J. CHEM. SOC., CHEM. COMMUN., 1983

The Participation and Migration of a Sulphur Atom Substituent in the Decomposition of Pyrazolines

Masashi Hamaguchi,* Shin-ichi Miyazaki, and Toshikazu Nagai

Department of Chemistry, College of General Education, Osaka University, Toyonaka, Osaka 560, Japan

When appropriate vinyl sulphides, which are activated by two electron-withdrawing groups at the 2-position, react with diazoalkanes they give 4-arylthio-substituted pyrazolines; these undergo accelerated thermal decomposition in which the arylthio-group migrates to the 5-position, with loss of nitrogen, to furnish exclusively the substituted allyl sulphides.

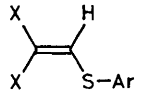
1-Pyrazolines, geminally substituted with two electron-withdrawing groups at the 3-position, are known to undergo thermal decomposition to form products by loss of nitrogen and migration of hydrogen, aryl, or alkyl groups, as well as cyclopropane products.[1]

We have found that 4-arylthio-substituted pyrazolines (**2**) with two electron-withdrawing groups at the 3-position undergo accelerated thermal decomposition and that the 4-arylthio-group participates and migrates to C(5) with loss of nitrogen to give allyl sulphides.† Neither the formation of cyclopropanes nor the migration of hydrogen was observed.

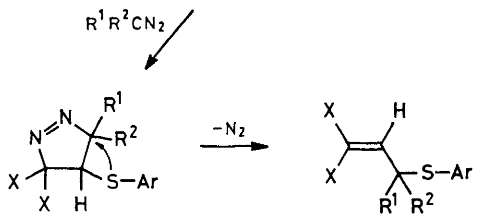
Dimethyl (*p*-nitrophenylthiomethylene)malonate (**1a**) was

---

† Compounds decompose thermally much faster than pyrazolines without the sulphur substituent at the 4-position.

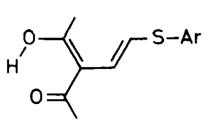


(1a) Ar = p-$NO_2C_6H_4$, X = CO_2Me
(1b) Ar = Ph, X = CO_2Me
(1c) Ar = p-$NO_2C_6H_4$, X = Ac

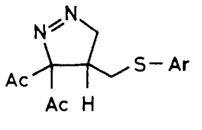


(2a) Ar = p-$NO_2C_6H_4$, $R^1 = R^2 = H$, X = CO_2Me
(2b) Ar = Ph, $R^1 = R^2 = H$, X = CO_2Me
(2c) Ar = p-$NO_2C_6H_4$, $R^1 = H$, $R^2 = Me$, X = CO_2Me
(2d) Ar = p-$NO_2C_6H_4$, $R^1 = R^2 = Me$, X = CO_2Me
(2e) Ar = p-$NO_2C_6H_4$, $R^1 = R^2 = H$, X = Ac

(3a) Ar = p-$NO_2C_6H_4$, $R^1 = R^2 = H$, X = CO_2Me
(3b) Ar = Ph, $R^1 = R^2 = H$, X = CO_2Me
(3c) Ar = p-$NO_2C_6H_4$, $R^1 = H$, $R^2 = Me$, X = CO_2Me
(3d) Ar = p-$NO_2C_6H_4$, $R^1 = R^2 = Me$, X = CO_2Me
(3e) Ar = p-$NO_2C_6H_4$, $R^1 = R^2 = H$, X = Ac

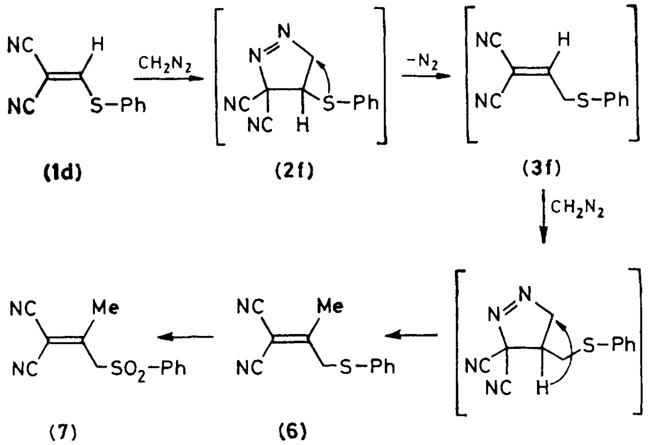


(4) Ar = p-$NO_2C_6H_4$



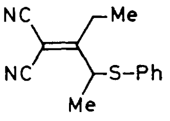
(5) Ar = p-$NO_2C_6H_4$

allowed to react with diazomethane at −10 °C for 1 day and gave the pyrazoline (**2a**), quantitatively, m.p. 106 °C (decomp.), ^{1}H n.m.r. δ 3.77 (s, 3H), 3.95 (s, 3H), 4.48 (dd, 1H, J 8.7, 5.4 Hz), 4.71 (dd, 1H, J 18.8, 5.4 Hz), 5.25 (dd, 1H, J 18.8, 8.7 Hz), and 7.53, 8.17 (ABq, $C_6H_4NO_2$-p).[‡] The pyrazoline (**2a**) decomposed slowly in solution at room temperature with evolution of nitrogen to give the alkene (**3a**), quantitatively, m.p. 56—57 °C; ^{1}H n.m.r. δ 3.82 (s, 3H), 3.85 (s, 3H), 3.95 (d, 2H, J 7.7 Hz), 7.00 (t, 1H, J 7.7 Hz), and 7.40, 8.12 (ABq, $C_6H_4NO_2$-p). Similar results were found when (**1b**) was treated with excess of diazomethane. The structure of the resulting alkene (**3b**) was confirmed by oxidation with *m*-chloroperbenzoic acid (MCPBA) to the corresponding sulphone, m.p. 76—78 °C. Compounds (**3a**) and (**3b**) are products arising from migration of sulphur to C(5) with elimination of nitrogen. When diazoethane was employed, the ^{1}H n.m.r. spectrum of the reaction mixture with (**1a**) showed the presence of *trans*- and *cis*-(**2c**) together with the alkene (**3c**). The alkene (**3c**) was formed quantitatively by heating the reaction mixture, m.p. 58—60 °C. Treatment of (**1a**) with 2-diazopropane gave the pyrazoline (**2d**), m.p. 97—103 °C which decomposed quantitatively to the alkene (**3d**), m.p. 61—62 °C.

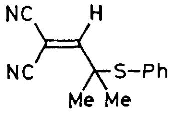


(1d) **(2f)** **(3f)**

(7) **(6)**



(8)



(9)

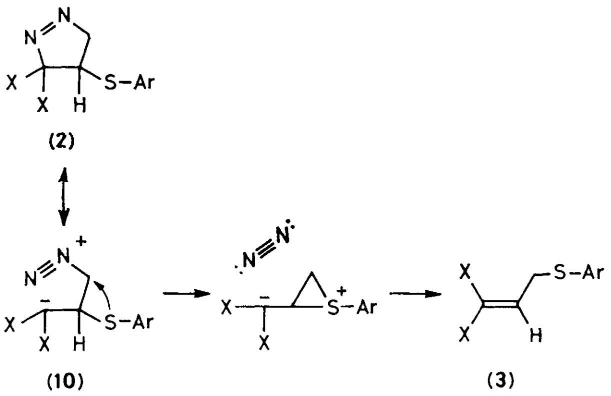
2,2-Diacetyl-*p*-nitrophenylthioethylene (**1c**) was allowed to react with diazomethane at −30 °C for 1 day. Immediately after evaporation of the solvent, the ^{1}H n.m.r. spectrum of the residue showed the presence of a major amount of the pyrazoline (**2e**) and a small amount of (**3e**) together with the ketone (**4**). Fifteen minutes later, the ^{1}H n.m.r. spectrum showed an increase in the amount of (**4**) present. After 4 h, (**2e**) had disappeared completely and the spectrum showed (**4**) and a trace of (**3e**). The presence of only small amounts of (**3e**) at all times is an indication of the fast isomerization of (**3e**) to (**4**). When (**1c**) was allowed to react with excess of diazomethane at room temperature, (**3e**) was trapped with diazomethane to give (**5**) in fairly good yield.

In comparison with (**1a**—**c**) the reaction of phenylthiomethylenemalononitrile (**1d**), bearing stronger electron-withdrawing groups, with diazomethane was extremely fast. When solutions of (**1d**) and diazomethane were mixed at 0 °C, evolution of nitrogen was observed immediately and ceased within ten seconds. Evaporation of the volatile component left an oily residue, the ^{1}H n.m.r. spectrum of which showed the formation of the alkene (**6**), from the reaction of (**1d**) with two moles of diazomethane. The alkene (**6**) was oxidized with MCPBA to the corresponding sulphone (**7**), m.p. 91—93 °C. The 1 : 1 product (**3f**) was not detected even under conditions which allow the recovery of a large amount of the starting material. This indicates that pyrazoline (**2f**) is unstable and that the alkene (**3f**) is more reactive towards diazomethane than (**1d**). The reaction with diazoethane also gave the 1 : 2 product (**8**) together with a trace of the 1 : 1 product. A bulky substituent on the 1 : 1 product might cause it to be less reactive than the starting material and allow it to be isolated. When (**1d**) was treated with 2-diazopropane, the 1 : 1 product (**9**) was isolated in good yield, since the bulky 1-phenylthio-1-methylethyl group hinders further reaction.

As described above, migration of the 4-sulphur substituent of pyrazolines and elimination of nitrogen has occurred. However, it has been shown that a 4-oxygen substituent on pyrazolines, with two electron-withdrawing groups at the 3-position, does not migrate, but instead the hydrogen on

---

[‡] The structures of all the isolated products were supported by ^{1}H n.m.r., i.r., and elemental analysis.



Scheme 1

C(4) migrates exclusively to C(5) with elimination of nitrogen on decomposition.[2] We believe that 1-pyrazoline geminally substituted with two electron-withdrawing groups has a large contribution from the intramolecular diazonium salt (**10**) as a resonance form owing to stabilization of the anion by the two electron-withdrawing groups. The ability of sulphur substituents to accelerate the decomposition by migration and the reluctance of oxygen substituents to migrate could be explained by the mechanism shown in Scheme 1.[3]

Received, 1st October 1982; Com. 1162

References

1 D. S. Wulfman, G. Linstrumelle, and C. F. Cooper, 'Synthetic Applications of Diazoalkanes,' in 'The Chemistry of Diazonium and Diazogroups,' ed. S. Patai, Wiley, New York, 1978, p. 821.

2 The ^{1}H n.m.r. spectra of the reaction mixture from the thermal decomposition of the analogue of (**1**) (OMe in place of SAr) showed the quantitative formation of hydrogen-migration products. Also see, F. D. Popp and A. Catala, *J. Org. Chem.*, 1960, **26**, 2738.

3 It has been shown that a 2-sulphur substituent accelerates a S_N1 reaction to give an episulphonium intermediate owing to strong neighbouring-group participation. Oxygen substituents do not seem to participate as strongly as those of sulphur. See, H. Böhme and K. Sell, *Chem. Ber.*, 1948, **81**, 123.