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DECOMPOSITION OF THE PHENYL AZIDE ADDUCT OF NORBORNYLENE

R. S. McDaniel and A. C. Oehlschlager*

Department of Chemistry, Simon Fraser University, Burnaby 2, B.C., Canada

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Abstract—The pyrolysis of the triazoline adduct formed upon the reaction of phenyl azide with bicyclo (2.2.1) heptene results in the elimination of nitrogen and the formation of at least five products. The major products of pyrolysis in decalin were 3-azatricyclo ($3.2.1.0^{2,4\,exo}$) octane (**19**) and N-phenylbicyclo (2.2.1) hept-2-imine (**20**). Also formed in substantial amounts were *syn*-7-N-phenylaminobicyclo (2.2.1) hept-2-ene (**22**), 3-N-phenylaminotricyclo ($2.2.1.0^{2,6}$) heptane (**23**), and 3-azatricyclo($3.2.1.0^{2,4\,endo}$) octane (**21**). The mechanism of decomposition of the triazoline adduct is considered to proceed via a multistep mechanism involving initial heterolytic cleavage of the N–N single bond to give a diazonium betaine (**16**) which undergoes C—C bond cleavage to give a diazoimine (**17**) prior to loss of nitrogen. Both kinetic and chemical evidence is offered to support the proposed mechanism.

INTRODUCTION

Organic azides (**1**) react most readily with activated alkenes (**2**) via 1,3-dipolar cycloadditions.[1,2] Alkenes are activated toward 1,3-dipolar cycloadditions by angular strain, conjugation with aryl **2** (X = aryl) or carbonyl groups **2** ($X = \overset{\overset{O}{\|}}{C}$—) and by the presence of adjacent nitrogen and oxygen such as in enamines **2** (X = N) and vinyl ethers **2** (X = O—).

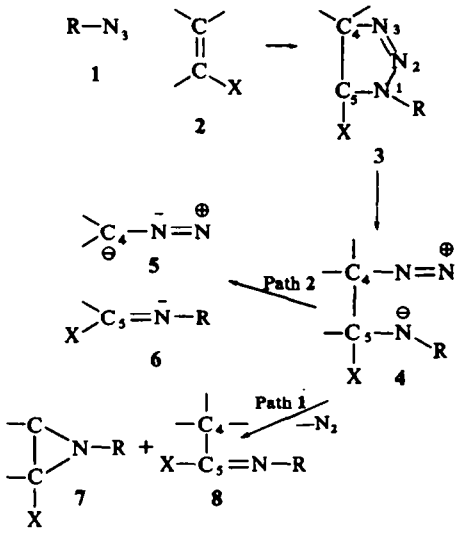
The initial products of these reactions are usually 1,2,3,Δ^2-triazolines (**3**), however in cases where the reacting azide (**1**) possesses a strong electron withdrawing group the products of the thermal decomposition (**5**,**6**,**7**,**8**) of the initially formed triazolines are isolated.[3,4] The thermal decomposition of triazolines is considered to proceed *via* initial heterolytic cleavage of the N_1—N_2 bond to produce diazonium-betaine intermediates (**4**).[1,3–5] These intermediates may decay by several pathways depending upon the substituents. Two principle modes of decomposition of diazonium-betaines such as **4** are cleavage of the N_3—C_4 bond (Path **1**) and cleavage of the C_4—C_5 bond (Path **2**). The former of these possibilities has been reported in the pyrolysis of triazolines produced from the reaction of organic azides with bicyclo (2.2.1) heptenes[3,6] (**9**), enol ethers and enamines which possess at least one alkyl substituent attached to the carbon β to the heteroatom.[4] This mode of decomposition may be followed by loss or migration (to C_4) of a C_5 substituent.

The second mode of decomposition (Path **2**) has been reported in those triazolines which arise from the reaction of organic azides with vinyl ethers and enamines which are unsubstituted at the carbon β to the heteroatom or possess an electron withdrawing group in this position.[7] This mode of decomposition also forms the basis of a good synthetic route to a α-diazocarbonyls by decomposition of triazoline

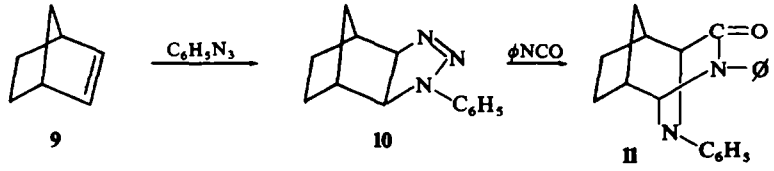
* To whom inquiries should be addressed.

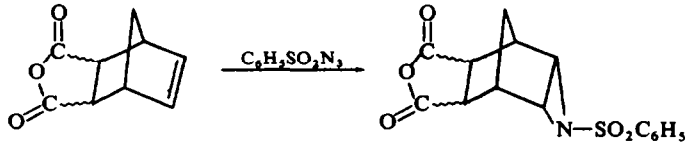
intermediates produced upon the reaction of azides with α,β-unsaturated aldehydes and ketones.[8]

Scheme 1



We wish to present evidence that the decomposition of triazoline **10**, formed from the reaction of phenyl azide with bicyclo (2.2.1) heptene (**9**) proceeds via a diazonium-betaine intermediate and involves C—C bond cleavage (Path **2**). The question of C—C bond cleavage in this type of triazoline system has been raised recently by the observation that **11** is produced from the decomposition of **10** in phenyl isocyanate[9] and that the reaction of benzenesulfonylazide with **12** and **13** produced predominantly the *endo*-aziridines **14** and **15** respectively.[10]





12 *endo*-anhydride
13 *exo*-anhydride
14 *endo*-anhydride
15 *exo*-anhydride

RESULTS

We have studied the decomposition of **10** under various conditions and have found **19–23** (Scheme 2) to be the products of decomposition. The amount of each

product was determined by gas chromatography and the results are recorded in Table 1.

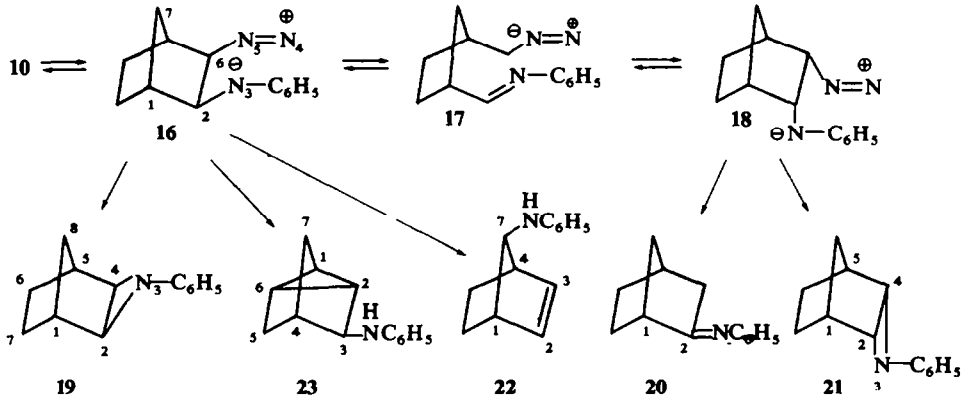
The *exo*-aziridine, **19**, was isolated from the pyrolysate of **10** in decalin by preparative gas chromatography. It was identical with a sample of **19** prepared by photolysis of **10**[6a,b]. Huisgen and coworkers have previously reported **19** as a product of the pyrolysis and photolysis of **10**[6b]. The structure of **19** was further confirmed by its characteristic NMR spectrum which exhibited a high field doublet (J = 9·5 c/s) at δ 0·72 attributable to the *anti*-C_8 hydrogen, a doublet of triplets (J = 9·5 and J = 1·8 c/s) at δ 1·62 attributable to the *syn*-C_8-hydrogen and a sharp singlet at δ 2·10 which was assigned to the hydrogens attached to C_2 and C_4.[6b] These signals are particularly characteristic of 3-azatricyclo (3,2.1.$0^{2,4\text{-}exo}$) octanes.[11]

TABLE 1. PRODUCTS OF DECOMPOSITION OF TRIAZOLINE **10**[a]

Conditions	19	20	21	22	23
Decalin[b]	49	18	9	11	10
Dimethyl Sulfoxide[b]	36	42	5	9	7
Nitrobenzene[b]	54	20	5	16	<1
Dimethyl Formamide[c]	37	46	5	8	3
3,5-Lutidine[b]	43	31	≈1	18	7
Photolysis	100				
Acetone, HCl excess[d,e]				73	21

[a] determined after 85–95% reaction
[b] at 160°
[c] at 148°
[d] see experimental
[e] ~5% 7-*syn*-N-phenylamine-2-*exo*-bicyclo (2.2.1) heptanol[d]

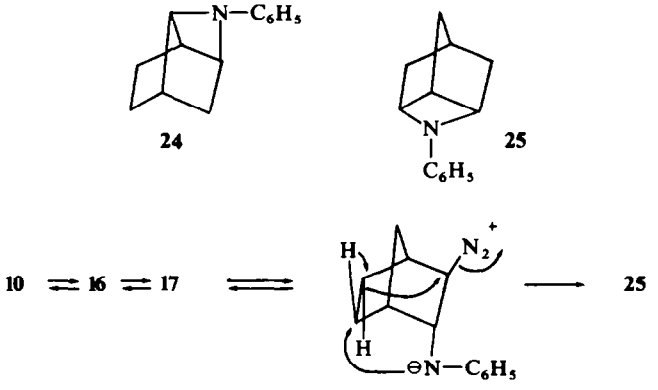
SCHEME 2



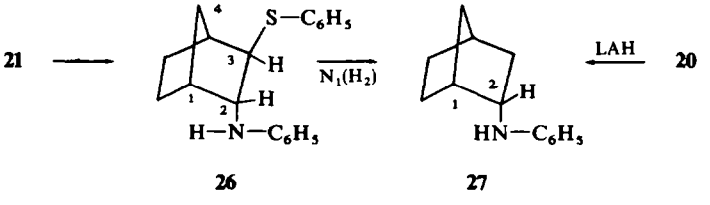
The imine, **20**, was identified by its hydrolysis to bicyclo (2.2.1) heptanone and aniline and by comparison with a sample prepared by condensation of these latter two reagents by standard procedures. Huisgen *et al.* have previously reported **20** as a product of the pyrolysis of **10**.[6b]

The structure of **21** was determined by a combination of spectroscopic analysis and chemical degradation. Significantly the infrared spectrum of the compound in question contained no N—H absorption. The NMR spectrum of this compound exhibited four distinct signals in the ratio of 5:2:2:6 in the direction of stronger field. Specifically the signals appeared as a multiplet centered at δ 6·90, a triplet (J = 2·0 c/s) centered at δ 2·69, a multiplet centered at δ 2·37 and a complex signal in the region between δ 1·1 and δ 1·7. The δ 2·69 signal may be assigned to hydrogens attached to carbon bearing nitrogen and the δ 2·37 signal to bridgehead hydrogens. Three structures may be proposed which are consistent with the spectral data and which are reasonable on mechanistic grounds. These are **21**, **24**, and **25**. The formation of **24** from **10** would be analogous to the formation of 2-*exo*-7-*syn*-dibromobicyclo (2.2.1) heptane during the bromination of **9**. Azetidines of this type have been considered previously as possible products of triazoline decomposition.[12] The azetidine **25** could arise as shown in Scheme 3.

SCHEME 3



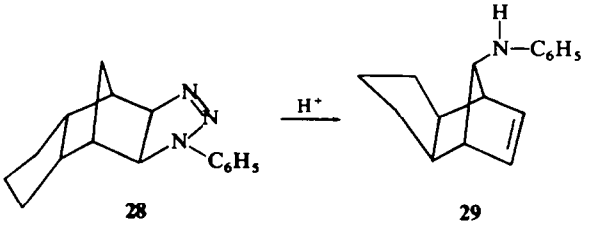
The equivalence of the bridgehead hydrogens in the NMR spectrum of the compound in question and the appearance of a triplet for the hydrogens attached to carbon bearing nitrogen[10] led us to favor structure **21** for this compound. To confirm the structure the compound was treated with hot potassium thiophenate in alcohol, conditions which should lead to S_n2 opening of **21**, **24** and **25** and give no skeletal rearrangement.[3a] Such cleavage would be expected to yield a *trans*-2,3-disubstituted bicyclo (2.2.1) heptane derivative only in the case of structure **21**. The product of this reaction exhibited an NMR spectrum clearly indicating the *trans*-2,3-disubstituted bicyclo (2.2.1) heptane, **26**. A quartet ($J_{2,2}$ = 4·0 c/s; $J_{3,7a}$ = 2·5 c/s) centered at δ 2·58 was observed for the 3-*endo* hydrogen and a triplet ($J_{2,3} = J_{2,4}$ = 4·0 c/s) centered at δ 3·50 was observed for the 2-*exo*-hydrogen. The assigned couplings are consistent with those observed in similar systems.[13]



26 **27**

Treatment of **26** with Raney nickel in isopropanol gave an aminobicyclo (2.2.1) heptane. This amine was identical in all respects with that formed upon the LAH reduction of **20**. Since this latter reduction should proceed from the *exo* side of the carbon-nitrogen double bond of **20**, the product must be 2-*endo*-N-phenylamino-bicyclo (2.2.1) heptane (**27**).

The structure of **22** was determined by an analysis of its infrared and NMR spectra. The infrared spectrum significantly exhibited absorptions at 3450 and 3070 and 1701 cm^{-1} which were assigned to the N—H and olefinic groups respectively. The NMR spectrum of **22** contained signals in the ratio of 5:2:1:1:2:4 in the direction of stronger field. Two olefinic hydrogens appeared as a symmetrical triplet (J = 2·0 c/s) centered at δ 5·97. A broad signal at δ 2·90 was assigned to the two bridgehead hydrogens. A one hydrogen singlet at δ 3·74 which was easily exchanged with deuterium oxide was assigned to the hydrogen attached to nitrogen. This treatment did not significantly alter the appearance of the singlet at δ 3·42 which was assigned to the hydrogen attached to the carbon bearing the nitrogen function. Since this latter hydrogen was not significantly coupled to vincinal hydrogens the nitrogen function must be attached to C_7.[13] Mechanistic considerations lead to the assignment of the *syn*-7-stereochemistry to this nitrogen function. The formation of **22** during the pyrolysis of **10** is analogous to the formation of *syn*-2-norbornene-7-methyl carbamate during the pyrolysis of the corresponding triazoline.[3b] A sample of **22** was also prepared by treatment of **10** with acid. Under similar conditions **28** is reported to give **29**.[14]



28 **29**

The structure of **23** was also deduced by analysis of its infrared and NMR spectra. The infrared spectrum of **23** contained N—H absorption at 3475 cm^{-1} and absorption at 840 cm^{-1} which is attributed to the presence of the nortricyclene system.[15]

The NMR spectrum of **23** exhibited signals in the ratio 5:1:1:1:7 in the direction of stronger field. A high field signal (δ 1·02) which appeared as a relatively sharp signal was assigned to the three hydrogens attached to the cyclopropane ring. A four hydrogen signal which was observed as a complex multiplet between δ 0·9 and δ 1·7 was assigned to the C_5 and C_7 hydrogens. A broad singlet (1H) at δ 2·01 was assigned to the C_4 bridgehead hydrogen. This hydrogen absorbs at 0·39 ppm higher field than the C_1 hydrogen of **27**. This difference is readily attributable to diamagnetic shielding of C_4 by the cyclopropane ring in **23**.[16] Two further one hydrogen singlets were observed in the NMR spectrum of **23**. One occurred at δ 3·31 and was assigned to the hydrogen at C_3. The other (δ 3·47) disappeared upon the addition of deuterium oxide and was thus due to the hydrogen attached to the nitrogen. A sample of **23** was prepared by the treatment of **10** with acid (Table 1).

DISCUSSION

The formation of **19**, **20**, **22** and **23** during the pyrolysis of **10** is unexceptional and may be visualized as proceeding via the diazonium betaine intermediate **16**. The formation of **21**, however, is noteworthy for it requires a molecular rearrangement involving the cleavage of the C_2—C_6 bond of the bicyclo (2.2.1) heptyl system or several hydride shifts. We visualize the pyrolysis of **10** as proceeding via the initial heterolytic cleavage of the N_3—N_4 bond (**10** → **16**) followed by carbon–carbon bond cleavage to give **17**.* The diazoimine, **17**, may then undergo internal 1,3-dipolar cyclo-addition to give **10** and/or **18** which decompose in the usual fashion to give products (Scheme 2).

Table 2. Relative rates of decomposition of triazoline **10** in different solvents at 160°

Solvent	$T_{\frac{1}{2}}$
Decalin	74
Dimethyl Sulfoxide	66
Nitrobenzene	36

The first fundamental process in this mechanism is the heterolytic cleavage of the N_3—N_4 bond of **10** to give **16**. This proposal is based upon the observation by others[3b,d,5] and ourselves (Table 2) that the thermal decomposition of triazolines is accelerated in more polar solvents. The direction of heterolysis has been determined by substitution of electron withdrawing groups at N_3 of the triazoline ring.[3,4,7] Thus the reaction under investigation was found to be accelerated by such substitution (Table 3).

Table 3. Relative rates of decomposition of aryl substituted derivatives of **10** in nitrobenzene at 141·6 ± 0·1°

para Substituent	$T_{\frac{1}{2}}$ (min)
NO_2	39·3
Br	66·4
H	279·0
CH_3	473
CH_3O	521

The second fundamental process in the proposed mechanism is the cleavage of the C_2—C_6 bond of **16** to give the diazomine intermediate, **17**. In agreement with the postulation of a multistep mechanism is the observation that nitrogen evolution during the pyrolysis of **10** does not follow first order kinetics. The deviation from first order kinetics is greatest toward the end of the reaction and is positive deviation.

* Professor L. H. Zalkow at the Georgia Institute of Technology has independently reached similar conclusions. We wish to thank Professor Zalkow for numerous discussions concerning this problem and for his general scientific goodwill in providing many results of his investigations in advance of publication. A portion of this work is reported in the following paper.

That is, the rate of nitrogen loss is less than expected during the early stages of the reaction and more than expected in the latter stages. This type of deviation may be explained by the kinetic scheme diagramed below (Fig. 1).

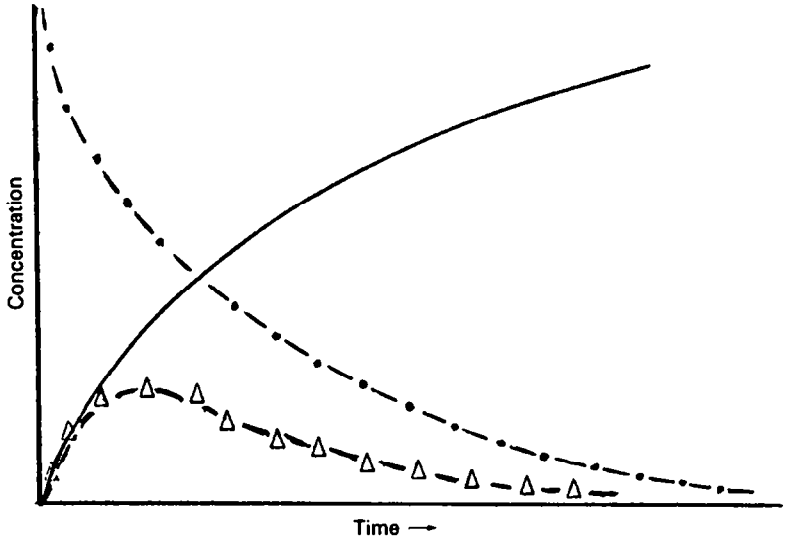
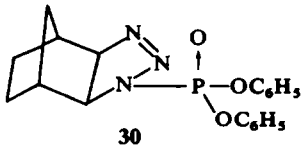


FIG. 1 Proposed variation of concentration of triazoline **10**(. – . –) intermediates (–Δ–) and nitrogen (——) with time during pyrolysis of **10**.

Berlin *et al.* have reported an analogous deviation from first order kinetics in the rate of nitrogen evolution during the pyrolysis of the phosphorylated triazoline, **30**. Their detailed analysis of the kinetic data favored a reaction scheme involving two consecutive first order reactions with accumulation of a diazo intermediate in the early stages of reaction.[3d] In the present case the deviation noted could arise from accumulation of the diazonium betaine, **16**, or the diazoimine, **17**, during the early stages of reaction. When the pyrolysis of triazoline, **10**, was carried out neat in a variable temperature infra red cell at 165° an absorption centered at 2175 cm^{-1} appeared and grew to a maximum intensity at thirty minutes. This absorption then decreased in intensity throughout the remaining portion of the pyrolysis. The absorption is not due to phenyl azide which absorbs at 2130 cm^{-1}. We feel this absorption is due to the presence of **16** or **17**. Although it is difficult to make a definite assignment of the observed absorption, **17** would be expected to have a finite existence as diazoalkanes and imines combine in 1,3-dipolar addition reactions only a moderate rates.[17]



30

Carbon–carbon bond cleavage during the pyrolysis of triazoline **10** has been elegantly employed by Baldwin and coworkers to account for the formation of **11** from **10** in phenyl isocyanate.[9] We have found that decomposition of triazoline **10** in phenyl isocyanate is very rapid and that the formation of both the imine (**20**) and *endo*-aziridine (**21**) are suppressed relative to the *exo*-aziridine (**19**).* Since the aziridine products are stable to phenyl isocyanate under the conditions of the decomposition, this result may represent a trapping of **17** before it is converted to *endo*-aziridine. It is interesting that Baldwin was able to obtain a 60% yield of **11** from decomposition of **10** in phenyl isocyanate but that only 5–10% of *endo*-aziridine is formed from the triazoline (**10**) in its absence. This may indicate that at least part of the diazoimine **17** is converted to *exo* products (e.g., **19**, **20**, and **21**). The **16** → **17** reaction would thus appear to be reversible.

There is a noticeable decrease in the amount of *endo*-aziridine formed when the decomposition is performed in more polar solvents (Table 1)' This is readily interpretable in terms of the proposed mechanism which allows decomposition of the diazonium betaine, **16**, to nitrogen and a norbornyl cation or the diazoimine **17**. Since the former of these modes of decomposition involves a greater charge separation, it would be expected to increase in importance in solvents of higher dielectric constant. Accordingly the amount of *endo*-aziridine (**21**), which is formed via the less polar mode of decomposition of **16** to the diazoimine, decreases in more polar solvents.

The mechanistic postulate outlined above to account for the formation of the *endo*-aziridine (**21**) upon pyrolysis of **10** has been used by Zalkow *et al.* to explain the reaction of benzenesulfonyl azide with the bicyclic anhydrides **12** and **13**.[10]* The reaction of benzenesulfonyl azide with **12** yields 60% of the *endo*-aziridine, **14**, and 19% of the corresponding *exo*-aziridine, while reaction with **13** gives 74% of the *endo*-aziridine, **15**, and 22% of the corresponding *exo*-aziridine. These reactions are considered to proceed via an unstable 1-benzenesulfonyl triazoline[10] which would be expected to decompose in a manner similar to **10**. It is interesting that in these latter cases the *endo*-aziridines **14** and **15** account for a major portion of the reaction products whereas in the present case only a minor amount of the *endo*-aziridine **21** is formed. These results and the isolation uf **11** in 60% yield[9] from the reaction of phenyl isocyanate with **10** indicate a similar amount of C_2—C_6 bond breakage occurs in both reactions. Evidently the inductive and field effects of the anhydride groups in **12** and **13** do not facilitate the development of negative charge on C_3 of the bicyclo (2.2.1) heptyl system which occurs during the formation of a diazoimine (e.g., **17**) from a diazonium betaine (e.g., **16**).[18]

One further aspect of the reaction which requires comment is the amount of imine **20** formed. Several investigators[3c,d] have suggested that imine products are formed in norbornyl triazoline decompositions from diazonium betaines (e.g., **16**) via 2,3-*endo* hydride shifts. This type of rearrangement is very slow in the norbornyl system. Indeed, even production of imine from *endo*-diazonium betaine analogs of **16** via 2,3-*exo* hydride shifts should be slow with respect to Wagner-Meerwein rearrange-

* We will report more fully upon the detailed investigation of this observation in a forthcoming communication.

* See footnote p. 11.

ment[19,20] in this system. If either 2,3-*endo* or 2,3-*exo* hydride shifts were occuring in the present case one would expect to find *much* more Wagner-Meerwein rearrangement products such as **22** and **23** than imine (this was not observed).

An attractive alternative which has been suggested recently [3b] is proton transfer from C_2 to nitrogen in diazonium betaines analogous to **16** to give the enamine form of **20**. Another possible pathway to compounds of the imine type is via rearrangement of initially formed aziridines.[21] In the present case all products including **19** and **21** were stable under the pyrolysis conditions.

EXPERIMENTAL

C, H and N analyses were performed by Alfred Bernhardt, Microanalytical Laboratory, Mulheim, West Germany. IR spectra were obtained with a Unicam SP-200 or Beckman IR—12 spectrophotometer. NMR spectra were taken on a Varian A-56–60 spectrometer. $CDCl_3$ was used as the solvent and line positions are reported as δ units using TMS as an internal standard (δ0). M.ps were obtained on a Fisher-Johns melting point apparatus and are uncorrected. Gas-liquid partition chromatography was performed on Varian Aerograph Autoprep A-705 and *Hi-Fi* gas chromatography units. Peak areas were determined with the aid of a disc integrator and were easily reproduced to within ±2%. The yields reported in Table 1 are absolute and were obtained by calibration measurements of weight injected *vs* peak area using standard solutions of the pure materials or a substance, often an isomer, of similar peak shape and retention time. The following columns were used: column A, 1·5 ft × 0·25 in, containing 20% SE 550 Silicon oil stationary phase on 60–80 mesh Chromosorb W support; column B, 6 ft × 0·25 in, containing 20% XF-1150 Cyano Silicon oil stationary phase on 60–80 mesh Chromosorb W support; column C, 5 ft × 0·50 in, containing packing identical to column B; column D, 5 ft × 0·125 in, containing packing material identical to column B; column E, 20 ft × 0·375 in, containing 30% SE 30 Silicon oil stationary phase on 40–60 mesh Chromosorb W support.

Preparation of 3-*phenyl*-3,4,5-*triazotricyclo* (5.2.1.0) *dec*-4-*ene* (**10**). The phenyl azide adduct of bicyclo (2.2.1) hept-2-ene was prepared in the usual manner[21] and had m.p. 99–100°; recorded[21] m.p. 101–102°.

Preparation of 3-p-*anisyl*-3,4,5-*triazatricyclo* (5.2.1.0) *dec*-4-*ene*. The *p*-anisyl azide adduct of bicyclo (2.2.1) hept-2-ene was prepared in the usual manner[21] and had m.p. 89·3–90·3°, recorded[21] m.p. 90–91°.

Preparation of 3-p-*bromophenyl*-3,4,5-*triazabicyclo* (5.2.1.0) *dec*-4-*ene*. The *p*-bromophenyl azide adduct bicyclo (2.2.1) hept-2-ene was prepared in the usual manner[21] and had m.p. 121·6–122·6°, recorded[21] m.p. 123–124°.

Preparation of 3-p-*tolyl*-3,4,5-*triazatricyclo* (5.2.1.0) *dec*-4-*ene*. The *p*-tolyl azide adduct of bicyclo (2.2.1)hept-2-ene was prepared in the usual manner[21] and had m.p. 79–80·5; recorded[23] m.p. 79–80°.

Preparation of 3-p-*nitrophenyl*-3,4,5-*triazatricyclo* (5.2.1.0) *dec*-4-*ene*. The *p*-nitrophenyl azide adduct of bicyclo(2.2.1)hept-2-ene was prepared in the usual manner[23] and had m.p. 164·5–165·5; recorded[23] m.p. 164–165°.

Kinetic determinations of the pyrolysis of triazolines. The extent and rates of pyrolysis of the triazolines studied were determined by measurement of N_2 gas evolution. The temp of the reaction was regulated by immersion of the reaction vessel in an oil bath maintained at constant temp (±0·2°). The measurements of gas evolution were made with the aid of a thermostated 100 ml gas burette attached to the reaction vessel and the results were reproducible to within ±2%. A typical kinetic determination is as follows: The solvent (30 ml) was placed in the reaction vessel and the soln was allowed to equilibrate with stirring for 10 min. During this time the system was flushed continuously with dry N_2. The triazoline (0·002 mol to 0·002 mol) was then injected into the stirred soln with a solid plug injector and the system was sealed. The zero reading on the gas measuring burette was taken and the time for generation of each 2 ml sample was recorded until 90% reaction. Plots of log $(V_\infty/V_\infty - V_t)$ *vs* t gave smooth lines which exhibited divergence from linearity in the initial and latter stages of reaction. The $t_{\frac{1}{2}}$ values from various determinations are recorded in Tables 2 and 3.

Isolation of products of pyrolysis of **10** *in decalin*. A soln of 16 g of **10** in 600 ml decalin was heated for 5 hr at 160° after which time N_2 evolution ceased. The solvent was removed at 40° under vacuum (2 mm). gas chromatographic analysis of the pyrolysate on column B (injector 180°, column 160°) gave the product distribution recorded in Table 1. The five components were separated by preparative gas chromatography

on column E (injector 180°, column 160°). The first component of the pyrolysate to be eluted was **21** which was isolated as an oil, b.p. 80° (0·10 mm). (Found: C, 84·00; H, 7·99. Calc. for $C_{13}H_{15}N$: C, 84·28; H, 8·16%). The second component to be eluted from the column was **19**. This component was isolated as an oil b.p. 80° (0·10 mm). (Found: C, 83·89; H, 8·08. Calc. for $C_{13}H_{15}N$: C, 84·28; H, 8·16%). This component was identical in all respects with the product of photolysis of **10** which is described below. The anil, **20**, was eluted third and was identical with an authentic sample prepared as described below. The component eluted fourth was **22**. This component was distilled at 100° (0·1 mm) and melted at room temp (27°). (Found: C, 84·11; H, 8·22; N, 7·54. Calc. for $C_{13}H_{15}N$: C, 84·28; H, 8·16; N, 7·56%). The last component to be eluted was **23**. This nortricyclene derivative was isolated as an oil, b.p. 97 (0·13 mm). (Found: C, 83·78; H, 8·11, Calc. for $C_{13}H_{15}N$: C, 84·28; H, 8·16%). These latter two components (**22** and **23**) were prepared in larger quantity by the treatment of the triazoline, **10**, with acid as described below.

Each component isolated was reinjected and found to be stable under the gas chromatographic conditions. In addition each component gave a single spot upon thin layer chromatography in several solvent systems.

Preparation of 3-*phenyl*-3-*azatricyclo*(3.2.1.$0^{2,4\,exo}$) *octane* (**19**) *by photolysis of* **10**. A soln of 10·0 g of **10** in 250 ml ether was irradiated in a quartz vessel with a 200 watt Hanovia lamp for 1 hr. The ether was evaporated and the product was vacuum distilled b.p. 84·5–85·0° (0·11 mm) (reported[6b] b.p. 90° at 0·06 mm).

The exo-aziridine **19** was isolated in 75% yield. Analysis of both the crude photolysate and the distilled product by TLC and by gas chromatography on column A (injector 180°; column 163°) and column B (injector 180°; column 163°) indicated a single component.

Preparation of N-*phenyl-bicyclo*(2.2.1)*hept*-2-*imine* (**20**). A soln of 2·6 g bicyclo (2.2.1) heptane-2-one and 2·1 g aniline in 10 ml benzene containing a catalytic amount (30 mg) of *p*-toluenesulfonic acid was refluxed for 6 hr. The benzene was removed and the product (**20**) was distilled under reduced press b.p. 83·0–85·5° (0·10 mm) (reported[6b] b.p. 85·93° at 0·03 mm). Analysis of the distillate by gas chromatography on column B (injector 180°, column 160°) revealed a single component which was identical in all respects to the imine (**20**) isolated from the pyrolysis of 10 NMR δ 7·4–6·6 (5H), 2·85 (1H), 2·47 (1H), 2·22 (1H) and 2·0–1·2 (7H).

Treatment of **10** *with acid*. A soln of 3 g of **10** in 60 ml acetone was treated in a dropwise manner with 5 ml 2N HCl at room temp. The reaction was neutralized with sat Na_2CO_3 aq, concentrated *in vacuo* and extracted with ether. The ether extract was dried over $MgSO_4$, filtered and the ether evaporated. The resulting product mixture was chromatographed on 200 g of neutral alumina. Elution with pet ether: ether (9:1) gave, in the initial fractions, pure **22**. Continued elution with this eluent gave a mixture of **22** and **23** which was separated into the pure components by preparative gas chromatography on column E (injector 230°, column 215°). Elution of the alumina column with pet ether: MeOH (8:2) gave *syn*-7-N-phenylamino-2-*exo*-bicyclo(2.2.1)heptanol. This substance was identical with an authentic sample prepared from the *exo* aziridine (**19**) by the method of Huisgen.[6b] The amount of each product was determined by gas chromatography of the crude ether extract (Table 1).

Preparation of 2-exo-*thiophenoxy*-2-endo-N-*phenylaminobicyclo* (2.2.1)*heptane* (**26**). To 4·3 ml of a 0·127 N potassium thiophenate in t-BuOH was added 0·2022 g of **21**. The reaction was refluxed for 50 hr then passed onto 20 ml water and the resulting mixture neutralized by the addition of dry ice. The suspension was extracted with ether which was dried over $MgSO_4$, filtered and evaporated. The crude ether extract (0·6 g) was chromatographed on 3 g of Silica Gel. Elution with pet. ether (b.p. 30–60°) gave 100 mg of pure **26** as an oil, b.p. 180° (1·0 mm). (Found: C, 77·32; H, 7·00. Calc. for $C_{19}H_{19}NS$: C, 77·26; H, 7·17%).

Raney nickel reduction of **26**. A soln of 0·050 g of **26** in 2 ml 2-propanol containing 1 g W-2 Raney Ni was stirred at room temp over night. The soln was filtered and the catalyst washed with 2-propanol. The alcohol was evaporated and the residue was analyzed by TLC and gas chromatography on columns A and B (injector 200°, column 185°). Analysis by these techniques revealed a single component which behaved in a fashion identical to **27**, prepared from **20** as described below. Samples of **27** prepared from **26** and **20** exhibited identical NMR and IR spectra.

Preparation of 2-endo-N-*phenylaminobicyclo*(2.2.1)*heptane* (**27**) *from* **20**. An etheral soln of 2·0 g of **20** was treated with excess LAH. The soln was stirred for 1 hr after which the reaction was poured onto water. The ether phase of the reaction mixture was separated, dried over $MgSO_4$, filtered and evaporated. The ether extract (2·34 g) showed one major component by TLC. This crude extract was chromatographed on 60 g of Silica Gel using pet. ether (b.p. 30–60°) and benzene as eluent. The product (**27**) was isolated as an oil, b.p. 85° (1·0 mm). (Found: C, 83·53; H, 9·31. Calc. for $C_{13}H_{17}N$: C, 83·37; H, 9·15%).

Pyrolysis of **10** *in an IR cell*. A variable temp cell manufactured by the Research and Industrial Instruments Co. (VLT-2) equipped with NaBr windows was filled with 0·5–1·0 g of **10** at room temp. The cell

was heated to 165° as rapidly as possible (1 min) while scanning the 2000–2300 cm^{-1} region continuously with a Beckmann IR 12 instrument as the cell was warmed an absorption at 2175 cm^{-1} was noted. This absorption was reproduced in three separate experiments and each time reached a maximum intensity about 30 min after the reaction had commenced. The maximum intensity of the absorption after this time was approximately ten times the noise level.

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