Pyrazolines IX. Chemistry of some 3-cyano-3-carbomethoxy-1-pyrazolines[1]

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Product and kinetic studies have been made on the pyrolysis of a series of 3-cyano-3-carbomethoxy-1-pyrazolines substituted at C-4 with a methyl and an aryl group (phenyl, *p*-methoxyphenyl, and *p*-nitrophenyl). Evidence is presented supporting a transition state structure in which little progress to bond breaking of the C-5 to N bond has taken place at the transition state. The product distribution is largely dependent on the stereochemistry of the initial pyrazoline and to a lesser degree on the nature of the aryl group at C-4. The *cis* pyrazolines gave products resulting primarily from aryl migration while the *trans* pyrazolines gave products predominantly from methyl migration.

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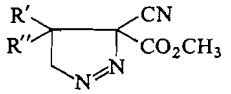
As a continuation of our interest in the mechanism of the pyrolysis of pyrazolines we have extended our studies to a series of 3-cyano-3-carbomethoxy-1-pyrazolines (**1**) substituted with a variety of groups at C-4 having a known stereo-



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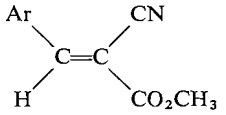
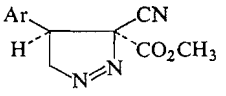
chemical relation to the substituents on C-3. As the mechanism for the pyrolysis reaction evolves it becomes apparent that a spectrum of mechanisms may develop based on the nature of substituents attached to the ring carbons. Earlier studies on the kinetics (1) and stereochemistry (2) for the pyrolysis of **1** have indicated a change of mechanism occurs in going from pyrazolines substituted with one electron withdrawing group at C-3 to those with two electron withdrawing groups at C-3. It is our purpose in the present paper to evaluate this change in more detail. Recently Hamelin and Carrie (3–5) have reported results on a closely related series of compounds which differ primarily by the use of a carboethoxy group at C-3 rather than a carbomethoxy group. Because of this overlap we will emphasize that chemistry which we can add to their contributions.

Preparation of Pyrazolines

The pyrazolines for this study were all prepared by the addition of diazomethane to the appropriate methyl α-cyanoacrylate and are shown in Chart 1. Compounds **2–4** are isolated in the *trans*[2] form, from the condensation of benzaldehyde with methyl cyanoacetate. The *trans* form of compounds **8–10** is isolated as the only product from the pyrazolines **5–7** (herein, 6, and 7). The *cis* form of **8** and **10** are derived from *cis–trans* isomeric mixtures obtained by equilibration followed by separation and purification.



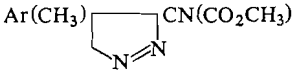
2 Ar = C_6H_5
3 Ar = *p*-$CH_3OC_6H_4$
4 Ar = *p*-$NO_2C_6H_4$



5 Ar = C_6H_5
6 Ar = *p*-$CH_3OC_6H_4$
7 Ar = *p*-$NO_2C_6H_4$

$Ar(CH_3)C{=}C(CN)CO_2CH_3$

cis and *trans* **8** Ar = C_6H_5
trans **9** Ar = *p*-$CH_3OC_6H_4$
cis and *trans* **10** Ar = *p*-$NO_2C_6H_4$



cis and *trans* **11** Ar = C_6H_5
trans **12** Ar = *p*-$CH_3OC_6H_4$
cis and *trans* **13** Ar = *p*-$NO_2C_6H_4$

CHART 1

A complication which continually appears in our work is the ease by which the *cis* and *trans* forms of the α-cyanoacrylates can be equilibrated. The sensitivity of **8** to base and heat can be illustrated by the following. After 2 h at room temperature a solution of 0.5 mmoles of *cis* **8** and 0.5 mmoles of pyridine in 0.6 ml of deuteriochloroform was found to be changed to a mixture of *trans* **8** and *cis* **8** in the ratio of 1:3 respectively.

[1]Taken in part from the Ph.D. Thesis of Y. Y. Wigfield, University of British Columbia, Vancouver, B.C., April, 1969.

[2]*Cis* and *trans* throughout this paper define the relative position of the carbomethoxy group to the aryl or benzyl group on the vicinal carbon.

After 30 min at 140° *trans* **8** is converted to the equilibrium mixture of *trans* **8** and *cis* **8** of 2:1. It has in fact been pointed out in the literature that similar olefins can be titrated reversibly as monobasic acids (8).

Base catalysis appears responsible for the following observations in the pyrazoline syntheses. Attempts to prepare *cis* **5**, as a mixture with *trans* **5**, from a mixture of *cis* and *trans* **2** gave only *trans* **5**; and examination of the reaction mixture after partial reaction showed that all of the *cis* **2** originally present had been converted to the more stable *trans* **2**. Synthesis of *trans* **13** from pure *trans* **10** gave yields of only 53% although *trans* **13** was easily isolated as it was only slightly soluble in the reaction medium. Examination of the remaining solution showed the presence of *cis* **13**. Reaction of *trans* **10** with less than one molar equivalent of diazomethane provided a reaction mixture containing *cis* and *trans* **10** and *cis* and *trans* **13**.

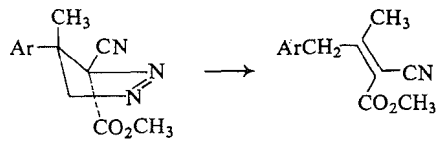
Our interpretation of these results is that the pyrazolines are sufficiently basic to induce equilibration of the α-cyanoacrylates and this is supported by some observations reported below. The degree to which isomerization occurs will depend on: (*1*) the rate of isomerization reactions, which is dependent on the olefin structure, (*2*) the concentration of the reactants, which is affected by the solubility of the pyrazolines, and (*3*) the time of contact between the pyrazoline and olefin, which is affected by the rate of pyrazoline formation and (see below) the rate of pyrazoline pyrolysis. We have not evaluated these three factors in detail in the present report.

The pyrazolines *trans* **11–13** and *cis* **13** were crystalline and as such were stable enough to be fully characterized. The pyrazolines *cis* **11** and **13** were readily distinguished from *trans* **11** and **13** in that the C-5 hydrogens gave a single broad peak for the *cis* series and an AB quartet for the *trans* series with $J \simeq 17$ Hz and $\Delta \simeq 0.5\,\tau$. Pyrazoline **7** on one occasion crystallized, indicating a definite occurrence of such a species, and gave an apparent m.p. of 45 °C. Recently the spectra of a number of such pyrazolines at low temperatures have been reported (*9*).

Pyrolysis of Pyrazolines

The only product formed in the reaction of **2–4** with diazomethane was the *trans* form of **8–10**. The formation of a single isomer has been noted earlier (6) and the *trans* stereochemistry is consistent with a mechanism involving concerted migration of hydrogen from C-4 to C-5 on the side *trans* to the leaving nitrogen (10,11).

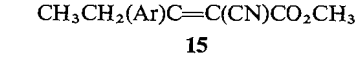
The pyrazolines *cis* **11** and *cis* **13** on pyrolysis gave the olefin **14**, resulting from migration of the aryl group, as the major product (see runs 20–24 in Table I). The stereochemistry of this olefin was predominantly *cis* as predicted by the model reaction. The *trans* **14** is believed to be



cis **14** chief product

formed by isomerization of the initially formed *cis* **14**.

The reaction products from the *trans* isomers of pyrazolines **11–13** are much more complicated and are presented in runs 1–19 in Table I. In addition to aryl migration there is also methyl migration to give the methyl α-cyano-β-ethylcinnamates (**15**) and the formation of appreciable amounts of methyl 2-methyl-2-aryl-1-cyanocyclopropanecarboxylates (**16**). Not all of the products have been isolated pure due to complications resulting from the ease of *cis–trans* isomerization



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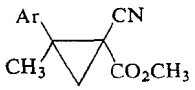

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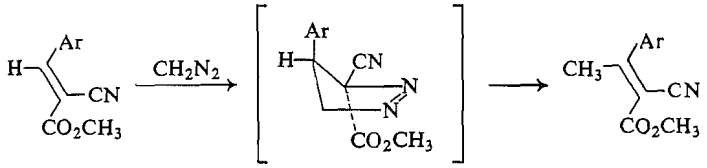


2–4 *trans* **8–10**

TABLE I

Product distribution for the pyrazoline decompositions under a variety of conditions

		Conditions			Products					
					Ar migration		methyl migration		cyclopropanes	
Run	Compound	solvent	time(h)	temperature (°C)	*trans* **14**	*cis* **14**	*trans* **15**	*cis* **15**	*trans* **16**	*cis* **16**
1	*trans* **11**	benzene	0.5	70	29	3	50	2	13	3
2	*trans* **11**	benzene	2.0	70	26	5	52	1	13	3
3	*trans* **11**	benzene	6.5	70	22	9	49	3	14	3
4	*trans* **11**	tetralin	8.0	60	19	13	30	20	9	9
5	*trans* **11**	nitrobenzene	2.0	70	20	13	49	4	5	9
6	*trans* **11**-5,5-d_2	nitrobenzene	2.0	70	20	16	48	4	2	10
7	*trans* **11**	neat	2 mos	room temperature	19	13	50	3	5	10
8	product from *trans* **11** (benzene)	$CDCl_3$(Py)	29.0	room temperature	18	13	50	3	13	3
9	product from *trans* **11** (benzene)	$CDCl_3$(Py)	equilibrium	room temperature	18	13	33	20	13	3
10	product from *trans* **11** (benzene)	neat	2.0	140	17	15	32	20	13	3
11	*trans* **12**	benzene	2.0	70	38	4	47	0	8	3
12	*trans* **12**	tetralin	8.0	60	27	17	39	11	0	6
13	*trans* **12**	nitrobenzene	2.0	70	27	11	52	0	2	8
14	*trans* **12**	neat	2 mos	room temperature	32	9	50	4	3	2
15	*trans* **12**	formamide	10 min	30	19	15	41	7	5	11
16	*trans* **13**	benzene	2.0	70	13	7	53	6	17	4
17	*trans* **13**	nitrobenzene	2.0	70	16	18	37	12	8	9
18	*trans* **13**	tetralin	2.0	70	10	10	25	27	20	7
19	*trans* **13**	formamide	10 min	30	8	8	49	9	4	22
20	*cis* **11**	benzene	2.0	70	5	91	0	0	0	4
21	*cis* **11**	nitrobenzene	2.0	70	36	64	0	0	0	0
22	*cis* **11**	neat	24.0	room temperature	11	86	0	0	0	3
23	*cis* **13**	benzene	4.0	70	7	77	0	0	0	16
24	*cis* **13**	nitrobenzene	20 min	70	8	84	0	0	0	8

in the olefin series. From *trans* **13** we have isolated *trans* **15**, *cis* **16**, *trans* **16**, a mixture of *cis* and *trans* **15**, and a mixture of *cis* and *trans* **14**. Hayashi (12) has reported the nuclear magnetic resonance (n.m.r.) spectra of related olefins and his data assists our stereochemical assignments. The stereochemistry of the cyclopropanes was readily determined since the *trans* **16** ring, when heated to 175° for 30 min, opened to a γ,δ-unsaturated ester (1,13) while *cis* **16** did not. Thus, characteristic n.m.r. peaks for all of the components in the product could be found so that product analysis on the crude mixtures could be made. In addition during the pyrolysis (for the *p*-nitrophenyl series only) some of the pyrazoline was isomerized to a 2-pyrazoline by tautomerization of a C-5 hydrogen.

Figures 1 and 2 show the n.m.r. analysis of runs 2 and 10 and clearly illustrate the presence of the indicated isomers due to changes in relative peak heights. Some of the *trans* cyclopropane **16** has rearranged as evidenced by the reduction of the τ 8.38 peak in Fig. 2. The data in Table I is reproducible to 2%.

Equilibration of the olefin products is achieved by the addition of a trace of pyridine (run 9) and heat (run 10) demonstrating the sensitivity of these compounds to base and heat. The product distribution in tetralin (runs 4, 12, 18) shows both olefins **14** and **15** close to equilibrium while in benzene (runs 2, 11, 16) shows mainly *trans* **14** and **15**. The pyrazolines are only slightly soluble in benzene. The greater solubility in tetralin maintains a higher concentration of pyrazoline to act as a base catalyst for the isomerization of these olefins. Nitrobenzene is intermediate in its effect.

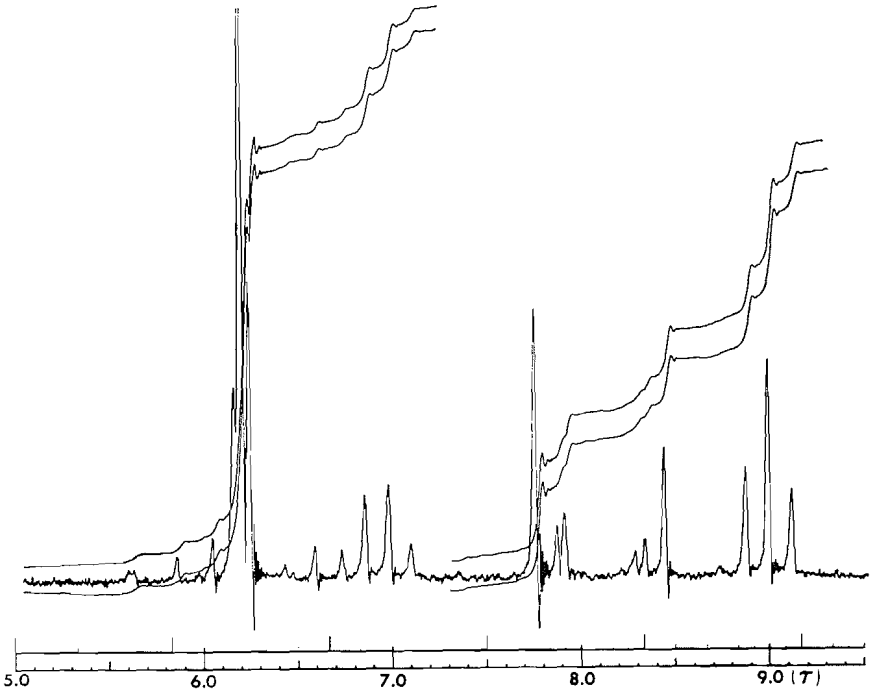


FIG. 1. The nuclear magnetic resonance spectrum of the product from run 2, Table I.

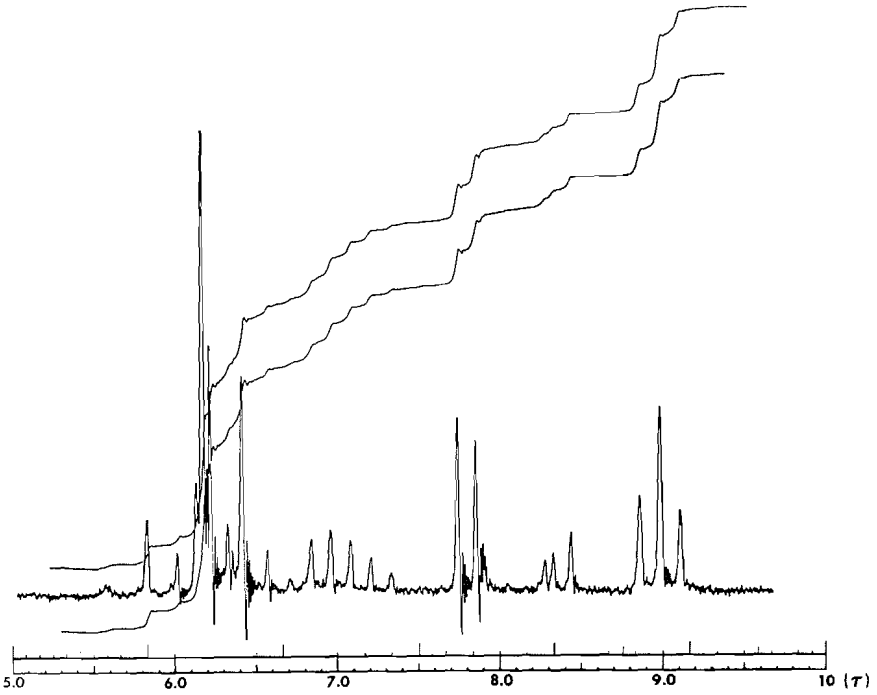


FIG. 2. The nuclear magnetic resonance spectrum of the product from run 10, Table I.

TABLE II

Rate constants and activation parameters for the pyrolysis of 1-pyrazolines

Compound	Solvent	Temperature (°C)	$k \times 10^4$(sec^{-1})	ΔH†(kcal/mole)	ΔS†(e.u.)
trans **11**	nitrobenzene*	44.9	2.06, 2.06		
trans **11**	nitrobenzene*	49.8	3.73±0.04		
trans **11**-5,5-d_2	nitrobenzene	49.8	3.66, 3.76		
trans **11**	nitrobenzene*	54.8	6.41±0.09	22.2	−5.67
trans **11**	tetralin	54.8	2.05, 2.05		
trans **11**	nitrobenzene*	64.9	18.0, 17.8		
trans **12**	nitrobenzene*	35.0	0.86 (calcd.)		
trans **12**	tetralin	35.0	0.024 (calcd.)		
trans **12**	formamide	35.0	88.5, 85.9		
trans **12**	nitrobenzene *	44.9	2.51, 2.52		
trans **12**	nitrobenzene *	49.8	4.22, 4.30		
trans **12**	nitrobenzene *	54.8	7.36±0.09	20.8	−9.58
trans **12**	tetralin	54.8	2.77, 2.79		
trans **12**	nitrobenzene *	64.9	19.5, 18.9		
trans **12**	nitrobenzene	75.2	49.8 (calcd.)		
trans **12**	tetralin	75.2	27.6, 27.5		
trans **12**	decalin	75.2	15.0, 15.1		
trans **13**	nitrobenzene*	44.9	2.09, 2.03		
trans **13**	nitrobenzene*	49.8	3.75, 3.78		
trans **13**	nitrobenzene*	54.8	6.62, 6.53	23.0	−3.19
trans **13**	tetralin	54.8	1.56, 1.56		
cis **13**	nitrobenzene	54.8	9.33, 9.23		
trans **13**	nitrobenzene*	64.9	18.9, 18.9		

*Runs used for the calculation of ΔH† and ΔS†.

Kinetics of the Pyrolysis Reaction

Further to the product studies we have carried out a kinetic study on the pyrolysis reaction for those pyrazolines which were crystalline. The apparatus and procedure for this study is described in a following paper (14). The weighed sample was added to 50 ml of solvent and the nitrogen evolved was measured in a gas burett. Runs were normally carried to over 80% completion. The V_∞ used was the calculated value and was shown to be within 2% of the observed value. A typical run is illustrated in Fig. 3. The results of this study are summarized in Table II. The solvents chosen were limited by the low solubility of the pyrazolines in benzene and hydrocarbon solvents. Standard error calculations showed that the limiting error is due to control of the temperature to ±0.1°.

Discussion

The value of the secondary α-deuterium kinetic isotope effect of $k_H/k_D = 1.01 \pm 0.07$ suggests that at the transition state there is little progress in the bond breaking of the C-5 to N bond. This is a major change in mechanistic detail from that found in 1-pyrazoline-α,α,α′,α′-d_4 ($k_H/k_D = 1.13$ per deuterium (15)), 3-methyl-3-carbomethoxy-5,5-d_2 ($k_H/k_D = 1.11$ per deuterium (14)), and the symmetric azo compound azobis-α-phenylethane-α,α′-d_2 ($k_H/k_D = 1.14$ per deuterium (16)). In the unsymmetric azo compound, α-phenylethylazomethane, with 3-deuteriums on the methyl, $k_H/k_D = 0.99$ per deuterium (16). The absence of an isotope effect in this case was attributed to a stepwise breaking of the two C—N bonds.

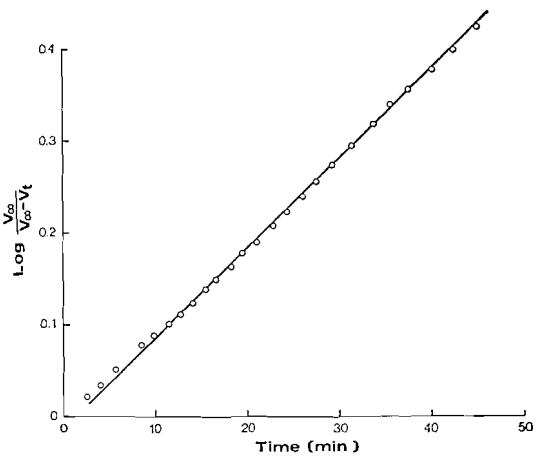
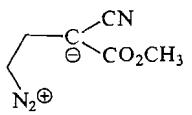


FIG. 3. Rate plot for *trans*-3-carbomethoxy-3-cyano-4-methyl-4-phenyl-1-pyrazoline (*trans* **11**) at 49.8 °C in nitrobenzene.

We also see from the kinetic results in Table II that there is negligible effect on the rate in going from *p*-methoxyphenyl to phenyl to *p*-nitrophenyl where the rate constants are 7.36, 6.41, and 6.57 respectively in nitrobenzene at 54.84°. This suggests that migration of the aryl group and the resulting effect of such participation has also progressed to a negligible degree in the transition state. Here again this is a major change from that observed in 3-methyl-3-carbomethoxy-1-pyrazoline-4,4-d_2 which showed an overall isotope effect of k_H/k_D of 1.36 attributable to considerable participation by the C-4 hydrogen in the transition state for that reaction (14).

The product analyses provide further information concerning the reaction mechanism. From this data we would like to be able to clearly determine whether after the transition state there is the opportunity for bond rotation as might be anticipated for an intermediate of the zwitterion type illustrated by **17**. The occurrence of olefin products of mixed stereochemistry suggests that



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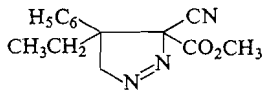

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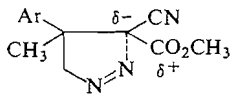
such is the case. However, the mixed stereochemistry in the olefin products can also be explained by isomerization after initial product formation. To clearly demonstrate this possibility, we pyrolized a pyrazoline **18** in the presence of a less than equimolar amount of *cis* **14**. Upon completion of the pyrolysis a mixture of *cis* **14** and *trans* **14** could clearly be shown to be present due to their n.m.r. peaks at τ 7.87 and 7.77 in the ratio of 54:46 respectively. It is significant that the benzyl olefins (**14**) are more readily isomerized than the aryl olefins (**15**) (see run 8 Table I) and it is the benzyl olefins in the product mixtures which are closest to equilibrium. The following additional observations also speak against **17** occurring as a distinct intermediate with sufficient lifetime for rotation of the C-3 to C-4 bond. The product distribution is largely controlled by the stereochemistry of the initial pyrazoline (compare runs 1–19 with runs 20–24 in Table I). If **17** were a distinct intermediate, it should be common to pyrazolines of both stereochemistries. Product formation from **17** would be expected to be markedly influenced by the ionic character of **17**. Aryl and particularly *p*-methoxyphenyl migration should be markedly favored over methyl or *p*-nitrophenyl. In fact for the *trans* pyrazolines, methyl migration is preferred to aryl migration by a ratio of 1.2:1.8:3 for *p*-methoxyphenyl, phenyl, and *p*-nitrophenyl respectively in benzene. This suggests that at the time the product is determined there is little positive charge at C-5 and there is still a stereochemical restriction controlling which groups migrate. Occurrence of **17** as an intermediate would imply that the transition state should also have a high degree of ionic character. Ionic character in the transition state can be evaluated by the solvent effect on the kinetics (17). The *p*-methoxyphenylpyrazolene (*trans* **12**) gave relative rate constants in tetralin, nitrobenzene, and formamide of $1:34:3.4 \times 10^3$. The change from tetralin to nitrobenzene is less than expected for a truly ionic transition state. However, the change in going to formamide may certainly be attributed to a normal ionic transition state and may imply that in formamide formation of a structure like **17** is fully realized. The negative value of the entropy is not consistent with earlier studies on the pyrazoline pyrolysis reaction where positive values have previously been found (14,18). The negative values of the entropy are consistent with additional constraint in the degrees of freedom of the transition state compared to the starting material. Such an effect is frequently observed in reactions occurring via ionic transition states, however, here again the magnitude of the effect is not as large as found in fully ionized systems.

Conclusions

The pyrazolines in the present study react by a mechanism for which the transition state can be described by **19** in which bond breaking of the C-3 to N bond is well advanced over bond breaking of the N to C-5 bond. This structure has a



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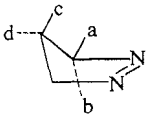

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polar character greater than the starting pyrazoline but less than expected for the zwitterion **17**. The product distribution is largely determined by the *cis* or *trans* geometry of the reacting pyrazoline presumably due to the steric requirements of the substituent groups and their influence on the conformational preference of the starting material and the transition state. This aspect has been

discussed elegantly by Hamelin and Carrie (5). It can be concluded that the smaller group (CN) on C-3 preferentially adopts the pseudo equatorial position (a) of structure **20**. This is particularly evident from the product analysis when (c) and (d) are both phenyl (5) but less evident when (c) and (d) are both methyl (1). The larger group on C-4 appears to prefer the pseudo equatorial position (d). This is evident from the reaction of 3,3-dicyano-1-pyrazolines substituted with different alkyl groups at C-4 (19), from the kinetic evidence of Crawford and co-worker on the reaction of 4,4-dimethyl-1-pyrazoline (18), and from the n.m.r. evaluation of the preferred conformation of some 1-pyrazolines with a hydrogen and an alkyl group at C-4 (11,20).

We prefer to attribute the nonstereospecific olefin formation to isomerization after product formation rather than the alternative formation of a zwitterion intermediate capable of bond rotation before product formation. The stereochemistry of the cyclopropane products is solvent dependent and evidence to date has not permitted a rationalization of this part of the reaction.

Experimental

*Methyl trans-α-Cyano-β-methylcinnamate (trans **8**)*

Treatment of methyl *trans*-α-cyanocinnamate (**2**) (21) in benzene with excess diazomethane at 0 °C gave, on evaporation of the solvent at 0 °C, an unstable oil which decomposed to give nitrogen and methyl *trans*-α-cyano-β-methylcinnamate (*trans* **8**), b.p. 122° at 0.2 mm, m.p. 43–44 °C. The absence of *cis* **8** was revealed through a comparison of the n.m.r. spectrum with that recorded in the literature for the *cis–trans* mixture (12).

*Methyl trans-α-Cyano-β-methyl-p-methoxycinnamate (trans **9**)*

Reaction of methyl *trans*-α-cyano-*p*-methoxycinnamate (**3**) (12) by the manner described above gave methyl *trans*-α-cyano-β-methyl-*p*-methoxycinnamate (*trans* **9**), m.p. 90.5–92 °C (lit. (22), m.p. 73–74 °C for the *cis–trans* mixture); n.m.r. ($CDCl_3$) τ 2.48 and 3.02 (doublets with J = 8.8 Hz), 6.08, 6.10, and 7.30.

Anal. Calcd. for $C_{13}H_{13}NO$: C, 67.50; H, 5.67; N, 6.06. Found: C, 67.79; H, 5.81; N, 5.98.

*Methyl trans-α-Cyano-β-methyl-p-nitrocinnamate (trans **10**)*

Addition of diazomethane in ether to methyl *trans*-α-cyano-*p*-nitrocinnamate (**4**), m.p. 177–178 °C (lit. (12), 153–154 °C) in benzene gave after 1 h an unstable solid, m.p. 45° (d), which decomposed to give nitrogen and methyl *trans*-α-cyano-β-methyl-*p*-nitrocinnamate (*trans* **10**), m.p. 119–121 °C (lit. (12), m.p. 153–154 °C); n.m.r. ($CDCl_3$) τ 1.17 and 2.37 (doublets with J = 8.8 Hz), 6.07, and 7.25.

Anal. Calcd. for $C_{12}H_{10}N_2O_4$: C, 58.55; H, 4.09; N, 11.39. Found: C, 58.62; H, 4.29; N, 11.49.

*Methyl cis-α-Cyano-β-methylcinnamate (cis **8**)*

A solution of 8.0 g of distilled methyl *trans*-α-cyano-β-methylcinnamate in 70 ml of ether was irradiated in a silica tube in a Rayonet Photochemical Reactor using 75 W, 250 V, 2537 Å lamps for 2 days. Evaporation of the ether and filtration gave 3.0 g of methyl *cis*-α-cyano-β-methylcinnamate (*cis* **8**), m.p. 75–76 °C; n.m.r. (CCl_4) τ 2.60–3.05 (multiplet), 6.40, and 7.50.

Anal. Calcd. for $C_{12}H_{11}NO_2$: C, 71.64; H, 5.51; N, 6.96. Found: C, 71.78; H, 5.57; N, 7.08.

*Methyl cis-α-Cyano-β-methyl-p-nitrocinnamate (cis **10**)*

Methyl *trans*-α-cyano-β-methyl-*p*-nitrocinnamate (*trans* **10**) was heated at 150° for 2 h, cooled, and slurried with ether (3 × 70 ml). The remaining solid (0.4 g) was crystallized 3 times from methanol to give methyl *cis*-α-cyano-β-methyl-*p*-nitrocinnamate (*cis* **10**), m.p. 158–159 °C; n.m.r. ($CDCl_3$) τ 1.73 ar d 2.67 (doublets with J = 8.5 Hz), 6.30, and 7.43.

Anal. Calcd. for $C_{12}H_{10}N_2O_4$: C, 58.55; H, 4.09; N, 11.39. Found: C, 58.57; H, 4.17; N, 11.53.

*trans-3-Carbomethoxy-3-cyano-4-methyl-4-phenyl-1-pyrazoline (trans **11**)*

Reaction of *trans* **8** with diazomethane in ether gave in quantitative yield after standing overnight white crystals of *trans* **11**, m.p. 93–94 °C (d); n.m.r. ($CDCl_3$) τ 2.68 (multiplet), 4.70, and 5.22 (doublets with J = 18.0 Hz), 6.06, and 8.53.

Anal. Calcd. for $C_{13}H_{13}N_3O_2$: C, 64.16; H, 5.39; N, 17.27. Found: C, 63.95; H, 5.51; N, 17.16.

*trans-3-Carbomethoxy-3-cyano-4-methyl-4-p-methoxyphenyl-1-pyrazoline (trans **12**)*

By a procedure similar to the above *trans* **9** was converted in quantitative yield to *trans* **12**, m.p. 82–83 °C (d); n.m.r. ($CDCl_3$) τ 2.88, and 3.13 (doublets with J = 9.0 Hz), 4.70 and 5.25 (doublets with J = 17.7 Hz), 6.05, 6.20, and 8.52.

Anal. Calcd. for $C_{14}H_{15}N_3O_3$: C, 61.53; H, 5.53; N, 15.37. Found: C, 61.41; H, 5.71; N, 15.21.

*trans-3-Carbomethoxy-3-cyano-4-methyl-4-p-nitrophenyl-1-pyrazoline (trans **13**)*

By a procedure similar to the above *trans* **10** was converted in 50% yield to *trans* **13**, m.p. 101–102 °C (d); n.m.r. ($CDCl_3$) τ 1.80, and 2.63 (doublets with J = 9.0 Hz), 4.65, and 5.06 (doublets with J = 16.4 Hz), 5.95, and 8.46.

Anal. Calcd. for $C_{13}H_{12}N_4O_4$: C, 54.15; H, 4.20; N, 19.43. Found: C, 54.20; H, 4.30; N, 19.20.

The filtrate from the above preparation was evaporated and examined by n.m.r. and found to contain *trans* **13** (5%), *cis* **13** (35%); n.m.r. ($CDCl_3$) τ 1.78 and 2.58 (doublets with J = 8.5 Hz), 4.74, 6.48, and 8.50 and 4-methyl-4-*p*-nitrophenyl-5-carbomethoxy-5-cyano-2-pyrazoline (see below) (60%); n.m.r. ($CDCl_3$) τ 1.73, and 2.40 (doublets with J = 8.8 Hz), 3.19, 3.49, 6.00, and 8.33.

*cis-3-Carbomethoxy-3-cyano-4-methyl-4-phenyl-1-pyrazoline (cis **11**)*

The liquid pyrazoline *cis* **11** was obtained in quantitative yield from the reaction of *cis* **8** with one mole of diazomethane in ether followed by evaporation of the solvent at 0 °C; n.m.r. ($CDCl_3$) τ 2.55–3.0 (multiplet), 4.80, 6.65, and 8.56. No further data could be obtained due to the instability of this compound.

*cis-3-Carbomethoxy-3-cyano-4-methyl-4-p-nitrophenyl-1-pyrazoline (cis **13**)*

Reaction of *cis* **10** with diazomethane gave on evaporation of the solvent at 0° a quantitative yield of *cis* **13**, m.p. 90–91 °C (d); n.m.r. ($CDCl_3$) τ 1.78 and 2.58 (doublets with J = 8.5 Hz), 4.74, 6.48, and 8.50.

Anal. Calcd. for $C_{13}H_{12}N_4O_4$: C, 54.15; H, 4.20; N, 19.43. Found: C, 54.08; H, 4.20; N, 19.41.

Pyrolysis of the Pyrazolines

The conditions for the pyrolyses and the analysis of the product mixtures are given in Table I. When benzene and decalin were used as solvents these solvents were evaporated under reduced pressure after complete pyrolysis and the product analyses were made from the n.m.r. spectrum of the residue in deuteriochloroform. When nitrobenzene and tetralin were used as decomposition solvents the product compositions were measured directly in the same solvents. When formamide was used, the products which were insoluble in these solvents were dissolved in deuteriochloroform to an equivalent volume to the formamide used and n.m.r. spectra were measured in both solvents under identical conditions.

A typical spectrum for the analysis of the product from *trans* **11** is given in Fig. 1. Peak positions characteristic of the individual products for the phenyl, *p*-methoxyphenyl, and *p*-nitrophenyl respectively in $CDCl_3$ in units of τ were: *trans* **14**: 7.77, 7.80, 7.70; *cis* **14**: 5.86, 5.97, 5.72 and 7.87, 7.90, 7.80; *trans* and *cis* **15**: 9.03, 9.00, 8.95 (triplets); *cis* **15**; 6.52, 6.43, 6.32; *trans* **16**: 8.50, 8.50, 8.38; *cis* **16**: 6.67, 6.58, 6.41. In addition the 2-pyrazoline from *trans* **13** was identified by peaks at τ 3.19 and 3.49. The following new compounds were characterized from the product mixtures.

Methyl α-Cyano-β-ethyl-p-nitrocinnamate

The decomposition products from *trans* **13** in benzene were separated by preparative thin layer chromatography (t.l.c.) on silica with carbon tetrachloride and ether (2:1) as solvent. Extraction of the component with R_f = 0.39 with chloroform and crystallization from methanol gave methyl *trans*-α-cyano-β-ethyl-*p*-nitrocinnamate, m.p. 100–101 °C; n.m.r. ($CDCl_3$) τ 1.68 and 2.46 (doublets with J = 8.5 Hz), 6.09, 6.85 (quartet with J = 7.5 Hz), and 8.95 (triplet with J = 7.5 Hz).

Anal. Calcd. for $C_{13}H_{12}N_2O_4$: C, 59.98; H, 4.65; N, 10.76. Found: C, 59.78; H, 4.63; N, 10.88.

A 1:1 mixture of methyl *cis* and *trans*-α-cyano-β-ethyl-*p*-nitrocinnamate was isolated from a thin layer chromatogram on alumina with chloroform. Analysis of the component with R_f = 0.8 provided the following n.m.r. assignments for the *cis* isomer ($CDCl_3$); τ 1.73 and 2.68 (doublets with J = 9.0 Hz), 6.32, 7.09 (quartet with J = 7.5 Hz), and 8.90 (triplet with J = 7.5 Hz).

Methyl trans-2-p-Nitrophenyl-2-methyl-1-cyano-1-cyclopropanecarboxylate

The fraction from the above separation on silica with an R_f of 0.29 was a mixture of the *trans* cyclopropane component and the *cis* and *trans* benzyl olefins (**14**). Recrystallization from methanol gave methyl *trans*-2-*p*-nitrophenyl-2-methyl-1-cyano-1-cyclopropanecarboxylate, m.p. 142–143 °C; n.m.r. ($CDCl_3$) τ 1.75 and 2.48 (doublets with J = 8.8 Hz), 6.10, 7.82, and 8.38.

Anal. Calcd. for $C_{13}H_{12}N_2O_4$: C, 59.98; H, 4.65; N, 10.76. Found: C, 59.70; H, 4.71; N, 10.91.

A sample of this cyclopropane was heated to 175° for 3 h and the residue purified by t.l.c. to give methyl 2-cyano-4-*p*-nitrophenylpent-4-enoate as an oil; n.m.r. ($CDCl_3$) τ 1.79 and 2.45 (doublets with J = 8.5 Hz), 4.41, 4.53, 6.26, 6.44 (quartet with J = 9.0 Hz and 5.8 Hz), 6.71 (quartet with J_{gem} = 14.2 Hz and J = 5.8 Hz), and 6.96 (J_{gem} = 14.2 Hz and J = 9.0 Hz). There was not sufficient sample for microanalysis.

Methyl cis-2-Methyl-2-p-nitrophenyl-1-cyano-1-cyclopropanecarboxylate

Pyrolysis of *cis* **13** in the absence of solvent gave on standing a small amount of crystalline material in addition to the major oily product. Filtration and crystallization from methanol gave the methyl *cis*-2-methyl-2-*p*-nitrophenyl-1-cyano-1-cyclopropanecarboxylate, m.p. 167.5–168.5 °C; n.m.r. ($CDCl_3$) τ 1.78 and 2.54 (doublets with J = 8.8 Hz), 6.41, 7.52, and 8.12 (doublets with J = 5.8 Hz), and 8.19.

Anal. Calcd. for $C_{13}H_{12}N_2O_4$: C, 59.98; H, 4.65; N, 10.76. Found: C, 59.78; H, 4.47; N, 10.67.

This sample was heated at 170° for 2 h with no change.

4-Methyl-4-p-nitrophenyl-5-cyano-5-carbomethoxy-2-pyrazoline

During pyrolysis of *trans* **13** in tetrachloroethylene a precipitate formed which was isolated and crystallized from chloroform to give the 2-pyrazoline (**18**), m.p. 171–172.5 °C; n.m.r. ($CDCl_3$) τ 1.73 and 2.40 (doublets with J = 8.8 Hz), 3.19, 3.49, 6.00, and 8.33. The peak at 3.49 disappeared on the addition of D_2O.

Anal. Calcd. for $C_{13}H_{12}N_4O_4$: C, 54.14; H, 4.20; N, 19.43. Found: C, 54.17; H, 4.35; N, 19.29.

*Methyl cis-4-Phenyl-3-methyl-2-cyano-2-butenoate (cis **14**)*

The product from the pyrolysis of *cis* **11** in benzene was distilled to give a liquid which was 91% *cis* **14** in the presence of 5% of *trans* **14** and 4% of *cis* **16**. The n.m.r. spectrum ($CDCl_3$) showed peaks for *cis* **14** at τ 2.79, 5.86, 6.22, and 7.87.

Anal. Calcd. for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.50. Found: C, 72.74; H, 6.29; N, 6.30.

Equilibration of *cis* **14** with a trace of pyridine gave a ratio of *cis* **14** to *trans* **14** of 42:58 respectively. Peaks in the n.m.r. due to *trans* **14** appeared at τ 2.79, 6.16, 6.22, and 7.77.

trans-3-Carbomethoxy-3-cyano-4-methyl-4-phenyl-5,5-dideuterio-1-pyrazoline

Dideuteriodiazomethane was prepared from diazomethane in ether by exchange with D_2O catalyzed by potassium carbonate. The deuteriodiazomethane was reacted with *trans* **8** to give *trans* **11**-5,5-d_2 which contained 80% deuterium at C-5 as estimated by n.m.r. and mass spectral analysis.

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