(δ CH diene), 14.65 μ; nmr (DMSO-d_6) δ 4.98–5.73 (m, 3 H), 6.70–7.38 (m, 2 H), 8.02–8.41 (m, 4, aromatic); mass spectrum *m/e* 218 (molecular ion), 150 (as expected for loss of the fragment NHCH=CHCH=CH_2).

Anal. Calcd for $C_{11}H_{10}N_2O_3$: C, 60.54; H, 4.61; N, 12.84. Found: C, 60.57; H, 4.76; N, 12.82.

Isomerization of 1 to 5 by Thermolysis.—A mixture of 150 mg of **1** in 10 ml of decane was heated under reflux for 1 hr in a quartz tube. The mixture was cooled and filtered to give 77 mg of **5**.

Rearrangement of 1 to 5 by Sodium Chloride in DMSO.—A mixture of 170 mg **1**, 650 mg NaCl, and 1.4 ml of DMSO was heated at 80° for 1 hr. The mixture was cooled and water was added dropwise. The precipitate of **5** was filtered, dried, and weighed (158 mg, 93%). A control run of **1** in DMSO resulted in isolation of starting material.

Rearrangement of 1 to 5 by KSCN.—A mixture of 206 mg of **1** and 440 mg of KSCN in 13 ml of commercial CH_3CN was heated under reflux for 2 hr. Evaporation of the solvent and addition of water to the residue followed by filtration gave 204 mg of **5**.

Isomerization of 5 to 6.—A solution of 418 mg of **5** in 140 ml of CH_3OH was irradiated at room temperature for 2 days, using a water-cooled immersion well and a 100-W GE mercury lamp type H-100 A4/T from which the glass jacket was removed. Evaporation of the solvent gave 392 mg of crude **6** (94%) melting at 170–174°. Four recrystallizations from aqueous CH_3CN gave **6**: mp 192–194°; ir (Nujol) 3.10 (NH), 5.54 (weak overtone of terminal vinyl), 6.08 (C=O), 6.23, 6.55, 6.60, 7.30, 7.35, 7.42, 7.60, 7.68 (CH=CH_2), 7.73, 8.36, 9.00, 9.89, 10.05 (CH=CH_2), 10.79, 11.10 (CH=CH_2), 11.52, 11.71, 11.82, 13.95, 14.10 (very broad peaks, δ CH diene); nmr (DMSO-d_6) δ 4.90–5.35 (m, 2 H), 5.98–7.24 (m, 3 H), 8.0–8.40 (m, 4 H, aromatic).

Anal. Calcd for $C_{11}H_{10}N_2O_3$: C, 60.54; H, 4.61; N, 12.84. Found: C, 60.65; H, 4.80; N, 12.84.

Compound **6** was also prepared by heating 100 mg of **5** in 15 ml of CH_3CN containing 2 ml of triethylamine for 2 hr. Evaporation of volatiles gave 92 mg of **6**.

Reaction of 6 with Maleic Anhydride.—A suspension of 283 mg of **6** and 127 mg of maleic anhydride in 15 ml of benzene was heated under reflux with vigorous shaking for 15 min. The reaction mixture was cooled and crude **7** (302 mg) was collected by filtration and recrystallized from acetonitrile: mp 234–236°; mass spectrum *m/e* 316 (molecular ion).

Anal. Calcd for $C_{15}H_{12}N_2O_6$: C, 56.97; H, 3.82; N, 8.86. Found: C, 56.76; H, 3.91; N, 8.73.

Under comparable conditions but with a reaction time of over 1 hr compound **5** failed to react with maleic anhydride.

Rearrangement of 1-*p*-Nitrobenzoyl-2-vinylaziridine to 3 by KCNS.—A mixture of 177 mg of the aziridine[1] and 440 mg of KCNS in 10 ml of CH_3CN was allowed to stand at room temperature for 24 hr. The solvent was evaporated and the residue washed with water and filtered giving 175 mg (98%) of **3**.

***cis*-*N*-(4-Iodo-2-butenyl)-*p*-nitrobenzamide (4a).**—To a chilled mixture of 383 mg of **1** in 5 ml of acetone was added 2 ml of 47% hydriodic acid. After 3 min water was added dropwise to the reaction mixture and the precipitate of 570 mg (73%) of crude **4a** was collected by filtration. The crude **4a** was purified by heating it in CCl_4 for a very brief period of time and then filtering the undissolved **4a**. Cooling the filtrate gave **4a** melting at 118–119°. Prolonged heating of **4a** in CCl_4 caused decomposition.

The nmr spectrum of **4a** taken in $CDCl_3$ showed clearly four aromatic protons centered at δ 8.09, two olefinic protons as a multiplet extending from δ 5.32 to 6.25, four aliphatic protons as a series of peaks centered at δ 4.09, and the NH as a broad peak at approximately δ 6.80.

Anal. Calcd for $C_{11}H_{11}IN_2O_3$: C, 38.16; H, 3.20. Found: C, 38.54; H, 3.41.

***N*-(2-Iodo-3-butenyl)-*p*-nitrobenzamide (12).**—To a chilled solution of 305 mg of 1-*p*-nitrobenzoyl-2-vinylaziridine in 5 ml of acetone was added 2 ml of 47% hydriodic acid. Water was immediately added dropwise and the crude **12** (317 mg, 51%) was isolated by filtration and purified by the same procedure as **4a** to give 12 melting at 103–105°.

The nmr spectrum of **12** taken in $CDCl_3$ showed four aromatic protons centered at δ 8.10, the NH as a broad peak at approximately δ 6.68, three olefinic protons as a multiplet extending from δ 4.68 to 6.42, and three aliphatic protons as a multiplet extending from δ 3.70 to 4.17.

Anal. Calcd for $C_{11}H_{11}IN_2O_3$: C, 38.16; H, 3.20. Found: C, 38.21; H, 3.31.

Conversion of 4a into 13.—To 15 ml of an ether suspension of excess sodium hydride was added 157 mg of **4a**. The reaction mixture stood overnight at room temperature after which time the ether was decanted and evaporated. Water was added to the residue and the resulting slurry filtered to give 96 mg (97%) of **13**. The infrared spectrum of **13** obtained in this manner was identical with that of a sample of **13** prepared by reaction of 3-pyrroline with *p*-nitrobenzoyl chloride.[1]

Conversion of 12 into 3.—To 15 ml of an ether suspension of excess sodium hydride was added 204 mg of **12**. After the reaction mixture was allowed to stand for 12 hr at room temperature the ether was decanted and evaporated giving **3** (110 mg, 86%).

Registry No.—**1**, 17659-01-3; **2**, 31420-37-8; **3**, 17659-08-4; **4**, 31420-39-0; **4a**, 31420-40-3; **5**, 31420-41-4; **5**, 31420-42-5; **7**, 31443-68-2; **12**, 31420-43-6.

Acknowledgment.—This investigation was supported by Public Health Research Grant CA 10015.

Pyrazoles. VIII. Rearrangement of *N*-Nitropyrazoles. The Formation of 3-Nitropyrazoles[1,2]

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1-Nitropyrazole (**1**) undergoes an uncatalyzed intramolecular thermal rearrangement at 140° to 3(5)-nitropyrazole (**5**). 3-Methyl-1-nitropyrazole (**3**) and the 5-methyl isomer **4** were prepared and separated. Thermal rearrangement of **3** gave exclusively 3(5)-methyl-5(3)-nitropyrazole (**7**); rearrangement of **4** gave 3(5)-methyl-4-nitropyrazole (**9**) in 93% yield plus 7% **7**.

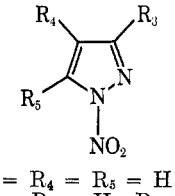
The synthesis and properties of 1-nitropyrazole (**1**) and some substituted *N*-nitropyrazoles have been reported by Hüttel and Büchele.[3] They also described the rearrangement of *N*-nitropyrazoles to the 4-nitro derivatives in H_2SO_4 solution in the cold. We have found that several *N*-nitropyrazoles also can undergo a thermal rearrangement. For our investigations on this thermal rearrangement we have studied in addition to 1-nitropyrazole (**1**) the newly synthesized compounds 4-ethyl-1-nitropyrazole (**2**), 3-methyl-1-nitropyrazole (**3**), and 5-methyl-1-nitropyrazole (**4**). These compounds were synthesized according to the same procedure that was used for the synthesis of **1**.

(1) Part VII: C. L. Habraken, P. Cohen-Fernandes, S. Balian, and K. C. van Erk, *Tetrahedron Lett.*, 479 (1970).

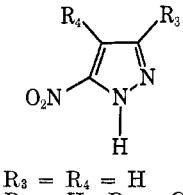
(2) This research was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

(3) R. Hüttel and F. Büchele, *Chem. Ber.*, **88**, 1586 (1955).

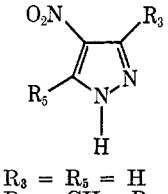
Compounds **3** and **4**, formed by N-nitration of 3(5)-methylpyrazole, were separated by column chromatography. The structure assignments for **3** and **4** were based on the following nmr spectral evidence. From the investigations of Elguero, *et al.*,[4] it is known that in several solvents the 5-proton resonance signal of 1-substituted pyrazoles is distinguished in two ways from the signal of the 3 proton, namely by appearing at lower field and with a larger coupling constant ($J_{45} > J_{34}$). In addition, it is reasonable to expect a larger chemical shift for the 5 proton due to the presence of the adjacent nitro group. In the nmr spectra of **1**, determined in five different solvents (see Experimental Section), only one signal was found to be a distinct doublet. In all spectra this doublet also appeared to be the one with the larger chemical shift and was therefore assigned to the 5 proton. Consequently, compound **3**, the isomer showing a distinct doublet in the nmr spectrum, was assigned the structure with a proton at C-5 and a methyl group at C-3. In addition, this doublet had a larger chemical shift than the unresolved signal at low field in the spectrum of its isomer **4**.



1, $R_3 = R_4 = R_5 = H$
2, $R_3 = R_5 = H$; $R_4 = C_2H_5$
3, $R_3 = CH_3$; $R_4 = R_5 = H$
4, $R_3 = R_4 = H$; $R_5 = CH_3$



5, $R_3 = R_4 = H$
6, $R_3 = H$; $R_4 = C_2H_5$
7, $R_3 = CH_3$; $R_4 = H$



8, $R_3 = R_5 = H$
9, $R_3 = CH_3$; $R_5 = H$

The ir spectra of the *N*-nitropyrazoles showed a symmetric NO_2 stretching vibration (1295–1275 cm^{-1}) at lower frequency and an asymmetric vibration (1625–1605 cm^{-1}) at higher frequency than is generally found for *C*-nitro groups (ν_{sym} 1385–1360 and ν_{asym} 1565–1545 cm^{-1});[5] for *C*-nitro groups in nitropyrazoles we found ν_{sym} 1375–1330 and ν_{asym} 1545–1490 cm^{-1}.[6]

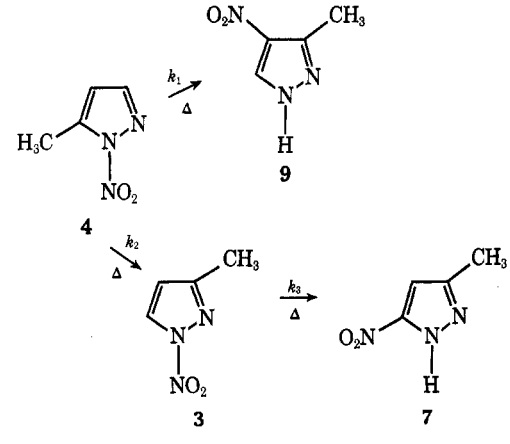
1-Nitropyrazole (**1**), on heating at 140–150° either neat in a melting point tube or on a preparative scale in anisole solution, rearranged quantitatively into 3(5)-nitropyrazole (**5**), which was identified by its ir and nmr spectra. The rearrangement in anisole or in the presence of phenol did not result in the formation of nitration products of these compounds. Control experiments established that the isomerization of **1** in H_2SO_4 solution in the cold resulted, as reported,[3] in the formation of 4-nitropyrazole (**8**). In these instances, however, the addition of anisole or of phenol was accompanied by the formation of nitroanisoles or of nitrophenols. The thermal isomerization of **1**, carried out in the presence of 3,5-dimethylpyrazole, a compound which on N-nitration conditions forms 1,4-dinitro-3,5-dimethylpyrazole very readily,[3] also did not result in the formation of nitration products of this compound. No difference was observed when this isomerization was carried out in the presence of quinoline, indicating that a proton is not involved; the presence of bibenzyl could not be demonstrated when this isomerization was run in toluene solution. Kinetic experiments (nitrobenzene solution, 166°, nitrogen atmosphere) showed perfect first-order behavior ($k = 0.021$ min^{-1}) even at conversions up to 95%. These observations suggest that this novel rearrangement is an uncatalyzed intramolecular process, not involving free radicals.

Thermolysis of the 4-ethyl compound **2**, though accompanied by decomposition, afforded 4-ethyl-3(5)-nitropyrazole (**6**), while treatment of **2** with H_2SO_4 gave, besides a small amount of **6**, mainly 4-ethylpyrazole.

Heated at 140–145° neat or in anisole solution, compound **3** rearranged cleanly to 3(5)-methyl-5(3)-nitropyrazole (**7**), which was identified by its ir and nmr spectra. Rearrangement of **3** in H_2SO_4 solution gave 3(5)-methyl-4-nitropyrazole (**9**) in addition to a small amount of **7**. The latter compound could not be detected in a control experiment of the nitration of 3(5)-methylpyrazole with mixed acid. For the thermal rearrangement of **3** into **7**, carried out in anisole solution at 140°, a first-order rate constant, $k = 0.0214$ min^{-1}, was found.

Thermal rearrangement of compound **4** in anisole solution (140°) ultimately led to 93% of **9** and 7% of **7**. During this reaction, up to 3% of **3** is present as intermediate. Kinetic data are in perfect agreement with the structures of first-order reactions as shown in Scheme I, with $k_1 + k_2 = 0.0252$ min^{-1}, $k_1/k_2 = 93/7$, and $k_3 = 0.0214$ min^{-1}.

SCHEME I



From the data presented here, and from our findings on the thermal isomerization of 2-nitroindazoles into 3-nitroindazoles,[7] it appears that this thermally induced migration of a nitro group from an N atom to a C atom is a characteristic property of *N*-nitroazoles. Furthermore, this rearrangement reaction provides a convenient method for the synthesis of 3-nitropyrazoles. We are continuing our studies in an effort to understand the mechanism of this new reaction.

(4) J. Elguero, R. Jacquier, and H. C. N. Tien Duc, *Bull. Soc. Chim. Fr.*, 2327 (1966).

(5) A. D. Cross and R. A. Jones, "An Introduction to Practical Infrared Spectroscopy," 3rd ed, Butterworths, London, 1969.

(6) Ir spectra of 3(5)- and 4-nitropyrazoles, unpublished results.

(7) P. Cohen-Fernandes and C. L. Habraken, *J. Org. Chem.*, **36**, 3084 (1971).

Experimental Section

General.—Elemental analyses were performed by Mr. W. J. Buis, TNO Laboratory of Organic Chemistry, Utrecht, The Netherlands. Ir and mass spectra were recorded on Perkin-Elmer IR-137 and AE MS-902 spectrometers, respectively; nmr spectra (δ expressed in parts per million) were recorded on a JEOLCO Minimar 60-MHz instrument; glc analyses were performed on a Varian Aerograph 1400 instrument. Orienting thermolyses of *N*-nitropyrazoles were carried out in sealed melting point tubes, inserted in the oil bath of a Büchi melting point apparatus; reaction products were analyzed by tlc and/or glc. All melting points are uncorrected.

Materials.—Pyrazole, 4-ethylpyrazole, 3(5)-methylpyrazole, and 3,5-dimethylpyrazole were synthesized by standard procedures. 3(5)-Methyl-4-nitropyrazole was prepared by the method of Morgan and Ackerman;[8] 1-acetyl-4-ethylpyrazole was prepared according to the method of Barthel and Schmeer.[9] Anisole and nitrobenzene, used for kinetic experiments, were distilled before use; all other chemicals were used without special purification.

General N-Nitration Procedure.—Nitric acid (0.7 ml, *d* 1.5) was carefully added to a cooled solution of the pyrazole (0.014 mol) in 3 ml of acetic acid. Acetic anhydride (2 ml) was added, and the reaction mixture was allowed to stand for 30 min and poured on ice. After being diluted with water the mixture was neutralized with $NaHCO_3$ and extracted with ether, the extracts were dried ($MgSO_4$) and filtered, and ether was removed by evaporation.

1-Nitropyrazole (**1**).—This compound was prepared as described by Hüttel, *et al.*,[3] mp 91–92° (lit.[3] 93°), ir (KBr) 1610 and 1280 cm^{-1} (*N*-nitro). Nmr spectra were determined in mesitylene, $CDCl_3$, acetone, DMSO, and hexamethylene phosphoramide (HMPA). The results are summarized in Table I.

TABLE I
CHEMICAL SHIFTS OF THE PROTONS OF **1** IN VARIOUS SOLVENTS

Solvent	5-H	3-H	4-H
Mesitylene	7.38 (d)[a]	6.92 (s)	5.59 (m)
$CDCl_3$	8.39 (d)	7.67 (s)	6.50 (m)
Acetone	8.64 (d)	7.77 (s)	6.64 (m)
DMSO	8.79 (d)	7.89 (s)	6.70 (m)
HMPA	9.14 (d)	8.07 (s)	6.83 (m)

[a] J_{45} = 2.8–3.0 Hz in all solvents.

4-Ethyl-1-nitropyrazole (**2**).—4-Ethylpyrazole (1.4 g), N-nitrated by the general procedure, gave 1.8 g of **2**, contaminated with a few per cent of 1-acetyl-4-ethylpyrazole, which could be identified in the ir spectrum and on glc after comparison with a pure sample of 1-acetyl-4-ethylpyrazole. An analytical pure sample of **2** was obtained after preparative glc (on SE-30 at 130°): a yellow, oily liquid; ir (liquid film) 1610 and 1287 cm^{-1} (*N*-nitro); nmr ($CDCl_3$) 8.11 (s, 1, 5-H), 7.50 (s, 1, 3-H), 2.55 (quartet, 2, CH_2), and 1.26 (t, 3, CH_3); mol wt (calcd for $C_5H_7N_3O_2$) 141.0437 (found 141.0555).

3-Methyl-1-nitropyrazole (**3**).—N-Nitration of 3(5)-methylpyrazole by the general method gave a mixture of nearly equal quantities of **3** and **4** (shown by glc and nmr analysis). Some unreacted 3(5)-methylpyrazole was removed by extraction with diluted sulfuric acid; the isomers were separated by column chromatography (technique of Hunt and Rigby[10]) on aluminium oxide G type E (Merck) with benzene as eluent, **3** being the faster moving isomer. An analytical sample of **3** was obtained by crystallization from hexane: colorless crystals; mp 54–55°; ir (Nujol) 1620 and 1297 cm^{-1} (*N*-nitro); nmr ($CDCl_3$) 8.25 (d, 1, J = 2.9 Hz, 5-H), 6.31 (d, 1, J = 2.9 Hz, 4-H), and 2.39 (s, 3, CH_3).

Anal. Calcd for $C_4H_5N_3O_2$: C, 37.80; H, 3.97; N, 33.06. Found: C, 37.53; H, 3.85; N, 33.31.

5-Methyl-1-nitropyrazole (**4**).—This compound, the slower moving isomer in the preparation of **3**, was purified by column chromatography[10] (aluminium oxide G type E; hexane, gradually replaced by successively benzene and chloroform): a slightly yellow oily liquid, gas chromatographically pure (OV-17 column); ir (liquid film) 1619 and 1294 cm^{-1} (*N*-nitro); nmr ($CDCl_3$) 7.47 (s, 1, 3-H), 6.23 (s, 1, 4-H), and 2.67 (s, 3, CH_3).

Anal. Calcd for $C_4H_5N_3O_2$: C, 37.80; H, 3.97; N, 33.06. Found: C, 37.84; H, 4.02; N, 33.21.

3(5)-Nitropyrazole,[11,12] (**5**).—A solution of 2.2 g of **1** in *ca.* 180 ml of anisole was heated for 10 hr in an oil bath at 145°. After being cooled a white, crystalline solid precipitated; filtration and drying at reduced pressure afforded 1.05 g of **5**. Extraction with 1 *N* NaOH solution of the anisole filtrate (diluted with ether), followed by acidification with dilute sulfuric acid and extraction with ether, afforded an additional amount of 1.0 g of **5**: mp (after recrystallization from benzene) 174–175° (lit.[12] 175°); ir (KBr) 3180 (NH), 1520 and 1351 cm^{-1} (NO_2); nmr (DMSO) 7.96 (d, 1, J = 2.0 Hz, 5(3)-H) and 6.96 (d, 1, J = 2.0 Hz, 4-H).

Anal. Calcd for $C_3H_3N_3O_2$: C, 31.86; H, 2.67; N, 37.16. Found: C, 32.19; H, 2.84; N, 37.18.

4-Ethyl-3(5)-nitropyrazole (**6**). **A.**—While being cooled in a salt–ice mixture, **2** was suspended in an excess of concentrated H_2SO_4. The mixture was allowed to stand overnight, poured on ice, diluted with water, and extracted with ether. The extracts were dried ($MgSO_4$) and the solvent was evaporated. The residue, containing mainly 4-ethylpyrazole and some **6**, was purified by column chromatography[10] (silica gel H according to Stahl, chloroform–ethyl acetate 1:1) and sublimation to obtain an analytical sample of **6**: a white solid; no sharp melting point (135–143°); ir (KBr) 3130 (NH), 1512 and 1349 cm^{-1} (NO_2); nmr ($CDCl_3$) 7.71 (s, 1, 5(3)-H), 2.88 (quartet, 2, CH_2), and 1.31 (t, 3, CH_3).

Anal. Calcd for $C_5H_7N_3O_2$: C, 42.55; H, 5.00; N, 29.78. Found: C, 42.26; H, 5.28; N, 29.66.

B.—A better yield could be obtained on heating a 5% solution of **2** in anisole for *ca.* 50 hr at 145°. In the work-up of the reaction mixture the same procedure was followed as described for the preparation of compound **5**.

3(5)-Methyl-5(3)-nitropyrazole (**7**). **A.**—In a closed screw cap vial 550 mg of **3** was heated for 2 hr at 140–145° (drying oven). Sublimation under reduced pressure, first at 40° to remove traces of **3** and thereafter at 140°, afforded 530 mg of pure **7**: a white solid; mp 156–157°; ir (KBr) 3150 (NH), 1533 and 1335 cm^{-1} (NO_2); nmr (DMSO) 6.75 (s, 1, 4-H) and 2.37 (s, 3, CH_3).

Anal. Calcd for $C_4H_5N_3O_2$: C, 37.80; H, 3.97; N, 33.06. Found: C, 37.97; H, 3.88; N, 33.03.

B.—For preparing larger quantities a 5% solution of **3** in anisole was heated for 2 hr at 145° and worked up as described for the synthesis of **5**.

Kinetic Measurements.—A tube, containing approximately 1 ml of a solution of the *N*-nitropyrazole and *n*-pentadecane

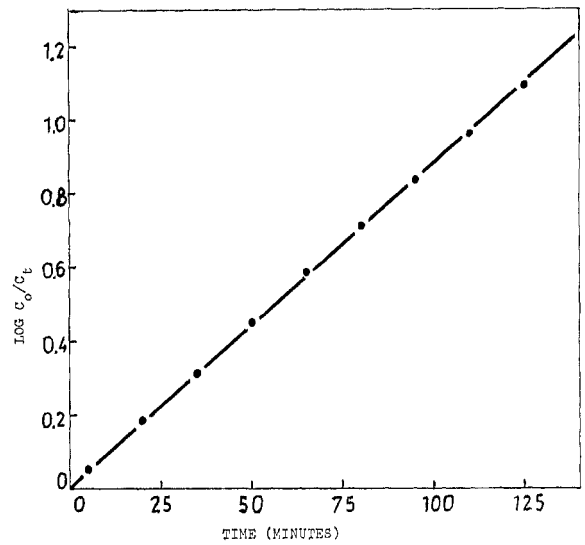


Figure 1.—Graph of a typical kinetic run (1-nitropyrazole).

(8) J. T. Morgan and I. Ackerman, *J. Chem. Soc.*, **123**, 1308 (1923).

(9) J. Barthel and G. Schmeer, *Justus Liebigs Ann. Chem.*, **738**, 195 (1970).

(10) B. J. Hunt and W. Rigby, *Chem. Ind. (London)*, 1868 (1967).

(11) After completion of this work a publication by M. A. Khan and B. M. Lynch [*J. Heterocycl. Chem.*, **7**, 1237 (1970)] informed us of the synthesis of 3(5)-nitropyrazole from 3(5)-aminopyrazole, reported by Bagal, *et al.*[12]

(12) L. I. Bagal, M. S. Pevzner, A. N. Forlov, and N. I. Sheludyakova, *Khim. Geterosikl. Soedin.*, 259 (1970); *Chem. Abstr.*, **72**, 111383h (1970).

(weighed amounts, concentration of the *N*-nitropyrazole *ca.* 1%, *n*-pentadecane added as internal standard) in anisole, or, in the case of the rearrangement of **1**, in nitrobenzene, was inserted in a thermostated oil bath (166° for 1, 140° for **3** and **4**). A small stream of nitrogen was passed over. Aliquots were removed at 15- or 20-min intervals and analyzed by glc (column 1.5 m × 0.125 in., 4% OV-17 on 80–100 mesh Gas-Chrom Q), column temperature 160° (rearrangement of **1**), or ballistic programmed from 130° to 200° (rearrangement of **3** and **4**). The amounts of the *N*-nitropyrazoles and of the rearrangement products, relative to *n*-pentadecane, were calculated, using graphs obtained by injection (under the same glc conditions) of standard solutions of the various nitropyrazoles and *n*-pentadecane in anisole or in nitrobenzene. Reactions were followed to 90–95% conversion. During each run the sum of *N*-nitropyrazoles and *C*-nitropyrazoles was constant within experimental error. Plots of log C_0/C_t *vs.* time always gave straight lines (see Figure 1); k values for the isomerization of **1** and **3**, and $k_1 + k_2$ for the isomerization of **4**, were calculated from these graphs. To determine k_1/k_2 for the isomerization of **4**, the reaction mixture was analyzed after 3 hr of isomerization (completeness). It contained 93% of **9** and 7% of **7**. To control the proposed scheme for the isomerization of **4**, the amounts of **3** theoretically present during the reaction, calculated with the expression

$$x = \frac{C_0 k_2}{k_1 + k_2 - k_3} [e^{-k_3 t} - e^{-(k_1 + k_2)t}] \text{ (see Scheme I)}$$

were compared with the amounts found. The results are summarized in Table II.

TABLE II

COMPARISONS OF THE AMOUNTS OF **3**, PRESENT DURING A KINETIC RUN OF **4**, CALCULATED AND FOUND

Reaction time, min	Calcd, %[a]	Found, %[a,b]
5	0.8	0.5
25	2.4	2.5
45	2.8	3
65	2.5	2.5
85	2.0	2
105	1.6	1.5
125	1.2	1

[a] Per cents from C_0. [b] Approximations.

Registry No.—**1**, 7119-95-1; **2**, 31163-83-4; **3**, 31163-84-5; **4**, 31163-85-6; **5**, 26621-44-3; **6**, 31163-87-8; **7**, 31163-88-9.

Acknowledgment.—We thank Dr. R. Louw for his advice on the kinetic experiments and Drs. J. v. Thuyl, K. Klebe, and J. v. Houte for the mass spectral analyses. We are also very grateful to C. Kruse, C. v.d. Laken, and A. Vink for carrying out some of the experiments and to Mr. B. de Boo for his technical assistance on the nmr spectra.

Nitration of Indazoles in the 3 Position

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Nitration of indazole with nitric acid and acetic anhydride gives the 3-nitro and 3,5-dinitro derivatives. With this reagent, the four Bz-mononitro indazoles undergo nitration at N-2. The N-2 nitro group in these compounds rearranges to C-3 on heating. The mechanism of the reagent-dependent nitration of indazoles is discussed.

Although numerous indazoles containing nitro groups are known,[1] to our knowledge no 3-nitroindazoles have been described in the literature. The majority of the reported nitroindazoles were obtained directly by ring closure reactions. Nitration of indazole with nitric acid yields the 5-nitro derivative[2] which according to Davies[3] gives a *m*-dinitroindazole on further nitration with mixed acid.[4] Nmr analysis (see Experimental Section) clearly indicated this compound to be 5,7-dinitroindazole. The formation of 5,6-dinitroindazole on nitration of 6-nitroindazole, first reported by Fries,[5] was confirmed by Davies.[3]

We have discovered a facile nitration of indazole in the 3 position. Treatment of an acetic acid solution of indazole in the cold, with nitric acid and acetic anhydride successively, afforded a mixture of two products, 3-nitroindazole (**1**, 55%) and 3,5-dinitroindazole (**2**, 20%), which were easily separated by column chromatography. The nitration of 5-nitroindazole by the same procedure also gave **2** (42%) in addition to the *N*-nitro derivative 2,5-dinitroindazole (**3**, 51%). From the nitration of 6-nitroindazole only 3,6-dinitroindazole (**4**, 97%) was obtained. On the other hand, nitration of 4-nitro- and of 7-nitroindazole gave the *N*-nitro compounds 2,4-dinitroindazole (**5**, 95%) and 2,7-dinitroindazole (**6**, 85%). On heating[6] in anisole solution these *N*-nitro compounds **3**, **5**, and **6** could easily be converted to the 3-nitro derivatives **2**, 3,4-dinitroindazole (**7**), and 3,7-dinitroindazole (**8**). Moreover, **3** appeared to disproportionate in solution at room temperature as observed in tlc experiments. 2,6-Dinitroindazole (**9**, 75%) and 2,3-dinitroindazole (**10**, 30%) were obtained on nitration of 6-nitro- and 3-nitroindazole, respectively, at room temperature in acetic acid solution by treatment with acetylnitrate. On heating **9** rearranged into the 3-nitro compound **4**, but the 2,3-dinitroindazole (**10**) decomposed on heating. **1** was identified on comparison (ir and nmr spectra, tlc, and mixture melting points) with authentic samples of 4-, 5-, 6-, and 7-nitroindazole. The nmr spectrum consisted of two multiplets centered at δ 8.13 and 7.60, with relative intensities of 1:3 for the C–H protons and the ir spectrum showed a strong absorption at 748 cm^{-1} indicating four vicinal aromatic protons. The structure assignments of **2**, **4**, **7**, amd **8** were based on their nmr spectra and on comparison of these spectra with those of

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(6) Similar rearrangements have been observed in the case of *N*-nitropyrazoles where isomerization takes place thermally[7] as well as under acid conditions.[7,8]
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