Experimental Section

The alkylphenols were obtained from the Aldrich Chemical Co., Milwaukee, and had the following purities in mole per cent: *o*-alkylphenol, 99.2% *ortho*, <0.3% *meta*, and 0.5% *para; m*-alkylphenol, <0.5% *ortho*, 98.1% *meta*, and 1.4% *para; p*-alkylphenol, <0.3% *ortho*, <0.3% *meta*, and 99.4% *para*.

The isomerization reactions were carried out in a sealed magnetically stirred 100-ml flask immersed in a constant-temperature bath. The catalyst, 45% rare earth cation-exchanged–45% decationized Type Y Molecular Sieve with a SiO_2–Al_2O_3 molar ratio of 5.0, was prepared by repeatedly contacting NaY with a 10% aqueous solution of ammonium chloride until the sodium cation-exchange level was reduced to 10% of the total base exchange capacity. This zeolite was then ion exchanged with the theoretical amount of rare earth chloride required to effect a 45% rare earth cation exchange. The catalyst was decationized by calcination at 550° in an air purge for 2 hr. A 1-g sample of catalyst was used with 50 g of monoalkylphenol. Samples of the reaction mixture were removed periodically and analyzed by glpc. Isomer distributions in the tables are given in normalized mole per cent. The similar boiling points and polarities of the alkylphenols make the effective separation of the isomers difficult to achieve by normal chromatographic techniques. However, when these isomers are converted into their silyl ethers, an effective separation[5] is obtained. Component identification and distribution was verified by ir analyses. The analyses of the silyl ether derivatives of the alkylphenols were carried out on a Perkin-Elmer 154 vapor fractometer fitted with a 100-ft squalene column and operated at 65° with a He carrier gas pressure of 30 psi. The dialkylphenol isomers were separated on 150-ft SE-30 column, programmed at 7°/min from 50° with a He carrier gas pressure of 5 psi.

Registry No.—*o-t*-Butylphenol, 88-18-6; *m-t*-butylphenol, 585-34-2; *p-t*-butylphenol, 98-54-4; 2,6-di-*t*-butylphenol, 128-39-2.

[5] R. W. Martin, *J. Amer. Chem. Soc.*, **74**, 3024 (1952).

The Photolysis and Pyrolysis of *trans*-β-Azidovinyl *p*-Tolyl Sulfone

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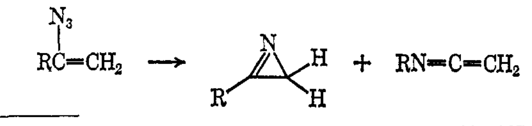
The pyrolysis and photolysis of a terminal vinyl azide, *trans*-β-azidovinyl *p*-tolyl sulfone (**1**), was studied in an effort to learn about possible intermediates in these decompositions. When pyrolysis of **1** was carried out in aqueous ethanol and other solvents, *p*-toluenesulfonylacetonitrile (**2**) was formed. When photolysis in aqueous ethanol or other moist solvents was used, 2,3-di-*p*-toluenesulfonylaziridine (**3**) was formed. No **3** was found in the pyrolysis and no **1** was detected in the irradiation (at about 0°) observations which indicate that different pathways are involved. Irradiation of 4(5)-*p*-toluenesulfonyltriazole, isomeric with **1**, did not give rise to **2** or **3**. The photolysis is believed to give 3-*p*-toluenesulfonyl-3H-azirine (**4**) some of which is hydrolyzed to give *p*-toluenesulfinic acid which then condenses with remaining **4** to give **3**. When the photolysis was carried out in the presence of benzenesulfinic acid, 2-benzenesulfonyl-3-*p*-toluenesulfonylaziridine was formed. This new reaction of the 3H-azirine system was also shown by the addition of *p*-toluenesulfinic acid to 2,3-diphenyl-3H-azirine and to 2-phenyl-3-methyl-3H-azirine. Attempts to isolate **4** gave material having absorption in the infrared spectrum, characteristic of the 3H-azirine system, but the material rapidly gave polymeric material behaving similarly to other 3H-azirines lacking a substituent in the 2 position.

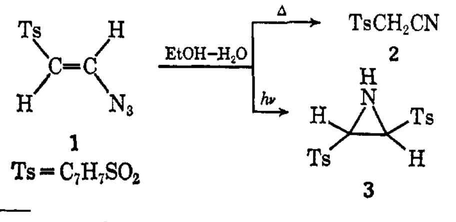
The production of different intermediates in the photolytic and pyrolitic loss of nitrogen from organic azides is of current interest and has been discussed recently.[2] Although the photolysis and pyrolysis of triarylmethyl azides gives qualitatively the same products, the migratory aptitudes of phenyl and substituted phenyl groups are markedly different.[2] Lewis and Saunders suggested that a discrete nitrene intermediate is involved in the photochemical process but probably not in the thermal process, and they have discussed the possible multiplicity of the nitrene involved in the photochemical process.[3]

In other recent work it is believed that neither singlet nor triplet pivaloyl nitrene is an intermediate in the thermal or in the photoinduced Curtius rearrangement of pivaloyl azide. Both arrangements are most likely concerted processes.[4]

The pyrolysis of vinyl azides has been investigated by Smolinsky[5] who has isolated 3H-azirines and observed N-alkyl ketenimines from this reaction. Hassner and Fowler[6] have developed a general synthesis of 3H-azirines from the photolysis of vinyl azides obtainable from olefins. Others[7,8] have also observed the formation of 3H-azirines and unstable ketenimines from the photolysis and pyrolysis of vinyl azides. Boyer[9] has reported that the photolysis and pyrolysis of β-styryl azide yield phenylacetonitrile. In no case has it previously been shown that the photolysis and pyrolysis of a given vinyl azide proceed along different pathways to the observed products.



At this point it is stressed that in the photolysis and pyrolysis of β-azidovinyl *p*-tolyl sulfone (**1**) the products are different and exclusive; that is, no *p*-toluenesulfonylacetonitrile (**2**) is detected in the photolysis of **1** and no 2,3-di-*p*-toluenesulfonylaziridine (**3**) is produced in the pyrolysis of **1**. This is evidence that different



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[1] National Institutes of Health Predoctoral Fellow, 1966–1967.

[2] W. H. Saunders, Jr., and E. A. Caress, *J. Amer. Chem. Soc.*, **86**, 861 (1964).

[3] F. D. Lewis and W. H. Saunders, Jr., *ibid.*, **89**, 645 (1967).

[4] S. Linke, G. T. Tisue, and W. Lwowski, *ibid.*, **89**, 6308 (1967).

[5] G. Smolinsky, *ibid.*, **83**, 4483 (1961); G. Smolinsky, *J. Org. Chem.*, **27**, 3557 (1962).

[6] A. Hassner and F. W. Fowler, *Tetrahedron Lett.*, 1545 (1967).

[7] R. Harvey and K. W. Ratts, *J. Org. Chem.*, **31**, 3907 (1966).

[8] C. S. Cleaver and C. G. Krespan, *J. Amer. Chem. Soc.*, **87**, 3716 (1965).

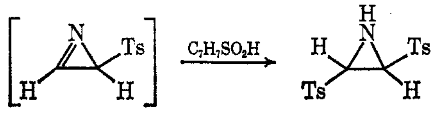
[9] J. H. Boyer, W. E. Krueger, and G. J. Mikol, *ibid.*, **89**, 5505 (1967).

intermediates are involved in these reactions. The purpose of this paper is to describe the origin of **2** and **3**.

Photolysis of **1** in dry cyclohexene was attempted in order to trap a nitrene but only a reddish brown, apparently polymeric, material formed.

Irradiation of **1** in dry tetrahydrofuran gave an oil which showed infrared absorptions at 3.05, 5.65, and 5.8 μ. The infrared absorption at 5.65 μ is characteristic of the C=N stretch of the 3H-azirine ring system.[5] On standing, the oil slowly became semicrystalline suggestive of the known reaction of 3H-azirines involving hydrolysis to the amino ketone followed by self-condensation and oxidation to a pyrazine.[10]

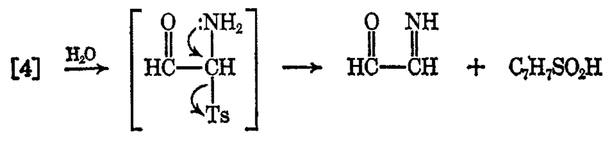
The crystallization process was speeded up by methanolic hydrochloric acid. When the photolysis of **1** was carried out in cyclohexene which had been saturated with water, the product crystallized during the reaction. A higher yield of the photolysis product was obtained in aqueous ethanol. This product melted at 190°, and its analysis corresponded to $C_{16}H_{17}NO_4S_2$. The infrared spectrum showed an NH absorption at 3.1 μ, and the absorptions at 5.65 and 5.8 μ had disappeared with no new absorption in the carbonyl region. The nmr spectrum in acetone-d_6 showed a signal at 4.05 ppm (two protons), a broadened signal at 2.9 ppm [one proton (NH)], and signals for two *p*-toluenesulfonyl groups. These data definitely excluded 2,5-di-*p*-toluenesulfonylpyrazine ($C_{18}H_{16}N_2O_4S_2$) as the structure and a structural assignment of 2,3-di-*p*-toluenesulfonylaziridine was made. The absorption of the crude oil at 5.65 μ indicated that 3-*p*-toluenesulfonyl-3H-azirine (**4**) was formed as an unstable intermediate. Hydrolysis of some of the azirine **4** could give *p*-toluenesulfinic acid which on addition to the imine linkage of the azirine would lead to aziridine **3**.



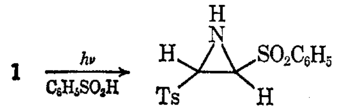
4 **3**

This compound is probably the *trans* compound since approach of *p*-toluenesulfinic acid from the least-hindered face of the molecule would lead to formation of the *trans* aziridine. The reduction of 3H-azirines with lithium aluminum hydride has been shown to yield *cis* aziridines thus demonstrating that lithium aluminum hydride approaches from the least-hindered face of the 3H-azirine ring system.[6]

The slow hydrolysis of azirine **4** by water in the reaction mixture to give *p*-toluenesulfinic acid seems probably due to the presence of a geminal amino and *p*-toluenesulfonyl group. Miller and Kalnins have reported a similar formation of *p*-toluenesulfinic acid from a geminal *p*-toluenesulfonyl alcohol.[11]

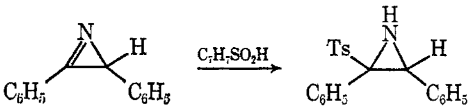


If azirine **4** is an intermediate in the formation of **3**, then the photolysis of vinyl azide **1** under anhydrous conditions in the presence of a different sulfinic acid should lead to the incorporation of this sulfinic acid into the molecule. This proved to be the case. Photolysis of **1** in the presence of benzenesulfinic acid yielded 2-benzenesulfonyl-3-*p*-toluenesulfonylaziridine (**5**). The chemical shifts of the C-2 and C-3 protons were the same; so a definite *cis* or *trans* assignment could not be made for **5**. Although a high yield of aziridine **5** was expected since the hydrolysis step was by-passed, only a small amount of **5** was isolated. This is most likely due to the instability of benzenesulfinic acid to ultraviolet light. On irradiation by itself, benzenesulfinic acid broke down to a foul-smelling oil.



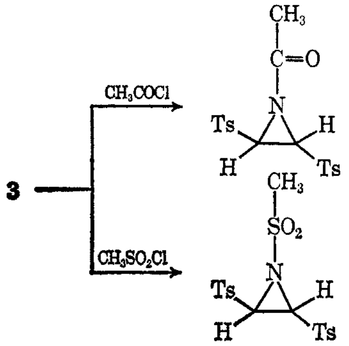
5

As no addition of a sulfinic acid to a 3H-azirine has been reported, 2,3-diphenyl-3H-azirine was allowed to react with *p*-toluenesulfinic acid at room temperature in acetone; 2,3-diphenyl-2-*p*-toluenesulfonylaziridine (**6**) crystallized from the reaction mixture within 30 min. *p*-Toluenesulfinic acid also condensed with 2-phenyl-3-methyl-3H-azirine.



6

Aziridine **3** can be acetylated and mesylated to yield the N-substituted aziridines. Aziridine **6** was also mesylated. It has been reported that deamination to aziridines is stereospecific, and it was hoped that this reaction would prove the *trans* assignment of **3** made above. However, attempts to deaminate **3** with either nitrosyl chloride in triethylamine[12] or 3-nitro-9-nitrosocarbazole[13] failed. Evidently the pair of electrons on the aziridine is not sufficiently nucleophilic to react with the nitroso compounds. Hydrolysis of **3** with sodium hydroxide gave *p*-toluenesulfinic acid. Aziridine **3** was not affected by hot methanolic hydrochloric acid.



The instability of azirine **4** is not surprising. The 3H-azirines prepared to date have all been derived from vinyl azides in which the azido function occupies an internal position; hence, the azirine produced bears a substituent at the carbon atom of the imine linkage.

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(10) P. W. Neber and G. Huh, *Ann.*, **515**, 283 (1935).

(11) B. Miller and M. V. Kalnins, *Tetrahedron*, **23**, 1145 (1967).

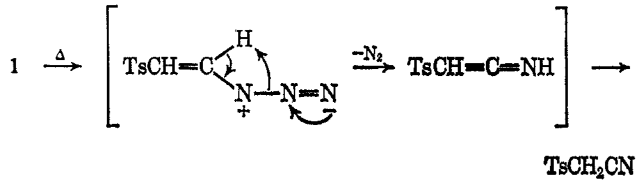
(12) R. D. Clark and G. K. Helmkamp, *J. Org. Chem.*, **29**, 1316 (1964).

(13) C. L. Bumgardner, K. S. McCallum, and J. P. Freeman, *J. Amer. Chem. Soc.*, **83**, 4417 (1961).

Hassner and Fowler[14] have found that 1-azido-3,3-dimethyl-1-butene, a vinyl azide with the azido function on the terminal carbon atom, gave mostly polymer and a small amount to 2,5-di-*t*-butylpyrazine on photolysis. No 3-*t*-butyl-3H-azirine was isolated. Boyer, Krueger, and Mikol[9] have reported that photolysis and pyrolysis of β-styryl azide, a terminal vinyl azide, yield phenylacetonitrile. However, in the pyrolysis a 74% yield of the nitrile was isolated while in photolysis a maximum of 8% nitrile was detected along with 74% polymeric solid. This difference in products is indicative of different intermediates in the two processes. The possibility that nitrile formation in the photolysis of β-styryl azide is occurring through pyrolysis has not been ruled out in Boyer's work since the temperature of the Rayonet reactor was not reported. We also observed nitrile formation when **1** was photolyzed without external cooling; however, nitrile formation could be prevented by keeping the azide below room temperature during photolysis. This coupled with our data indicates that 3H-azirines with a hydrogen atom on the unsaturated carbon are unstable, possibly owing to the absence of steric hindrance to polymerization.

Qualitatively the behavior of the *cis*-β-azidovinyl *p*-tolyl sulfone resembled the behavior of the *trans* isomer. Irradiation of the *cis* azide in one experiment gave a 29% yield of **3**. When *cis*-1,2-di-*p*-toluenesulfonylethene was treated with sodium azide in dimethylformamide on a steam bath, the azide which formed was immediately decomposed and gave the nitrile **2**. It has been found that the *cis* azide is formed first in the sulfone sodium azide reaction in dimethyl sulfoxide and in aqueous methanol,[15,16] and it was assumed that in the hot dimethylformamide the nitrile was arising from the *cis* azide.

In summary, the pyrolysis of **1** to yield *p*-toluenesulfonylacetonitrile can be explained by invoking either nitrogen loss to form a singlet nitrene which inserts into the carbon–hydrogen bond or a concerted loss of nitrogen and migration of hydrogen as is indicated in the following diagram.[17] The observation that no azirine formation occurs is attributed to the high electrophilicity of the π bond α to the sulfone group which raises the activation energy for this reaction.



The photolysis of **1** to produce the unstable azirine **4** indicates that the photolytic decomposition of **1** produces an intermediate in which π-bond migration is favored over hydrogen-atom migration. The ability of the electron-deficient π bond to interact with the azide or nitrene can be explained by invoking a triplet azide or nitrene which would have the properties of a diradical rather than an electrophilic species.

Cleaver and Krespan[8] discarded a triazole as an intermediate in the pyrolysis of 1-azidopentafluoropropene since fluorinated tetrazoles are stable at 100°. Irradiation of the triazole related to **1** failed to give either **2** or **3** and cannot be an intermediate.

Experimental Section

All nmr spectra were run on Varian A-60 and A-60A spectrophotometers with TMS as an internal standard. Elemental analyses were carried out by Galbraith Laboratories, Knoxville, Tenn. Melting points were determined on a Fisher-Johns melting point apparatus and are corrected. Mass spectra were obtained by Mr. R. Sadecky using a CEC 21-103C mass spectrometer.

Pyrolyses Giving *p*-Toluenesulfonylacetonitrile (2).—A solution of 0.5 g of the vinyl azide in 21 ml of methanol was refluxed for 11 hr. The methanol was removed leaving 0.422 g (96%) of a tan solid, mp 140–147°. After recrystallization from methanol the material weighed 0.225 g (53%) and melted at 147–148° (lit.[11] mp 149.5–150.5° for *p*-toluenesulfonylacetonitrile). The infrared spectrum showed sharp absorption at 4.43 μ and the nmr spectrum (acetone-d_6) showed one *p*-toluenesulfonyl group and two signals for the methylene protons at 4.7 and 2.94 ppm which gradually exchange for deuterium. Possibly tautomerization is involved in this solvent. In deuteriochloroform the nmr spectrum showed a quartet between 8.1 and 7.8 for four aromatic hydrogen atoms, a singlet for the two methylene protons at 4.11, and a singlet for the *p*-methyl group at 2.53 ppm.

Anal. Calcd for $C_9H_9NO_2S$: C, 55.37; H, 4.65; N, 7.17. Found: C, 55.54; H, 4.70; N, 6.99.

p-Toluenesulfonylacetonitrile was also isolated from the pyrolysis of **1** in benzene.

In a similar experiment the vinyl azide **1** was pyrolyzed to *p*-toluenesulfonylacetonitrile in 15% aqueous ethanol. An infrared spectrum of the crude product showed that no 2,3-di-*p*-toluenesulfonylaziridine was present.

A 0.100-g sample of the *trans* azide, dissolved in acetone-d_6, was placed in a mailing tube and then in a Rayonet photoreactor. Although the fan was turned on, the temperature in the reactor was sufficient to give a 30% conversion into the nitrile in 22 hr.

cis-1,2-Di-*p*-toluenesulfonylethene (2 g) and sodium azide (2 g) in 90 ml of dimethylformamide were heated on a steam bath for 30 hr until the initially bright yellow color was almost discharged. After recrystallization from water the nitrile melted at 146–148° (0.7 g). Similar results were obtained using boiling isobutyl alcohol or aqueous acetonitrile.

Photolyses of I.—A solution of 0.5 g of the *trans*-vinyl azide in 10 ml of cyclohexene (distilled from calcium hydride) in a Pyrex test tube cooled by an ice bath was irradiated for 40 hr in a Rayonet photolysis apparatus with black phosphor lamps. The solvent on evaporation left 0.710 g of an intractable tar contaminated with solvent. A solution of 0.676 g of the vinyl azide in 60 ml of tetrahydrofuran (distilled from lithium aluminum hydride) was irradiated for 8 hr in a quartz flask. The solution was concentrated by means of a rotary evaporator and gave a brown oil. The infrared spectrum (smear) of this oil showed absorption at 3.05, 5.65, and 5.8 μ. The oil was dissolved in 10 ml of ethanol and 9 ml of 10% hydrochloric acid and boiled on a steam bath for 20 min. On cooling, the solution gave 0.25 g of white needles: mp 188.5–190.5°; mass spectrum (70 eV), *m/e* (rel intensity) 351 (1), 287 (5), 196 (9), 156 (11), 139 (100), 92 (83), 91 (46), 65 (24), 40 (14), 39 (14); other spectral data are given above for **3**.

Anal. Calcd for $C_{16}H_{17}NO_4S_2$: C, 54.68; H, 4.88; N, 3.99; S, 18.25. Found: C, 54.80; H, 4.96; N, 3.61; S, 18.32.

A solution of 0.5 g of the vinyl azide was irradiated with cooling for 16 hr. At the end of this time 0.17 g of a white solid which had crystallized from the reaction mixture was filtered, mp 179–182°. The nmr spectrum showed that it was identical with 2,3-di-*p*-toluenesulfonylaziridine.

A solution of 1.71 g of the vinyl azide in 20 ml of 15% aqueous ethanol in a Pyrex test tube was photolyzed for 40 hr. The temperature was not allowed to rise above 20°. The solvent was removed using a stream of air, and a small quantity of methanol (2–5 ml) was added. The reaction mixture was chilled

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(14) A. Hassner, University of Colorado, private communication, 1967.

(15) J. S. Meek and J. S. Fowler, *J. Amer. Chem. Soc.*, **89**, 1967 (1967).

(16) J. S. Meek and J. S. Fowler, *J. Org. Chem.*, **33**, 985 (1968).

(17) A. N. Nesmeyanov and M. I. Rybinskaya [*Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 816 (1962)] have reported the formation of benzoylacetonitrile from the acid-catalyzed decomposition of β-azidovinyl phenyl ketone.

and filtered to yield 0.765 g (56%) of a white solid, mp 175–180°. The ir and nmr spectra were identical with those of the product obtained from photolysis of the vinyl azide in tetrahydrofuran.

A 0.795-g sample of *cis*-β-azidovinyl *p*-tolyl sulfone in 14 ml of methanol was diluted with 1 ml of water containing 15 mg of hydroquinone. After irradiation 0.18 g (29%) of **3** was isolated: mp 179–181°.

Photolysis of *trans*-β-Azidovinyl *p*-Tolyl Sulfone in the Presence of Benzenesulfinic Acid.—A solution of 1.0 g of **1** and 0.54 g of benzenesulfinic acid in 3.2 ml of glyme (distilled from calcium hydride) was photolyzed for 40 hr, and the temperature was maintained below 20°. The glyme was removed using a stream of air and a few milliliters of methanol was added. The reaction mixture was chilled and filtered yielding 0.28 g of a semicrystalline material which after one recrystallization from chloroform–pentane had mp 149–152° (wt, 0.16 g). Six recrystallizations from chloroform–pentane yielded an analytical sample, mp 152.5–154°. The nmr spectrum ($CDCl_3$) showed signals at 3.92 ppm (2 H singlet) in addition to a singlet at 2.45 ppm covering a broadened signal integrating for a total of four protons, and a multiplet between 7 and 8 ppm (9 H).

Anal. Calcd for $C_{15}H_{15}NO_4S_2$: C, 53.39; H, 4.48; N, 4.15. Found: C, 53.12; H, 4.43; N, 4.15.

Reaction of 2,3-Diphenyl-3H-azirine with *p*-Toluenesulfinic Acid.—To 0.56 g of the azirine[18] in 5.5 ml of acetone (distilled from magnesium sulfate) was added 0.50 g of *p*-toluenesulfinic acid (prepared by acidifying sodium *p*-toluenesulfinate dihydrate). Within 15 min a bright yellow color had developed, and within 0.5 hr white needles precipitated from the reaction mixture. Filtration yielded 0.61 g, mp 198–200°. The infrared spectrum showed sharp NH absorption at 3.02 μ. The mass spectrum showed a weak molecular ion at *m/e* 349 and a very intense fragment at *m/e* 193 corresponding to the loss of *p*-toluenesulfinic acid to yield the parent azirine.

Anal. Calcd for $C_{21}H_{19}NO_2S$: C, 72.18; H, 5.48; N, 4.01. Found: C, 72.11; H, 5.50; N, 4.04.

2-Phenyl-2-*p*-toluenesulfonyl-3-methylaziridine.—When 0.68 g of *p*-toluenesulfinic acid and 0.55 g of 3-methyl-2-phenyl-3H-azirine[18] were allowed to react in 3 ml of acetone for 30 min a 60% crude yield of product was obtained by filtration. The analytical sample melted at 98–99° after recrystallization from ether: nmr ($CDCl_3$), δ 7.9–6.9 (m, 9), 4.8 (broad s, 1, N–H), 3.27 (q, 1 H-3, J = 5.5 Hz), 2.37 (s, 3), and 0.97 ppm (d, 3, J = 5.5 Hz).

Anal. Calcd for $C_{16}H_{17}NO_2S$: C, 66.87; H, 5.96; N, 4.88. Found: C, 66.58; H, 5.76; N, 4.69.

Acetylation of 2,3-Di-*p*-toluenesulfonylaziridine.—A solution of 0.15 g of the aziridine, 0.5 ml of triethylamine, and 0.5 ml of acetyl chloride in 10 ml of benzene was refluxed for 21 hr. At the end of this time the salt was filtered, and the benzene, excess triethylamine, and acetyl chloride were removed using a stream of air. Ether was added to the residue and 0.125 g of a white solid formed, mp 188.5–191°. Three recrystallizations from ether–chloroform gave an analytical sample: mp 195.5–196°; mass spectrum (70 eV), *m/e* (rel intensity) 393 (<1), 352 (1), 238 (32), 139 (100), 91 (56), 43 (50). The nmr spectrum showed signals at δ 4.33 (s, 2) and 2.22 ppm (s, 3) in addition to signals for two *p*-toluenesulfonyl groups.

Anal. Calcd for $C_{18}H_{19}NO_5S_2$: C, 54.94; H, 4.87; N, 3.56. Found: C, 54.78; H, 4.78; N, 3.53.

Mesylation of 3.—A solution of 0.35 g of the aziridine, 1.5 ml of methanesulfonyl chloride, and 1.5 ml of triethylamine in 20 ml of benzene was allowed to stand at room temperature overnight. The benzene was washed with water and removed using a stream of air. The residue was crystallized by the addition of a few milliliters of ether to yield 0.31 g of a white solid, mp 171–175°. An nmr spectrum ($CDCl_3$) showed signals at 4.58 (2 H singlet) and 3.0 ppm (3 H singlet) in addition to signals for two *p*-toluenesulfonyl groups.

Anal. Calcd for $C_{17}H_{19}NO_6S_3$: S, 22.39. Found: S, 22.46.

Mesylation of 2-Phenylsulfonyl-3-*p*-toluenesulfonylaziridine.—A solution of 0.235 g of the aziridine, 1 ml of methanesulfonyl chloride, and 1 ml of triethylamine in 10 ml of benzene was allowed to stand for 48 hr at room temperature. The reaction mixture was washed with water, and the benzene was removed using a stream of air. The addition of a few milliliters of methanol caused the precipitation of 0.182 g of a white solid, mp 172–174°. An nmr spectrum ($CDCl_3$) showed signals at 2.45 (3 H, singlet, tolyl methyl), 3.02 (3 H, singlet, mesyl methyl), 4.62 (2 H, singlet, aziridine ring protons), 7–8 ppm (9 H, multiplet, aromatic protons). Five recrystallizations from methanol yielded an analytical sample, mp 177.5–178°.

Anal. Calcd for $C_{16}H_{17}NO_6S_3$: C, 46.25; H, 4.12; N, 3.37. Found; C, 46.50; H, 4.30; N, 3.45.

Reaction of 3 with Methanolic Potassium Hydroxide.—A solution of 90 mg of the aziridine, 0.37 g of sodium hydroxide, and 4 ml of a 1:1 methanol–water solution was refluxed for 7 hr. The reaction mixture was acidified with 10% hydrochloric acid and extracted with ether. The ether yielded 0.062 g of a white solid, mp 84–87° (lit.[19] mp 81–83° for *p*-toluenesulfinic acid). The nmr spectrum was identical with that of *p*-toluenesulfinic acid. No basic component was detected.

Attempted Acidic Hydrolysis of 3.—A solution of 0.25 g of the aziridine in 13 ml of methanol and 2 ml of 10% hydrochloric acid was refluxed for 24 hr. Cooling and filtering yielded 0.14 g, mp 187–188°, identical with **3**.

Irradiation of 4(5)-*p*-Toluenesulfonyltriazole.[16]—The triazole related to **1** was unstable to conditions which converted **1** into **3**, and the formation of **2** and **3** was not detected.

Registry No.—**1**, 15645-79-1; **2**, 5697-44-9; **3**, 17037-76-3; **3** (acetylated), 17037-77-3; **3** (mesylated), 17037-78-4; **5**, 17037-79-5; **5** (mesylated), 17037-82-0; **6**, 17037-80-8; 2-phenyl-2-*p*-toluenesulfonyl-3-methylaziridine, 17037-81-9.

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