens, R. M.; Wright, J. S. *Ibid.* **1972**, *94*, 279.

(24) The dihedral angle between the plane of the three carbon atoms and the plane of C-3, C-5, and the two nitrogens is 11–31°, depending on substituents. It has been reported that the more substituents a pyrazoline bears, the smaller the dihedral angle becomes: (a) Kao, J.; Huang, T. N. *J. Am. Chem. Soc.* **1979**, *101*, 5546. (b) See ref 4b.

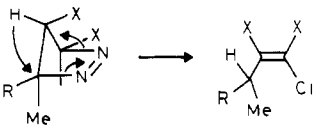
**Scheme V**




cess.[12,21a,25] However, Hiberty reported on the basis of MO calculation for the thermal decomposition of 1-pyrazoline that the difference in the activation energy between the symmetry-forbidden process and the symmetry-allowed process in nitrogen extrusion from the parent 1-pyrazoline is 3.7 kcal/mol.[12b] And also Epiotis indicated that configuration interaction can reverse the stereoselectivity of 2 + 2 cycloaddition when two cycloaddends have widely different polarity and that the increase of polarity of substituents increases the tendency to allowance for the thermal forbidden process of $2_s + 2_s$.[26] These suggest that the symmetrically forbidden process of (90,90) trimethylene formation in the thermal decomposition of multisubstituted pyrazoline might become a possible pathway. Configuration interaction is also important in the ring closure process of the multisubstituted (90,90) trimethylene and ultimately the disrotatory ring closure can proceed with retention (least motion process[27]). The inversion process can compete with the retention process in ring closure when there are large steric repulsions between bulky vicinal substituents within the (90,90) trimethylene intermediate.

**Formation of Olefins.** The thermal decomposition of the five pyrazolines (**8**, **11Z**, **20**, **21**, and **24Z**) among all pyrazolines studied here gave olefins (**34**, **36**, **38**, **40**, and **42**) as minor products, as well as cyclopropanes. Investigation of the stereochemistry of the olefins formed is useful in obtaining information on the mechanism of the olefin formation. In order to determine the stereostructures of **34** from **8** and **36** from **11Z**, authentic samples of **34** and **36** were prepared as outlined in Scheme V. Thermal decomposition of the pyrazoline **47Z** in refluxing benzene, which was prepared by the reaction of 1-phenyldiazoethane (**2**) with chloromaleic anhydride (**43**), gave a mixture of olefin **48** and cyclopropanes (**49Z** and **49E**) in a ratio of 1:1. The treatment of the olefin **48** with methanol followed by diazomethane gave the dimethyl maleate derivative **36Z**. Photochemical isomerization of **36Z** gave a mixture of **36E** and **36Z**. The NMR spectrum of **36** obtained by thermolysis of **11Z** proved identical with that of **36Z**. Structure of **34** was also determined to be the maleate derivative **34Z** by comparison with an authentic sample prepared in a similar manner. Here we consider two possible mechanisms for the formation of olefins: (i) a mechanism involving the trimethylene, which is a common intermediate for the cyclopropane formation, followed by hydrogen migration[6,22b,c] and (ii) a concerted mechanism[4] as shown in Scheme VI. If the trimethylene mechanism was operative, **11Z** should give a mixture of the olefins **36Z** and **36E** together with the cyclopropanes and all pyrazolines should have the possibility of producing olefins via such a process as well as cyclopropanes. However, the fact that only single olefins were formed among possible olefins in decomposition of **8** and **11Z** and that olefin formation was observed in only less decomposable pyrazolines (**8**, **11Z**, **20**, **21**, and **24Z**) excludes the trimethylene mechanism. These observations can be rationalized by the concerted mechanism (Scheme VI). Retardation of pyrazoline decomposition to a trimethylene leading to cyclopropanes allows a competitive alternative reaction path, olefin formation by the concerted mechanism.

**Scheme VI**



## Conclusion

The thermal stability of the pentasubstituted pyrazolines described here decreases with the variation of the substituents at C-5 in the series Me, Me > Me, Ph > Ph, Ph > biphenylylene. Pyrazolines bearing bulky vicinal substituents at C-3, C-4, and C-5 in the cis configuration are substantially more stable than other isomers. This abnormal stability is due to steric interactions between the substituents: bulky substituents at C-4 partly inhibit conformations of the cis-conjugated substituents at C-3 or C-5 such as a phenyl and a methoxycarbonyl group favorable for the decomposition, which results in increase of the activation energy for decomposition. Although most of the thermal transformations of the pyrazolines to the cyclopropanes proceed with retention of the stereochemistry of the starting materials, some pyrazolines bearing bulky vicinal cis groups gave mixtures of stereoisomeric cyclopropanes. The mechanism for the cyclopropane formation from these pyrazolines is explained on the basis of stereochemical distribution of decomposition products by (90,90) trimethylene intermediates.

## Experimental Section

The NMR spectra were obtained with a Varian EM-390 (90 MHz) instrument, with tetramethylsilane as the internal standard. The IR spectra were recorded on Perkin-Elmer 983G infrared spectrophotometer. All melting points were uncorrected. The reactions of diazomethane derivatives with olefins were carried out under dark condition.

**Reaction of 2-Diazopropane (1) with Olefins.** When an ethereal solution containing a slight excess of 2-diazopropane was added to a solution of an olefin (5 mmol) in dichloromethane (10 mL) at 0 °C, the reaction rapidly occurred. Solvent was removed under reduced pressure and the residue was purified by recrystallization from ether/pentane, giving pure pyrazolines.

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

(26) (a) Epiotis, N. D. *J. Am. Chem. Soc.* **1972**, *94*, 1924. (b) Epiotis, N. D. *Ibid.* **1972**, *94*, 1935. (c) Epiotis, N. D. *Ibid.* **1973**, *95*, 1191. (d) Epiotis, N. D. *Ibid.* **1973**, *95*, 1200.

(27) (a) Rice, F. O.; Teller, E. *J. Chem. Phys.* **1938**, *6*, 489. (b) Rice, F. O.; Teller, E. *Ibid.* **1939**, *7*, 199. (c) Hine, J. *J. Org. Chem.* **1966**, *31*, 1236.

***trans*-3,4-Bis(methoxycarbonyl)-3-chloro-5,5-dimethyl-1-pyrazoline (7).** Reaction of dimethyl chlorofumarate (**5**) with **1** gave a colorless crystalline solid (**7**) (85%): mp 57.5–58.5 °C; NMR δ 1.51 (s, 3 H), 1.68 (s, 3 H), 3.41 (s, 1 H), 3.75 (s, 3 H), 3.96 (s, 3 H); IR (KBr) 1762 $cm^{-1}$. Anal. Calcd for $C_9H_{13}N_2O_4Cl$: C, 43.47; H, 5.29; N, 11.27. Found: C, 43.62; H, 5.29; N, 11.32.

***cis*-3,4-Bis(methoxycarbonyl)-3-chloro-5,5-dimethyl-1-pyrazoline (8).** Reaction of dimethyl chloromaleate (**6**) with **1** gave a colorless crystalline solid (**8**) (78%): mp 55–56 °C; NMR δ 1.46 (s, 3 H), 1.64 (s, 3 H), 3.13 (s, 1 H), 3.69 (s, 3 H), 3.87 (s, 3 H); IR (KBr) 1764, 1725 $cm^{-1}$. Anal. Calcd for $C_9H_{13}N_2O_4Cl$: C, 43.47; H, 5.29; N, 11.27. Found: C, 43.36; H, 5.12; N, 11.28.

**3a,4,9,9a-Tetrahydro-9a-chloro-3,3-dimethyl-4,9-dioxo-3*H*-benz[*f*]indazole (20).** Reaction of 2-chloro-1,4-naphthoquinone (**18**) with **1** gave lemon yellow needles (**20**) (96%): mp 90 °C dec; NMR δ 1.04 (s, 3 H), 1.86 (s, 3 H), 3.23 (s, 1 H), 7.43–7.98 (m, 2 H), 8.02–8.27 (m, 2 H); IR (KBr) 1697, 1683, 1587 $cm^{-1}$. Anal. Calcd for $C_{13}H_{11}N_2O_2Cl$: C, 59.43; H, 4.22; N, 10.67. Found: C, 59.57; H, 4.24; N, 10.68.

**3a,4,6,6a-Tetrahydro-6a-chloro-3,3-dimethyl-4,6-dioxo-5-tolyl-3*H*-pyrrolo[3,4-*c*]pyrazole (21).** Reaction of *N*-tolylchloromaleimide (**19**) with **1** gave a white crystalline solid (**21**) (97%): mp 132–133 °C dec; NMR δ 1.63 (s, 3 H), 1.65 (s, 3 H), 2.38 (s, 3 H), 3.05 (s, 1 H), 7.09 (AB q, 2 H, $J$ = 8.1 Hz), 7.21 (AB q, 2 H, $J$ = 8.1 Hz); IR (KBr) 1719, 1514 $cm^{-1}$. Anal. Calcd for $C_{14}H_{14}N_3O_2Cl$: C, 57.63; H, 4.84; N, 14.40. Found: C, 57.72; H, 4.84; N, 14.42.

**Reaction of 1-Phenyldiazoethane (2) with Olefins. Reaction with Dimethyl Chlorofumarate (5).** To a solution of **5** (10.0 mmol) in ether (25 mL) at 0 °C was added a solution of **2** (ca. 11.2 mmol) in ether (25 mL) and the solution was kept at 0 °C for 1 h. Solvent was removed under reduced pressure, leaving a red oil, which solidified on standing under pentane/ether to give 3-chloro-*r*-3,*t*-4-bis(methoxycarbonyl)-*c*-5-methyl-*t*-5-phenyl-1-pyrazoline (**9Z**) as a white crystalline solid (63%): mp 89–90 °C; NMR δ 1.66 (s, 3 H), 3.27 (s, 3 H), 3.94 (s, 4 H), 7.22–7.38 (m, 5 H); IR (KBr) 1735, 1702 $cm^{-1}$. Anal. Calcd for $C_{14}H_{15}N_2O_4Cl$: C, 54.11; H, 4.87; N, 9.02. Found: C, 53.92; H, 4.80; N, 8.98. The residual solution was concentrated to give an oil, which was separated by column chromatography on silica gel with hexane–ether (1:1).[29] The main fraction gave *r*-1,*t*-3-bis(methoxycarbonyl)-1-chloro-*t*-2-methyl-*c*-2-phenylcyclopropane (**10E**) (25%) as a colorless oil: NMR δ 1.75 (s, 3 H), 3.36 (s, 1 H), 3.40 (3 H), 3.79 (s, 3 H), 7.10~7.40 (m, 5 H); IR (film) 1735 $cm^{-1}$. Anal. Calcd for $C_{14}H_{15}O_4Cl$: C, 59.47; H, 5.35. Found: C, 59.47; H, 5.36.

**Reaction with Dimethyl Chloromaleate (6).** An ethereal solution (40 mL) of **6** (15.1 mmol) and **2** (ca. 15.8 mmol) was allowed to stand at 0 °C for 2 days. A white precipitate was separated from the solution, washed with pentane, and dried to give *r*-3,*c*-4-bis(methoxycarbonyl)-3-chloro-*t*-5-methyl-*c*-5-phenyl-1-pyrazoline (**11Z**) (54%): mp 113–114 °C; NMR δ 1.90 (s, 3 H), 3.02 (s, 3 H), 3.53 (s, 1 H), 3.86 (s, 3 H), 7.30 (s, 5 H); IR (KBr) 1748, 1727 $cm^{-1}$. Anal. Calcd for $C_{14}H_{15}O_4N_2Cl$: C, 54.11; H, 4.87; N, 9.02. Found: C, 54.12; H, 4.88; N, 8.99. The filtrate was concentrated to an oil, which gave a mixture of white powders and white prisms by recrystallization from ether. Hand separation of the species showed the white powders to be **11Z** (3%, total 57%). The major white prisms were recrystallized from ether to give *r*-3,*c*-4-bis(methoxycarbonyl)-3-chloro-*c*-5-methyl-*t*-5-phenyl-1-pyrazoline (**11E**) (26%): mp 81–82 °C; NMR δ 1.77 (s, 3 H), 3.58 (s, 1 H), 3.74 (s, 3 H), 3.90 (s, 3 H), 7.35 (s, 5 H); IR (KBr) 1748 $cm^{-1}$. Anal. Calcd for $C_{14}H_{15}O_4N_2Cl$: C, 54.11; H, 4.87; N, 9.02. Found: C, 53.97; H, 4.96; N, 9.00.

**Reaction with 2-Chloro-1,4-naphthoquinone (18).** A solution of **18** (5.00 mmol) and **2** (ca. 5.6 mmol) in ether (25 mL) was maintained at 0 °C for 1 h. The precipitate was filtered and washed with hexane to give 3a,4,9,9a-tetrahydro-9a-chloro-*exo*-3-methyl-*endo*-3-phenyl-4,9-dioxo-3*H*-benz[*f*]indazole (**22Z**) (44%): mp 99–100 °C; NMR δ 2.25 (s, 3 H), 3.42 (s, 1 H), 6.57–6.75 (m, 2 H), 6.83–7.04 (m, 3 H), 7.45–7.68 (m, 3 H), 7.79–7.96 (m, 1 H); IR (KBr) 1677, 1589 $cm^{-1}$. Anal. Calcd for $C_{18}H_{13}O_2N_2Cl$: C, 66.57; H, 4.04; N, 8.63. Found: C, 66.58; H, 4.04; N, 8.47. The filtrate was concentrated, leaving an oil which was chromatographed over silica gel using ether/hexane (1:1) as an eluent. The main fraction was recrystallized from ether/hexane to give 1a,7a-dihydro-1a-chloro-*endo*-1-methyl-*exo*-1-phenyl-1*H*-cyclopropa[*b*]naphthalene-2,7-dione (**23E**) as white needles (34%): mp 122.5–124 °C; NMR δ 1.45 (s, 3 H), 3.33 (s, 1 H), 7.23–7.49 (m, 5 H), 7.62–7.87 (m, 2 H), 8.06–8.33 (m, 2 H); IR (KBr) 1683, 1589 $cm^{-1}$. Anal. Calcd for $C_{18}H_{13}O_2Cl$: C, 72.85; H, 4.42. Found: C, 72.47; H, 4.61.

**Reaction with *N*-Tolylchloromaleimide (19).** To a soution of **19** (5.01 mmol) in dichloromethane (15 mL) at 0 °C was added a solution of **2** (ca. 6.4 mmol) in ether (15 mL), and the mixture was maintained at 0 °C for 1 h. The precipitate was filtered and washed with pentane to give 3a,4,6,6a-tetrahydro-6a-chloro-4,6-dioxo-*exo*-3-methyl-*endo*-3-phenyl-5-tolyl-3*H*-pyrrolo[3,4-*c*]-pyrazole (**24Z**) (37%). Recrystallization of **24Z** from $CH_2Cl_2$ gave a white crystalline solid: mp 151 °C; NMR δ 2.11 (s, 3 H), 2.31 (s, 3 H), 3.25 (s, 1 H), 6.60 (d, 2 H, $J$ = 8.7 Hz), 6.98–7.47 (m, 7 H); IR (KBr) 1723, 1514 $cm^{-1}$. Anal. Calcd for $C_{19}H_{16}O_2N_3Cl \cdot {}^1/_2H_2O$: C, 63.07; H, 4.46; N, 11.62. Found: C, 63.36; H, 4.52; N, 11.45. The filtrate was concentrated under reduced pressure, leaving an oil which was crystallized from ether/pentane to give 3a,4,6,6a-tetrahydro-6a-chloro-4,6-dioxo-*endo*-3-methyl-*exo*-3-phenyl-5-tolyl-3*H*-pyrrolo[3,4-*c*]pyrazole (**24E**) as colorless plates (48%): mp 98–100 °C; NMR δ 1.87 (s, 3 H), 2.40 (s, 3 H), 3.47 (s, 1 H), 7.13 (AB q, 2 H, $J$ = 8.4 Hz), 7.25 (AB q, 2 H, $J$ = 8.4 Hz), 7.32–7.41 (m, 5 H); IR (KBr) 1735, 1512 $cm^{-1}$. Anal. Calcd for $C_{19}H_{16}O_2N_3Cl$: C, 64.50; H, 4.56; N, 11.88. Found: C, 64.55; H, 4.63; N, 11.73.

**Reaction of Diphenyldiazomethane (3) with Olefins. Reaction with Dimethyl Chlorofumarate (5).** A benzene solution (5 mL) of **3** (2.00 mmol) and **5** (2.40 mmol) was allowed to stand at room temperature for 2 days. Solvent was removed under reduced pressure and the residue was separated by column chromatography on silica gel with benzene. The main fraction gave *trans*-1,3-bis(methoxycarbonyl)-1-chloro-2,2-diphenylcyclopropane (**13E**) (90%). Recrystallization of **13E** from $CH_2Cl_2$ gave colorless prisms: mp 138–139 °C; NMR δ 3.47 (s, 3 H), 3.72 (s, 4 H), 7.06–7.47 (m, 10 H); IR (KBr) 1735 $cm^{-1}$. Anal. Calcd for $C_{19}H_{17}O_4Cl$: C, 66.19; H, 4.97. Found: C, 66.22; H, 4.95.

**Reaction with Dimethyl Chloromaleate (6).** A benzene solution (1.5 mL) of **3** (1.00 mmol) and **6** (1.22 mmol) was allowed to stand at room temperature for 12 days. The reaction mixture was treated with $CH_2Cl_2$/hexane, giving *cis*-3,4-bis(methoxycarbonyl)-3-chloro-5,5-diphenyl-1-pyrazoline (**14**) as a white crystalline solid (73%): mp 128.5–129.5 °C; NMR δ 3.09 (s, 3 H), 3.89 (s, 3 H), 4.39 (s, 1 H), 7.00–7.47 (m, 8 H), 7.51–7.69 (m, 2 H); IR (KBr) 1764, 1725 $cm^{-1}$. Anal. Calcd for $C_{19}H_{17}O_4N_2Cl$: C, 61.21; H, 4.60; N, 7.52. Found: C, 61.16; H, 4.58; N, 7.50.

**Reaction with 2-Chloro-1,4-naphthoquinone (18).** A benzene solution (5.0 mL) of **3** (2.00 mmol) and **18** (2.40 mmol) was permitted to stand at room temperature for 18 days. The precipitate was filtered and washed with hexane/benzene to give 1a,7a-dihydro-1a-chloro-1,1-diphenyl-1*H*-cyclopropa[*b*]-naphthalene-2,7-dione (**26**) (59%). After removal of the solvent from the filtrate, the residue was separated by column chromatography on silica gel with benzene. The main fraction gave **26** (19%, total 78%): mp 212–214 °C; NMR δ 3.72 (s, 1 H), 6.77–6.93 (m, 2 H), 7.07–7.57 (m, 10 H), 7.67–7.97 (m, 2 H); IR (KBr) 1691, 1676, 1591 $cm^{-1}$. Anal. Calcd for $C_{23}H_{15}O_2Cl$: C, 76.99; H, 4.21. Found: C, 76.68; H, 4.22.

**Reaction with *N*-Tolylchloromaleimide (19).** By using the similar procedure as described above (reaction time; for 1 day), 3a,4a-dihydro-3a-chloro-4,4-diphenyl-2-tolyl-4*H*-cyclopropa[*c*]-pyrrole-1,3-dione (**30**) (94%) was obtained from **3** (2.00 mmol) and **19** (2.40 mmol). Recrystallization of **30** from $CH_2Cl_2$/hexane

(28) Bulk of substituent in the present case should be considered on the basis of Berg's ortho steric parameter ($S°$).[20a] Eliel's popular steric parameter[20b] on the basis of 1,3-diaxial interaction in cyclohexane derivatives is not suitable for the present case, because the steric effects described in this study are predominantly due to 1,2-steric interactions rather than 1,3-steric interactions. Substituent bulkiness in this study could follow Berg's parameter ($S°$) on the basis of 1,2-steric interaction, which was derived from N-methylation of ortho-substituted pyridines. According to the $S°$ value, a series of bulkiness of substituents is in the following order: H (0) < Cl (−0.54) < Me (−0.73) < COOMe (−1.04) < Ph (−1.82).

(29) We checked that the chromatographic treatment did not cause any chemical change by means of NMR in all procedures described here.

gave a white crystalline solid: mp 185–187 °C; NMR δ 2.25 (s, 3 H), 3.61 (s, 1 H), 6.19 (d, 2 H, $J$ = 8.3 Hz), 6.99 (d, 2 H, $J$ = 8.3 Hz), 7.18–7.57 (m, 10 H); IR (KBr) 1785, 1720, 1513 cm$^{-1}$. Anal. Calcd for $C_{24}H_{18}O_2NCl$: C, 74.32; H, 4.68; N, 3.61. Found: C, 74.32; H, 4.78; N, 3.67.

**Reaction of 9-Diazofluorene (4) with Olefins. Reaction with Dimethyl Chlorofumarate (5).** A benzene solution of **4** (2.00 mmol) and **5** (2.40 mmol) was allowed to stand at room temperature for 2 days. The reaction mixture was separated by column chromatography on silica gel using benzene as an eluent.

The main fraction gave *trans*-2,3-bis(methoxycarbonyl)-2-chlorospiro[cyclopropane-1,9′-fluorene] (**16E**) (87%). Recrystallization of **16E** from $CH_2Cl_2$/hexane gave a pale yellow crystalline solid: mp 132.5–134.0 °C; NMR δ 3.64 (s, 3 H), 3.74 (s, 4 H), 6.97–7.52 (m, 5 H), 7.66–7.83 (m, 3 H); IR (KBr) 1743 cm$^{-1}$. Anal. Calcd for $C_{19}H_{15}O_4Cl$: C, 66.42; H, 4.41. Found: C, 66.57; H, 4.39.

**Reaction with Dimethyl Chloromaleate (6).** By using a similar procedure to that described above (reaction time 12 days), *cis*-2,3-bis(methoxycarbonyl)-2-chlorospiro[cyclopropane-1,9′-fluorene] (**16Z**) (88%) was obtained from **4** (1.01 mmol) and **6** (1.20 mmol) in benzene (2.0 mL). Recrystallization of **16Z** from $CH_2Cl_2$/hexane gave colorless prisms: mp 117.5–118.0 °C; NMR δ 3.30 (s, 1 H), 3.72 (s, 3 H), 3.80 (s, 3 H), 7.08–7.51 (m, 6 H), 7.69–7.82 (m, 2 H); IR (KBr) 1741 cm$^{-1}$. Anal. Calcd for $C_{19}H_{15}O_4Cl$: C, 66.57; H, 4.41. Found: C, 66.43; H, 4.46.

**Reaction with 2-Chloro-1,4-naphthoquinone (18).** By using a similar procedure to that described above (reaction time 18 days), 1a,7a-dihydro-1a-chlorospiro[1*H*-cyclopropa[*b*]naphthalene-1,9′-fluorene]-2,7-dione (**28**) (92%) was obtained from **4** (2.00 mmol) and **18** (2.41 mmol) in benzene (7.0 mL). Recrystallization of **28** from $CH_2Cl_2$/hexane gave a yellow crystalline solid: mp 137–139 °C; NMR δ 3.85 (s, 1 H), 6.17 (d, 1 H, $J$ = 7.8 Hz), 6.72 (t, 1 H, $J$ = 7.8 Hz), 7.18 (d, 1 H, $J$ = 7.8 Hz), 7.29–7.58 (m, 3 H), 7.65–7.97 (m, 4 H), 8.11–8.36 (m, 2 H); IR (KBr) 1685, 1588 cm$^{-1}$. Anal. Calcd for $C_{23}H_{13}O_2Cl$: C, 77.42; H, 3.67. Found: C, 77.27; H, 3.63.

**Reaction with *N*-Tolylchloromaleimide (19).** By using a similar procedure to that described above (reaction time 1 day), 3a,4a-dihydro-3a-chloro-2-tolylspiro[4*H*-cyclopropa[*c*]pyrrole-4,9′-fluorene]-1,3-dione (**32**) (86%) was obtained from **4** (2.00 mmol) and **19** (2.40 mmol) in benzene (8.0 mL). Recrystallization from benzene gave a pale yellow crystalline solid: mp 147–149 °C; NMR δ 2.42 (s, 3 H), 3.66 (s, 1 H), 7.02–7.20 (m, 2 H), 7.23–7.55 (m, 8 H), 7.67–7.84 (m, 2 H); IR (KBr) 1725, 1511 cm$^{-1}$. Anal. Calcd for $C_{24}H_{16}O_2NCl$: C, 74.71; H, 4.18; N, 3.63. Found: C, 74.65; H, 4.19; N, 3.59.

**Thermal Decomposition of Pyrazolines.** A solution of a pyrazoline (1.0 mmol) was refluxed for 2–9 h. Removal of the solvent by rotary evaporator left an oil, which was chromatographed over silica gel using hexane–ether or hexane–benzene as an eluent.

**Thermal Decomposition of 7.** **7** in refluxing toluene for 2 h gave *trans*-1,3-bis(methoxycarbonyl)-1-chloro-2,2-dimethylcyclopropane (**33E**) (97%) as a colorless oil: bp 140–141.5 °C (26 mmHg); NMR δ 1.25 (s, 3 H), 1.50 (s, 3 H), 2.63 (s, 1 H), 3.70 (s, 3 H), 3.80 (s, 3 H); IR (film) 1732 cm$^{-1}$. Anal. Calcd for $C_9H_{13}O_4Cl$: C, 48.99; H, 5.94. Found: C, 48.84; H, 5.85.

**Thermal Decomposition of 8.** **8** in refluxing toluene for 2 h gave a mixture of **33E** (9%) and dimethyl 1-chloro-2-isopropylmaleate (**34**) (4%) as one fraction and *cis*-1,3-bis(methoxycarbonyl)-2,2-dimethylcyclopropane (**33Z**) (70%): bp 81.0–81.5 °C (3 mmHg); NMR δ 1.42 (s, 3 H), 1.44 (s, 3 H), 2.03 (s, 1 H), 3.72 (s, 3 H), 3.77 (s, 3 H); IR (film) 1743 cm$^{-1}$. Anal. Calcd for $C_9H_{13}O_4Cl$: C, 48.99; H, 5.94. Found: C, 48.66; H, 5.83.

**Thermal Decomposition of 9Z.** **9Z** in refluxing benzene for 8 h gave **10E** (21%) and 1-chloro-*r*-1,*t*-3-bis(methoxycarbonyl)-*c*-2-methyl-*t*-2-phenylcyclopropane (**10Z**) (72%): mp 54.5–55.0 °C; NMR δ 1.46 (s, 3 H), 2.95 (s, 1 H), 3.64 (s, 3 H), 3.83 (s, 3 H), 7.27 (s, 5 H); IR (KBr) 1748, 1735 cm$^{-1}$. Anal. Calcd for $C_{14}H_{15}O_4Cl$: C, 59.47; H, 5.35. Found: C, 59.60; H, 5.41.

**Thermal Decomposition of 11E.** **11E** in refluxing toluene for 2 h gave **10E** (7%) and 1-chloro-*r*-1,*c*-3-bis(methoxycarbonyl)-*c*-2-methyl-*t*-2-phenylcyclopropane (**35E**) (93%): mp 67–67.5 °C; NMR δ 1.69 (s, 3 H), 2.68 (s, 1 H), 3.78 (s, 3 H), 3.83 (s, 3 H), 7.31 (s, 5 H); IR (KBr) 1741, 1724 cm$^{-1}$. Anal. Calcd for $C_{14}H_{15}O_4Cl$: C, 59.47; H, 5.35. Found: C, 59.33; H, 5.38.

**Thermal Decomposition of 11Z.** **11Z** in refluxing toluene for 2 h gave a mixture of **10E** (6%), **35E** (50%), and dimethyl 1-chloro-2-(1-phenethyl)maleate (**36**) (4%) as one fraction and **10Z** (15%) and 1-chloro-*r*-1,*c*-3-bis(methoxycarbonyl)-*t*-2-methyl-*c*-2-phenylcyclopropane (**35Z**) (16%). Recrystallization of **35Z** from ether/hexane gave a white crystalline solid: mp 66.0–67.5 °C; NMR δ 1.68 (s, 3 H), 2.45 (s, 1 H), 3.53 (s, 3 H), 3.63 (s, 3 H), 7.12–7.42 (m, 5 H); IR (KBr) 1751, 1729 cm$^{-1}$. Anal. Calcd for $C_{14}H_{15}O_4Cl$: C, 59.47; H, 5.35. Found: C, 59.53; H, 5.40.

**Thermal Decomposition of 14.** **14** in refluxing benzene for 3 h gave **13E** (56%) and 1-chloro-*cis*-1,3-bis(methoxycarbonyl)-2,2-diphenylcyclopropane (**13Z**) (44%). **13Z** was recrystallized from hexane gave a white crystalline solid: mp 95–96 °C; NMR δ 3.11 (s, 1 H), 3.67 (s, 3 H), 3.69 (s, 3 H), 7.06–7.52 (m, 10 H); IR (KBr) 1741 cm$^{-1}$. Anal. Calcd for $C_{19}H_{17}O_4Cl$: C, 66.18; H, 4.97. Found: C, 66.26; H, 4.97.

**Thermal Decomposition of 20.** A benzene solution of **20** (0.782 mmol) was refluxed for 2 h. The reaction mixture was chromatographed on silica gel. Elution with hexane/benzene gave 2-chloro-3-isopropyl-1,4-naphthoquinone (**38**) (15%). Recrystallization of **38** from $CH_2Cl_2$/hexane yielded a yellow crystalline solid: mp 65–66 °C; NMR δ 1.40 (d, 6 H, $J$ = 7.2 Hz), 3.58 (hep, 1 H, $J$ = 7.2 Hz), 7.60–7.80 (m, 2 H), 7.95–8.22 (m, 2 H); IR (KBr) 1664, 1593, 1566 cm$^{-1}$. Anal. Calcd for $C_{13}H_{11}O_2Cl$: C, 66.53; H, 4.72. Found: C, 66.37; H, 4.66. Further elution gave 1a,7a-dihydro-1a-chloro-1,1-dimethyl-1*H*-cyclopropa[*b*]naphthalene-2,7-dione (**37**) (81%). Recrystallization of **37** from $CH_2Cl_2$/hexane yielded a white crystalline solid: mp 111.5–112.0 °C; NMR δ 1.17 (s, 3 H), 1.61 (s, 3 H), 2.71 (s, 1 H), 7.63–7.82 (m, 2 H), 7.97–8.21 (m, 2 H); IR (KBr) 1686, 1590 cm$^{-1}$. Anal. Calcd for $C_{13}H_{11}O_2Cl$: C, 66.53; H, 4.72. Found: C, 66.33; H, 4.74.

**Thermal Decomposition of 21.** A toluene solution of **21** was refluxed for 2 h. The reaction mixture was chromatographed on silica gel. Elution with hexane–ether (1:1) gave 3-chloro-4-isopropylpyrrole-2,5-dione (**40**) (43%). Recrystallization of **40** from $CH_2Cl_2$/hexane yielded colorless prisms: mp 92–93 °C; NMR δ 1.37 (d, 6 H, $J$ = 6.9 Hz), 2.35 (s, 3 H), 3.21 (hep, 1 H, $J$ = 6.9 Hz), 7.20 (s, 4 H); IR (KBr) 1721 cm$^{-1}$. Anal. Calcd for $C_{14}H_{14}O_2NCl$: C, 63.76; H, 5.35; N, 5.31. Found: C, 63.87; H, 5.39; N, 5.38. Further elution gave 3a,4a-dihydro-3a-chloro-4,4-dimethyl-2-tolyl-4*H*-cyclopropa[*c*]pyrrole-1,3-dione (**39**) (54%). Recrystallization of **39** from $CH_2Cl_2$/hexane yielded colorless needles: mp 134.5–135 °C; NMR δ 1.43 (s, 3 H), 1.48 (s, 3 H), 2.35 (s, 3 H), 2.53 (s, 1 H), 7.10 (AB q, 2 H, $J$ = 9.0 Hz), 7.20 (AB q, 2 H, $J$ = 9.0 Hz); IR (KBr) 1778, 1707 cm$^{-1}$. Anal. Calcd for $C_{14}H_{14}O_2NCl$: C, 63.76; H, 5.35; N, 5.31. Found: C, 63.55; H, 5.39; N, 5.37.

**Thermal Decomposition of 22Z.** **22Z** in refluxing benzene for 9 h gave a mixture of **23E** (7%) and 1a,7a-dihydro-1a-chloro-1-methyl-*endo*-1-phenyl-1*H*-cyclopropa[*b*]naphthalene-2,7-dione (**23Z**) (91%). Recrystallization of the mixture from $CH_2Cl_2$/hexane yielded **23Z** as a white crystalline solid: mp 134.0–134.5 °C; NMR δ 1.85 (s, 3 H), 3.07 (s, 1 H), 6.77–7.07 (m, 5 H), 7.22–7.45 (m, 2 H), 7.57–7.81 (m, 2 H); IR (KBr) 1685, 1592 cm$^{-1}$. Anal. Calcd for $C_{18}H_{13}O_2Cl$: C, 72.85; H, 4.42. Found: C, 72.69; H, 4.45.

**Thermal Decomposition of 24E.** **24E** in refluxing benzene for 2 h gave 3a,4a-dihydro-3a-chloro-4-methyl-*exo*-4-phenyl-2-tolyl-4*H*-cyclopropa[*c*]pyrrole-1,3-dione (**41E**) (100%): mp 173 °C; NMR δ 1.68 (s, 3 H), 2.37 (s, 3 H), 3.20 (s, 1 H), 7.09–7.23 (m, 4 H), 7.36 (s, 5 H); IR (KBr) 1782, 1719 cm$^{-1}$. Anal. Calcd for $C_{19}H_{16}O_2NCl$: C, 70.04; H, 4.95; N, 4.30. Found: C, 70.10; H, 5.09; N, 4.04.

**Thermal Decomposition of 24Z.** A suspension of **24Z** in benzene was refluxed for 2 h. The reaction mixture was chromatographed on silica gel. Elution with benzene/hexane (1:1) gave 3-chloro-4-(1-phenethyl)-1-tolylpyrrole-2,5-dione (**42**) (11%). Recrystallization of **42** from ether/hexane yielded a white crystalline solid: mp 87–89 °C; NMR δ 1.77 (d, 3 H, $J$ = 7.4 Hz), 2.35 (s, 3 H), 4.32 (q, 1 H, $J$ = 7.4 Hz), 7.19 (s, 5 H), 7.25–7.40 (m, 4 H); IR (KBr) 1727, 1632 cm$^{-1}$. Anal. Calcd for $C_{19}H_{16}O_2NCl$: C, 70.04; H, 4.95; N, 4.30. Found: C, 69.82; H, 4.97; N, 4.36. Further elution gave **41E** (41%) and 3a,4a-dihydro-3a-chloro-4-methyl-*endo*-4-phenyl-2-tolyl-4*H*-cyclopropa[*c*]pyrrole-1,3-dione (**41Z**) (48%). Recrystallization of **41Z** from $CH_2Cl_2$/hexane yielded a

white crystalline solid: mp 148 °C; NMR δ 1.69 (s, 3 H), 2.20 (s, 3 H), 2.85 (s, 1 H), 6.13 (d, 2 H, $J$ = 8.4 Hz), 6.95 (d, 2 H, $J$ = 8.4 Hz), 7.33 (s, 5 H); IR (KBr) 1781, 1719 cm$^{-1}$. Anal. Calcd for $C_{19}H_{16}O_2NCl$: C, 70.04; H, 4.95; N, 4.30. Found: C, 70.15; H, 4.96; N, 3.97.

**Preparation of Dimethyl 1-Chloro-2-isopropylmaleate (34Z).** To a solution of **43** (30.0 mmol) in ether (30 mL) was added dropwise a solution of 1 (ca. 31.5 mmol) in ether (70 mL) at 0 °C. After 0.5 h, 100 mL of benzene was added to the reaction mixture and then ether was removed from the solution and the solution was refluxed for 30 min. Removal of solvent left an oil which was chromatographed on silica gel. Elution with ether-hexane (10:90) gave 1-chloro-2-isopropylmaleic anhydride (**45**) (76%): bp 104-106 °C (6 mmHg); NMR δ 1.35 (d, 6 H, $J$ = 7.1 Hz), 3.09 (hep, 1 H, $J$ = 7.1 Hz); IR (film) 1862, 1832, 1775, 1633 cm$^{-1}$. Anal. Calcd for $C_7H_7O_3Cl$: C, 48.15; H, 4.04. Found: C, 48.33; H, 4.32. **45** (9.99 mmol) was dissolved in methanol (40 mL) and refluxed for 5 h. Removal of methanol left an oil, which was dissolved in dichloromethane (10 mL) and treated with diazomethane (ca. 15 mmol) in ether. After few minutes, solvent was removed under reduced pressure and the residue was chromatographed on silica gel. Elution with ether-hexane (10:90) gave **34Z** (89%): bp 121.5-122.5 °C (6 mmHg); NMR δ 1.15 (d, 6 H, $J$ = 6.9 Hz), 3.18 (hep, 1 H, $J$ = 6.9 Hz), 3.82 (s, 3 H), 3.83 (s, 3 H); IR (film) 1735, 1610 cm$^{-1}$. Anal. Calcd for $C_9H_{13}O_4Cl$: C, 48.99; H, 5.94. Found: C, 48.91; H, 6.03.

**Preparation of Dimethyl 1-Chloro-2-(1-phenethyl)maleate (36Z).** To a solution of chloromaleic anhydride (**43**) (30.0 mmol) in ether (30 mL) was added dropwise a solution of 1-phenyldiazoethane (ca. 31.5 mmol) in ether (45 mL) for 15 min and was kept at 0 °C for 1 h. The precipitate was filtered and washed with cold ether/pentane, giving **47Z** (18%), which decomposed gradually at room temperature. **47Z** was refluxed in benzene (20 mL) for 30 min and then removal of solvent left an oil, the NMR spectrum of which showed 1:1 mixture of **48** and **49**. Elution with benzene-hexane (1:1) gave 1-chloro-2-(1-phenethyl)maleic anhydride (**48**) (39%): mp 52.5-53.5 °C; NMR δ 1.74 (d, 3 H, $J$ = 7.2 Hz), 4.24 (q, 1 H, $J$ = 7.2 Hz), 7.33 (s, 5 H); IR (KBr) 1860, 1796, 1634 cm$^{-1}$. Anal. Calcd for $C_{12}H_9O_3Cl$: C, 60.90; H, 3.83. Found: C, 60.66; H, 3.87. A solution of **48** (1.67 mmol) in methanol (40 mL) was refluxed for 5 h. Removal of methanol left an oil, which was dissolved in dichloromethane (10 mL) and reacted with diazomethane (2.5 mmol) in ether. After a few minutes, solvent was removed under reduced pressure and the residue was chromatographed on silica gel. Elution with benzene/hexane (1:1) gave **36Z** (96%): NMR δ 1.54 (d, 3 H, $J$ = 7.2 Hz), 3.56 (s, 3 H), 3.75 (s, 3 H), 4.37 (q, 1 H, $J$ = 7.2 Hz), 7.26 (s, 5 H); IR (film) 1737, 1608 cm$^{-1}$. Anal. Calcd for $C_{14}H_{15}O_4Cl$: C, 59.47; H, 5.35. Found: C, 59.36; H, 5.36.

**Photochemical Isomerization of Dimethyl 1-Chloro-2-(1-phenethyl)maleate (36Z).** A solution of **36Z** (1.48 mmol) in benzene (130 mL) was irradiated under nitrogen with a low pressure mercury lamp at room temperature for 1 h. Solvent was removed under reduced pressure, leaving an oil, the NMR spectrum of which showed a mixture of **36Z** and dimethyl 1-chloro-2-(1-phenethyl)fumarate (**36E**) (δ 1.56 (d, 3 H, $J$ = 7.2 Hz), 3.53 (s, 3 H), 3.79 (s, 3 H), 4.75 (q, 1 H, $J$ = 7.2 Hz), 7.29 (s, 5 H)).

# Reactions of Carboxylic Acids with "Phosphonium Anhydrides"

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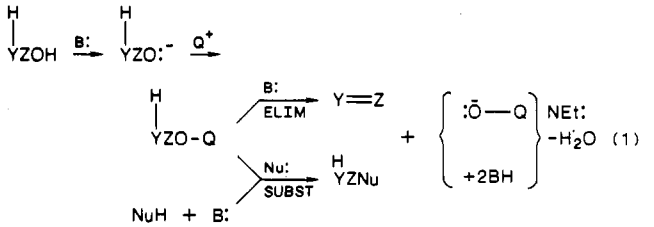
General considerations are outlined for a reagent to extract oxygen from organic molecules by an equivalent of dehydration. Reagents, $(R_3P^+)_2O$, $2OTf^-$, were created for the purpose and subjected to a preliminary study. They were found to convert carboxylic acids readily and rapidly to anhydrides, esters, amides, amidines, benzimidazoles, and cyclic aryl ketones in good yields.

We wished to design a general reagent for the activation of oxygen in organic molecules to effect its removal in an isohypsic manner.[1] The synthetic importance of such a reagent lies in the ubiquitous presence of oxygen in common functional groups and the fact that many important organic transformations involve loss of water. Although many such reagents exist,[2] they are commonly either flawed in some aspect or narrow in their range of activity. The features we sought were (1) selectivity for oxygen; (2) enough reactivity for rapid reaction at moderate temperatures; (3) no potential for redox reactions; (4) no nucleophiles present or formed to create competitive substitution reactions; (5) utility in a range of common solvents and pH values.

The key to a general view of the utility of such a reagent is the summary of eq 1, which shows the reagent Q bonding first as electrophile to an oxygen atom electron pair. This in turn creates a good leaving group of that oxygen atom for elimination or nucleophilic substitution reactions. The




net effect is removal of the elements of $H_2O$ from the reactants.

The design of the ideal reagent requires an element that forms an unusually strong bond to oxygen so that its initial bond formation and its final removal of the oxygen as R-O:$^-$ will be thermodynamically favored. Thus, the central work of the reagent may be seen as the extraction of the oxygen atom from the molecule, with two protons released in its wake to some base. The strongest bond oxygen forms is its bond to phosphorus in the phosphoryl group. Furthermore, although sulfur forms strong bonds also, it is more prone to oxidation-reduction changes, which can create unwanted side reactions (Martin's sulfurane reagent[3] is a powerful dehydrating reagent based on sulfur, which also initiates oxidation-reduction). We

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