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On the Mechanism of the Thermal *N*-Nitropyrazole Rearrangement. Evidence for a [1,5] Sigmatropic Nitro Migration¹

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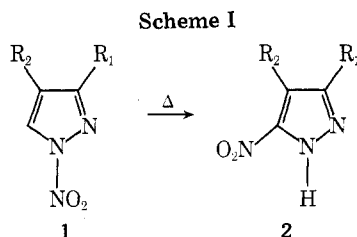
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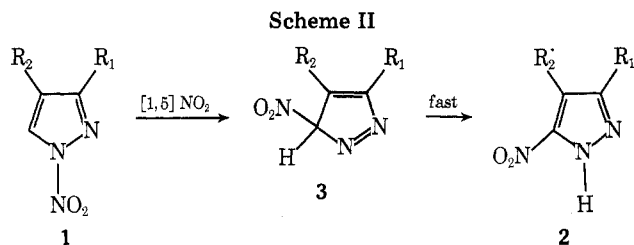
The title reaction, which smoothly proceeds at ca. 150 °C, displays first-order kinetics and is affected neither by acids or bases, nor scavengers for free radicals or for NO_2^+ . Our kinetic studies further showed that replacement of 3(5)H by D has no effect on the rate of this intramolecular process. Solvent effects are surprisingly small. Substituents at the 3, 4, or 5 position exert only modest influence on rates and activation parameters; ΔH^\ddagger values are in the range 30–36 kcal mol⁻¹, ΔS^\ddagger being 2 ± 5 eu. The reaction, which can also be performed in the vapor phase, apparently does not proceed heterolytically; the type of solvent effect points to a transition state which is somewhat less polar than the starting compound. Isomerizations in benzene lead to trace amounts only of the corresponding (1-) phenylpyrazoles. The N–NO₂ bond strength is estimated to be 45–50 kcal mol⁻¹. Hence, a homolytic mechanism involving free (1-) pyrazolyl radicals is highly unlikely. All experimental data are compatible with a rate-determining [1,5] shift of NO₂ to give a 3*H*-pyrazole as an intermediate, which subsequently isomerizes into the 3(5)-nitropyrazole. The first step is discussed in some detail. As the reverse reaction could not be observed, the overall process is markedly exothermic. With 4-substituted 1-nitropyrazoles some denitration (apparently caused by steric hindrance) is competing with rearrangement.

Thermal rearrangement of *N*-nitropyrazoles unsubstituted at the 5 position (1) has been proven to be a convenient method for the preparation of 3(5)-nitropyrazoles (2)^{2,3} (Scheme I). The isomerizations can be performed at moderate temperatures (120–190 °C) in various solvents. Normally, the 3(5)-nitropyrazoles are formed quantitatively; in some instances side reactions, particularly denitration, are observed.

Thermal N → C migration of NO₂ is not restricted to py-

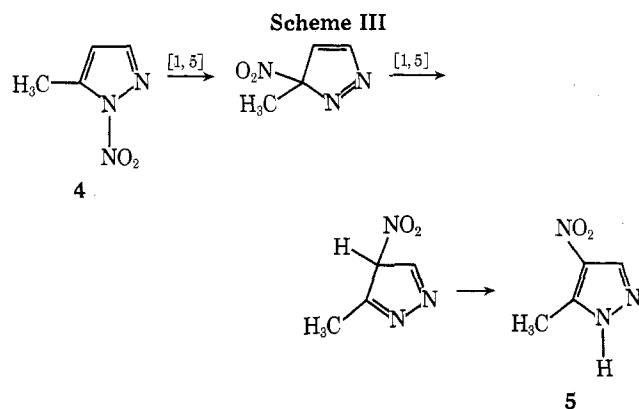


- a, $R_1 = R_2 = \text{H}$
 b, $R_1 = \text{CH}_3$; $R_2 = \text{H}$
 c, $R_1 = \text{C}(\text{CH}_3)_3$; $R_2 = \text{H}$
 d, $R_1 = \text{C}_6\text{H}_5$; $R_2 = \text{H}$
 e, $R_1 = p\text{-NO}_2\text{C}_6\text{H}_5$; $R_2 = \text{H}$
 f, $R_1 = \text{NO}_2$; $R_2 = \text{H}$
 g, $R_1 = \text{H}$; $R_2 = \text{CH}_3$
 h, $R_1 = \text{H}$; $R_2 = \text{C}_2\text{H}_5$



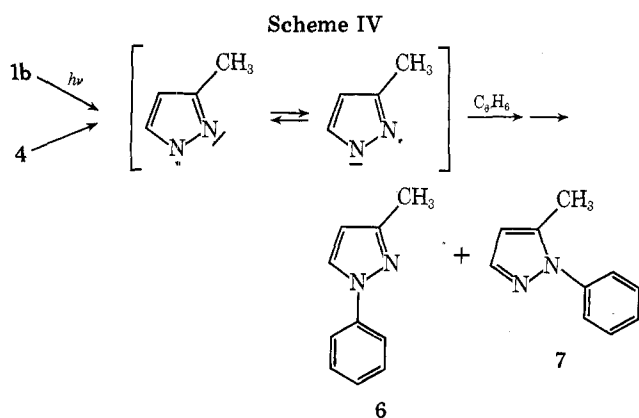
razoles; analogous migrations were found in *N*-nitroindazoles,⁴ triazoles,⁵ and imidazoles.⁶

For the mechanism of the rearrangement of *N*-nitro(pyrazoles), a two-step process has been proposed,^{3,5} involving an unprecedented [1,5] sigmatropic shift of the nitro group and fast rearomatization of the intermediately formed 3*H*-pyrazole (3) (Scheme II). For thermal N → C migrations of alkenyl groups in pyrroles and, recently, imidazoles, similar mechanisms have been suggested.^{7,8} Our proposition was based on the apparent intramolecularity of the *N*-nitropyrazole rearrangement. The isomerization obeys first-order kinetics perfectly and no divergent reaction paths were observed when the thermolyses were performed in the presence of reagents (e.g., phenol, quinoline, and toluene) which may act as catalyst or scavenger of intermediates (see ref 2). Moreover, a sigmatropic process adequately accounts for NO₂ migration to the 5(3) position. Migration to the 4 position has only been ob-

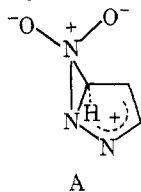


served^{2,3} with a 5-substituted 1-nitropyrazole: 5-methyl-1-nitropyrazole (4) gives 3(5)-methyl-4-nitropyrazole (5) as major product. In this case, formation of a 4-nitropyrazole can be explained by assuming two sequential [1,5] nitro shifts (Scheme III). Formation of a small amount of the 5(3)-nitro isomer **2b** on thermolysis of 4 is the result of a noteworthy side reaction: slow isomerization into the less strained *N*-nitro compound **1b**, followed by rearrangement to **2b**.²

In itself, the differing behavior of 3- and 5-methyl substituted 1-nitropyrazoles excludes a common intermediate. Hence dissociation, viz., initial homo- or heterolysis of the *N*-NO₂ bond, is not involved, as in these cases the resulting pyrazolyl fragments (radical or anion) should give rise to the same (ratio of) products. Recently we showed that *N*-pyrazolyl radicals generated from 3- and 5-methyl substituted pyrazole precursors are, at least at room temperature, indistinguishable.⁹ Thus, photolysis of *N*-nitropyrazoles **1b** and **4** in benzene leads to the same products, viz., isomeric *N*-phenylpyrazoles **6** and **7**, in a 4:1 ratio; apparently these derivatives arose via homolytic aromatic substitution (Scheme IV).



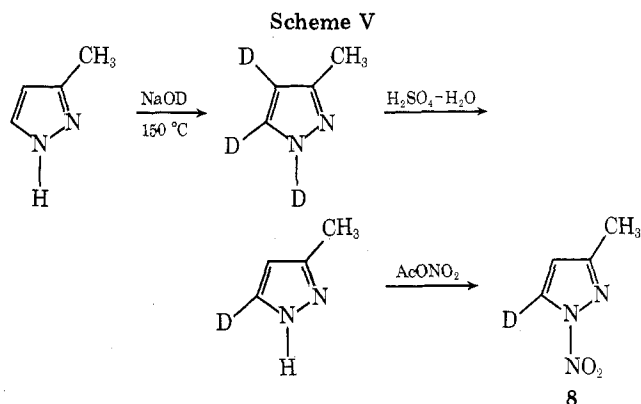
Although the thermally induced, intramolecular rearrangement of *N*-nitropyrazoles obviously proceeds with a high degree of selectivity, more data are needed to define the transition state(s) involved in the NO₂ shift. Information on other, possibly sigmatropic, NO₂ shifts is very scarce,¹⁰ and on the basis of the available data processes involving tight (caged) radical¹¹ or ion pairs cannot be excluded rigorously. Another possibility is that of migration via a reactive intermediate, particularly bicyclic structure A. For the thermal



rearrangements of 3*H*-pyrazoles into *N*-substituted pyrazoles (van Alphen rearrangements,¹² the migrating groups being, e.g., cyano or acyl), analogous bicyclic intermediates have been proposed,¹³ although most authors favor a sigmatropic mechanism.¹⁴

A way to discriminate between these possible modes of NO₂ migration might be determination of activation parameters. However, then first the possibility of tautomerization **3** → **2** (see Scheme II) being rate determining has to be eliminated. Note that intermediate **3** is a 3*H*-pyrazole, and these compounds can only be isolated when the 3 position is disubstituted.¹⁵ Thus tautomerization **3** → **2**, which can be either a [1,5] hydrogen shift or a solvent-assisted proton transfer, is probably faster than remigration of the nitro group. Kinetic parameters for the overall reaction then bear upon the first step(s). Alternatively, if remigration of NO₂ is faster than tautomerization, introduction of D at the 5 position should give rise to a primary kinetic H/D isotope effect.

5-Deuterio-3-methyl-1-nitropyrazole (**8**) was prepared according to Scheme V (cf. ref 16 and 3). A competition experiment with the nondeuterated derivative **1b** at 140 °C (hexachloroacetone solution, isomerization followed by NMR, see Experimental Section) did not reveal a primary isotope effect: $k_{\text{H}}/k_{\text{D}} = 1.0 \pm 0.1$. Hence, hydrogen migration is not involved in the rate-determining step(s).



Results and Discussion

Kinetic Measurements. First, the solvent effect on the rearrangement of a representative *N*-nitropyrazole was studied. The isomerization rate of the 3-methyl derivative **1b** at 140 °C was measured in six solvents of differing polarity (see Table I). Kinetic data are based on the decay of *N*-nitropyrazole, followed by GLC. TLC analysis after completion of the reactions revealed that in all solvents studied the expected product **2b** was formed without detectable amounts of side products.¹⁷ In all solvents, first-order kinetics was observed.

In three solvents of markedly different character (*n*-decane, nitrobenzene, and propylene glycol), rate constants were determined at different temperatures, and from the Arrhenius plots obtained the activation parameters were calculated. The results, together with rate constants at 140 °C in the different solvents, are listed in Table I.

In order to learn about substituent effects, activation parameters were determined for the isomerization of the parent 1-nitropyrazole **1a**, and for the 3-phenyl (**1d**) and 3-nitro derivative (**1f**), in nitrobenzene solution. In addition, the effect of variation in *position* of a (methyl) substituent was examined by measuring the activation parameters for the rearrangement of the 4- and 5-methyl derivatives **1g** and **4**, in *o*-nitrotoluene solution. Again, in all cases first-order behavior was observed.

The kinetic data for the rearrangement of **4** were corrected

Table I. Rate Constants and Activation Parameters for the Rearrangement of 3-Methyl-1-nitropyrazole (1b) in Various Solvents

Solvent	$10^4 k, \text{s}^{-1}$ (140 °C)	$\Delta H^\ddagger, ^a$ kcal mol ⁻¹	$\Delta S^\ddagger, ^a$ eu
<i>n</i> -Decane	3.4 ^b	29.7	-3
Mesitylene	3.8		
Anisole	3.6		
Nitrobenzene	3.5	33.9	+7
<i>N</i> -Methylformamide	4.6		
Propylene glycol	6.4	30.5	0

^a Temperature range 130–170 °C; parameters calculated for 150 °C. ^b The same rate constant was found in 0.08 and 0.008 M solutions.

Table II. Rate Constants and Activation Parameters for the Rearrangement of Some Substituted *N*-Nitropyrzoles in Nitrobenzene

Compd	Substitution	Temp, °C	$10^4 k_{150^\circ}, \text{s}^{-1}$	$\Delta H^\ddagger, ^a$ kcal mol ⁻¹	$\Delta S^\ddagger, ^a$ eu
1a		150–190	0.7	34.9	+4
1b	3-Methyl	130–170	9.3	33.9	+7
1d	3-Phenyl	110–140	72 ^c	30.2	+2
1f	3-Nitro	160–200	0.3 ^{c-e}	37 ^{d,e}	+6 ^{d,e}
1g	4-Methyl	150–190 ^b	0.7 ^e	35.8 ^e	+6 ^e
4	5-Methyl	130–160 ^b	11 ^f	32.7 ^f	+4 ^f

^a Calculated for 150 °C. ^b In *o*-nitrotoluene rather than nitrobenzene. ^c Extrapolated from Arrhenius parameters. ^d Approximation (owing to poorly reproducible GLC analyses). ^e Not corrected for concurrent denitration (see text); denitration of 1g ~10% at 150 °C, ~20% at 190°. ^f Corrected for concurrent N₁ → N₂ nitro migration.

for the concurrent (slow) N₁ → N₂ (→C₃) nitro shift (see Experimental Section). For this side reaction approximate activation parameters could be calculated: log *A* ≈ 16 and *E_A* ≈ 40 kcal mol⁻¹. Kinetic data for the other rearrangements are based merely on decay of starting material. Hence, denitration, as observed on thermolyzing 1f and 1g,³ is not treated as an independent side reaction (vide infra).

Results are summarized in Table II.

Although in solvents of entirely different character *k*_{140°} only varies within a twofold range (Table I); the solvent effect on the activation parameters is evident. As the starting materials have distinct dipole moments (~4.0 D for 1b, benzene solution),^{1a} the higher ΔH^\ddagger and ΔS^\ddagger values in nitrobenzene than in *n*-decane can be understood if the transition state for the rate-determining step has less (di)polar character than the starting material. In nitrobenzene, solvation lowers the energy content of the initial state relative to that in *n*-decane, while for the transition state the differences in solvation are small(er). The relatively high activation entropy in nitrobenzene solution also is a result of decreased solvation in the transition state. The rather low activation parameters observed for the rearrangement of 1b in propylene glycol may result from hydrogen bonding interactions in the probably 3*H*-pyrazole-like transition state.

In the light of the above considerations, a transition state with a marked degree of charge separation is highly unlikely. This also follows from the small substituent effects found (Table II): the fact that a 3-phenyl substituent affects the activation energy more than 3-nitro is incompatible with a polar transition state.

Thus, the most obvious possibilities are those of a concerted NO₂ migration, or migration via an intimate radical pair. A

concerted reaction involving a cyclic transition state normally has $\Delta S^\ddagger < 0$, although for, e.g., [1,5] sigmatropic shifts in cyclopentadienes, values up to +6 eu have been reported.¹⁸ As suggested by both dipole moments and ultraviolet spectra,^{1a} the N–NO₂ bond in *N*-nitropyrzoles has a restricted rotational freedom. Hence, the entropy content of the transition state need not be less than that of the initial state. As the activation parameters in *n*-decane are the least affected by solvation, they are the most appropriate to consider. The value of -3 eu found for the rearrangement of 1b in *n*-decane tallies, in our opinion, with a sigmatropic NO₂ migration.

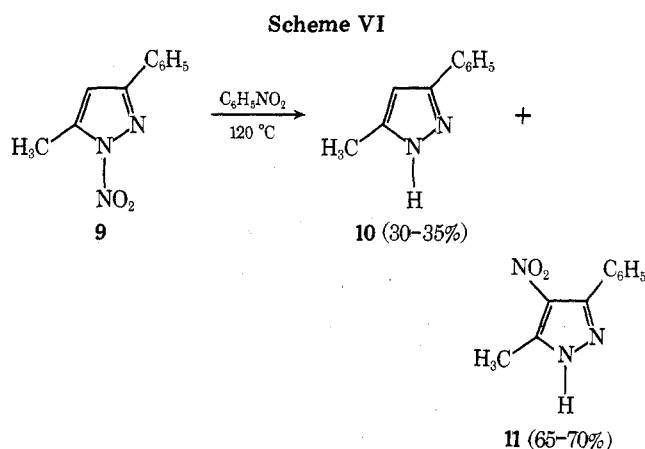
The magnitude of the activation energy is also more compatible with a concerted rearrangement than with a radical-pair process. The value of the N–NO₂ bond dissociation energy is unknown, but *N*-nitropyrzoles may be compared with dialkylnitroamines. For *D*_(N–NO₂) in *N,N*-dimethylnitroamine, values ranging from 41 to 53 kcal mol⁻¹ have been reported.¹⁹ On the basis of the heats of formation of dimethylnitroamine ($\Delta H_{f(g)}^\circ = 0$)²⁰ and the dimethylamino²¹ and nitrogen dioxide²² radicals ($\Delta H_f^\circ = +39$ and +8, respectively), we expect *D*_(N–NO₂) ≈ 47 kcal mol⁻¹. Consequently, for *N*-nitropyrzoles a N–NO₂ bond strength of 45–50 kcal mol⁻¹ seems realistic. The ΔH^\ddagger values for the N → C NO₂ migrations do not exceed 37 kcal; moreover, ΔH^\ddagger for the rearrangement of 1b in *n*-decane is only 30 kcal mol⁻¹. The difference of ≥15 kcal with the (estimated) bond dissociation energy is thought to be sufficient for excluding N–NO₂ bond homolysis as the rate-determining step.

To reveal possible "borderline" character of the mechanism, thermolyses of the methyl substituted *N*-nitropyrzoles 1b, 1g, and 4 were performed in benzene solution, and the reaction mixtures were analyzed for *N*-phenylpyrazoles, diagnostic for free pyrazolyl radicals.⁹ *N*-Phenylpyrazoles were found to be present at extremely low levels (<<0.1%) only (see Experimental Section). Perhaps impurities have played a part. However, if the proportions of *N*-phenylpyrazoles are considered to be correct indications for competitive N–NO₂ bond homolysis, and accepting log *A* = 16, the corresponding rates lead to *E_A* ≈ 45 kcal mol⁻¹, in reasonable agreement with the estimated bond strength. Hence, homolytic scission of the N–NO₂ bond can be considered as an unimportant parallel reaction of the (apparently molecular) N → C NO₂ migration.

Recapitulating, the best fitting mechanism for the thermal *N*-nitropyrzole rearrangement involves a rate-determining, concerted migration of NO₂ giving a nonaromatic 3-nitro-3*H*-pyrazole (3) as intermediate (cf. Scheme II). This endothermic step is followed by rapid tautomerization to give a 3(5)-nitropyrzole 2; hence the driving force for the overall isomerization is the greater stability of a *C*-nitro- as compared to a *N*-nitropyrzole.²³

In the first step of the rearrangement, the nitro group has to move out of the pyrazole plane; therefore, the nitro migration may be classified as a symmetry-allowed suprafacial [1,5] sigmatropic shift²⁴ (cf. [1,5] migrations in cyclopentadienes). The N₁ → N₂ nitro migration as observed during the isomerization of 4 might well be a *suprafacial* (i.e., over the pyrazole plane) shift too, rather than an in-plane migration. Although a planar process is the least motion mode and aromaticity of the pyrazole ring is conserved, it is unlikely as it, when concerted, is a [_σ2_s + ω2_s], symmetry forbidden process.^{24,25} The relatively high activation energy for a N₁ → N₂ nitro shift may be a result of the interaction of *three* nitrogen centers in the transition state.

Although the N → C nitro migration apparently is a concerted process, the rather small (and insufficiently examined as yet) *substituent* effects (see Table II) might be indicative for polar contributions to the pericyclic transition state. So rate enhancement by a 3-methyl and retardation by a 3-nitro substituent is suggestive of a *minor* contribution of bicyclic



structure A (vide supra). On the other hand, the effect of the position of a (methyl) substituent is not easily understood.

As mentioned above, isomerization of *N*-nitropyrazoles is sometimes accompanied by denitration. Especially this is the case when the 4 position is substituted (cf. ref 3). It is difficult to imagine how a substituent at the 4 position should affect the first step of the isomerization. During the second step (that of rearomatization), however, the nitro group has to return in the pyrazole plane. From dissociation constants and ultraviolet spectra of "ortho"-substituted *C*-nitropyrazoles²⁶ it follows that these compounds are strained.²⁷ Hence the activation barrier for tautomerization into 4-substituted 3(5)-nitropyrazoles may well be increased, and alternative reactions may take place. To test this thesis, the thermolysis of 5-methyl-1-nitro-3-phenylpyrazole (9) was studied. Neither 5-methyl-1-nitro-3-phenylpyrazole (4) nor 1-nitro-3-phenylpyrazole (1d) give denitration, but the expected rearrangement product of 9, 3(5)-methyl-4-nitro-5(3)-phenylpyrazole (11), is highly strained, and denitration should be observed. Heating 9 in nitrobenzene at 120 °C indeed yields 11, but also for ~30% the denitrated pyrazole 10 (see Scheme VI); k_{120° for the disappearance of 9 is $\sim 4.2 \times 10^{-4} \text{ s}^{-1}$ (see Experimental Section), and the product ratio 10:11 does not depend on the degree of conversion (tallying with the observation that 11 is stable under the experimental conditions). Hence, it is likely that the denitration reaction competes with the rearomatization step(s). The way in which the nitro group is lost is, as yet, far from clear, however. Possibly some radical pathway obtains.²⁸

The denitration accompanying isomerization of 1,3-dinitropyrazole (1f) may not be due to steric factors. As addition of quinoline appeared to suppress this side reaction,³⁰ a heterolytic mechanism is indicated. Here, the product, 2f, with $\text{p}K_a = 3.1$,²⁶ may be acidic enough to entail protodenitration.³¹

In conclusion, the mechanism suggested earlier for the thermal *N*-nitropyrazole rearrangement seems in accord with all experimental data: the rearrangement is intramolecular; solvent and substituent effects rule out a polar (or ionic) transition state for the rate-determining NO_2 migration step, while the low ΔH^\ddagger values make a radical-pair process highly unlikely. The most plausible mechanism, then, is that of sigmatropic NO_2 migration.

Experimental Section³²

Materials. The syntheses of the *N*-nitropyrazoles used for the kinetic measurements, as well as those for the *C*-nitropyrazoles used as reference materials, have been described in ref 2 and 3. Other pyrazoles, such as 3(5)-methyl-5(3)-phenylpyrazole (10), were synthesized by standard procedures. The solvents used for the kinetic measurements were redistilled over either a spinning band column or a 1-m Vigreux column, *n*-decane after treatment with concentrated sulfuric acid. Other chemicals (including those used as internal standard), being high-grade commercial products, were used as such.

3(5)-Deuterio-5(3)-methylpyrazole.²⁹ A solution of 5 g of 3(5)-methylpyrazole in 25 ml of 1 N sodium deuterioxide (prepared by

dissolving sodium in deuterium oxide, 99.75%) was heated in an autoclave at 150 °C for 4 h. The reaction mixture was neutralized with deuterated (98–99%) trifluoroacetic acid, and the deuterated pyrazole was isolated by means of continuous extraction (15 h) with methylene chloride, followed by evaporation of the solvent; this alkaline exchange was repeated once. The deuterated pyrazole was then refluxed for 15 h in 1 N aqueous sulfuric acid, and worked up (after neutralization with sodium bicarbonate) by continuous extraction with methylene chloride. This acid exchange was repeated once. The resulting pyrazole was distilled in vacuo: yield 3.2 g; bp 105 °C (18 mm); NMR (60 MHz, CDCl_3 solution) δ 5.8 (s, 1, 4-H) and 2.1 ppm (s, 3, CH_3); isotopic composition (MS analysis,) 7.4% d_0 , 86% d_1 , and 6.6% d_2 .

5-Deuterio-3-methyl-1-nitropyrazole (8).²⁹ A preformed mixture of 6 ml of acetic anhydride and 2.5 ml of nitric acid (100%) was added carefully to a solution of 2.0 g of 3(5)-deuterio-5(3)-methylpyrazole in 2 ml of acetic acid at 0 °C. After 2 h, the reaction mixture was poured onto ice and neutralized with potassium carbonate, and the resulting precipitate was collected through filtration. The crude product (1.4 g) was crystallized from hexane: mp 54–55 °C; NMR (100 MHz, CDCl_3) δ 6.2 (s, 1, 4-H) and 2.3 ppm (s, 3, CH_3); no 5-H signal could be detected. Accurate MS analysis appeared to be impeded by D/H randomization in the mass spectrometer.

Measurement of the Kinetic Isotope Effect.²⁹ About equal quantities of both the deuterated 8 and the nondeuterated 3-methyl-1-nitropyrazole (1b) were dissolved in hexachloroacetone; *p*-dichlorobenzene was added as internal standard. NMR spectra (100 MHz) were recorded before and after heating of the solution in an oil bath at 140 °C. The results of a typical experiment are as follows.³³

	Integrated signals (relative to internal standard)			Obsd ratio ^b 1b/8
	5-H	4-H	4'-H ^a	
Initial solution ^c	0.761	1.412	—	1.17
After 20 min at 140 °C	0.514	0.951	0.439	1.18

^a 4-Proton from the rearrangement product. ^b Calculated from 5-H/(4-H - 5-H). ^c Weight ratio 1b/8 = 1.05.

Kinetic Measurements. A. Determination of the Rate Constants. General Procedure. A small, thin-wall tube, containing ~0.5 ml of a ca. 0.1 M solution of the *N*-nitropyrazole and an internal standard³⁴ in the appropriate solvent, was placed in a thermostated oil bath; a small stream of nitrogen was passed over. Aliquots were removed at regular time intervals and analyzed by GLC (using a 2 m \times 0.125 in., OV-17 on Gas-Chrom Q column,³⁵ at temperatures at which rearrangement of the *N*-nitropyrazole was negligible, normally 120–150 °C). The isomerizations were followed for about 2 half-lives. The relative amounts of *N*-nitropyrazoles present in the samples (C_i) were calculated from the peak areas. First-order rate constants were calculated from plots of $\ln C_0/C_t$ vs. time.

B. Correction of the Kinetic Data for the Rearrangement of 5-Methyl-1-nitropyrazole (4). To correct for the concurrent (slow) $\text{N}_1 \rightarrow \text{N}_2$ ($\rightarrow \text{C}_3$) nitro shift, the product ratios 3(5)-methyl-5(3)-nitropyrazole (2b)/3(5)-methyl-4-nitropyrazole (5), representing $k(\text{N}_1 \rightarrow \text{N}_2)/k(\text{N}_1 \rightarrow \text{C}_5)$, were determined by analyzing the reaction mixtures after more than 10 half-lives by GLC, using standard mixtures of the isomeric *C*-nitropyrazoles. Although the *C*-nitropyrazoles were incompletely separated, $k(\text{N}_1 \rightarrow \text{C}_5)$ could be calculated with appropriate accuracy. From the (less accurate) values of $k(\text{N}_1 \rightarrow \text{N}_2)$, activation parameters for this isomerization were calculated (vide supra).

Thermolysis of *N*-Nitropyrazoles in Benzene Solution. Solutions (ca. 5%) of the relevant *N*-nitropyrazoles in benzene, containing 0.01% of *p*-di-*tert*-butylbenzene as internal standard, were heated in sealed tubes. The resulting solutions were analyzed by GLC on a 55-m capillary OV-17 column. Quantitative analyses were made for *N*-phenylpyrazoles only: 3-methyl-1-nitropyrazole (1b), 2 h at 150 °C, gave ca. 0.006% of 3-methyl-1-phenylpyrazole (6) (close to the lower limit of detection; the 5-methyl isomer 7 could not be detected); 5-methyl-1-nitropyrazole (4) gave, under the same conditions, ca. 0.015% of a mixture of the isomeric *N*-phenylpyrazoles 6 and 7; 4-methyl-1-nitropyrazole (1g), 2 h at 190 °C, gave ca. 0.03% of 4-methyl-1-phenylpyrazole; in the latter reaction mixture, semiquantitative analysis revealed ~16% of 4-methylpyrazole, 0.7% of nitrobenzene, and ~0.1% of biphenyl.

5-Methyl-1-nitro-3-phenylpyrazole (9)²⁹ was prepared from 10 (2 g) by nitration in acetic acid (12 ml) with acetyl nitrate (1.7 ml of HNO₃, *d* 1.52, and 4 ml of acetic anhydride), during 2 h at room temperature. After working up with ice-cold water, filtration, and recrystallization from methanol, 0.9 g of 9 was obtained: mp 99–100 °C; ir (KBr) 1615 and 1265 cm⁻¹ (NNO₂); NMR (CDCl₃) δ 7.6 (m, 5, C₆H₅), 6.56 (s, 1, 4-H), and 2.68 (s, 3, CH₃).

Anal. Calcd for C₁₀H₉N₃O₂: C, 59.10; H, 4.46; N, 20.68. Found: C, 59.02; H, 4.67; N, 20.48.

Thermolysis of 9.²⁹ **A. Preparative Scale.** A solution of 0.8 g of 9 in 10 ml of chlorobenzene was heated for 4 h at 110 °C under a nitrogen atmosphere. After evaporation of the solvent, the products were chromatographed over a silica gel column using a chloroform-ethyl acetate mixture as eluent. In addition to 0.18 g of unreacted 9, 0.35 g of 3(5)-methyl-4-nitro-5(3)-phenylpyrazole (11) and 0.20 g of denitrated product 10 were isolated. Compound 11 was recrystallized from benzene and had mp 140 °C; ir (KBr) 1600 and 1360 cm⁻¹ (CNO₂); NMR (CDCl₃) δ 8.27 (s, 1, N-H), 7.36 (s, 5, C₆H₅), and 2.26 (s, 3, CH₃).

Anal. Calcd for C₁₀H₉N₃O₂: C, 59.10; H, 4.46; N, 20.68. Found: C, 59.42; H, 4.77; N, 20.14.

B. NMR Scale. A 0.2 M solution of 9 in nitrobenzene, containing *p*-di-*tert*-butylbenzene as internal standard, was heated (under a nitrogen atmosphere) in a thermostated oil bath at 120 °C. Samples were withdrawn at six 15-min intervals. Product compositions were determined via careful integration of NMR (100 MHz) spectra.

Registry No.—1a, 7119-95-1; 1b, 31163-84-5; 1d, 38859-26-6; 1f, 38858-81-0; 1g, 38858-82-1; 4, 31163-85-6; 8, 58311-77-6; 9, 58311-78-7; 10, 3440-06-0; 11, 58311-79-8; 3(5)-deuterio-5(3)-methylpyrazole, 58311-80-1; 3(5)-methylpyrazole, 1453-58-3.

References and Notes

- (1) (a) Partly abstracted from the Ph.D. Thesis of J.W.A.M.J. (Leiden, 1975), to be referred to as 1a. (b) This research was supported by the Netherlands Foundation for Chemical Research (S.O.N.) with financial aid from the Netherlands Organization for the Advancement of Pure Research (Z.W.O.).
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- (27) Although strained, the investigated "ortho"-substituted *C*-nitropyrazoles were stable under the experimental conditions for the rearrangement reactions.
- (28) In the product of thermolysis of 1g in anisole (2 h at 190 °C), 0.7% of nitroanisole (mainly *m*- and *p*-; GLC analysis²⁹) was found to be present. Cf. thermolysis of 1g in benzene, yielding 0.7% of nitrobenzene (see Experimental Section). Note also that in the latter case only a trace amount of 4-methyl-1-phenylpyrazole is formed; this seems to exclude formation of NO₂ via homolysis of starting compound 1g.
- (29) This experiment was performed by M. Timmer, this laboratory.
- (30) In contrast, addition of quinoline to 4-methyl-1-nitropyrazole (1g) seems to have no effect on the denitration reaction (GLC analysis).²⁹
- (31) When thermolyzing 1f in benzene at 190 °C, ca. 1% of nitrobenzene is formed; the use of anisole as a solvent (170 °C) led to 2–3% of *o*- and *p*-nitroanisole (ratio ca. 1.5:1, GLC analysis),²⁹ indicative of electrophilic nitration. Compare J. G. Hoggett, R. B. Moodle, J. R. Penton, and K. Schofield, "Nitration and Aromatic Reactivity", Cambridge University Press, New York, N.Y., 1971, p 95.
- (32) The following instruments were used: Varian Aerograph 1400 and Hewlett-Packard HP 5700 gas chromatographs; JEOL PS-100 and Minimar NMR apparatus; an AEI-MS 902 mass spectrometer; and a Beckman IR-10 spectrophotometer.
- (33) From these data it can also be concluded that (1) the rate of the rearrangement in hexachloroacetone is about 3×10^{-4} s⁻¹, comparable to that in the other solvents used (cf. Table I), and (2) the rearrangement in hexachloroacetone proceeds cleanly (4-H₁₌₀ = 4-H₁₌₂₀ + 4'-H₁₌₂₀).
- (34) The following internal standards were used: nitrobenzene (rearrangement of 1b in *N*-methylformamide and propylene glycol); *n*-tridecane (1b in *n*-decane); methyl myristate (rearrangement of 1d); and *n*-pentadecane (all other cases).
- (35) To follow the rearrangement of 1d, a comparable 0.5-m column was used.