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# TRIAZOLINE PHOTODECOMPOSITION

## THE PREPARATION OF AZIRIDINES

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**Abstract**—Triazoline photodecomposition has been found suitable for the preparation of aziridines bearing a variety of substituents. The nature and position of substituents in the starting triazoline does not generally hinder the reaction, although difficulties were encountered when photoreactive groups were present. A quantitative study of the effect of alkyl and cycloalkyl groups on the aziridine yield revealed a dependence on triazoline geometry. The effect, however, was not large.

PHOTODECOMPOSITION of $\Delta^2$-1,2,3-triazolines produces aziridines.[1] While thermolysis generally gives mixtures of imines and aziridines, triazoline photolysis has afforded dramatically higher yields of aziridines, relatively uncontaminated with isomeric products.[1-3] The mild conditions (inert solvents, low temps) associated with triazoline photodecomposition are advantageous, and contrast with those employed in classical aziridine preparative methods.[4] In view of recent extensions of the azide-olefin reaction to include simple olefins and dienes,[5] fluorinated olefins,[6] phosphorous azides,[7] enamines,[8] and enol ethers,[9] and the consequent availability of variously substituted triazolines, the photolytic route to aziridines appears to have wide synthetic potential. The present paper deals with synthetic aspects of the reaction; the mechanism of triazoline photodecomposition is discussed elsewhere.[10]

### RESULTS AND DISCUSSION

*Spectra and solvent effects.* Triazolines irradiated in the region of their UV absorption maxima (>240 mμ) undergo decomposition. The UV absorption spectra of triazolines display a marked sensitivity to the nature of substituents at the 1-position. The data in Table 1 indicate the effect of such substituents on both the position and intensity of the maximum absorption. On the other hand, the triazoline chromophore is not significantly influenced by substituents at the carbon positions of the triazoline nucleus; the UV spectra of several 4- and 5-substituted 1-phenyl triazolines are essentially identical to the first example in Table 1.

Provided the starting material or product is not attacked,* the course of reaction is independent of the solvent. Photolysis of I in solvents n-hexane, cyclohexene, tetrahydrofuran, acetone, ethyl acetate, *p*-dioxane and benzene all resulted in quantitative conversions to the aziridine. Similarly, the photodecomposition of II occurred smoothly in either anhydrous or 20%-aqueous dimethylformamide.

*Substituents at the 1-position.* The high reactivity or norbornene and organic azides

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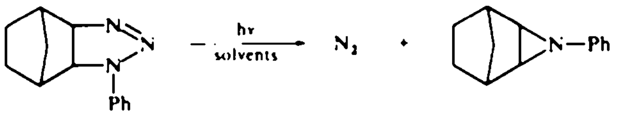
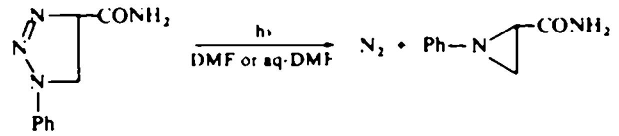
* Triazolines are rapidly decomposed by acids. Aziridines are attacked by acids and strong nucleophiles

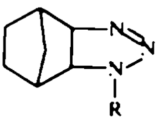


I



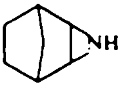
II

TABLE 1. UV ABSORPTION OF TRIAZOLINES

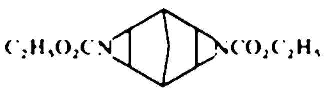
|  R | $\lambda_{max}$, mμ[a] | $\varepsilon_{max}$, l mole$^{-1}$ cm$^{-1}$ |
|---|---|---|
| Ph | 309 | 10,700 |
| C(Ph)=CH₂ | 274 | 6670 |
| CH₂Ph | 270 | 4860 |
| —SiMe₃ | 257 | 3580 |
| CO₂Et | 244 | 3320 |

[a] Acetonitrile and EtOH solns.

was utilized to prepare triazolines possessing various substituents at the 1-position. Prior to this study, 1-alkyl,[1,11] 1-carbethoxy,[1] and 1-aryl[1,2] triazolines had been successfully photolyzed. It was therefore not surprising that triazolines IIIa–h afforded excellent yields (> 90%) of the corresponding aziridines (Table 2). However, in contrast to IIIa–h, nitrogen was evolved slowly and incompletely from the 1-*p*- and 1-*m*-nitrophenyl triazolines (IIIi, j); the formation of highly coloured materials was observed. Although a low yield (18%) of aziridine IVi was obtained, no characterizable product was isolated from IIIj. The failure of IIIi, j to give satisfactory yields of aziridine is probably due to competing processes associated with the excited aromatic nitro group.[12] Other 1-nitrophenyl triazolines exhibited similar photolytic behaviour.



V



VI

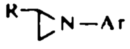
3-Azatricyclo[3.2.1.0$^{2,4}$]octane (V) was conveniently obtained from IVa. The facile cleavage of Si-N bonds by alcohols[13] was employed, suggesting a general method for aziridines unsubstituted on nitrogen. *bis*-Aziridine (VI) was also prepared by photodecomposition.

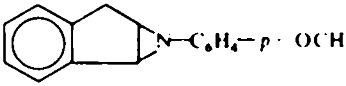
*Substituents on carbon.* In general, the course of the photolysis was not affected by the nature of substituents on the triazoline nucleus. Thus photodecomposition of

TABLE 2 PHOTOLYSIS OF 1-SUBSTITUTED TRIAZOLINES

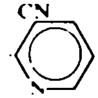
| | III<br>R | | IV<br>R |
|---|---|---|---|
| a | $SiMe_3$ | f | $C_6H_4$—p-Cl |
| b | $C(Ph)=CH_2$ | g | $C_6H_4$—p-OMe |
| c | $CO_2Et$ | h | $C_6H_4$—m-OMe |
| d | $C_6H_4$—m-Me | i | —$C_6H_4$ p-$NO_2$ |
| e | $C_6H_4$—m-Br | j | —$C_6H_4$ m-$NO_2$ |

triazolines bearing amide, nitrile and 2-pyridyl groups occurred smoothly and produced the corresponding aziridines (VIIa-c). The synthesis of a 2-alkoxyaziridine by this method has recently been described.[3]



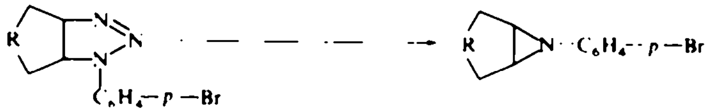


VII a R = $CONH_2$
b[14] R = CN
c R =



VIII

Carbocyclic ring-fused aziridines, e.g. VIII, were readily prepared by triazoline photolysis. Therefore, it was of interest to determine the effect of additional heteroatoms incorporated into such structures. In part, we were prompted to apply the

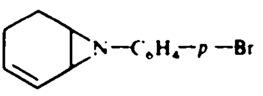


IXa R = O
b R = NH

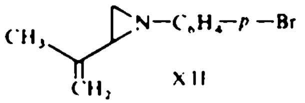
X

photolytic method to compare it with the reported synthesis of related compounds by the Wenker procedure.[15] Accordingly, triazolines IXa, b were prepared (>90%) by the addidion of p-bromophenyl azide to 2,5-dihydrofuran and 3-pyrroline. Photolysis afforded a quantitative yield of Xa, while a somewhat lower yield (61%) of Xb was obtained. In the latter case, photo-induced side reactions appear to have occurred; prolonged irradiation gave rise to a dark, tarry mixture.

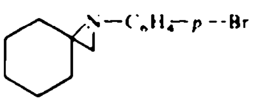
5-Vinyltriazolines, available by the addition of azide to 1,3-dienes,[5] photolyzed without difficulty. The method thus provides a simple route to 2-vinylaziridines, such as XI and XII.[16] Spiroaziridine XIII also conveniently prepared from the corresponding triazoline.



XI

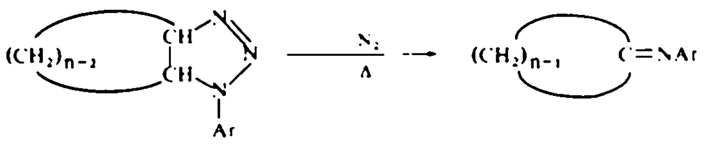


XII



XIII

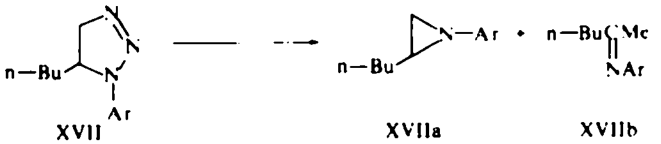
*Structural effects.* Alder and Stein reported the pyrolysis of azide-cycloalkene adducts to cyclic imine derivatives.[17] But photolysis of a cyclopentene adduct



(n = 5) gave the aziridine and only traces of the imine. This observation, and interest in structural effects on the photodecomposition, led us to examine the influence of structure on the yield of aziridine.

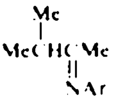
Under standardized conditions, a series of triazolines was photolyzed in dilute benzene solution. In each case, VPC analysis revealed only two products; aziridine and imine. For comparative purposes, the triazolines were thermally decomposed by injecting benzene solutions into the vapor phase chromatograph. The results of duplicate runs are summarized in Table 3.

The imine products from both thermal and photodecompositions (except from XIX) arose by hydrogen rather than alkyl migration. Triazoline XVII, for example, gave aziridine XVIIa and 2-hexylidene-*p*-bromoaniline (XVIIb). Methyl migration was



XVII XVIIa XVIIb

observed in the decompositions of XIX, forming 3-methyl-2-butylidene-*p*-bromoaniline (XIXb), as well as the aziridine.



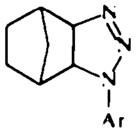
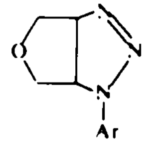
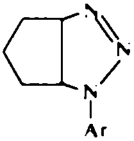
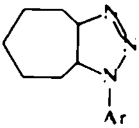
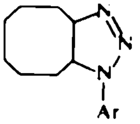
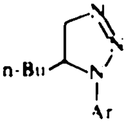
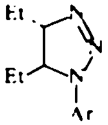
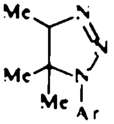
$$\mathrm{Me\overset{\overset{\displaystyle Me}{|}}{C}HC\underset{\underset{\displaystyle NAr}{\|}}{}Me}$$

XIXb

From the preparative standpoint, the photolytic yields of aziridine were quite satisfactory, and in all instances better than the thermal reactions. Furthermore, the data in Table 3 suggest a correlation between triazoline structure and the photolytic product distribution. Increased flexibility (rotational freedom) about the $C_4$–$C_5$ triazoline bond apparently results in substantially larger amounts of imine. Alkyl substitution at the 4-position may also have a somewhat deleterious effect on the yield of aziridine (cf. XVII, XVIII, XIX).

*Conclusions.* Triazoline photodecomposition has been found excellent for the preparation of aziridines. The results indicate a wide scope for the reaction. Provided that the substituents themselves were not photoreactive, high yields were obtained.

TABLE 3. PHOTO AND THERMAL DECOMPOSITION OF 1-$p$-BROMOPHENYL TRIAZOLINES

| | Triazoline$^c$ | Photodecomposition$^a$ Aziridine, %$^d$(a) | Photodecomposition$^a$ Imine, %$^d$ (b) | Thermal decomposition$^b$ Aziridine, % (a) | Thermal decomposition$^b$ Imine, % (b) |
|---|---|---|---|---|---|
| XIV |  | 100 | < 1 | $^e$ | $^e$ |
| IXa |  | 96 | 4 | 47 | 53 |
| |  | 94 | 6 | 21 | 79 |
| XV |  | 89 | 11 | 54 | 46 |
| XVI |  | 88 | 12 | 55 | 45 |
| XVII |  | 88 | 12 | 64 | 36 |
| XVIII |  (*trans*) | 84$^{f,g}$ | 16 | .. | |
| XIX |  | 83 | 17 | 69 | 31 |

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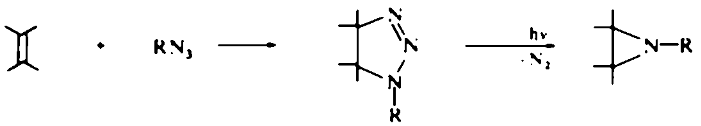
$^a$ Benzene solutions, 0·025 0·030M. $^b$ 315 ± 5°. Injection chamber of vapor phase chromatograph. $^c$ Ar = $p$-$C_6H_4Br$. $^d$ Area under recorded peaks ±2%. $^e$ Additional products present. $^f$ Analysis by infrared technique. $^g$ Stereochemistry not determined

With various alkyl- and cycloalkyl substituents, the yield of aziridine appears to be a function of triazoline geometry, and perhaps the degree and position of substitution. But these structural effects were not great. Since triazolines are available by azide-olefin addition (as well as other methods[18]) the two-step sequence outlined below offers a convenient and general route to aziridines.



## EXPERIMENTAL

NMR spectra were determined in $CDCl_3$ with a Varian A-60 instrument, using TMS as an internal standard. M.ps, uncorrected, were obtained with a Fisher Johns m.p. apparatus. IR spectra were determined for $CHCl_3$ solns with a Perkin-Elmer Model 237 instrument. UV spectra were recorded with a Carey Model 14 instrument. VPC was carried out with an F & M Model 810, using He as the carrier gas, and a thermal conductivity detector.

*General photolysis procedure*. Solns of the triazolines in cylindrical tubes were immersed in a water bath (25° ± 1°), approximately 10 cm from the light source. A Hanovia 450 w medium press Hg arc, immersed in the water bath in a large quartz test tube, provided the light. Evolved $N_2$ was measured by means of a thermostatted gas buret, connected to the top of the reaction tube. Reactions were terminated after the theoretical volume had been evolved.

3-*Trimethylsilyl*-3,4,5-*triazatricyclo*[5.2.1.$0^{2,6}$]*dec*-4-*ene* (IIIa). Norbornene, 7·5 g (0·08 mole), trimethylsilyl azide,[19] 9·3 g (0·08 mole), and 30 ml cyclohexane were refluxed for 8 days. Removal of the volatile materials (1·0 mm, 50°) gave 13·3 g (79%) of a light orange oil. This material (IIIa) showed a strong Si—$Me_3$ absorption[20] at 1250 $cm^{-1}$ and $\lambda_{max}$ 257 mμ, ε = 3580 in acetonitrile. Treatment with dilute aqueous acid caused the vigorous evolution of $N_2$ characteristic of $\Delta^2$-1,2,3-triazolines. Attempts to purify this material by distillation caused extensive decomposition.

3-*Trimethylsilyl*-3-*azatricyclo*[3.2.1.$0^{2,4}$]*octane* (IVa). A soln of 6·6 g (0·032 mole) of IIIa in 150 ml THF was irradiated in a quartz tube for 20 hr. 90% of the theoretical $N_2$ was evolved. Removal of the solvent gave 5·5 g of pale yellow oil, b.p. 42° (2·5 mm). The IR spectrum showed a strong peak at 1250 $cm^{-1}$, but no absorption in the C═N region, 1690–1640 $cm^{-1}$.[21] The analytical sample was collected by VPC from a 10-ft column (20% silicone rubber SE-30 on Diatoport S) at 170° (Found: C, 66·39; H, 10·49; N, 7·62. Calc for $C_{10}H_{19}NSi$: C, 66·23; H, 10·56; N, 7·73%)

3-*Azatricyclo*[3.2.1.0]*octane* (V). A sample of IVa (1·0 g) was dissolved in 3 ml MeOH and the soln remained overnight at room temp. Analysis by VPC (10-ft silicone rubber column, 160°) showed that the starting material had been completely transformed to V and more volatile materials. An analytical sample of V, m.p. 81–84° with sublimation, was collected by VPC. The IR spectrum showed it to be a secondary amine and the NMR spectrum accorded with that reported for V.[22] (Found: C, 76·89; H, 10·00; N, 12·74. Calc. for $C_7H_{11}N$: C, 77·01; H, 10·16; N, 12·83%).

A sample of V treated with excess phenylisothiocyanate at room temp afforded the phenylthiourea derivative, m.p. 119–120° after recrystallization from n-hexane–benzene (5:1). The same compound was obtained from the hydrolysis product of IVc.[1] (Found: C, 69·10; H, 6·57; N, 11·21. Calc for $C_{14}H_{16}N_2S$: C, 68·81; H, 6·60; N, 11·47%).

3-α-*Styryl*-3,4,5-*triazatricyclo*[5.2.1.$0^{2,6}$]*dec*-4-*ene* (IIIb). A soln of 4·7 g (0·05 mole) norbornene, 7·3 g (0·05 mole) α-azidostyrene[23] and 30 ml of n-hexane was refluxed for 16 hr. Evaporation of the solvent under reduced press gave 9·4 g (78%) of an orange oil. Chromatography on 150 g alumina (petroleum ether–diethyl ether eluent) gave 8·2 g of IIIb. Treatment with dilute acid resulted in vigorous gas evolution. The IR spectrum showed no azide absorption, but a medium intensity peak at 1620 $cm^{-1}$ (terminal methylene), and the UV spectrum showed $\lambda_{max}$ 274 mμ, ε = 6,670 in acetonitrile. In addition to the usual norbornene-azide adduct spectrum,[2] the NMR showed singlets (1H each) at τ 5·42 and 5·57 (terminal methylene). The compound deteriorated on standing.

3-α-*Styryl*-3-*azatricyclo*[3.2.1.$0^{2,4}$]*octane* (IVb). A soln of 4·0 g (0·017 mole) of IIIb in 120 ml THF was irradiated in a quartz tube for 7 hr. The solvent was removed and the residue distilled at 128–138° (1·5

2·0 mm), giving 2·7 g of IVb. Redistillation, 128–130° (1·5 mm) gave the analytical sample. (Found: C, 85·06; H, 8·29; N, 6·51. Calc. for $C_{15}H_{17}N$: C, 85·26; H, 8·11; N, 6·63%).

IR peaks at 1686 $cm^{-1}$ (enamine) and 1620 $cm^{-1}$ (terminal methylene) were observed. The NMR spectrum showed two singlets (1H each) at $\tau$ 5·17 and 5·60 (terminal methylene), five aromatic H's and the typical 3-azatricyclo[3.2.1.$0^{2,4}$]octane pattern[22] (10 H).

*Aziridines* IVd-i. These compounds were prepared by photolysis of the corresponding triazolines[24] as previously described for 3-*p*-bromophenyl-3-azatricyclo[3.2.1.$0^{2,4}$]octane.[1]

TABLE 4 AZIRIDINES IVd-i

| Aziridine IV | m.p. or b.p. (mm) | Recryst solvent* | Anal. data Calcd; Found C | H | N |
|---|---|---|---|---|---|
| d | 96 (0·5) | | 84·37<br>84·12 | 8·60<br>8·70 | 7·03<br>6·82 |
| e | 46·5–47·0 | A | 59·10<br>59·31 | 5·34<br>5·31 | 5·30<br>5·56 |
| f | 93 94 | A | 71·06<br>70·93 | 6·42<br>6·66 | 6·38<br>6·36 |
| g | 39 40 | B | 78·10<br>78·31 | 7·96<br>8·20 | 6·51<br>6·51 |
| h | 108 (0·2) | | 78·10<br>77·97 | 7·96<br>8·11 | 6·51<br>6·64 |
| i | 121 122 | A | 67·81<br>67·65 | 6·13<br>6·05 | 12·17<br>12·11 |

* Recryst solvents A, methanol; B, pentane

3,7-*Dicarbethoxy*-3,7-*diazaquadricyclo*[3.3.1.$0^{2,4}$.$0^{6,8}$]*nonane* (VI). A soln of 4·6 g (0·05 mole) norbornadiene 13·2 g (0·12 mole) ethyl azidoformate and 10 ml n-hexane was allowed to stand at room temp for 3 days. The solid product, 13·4 g (83%), melted from 131–136°, and it reacted vigorously with dilute aqueous acid. In a quartz tube, 1·6 g (5·0 mmole) of this material in 60 ml benzene was irradiated for 19 hr. Removal of the solvent gave 1·4 g of viscous yellow oil which crystallized slowly on standing. The IR spectrum showed a single CO peak (1720 $cm^{-1}$) and no absorption in the imine region. The four equivalent *endo*-ring H's appeared as a singlet, $\tau$ 7·12. Two recrystallizations from n-heptane gave VI, m.p. 99 100 (Found: C, 58·43; H, 6·82. Calc. for $C_{13}H_{18}N_2O_4$: C, 58·63; H, 6·81%).

4-*Carboxamide*-1-*phenyl*-$\Delta^2$-1,2,3-*triazoline* (II). Acrylamide, 7·1 g (0·10 mole), phenyl azide, 11·9 g (0·10 mole), and 80 ml acetone were refluxed for 20 hr. The resulting suspension was filtered and 6·8 g (36%) of product was collected, 155 156° dec. Two recrystallizations from acetone gave II, 157° dec. With the exception of the amido hydrogens, the NMR was similar to that of related compounds.[14] (Found: C, 56·82; H, 5·35; N, 26·69. Calc for $C_9H_{10}N_4O$: C, 56·83; H, 5·30; N, 29·46%).

2-*Carboxamido*-1-*phenylaziridine* (VIIa). A suspension of 2·4 g (0·013 mole) 4-carboxamido-1-phenyl-$\Delta^2$-1,2,3-triazoline in 100 ml acetone was irradiated in a Pyrex tube for 16 hr. Removal of the solvent gave 1·9 g of solid, m.p. 137–139°. Recrystallization from benzene gave VIIa, m.p. 145–146°. The IR spectrum showed no absorption in the C=N region, and the NMR spectrum was similar to that of VIIb.[14] (Found: C, 66·41; H, 5·93; N, 17·5. Calc. for $C_9H_{10}N_2O$: C, 66·64; H, 6·21; N, 17·28%).

1-p-*Bromophenyl*-5(2-*pyridyl*)$\Delta^2$-1,2,3-*triazoline*. After 17 days at room temp, a mixture of 9·9 g (0·05 mole) *p*-bromophenyl azide and 5·3 g (0·05 mole) 2-vinylpyridine afforded 13·4 g (88%) of crude product, m.p. 95 100°. Two recrystallizations from n-hexane–EtOAc (2:1) gave the analytical sample, m.p. 147–148° dec. (Found: C, 51·38; H, 3·73; N, 18·55. Calc for $C_{13}H_{11}BrN_4$: C, 51·50; H, 3·66, N, 18·48%).

1-p-*Bromophenyl*-2(2-*pyridyl*)*aziridine* (VIIc). A soln of 1·9 g (6·3 mole) 1-*p*-bromophenyl-5(2-pyridyl)-$\Delta^2$-triazoline in 50 ml THF was irradiated in a Pyrex tube for 18 hr. Evaporation of the solvent under reduced press gave 1·8 g of product, m.p. 100–104°. Three recrystallizations from MeOH gave VIIc, m.p. 113·5–114·5° The IR spectrum showed no imine absorption, and the NMR spectrum displayed, in addition to the 8 aromatic H's, two multiplets centered at τ 7·50 (2H) and 6·75 (1H) (Found: C, 56·64; H, 4·03; N, 10·08. Calc. for $C_{13}H_{11}BrN_2$: C, 56·74; H, 4·03; N, 10·18%).

*7,8-Benzo-2-methoxyphenyl-2,3,4-triazabicyclo*[3.3.0]*octa-3,7-diene.* After 6 weeks at room temp, a mixture of 1·5 g (0·01 mole) *p*-methoxyphenyl azide and 1·2 g (0·01 mole) indene gave 1·0 g (38%) of adduct, m.p. 118–122. Three recrystallizations from n-hexane–EtOAc (3:1) gave material, m.p. 133 dec. The structure was assigned in agreement with those of other aryl azide-indene adducts.[25] (Found: C, 72·30; H, 5·66; N, 15·8. Calc. for $C_{16}H_{15}N_3O$: C, 72·43; H, 5·70; N, 15·84%.)

*2,3-Benzo-6-methoxyphenyl-6-azabicyclo*[3.1.0]*oct-2-ene* (VIII). Photolysis of 7,8-benzo-2-*p*-methoxyphenyl-2,3,4-triazabicyclo[3.3.0]octa-3,7-diene (EtOAc solvent, Pyrex tube) gave VIII (100%), m.p. 147–148°, lit.[26] m.p. 147–148.

2-p-*Bromophenyl-7-oxa-2,3,4-triazabicyclo*[3.3.0]*oct-3-ene* (IXa). A soln of 7·9 g (0·04 mole) *p*-bromophenyl azide in 25 ml 2,5-dihydrofuran was refluxed for 22 hr. Removal of the solvent gave 11·6 g (quantitative) of product, m.p. 135–140 dec. Four crystallizations from n-hexane–EtOAc (2:1) gave pure IXa, m.p. 151–152 dec. (Found: C, 44·79; H, 3·82; N, 15·7. Calc. for $C_{10}H_{10}BrN_3O$: C, 44·79; H, 3·76; N, 15·67%.)

6-p-*Bromophenyl-6-aza-3-oxabicyclo*[3.1.0]*hexane* (Xa). A soln of 3·0 g (11·2 mmole) of IXa in 50 ml benzene and 100 ml acetone was irradiated for 19 hr in a Pyrex tube. Crude product, 2·6 g, m.p. 125–129, was obtained. Three recrystallizations from n-hexane gave Xa, m.p. 135–136. The IR spectrum showed no imine absorption, and the NMR spectrum showed 4 aromatic H's and peaks centered at τ 6·87, 6·27 and 5·83 (2H each). (Found: C, 50·34; H, 4·37; N, 5·9. Calc. for $C_{10}H_{10}BrNO$: C, 50·02; H, 4·20; N, 5·83%.)

2-p-*Bromophenyl-2,3,4,7-tetraazabicyclo*[3.3.0]*oct-3-ene* (IXb). After 2 weeks at room temp, a mixture of *p*-bromophenyl azide, 5·9 g (0·03 mole) and 3-pyrroline, 2·1 g (0·03 mole) had completely solidified. The crude product, 7·2 g (90%), melted from 97–101. Four crystallizations from n-hexane–EtOAc (2:1) gave IXb, m.p. 112–113. (Found: C, 45·16; H, 4·28; N, 20·8. Calc. for $C_{10}H_{11}BrN_4$: C, 44·96; H, 4·15; N, 20·97%.)

6-p-*Bromophenyl-3,6-diazabicyclo*[3.1.0]*hexane* (Xb). Irradiation of 1·1 g (4·1 mmole) of IXb in 60 ml THF (quartz tube) for 6 hr produced an orange soln. The solvent was removed under reduced press and the resulting viscous oil crystallized on standing. Recrystallization from n-hexane gave 0·6 g (61%) of Xb, m.p. 115–116. The NMR spectrum showed peaks centered at τ 7·27, 7·17, 6·77 (2H each) and a singlet at τ 8·40 (1H, NH), as well as 4 aromatic H's. (Found: C, 50·17; H, 4·70; N, 11·62. Calc. for $C_{10}H_{11}BrN_2$: C, 50·22; H, 4·64; N, 11·72%.)

7-p-*Bromophenyl-7-azabicyclo*[4.1.0]*hept-2-ene* (XI). A soln of 1·4 g (5·0 mmole) 9-*p*-bromophenyl-7,8,9-triazabicyclo[4.3.0]nona-2,7-diene[5] in 55 ml THF was irradiated in a Pyrex tube for 17 hr. Removal of the solvent gave a yellow solid, 1·3 g, m.p. 76–80°. The IR spectrum showed a weak absorption at 1635 cm$^{-1}$. Three recrystallizations from pentane (−78°), followed by sublimation (70°, 0·5 mm) gave the analytical sample, m.p. 93–94°. The IR spectrum of this material showed no absorption in the imine region; four aromatic H's, 2 vinyl H's (multiplet centered at τ 3·75) and 6 aliphatic H's (multiplets, τ 7·1–9·0) comprised the NMR spectrum. (Found: C, 57·62; H, 4·85; N, 5·54. Calc. for $C_{12}H_{12}BrN$: C, 57·61; H, 4·84; N, 5·60%.)

1-p-*Bromophenyl-1-azaspiro*[2.5]*octane* (XIII). Irradiation of 2·1 g (7·2 mmole) 1-*p*-bromophenyl-1,2,3-triazaspiro[4.5]dec-2-ene[5] in 45 ml THF in a Pyrex tube for 13 hr gave 2·0 g of solid, m.p. 64–66. Three recrystallizations from pentane followed by sublimation (60°, 0·6 mm) gave XIII, m.p. 68–69. The IR spectrum showed no absorption from 1640–1690 cm$^{-1}$; the NMR spectrum showed 4 aromatic H's, 10 aliphatic H's, and a singlet at τ 8·02 (2 H, aziridine ring). (Found: C, 58·89; H, 6·12; N, 5·30. Calc. for $C_{13}H_{16}BrN$: C, 58·65; H, 6·06; N, 5·26%.)

*Photo and thermal decomposition of* 1-p-*bromophenyl triazolines* (*Table* 3)

*Procedure.* Freshly crystallized triazolines were dissolved in 25 ml anhyd benzene, to give 0·025–0·030M solns. Several runs at concentrations up to 0·06M showed that the results were not affected by concentration in this range. The solns were irradiated in a quartz cell, and evolved gas was measured with a gas buret at 27°. The incident light was filtered through two 3-mm plates of Pyrex glass and a Pyrex cell through which cold water was circulated. In operation, the temp of the reaction cell did not exceed 30°; controls showed no thermal decomposition under these conditions. After the theoretical quantity of $N_2$ had been observed (ca. 2 hr), the solns were irradiated for one additional hr, then analyzed by VPC using 3-ft columns packed with 10% Carbowax 20M on Chromosorb W (190–230°).

Overlap of the aziridine and imine peaks made chromatographic analysis unsuitable for XVIII. A previously described IR technique,[1] using the imine absorption at 6·05 μ, was employed

*Compounds*. Triazolines XV and XVI were prepared in 53% and 49% yield, respectively, by allowing mixtures of cycloheptene and cyclooctene (0·05 mole each), and *p*-bromophenyl azide (0·05 mole) to stand for 2 weeks at room temp. They were recrystallized from MeOH. The other triazolines have been previously reported.[1,5]

10-p-*Bromophenyl*-8,9,10-*triazabicyclo*[5.3.0]*dec*-8-*ene* (XV). M.p. 125–126° dec. (Found: C, 53·16; H, 5·35; N, 14·35. Calc. for $C_{13}H_{16}BrN_3$: C, 53·07; H, 5·48; N, 14·28%).

11-p-*Bromophenyl*-9,10,11-*triazabicyclo*[6.3.0]*undec*-9-*ene* (XVI). M.p. 131–132° dec. (Found: C, 54·49; H, 5·84; N, 13·69. Calcd. for $C_{14}H_{18}BrN_3$: C, 54·55; H, 5·89; N, 13·63%).

The aziridine products (isolated from larger runs) were characterized by their spectra. In each case, the IR spectrum showed no C=N absorption (1690–1640 cm$^{-1}$)[21] and the NMR spectrum displayed the requisite number of aromatic and aliphatic hydrogens. The solid compounds were recrystallized from n-pentane (−78°); analytical samples of the liquids were obtained by VPC, using Carbowax columns.

8-p-*Bromophenyl*-8-*azabicyclo*[5.1.0]*octane* (XVa). M.p. 58·5–59·0°. (Found: C, 58·70; H, 6·16; N, 5·27. Calc. for $C_{13}H_{16}BrN$: C, 58·65; H, 6·06; N, 5·26%).

9-p-*Bromophenyl*-9-*azabicyclo*[6.1.0]*nonane* (XVIa). M.p. 88·5–89·0°. (Found: C, 60·05; H, 6·44; N, 4·95. Calc. for $C_{14}H_{18}BrN$ C, 60·00; H, 6·47; N, 5·00%).

1-p-*Bromophenyl*-2-*butylaziridine* (XVIIa). (Found. C, 56·74; H, 6·39; N, 5·53. Calc. for $C_{12}H_{16}BrN$: C, 56·70; H, 6·35; N, 5·51%).

1-p-*Bromophenyl*-2,3-*diethylaziridine* (XVIIIa). (Found: C, 56·63, H, 6·39; N, 5·54. Calc. for $C_{12}H_{16}BrN$. C, 56·70; H, 6·35; N, 5·51%).

1-p-*Bromophenyl*-2,2,3-*trimethylaziridine* (XIXa) (Found: C, 54·93, H, 6·09; N, 5·88. Calc. for $C_{11}H_{14}BrN$: C, 55·01; H, 5·88; N, 5·83%).

For comparison with the decomposition products, authentic samples of the imines were prepared by refluxing 0·05 molar quantities of *p*-bromophenyl azide and the appropriate carbonyl compound with 0·5 ml conc HCl in 125 ml toluene. A Dean Stark trap removed water during the reaction. After 15–23 hr, the solvent was removed and the residue was distilled. The imines deteriorated rapidly on exposure to air; analytical samples were sealed in glass tubes after being collected from 3-ft Carbowax columns

*Cycloheptylidene*-p-*bromoaniline* (XVb). B.p. 129 130° (0·6 mm), $n_D^{24}$ 1·5836. (Found: C, 58·41; H, 5·92; N, 5·24. Calc. for $C_{13}H_{16}BrN$. C, 58·65; H, 6·06; N, 5·26%).

*Cyclooctylidene*-p-*bromoaniline* (XVIb). B.p. 148–153° (1·0 mm), $n_D^{24}$ 1·5839. (Found: C, 60·14, H, 6·52; N, 4·87. Calc. for $C_{14}H_{18}BrN$: C, 60·00; H, 6·47; N, 5·00%).

2-*Hexylidene*-p-*bromoaniline* (XVIIb). B.p. 90–100° (0·4 mm) $n_D^{24}$ 1·5522. (Found: C, 56·82, H, 6·59; N, 5·53. Calc. for $C_{12}H_{16}BrN$: C, 56·70; H, 6·35; N, 5·51%).

3-*Hexylidene*-p-*bromoaniline* (XVIIIb). B.p. 100–102° (0·7 mm). (Found: C, 56·50; H, 6·35; N, 5·52. Calc. for $C_{12}H_{16}BrN$: C, 56·70; H, 6·35; N, 5·52%).

3-*Methyl*-2-*butylidene*-p-*bromoaniline* (XIXb). B.p. 72 75° (0·4 mm), $n_D^{24}$ 1·5544. (Found: C, 54·86; H, 5·74; N, 5·86. Calc. for $C_{11}H_{14}BrN$: C, 55·01; H, 5·88; N, 5·83%).

The imine from IXa proved too unstable for elementary analysis. Its structure rests on its IR spectra.

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