other example is the conversion of 1-thiobenzoylazetidine in concentrated hydrochloric acid for 10 days at room temperature into 2-phenyl-4,5-dihydro-6*H*-1,3-thiazine while under identical conditions 1-benzoylazetidine gave only *N*-(3-chloropropyl)benzamide.[7]

Experimental Section

1-(*p*-Nitrocarbobenzoxy)-2-vinylaziridine (1).—A solution of 2.2 g of *p*-nitrocarbobenzoxy chloride in 45 ml of ether was added dropwise to a stirred solution of 1.0 g of 2-vinylaziridine[8] and 1.2 g of triethylamine in 100 ml of ether. The reaction mixture was stirred for 4 hr and then filtered free of the precipitated triethylamine hydrochloride. The filtrate was evaporated to give 2.5 g of a yellow oil. The oil was dissolved in 2-propanol and the solution was kept at −10° for 6 hr. The supernatant was decanted and the residue was washed with petroleum ether (bp 60–110°). Repetition of the purification procedure gave 1.11 g (46%) of **1** melting at 56–58°.

Anal. Calcd for $C_{12}H_{12}N_2O_4$: C, 58.07; H, 4.87; N, 11.28. Found: C, 57.81; H, 4.81; N, 11.43.

Rearrangement of 1 to 2.—A round-bottomed flask cleaned with chromic acid solution and repeatedly washed with distilled water and dried was charged with 249 mg of **1** and 10 ml of decalin. The reaction mixture was refluxed for 1 hr and then cooled to −10° and filtered. The crude product weighed 157 mg (63%) and as determined by nmr spectroscopy was 96% compound **2** and 4% compound **3**. Recrystallization four times from petroleum ether (bp 100–115°) gave **2** melting at 117.5–119.5°. The nmr spectrum of **2** is comparable to that of 2,3-dihydrofuran:[9] nmr ($CDCl_3$) δ 2.70 (t, 2, $=CHCH_2$), 2.84 (t, 2, NCH_2), 5.14 (m, 1, $=CHCH_2$), 5.29 (s, 2, CH_2O), 6.63 (q, 1, $NCH=$), 7.55 and 8.24 (m, 4, C_6H_4).

Anal. Calcd for $C_{12}H_{12}N_2O_4$: C, 58.07; H, 4.87; N, 11.28. Found: C, 58.41; H, 4.89; N, 11.08.

1-(*p*-Nitrocarbobenzoxy)-3-pyrroline (3).—A solution of 2.2 g of *p*-nitrocarbobenzoxy chloride in 30 ml of ether was added over 10 min to a stirred and cooled (ice bath) solution of 0.70 g of 3-pyrroline in 100 ml of ether. The reaction mixture was stirred for 2.5 hr and then filtered. Evaporation of the filtrate gave 1.6 g of crude **3**. Three recrystallizations from petroleum ether gave **3** melting at 129.5–131°: nmr ($CDCl_3$) 4.22 (s, 4, CH_2NCH_2), 5.26 (s, 2, CH_2O), 5.82 (s, 2, CH=CH).

Anal. Calcd for $C_{12}H_{12}N_2O_4$: C, 58.07; H, 4.87; N, 11.28. Found: C, 58.00; H, 4.84; N, 10.81.

1-(*p*-Nitrocarbobenzoxy)pyrrole (4).—To a solution of 0.50 g of pyrrole in 40 ml of C_6H_6 was added 0.80 g of potassium *tert*-butoxide. The mixture was stirred for 0.5 hr and then 1.20 g of *p*-nitrocarbobenzoxy chloride in 15 ml of C_6H_6 was added and the stirring was continued for an additional 2 hr. The reaction mixture was filtered and the filtrate was evaporated to give 1.35 g of yellow solid. The solid was dissolved in a little petroleum ether (bp 100–115°) and the solution was cooled and filtered. Repeated recrystallization from petroleum ether (bp 70–100°) and finally 2-propanol gave an analytical sample of **4** melting at 99–101°.

Anal. Calcd for $C_{12}H_{10}N_2O_4$: C, 58.53; H, 4.09; N, 11.38. Found: C, 58.36; H, 3.94; N, 11.20.

Oxidation of 2 to 4.—A mixture of 87 mg of **2** containing 2% **3** and 200 mg of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in 15 ml of toluene was refluxed for 5.5 hr. The solvent was evaporated to dryness and the residue extracted with chloroform. The chloroform extract was washed with 2% NaOH solution, dried over K_2CO_3, and decolorized with charcoal. The solution was evaporated to dryness to give 64 mg of crude **4** which had an infrared spectrum identical with that of authentic **4**.

2-Anilino-4,7-dihydro-1,3-thiazepine (6).—To a solution of 2.3 g of 2-vinylaziridine in 20 ml of ether cooled to 0° was added dropwise 4.5 g of phenyl isothiocyanate. A white solid precipitated. About 3 ml of petroleum ether (bp 30–60°) was added to complete the precipitation of **6**. The crude **6** was filtered and washed with a 1:1 mixture of ether–petroleum ether (bp 30–60°) giving 4.0 g (59%) of crude **6**; recrystallization from 4:1 petroleum ether (bp 100–115°)–1-propanol, gave **6**, mp 138–141°.

Anal. Calcd for $C_{11}H_{12}N_2S$: C, 64.67; H, 5.92; N, 13.71. Found: C, 64.63; H, 6.11; N, 13.56.

2-(*p*-Chlorophenyl)-4,7-dihydro-1,3-thiazepine (7).—To a slurry of 7.4 g of *p*-chlorothiobenzoylthioglycolic acid in 75 ml of water was added 3.1 g of sodium bicarbonate in small portions with shaking. About 100 ml of ether and 2.2 g of vinylaziridine was added to the reaction mixture which was then stirred for 1.5 hr. The ether layer was separated, the solvent evaporated, and the residue dissolved in hexane. The hexane solution was chromatographed on alumina using hexane as the eluent giving 3.4 g of crude **7**. Dissolution in hexane and cooling to −10° gave white crystals which melted at room temperature.

Registry No.—**1**, 31417-81-9; **2**, 31417-82-0; **3**, 31417-83-1; **4**, 31417-84-2; **6**, 31417-85-3; **7**, 31417-86-4.

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

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Reactions of 2-*p*-Nitrophenyl-4,7-dihydro-1,3-oxazepine

HAROLD W. HEINE* AND P. G. MENTE

Department of Chemistry, Bucknell University, Lewisburg, Pennsylvania 17837

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Reactions of 2-*p*-nitrophenyl-4,7-dihydro-1,3-oxazepine (**1**) with electrophilic reagents such as bromine or iodine form the ring-contracted products 2-*p*-nitrophenyl-5-(1,2-dibromoethyl)-2-oxazoline (**2**) and 2-*p*-nitrophenyl-5-vinyl-2-oxazoline (**3**), respectively. Compound **1** is also isomerized by sulfuric acid, iodide ion, and bromide ion into **3** but with methoxide ion, cyanide ion, triethylamine, and thiocyanate ion **1** is rearranged into *cis*-1-*p*-nitrobenzamido-1,3-butadiene (**5**). Treatment of *N*-(4-iodo-2-butenyl)-*p*-nitrobenzamide (**4a**) and *N*-(2-iodo-3-butenyl)-*p*-nitrobenzamide (**12**) with sodium hydride gave *N*-*p*-nitrobenzoyl-3-pyrroline (**13**) and **3**, respectively.

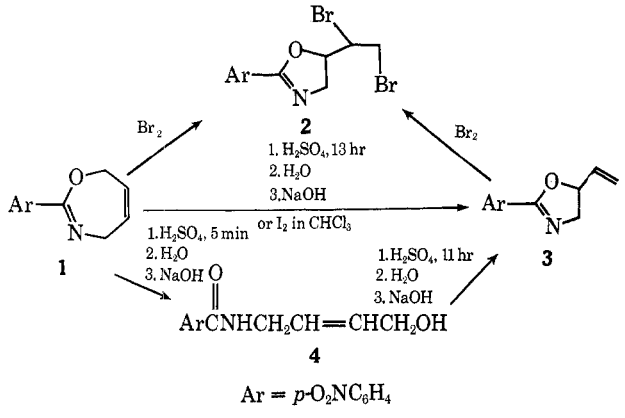
The synthesis and rearrangement of 1-*p*-nitrobenzoyl-2-vinylaziridine into 2-*p*-nitrophenyl-4,7-dihydro-1,3-oxazepine (**1**) has been recently reported.[1] In this paper the ring openings and rearrangements of **1** by various electrophiles, nucleophiles, and bases are described.

(1) P. G. Mente, H. W. Heine, and G. R. Scharoubim, *J. Org. Chem.*, **33**, 4547 (1968).

Results

Treatment of **1** with bromine formed 2-*p*-nitrophenyl-5-(1,2-dibromoethyl)-2-oxazoline (**2**) in 48% yield (Scheme I). The structure of **2** was established by an alternate synthesis involving the addition of bromine to the known 2-*p*-nitrophenyl-5-vinyl-2-oxazoline (**3**)[1] and by nmr spectroscopy. Other electrophilic reagents also caused the ring contraction of **1**. For example,

SCHEME I

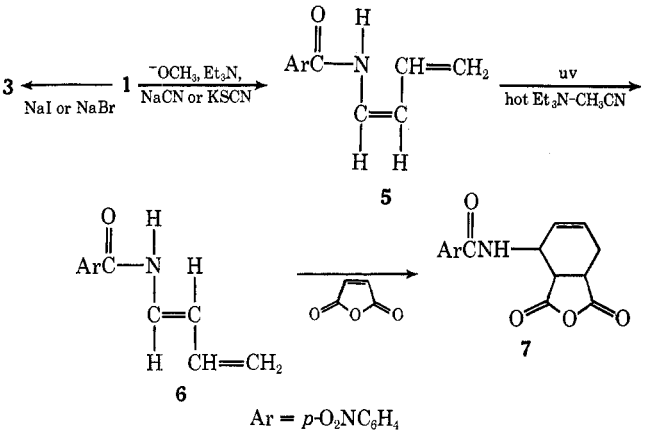


reaction of **1** with iodine in chloroform gave **3**. Reaction of **1** with concentrated sulfuric acid for 13 hr followed by the addition of water also gave **3**. However, isomerization of **1** to **3** did not occur if the reaction time in sulfuric acid was about 5 min. Under these conditions *N*-(4-hydroxy-2-butenyl)-*p*-nitrobenzamide (**4**) was obtained. Compound **3** was also formed by reaction of **4** with concentrated sulfuric acid for 11 hr at room temperature (Scheme I).

A ring-opening reaction similar to that observed with **1** and sulfuric acid to give **4** occurred when **1** was treated with 47% hydriodic acid. A 73% yield of *cis*-*N*-(4-iodo-2-butenyl)-*p*-nitrobenzamide (**4a**) was obtained.

Compound **1**, if reacted with an appropriate nucleophile or base, could be isomerized selectively into either **3** or *cis*-4-(*p*-nitrobenzamido)-1,3-butadiene (**5**). For example, **3** was formed by the treatment of **1** with sodium iodide in boiling butanone and by sodium bromide in boiling acetonitrile (Scheme II). On the other

SCHEME II



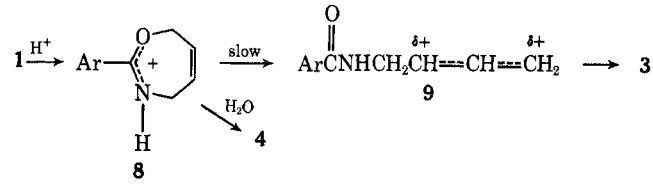
hand, **5** was obtained exclusively by the treatment of **1** with (a) sodium methoxide solution, (b) triethylamine in acetonitrile, (c) sodium cyanide or potassium thiocyanate in acetonitrile, or (d) sodium chloride in DMSO (Scheme II). Reaction of **1** with sodium bromide in DMSO gave a mixture of 50% of **3** and 10% of **5**. Compound **1** in refluxing decane also gave **5** in 50% yield.

Compound **5** was isomerized into *trans*-1-(*p*-nitrobenzamido)-1,3-butadiene (**6**) by reaction with triethylamine in refluxing acetonitrile. Under similar experimental conditions it was possible to convert **1** to **6**. Compound **6** could also be prepared by irradiating **5** in methanol for 48 hr (Scheme II). The structures of compounds **5** and **6** were elucidated by nmr spectroscopy, ir spectroscopy, mass spectrometry, elemental analyses, and by reactions of **5** and **6** with maleic anhydride. Assignment of the trans configuration to **6** was based on the ease of its reaction with maleic anhydride (several minutes in hot benzene) to give the Diels–Alder adduct **7** (Scheme II). Compound **5** did not react with maleic anhydride after 12 hr in hot benzene but did react with maleic anhydride after 2.5 hr in boiling *p*-xylene to give **7**. Undoubtedly in boiling *p*-xylene the cis diene **5** isomerized to **6** which subsequently reacted with the maelic anhydride to give **7**.

Discussion

The reactions of **1** in sulfuric acid can be explained by the initial formation of the protonated dihydrooxazepine **8** (Scheme III). Intermediate **8** in the ab-

SCHEME III



sence of a nucleophile, could slowly isomerize to the oxazolinium ion of **3** *via* the intermediate **9**. Intermediate **8** could also undergo nucleophilic attack at C_7 or C_2 to form **4** provided that water is added to the reaction mixture prior to the isomerization of **8** to **3**.

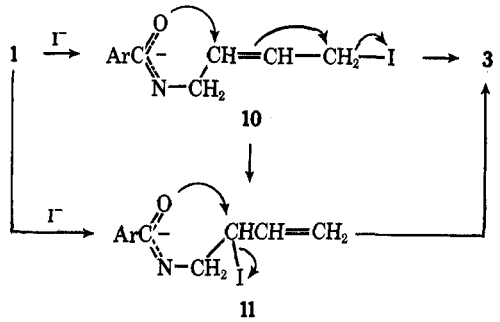
It can be presumed that the electrophilic reagents bromine and iodine act much like the sulfuric acid in bringing about the ring contraction of **1**. Subsequent addition of bromine to the oxazoline **3** forms compound **2**.

Several explanations can be put forth to account for the interesting iodide and bromide ion catalysis of **1** to **3**. For example, nucleophilic substitution by iodide ion on the C_7 atom of **1** could give the ambident anion **10** which by subsequent attack of the amido oxygen at the carbon–carbon double bond of **10** would yield **3** (Scheme IV). Alternatively, **10** may rearrange to the isomeric species **11** which by direct displacement of halide ion by the benzamido oxygen would form **3**. Indeed, it is possible to form **11** directly by attack of iodide ion on C-5 of **1** (Scheme IV). The ion **11** has already been proposed as the intermediate for the iodide ion catalyzed isomerization of 1-*p*-nitrobenzoyl-2-vinylaziridine into **3**.[1]

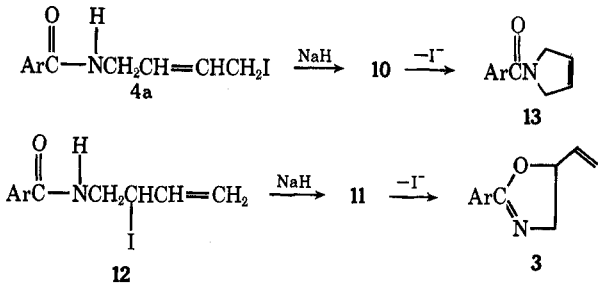
The intermediacy of **10** seems unlikely since treatment of *N*-(4-iodo-2-butenyl)-*p*-nitrobenzamide (**4a**) with excess sodium hydride in ether gave *N*-(*p*-nitrobenzoyl)-3-pyrroline (**13**)[1] in 97% yield (Scheme V). That intermediate **11** could be involved in the rearrangement of **1** to **3** is supported by the observation that *N*-(2-iodo-3-butenyl)-*p*-nitrobenzamide (**12**) (prepared by the reaction of 47% hydriodic acid with 1-*p*-nitrobenzoyl-2-vinylaziridine) gave **3** in quantitative yield when treated with sodium hydride (Scheme V).

The mechanism for the easy formation of butadiene **5** from **1** at ambient temperatures by basic reagents

SCHEME IV



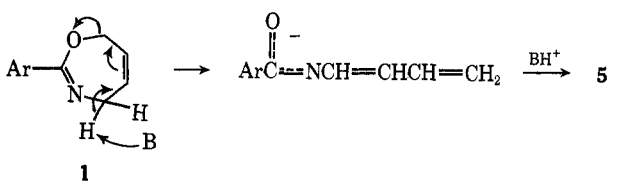
SCHEME V



Ar = p-$O_2C_6H_4$

such as methoxide ion, cyanide ion, or triethylamine can be viewed as a 1,4 elimination (Scheme VI). If

SCHEME VI

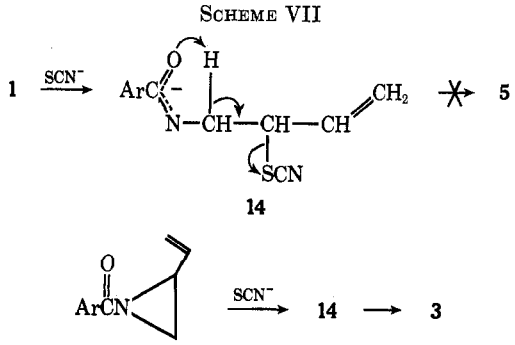


this be the case the elimination probably occurs in a concerted manner since **1** recovered from a reaction mixture of **1** in CH_3OD containing methoxide ion failed to exhibit deuterium incorporation. It is also to be noted that the elimination is stereospecific and gives the cis diene **5**.

Surprisingly, thiocyanate ion also catalyzed the rearrangement of **1** to the butadiene **5**. The increased basicity of the thiocyanate ion relative to iodide ion may suffice to favor the reaction pathway leading to the butadiene. Considerations such as thiocyanate ion reacting with **1** to form the anion **14** which because of the poorer leaving group qualities of thiocyanate relative to iodide ion would provide time for extraction of a proton by the amido oxygen and subsequent displacement of thiocyanate (Scheme VII) to give **5** are ruled out since 1-*p*-nitrobenzoyl-2-vinylaziridine with thiocyanate ion in acetonitrile gives a quantitative yield of the oxazoline **3**, presumably through the formation of **14** (Scheme VII).

The decreased nucleophilicity but increased basicity of bromide ion and chloride ion relative to iodide ion is probably responsible, too, for the formation of 10% of compound **5** and 50% of compound **3** when sodium bromide was allowed to react with **1** in DMSO and for the formation of 93% of **5** when sodium chloride was allowed to react with **1** in DMSO.

SCHEME VII



Experimental Section

Conversion of 1 to 2.—A 1% solution by weight of bromine in 17 g of $CHCl_3$ was added dropwise to a solution of 218 mg of **1** in 20 g of $CHCl_3$. The bromine color was slowly discharged. Evaporation of the reaction mixture to dryness and washing the residue with a small quantity of ethanol gave 180 mg (48%) of **2**. Recrystallization from ethanol gave **2** melting at 186–188°.

Anal. Calcd for $C_{11}H_{10}Br_2N_2O_3$: C, 34.95; H, 2.67; N, 7.41. Found: C, 34.88; H, 2.72; N, 7.51.

Conversion of 1 to 3 by Sulfuric Acid.—In 3.0 g of concentrated sulfuric acid was dissolved 100 mg of **2**. The solution was left at room temperature for 13 hr. Ice was then added to the reaction mixture followed by sodium hydroxide solution until neutrality was achieved. The precipitate was collected by filtration giving 65 mg (65%) of **3**, mp 96–98°. The infrared spectrum of **3** was identical with that of an authentic sample.[1]

Rearrangement of 1 to 3 by Iodine.—To 0.5 ml of $CDCl_3$ was added 102 mg of **1** and 47 mg of iodine. The nmr spectrum showed complete conversion of **1** to **3** within 24 hr. The contents of the nmr tube were drained into 25 ml of 5% sodium thiosulfate solution. The solution was extracted with $CHCl_3$, the $CHCl_3$ was evaporated, and the residual oil dissolved in CH_3OH. Addition of water precipitated 40 mg (40%) of **3**.

Rearrangement of 1 to 3 by Sodium Iodide.—A mixture of 157 mg of **1** and 289 mg of sodium iodide in 15 ml of butanone was heated under reflux for 5 hr. Evaporation of the solvent, addition of water to the residue, and filtration gave 147 mg (93%) of **3**. A control run of **1** in boiling butanone gave back starting material.

Rearrangement of 1 to 3 by Sodium Bromide.—A mixture of 140 mg of **1** and 400 mg NaBr in 15 ml of CH_3CN was heated under reflux 48 hr (not all of the NaBr dissolved). The reaction mixture was worked up as in the previous experiment to give 134 mg (95%) of **3**. A shorter reaction time (24 hr) gave incomplete conversion of **1** to **3**.

Conversion of 1 to 4.—To 2.8 g of concentrated sulfuric acid was added 250 mg of **1**. After about 1 min ice was added followed by sodium hydroxide solution until the reaction mixture was neutral. Filtration gave 123 mg (42%) of **4**. Recrystallization from water gave **4** melting at 146–149°. The nmr spectrum of **4** taken in a mixture of DMSO and $CDCl_3$ showed clearly two olefinic protons centered at δ 5.55, four aromatic protons at δ 8.10, four aliphatic protons centered at δ 4.1, and the NH and OH protons at approximately δ 8.16 and 4.0, respectively.

Anal. Calcd for $C_{11}H_{12}N_2O_4$: C, 55.93; H, 5.12; N, 11.86. Found: C, 56.26; H, 5.30; N, 11.79.

Conversion of 4 to 3.—A mixture of 78 mg of **4** and 1 g of concentrated sulfuric acid was kept at room temperature for 10.5 hr. Ice was added to the mixture and then sodium hydroxide solution until the mixture was basic. Filtration gave 65 mg (90%) of **3**.

Rearrangement of 1 to *cis*-1-*p*-Nitrobenzamido-1,3-butadiene (5) by Sodium Methoxide.—To 10 ml of 0.3 M sodium methoxide solution was added 146 mg of **1**; the reaction mixture was heated for 1–2 min to dissolve all of the **1**. Evaporation of the methanol gave a bright yellow solid which was washed with water and collected by filtration. The crude **5** (137 mg, 94%) was recrystallized from a small quantity of aqueous CH_3CN or acetonitrile itself to give pure **5**: mp 183–185°; ir (Nujol) 3.10 (NH), 5.53 (overtone of terminal vinyl), 6.10 (amide C=O), 6.23 (conjugated diene), 7.65 ($CH=CH_2$), 7.80, 8.42, 8.50, 9.01, 9.58, 9.87, 10.01 ($CH=CH_2$), 11.08 ($CH=CH_2$), 11.46, 11.75 ($>C=CH_2$), 12.30, 12.40, 12.79, 13.82 (δ CH diene), 13.95

(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]

J. W. A. M. JANSSEN AND CLARISSE L. HABRAKEN*

Laboratory of Organic Chemistry, The University, Leiden, The Netherlands

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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).

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