Tetrahedron. Vol. 26, pp. 3245 to 3263. Pergamon Press 1970. Printed in Great Britain

THE DECOMPOSITION OF N-ARYLAZOAMINES

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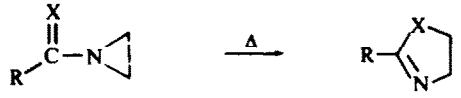
(*Received in USA* 4 *October* 1969; *Received in the UK for publication* 16 *March* 1970)

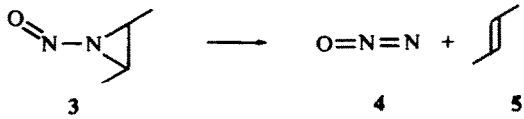
Abstract—The thermal decomposition of N-arylazoaziridines follows two routes; one giving arylazide and alkene (stereospecifically) and the other giving products typical of homolysis of the azo-linkage. The products of the homolytic route in benzene solvent are aziridines, biaryls and arenes. Both the rate and extent of azide and alkene formation are favoured by increasing the electronegativity of substituents in the aryl ring and performing the reaction in more polar solvent ($CHCl_3$). Pyrolysis and photolysis of N-arylazo derivatives of larger cyclic amines proceeds via homolysis of the azo linkage to the exclusion of fragmentation of azide and unsaturate. The mechanisms of these reactions are discussed. The application of the Woodward–Hoffman orbital symmetry theory and related treatments for nonsymmetrical systems to the elimination of aryl azide from N-arylazocycloamines are discussed.

THERMALLY induced rearrangements of aziridines possessing π-conjugative groups attached to the nitrogen usually result in enlargement of the aziridine ring or expulsion of the aziridine nitrogen with concommitant alkene formation. Thus, thermolysis of the N-acylaziridine[1] (1) and the sulfur containing analog[2] give ring expanded products (2) in good yield.



1a: X = O, R = C_6H_5 **2a**: X = O, R = C_6H_5
b: X = S, R = N—C_6H_5 **b**: X = S, R = NHC_6H_5

By contrast thermolysis of N-nitrosoaziridines (3) yield nitrous oxide (4) and alkenes (5).[3] The elimination is highly stereospecific yielding substituted alkenes which possess the same stereochemistry as the aziridine from which they are derived. The



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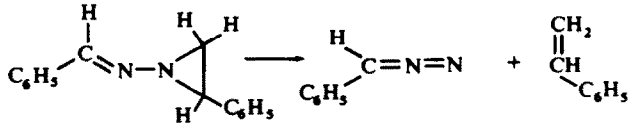
thermal decomposition of N-phenyliminoaziridine (6) has been reported to follow a similar course yielding phenyldiazomethane (7) and styrene (8).[4]



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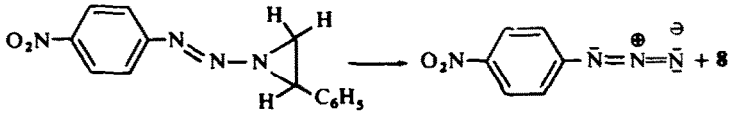
Likewise, Huisgen[4] *et al.* found that N-arylazoaziridine (**9**) underwent smooth thermal fragmentation to *p*-nitrophenyl azide (**10**) and (**8**).



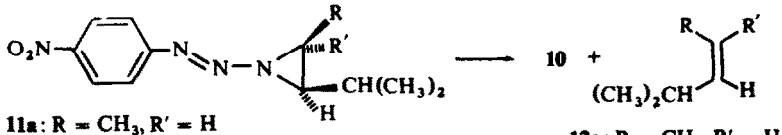
9 **10**

This observation supports the report by Rondestvedt and Davis[5] of the formation of aryl azides upon the dry distillation of impure N-arylazoaziridines.

The cycloeliminations of N-nitroso, N-imino, and N-azo aziridines are apparent examples of electrocyclic reactions. In an effort to determine the applicability of the Woodward–Hoffmann orbital symmetry theory[6] to the prediction of the stereospecificity of nitrogen elimination from the heterocyclic ring in these cycloeliminations[7] and to determine the extent to which cycloelimination would occur in larger cyclic amine derivatives we have investigated the thermal and photochemical decomposition of several N-arylazoamines. The choice of the N-arylazoamine system was based on the ease with which the electronic nature of the triazo-group could be changed by proper substitution.

RESULTS

The N-arylazoaziridines studied were prepared by coupling variously substituted aryl diazonium salts with the appropriate aziridine in buffered aqueous solution according to the procedure of Rondestvedt and Davis.[5] Because of the thermal instability of the triazenes studied, elemental analyses were not attempted. The triazenes studied were characterized by NMR, IR and UV spectra and by their ready arrangement into 1,2,3,-Δ^2-triazolines by iodide ion in acetone.[8] The aziridines used were either commercially available or were synthesized by well established procedures and were of known stereochemistry.[9] In agreement with earlier reports[4, 5] the *N*-nitrophenylazoaziridines were found to undergo facile thermal decomposition. Thermolysis of *cis* and *trans*-2-isopropyl-3-methyl-N-*p*-nitrophenylazoaziridines (**11a** and **11b**) at 80° in benzene gave a 78–82% yield of *p*-nitrophenyl azide (**10**) and 67–71% yield 4-methyl-2-pentenes (**12a** and **12b**) which were of the same configuration as the N-arylazoaziridine from which they were derived.



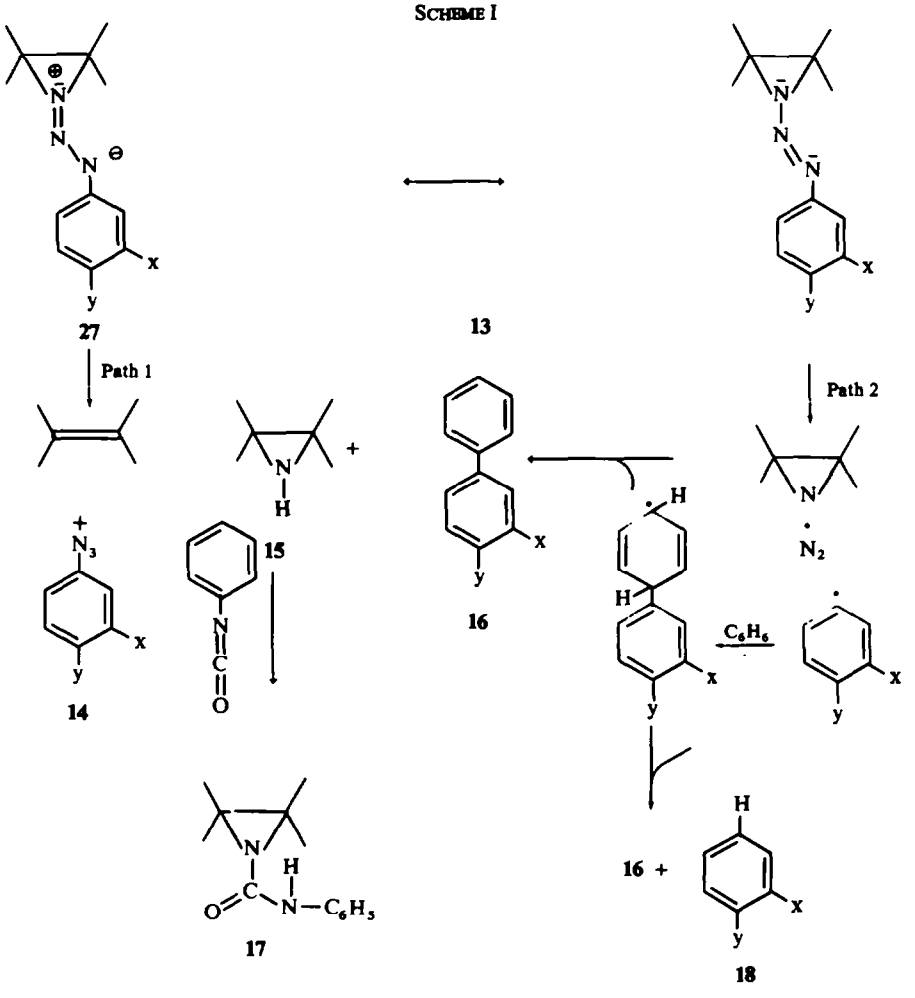
11a: R = CH_3, R′ = H
b: R = H, R′ = CH_3

12a: R = CH_3, R′ = H
b: R = H, R′ = CH_3

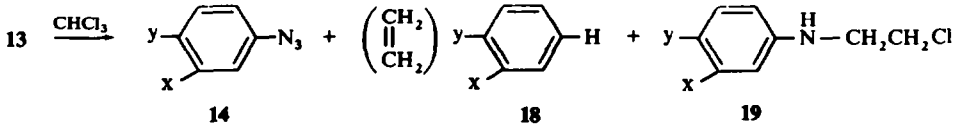
The thermolysis of N-arylazoaziridines **13a–c** in refluxing benzene (Table 1) gave aryl azides (**14**), ethylenimine (**15**), substituted biphenyls (**16**), and substituted arenes (**18**) (Scheme I). A GLPC search for biphenyl, N-arylethylenimine and symmetrically

substituted biphenyls in these reaction mixtures was negative. The limits of experimental detection of these possible products was 2–3%. Each of these possible products was stable in refluxing benzene.

SCHEME I



When the thermolyses of N-arylazoaziridines **13a, d–e** were carried out in chloroform, aryl azides (**14**), substituted arenas (**18**), and N-(2-chloroethyl)anilines (**19**) were formed (Table 1).



A GLPC search for N-arylethylenimines in these reaction mixtures was negative. In separate experiments it was determined that N-arylethylenimines were stable in

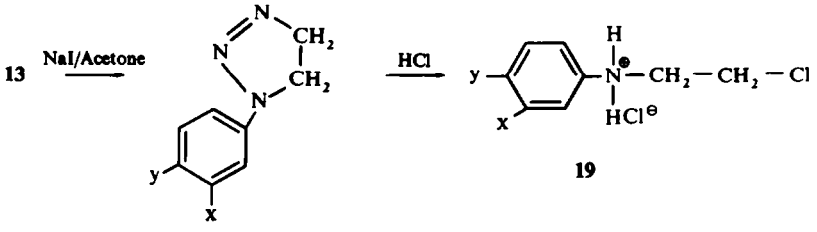
TABLES 1. PRODUCTS OF DECOMPOSITION OF N-ARYLAZOAZIRIDINES IN BENZENE AND CHLOROFORM

N-Arylazoaziridine	σ	Solvent	Aryl azide[b] 14	Ethylenimine as 17	Biphenyl deriv 16	Benzene deriv 18	N-2-Chloro ethyl deriv 19
13a: x = H, y = Cl		C_6H_6	*a*	84	92	3–4	
		$C_6H_6(h\nu)$			57	17	28[c]
		$CHCl_3$	30			50	10
b: x = H, y = Br		C_6H_6	*a*	63	84	6	
c: x = H, y = NO_2		C_6H_6	89				
d: x = NO_2, y = CH_3		C_6H_6	9	53	77	10	
		$CHCl_3$	52			28	12
e: x = y = Cl		C_6H_6	13	50	71	9	
		$CHCl_3$	68			14	9

[a] Azide not detected by infrared analysis of reaction mixture
[b] Ethylene is presumed to be formed also but was not sought
[c] N-*p*-chlorophenylethylenimine

refluxing chloroform. The structures of the N-2-chloroethyl anilines were determined by synthesis from the corresponding 1,2,3-Δ^2-triazolines (**20**).[8]

The thermal decomposition of **13b** in cyclohexene solution gave bromobenzene (34%), 3,3'-biscyclohexenyl (50%), ethylenimine (20%) and N-(*p*-bromophenyl)-ethylenimine (40%). The photolysis of **13b** in this solvent gave very nearly the same product distribution. The N-(*p*-bromophenyl)ethylenimine was identified by comparison with an authentic sample obtained by photodecomposition of triazoline, **20b**.[8, 10]

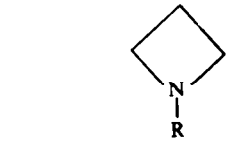


The rate of the azide formation from the N-arylazoaziridines (**13**) was determined by IR analysis. The reaction followed good first order kinetics in benzene and chloroform as long as the reaction was run in a non-pressured vessel. If the sealed tube technique was used as the method of performing the reaction the apparent rate of azide formation decreased steadily from initial values as the reaction progressed. That this was due to the reaction of the azide with ethylene formed in the decomposition and trapped in the sealed tube was indicated by performing the reaction under a nitrogen blanket, at atmospheric pressure, conditions which should allow the ethylene to escape into the vapour phase. Under these conditions the reaction of **13** to give azide followed first order kinetics. As shown in Table 2 the rate of azide formation from N-arylazoaziridines (**13**) is much faster in chloroform than it is in benzene. It is also obvious that the rate of azide formation from **13** increases as the electronegativity of the aryl substituent increases.

TABLE 2. RATES OF ARYL AZIDE FORMATION FROM N-ARYLAZOAZIRIDINES IN BENZENE AND CHLOROFORM

N-arylazoaziridine	Solvent	Temp	$k_1 \times 10^6$ sec^{-1}
13a: x = H, y = Cl	$CHCl_3$	51 ± 0·05°	36 ± 2·5
c: x = H, y = NO_2	C_6H_6	80 ± 0·05°	140 ± 7·3
	C_6H_6	70 ± 0·05°	45 ± 2·1
	C_6H_5	60 ± 0·05°	13 ± 1·5
	C_6H_6	50 ± 0·05°	3·8 ± 0·7
d: x = NO_2, y = CH_3	C_6H_6	80 ± 0·05°	4·5 ± 0·7
	$CHCl_3$	50 ± 0·05°	50·7 ± 3·4
e: x = y = Cl	C_6H_6	80 ± 0·05°	7·1 ± 1·2
	C_6H_6	70 ± 0·05°	1·5 ± 0·6
	$CHCl_3$	50 ± 0·05	79 ± 1·3

In an attempt to extend this azide elimination reaction to other N-arylazocycloamines the N-arylazoderivatives of azetidine, **21a**, Δ^3-pyrroline, **22a**, 2,3-dihydro-*H*-benz[*de*]isoquinoline, **23a**, and 2,7-dihydro[3,4,5,7]dibenzazepine, **24a**, were prepared by coupling the free amine with the appropriate aryl diazonium salt in buffered aqueous solution.

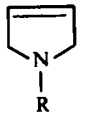


21a: R = H

b: R = —N=N—C$_6$H$_4$—Br

c: R = —N=N—C$_6$H$_4$—NO$_2$

d: R = —C$_6$H$_4$—Br

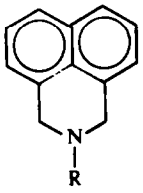


22a: R = H

b: R = —N=N—C$_6$H$_4$—Cl

c: R = —N=N—C$_6$H$_4$—NO$_2$

d: R = —C$_6$H$_4$—Cl



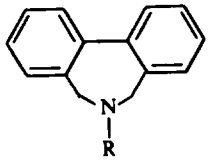
23a: R = H

b: R = —N=N—C$_6$H$_5$

c: R = —N=N—C$_6$H$_4$—NO$_2$

d: R = —C$_6$H$_5$

e: R = —N=O



24a: R = H

b: R = —N=N—C$_6$H$_4$—Cl

c: R = —C$_6$H$_4$—Cl

d: R = —N=O

In addition the known N-nitroso derivatives **23e** and **24d** were studied.

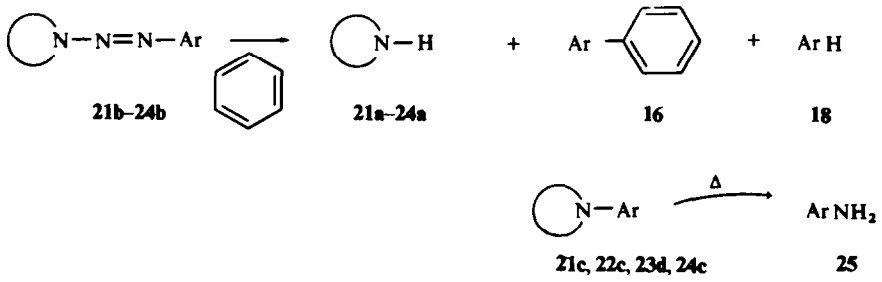
The rates of thermal decomposition of the N-arylazoderivatives of **21a–24a** were much lower than those of the N-arylazoaziridines studied. Thus in refluxing benzene or chloroform **21b**, **c–23b**, **c** and **24c**, were unchanged after 34 hrs. Heating **21b**, **c–23b**, **c** and **24b**, in benzene solution in a sealed tube at 170°–200° for twelve hrs. resulted in loss of nitrogen and formation of the several products shown below (Scheme II).

TABLE 3. PRODUCT DISTRIBUTION FROM PYROLYSIS AND PHOTOLYSIS OF N-ARYLAZOCYCLOAMINES IN BENZENE SOLUTION (% YIELD)

N-arylazo derivative	Conditions	Amine	Biphenyl derivative[b]	Benzene derivative[b]	N-arylamine	Subst. aniline[b]
21b	200°C/12 hr	42 (**21a**)	45 (**16b**)	28 (**18b**)	12 (**21d**)	4 (**25b**)
	hν	30 (**21a**)	41 (**16b**)	20 (**18b**)	25 (**21d**)	3–5 (**25b**)
22b	170°C/12 hr	12 (**22a**)	45 (**16a**)	21 (**18a**)	5 (**22d**)	3 (**25a**)
	hν	16 (**22a**)	49 (**16a**)	18 (**18a**)	14 (**22d**)	3 (**25a**)
23b	170°C/12 hr	53 (**23a**)	55[c]	[a] (**18f**)	16 (**23d**)	3[d]
	hν	49 (**23a**)	60[c]	[a] (**18f**)	11 (**23d**)	
24b	170°C/8 hr	41 (**24a**)	44 (**16a**)	16 (**18a**)	13 (**24c**)	(**25a**)
	hν	47 (**24a**)	53 (**16a**)	13 (**18a**)	20 (**24c**)	(**25a**)

[a] Benzene, could not be detected.
[b] Letter in the column refers to substituent as evident from Table 1
[c] Biphenyl
[d] Aniline

SCHEME II



The product distribution observed in the photodecomposition differed very little from that observed in the pyrolysis as can be seen from Table 3. The small amounts of substituted anilines (**25**) which were observed by GLPC were found to arise from thermal decomposition of the N-arylamines in the injection port of the gas chromatograph. This interesting observation is under further study. Although the product distribution from the thermolysis of **21c–23c** was not investigated in detail the absence (> 2%) of *p*-nitrophenyl azide and its thermal decomposition products (e.g. *p*-nitroaniline) was indicated by GLPC and TLC. A search for acenaphthene in the pyrolysate and photolysate of both **23c** and **23d** was negative.

The thermolysis of the N-nitrosoderivatives **23e** and **24d** in *o*-xylene at reflux for two days produced no acenaphthene or 9,10-dihydrophenanthrene. High yields of starting material were obtained from these thermolyses.

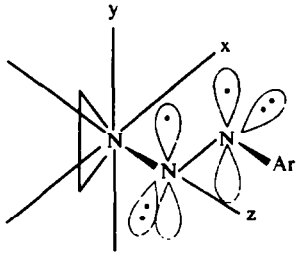
DISCUSSION

The thermal decomposition of N-arylazoaziridines takes two paths (Scheme I). The competition between these two paths depends primarily on the aryl substituent. When electron withdrawing substituents are present in the aryl ring a cycloelimination occurs (Path 1) to give alkene and aryl azide. When no electron withdrawing group is present thermal fragmentation occurs (Path 2) to give nitrogen, ethylenimine, and products arising from reaction with the solvent. This latter path (Path 2) leads to production of ethylenimine (**15**), biphenyls (**16**), and substituted arenes (**18**) in benzene and is considered to involve homolytic expulsion of nitrogen to give aziridinyl and aryl radicals.[11–15] The mechanism considered most accurate is given in Scheme I. As this mode of reaction has ample precedent[12–15] and was not of primary interest in the present investigation, the mechanistic complications such as the sequence of cleavage of the two bonds to the departing nitrogen and the possibility of induced reaction were not investigated. The absence of biphenyl in the pyrolysis mixture is noteworthy since this indicates that ethylenimine is not formed by the abstraction of hydrogen from the benzene solvent. Such a reaction would yield phenyl radicals which would readily couple.[14] The proposed sequence readily explains the observation that the yield of ethylenimine (**15**) is greater than the aryl derivative (**18**) and the total yield of **15** and **18** is not greater than that of the biphenyl derivative **16**). A radical mechanism is also indicated by the formation of high yields of 3,3'-biscyclohexenyl when **13b** is thermally or photochemically decomposed in cyclohexene.

The origin of the N-2-chloroethylanilines (**19**) from N-arylazoaziridines (**13**) in chloroform solution is unclear. These products (**19**) as well as the substituted arenes

(18) detected are undoubtedly formed via homolytic cleavages of the N-arylazoaziridine as discussed above. In chloroform the aryl and aziridinyl radicals thus formed would be expected to couple as well as abstract hydrogen from the solvent. While the latter process explains the origin of the substituted arenes, the former would yield N-arylaziridines which were stable in refluxing chloroform. Furthermore, in the presence of benzoyl peroxide in refluxing chloroform we found that N-arylaziridines unchanged after one day. The possibility of their formation via N-arylazoaziridine to triazoline isomerization followed by decomposition of the latter was also ruled out since the triazolines in question were stable in refluxing chloroform.

Competing with azo type homolysis of N-arylazoaziridines is cycloelimination to give aryl azide and alkene. The high degree of stereospecificity observed in the cycloelimination of N-arylazoaziridines **11a** and **11b** strongly suggests that both aziridinyl C—N bonds are broken simultaneously. Indeed the ease with which the thermal cycloelimination of azide, nitrous oxide[3] and isoelectronic species[4] occurs from appropriately N-substituted aziridines indicates a general reaction type. The cycloelimination of aryl azide from N-arylazoaziridines is symmetry allowed (σ^{2s} σ^{2s})[16] from either the conformation of the N-arylazoaziridine in which the plane of the π-bond is orthogonal to the lone pair on the aziridinyl nitrogen (**26**) or the conformation in which the aziridinyl lone pair is in the same plane as the aso π-bond (**27**).



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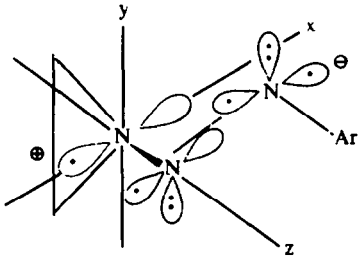

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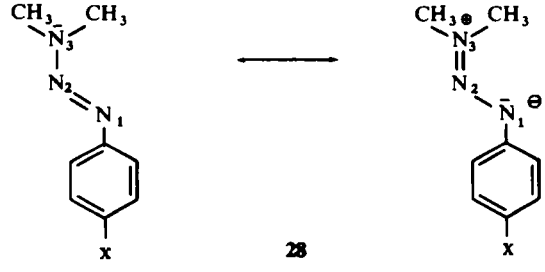
We have determined that the proportion of cycloelimination obtained increases with increasing π-overlap between N_2 and N_3 of the reacting arylazoaziridine. This trend suggests very strongly that conformation **27** is the preferred conformation in the cycloelimination reaction. Recent studies[17] in this laboratory have shown that there is appreciable π-overlap between N_2 and N_3 of N-arylazoamines such as **28**.*



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* This overlap gives rise to a relatively high barrier to rotation about the N_2—N_3 bond ($\Delta F^{\ddagger}_{298}$ = 12·7–15·7 kcal/mole). The rate of rotation about the N_2—N_3 bond obeys a linear free energy relationship decreasing with increasing electronegativity of the substituent ($\rho = -2{\cdot}1$).

This π-overlap increases with increasing electronegativity of the aryl substituent since the dipolar resonance hybrids of these N-azo amines are stabilized. Although placing the amino nitrogen in a 3-membered ring such as in the N-azoaziridines, **13**, would be expected to decrease N_2–N_3 π-overlap appreciably, any trends in amount of π-overlap between these two nitrogens would be expected to be in the same direction.*

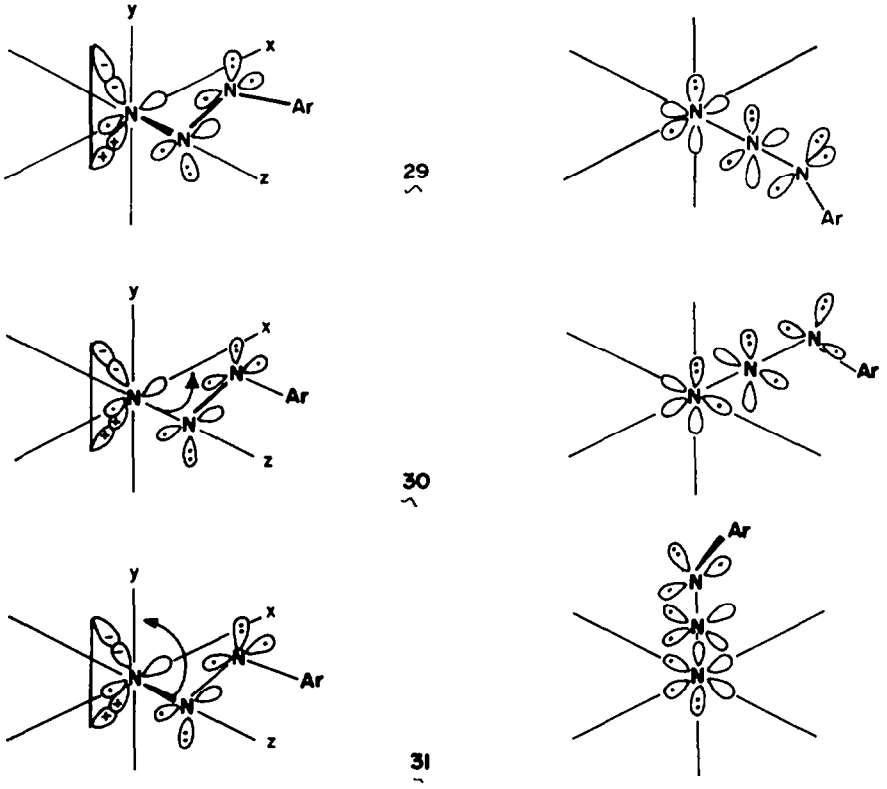
The thermolysis (Table 1) of those N-arylazoaziridines expected to have the larger degree of N_2–N_3 π-overlap (**13**; x = NO_2, y = H, x = y = Cl) gave proportionally more cycloelimination and at a faster rate (Table 2). Thermolysis of those N-arylazoaziridines expected to have the lowest amount of N_2–N_3 π-overlap (**13**, x = Br, Cl; y = H) resulted in cleavage of the azo linkage (Path 1) at the expense of cycloelimination.

As N_2–N_3 π character increases in the N-arylazoaziridines the triazo group becomes dipolar in character, the 1,3-dipolar resonance hybrid being represented by **27** (Scheme I). The increased rate of azide formation as well as the increased yield of azide from N-arylazoaziridines **13d** and **13e** in chloroform as compared to benzene (Table 1 and 2) are readily interpretable in terms of a dipolar transition state in the cycloelimination which is stabilized in the more polar solvent. It is noteworthy that the rate of cycloelimination of nitrous oxide from N-nitrosoaziridines is also increased by increasing solvent polarity.[3]

Woodward and Hoffmann have recently[16] pointed out that cycloeliminations which involve concerted cleavage of two σ bonds terminating at a single atom have definite symmetry requirements. In the case of cycloelimination of aryl azide from N-arylazoaziridines the electrons in the symmetric aziridinyl σ orbital of the two σ bonds undergoing cleavage may be delivered to the π bonding orbital of the alkene maintaining stereospecificity during the reaction. In this event the electrons in the corresponding antisymmetric aziridinyl σ orbital must be delivered with conservation of symmetry to an orbital in the cycloeliminated group, i.e. a y symmetric p or sp orbital on N_3 of the azide. This consideration dictates the direction in which the departing group moves away from the developing alkene in order to preserve maximum bonding during the elimination. Consideration of the present cycloelimination in an invariant coordinate system using conformation **27** reveals that the departing azide (N_3) can move away from the developing alkene in three distinct ways: (a) in a linear fashion along the z axis (**29**), (b) in a nonlinear fashion in the xz plane (**30**), or (c) in the yz plane (**31**); each of which allows electrons in the antisymmetric aziridinyl σ orbital to be delivered to an orbital on N_3 of the developing azide possessing the proper symmetry. Only in the case of nonlinear motion in the yz plane are the electrons in the antisymmetrical aziridinyl σ orbital delivered to the nonbonding sp lone pair on N_3 in such a manner as to allow simultaneous development of the yz symmetric N_2–N_3 π bond as well as maintainance of the xy symmetric 4π system of the azide. This nonlinear mode of reaction would then appear to be the most energetically favourable in the stereospecific aziridine-alkene transformation observed.

Alternatively, conservation of symmetry may be maintained by delivery of the

* In agreement with this the coalescence temperature of the aziridinyl hydrogens of **13c** was observed to be $-57 \pm 1°$ and that of **13a** below 60°. Although we suspect the origin of the temperature dependence in this system is restricted N_2—N_3 rotation we have not yet ruled out the possibility of slow aziridinyl nitrogen inversion.



electrons in the symmetric aziridinyl σ orbital to an orbital of proper symmetry on N_3 of the departing azide (this would be of necessity a z symmetric p or sp orbital). In this event the electrons in the antisymmetric aziridinyl σ orbital would be delivered to the antibonding π orbital of the alkene resulting in a stereorandom aziridine–alkene transformation. Geometric analysis of this alternative reveals the most energetically favorable mode of cycloelimination is the linear one (i.e. the departing azide moves along the z axis).

By this analysis[16] linear cycloelimination is favored in those cases where the electrons in the antisymmetric σ orbital of the σ bonds undergoing cleavage are delivered to the carbon skeleton of the ring opened species and nonlinear cycloelimination as indicated is favored in those cases where the electrons in this antisymmetric σ orbital are delivered to the cycloeliminated group. In the hope of determining if linearity or nonlinearity, as discussed above, is a characteristic of this type of cycloelimination we undertook the investigation of the thermolysis and photolysis of N-arylazoazetidines (**21b** and **21c**), N-arylazo-Δ^3-pyrrolines (**22a** and **22c**), N-arylazo (and N-nitroso) 2,3-dihydrobenzisoquinolines (**23b**, **23c** and **23e**) and 2,7-dihydrodibenzazepines (**24b** and **24d**). The possible thermal cycloelimination of arylazide from N-arylazoazetidines to produce cyclopropane was of primary interest since stereochemistry is maintained in the azetidine → cyclopropane transformation the process would be nonlinear by the

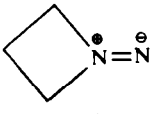
above treatment.* Our efforts in this direction were completely thwarted by the complete dominance of azo type cleavage (Scheme II, Table 3) in the derivatives studied.

A more intriguing approach to deduction of the linearity or nonlinearity of the present cycloelimination in larger systems was attempted by study of the thermolysis and photolysis of N-arylazo-Δ^3-pyrrolines. The production of butadiene via thermal cycloelimination of arylazide from these derivatives can take place in a controtatory or disrotatory fashion. If the process is disrotatory the reaction would be predicted to involve linear departure of the azide since the electrons in the symmetric pyrroline σ orbital are delivered to the z symmetric sp lone pair on N_3 of the azide. In this instance the electrons in the antisymmetric pyrroline σ orbital are delivered to the highest occupied (xz antisymmetric) orbital of the butadiene. A conrotatory cycloelimination in this system should, by the above analysis, involve a nonlinear departure of azide.†

Our efforts in this direction were again completely thwarted by the predominance of azo type cleavage (Scheme II, Table 3) in these derivatives as well as in the N-arylazo (and N-nitroso) 2,3-dihydrobenzisoquinolines and 2,7-dihydrodibenzazepines.

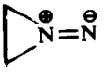
The predominance of azo type cleavage in the N-arylazocycloamines possessing rings larger than the N-arylazoaziridines was at first surprising. Cycloelimination was symmetry allowed in each case studied and the extent to which N_2—N_3 π-overlap could occur in the N-arylazocycloamine possessing larger rings was larger than in the N-arylazoaziridines.[20] A consistent and qualitative rational emerges from a consideration of the electronic reorganization occurring during the cycloelimination process. In the simplest description of the electronic reorganization of the N-arylazoaziridines during cycloelimination, for example, the σ C—N bonds and a sp^3 lone pair on N_3 are transformed into a π C—C bond, a π N_2—N_3 bond, and a sp

* The cycloelimination producing N_2 and cyclopropane from azetidines treated with difluoroamine has been reported.[18] This reaction presumably proceeds via diazene i and should be stereospecific if the nitrogen departs in a nonlinear fashion.



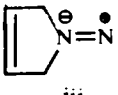
i

† The elimination of N_2 from aziridines treated with difluoroamine produces alkenes stereospecifically. The reaction is presumed to proceed via diazene ii[7] which by the geometric analysis given above must decompose in a nonlinear fashion.[16]



ii

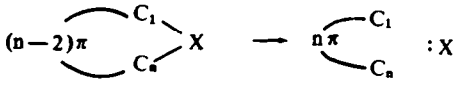
Similar deamination of Δ^3-pyrrolines give butadiene presumably via diazene iii. The reaction is highly stereospecific and disrotatory[19] suggesting a linear process is favored in this case.[16]



iii

lone pair on N_3. It becomes apparent from this viewpoint that the reaction should proceed with most facility in those systems in which the C—N bonds as well as the lone pair on N_3 possess the greatest amount of p character. In such cases π bond formation between the two ring carbons as well as overlap in the 4π system of the developing azide are more advanced in the reactant. Simultaneously the more energy is available to the system from rehybridization of one of the reactant orbitals to sp on N_3 of the azide.

The geometric analysis[16] applied above implies a direct relationship between the rotatory motion involved in cycloeliminations (e.g. in the Δ^3-pyrroline and 2,7-dihydroazepine systems) and the direction of departure of the cycloelimination group. A most intriguing question raised by this treatment is whether cycloelimination of a type will be characteristically linear or nonlinear. Both paths are symmetry allowed and may be characterized by determining the stereochemical course of reactions in a homologous series, e.g.



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 Beckmann IR-12 spectrophotometer. UV spectra were obtained with a Cary 14 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 (δO).

Mass spectra were obtained on a Perkin–Elmer Hatachi spectrometer using an ionization voltage of 70 eV and an inlet temp of 200°.

Gas–liquid partition chromatography was performed on Varian Aerograph Autoprep and HiFi gas chromatography units. The following columns were used: column A, 5 ft × 0·125 in, containing 20% SE 550 silicone oil stationary phase on 100–120 mesh Chromosorb W support; column B, 5 ft × 0·125 in, 25% of 30% silver nitrate in triethylene glycol stationary phase on 100–120 mesh Firebrick; column C, 5 ft × 0·125 in, containing 20% XF 1150 Cyanosilicon stationary phase on 100–120 mesh Chromosorb W support.

Preparation of the aziridines

Ethylenimine was used as supplied by Matheson, Coleman and Bell. The *cis* and *trans*-2-isopropyl-3-methyl aziridines were prepared by the method of Hassner[9] from the *cis* and *trans*-4-methyl-2-pentenes supplied by J. T. Baker Chemical Co. The pure aziridines were obtained by this method in 50–60% yield. Each aziridine was shown to be uncontaminated with its geometrical isomer by GLPC analysis on column B at 50°. The phenylurethane of the *trans*-2-isopropyl-3-methyl aziridine had m.p. 67–69°. (Found: C, 71·69; H, 8·27. Calc. for $C_{13}H_{28}N_2O$: C, 71·53; H, 8·31%.) The phenylurethane of the *cis*-2-isopropyl-3-methyl aziridine had m.p. 71–73°. Found: C, 71·47; H, 8·46%.

Preparation of N-*arylazoaziridines*, **13a–e**. The N-arylazoaziridines studied were prepared by coupling various substituted aryl diazonium salts with the appropriate aziridine in buffered aqueous solution according to Procedure F of Ref. 5. Each N-arylazoaziridine was extracted with ether and where possible crystallized from ether–light petroleum. The yield in these coupling reactions ranged from 50–80%. Confirmation of the structure of the N-arylazoaziridines was obtained by conversion of each into the respective 1-aryl-1,2,3-Δ^2-triazoline by reaction with NaI in acetone.[8] The yields of these conversions were 75–85% after purification of the triazoline product by crystallization. See Table 4.

TABLE 4. PROPERTIES OF N-ARYLAZOAZIRIDINES

N-Arylazoaziridine	m.p.	Aziridinyl Hydrogen (δ_{TMS})	λ_{max} (ε) in hexane	1,2,3-Δ^2-triazoline isomer m.p.
13a	30–31° (lit.[8] red liquid)	2·07	260 (8,710)	100–101·5° (lit.[8] 99–100·5°C)
13b	57–58° (lit.[8] 56–57°)	2·07	263 (8,610) 240 (12,200)	120–121° (lit.[8] 121–122°)
13c	71–72° (lit.[5] 70–70·5°)	2·28	287 (8,500)	144–145·5° (lit.[8] 145–146°)
13d	45–47° (lit.[8] 44·5–45·5)	2·16	230 (14,950)	99–101° (lit.[8] 99–100·5°C)
13e	16–17°	2·19	265 (5,533) 238 (11,250) 224 (10,880)	95–96·5° — —
11a	red liquid[a]	2·13	292 (8,470)	—
11b	red liquid[a]	2·13	291 (8,550)	—

[a] Repeated attempts to crystallize these compounds failed. Their structure is based on their NMR spectra and on determination of their mol wt by the cryoscopic method using benzene as a solvent. For **11a**. Found: 235–238; **11b**. Found: 237–239. Calc. for $C_{12}H_{16}N_4O_2$: 248

Thermal decomposition of N-p-*nitrophenylazo-2-isopropyl-3-methylaziridines* **11a** *and* **11b**.

A benzene (15 ml) soln of 0·54 g of **11a** was heated at reflux for 12 hr. Flash evaporation of the solvent into a cold trap (−70°) yielded 0·307 g of residue which was chromatographed on 35 g neutral alumina. Using light petroleum (b.p. 30–60°) as the eluent, 0·281 g (78·2%) **10** was isolated m.p. 71–72·5° (lit.[21] m.p. 74) mmp with an authentic sample[22] 71–73. TLC analysis of the crude reaction mixture revealed the absence of **16c**.

The portion of the reaction mixture which was evaporated into the cold trap was analysed by GLPC on column B and revealed the presence of **12a** and the absence of (<0·5%) of *trans* **12b**. By comparison of the trap contents with standard solns of the methylpentene in benzene the yield of alkene was determined to be 67%.

Decomposition of **11b** in benzene yielded 82% **10** and 71% *trans* **12b**.

Thermal decomposition of N-p-*nitrophenylazoaridine*, **13c**, *in benzene*

A benzene soln (10 ml) of 0·482 g of **13c** was refluxed until IR spectral analysis revealed the concentration of *p*-nitrophenyl azide (2090 and 2135 cm^{-1}) to be constant (6 hr). The soln was refluxed for an additional 6 hr after which time IR revealed no change in azide concentration. The solvent was removed under vacuum to give a reddish residue (0·42 g) which crystallized (m.p. 69–74°) on standing. A portion (0·35 g) of the residue was chromatographed on 40 g neutral alumina. Elution with light petroleum (b.p. 30–60°) gave 0·30 g (87%) *p*-nitrophenyl azide m.p. 71–72°, (lit.[22] m.p. 71–73°). TLC analysis of the crude reaction mixture revealed the absence of *p*-nitrobiphenyl. The yield of *p*-nitrophenyl azide calculated in the reaction mixture by use of the 2090 and 2135 cm^{-1} absorptions from a Beer's law analysis was 91%.

Thermal decomposition of N-*arylazoaziridines*, **13a**, **b**, **d** *and* **e** *in benzene*

The decomposition of **13a**, **b**, **d** and **e** was carried out in the manner described above for **13c** using 0·5 g–0·75 g samples in 10–15 ml benzene. The decomposition vessel was equipped with a side arm venting to a flask containing a benzene soln of phenyl isocyanate. The reaction was run under a N_2 gas purge. In this manner the ethylenimine formed was swept into the isocyanate soln. The N-aziridinyl-N′-phenylurea (**17**) formed was isolated by crystallization, m.p. 75–77°. The yields for each reaction are reported in Table 1. Compound **17** had m.m.p. 75–77·5° with authentic sample (m.p. 77–78·5°) prepared from ethylenimine and phenylisocyanate. (Found: C, 66·83; H, 6·37. Calc. for $C_9H_{10}NO_2$: C, 66·64; H, 6·21%).

The non-volatile reaction products were concentrated and chromatographed on neutral alumina. Elution with light petroleum (b.p. 30–60°) gave aryl azides which were identified by comparison with authentic sample prepared by treatment of the corresponding aniline derivative with nitrous acid then sodium azide (Table 5). Elution with light petroleum:ether, 9:1 gave biphenyl derivatives which were identified by comparison of their UV spectra and m.p. with literature values. The yields of each of these products are recorded in Table 1. Each aryl azide was independently demonstrated to be stable under the reaction conditions. GLPC analysis of the crude reaction mixture on column A indicated the absence of (>2%) of biphenyl in each pyrolysate. Similarly the pyrolysates of **13a** and **13b** were shown to contain no 4,4′-dichlorobiphenyl or 4,4′-dibromobiphenyl respectively. The N-arylaziridines corresponding to loss of nitrogen from **13a**, **b**, **d**, **e** were shown by GLPC analysis (Column A) to be absent from the reaction mixtures and were independently shown to be stable in refluxing benzene.

Thermal decomposition of N-*arylazoaziridines* **13** *in chloroform*

The typical procedure for the isolation of the products of the thermal decomposition of the N-arylazoaziridines in chloroform is illustrated below.

A chloroform soln (10 ml) of 1·1 g of **13** was refluxed for 2 hr. During this time the reaction vessel was purged with N_2 gas, the effluent being carried via a side arm to a flask containing a benzene solution of phenylisocyanate. Work up of the benzene solution after the thermal decomposition was complete, revealed no **17**, had been formed in any case. The decomposition of **13** was followed by IR analysis in the 2090–2135 cm^{-1} region. After 2 hr, IR analysis revealed that in all cases the production of azide had stopped. Refluxing the soln for an additional 2 hr did not alter the amount of azide. The reaction was allowed to reflux for an additional 10 hr after which time the solvent was removed *in vacuo*. NMR analysis of the nonvolatile residue revealed that all the N-arylazoaziridine had been consumed. Analysis of the residue by GLPC on column A using a linear temp program rate of 10°/min from 60° to 250° revealed the presence of arene, aryl azide and a third component which was isolated by column chromatography as described below.

A portion of the reaction mixture was chromatographed on ~60 g of neutral alumina. Using light

petroleum (b.p. 30–60°) as the eluent the aryl azide and arene were eluted together. GLPC analyses on column A using comparison with standard solns revealed the composition of the mixture. Elution with light petroleum : ether (3 : 1) gave **19**, the structures of which were confirmed by their spectral properties (Table 6) and by comparison with an authentic sample prepared by the method of Heine.[8]

Photodecomposition of N-p-*chlorophenylazoaziridine* **13a** *in benzene*

A benzene soln (100 ml) of **13a** (1·5 g) was irradiated with a 250 watt medium press Hanovia mercury lamp through a Pyrex filter for 1·5 hr. During this time the soln was purged with N_2 gas, the effluent being passed through a benzene soln of phenyl isocyanate. Work up of this soln after the photoreaction was complete gave only a few mg of **17**. The solvent was removed from the photoreaction *in vacuo*. IR analysis of the residue revealed no azide absorption, GLPC analysis of the mixture on column A showed the presence of chlorobenzene (17%), *p*-chlorobiphenyl (47%) and N-*p*-chlorophenylaziridine (28%) (b.p. 65–67°/05mm). The structure of the latter compound was ascertained from its spectra: IR ν_{neat} (cm^{-1}), 1595, 1490, 1325, 1160, 1095, 1015, 910, 843 and 750. N.M.R. (δ) 1·86 (s, 4H), 6·91 (A_2B_2, J = 8·5 Hz, 4H). Mass spec $(M)^+$ 153; $(M + 2)^+/(M)^+$ 0·30. This compound was identical in all respects to the product formed upon photodecomposition of **20a** in benzene, a reaction known to lead to N-arylaziridinyl products in high yield.[10]

Kinetic procedure for the determination of the rate of azide production from the N-*arylazoaziridines*, **13**.

Sealed tube method. Solns of **13** 0·05–0·1 M in benzene (or chloroform) were prepared, at room temp and transferred to small open tubes. These tubes were immediately cooled to − 70° and sealed. IR analysis of the freshly prepared soln revealed no azide absorption. All but three of the tubes (which were retained for zero time calculations) were allowed to warm to room temp after which time they were placed in a constant temp bath. Ten to twelve sets of three tubes were withdrawn at regular intervals and analysed by IR using balanced soln cells. The analysis was performed between 2090 and 2135 cm^{-1}, a region where solvent and other products did not absorb. A typical run involved a change in absorbance. of 0·65. The rate of aryl azide production was calculated by comparison of the 2090–2135 cm^{-1} absorption intensity with that of solns of known concentration of the same aryl azide in the same solvent. The reactions followed good first order kinetics on duplicate runs (log a/(a–x) *vs* t) to 45% reaction then showed definite negative deviations. It was assumed that the azide and ethylene formed were reacting. This assumption was apparently justified when no such deviation was observed when the reactions were run in open vessels as described below.

Open vessel method. Solns of the N-arylazoaziridines 0·05–0·1 M benzene or chloroform were made at room temp under a N_2 gas blanket and immediately immersed in constant temp baths. After the temp of the reaction reached the bath zero time readings were taken and thereafter 10–12 sets of duplicate samples were withdrawn and analyzed by IR as described above. The rate of azide production from the N-arylazoaziridines was cleanly first order.

Preparation of N-*arylazoazetidines*, **21b–c**

N-(p-*Bromophenylazo*)-*azetidine* **21b**. A soln of 3·55 g (0·02M) of p-bromoaniline in 10 ml 12N HCl and 15 ml water was treated with 1·4 g (0·021 m) $NaNO_2$ at 0–5°. After 10 min a sat NaOAc aq was added until the pH of the reaction mixture was maintained at 5·9–6·0°. The soln was then treated with decolorizing charcoal and filtered. Addition of azetidine,[27] **21a** (1·5 M excess), to this soln gave a thick ppt which was filtered off, washed with water, and dried to give 3·3 g (69%) of **21b** m.p. 71–74°. Recrystallization from MeOH gave m.p. 73–74°. NMR (δ, $CDCl_3$) 2·39 (quint, 2H), 4·19 (t, 4H), 7·28 (m, 4H), $\lambda_{max}^{CH_3OH}$, mμ(ε), 320 (16,600), 292 (16,350); $\nu_{KBr(cm^{-1})}$ 1470, 1420, 1380, 1260, 1080, 1000 and 930. Calc. for $C_9H_{10}BrN_3$: 239 $(M)^+$; $(M + 2)^+/(M^+)$, 0·98. Found: Mass spec. 239 (M^+); $(M + 2)^+/(M)^+$, 0·99.

The preparation of **21c** was effected in 83% yield by the above procedure from *p*-nitroaniline and azetidine, m.p. (MeOH) 148–149°; ν_{KBr} (cm^{-1}) 1585, 1505, 1390, 1330, 1265, 1100, 865, 845, 760 and 700; $\lambda_{max}^{CH_3OH}$, mμ/ε) 340 (18,700), 275 (17,500); NMR $\delta(CDCl_3$ 2·41 (qunit, 2H), 4·41 (t, 4H), 7·78 (m, 4H). Calc. for $C_9H_{10}N_4O_2$: 206 (M^+); $(M + 1)^+/(M)^+$, 0·114. Found: mass spec. 206 (M^+); $(M + 1)^+/(M)^+$, 0·118.

Preparation of N-*arylazo*-3-*pyrroline*, **22b–c**.

The N-(*p*-chlorophenylazo)-3-pyrroline (**22b**) was prepared in 81% yield from *p*-chlorobenzenediazonium chloride and **22a** (Aldrich Chemical Co) in the manner described for the preparation of the N-arylazoazetidines. Recrystallization from MeOH-light petroleum gave m.p. 97–98°; ν_{KBr} (cm^{-1}) 1487, 1430, 1402,

1360, 1241, 840 and 687; $\lambda_{max}^{CH_2OH}$ (ε) 320 (16,800) and 290 (16,400); NMR δ ($CDCl_3$), 4·47 (s, 4H), 5·88 (s, 2H) and 7·25 (s, 4H). Calc. for $C_{10}H_{10}ClN_3$: 207 (M^+), $(M+2)^+/(M)^+$, 0·37. Found: mass spec. 207 $(M)^+$; $(M+2)^+/(M)^+$, 0·35.

The N-(*p*-nitrophenylazo)-3-pyrroline (**22c**) was prepared by a similar procedure in 77% yield, m.p. 201–202°, ν_{KBr} (cm^{-1}) 1590, 1510, 1395, 1330, 1295, 1285, 1240, 1100, 750 and 680; NMR δ (TFA) δ 4·10 (s, 4H), 5·71 (s, 2H) and 8·31 (m, 4H). Calc. for $C_{10}H_{10}N_4O_2$: 218 $(M)^+$; $(M+2)^+/(M)^+$, 0·011. Found: mass spec. 218 $(M)^+$; $(M+2)^+/(M)^+$, 0·009.

Preparation of N-(p-*chlorophenyl*)-3-*pyrroline* **22d**.

A benzene soln (90 ml) of 4·1 g (0·03 M) of *cis*-1,4-dichloro-2-butene,[28] 3·8 g (0·03 M) *p*-chloroaniline and 10 g (0·1 M) triethylamine was stirred at 40–45° for 25 hr. The ppt of triethylamine hydrochloride was removed by filtration. The supernatant was washed first with 5% HCl and then with cold water. The organic layer was dried, the drying agent was removed by filtration, then the solvent was removed to give 2·8 g (53%) **22d**, m.p. 109–112°. Recrystallization from MeOH gave m.p. 113–114·5°, ν_{KBr} (cm^{-1}) 1603, 1505, 1380, 1360, 1180, 1005, 950, 810 and 677; NMR δ ($CDCl_3$) 3·95 (s, 4H), 5·81 (s, 2H), and 7·31 (A_2B_2, J = 9 Hz, 4H). Calc. for $C_{10}H_{10}ClN$: 179 $(M)^+$; $(M+2)^+/(M)^+$, 0·37. Found: mass spec. 179 $(M)^+$; $(M+2)^+/(M^+)$, 0·36.

Preparation of N-(*Arylazo*)-2,3-*dihydro*-1H-*benz* [de] *isoquinolines*, **23b–c**.

The N-(phenyl)-2,3-dihydro-1*H*-benz-[*de*] isoquinoline (**23b**) was prepared in 77% yield from benzenediazonium chloride and **23a** [29] in the manner described for the preparation of the N-arylazoazetidines. Recrystallization from MeOH gave m.p. 103–104·5°; ν_{KBr} (cm^{-1}) 1659, 1433, 1360, 1244, 1141, 820, 770, 760 and 695; $\lambda_{max}^{CH_2OH}$ (Mμ (ε) 299 (21,360); NMR δ ($CDCl_3$) 5·10 (s, 4H) and 7·34 (m, 11H). Calc. for $C_{18}H_{15}N_3$: 273 $(M)^+$; $(M+1)^+/(M)^+$, 0·209; $(M+2)^+/(M)^+$, 0·022. Found: mass spec. 273 $(M)^+$; $(M+1)^+/(M)^+$, 0·21; $(M+2)/(M)^+$, 0·025.

Compound **23c** was prepared in 80% yield in the manner described above for **23b**. Recrystallization from MeOH gave m.p. 183–184°; ν_{KBr} (cm^{-1}) 1580, 1505, 1430, 1420, 1395, 1330, 1305, 1175, 1105, 860, 820 and 770; NMR δ ($CDCl_3$) 5·54 (s, 4H) and 7·61 (m, 10H). Calc. for $C_{18}H_{15}N_4O_2$: 319 $(M)^+$; $(M+2)^+/(M)^+$, 0·023. Found: mass spec. 319 $(M)^+$; $(M+2)^+/(M)^+$ = 0·024.

Preparation of 2-*aryl*-2,3-*dihydro*-1H-*benz*[de]*isoquinolines*, **23b–e**. N-(*phenyl*)-2,3-*dihydro*-1H-*benz*-[de]-*isoquinoline*, **23b**.

To a warm (40–45°) benzene soln (25 ml) of 2·1 g (0·066M) of 1,8-bis(bromomethyl)-naphthalene[29] was added to 15 ml benzene containing 1·8 g (0·19M) aniline over a period of 20 min. After the addition was complete, the soln was allowed to reflux for 12 hr. After this time aniline hydrobromide was removed by filtration, the supernatant was washed with two (10 ml) portions of 5% HCl then with water. The organic layer was separated, dried and concentrated *in vacuo*. The residue remaining after removal of the solvent, 1·2 g (74%) solidified upon standing. Recrystallization from ether-light petroleum gave orange plates, m.p. 52–53° (Lit.[30] m.p. 57–59°); ν_{KBr} (cm^{-1}) 3005, 1605, 1500, 1455, 1385, 1220, 955, 810, 760 and 630; NMR δ ($CDCl_3$) 4·48 (s, 4H) and 7·15 (m, 15H).

Preparation of N-(p-*chlorophenylazo*)-2,7-*dihydro*-3,4,5,7-*dibenzazepine*, **24b**.

Compound **24b**, was prepared in 50% yield from *p*-chlorobenzenediazonium chloride and the hydrochloride of **24a**,[31] as described for the preparation of the N-arylazoazetidines. Recrystallization from MeOH-light petroleum gave m.p. 114–115·5°; ν_{KBr} (cm^{-1}) 1485, 1460, 1440, 1150, 1100, 1090, 845, 785, 755, 740 and 720; $\lambda_{max}^{CH_2OH}$ (mμ) (ε) 316 (25,400), 288 (25,800); NMR δ ($CDCl_3$) 4·56 (s, 4H) and 7·23 (m, 12H). Calc. for $C_{20}H_{16}N_3Cl$: 333 (M^+); $(M+2)^+/(M)^+$ 0·340. Found: mass spec 333 (M^+); $(M+2)^+/(M)^+$ 0·338.

Preparation of N-(p-*chlorophenyl*)-2,7-*dihydro*-3,4,5,7-*dibenzazepine*, **24c**.

A benzene soln (45 ml) of 2 g (0·0058M) 2,2′-bis (bromomethyl)biphenyl[32] and 2·3 g (0·018M) p-chloroaniline was refluxed overnight. The soln was filtered and the supernatant washed with water, dried, and the solvent was evaporated *in vacuo*. Recrystallization of the residue from MeOH-light petroleum gave 1·4 g (78%) of **24c**, m.p. 147–148·5° (Lit.[33] m.p. 147–149°); ν_{KBr} (cm^{-1}) 1590, 1500, 1210, 830, 805, 760 and 665; NMR δ ($CDCl_3$) 4·08 (s, 4H), and 7·20 (m, 12H).

Preparation of 1-*nitroso*-2,7-*dihydro*-3,4,5,7-*dibenzazepine*, **24d**.

To a suspension 4·5 g (0·019M) of **24a** hydrochloride in 5 ml of water and 50 ml glacial AcOH was added 3·5 g (0·05M) $NaNO_2$ in 10 ml water. Spontaneous warming occurred and the suspended hydrochloride gradually dissolved. The reaction was allowed to stand at room temp for 15 hr then diluted with water (200 ml) to precipitate the N-nitrosoamine (3·2g, 73%). Recrystallization of **24d** from hot EtOH gave m.p. 109–110·5°; ν_{KBr} (cm^{-1}) 1428, 1350, 1130, 1090, 968, 755 and 700; $\lambda_{max}^{CH_3OH}$ (mμ) (ε) 347 (100); NMR δ ($CDCl_3$) 4·51 (s, 2H), 5·10 (s, 2H) and 7·35 (m, 12H). Calc. for $C_{14}H_{12}N_2O$: 224 $(M)^+$; $(M+1)^+/(M)^+$ 0·161; $(M+2)^+/(M)^+$ 0·014. Found: mass spec. 224 $(M)^+$; $(M+1)^+/(M)^+$ 0·161; $(M+2)^+/(M)^+$ 0·015.

Thermal decomposition of the N-*arylazo derivative of the cyclic amines*, **21b–24b**

Benzene solns 10% in N-arylazoamine were heated in sealed tubes at 170–200° for 8–12 hr. After this time the tubes were cooled, opened, and the contents analyzed by IR and GLPC on columns A and C using temp program rate of 10°/min from 60° to 250° and 60° to 190° respectively. The products of each reaction were determined by mixed injection comparison with authentic samples described above. In the case of identification of **21d** comparison was made with the sample of **21d** prepared from irradiation of **21b** as described below. The product yields were determined by comparison of peak areas generated upon injection of standard solns of pure sample of each product with those obtained from injection of the reaction mixture. The product yields from decomposition of the N-arylazoamines given in Table 3 are averaged for duplicate runs which were reproducible within ± 2%.

Photolysis of N-(p-*bromophenylazo*)*azetidine*, **21b**

A 1·0 g sample of N-(*p*-bromophenylazo)azetidine was dissolved in 100 ml anhyd benzene and was irradiated under N_2 with a 250 watt Hanovia lamp for 10 hr. The excess solvent, removed under vacuum, was collected at − 30°. The NMR of the red residue indicated the complete consumption of the azoazetidine. Analysis of the mixture on column A showed the presence of bromobenzene, *p*-bromobiphenyl, a small amount of *p*-bromoaniline, and an unidentified product. A fraction (750 mg) of the mixture was chromatographed on 45 g of neutral alumina using 30–60 light petroleum as the eluent. The 30–60 light petroleum fraction gave bromobenzene (120 mg, 20%), further elution with 10% benzene-light petroleum gave a pale yellow compound, *p*-bromobiphenyl (380 mg, 41%), m.p. 87–89°. Further elution with 20% benzene-light petroleum gave a yellow liquid (220 mg, 25%), which solidified on cooling, m.p. 39–42°. Recrystallization of this solid from light petroleum gave m.p. 42·43·5°; ν_{max}^{KBr} (cm^{-1}) 1600, 1470, 1395, 1290, 1015, 905, 835, 770 and 700; NMR δ ($CDCl_3$), 2·99 (m, 4H), 5·97 (t, 4H) and 7·84 (quint, 2H). Calc. for $C_{10}H_{11}N_2O$: 2[illegible] $(M)^+$; $(M+2)^+/(M)^+$, 0·98. Found: 212 $(M)^+$; $(M+2)^+/(M)^+$, 0·975. On the basis of the observed spectra the solid was assigned the structure of **21d**. Attempted preparation of **21d** from 1,2-dibromopropane and p-bromoaniline was unsuccessful. The solvent evaporated from the above photolysis reaction was treated with phenyl isocyanate. Work up in the usual manner gave 198 mg (30%) of N-azetidinyl-N'-phenylurea m.p. 189–191°, m.m.p. 189–191° with an authentic sample prepared from azetidine and phenyl isocyanate.

Photodecomposition of N-*arylazoderivatives of the cyclic amines*, **22b–24b**

Benzene solns 1–2% in N-arylazoamine were irradiated in Pyrex under N_2 with a 250 watt Hanovia medium press mercury lamp for 12–18 hr. After this time the solvent was removed *in vacuo* and the reaction mixture was analyzed by GLPC on columns A and C as described above for the thermal decomposition. The yield of **22a** was obtained by treating the solvent removed from the photolysate with phenyl isocyanate as described above for azetidine. The yields are recorded in Table 3.

Attempted thermal decomposition of N-*nitrosocycloamines* **23e** *and* **24d**

A soln of 0·11 g. of **24d** in 10 ml *o*-xylene was refluxed for 47 hr. Upon cooling and evaporation of the solvent, 0·085 g **24d** was recovered.

This experiment was repeated using 0·1 g of **23e** in 10 ml *o*-xylene at reflux for 47 hr. Evaporation of the solvent gave 0·09 g **23e**. Analysis of the crude reaction mixtures by GLPC on column A in both vases failed to reveal any acenaphthene or 9,10-dihydrophenanthrene.

Acknowledgements—We wish to thank the National Research Council of Canada for generous financial support. We also thank Professor Lwowski for a sample of 3,3'-biscyclohexenyl.

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