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MIGRATION OF DOUBLE BOND IN DECOMPOSITION OF METHYLENEPYRAZOLINE

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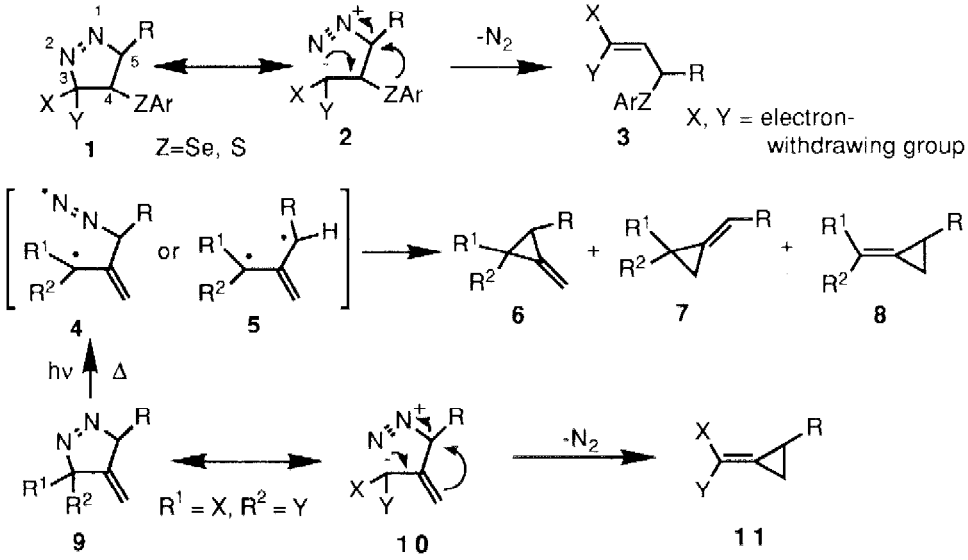
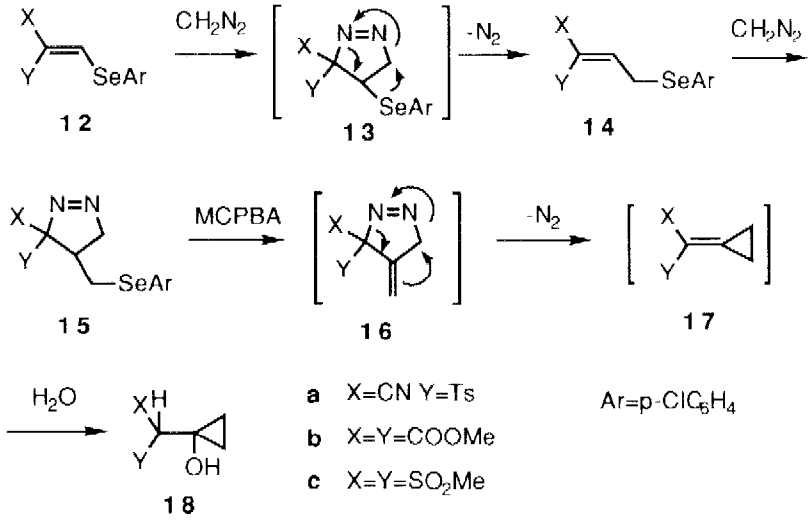
Abstract: Thermal decomposition of 4-methylenepyazolines bearing an electron-withdrawing group at C-3 results in the formation of methylenecyclopropanes derived from migration of the double bond with the breaking of the C-N bond.

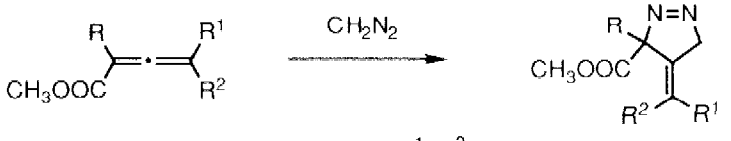
We found that 4-arylseleno or arylthio pyrazolines **1** bearing two electron-withdrawing groups at C-3 underwent facile decomposition with migration of the arylseleno or arylthio group to the C-5 under extrusion of nitrogen, to give allyl selenide or sulfide derivatives **3**, quantitatively.[1,2] These phenomena were explained by a resonance contribution from intramolecular diazonium salt **2**, in which arylseleno or arylthio group migrates concertedly with the breaking of the C-N bond.

Pyrolysis of methylenepyrazolines has been known to give a mixture of isomeric cyclopropanes **6**, **7**, and **8**, resulting from three modes of cyclization derived from a diazenyl radical **4** or a trimethylenemethane intermediate **5**.[3] We study on 4-methylenepyrazolines **9** bearing an electron-withdrawing group at C-3 to investigate the effect of double bond on decomposition of the pyrazoline, in which the double bond is expected to participate in the breaking of the C-N bond under a resonance contribution of intramolecular diazonium salt **10** as shown in scheme, giving a methylenecyclopropane **11**.





When the pyrazoline **15a**, prepared from the reaction of vinyl selenide **12a** bearing two electron withdrawing groups at β-position with excess of diazomethane, was oxidized by MCPBA in dichloromethane at -10°C, the cyclopropyl alcohol **18a** was isolated in 92 % yield. The formation of **18a** can reasonably be explained by the addition of water to the methylenecyclopropane **17a**, which was formed by decomposition of the unstable methylenepyrazoline **16a**, generated by elimination of selenoxide moiety, in a concerted manner with participation of the double bond in the breaking of the C-N bond. It is known that a carbon atom bearing two electron-withdrawing groups chemically behaves like oxygen,[4] suggesting that the methylenecyclopropane **17a** substituted by two electron-withdrawing groups is expected to have chemical properties similar to those of a cyclopropanone which undergoes facile addition of water to give geminal diol.[5] The oxidation of the pyrazolines **15b** and **15c** by MCPBA also gave the cyclopropyl alcohols **18b** and **18c**.



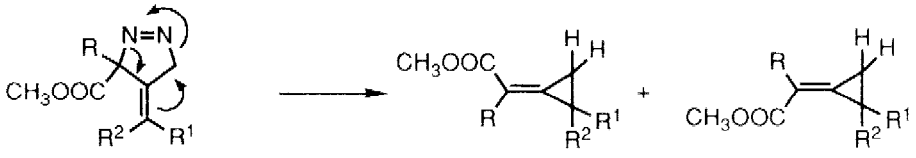
19 a R=p-ClC$_6$H$_4$CH$_2$ R^1=R^2=Ph

b R=p-ClC$_6$H$_4$CH$_2$ R^1=H R^2=ClC$_6$H$_4$

c R=R^1=R^2=Ph

The 4-methylenepyrazolines **20a** and **20b**, bearing an electron-withdrawing group at C-3, were prepared by the reaction of the corresponding allenecarboxylates **19a** and **19b** with diazomethane. These methylenepyrazolines are stable at room

temperature. The 4-diphenylmethylenepyrazoline **20a** was refluxed in benzene for 1 hr to give methylenecyclopropanes **21a** and **22a** in a ratio of 5 : 1, quantitatively. Equivalency of methylene protons of chlorobenzyl group and also cyclopropane methylene protons of these products[6] excludes the methylenecyclopropane **23a**, a normal pyrazoline decomposition product, as **23a** should show nonequivalency of these methylene protons. We assigned the major and the minor products to **21a** and **22a**, respectively, by the following reasons. *p*-Chlorophenyl protons of the major product and cyclopropane methylene protons of the minor product appeared at high fields due to the anisotropy effect of diphenyl groups and *p*-chlorophenyl group, respectively. These two methylenecyclopropanes were also formed by extrusion of nitrogen with participation of the double bond.

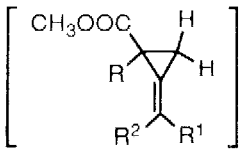


20 **21** **22**

a R=p-ClC$_6$H$_4$CH$_2$ R^1=R^2=Ph

b R=p-ClC$_6$H$_4$CH$_2$ R^1=H R^2=ClC$_6$H$_4$

c R=R^1=R^2=Ph



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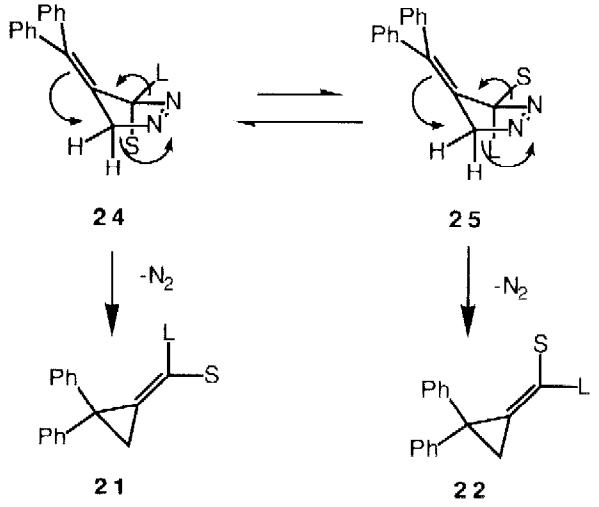
The thermal decomposition of **20b** in refluxing benzene for 1 hr gave two methylenecyclopropanes **21b** and **22b** in a ratio of 3 : 1. The protons *syn* to *p*-chlorobenzyl group in these products appeared at high field. The cyclopropyl methine proton of **21b** and cyclopropyl methylene protons of **22b** appeared at 0.3 ppm higher field compared with the correponding protons of the other isomers.

The methylenepyrazoline **20c**, prepared from the reaction of the allenecarboxylate **19c** with diazomethane, was unstable at room temperature and slowly decomposed to give the methylenepyrazolines **21c** and **22c** in a ratio of 3 : 1 along with a trace amount of **23c**. The methylenecyclopropane **23c** was not primarily formed from **20c** but by secondary isomerization from **21c** and **22c**. The methylenecyclopropane **21c** and **22c** isomerized to **23c** on prolong standing or heating.

In thermal decomposition of **20a,b,c**, sterically less stable methylenecyclopropanes **21a,b,c** were formed as major products: the methylenecyclopropanes **21** with a methoxycarbonyl group *anti* to R^1 and R^2 are sterically less stable than **22** with a methoxycarbonyl group *syn* to R^1 and R^2 because p-chlorobenzyl and phenyl groups

are larger than a methoxycarbonyl group.[7] These results can be rationalized by following consideration. Methylenepyrazoline is expected to prefer a folded conformation such as **24** and **25**, which leads to overlap between the π-bond of a alkylidene substituent and the breaking C-N bonds. The conformation **24** where the large substituent is located at pseudo-equatorial position is more preferred to **25** with the large substituent at pseudo-axial position. The methylenepyrazolines are expected to undergo thermolysis from the folded conformer **24** and **25**. Preferred conformer **24** results in the formation of sterically unstable methylenecyclopropane **21**, while **25** results in the formation of **22** as shown in scheme.



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6. NMR spectrum of **21a**($CDCl_3$): δ 2.33(s, 2H), 3.71(s, 3H), 3.86(s, 2H), 6.80(d, 2H, J=8.3), 7.05(d, 2H, J=8.3), 7.17-7.32(m, 10H). **22a**: δ 1.89(s, 2H), 3.65(s, 3H), 3.80(s, 2H), 7.12-7.30(m, 14H). **21b**: δ 1.59(dd, 1H, J=6.3, 10.9), 2.07(br t, J=10.6), 2.55(dd, J=6.3, 9.9), 3.55(d, 1H, J=15.0), 3.71(d, 1H, J=15.0), 3.77(s, 3H), 6.84(t, 2H, J=8.6), 6.91(d, 2H, J=8.3), 7.06(d, 2H, J=8.6), 7.18(d, 2H, J=8.3). **22b**: δ 1.26(dd, 1H, J=6.3, 10.6), 1.75(br t, 1H, J=10.2), 2.87(dd, 1H, J=6.3, 10.2), 3.57(s, 3H), 3.79(s, 2H), 6.98(d, 2H, J=8.6), 7.16-7.27(m, 6H).
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