washed with saturated brine and dried over anhydrous magnesium sulfate.[15b] The hexane was removed under reduced pressure and the residue was distilled giving 0.14 g (55%) of pale yellow oil. This material was chromatographed on 5 g of neutral alumina (Woelm, activity I) and the material eluted with pentane was distilled giving 0.07 g of decalin **9** as a colorless liquid: $\lambda_{max}^{film}$ 6.89, 7.24, 8.51, 10.10, and 10.42 $\mu$; $\delta_{TMS}^{CCl_4}$ = 0.98 ($CH_2CH_3$, triplet, $J$ = 7 cps), and 0.82 ppm (C-10 $CH_3$).

*Anal.* Calcd for $C_{13}H_{24}$: C, 86.58; H, 13.42. Found: C, 86.9; H, 13.2.

The gas chromatogram obtained using a 13 ft by 1/8 in. 10% DC-550 oil on 60–80 Chromosorb W column at 100° with a helium flow rate of 50 cc/min showed one peak at 22.8 min (**9**) with a shoulder at 24.4 min corresponding to the epimeric decalin **16** (see below).

**B. From Decalylacetic Acid 10.**—A solution of 20 mg of decalylacetic acid **10**[10] in 5 ml of 1,2-dimethoxyethane was added to a solution containing 50 mg of lithium aluminum hydride in 5 ml of 1,2-dimethoxyethane. The mixture was stirred at reflux for 3 hr, cooled, and treated with 0.1 ml of water and 0.08 ml of 10% aqueous sodium hydroxide. After stirring for several hours the mixture was filtered and the filtrate was distilled giving 19 mg of decalylethanol **11**: $\lambda_{max}^{film}$ 3.02 (OH), 6.91, 9.42, 11.46, and 11.77 $\mu$.

A 15-mg portion of this alcohol in 0.5 ml of pyridine was treated with 45 mg of methanesulfonyl chloride.[15c] After 3.5 hr, the mixture was diluted with ice–water and thoroughly extracted with ether and benzene. The extracts were washed successively with water, 2% sulfuric acid, water, 10% sodium bicarbonate, and saturated brine and dried. The solvent was removed under reduced pressure affording 22 mg of oily methanesulfonate **12**: $\lambda_{max}^{film}$ 7.37, 8.49, 10.55, and 12.25 $\mu$.

The above sample of methanesulfonate **12** in 0.5 ml of absolute ethanol and 5 ml of ether was added to 25 ml of liquid ammonia containing 57 mg of lithium wire. After 10 min, an additional 50 mg of lithium wire and 0.5 ml of ethanol was added. The solution was stirred for 1.5 hr, 5 g of ammonium chloride was added, and the ammonia was allowed to evaporate. The residue was treated with saturated brine and extracted with ether. The extracts were dried, the solvent was removed under reduced pressure, and the residue was chromatographed on alumina giving 6 mg (42%) of colorless decalin **9**. The infrared spectrum and gas chromatographic retention time were identical with the material described in part A.

***trans*-10β-Methyl-7β-ethyldecalin (16).**[15e]—A 35-mg sample of acid **13**[10] was reduced with lithium aluminum hydride according to the procedure described above for acid **10**. The resulting alcohol **14** (30 mg, 92%) was distilled: bp 70° (bath temperature) (0.1 mm); $\lambda_{max}^{film}$ 3.02 (OH), 6.89, 9.52, 11.20, and 11.73 $\mu$.

The methanesulfonate derivative **15** ($\lambda_{max}^{film}$ 6.89, 7.37, 8.49, 10.55, 12.07, and 12.40 $\mu$) was prepared from 200 mg of alcohol **14** according to the procedure described above for **12**.

A 274-mg sample of methanesulfonate was reduced as described above for the preparation of **9**. The resulting decalin **16** (100 mg, 55%) exhibited $\lambda_{max}^{film}$ 6.89, 7.22, 8.49, 10.03, 10.13, and 12.41 $\mu$.

*Anal.* Calcd for $C_{13}H_{24}$: C, 86.58; H, 13.42. Found: C, 86.6; H, 13.6.

The retention time (24.4 min) observed in the gas chromatogram of this material corresponded exactly with that of the minor component obtained *via* degradation of the mixture of octalones **5b** and **6b** (see above).

**Attempted 1,6 Addition of Phenylmagnesium Bromide to Dienone 2.**—The general procedure was followed using 35 ml of 0.6 *M* phenylmagnesium bromide in ether. The resulting viscous dark brown oil was chromatographed on alumina giving 0.32 g of biphenyl and 0.60 g of thick oil [$\lambda_{max}^{film}$ 5.83, 5.93 (CO), 13.05, and 14.30 $\mu$], which did not distil at 150° (0.1 mm).

**Attempted 1,6-Addition of Isopropylmagnesium Bromide to 1,10-Dimethyl-1(9),7-hexal-2-one (17).**[15e]—To 0.50 g of dienone **17**[16] in 50 ml of tetrahydrofuran containing 0.20 g of cupric acetate hydrate was added 25 ml of 0.41 *M* isopropylmagnesium bromide at −10 to −20° according to the general procedure. The crude product was triturated with ether giving 0.15 g of white solid which exhibited mp 222–223° after two recrystallizations from ether–chloroform; $\lambda_{max}^{KBr}$ 6.01 (CO), 6.31 (C=C), 6.83, 7.66, and 8.34 $\mu$; $\lambda_{max}^{95\%\ EtOH}$ 263 m$\mu$ ($\epsilon$ 22,000 for molecular wt 439); $\delta_{TMS}^{CDCl_3}$ = 0.85 (triplet, or two doublets 12 H), 1.41 (singlet, 6 H), 2.00 (singlet, 6 H), 3.45 ppm (singlet, 2 H) assuming $C_{30}H_{46}O_2$.

*Anal.* Calcd for $C_{30}H_{46}O_2$ (two isopropyl groups): C, 82.13; H, 10.57; mol wt, 438.7. Calcd for $C_{27}H_{40}O_2$ (one isopropyl group): C, 81.76; H, 10.17; mol wt, 396.6. Calcd for $C_{24}H_{34}O_2$ (no isopropyl groups): C, 81.31; H, 9.67; mol wt, 354.5. Found: C, 81.14; H, 10.42; mol wt, 399.[20]

**Acknowledgments.**—Support of this work by the National Science Foundation through a Research Grant GP-4174 and the National Institutes of Health through a Predoctoral Fellowship 1-Fl-GM-29,696 (to H. Roebke) is gratefully acknowledged.

(20) Analysis was by Miss H. Beck using a Mechrolab Model 303 vapor pressure osmometer.

# Aziridines. XVI. 1-Azaspiro[2.5]octane and 1-Azaspiro[2.4]heptane[1]

PAUL E. FANTA, ROBERT J. SMAT, LEO F. PIECZ, AND LAWRENCE CLEMENS

*Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois 60616*

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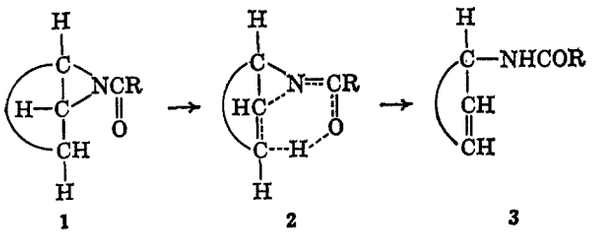
Under conditions found suitable for the preparation of 1-*p*-nitrobenzoyl-2,2-dimethylaziridine, 1-azaspiro[2.5]-octane and 1-azaspiro[2.4]heptane gave instead of the expected N-*p*-nitrobenzoyl derivatives the isomeric N-cycloalkenylmethyl *p*-nitrobenzamides, which were readily cyclized to the isomeric spirooxazolines. The N-*p*-iodobenzenesulfonyl and N-*p*-nitrobenzenesulfonyl derivatives of 1-azaspiro[2.5]octane were prepared and found to rearrange smoothly to the unsaturated sulfonamides upon gentle heating. Attempted preparation of the same derivatives of 1-azaspiro[2.4]heptane gave directly the isomeric, unsaturated sulfonamides. A higher temperature and longer time was required for the analogous rearrangement of 1-*p*-nitrobenzenesulfonyl-2,2-dimethylaziridine. The relative ease of rearrangement in the three aziridine systems is better accounted for in terms of a concerted transition state than a zwitterion intermediate.

In previous work from this laboratory,[2] it was found that the temperature required for the pyrolytic rearrangement of N-acyl, fused, bicyclic aziridines (**1**) to unsaturated amides (**3**) was greatly dependent on the size of the ring. Thus, when the three contiguous carbon atoms of part structure **1** were part of an eight- or ten-membered ring, the reaction occurred readily even below 80°. A much higher temperature was required when the three carbon atoms were part of a six-membered ring or a five-membered ring.[3] These observations are in accord with the view that the isom-

(1) Supported in part by Public Health Service Research Grant No. GM-11883 from the National Institute of General Medical Sciences. Abstracted from the Ph.D. thesis of R. J. S., Illinois Institute of Technology, June 1966, which includes complete details of the spectral data. Some preliminary work was initiated by L. C. as a National Science Foundation Undergraduate Research Participate, 1958–1959, and also appears in the M.S. thesis of L. F. P., Illinois Institute of Technology, June 1962.

(2) P. E. Fanta and E. N. Walsh, *J. Org. Chem.*, **30**, 3574 (1965), and previous papers in this series.

(3) P. E. Fanta and R. J. Smat, manuscript in preparation.

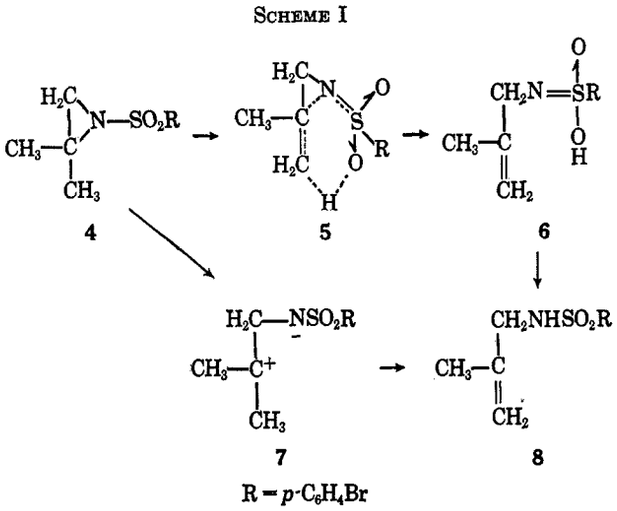


1 2 3

erization of **1** to **3** occurs *via* a stereospecific, cyclic transition state **2**.

It has also been found that an analogous pyrolytic rearrangement of 1-*p*-bromobenzenesulfonyl-2,2-dimethylaziridine (**4**) to N-β-methallyl-*p*-bromobenzenesulfonamide (**8**) occurs, although somewhat higher temperatures are required. For this reaction the following alternative mechanisms were suggested: either a concerted ring opening and proton transfer *via* a cyclic transition state **5** and sulfonamide tautomer **6**; or ring opening to give a zwitterion **7**, followed by proton transfer (Scheme I).[4]

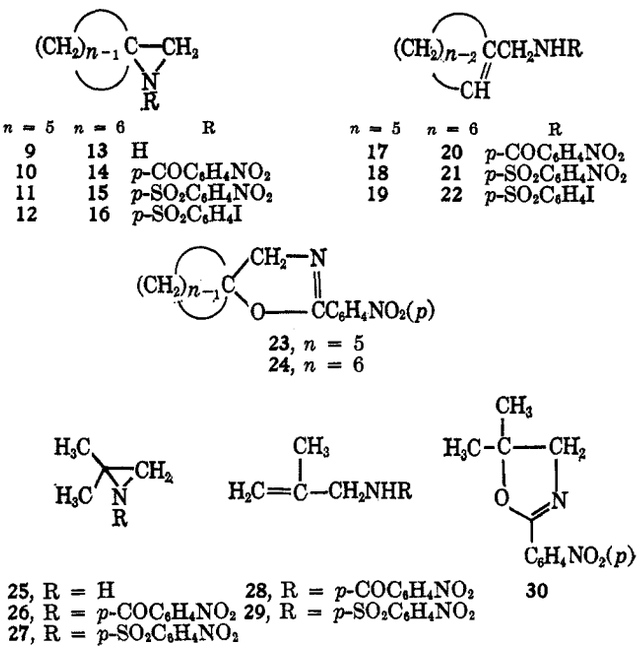
SCHEME I



4 5 6 7 8

R = *p*-$C_6H_4Br$

The present work was undertaken with the objective of determining the effect on these rearrangements of inclusion of the aziridine ring in a spiro skeleton with a carbocyclic ring. For this purpose, we selected the two compounds 1-azaspiro[2.5]octane (**13**), the preparation of which has already been described,[5] and 1-azaspiro-[2.4]heptane (**9**), which was prepared from nitrocyclopentane by a conventional sequence of reactions. Nitrocyclopentane was prepared from bromocyclopentane by the method of Kornblum[6] and converted to (1-nitrocyclopentane)methanol in 86% yield by treatment with paraformaldehyde and methanolic potassium hydroxide. The low-pressure hydrogenation of the nitro alcohol in the presence of either palladium- or rhodium-on-carbon catalyst gave (1-aminocyclopentane)methanol in up to 77% yield. The sulfate ester was prepared from the amino alcohol by treatment with either sulfuric acid or chlorosulfonic acid. The previously unreported 1-azaspiro[2.4]heptane (**9**) was prepared in 57% yield by treatment of the sulfate ester with excess aqueous sodium hydroxide, and characterized by the preparation of a crystalline N-phenylthiocarbamoyl derivative. Further support for the structure was provided by the infrared and nmr spectra.



| *n* = 5 | *n* = 6 | R |
|---|---|---|
| 9 | 13 | H |
| 10 | 14 | *p*-$COC_6H_4NO_2$ |
| 11 | 15 | *p*-$SO_2C_6H_4NO_2$ |
| 12 | 16 | *p*-$SO_2C_6H_4I$ |

| *n* = 5 | *n* = 6 | R |
|---|---|---|
| 17 | 20 | *p*-$COC_6H_4NO_2$ |
| 18 | 21 | *p*-$SO_2C_6H_4NO_2$ |
| 19 | 22 | *p*-$SO_2C_6H_4I$ |

23, *n* = 5
24, *n* = 6

25, R = H
26, R = *p*-$COC_6H_4NO_2$
27, R = *p*-$SO_2C_6H_4NO_2$
28, R = *p*-$COC_6H_4NO_2$
29, R = *p*-$SO_2C_6H_4NO_2$

30

The two spiroaziridines were each treated with *p*-nitrobenzoyl chloride in excess triethylamine with the expectation that the nitrobenzoyl derivatives **10** and **14** would be formed. Surprisingly, only the unsaturated amides **17** and **20** were isolated. The structures assigned to these amides were supported by the infrared spectra with distinctive bands indicating the presence of NH at 3500 $cm^{-1}$, amide C=O at 1670 $cm^{-1}$, and =CH— at 3050 $cm^{-1}$. The nmr spectra also clearly support the unsaturated amide structures. Both compounds instantly discharged the purple color of potassium permanganate in aqueous methanol.

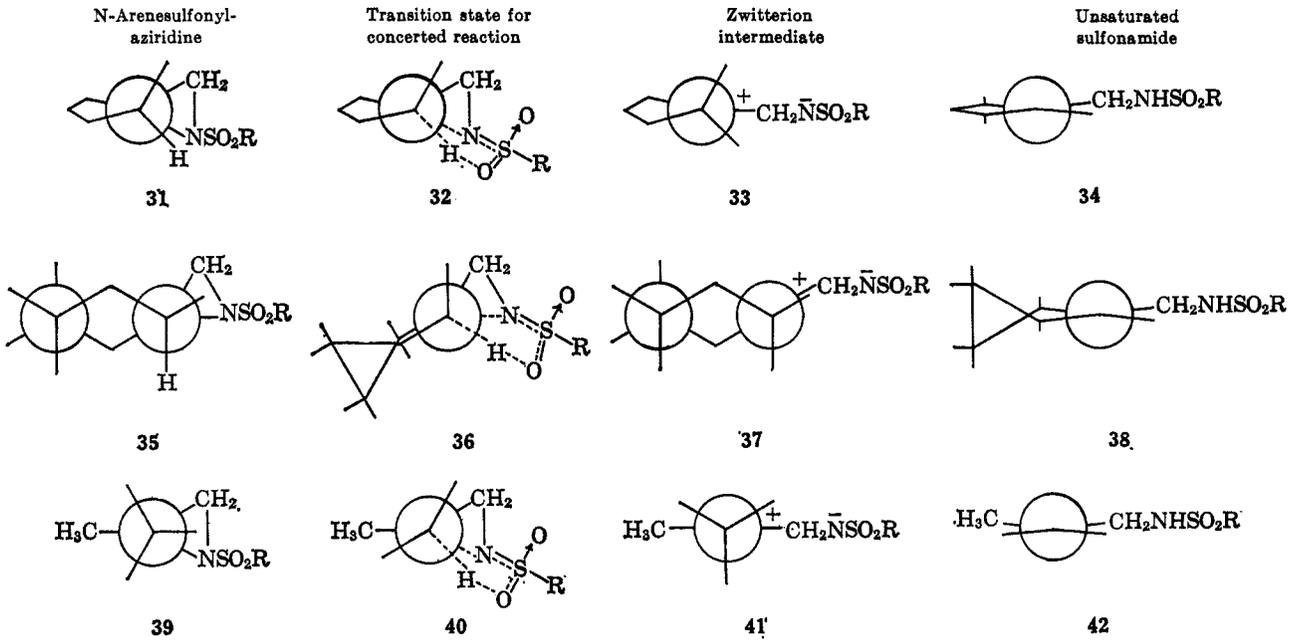
Apparently in both instances the formation of the N-acylaziridine was quickly followed by a facile isomerization to the unsaturated amide, so that no conclusion about a ring-size effect is possible. The unsaturated amides were cyclized by treatment with cold, concentrated sulfuric acid to give the spirooxazolines **23** and **24** in quantitative yield.

In contrast, 1-(*p*-nitrobenzoyl)-2,2-dimethylaziridine (**26**) was obtained in good yield by treatment of 2,2-dimethylaziridine (**25**) with *p*-nitrobenzoyl chloride in the presence of excess triethylamine. The acylaziridine **26** is readily isomerized to the unsaturated amide **28**,[7] which is quantitatively cyclized to the oxazoline **30** in sulfuric acid.[8]

On the other hand, a distinct ring-size effect was found in the behavior of the *p*-nitrobenzenesulfonyl and *p*-iodobenzenesulfonyl derivatives of the two spiroaziridines. The azaspirooctane derivatives **15** and **16** were readily prepared in the usual manner and purified by recrystallization from ethanol or benzene–hexane mixture. Upon refluxing in toluene for 16 hr, each compound was isomerized in high yield to the respective unsaturated sulfonamides, **21** and **22**. In contrast, attempted preparation of the azaspiroheptane

(4) D. V. Kashelikar and P. E. Fanta, *J. Org. Chem.*, **26**, 1841 (1961).
(5) P. B. Talukdar and P. E. Fanta, *ibid.*, **24**, 526 (1959).
(6) N. Kornblum and J. W. Powers, *ibid.*, **22**, 455 (1957).
(7) P. E. Fanta and M. K. Kathan, *J. Heterocyclic Chem.*, **1**, 293 (1964).
(8) H. W. Heine, M. E. Fetter, and E. M. Nicholson, *J. Am. Chem. Soc.*, **81**, 2202 (1959).

CHART I




derivatives **11** and **12** gave directly the rearrangement products **18** and **19**.

As expected from the earlier observations,[4] a much higher temperature and longer reaction time was required for the rearrangement of 1-*p*-nitrobenzenesulfonyl-2,2-dimethylaziridine (**27**) than for the azaspirooctane derivative **15**. Only unreacted starting material was obtained when a toluene solution of **27** was refluxed for 50 hr. At 150°, **27** was isomerized to N-(β-methallyl)-*p*-nitrobenzenesulfonamide (**29**).

The nmr spectra of all the isolated compounds were in accord with the assigned structures. The spectra of the spiroaziridines **9** and **13** had three distinctive bands due to the proton on nitrogen, the methylene group in the aziridine ring, and a more complex band assignable to the methylene groups in the carbocyclic ring. In the spectrum of the aziridine derivative **15** the singlet due to the methylene group in the aziridine ring was shifted downfield. The spectra of the unsaturated benzamides **17** and **20** were very similar, each having five distinctive bands due to the five different kinds of protons present. The spectra of the unsaturated benzenesulfonamides were also very similar, except that a band believed to be due to the proton on nitrogen was found only in the spectrum of **18**.

## Discussion

A study of the three-dimensional models or Newman projection formulas of 1-arenesulfonyl-1-azaspiro[2.4]-heptane (**31**) and 1-arenesulfonyl-1-azaspiro[2.5]octane (**35**) suggests that sterically the three-membered ring of these spiro systems is somewhat analogous to an *exo* double bond attached to a cyclopentane or cyclohexane ring.[9] Thus, it appears that **31** has less Pitzer strain in the five-membered ring than does cyclopentane, while **35** has more Pitzer strain in the six-membered ring than does cyclohexane. Taken alone, this consideration is inadequate to explain the observed ring-size effect, since it leads to the erroneous expectation that 1-arenesulfonyl-1-azaspiro[2.5]octane should undergo a greater decrease of strain upon rearrangement to the isomeric, unsaturated sulfonamide (**35** → **38**), and therefore should rearrange more readily than the corresponding 1-arenesulfonyl-1-azaspiro[2.4]heptane derivative (**31** → **34**; see Chart I).

A different result is to be expected if the possible mechanisms of the reaction are considered in further detail. If the rearrangement is a concerted reaction requiring coplanarity of the elements in the quasi-six-membered ring, then little additional strain is involved in going from the ground state to the transition state for the rearrangement of 1-arenesulfonyl-1-azaspiro[2.4]heptane (**31** → **32**). In contrast, it appears that the cyclohexane ring of 1-arenesulfonyl-1-azaspiro[2.5]octane must go from a favorable chair conformation in the ground state to a comparatively strained twist conformation in the transition state to attain coplanarity of the quasi six-membered ring in the analogous transition state (**35** → **36**).[10] The even higher temperature and longer time required for the isomerization of 1-arenesulfonyl-2,2-dimethylaziridine may be ascribed to a comparatively large entropy effect associated with the attainment of the transition state (**39** → **40**), which places a relatively high constraint on the rotational degrees of freedom of the parent molecule.

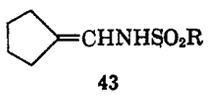
If the reaction proceeds through the formation of a zwitterion intermediate, it would also be expected that the formation of the cyclopentyl cation **33**, would

(9) As a result of a comprehensive survey of the literature, H. C. Brown, J. H. Brewster, and H. Schechter [*J. Am. Chem. Soc.*, **76**, 467 (1954)] observed that "reactions will proceed in such a manner as to favor the formation or retention of an *exo* double bond in the 5-ring system and to avoid the formation or retention of the *exo* double bond in the 6-ring system...for a first approximation attention may be focused on the relative stabilities of the *exo* double bonds and the smaller differences in stabilities of the *endo* double bonds may be ignored."

(10) It is assumed that the nitrogen atom is in the equatorial position as shown in formula **35**. A determination of the molecular structure of compound **16** in the crystalline state by means of single-crystal X-ray diffraction is underway in the laboratory of L. M. Trefonas at the University of Louisiana in New Orleans. For a cyclohexane ring fused *cis* to a small planar ring the twist conformation is favored over the boat conformation: E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw Hill Book Co., Inc., New York, N. Y., 1962, p 278.

be greatly favored over the cyclohexyl cation **37**, as has been found for the SN1 type solvolysis of 1-methylcycloalkyl chlorides.[11] The ring-size effect here may be clearly ascribed to the greater strain in the cyclohexyl cation owing to increased bond oppositions, compared to the decreased bond oppositions in the cyclopentyl cation. On the other hand, if the rate of reaction is dependent on carbonium ion stability, **41** should be more stable than **37**, in agreement with the relative rate data for tertiary chloride solvolysis,[11] and **39** should rearrange more readily than **35**. In summary, it appears that the relative ease of rearrangement of the three different aziridine systems is better accounted for in terms of a concerted transition-state mechanism than a zwitterion intermediate mechanism.

An intermediate zwitterion such as **33** could also undergo transfer of a proton from the side-chain methylene group to give a vinylamine derivative **43**, in which the ring strain would be at a minimum. The fact that such a product was not observed argues strongly against the zwitterion mechanism, but does not conclusively exclude it.[12]



**43**

## Experimental Section

All melting points and boiling points are uncorrected. Melting points were determined on a Thomas–Hoover capillary melting point apparatus. Microanalyses were performed by Micro-Tech Laboratories, Inc., Skokie, Ill. Infrared spectra were determined on a Perkin-Elmer Model 21 infrared spectrometer using sodium chloride optics and either neat liquids or chloroform solutions (*ca.* 3% by weight). Nmr spectra were obtained using a Varian A-60 spectrometer and either neat liquids or dilute solutions (*ca.* 10% by weight) of deuteriochloroform; tetramethylsilane was used as an internal standard. Chemical shifts are given on the $\delta$ scale in parts per million relative to tetramethylsilane ($\delta$ 0.0). 2,2-Dimethylaziridine was obtained from K and K laboratories, Inc. Sodium nitrite (Eastman White Label) was dried overnight in an electric oven at 125–130° and placed in a desiccator until just prior to use. Dimethyl sulfoxide (Crown-Zellerbach) was dried over calcium hydride for 2 weeks and distilled (reduced pressure) from calcium hydride. "Dry" solvents were redistilled prior to use.

**Nitrocyclopentane.**—The procedure employed was essentially that developed by Kornblum.[6] Cyclopentyl bromide (332.0 g, 2.23 moles) was added dropwise over 1.0 hr to a well-stirred mixture of 270.0 g (3.92 moles) of dried sodium nitrite contained in 1500 ml of dried dimethyl sulfoxide. The reaction was carried out at 15° with external cooling in an ice bath. The reaction mixture was then stirred for an additional 5.0 hr at 15–20° and then poured into 1 l. of ice–water layered over with 250 ml of petroleum ether (bp 60–70°). After separation, the aqueous phase was further extracted with five 250-ml portions of petroleum ether. The combined extracts were washed with four 250-ml portions of water and dried over anhydrous magnesium sulfate. The drying agent was removed by filtration and the solvent removed *in vacuo* leaving a yellow oil. Distillation of the oil gave 111.5 g (49%) of colorless nitrocyclopentane, bp 59° (7.0 mm), $n^{26}$D 1.4514 [lit.[6] bp 62° (8.0 mm), $n^{20}$D 1.4538]. The infrared spectrum was as follows: $\nu_{max}^{neat}$ 3010, 2900 (sh), 1550, and 1380 cm$^{-1}$.

*Anal.* Calcd for $C_5H_9NO_2$: C, 52.24; H, 7.89; N, 12.17. Found: C, 52.38; H, 8.04; N, 11.38.

**(1-Nitrocyclopentane)methanol.**—The method used was similar to that used by Noland for the preparation of (1-nitrocyclohexane)methanol.[13] Ten milliliters of a 30% solution of potassium hydroxide in methanol was added to a magnetically stirred mixture of 115.0 g (1.0 mole) of nitrocyclopentane and 30.0 g (1.0 mole) of paraformaldehyde in 80 ml of methanol. The addition took place over 10.0 min (slightly exothermic) with the initial white slurry changing to a pale yellow solution. The solution was refluxed for an additional 1.0 hr and held at 30–40° for 24.0 hr. The yellow reaction mixture was acidified with acetic acid (1 equiv) and then poured into 1 l. of benzene. The solution was filtered free of potassium acetate and the benzene filtrate was dried over anhydrous magnesium sulfate. The drying agent was removed by filtration and the benzene removed *in vacuo* leaving a brown oil. Distillation of the oil gave 125.0 g (86%) of colorless, viscous liquid, bp 76° (0.5 mm), $n^{27}$D 1.4759. The infrared spectrum showed the following bands: $\nu_{max}^{CHCl_3}$ 3720, 3530, 3010, 2920 (sh), 1540, 1455, 1355, and 1060 (broad) cm$^{-1}$.

*Anal.* Calcd for $C_6H_{11}NO_3$: C, 49.64; H, 7.65; N, 9.65. Found: C, 49.46; H, 7.72; N, 9.59.

Reaction of the nitro alcohol with phenylisocyanate gave the **phenylurethan** as white plates from ethanol–carbon tetrachloride, mp 117–118°.

*Anal.* Calcd for $C_{13}H_{16}N_2O_4$: C, 59.07; H, 6.11; N, 10.60. Found: C, 59.37; H, 6.27; N, 10.71.

**Catalytic Reduction of (1-Nitrocyclopentane)methanol to (1-Aminocyclopentane)methanol.**—In a pressure-resistant glass bottle, 22.0 g (0.15 mole) of (1-nitrocyclopentane)methanol was dissolved in 100 ml of absolute ethanol and 1.0 g of 5% palladium-on-carbon catalyst was added. The bottle was placed on a low-pressure Parr hydrogenation apparatus and the system was evacuated (water pump). Hydrogen was introduced and shaking was commenced. After 1.5 hr of shaking at 3–4 atm (room temperature), the theoretical amount of hydrogen was absorbed (0.45 mole). The bottle was removed from the shaker and the catalyst removed by filtration. The solvent was removed by distillation through a short low-hold-up distillation column and the pale yellow oily residue was fractionally distilled under reduced pressure giving 11.25 g (65%) of colorless, viscous product having a distinct spermlike odor, bp 60.5–61.5° (0.6 mm), $n^{27}$D 1.4877 [lit.[14] bp 68–69° (1 mm), $n^{25}$D 1.4879]. The infrared spectrum was as follows: $\nu_{max}^{CHCl_3}$ 3750, 3450 (broad), 3010, 2910 (sh), 1600, 1450, and 1040 cm$^{-1}$.

*Anal.* Calcd for $C_6H_{13}NO$: C, 62.57; H, 11.36; N, 12.16. Found: C, 63.29; H, 11.37; N, 12.14.

Reaction of the amino alcohol with phenyl isothiocyanate gave the **N-phenylthiocarbamyl derivative**, white plates from ethanol, mp 156–158°.

*Anal.* Calcd for $C_{13}H_{18}N_2OS$: C, 62.36; H, 7.25; N, 11.19. Found: C, 62.66; H, 7.21; N, 11.22.

The reduction could also be carried out using 5% rhodium-on-carbon catalyst, giving yields of up to 77% of the amino alcohol. Platinum dioxide and 5% platinum-on-carbon catalysts gave mixtures of the amino alcohol and starting material and were unsuitable for use in this reduction.

**1-Aminocyclopentanemethyl Hydrogen Sulfate. A. Sulfuric Acid Method.**—A cold solution of 1.96 g (0.02 mole) of concentrated sulfuric acid in 6 ml of water was cautiously added to 2.30 g (0.02 mole) of (1-aminocyclopentane)methanol, and water was slowly removed from the solution by heating it first at atmospheric pressure and finally for 10 min at 145–155° (25 mm) (Wood's metal bath). The brown viscous residue that remained solidified upon cooling and formed a hard dark brown cake. A solution of the brown, solid residue in the minimum of water was treated with charcoal, filtered, and diluted with an equal volume of ethanol, giving 1.62 g (42%) of white solid, mp 243–245° dec. Recrystallization from aqueous acetone gave fine, white crystals which darkened at 240° and melted at 245–246° dec.

*Anal.* Calcd for $C_6H_{13}NO_4S$: C, 36.90; H, 6.72; N, 7.17. Found: C, 36.65; H, 6.77; N, 7.39.

**B. Chlorosulfonic Acid Method.**—In a 500-ml, three-necked, round-bottomed flask, equipped with mechanical stirrer, reflux condenser, and dropping funnel was placed 29.70 g (0.26 mole) of (1-aminocyclopentane)methanol and 250 ml of dry carbon tetrachloride. The solution was stirred vigorously with efficient cooling (ice bath) while 30.30 g (0.26 mole) of chlorosulfonic acid was added dropwise over a period of 20 min. At this point,

(11) J. Sicher, *Progr. Stereochem.*, **3**, 224 (1962).

(12) Analogous zwitterion intermediates have been proposed to account for the reactions of aziridinones: S. Sarel, F. D'Angeli, J. T. Klug, and Aviva Taube, *Israel J. Chem.*, **2**, 167 (1964).

(13) W. E. Noland, J. F. Kneller, and D. E. Rice, *J. Org. Chem.* **22**, 695 (1957).

(14) H. Adkins and H. R. Billica, *J. Am. Chem. Soc.*, **70**, 3121 (1948).

a gummy, white precipitate formed and stirring became increasingly difficult. The mixture was stirred at room temperature for an additional 1.0 hr and the solvent was removed by decantation. The gummy white product was washed with three 100-ml portions of fresh carbon tetrachloride. The product was then treated with a 250-ml portion of acetone, and the white solid that separated was removed by suction filtration. The product was washed with three 100-ml portions of acetone and air dried; 34.60 g (68%) of white solid was obtained, mp 240–242° dec. Recrystallization from aqueous acetone gave the analytical sample, white needles, which darkened at 244° and melted at 248–249° dec.

*Anal.* Calcd for $C_6H_{13}NO_4S$: C, 36.90; H, 6.72; N, 7.17. Found: C, 37.43; H, 6.77; N, 7.02.

**1-Azaspiro[2.4]heptane (9).**—A solution of 11.70 g (0.06 mole) of the sulfate ester and 24.0 g of sodium hydroxide in 75 ml of water was heated in a distilling flask, and the distillate was collected in a cooled receiver containing 25 ml of ether over sodium hydroxide pellets. When the condensate no longer contained oily drops, the ether layer was separated and the aqueous layer was extracted with three 25-ml portions of ether. The combined ether extracts were dried over sodium hydroxide pellets. The ether was removed by distillation through a 12-in. Vigreux column and the resulting oily residue was fractionally distilled (from molecular sieves) to give 3.32 g (57%) of a colorless oil, having a sharp ammonialike odor, bp 52–54° (27 mm) (bp 138–139.5° at atmospheric pressure), $n^{27}D$ 1.4629. The infrared spectrum (neat liquid) exhibited an intense NH band at 3250 $cm^{-1}$. The nmr spectrum of this material (in $CDCl_3$) showed a broad singlet at $\delta$ 0.80 (1 H, >NH), a singlet at 1.55 (2 H, $CH_2$–N<), and a complex multiplet centered at 1.60–1.70 (8 H, ring protons).

*Anal.* Calcd for $C_6H_{11}N$: C, 74.15; H, 11.43; N, 14.42. Found: C, 74.37; H, 11.40; N, 13.86, 14.17.

Reaction of the imine **9** with phenyl isothiocyanate gave the N-phenylthiocarbamyl derivative as white, lustrous plates from benzene–hexane, mp 98–99°.

*Anal.* Calcd for $C_{13}H_{16}N_2S$: C, 67.19; H, 6.95; N, 12.06. Found: C, 66.65; H, 6.77; N, 11.57.

**Attempted Preparation of 1-(*p*-Nitrobenzoyl)-1-azaspiro[2.4]-heptane (10).**—To a solution of 3.88 g (0.04 mole) of 1-azaspiro-[2.4]heptane (**9**) and 4.04 g (0.04 mole) of triethylamine in 40 ml of dry benzene was added a suspension of 7.44 g (0.04 mole) of *p*-nitrobenzoyl chloride in 90 ml of dry benzene, while the mixture was stirred and maintained at 0–5°. After 3.0 hr of stirring at room temperature, the triethylamine hydrochloride was removed by filtration and the yellow filtrate was concentrated *in vacuo* leaving a pale yellow, crystalline solid. Recrystallization from benzene–hexane gave 7.0 g (71%) of pale yellow needles, mp 116–119°. Two more recrystallizations from benzene–hexane gave yellow needles, mp 118.5–119°. The infrared spectrum of this material was as follows: $\nu_{max}^{CHCl_3}$ 3580, 3450, 3180 (sh), 3100 (sh), 3050, 2990, 2900, 1940, 1820, 1670, 1620, 1540, 1495, 1350, 1290, 1165, 1115, 1020, 870, and 855 $cm^{-1}$. This product was evidently not the anticipated N-*p*-nitrobenzoyl derivative of the imine **9**, since it had an intense NH band at 3580 $cm^{-1}$ in the infrared and rapidly discharged the purple color of a solution of potassium permanganate in aqueous methanol. The nmr spectrum of the product (in $CDCl_3$) showed a quartet centered at $\delta$ 7.87 (4 H, aromatic, $J$ = 9 cps), a broad singlet at 6.70 (1 H, NH), a singlet at 5.37 (1H, HC=C), a doublet centered at 3.90 (2 H, $CH_2N$, $J$ = 6 cps), and a complex multiplet centered at 1.80–1.90 (6 H, ring protons). On the basis of the infrared and nmr data, the product was assigned the structure of N-(1-cyclopentenylmethyl)-*p*-nitrobenzamide (**17**). No 1-(*p*-nitrobenzoyl)-1-azaspiro[2.4]heptane (**10**) was detected.

*Anal.* Calcd for $C_{13}H_{14}N_2O_3$: C, 63.39; H, 5.74; N, 11.38. Found: C, 63.60; H, 5.88; N, 11.26.

**Isomerization of N-(1-Cyclopentenylmethyl)-*p*-nitrobenzamide (17) to 2-(*p*-Nitrophenyl)-5,5-tetramethylene-2-oxazoline (23).**—Concentrated sulfuric acid (10 ml) was added slowly with cooling and swirling to 1.5 g (0.006 mole) of N-(1-cyclopentenylmethyl)-*p*-nitrobenzamide (**17**) while the temperature was kept below 40°. After 2.0 hr of stirring at room temperature, the dark red solution was poured onto ice and the resulting solution was made neutral by careful addition of 15% aqueous sodium hydroxide solution (*ca.* 100 ml). The crude brown solid that precipitated was obtained in quantitative yield, mp 128–132°. Recrystallization from benzene–hexane gave pale yellow crystals, mp 131–132°. A second recrystallization from benzene–hexane gave white needles, mp 131.5–132.5°. The infrared spectrum showed the following bands: $\nu_{max}^{CHCl_3}$ 3150 (sh), 3100 (sh), 3020, 2910, 1950, 1810, 1650, 1610, 1540, 1415, 1350, 1275, 1110, 1100, 1020, 975, 870, and 855 $cm^{-1}$. The nmr spectrum in $CDCl_3$ showed a quartet centered at $\delta$ 7.90 (4 H, aromatic, $J$ = 10 cps), a sharp singlet at 3.68 (2 H, $CH_2N$), and a complex multiplet centered at 1.50–1.60 (8 H, ring protons).

*Anal.* Calcd for $C_{13}H_{14}N_2O_3$: C, 63.39; H, 5.74; N, 11.38. Found: C, 63.64; H, 5.73; N, 11.30.

**Attempted Preparation of 1-(*p*-Nitrobenzenesulfonyl)-1-azaspiro[2.4]heptane (11).**—To a solution of 0.97 g (0.01 mole) of 1-azaspiro[2.4]heptane (**9**) and 1.10 g (0.011 mole) of triethylamine in 60 ml of dry benzene was added a solution of 2.22 g (0.01 mole) of *p*-nitrobenzenesulfonyl chloride in 80 ml of dry benzene while the mixture was sitrred and maintained at 0°. The addition took place over 25 min. The reaction mixture was stirred an additional 2.5 hr at 5–10° and at room temperature for an additional 2.0 hr. The triethylamine hydrochloride was removed by suction filtration and the solvent was removed *in vacuo* leaving a pale yellow solid. Recrystallization from ethanol gave 2.33 g (83%) of yellow crystals, mp 113–115°. Another recrystallization from ethanol gave fine, pale yellow needles, mp 119–120°. A sample of this compound rapidly decolorized the purple color of a solution of potassium permanganate in aqueous methanol. The infrared spectrum was as follows: $\nu_{max}^{CHCl_3}$ 3480, 3390, 3180 (sh), 3100 (sh), 3030, 2920, 1950, 1800, 1620, 1540, 1410, 1355, 1315, 1170, 1100, 1070, 1020, and 860 $cm^{-1}$. The nmr spectrum of the product in $CDCl_3$ showed a quartet centered at $\delta$ 8.00 (4 H, aromatic, $J$ = 10 cps), a singlet at 5.32 (1 H, HC=C), a broad triplet centered at 4.93 (1 H, $HNSO_2$, $J$ = 6–7 cps), a doublet centered at 3.50 (2 H, $CH_2N$, $J$ = 5 cps), and a complex multiplet centered at 1.70–1.80 (6 H, ring protons). The compound was consequently characterized as the rearranged product, N-(1-cyclopentenylmethyl)-*p*-nitrobenzenesulfonamide (**18**); no 1-(*p*-nitrobenzenesulfonyl)-1-azaspiro[2.4]heptane (**11**) was isolated.

*Anal.* Calcd for $C_{12}H_{14}N_2O_4S$: C, 51.04; H, 5.01; N, 9.92. Found: C, 51.25; H, 5.27; N, 9.60.

**Attempted Preparation of 1-(*p*-Iodobenzenesulfonyl)-1-azaspiro[2.4]heptane (12).**—To a solution of 0.97 g (0.01 mole) of 1-azaspiro[2.4]heptane (**9**) and 1.10 g (0.011 mole) of triethylamine in 60 ml of dry benzene was added a solution of 3.03 g (0.01 mole) of *p*-iodobenzenesulfonyl chloride in 80 ml of dry benzene while the mixture was stirred and maintained at 0°. The mixture was stirred for an additional 2.0 hr at 0–5° and at room temperature for 2.0 hr. The triethylamine hydrochloride was removed by suction filtration and the filtrate was evaporated *in vacuo* leaving a pale brown oil, which formed fine, yellow crystals on cooling. Recrystallization from ethanol gave 2.58 g (71%) of fine, white needles, mp 97–99°. Another recrystallization from ethanol did not appreciably change the melting point, mp 97–98.5°. The infrared spectrum of the compound was as follows: $\nu_{max}^{CHCl_3}$ 3120 (sh), 3080 (sh), 3000, 2900 (sh), 1920, 1790, 1680, 1475, 1450, 1390, 1325, 1160, 1105, 1085, 1060, 1010, 970, and 820 (broad) $cm^{-1}$. The spectrum showed no NH band (*ca.* 3500 $cm^{-1}$) and the compound did not decolorize a solution of potassium permanganate in aqueous methanol.

*Anal.* Calcd for $C_{12}H_{14}INSO_2$: C, 39.68; H, 3.89; N, 3.86. Found: C, 42.35; H, 5.37; N, 3.29.

The above analysis was accurate for the molecular formula $C_{12}H_{14}INSO_2 \cdot 2C_2H_5OH$, and the compound was tentatively assigned the structure of 1-(*p*-iodobenzenesulfonyl)-1-azaspiro-[2.4]heptane (**12**) with 2 moles of ethanol of crystallization.

*Anal.* Calcd for $C_{12}H_{14}INSO_2 \cdot 2C_2H_5OH$: C, 42.30; H, 5.72; N, 3.08.

Recrystallization from benzene–hexane (2–3 min) gave white, lustrous plates, mp 123–124°. Another recrystallization from benzene–hexane raised the melting point to 125–126°. The infrared spectrum of this compound in chloroform was similar to that described above, except for the presence of an intense NH band at 3480 $cm^{-1}$. A sample of this compound also rapidly decolorized a solution of potassium permanganate in aqueous methanol. The nmr spectrum in $CDCl_3$ displayed an aromatic quartet centered at $\delta$ 7.72 (4 H, aromatic, $J$ = 10 cps), a broad band exhibiting some fine structure at 5.4–5.50 (1 H, HC=C), a doublet centered at 3.00 (2 H, $CH_2N$, $J$ = 6 cps), and a complex multiplet centered at 1.70–1.80 (6 H, ring protons). A band due to the NH was not observed. On the basis of the infrared and nmr data, the product was assigned the structure of N-(1-cyclopentenylmethyl)-*p*-iodobenzenesulfonamide (**19**).

*Anal.* Calcd for $C_{12}H_{14}INSO_2$: C, 39.68; H, 3.89; N, 3.86. Found: C, 38.47; H, 4.13; N, 3.81, 3.78.

**1-Azaspiro[2.5]octane (13).**—Prepared by the procedure of Fanta and Talukdar,[5] from nitrocyclohexane. The imine **13** was a colorless oil, having a sharp ammonialike odor, bp 55–57° (17 mm), $n^{30}D$ 1.4730 (lit.[5] bp 158–159°, $n^{30}D$ 1.4740). An infrared spectrum of the neat liquid displayed an NH band at 3270 $cm^{-1}$. Nmr spectrum (neat liquid) disclosed a broad singlet at $\delta$ 0.55 (1 H, >NH), a sharp singlet at 1.30 (2 H, $CH_2N<$), and a complex multiplet centered at 1.50 (12 H, ring protons).

*Anal.* Calcd for $C_7H_{13}N$: C, 75.60; H, 11.80; N, 12.60. Found: C, 75.18; H, 12.13; N, 11.87.

The imine was further characterized by preparation of the N-phenylthiocarbamyl derivative, white plates from ethanol: mp 96–97° (lit.[5] mp 104.7°).

*Anal.* Calcd for $C_{14}H_{18}N_2S$: C, 68.24; H, 7.38; N, 11.37. Found: C, 68.15; H, 6.91; N, 11.64.

**Attempted Preparation of 1-(*p*-Nitrobenzoyl)-1-azaspiro[2.5]-octane (14).**—To a solution of 2.22 g (0.02 mole) of 1-azaspiro-[2.5]octane (**13**) and 2.10 g (0.021 mole) of triethylamine in 50 ml of dry benzene was added a suspension of 3.72 g (0.02 mole) of *p*-nitrobenzoyl chloride in 80 ml of dry benzene, while the mixture was stirred and maintained at 0–5°. The reaction mixture was stirred an additional 2.0 hr at 5–10° and then was allowed to warm to room temperature. The triethylamine hydrochloride was removed by filtration and the filtrate was evaporated *in vacuo* leaving a pale yellow oil. Attempted crystallization from benzene–hexane gave only an oil. The oil was dissolved in the minimum of benzene and the benzene solution was chromatographed on a neutral alumina column. Elution with benzene gave, after removal of the solvent, 4.55 g (88%) of yellow solid, mp 103–106°. Recrystallization from benzene–hexane gave pale yellow needles, mp 107–108°. Infrared spectrum of the compound was as follows: $\nu_{max}^{CHCl_3}$ 3530, 3400, 3160 (sh), 3100 (sh), 3050, 2990, 2900, 1940, 1800, 1670, 1610, 1540, 1490, 1350, 1270, 1110, 1020, 870, 860 $cm^{-1}$. Nmr spectrum in $CDCl_3$ displayed a quartet centered at $\delta$ 7.80 (4 H, aromatic, $J$ = 9 cps), a broad singlet at 6.45 (1 H, NH), a singlet at 5.32 (1 H, HC=C), a doublet centered at 3.60 (2 H, $CH_2N$, $J$ = 5 cps), and a complex multiplet centered at 1.50–1.60 (8 H, ring protons). The compound also decolorized a solution of potassium permanganate in aqueous methanol. The compound was assigned the structure of N-(1-cyclohexenylmethyl)-*p*-nitrobenzamide (**20**). No 1-(*p*-nitrobenzoyl)-1-azaspiro[2.5]octane (**14**) was obtained.

*Anal.* Calcd for $C_{14}H_{16}N_2O_3$: C, 64.59; H, 6.21; N, 10.76. Found: C, 64.45; H, 6.29; N, 10.59.

**Isomerization of N-(1-Cyclohexenylmethyl)-*p*-nitrobenzamide (20) to 2-(*p*-Nitrophenyl)-5,5-pentamethylene-2-oxazoline (24).**—Concentrated sulfuric acid (10 ml) was added slowly with cooling and swirling to 0.70 g of N-(1-cyclohexenylmethyl)-*p*-nitrobenzamide (**20**) while the temperature was kept below 40°. After 5.0 hr of stirring at room temperature, the dark red solution was poured onto ice and the resulting solution was made neutral by careful addition of 15% aqueous sodium hydroxide (*ca.* 90 ml). The crude brown solid was obtained in quantitative yield. Recrystallization from ethanol gave white plates, mp 118–119°. The infrared spectrum was as follows: $\nu_{max}^{CHCl_3}$ 3100 (sh), 3080 (sh), 3020, 2920, 1950, 1820, 1660, 1620, 1540, 1460, 1420, 1360, 1090, 1020, 875, and 860 $cm^{-1}$. The nmr spectrum of the oxazoline in $CDCl_3$ showed a quartet centered at $\delta$ 8.05 (4 H, aromatic, $J$ = 10 cps), a sharp singlet at 3.70 (2 H, $CH_2N$), and a complex multiplet centered at 1.60 (10 H, ring protons).

*Anal.* Calcd for $C_{14}H_{16}N_2O_3$: C, 64.59; H, 6.21; N, 10.76. Found: C, 64.78; H, 6.24; N, 10.84.

**1-(*p*-Nitrobenzenesulfonyl)-1-azaspiro[2.5]octane (15).**—To a solution of 1.11 g (0.01 mole) of 1-azaspiro[2.5]octane (**13**) and 1.10 g (0.011 mole) of triethylamine in 60 ml of dry benzene was added a solution of 2.22 g (0.01 mole) of *p*-nitrobenzenesulfonyl chloride in 80 ml of dry benzene, while the mixture was stirred and maintained at 0°. The reaction mixture was stirred for an additional 2.5 hr at 0–5° and at room temperature for 1 hr more. The triethylamine hydrochloride was removed by filtration and the filtrate was evaporated *in vacuo* leaving a pale brown oil. Crystallization of the oil from ethanol gave 2.37 g (80%) of yellow crystals, mp 80–83°. Recrystallization from ethanol gave fine, white needles, mp 83–85°. The infrared spectrum was as follows: $\nu_{max}^{CHCl_3}$ 3180 (sh), 3100 (sh), 3010, 2910, 1950, 1810, 1620, 1540, 1460, 1410, 1390, 1250, 1165, 1140, 1110, 1100, 1085, 1029, 950, and 860 $cm^{-1}$. No NH band was observed in the infrared spectrum. The nmr spectrum in $CDCl_3$ displayed a quartet centered at $\delta$ 7.90 (4 H, aromatic, $J$ = 7–8 cps), a sharp singlet at 2.20 (2 H, $CH_2N<$), and a complex multiplet centered at 1.50-1.60 (10 H, ring protons).

*Anal.* Calcd for $C_{13}H_{16}N_2O_4S$: C, 52.68; H, 5.45; N, 9.45. Found: C, 53.10; H, 5.85; N, 9.18.

**Pyrolytic Isomerization of 1-(*p*-Nitrobenzenesulfonyl)-1-azaspiro[2.5]octane (15) to N-(1-Cyclohexenylmethyl)-*p*-nitrobenzenesulfonamide (21).**—A solution of 0.45 g (0.0015 mole) of 1-(*p*-nitrobenzenesulfonyl)-1-azaspiro[2.5]octane (**15**) in 35 ml of dry toluene was refluxed for 16.0 hr. After cooling, the solvent was evaporated *in vacuo* leaving a pale brown oil. Crystallization of the oil from benzene–hexane gave 0.30 g (67%) of pale yellow needles, mp 123–124°. Recrystallization from benzene–hexane gave lustrous white needles, mp 127.5–128°. The infrared spectrum was as follows: $\nu_{max}^{CHCl_3}$ 3480, 3150, (sh), 3100 (sh), 3000, 2920, 1950, 1810, 1620, 1540, 1450, 1410, 1350, 1170, 1100, 1010, 975, 940, 890, and 860 $cm^{-1}$. The nmr spectrum in $CDCl_3$ showed a quartet centered at $\delta$ 7.90 (4 H, aromatic, $J$ = 10 cps), a broad bond with some fine splitting at 4.80–4.90 (1 H, HC=C), an apparent doublet centered at 2.60–2.70 (2 H, $CH_2N$, $J$ = 4–5 cps), and a complex multiplet centered at 0.90–1.00 (8 H, ring protons). No NH band was observed. A sample of the compound rapidly discharged the purple color of a solution of potassium permanganate in aqueous methanol. The compound was assigned the structure of N-(1-cyclohexenylmethyl)-*p*-nitrobenzenesulfonamide (**21**).

*Anal.* Calcd for $C_{13}H_{16}N_2O_4S$: C, 52.68; H, 5.45; N, 9.45. Found: C, 52.67; H, 6.03; N, 9.16.

**1-(*p*-Iodobenzenesulfonyl)-1-azaspiro[2.5]octane (16).**—To a solution of 1.11 g (0.01 mole) of 1-azaspiro[2.5]octane (**13**) and 1.10 g (0.011 mole) of triethylamine in 60 ml of dry benzene was added a solution of 3.03 g (0.01 mole) of *p*-iodobenzenesulfonyl chloride in 80 ml of dry benzene, while the mixture was stirred and maintained at 0°. The reaction mixture was stirred for an additional 2.0 hr at 0–5° and 1.5 hr at room temperature. The triethylamine hydrochloride was removed by suction filtration and the filtrate was evaporated *in vacuo* leaving a tan solid. Recrystallization from ethanol gave 2.77 g (74%) of white crystals, mp 93.5–95°. Another recrystallization from ethanol gave fine, white crystals, mp 93.5–94.5°. The infrared spectrum was as follows: $\nu_{max}^{CHCl_3}$ 3120 (sh), 3080 (sh), 3000, 2900, 1930, 1780, 1570, 1455, 1390, 1320, 1270, 1160, 1135, 1110, 1095, 1080, 1060, 1035, 1015, 950, 870, and 840 $cm^{-1}$. No NH band was observed in the infrared spectrum. The nmr spectrum of the product in $CDCl_3$ displayed a quartet centered at $\delta$ 7.75 (4 H, aromatic, $J$ = 9 cps), a sharp singlet at 2.40 (2 H, $CH_2N<$), and a complex multiplet centered at 1.70 (10 H, ring protons).

*Anal.* Calcd for $C_{13}H_{16}INSO_2$: C, 41.38; H, 4.28; N, 3.71. Found: C, 41.15; H, 4.20; N, 3.88.

A small sample (0.50 g) of 1-(*p*-iodobenzenesulfonyl)-1-azaspiro[2.5]octane (**16**) was recrystallized from benzene–hexane; white lustrous needles were obtained, mp 95–96.5°. No NH band was observed in the infrared spectrum of the recrystallized product and the product did not decolorize a solution of potassium permanganate in aqueous methanol. Consequently, 1-(*p*-iodobenzenesulfonyl)-1-azaspiro[2.5]octane (**16**) was not converted to the isomeric unsaturated sulfonamide (**22**) by treatment with benzene–hexane, as was the case with 1-(*p*-iodobenzenesulfonyl)-1-azaspiro[2.4]heptane (**12**).

**Pyrolytic Isomerization of 1-(*p*-Iodobenzenesulfonyl)-1-azaspiro[2.5]octane (16) to N-(1-Cyclohexenylmethyl)-*p*-iodobenzenesulfonamide (22).**—A solution of 0.83 g (0.002 mole) of 1-(*p*-iodobenzenesulfonyl)-1-azaspiro[2.5]octane (**16**) in 35 ml of dry toluene was refluxed for 16.0 hr. The toluene was removed by evaporation *in vacuo* leaving a pale brown oil. Crystallization of the oil from benzene–hexane gave 0.74 g (89%) of white solid. Recrystallization from ethanol gave white plates, mp 141–142°. The product decolorized a solution of potassium permanganate in aqueous methanol, gave a positive Beilstein test, and displayed an intense NH band (*ca.* 3480 $cm^{-1}$) in its infrared absorption spectrum. The product was assigned the structure of N-(1-cyclohexenylmethyl)-*p*-iodobenzenesulfonamide (**22**).

*Anal.* Calcd for $C_{13}H_{16}INSO_2$: C, 41.38; H, 4.28; N, 3.71. Found: C, 41.07; H, 4.92; N, 3.40.

**1-(*p*-Nitrobenzoyl)-2,2-dimethylaziridine (26).**—To a solution of 2.84 g (0.04 mole) of 2,2-dimethylaziridine (**25**) and 4.55 g (0.045 mole) of triethylamine in 60 ml of dry benzene was added a suspension of 7.40 g (0.04 mole) of *p*-nitrobenzoyl chloride in

90 ml of dry benzene, while the mixture was stirred and maintained at 0° (20 min). The reaction mixture was stirred an additional 2.5 hr at 0–5° and then allowed to warm to room temperature (1.5 hr). The triethylamine hydrochloride formed in the reaction was removed by suction filtration and the pale yellow filtrate evaporated *in vacuo* leaving a viscous oil. The oil was dissolved in the minimum of benzene and chromatographed on a neutral alumina column. Elution with benzene–hexane (4:1) gave, after evaporation of the solvent, 4.81 g (55%) of pale yellow crystals, mp 65–68° [1-(*p*-nitrobenzoyl)-2,2-dimethylaziridine (**26**), lit.[8] mp 69–71°]. The infrared spectrum of the product was as follows: $\nu_{max}^{CHCl_3}$ 3180 (sh), 3100 (sh), 3030, 2990, 2930, 1950, 1820, 1670, 1620, 1540, 1460, 1415, 1400, 1390, 1350, 1290, 1175, 1115, 1095, 1025, 1018, 935, 875, and 855 cm$^{-1}$. No NH band was observed in the infrared spectrum of the product. The nmr spectrum of the product in $CDCl_3$ displayed a quartet centered at $\delta$ 7.88 (4 H, aromatic, $J$ = 9 cps), a singlet at 2.08 (2 H, $CH_2$), and a singlet at 0.98 (6 H, $CH_3$).

*Anal.* Calcd for $C_{11}H_{12}N_2O_3$: C, 59.98; H, 5.50; N, 12.72. Found: C, 60.23; H, 5.54; N, 12.53.

Elution of the column with benzene–methanol (4:1) gave, after removal of the solvent, 1.36 g (16%) of a second product as light brown crystals, mp 119–120.5°. Recrystallization from benzene–hexane gave lustrous white needles, mp 126–127.5° [N-(β-methallyl)-*p*-nitrobenzamide (**28**), lit.[8] mp 126–127.5°]. The infrared spectrum of this compound showed the following bonds: $\nu_{max}^{CHCl_3}$ 3560, 3420, 3140 (sh), 3100 (sh), 3030, 2970 (sh), 2900 (sh), 1940, 1810, 1670, 1620, 1540, 1495, 1450, 1350, 1290, 1150, 1115, 1020, 910, 872, and 860 cm$^{-1}$. The nmr spectrum in $CDCl_3$ showed a quartet centered at $\delta$ 7.78 (4 H, aromatic, $J$ = 9 cps), a broad singlet at 6.50 (1 H, NHCO), a singlet at 4.57 (2 H, $CH_2$=C), a doublet centered at 3.68 (2 H, $CH_2N$, $J$ = 5–6 cps), and a singlet at 1.45 (3 H, $CH_3$). The product rapidly discharged the purple color of a solution of potassium permanganate in aqueous methanol and was consequently characterized as N-(β-methallyl)-*p*-nitrobenzamide (**28**).

*Anal.* Calcd for $C_{11}H_{12}N_2O_3$: C, 59.98; H, 5.50; N, 12.72. Found: C, 59.92; H, 5.37; N, 12.83.

**Pyrolytic Isomerization of 1-(*p*-Nitrobenzoyl)-2,2-dimethylaziridine (26) to N-(β-Methallyl)-*p*-nitrobenzamide (28).**—A solution of 3.0 g (0.014 mole) of 1-(*p*-nitrobenzoyl)-2,2-dimethylaziridine (**26**) in 40 ml of dry toluene was refluxed for 48 hr. Cooling to room temperature gave 2.91 g (97%) of pale yellow needles, mp 127–128.5° [N-(β-methallyl)-*p*-nitrobenzamide (**28**), lit.[8] mp 126–127.5°]. Recrystallization from benzene–hexane gave fine, yellow needles, mp 127.5–128.5°. Mixture melting point with authentic N-(β-methally)-*p*-nitrobenzamide (**28**) showed no depression. The nmr and infrared spectra of this product and those of the N-(β-methallyl)-*p*-nitrobenzamide (**28**) isolated previously were identical.

*Anal.* Calcd for $C_{11}H_{12}N_2O_3$: C, 59.98; H, 5.50; N, 12.72. Found: C, 60.14; H, 5.41; N, 12.55.

**Isomerization of N-(β-Methallyl)-*p*-nitrobenzamide (28) to 2-(*p*-Nitrophenyl)-5,5-dimethyl-2-oxazoline (30).**—To 12 ml of concentrated sulfuric acid was added with cooling and swirling 1.50 g of N-(β-methallyl)-*p*-nitrobenzamide (**28**). The amber mixture was stirred at room temperature for 19 hr. The solution was cooled and added to 50 g of ice–water. The mixture was placed in an ice bath and carefully neutralized with 15% aqueous sodium hydroxide solution. The tan precipitate was filtered and the crude yield was quantitative, mp 141–143°. The oxazoline was recrystallized from 70% aqueous methanol and melted at 144–146° (lit.[8] mp 144–147°). The infrared spectrum of the oxazoline was as follows: $\nu_{max}^{CHCl_3}$ 3150 (sh), 3100 (sh), 3050, 2920, 1950, 1820, 1660, 1610, 1540, 1460, 1415, 1350, 1290, 1165, 1110, 1085, 1010, 972, 938, 870, and 853 cm$^{-1}$. The nmr spectrum in $CDCl_3$ displayed a quartet centered at $\delta$ 8.17 (4 H, aromatic, $J$ = 9 cps), a singlet at 3.82 (2 H, $CH_2$), and a singlet at 1.50 (6 H, $CH_3$).

*Anal.* Calcd for $C_{11}H_{12}N_2O_3$: C, 59.98; H, 5.50; N, 12.72. Found: C, 59.96; H, 5.50; N, 12.59.

**1-(*p*-Nitrobenzenesulfonyl)-2,2-dimethylaziridine (27).**—To a solution of 2.13 g (0.03 mole) of 2,2-dimethylaziridine (**25**) and 4.04 g (0.04 mole) of triethylamine in 60 ml of dry benzene was added a suspension of 5.37 g (0.024 mole) of *p*-nitrobenzenesulfonyl chloride in 80 ml of dry benzene, while the mixture was stirred and maintained at 0° (30 min). The reaction mixture was stirred for an additional 2.5 hr at 0–5° and for 2.0 hr at room temperature. The triethylamine hydrochloride was removed by suction filtration and the pale yellow filtrate was evaporated *in vacuo* leaving a pale yellow oil. Crystallization from benzene–hexane gave 5.74 g (94%) of white crystals, mp 90–92°. Recrystallization from benzene–hexane gave fine, white crystals, mp 90.5–92°. The infrared spectrum of the product was as follows: $\nu_{max}^{CHCl_3}$ 3220 (sh), 3200 (sh), 3100, 3000 (sh), 2930 (sh), 1950, 1820, 1620, 1540, 1390, 1360, 1175, 1140, 1115, 1095, 1085, 1022, 970, 955, 862, and 835 cm$^{-1}$. No NH band was observed in the infrared spectrum of the product. The nmr spectrum in $CDCl_3$ displayed a quartet centered at $\delta$ 7.90 (4 H, aromatic, $J$ = 7–9 cps), a sharp singlet at 2.22 (2 H, $CH_2$), and a sharp singlet at 1.25 (6 H, $CH_3$).

*Anal.* Calcd for $C_{10}H_{12}N_2O_4S$: C, 46.86; H, 4.73; N, 10.93. Found: C, 47.05; H, 4.82; N, 10.89.

**Isomerization of 1-(*p*-Nitrobenzenesulfonyl)-2,2-dimethylaziridine (27) to N-(β-Methallyl)-*p*-nitrobenzenesulfonamide (29).**—A solution of 1.67 g of 1-(*p*-nitrobenzenesulfonyl)-2,2-dimethylaziridine (**27**) in 50 ml of dry toluene was refluxed for 50 hr. The toluene was evaporated *in vacuo* leaving a pale brown oil. Crystallization from benzene–hexane gave 0.70 g (42%) of yellow crystals. Recrystallization from hexane gave fine, white needles, mp 89–90°. Mixture melting point with authentic 1-(*p*-nitrobenzenesulfonyl)-2,2-dimethylaziridine (**27**) showed no depression. The infrared spectrum of the product was identical with that of the 1-(*p*-nitrobenzenesulfonyl)-2,2-dimethylaziridine (**27**) obtained previously, showing no NH band at *ca.* 3500 cm$^{-1}$. Also, the product did not discharge the purple color of a solution of potassium permanganate in aqueous methanol. The product was obviously unreacted 1-(*p*-nitrobenzenesulfonyl)-2,2-dimethylaziridine (**27**) and consequently more vigorous conditions were necessary to isomerize 1-(*p*-nitrobenzenesulfonyl)-2,2-dimethylaziridine (**27**) to N-(β-methallyl)-*p*-nitrobenzenesulfonamide (**29**).

A solution of 0.45 g of 1-(*p*-nitrobenzenesulfonyl)-2,2-dimethylaziridine (**27**) in 20 ml of dry toluene was heated in a glass-lined steel bomb at 150 ± 5° for 9.0 hr. After cooling to room temperature, the solution was filtered to remove any suspended matter and the solvent was removed *in vacuo* leaving a brown syrup. The syrup was dissolved in the minimum amount of benzene and chromatographed on a neutral alumina column. Elution with benzene–ether (1:4) gave, after evaporation of the solvent, a light brown oil, which was crystallized from benzene–hexane giving 0.19 g (42%) of fine white needles, mp 73–75°. The infrared spectrum of the product showed a medium-intensity NH band at *ca.* 3450 cm$^{-1}$, and the product decolorized the purple color of a solution of potassium permanganate in aqueous methanol. The product was assigned the structure of N-(β-methallyl)-*p*-nitrobenzenesulfonamide (**29**).

*Anal.* Calcd for $C_{10}H_{12}N_2O_4S$: C, 46.86; H, 4.73; N, 10.93. Found: C, 47.04; H, 4.79; N, 11.02.