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EFFECTS OF HETERO ATOM SUBSTITUENTS IN THE DECOMPOSITION OF PYRAZOLINES: ABNORMAL BEHAVIOR OF METHOXY GROUP COMPARED WITH ARYLTHIO OR ARYLSELENO GROUP

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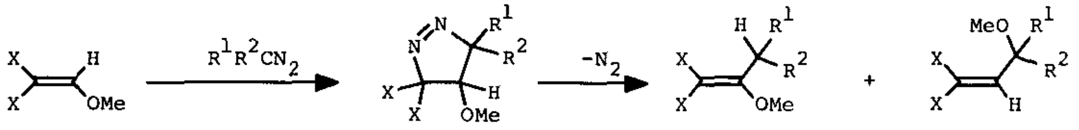
Abstract-Quantitative hydrogen migration was observed on the thermal decomposition of 4-methoxy-substituted pyrazolines with two electron-withdrawing groups at C(3) except some trans-5-alkyl-4-methoxypyrazolines accompanied with methoxy migration.

Decompositions of pyrazolines are a field of considerable interest for a long time[1]. We reported that vinyl sulfides, geminally substituted with two electron-withdrawing groups, reacted with diazoalkanes to give 4-arylthiopyrazolines, which decomposed to allyl sulfides by migration of 4-arylthio group to C(5) with loss of nitrogen, quantitatively[2]. We also found that 4-arylselenopyrazolines with two electron-withdrawing groups at C(3) undergo thermal decomposition at a lower temperature leading to a facile 4-arylseleno group migration to give allyl selenides. In this reaction, 4-arylseleno group appears to participate more strongly than 4-arylthio group[3]. These findings have prompted us to study 4-alkoxypyrazolines with two electron-withdrawing groups at C(3). In this study, we found quite a different behavior of methoxy group from that of arylthio or arylseleno groups.

Pyrazolines (3a-e) were obtained from the reactions of dimethyl methoxymethylenemalonate (1) with diazoalkanes, and the pyrazolines were much more stable than the pyrazolines bearing 4-arylthio and arylseleno groups. Pyrazoline (3a) on heating in xylene gave quantitatively 4a which is a product formed by hydrogen migration (instead of methoxy migration or cyclopropanation) to C(5) with elimination of nitrogen: mp 73-75°C; NMR δ2.44(s, 3H), 3.69(s, 3H), and 3.77(s, 6H). The thermal decomposition of the pyrazoline (3e) also afforded 4e, quantitatively.

The reaction of 1 with diazoethane gave two isomers of adducts, 3b-trans and 3b-cis



(1) X=COOMe

(2) X=CN

(3)

(4)

(5)

(a) X=COOMe, $R^1=R^2=H$

(b) X=COOMe, $R^1=H$, $R^2=Me$

(c) X=COOMe, $R^1=H$, $R^2=i\text{-}Pr$

(d) X=COOMe, $R^1=H$, $R^2=t\text{-}Bu$

(e) X=COOMe, $R^1=R^2=Me$

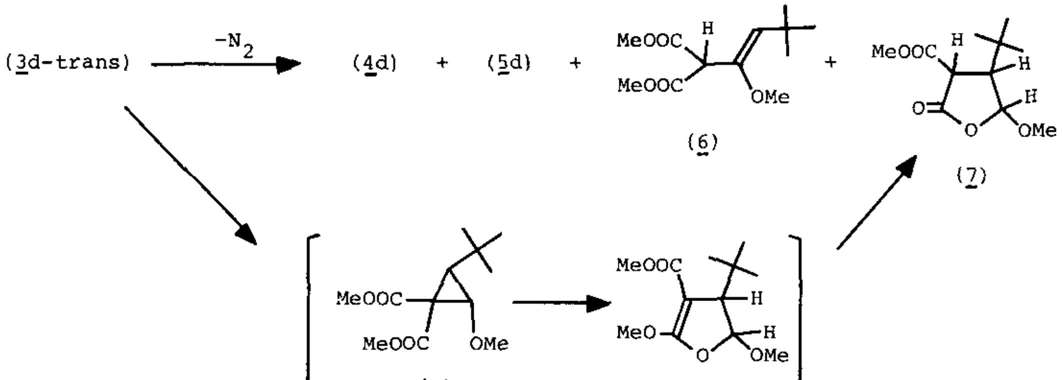
(f) X=CN, $R^1=R^2=H$

(g) X=CN, $R^1=H$, $R^2=Me$

(h) X=CN, $R^1=H$, $R^2=i\text{-}Pr$

(i) X=CN $R^1=H$, $R^2=t\text{-}Bu$

(j) X=CN, $R^1=R^2=Me$

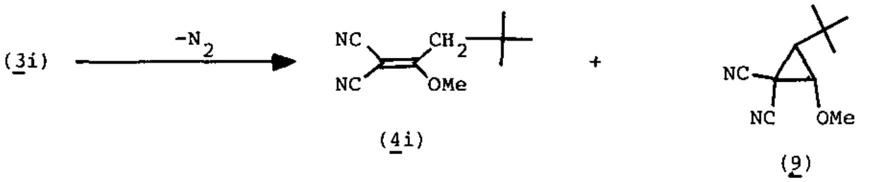


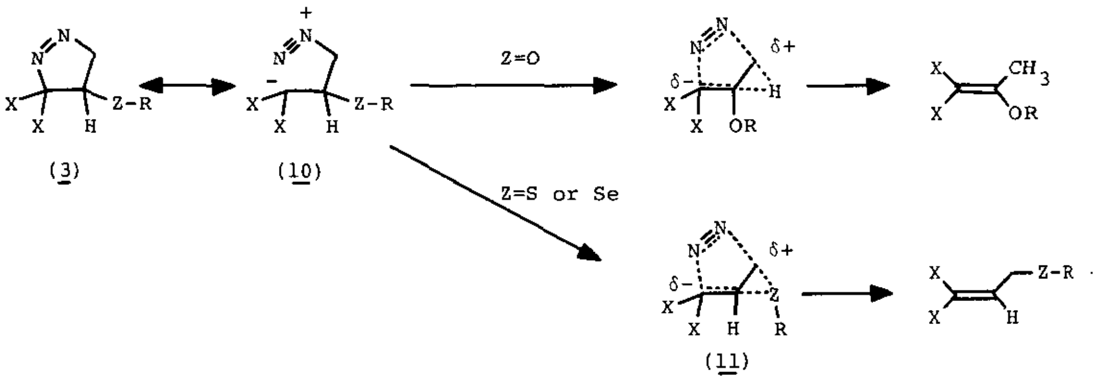
(6)

(7)

(8)

in a ratio of 4:1, which were separated by column chromatography on silica gel; (3b-trans): mp 46-47°C, NMR δ1.47(d, 3H, J=7.5Hz), 3.39(s, 3H), 3.83(s, 3H), 3.91(s, 3H), 4.08(d, 1H, J=3.4Hz), and 4.79(dq, 1H, J=3.4, 7.5 Hz); (3b-cis): mp 28-30°C, NMR δ1.65(d, 3H, J=7.3 Hz), 3.39(s, 3H), 3.83(s, 3H), 3.91(s, 3H), 4.20(d, 1H, J=5.3 Hz), and 4.49(dq, 1H, J=5.3, 7.3 Hz). Decomposition of 3b-cis resulted in quantitative formation of the hydrogen migration product (4b). On the other hand, decomposition of 3b-trans gave a 1:1 mixture of 4b and 5b, where 3b-trans decomposed more slowly than 3b-cis. Compound (5b) is the product formed by methoxy migration, NMR spectrum of which showed absorption at δ1.30(d, 3H, J=6.5 Hz), 3.26 (s, 3H), 3.76(s, 3H), 3.80(s, 3H), 4.07(dq, 1H, J=8.0, 6.5 Hz) and 6.84(d, 1H, J=8.0 Hz). When the pyrazoline (3c-trans) was decomposed, 4c and 5c were obtained in a ratio of 2:3. The decomposition of 3d-trans, substituted with t-butyl group at C(5), required a much higher temperature. The reaction mixture afforded on silica gel chromatography 6 and 7, along with 4d and 5d (4d:5d:6:7 = 9:47:16:28).

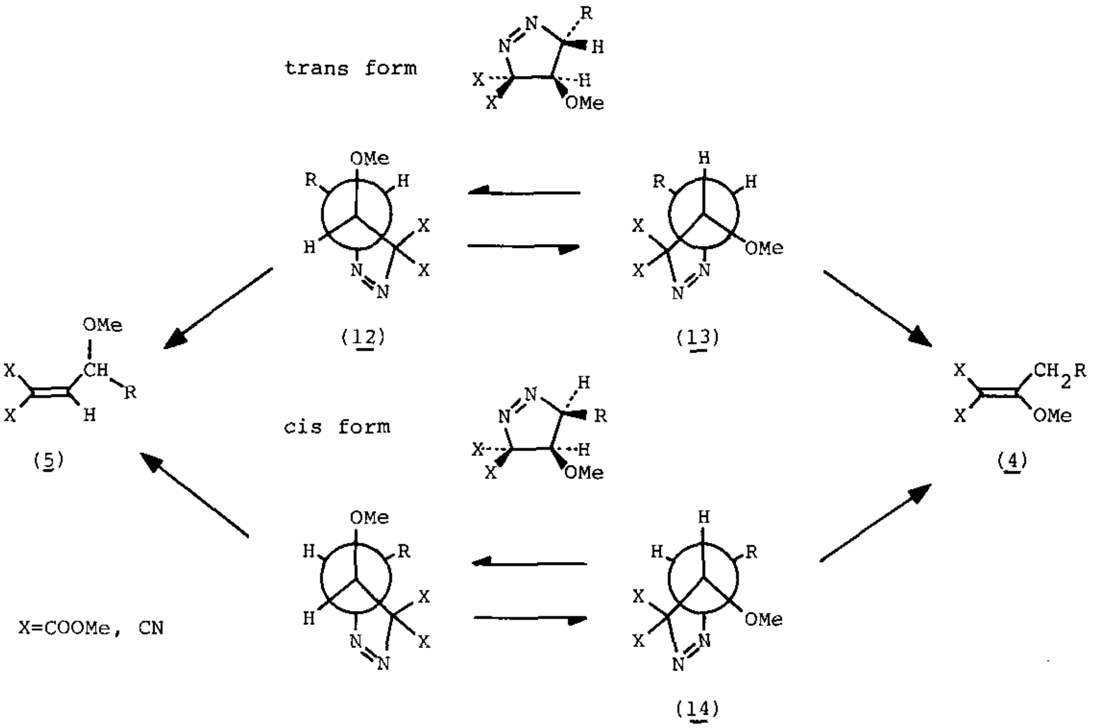




Compound (6) is the product, resulted by 1,3-hydrogen shift of 4d, while 7 is the product arising from cyclopropane (8): 8 undergoes ring opening followed by ring closure and hydrolysis to give the lactone (7) as a final product.

Our observation on the decomposition of 3a-d revealed that the ratio of methoxy migration versus hydrogen migration increases with bulkiness of the trans-substituents at C(5). The pyrazolines (3f-j) formed in the reaction of 2 with diazoalkanes are very unstable and undergo fast decomposition below room temperature without isolation of 3, due undoubtedly to stronger electron-withdrawing cyano groups. All cyanopyrazolines (3f, g, h, j), except for 3i arising from diazoneopentane, underwent only hydrogen migration with loss of nitrogen to give the alkenes (4f, g, h, j). However, 3i gave 4i and the cyclopropane derivative (9) in the ratio of 1:2. In general, as described above, 4-methoxypyrazolines (3) undergo hydrogen migration on decomposition which is contrary to the case of 4-arylthio and arylselenopyrazolines[4]. We believe that 1-pyrazoline geminally substituted with two electron-withdrawing groups has a large contribution from the intramolecular diazonium salt (10) owing to stabilization of the anion by the electron-withdrawing groups.

Thus the developing anion may assist 4-arylthio or arylseleno group participation in decomposition through episulfonium or episelenonium-like transition state (11) in a concerted manner, but methoxy group cannot participate so much as arylthio or arylseleno group: methoxy group would rather promote 1,2-hydride or alkyl shift in view of the facile Pinacol rearrangement or Tiffeneau reaction[5].



We observed that some trans-pyrazolines (3b, c, d) showed methoxy migration along with hydrogen migration. The decomposition is considered to proceed in a concerted manner with simultaneous breaking C-N bond and 1,2-migration of anti-periplaner migrating group. Therefore, hydrogen migration from the trans-pyrazoline requires the conformation (13) in which the repulsion between R (Me, i-Pr and t-Bu) and bulky $C(COOMe)_2$ groups are substantial and hence the energy barrier for hydrogen migration is high. Thus, reluctance of hydrogen migration may lead to the unfavorable methoxy migration to occur via another conformation (12), which does not have such steric repulsion. On the other hand, hydrogen migration in cis-pyrazoline (3b-cis) does not require such steric repulsion as shown in 14, which is in accord with the fact that the cis-pyrazoline decomposed faster than the trans-pyrazoline, to give the hydrogen migration product predominantly. Furthermore, in the decomposition of 3b-trans of which 4-methoxy was replaced by benzoyloxy, only hydrogen migration was observed, which is arising from reducing of migratory aptitude by benzoyl group. In the case of the pyrazoline (3e) formed from 2-diazopropane, both conformation for hydrogen migration and methoxy migration require same steric repulsion, so facile hydrogen migration occurred. These different migration behaviors on decomposition between pyrazolines having 3,3-dicyano and 3,3-bis-(carbomethoxy) substituents are considered to be due to the difference in their bulkiness as well as their electron-withdrawing abilities.

REFERENCES AND NOTES

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