g (88%) of pure **9c**, identical in all respects to purified **9c** prepared by method A.

Methyl 1,2-Dihydro-4-[(ethylenedioxy)methyl]-quinoline-1-carboxylate (9f) from 4-[(Ethylenedioxy)-methyl]quinoline (8f). Method B as described above for preparation of **9c** was used to obtain 0.279 g of crude **9f** (brown oil) from 0.215 g of **8f**. Rapid-elution chromatography on 60/200-mesh silica gel with CH_2Cl_2 gave 0.237 g (85%) of pure **9f** as a pale yellow oil: ^{1}H NMR δ 3.75 (3 H, s, OCH_3), 3.98 (4 H, br s, OCH_2CH_2O), 4.37 (2 H, dd, J = 4.4, 0.8 Hz, H2), 5.66 (1 H, dt, J = 1.0, 0.8 Hz, OCHO), 6.28 (1 H, td, J = 4.4, 1.0 Hz, H3), 6.87-7.25 (2 H, m, H6, H7), 7.25-7.65 (2 H, m, H5, H8). Anal. ($C_{14}H_{15}NO_4$): C, H.

Methyl 1,2-Dihydro-4-[(ethylenedioxy)methyl]-6-methoxyquinoline-1-carboxylate (9g) from 4-[(Ethylenedioxy)-methyl]-6-methoxyquinoline (8g). Method B as described above for preparation of **9c** was used to obtain 0.230 g of crude **9g** (brown oil) from 0.204 g of **8g**. Rapid-elution chromatography on 60/200-mesh silica gel with CH_2Cl_2 gave 0.217 g (90%) of pure **9g** as a pale yellow oil: ^{1}H NMR δ 3.74 (3 H, s, C6 OCH_3), 3.77 (3 H, s, CO_2CH_3), 4.01 (4 H, br s, OCH_2CH_2O), 4.37 (2 H, br d, J = 4.4 Hz, H2), 5.65 (1 H, br s, OCHO), 6.30 (1 H, br t, J = 4.4 Hz, H3), 6.75 (1 H, dd, J = 9.0, 2.9 Hz, H7), 7.04 (1 H, d, J = 2.9 Hz, H5), 7.43 (1 H, d, J = 9.0 Hz, H8). Anal. ($C_{15}H_{17}NO_5$): C, H.

Methyl 1,2-Dihydro-6-methoxyquinoline-1-carboxylate (9h) from 6-Methoxyquinoline (8h). Method B as described above for preparation of **9c** was used to obtain 0.254 g of crude **9h** (red-brown oil) from 0.185 g of **8h**. Bulb to bulb distillation of the crude material [140-143 °C (0.5 mm)] gave 0.228 g (89%) of pure **9h**: ^{1}H NMR δ 3.75 (6 H, s, C6 OCH_3 and CO_2CH_3), 4.35 (2 H, dd, J = 4.0, 1.8 Hz, H2), 5.96 (1 H, dt, J = 9.4, 4.0 Hz, H3), 6.42 (1 H, dt, J = 9.4, 1.8 Hz, H4), 6.53-6.87 (2 H, m, H5, H7), 7.44 (1 H, d, J = 8.8 Hz, H8). Anal. ($C_{12}H_{13}NO_3$): C, H.

Other dihydroquinoline urethanes prepared by this method include **9a** (90%), **9b** (87%), and **9e** (92%). See Table I for precise reaction conditions.

Variant of Method B: Reduction of 8c Using Catalytic 11. Quinoline-*N*-borane **10c** (1.0 mmol) was prepared from **8c** at -78 °C as described above. A catalytic amount of **11** (0.10 mmol) was added and the dry ice bath was removed. As the solution warmed above -20 °C, the characteristic deep yellow color began to develop. After 1 h at room temperature, the dry ice bath was replaced; and the reaction was quenched by addition of 4.0 mmol of methyl chloroformate. The workup procedure described above gave pure **9c** in 86% yield.

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Registry No. 8a, 91-22-5; **8b**, 491-35-0; **8c**, 4295-04-9; **8d**, 91-63-4; **8e**, 41037-26-7; **8f**, 56503-48-1; **8g**, 78513-88-9; **8h**, 5263-87-6; **9a**, 17718-14-8; **9b**, 78513-89-0; **9c**, 78513-90-3; **9d**, 78513-91-4; **9e**, 78513-92-5; **9f**, 78513-93-6; **9g**, 78513-94-7; **9h**, 78513-95-8; **10c**, 78529-62-1; **11**, 22722-98-1; quinoline-4-carboxaldehyde, 4363-93-3; 6-methoxyquinoline-4-carboxaldehyde, 4363-94-4.

Cyclization of Phenyl Azides with Homoallylic or Allylic Ortho Substituents and the Consequences of Triazoline Fragmentation

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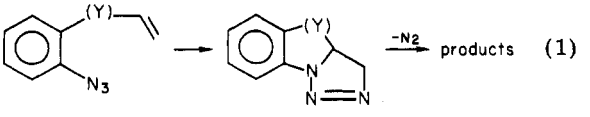
o-(Allyloxy)phenyl azide (**1**) and 14 derivatives substituted on the allyl group were thermolyzed at 110-120 °C to form benzoxazines (**16**), dihydroazirinobenzoxazines (**17**), or 3-alkenylbenzomorpholines (**18**, **19**) through fragmentation of intermediate triazolines. With substituted allyl groups, the geometrical isomers gave the same products in the same ratio, except in the case of *o*-(β,γ-dimethylallyl)phenyl azide. Rearrangement by phenyl migrations occurred with the β-phenylallyl compound. *o*-Allylphenyl azide (**27a**), (*o*-azidophenyl)acetaldehyde (**27b**), and *o*-[(*cis*-1-propenyl)oxy]phenyl azide (**27c**) required temperatures of 155-200 °C for thermolysis and yielded 2-methylindole, oxindole, and 2-ethylbenzoxazole, respectively, by nitrene insertion.

Thermolysis or photolysis of ortho-substituted aryl azides commonly leads to cyclization with loss of molecular nitrogen.[2] This may take place through formation of a nitrene intermediate, which may insert in an adjacent bond (generally C-H), or it may occur by addition of the azido group or nitrene to an adjacent unsaturated atom. Loss of nitrogen may thus precede ring closure, be synchronous with it, or follow it. Those azides that thermolyze more difficultly have been thought to form discrete nitrenes in the rate-determining step, whereas those that thermolyze at lower temperatures (<100 °C) and have lower activation energies (<28 kcal/mol) undergo loss of nitrogen synchronously with or subsequent to ring closure.[3-5]

Anchimerically assisted fragmentation of the azido group might require only a suitably placed nucleophilic center, in the form of an unshared electron pair or the π electrons of a multiple bond, or might additionally require the possibility of continuous conjugation embracing the azido group and the site of ring closure in an electrocyclic process.[4]

A further possibility is initial intramolecular 1,3-dipolar cycloaddition to form a stable intermediate (eq 1) that could subsequently lose nitrogen[5] to form the ultimate products in intermediate zwitterions or diradicals.

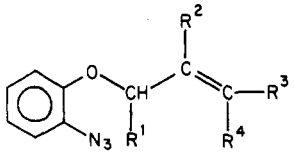


(1)

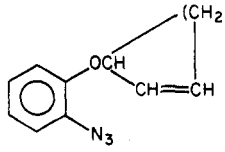
(1) From the doctoral dissertation of S.-S.P.C.
(2) P. A. S. Smith in "Nitrenes", W. Lwowski, Ed., Wiley, New York, 1970, Chapter 4.
(3) L. K. Dyall and J. E. Kemp, *J. Chem. Soc. B* 978 (1968).
(4) L. K. Dyall, *Aust. J. Chem.*, **28**, 2147 (1975); **30**, 2670 (1977).
(5) J. H. Hall, F. E. Behr, and R. L. Reed, *J. Am. Chem. Soc.*, **94**, 4952 (1972).

0022-3263/81/1946-3970$01.25/0

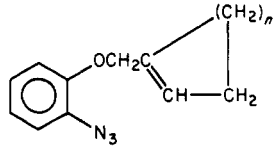
Chart I



1, $R^1 = R^2 = R^3 = R^4 = H$
2, $R^2 = CH_3$
3, $R^3 = C_6H_5$
4, $R^4 = C_6H_5$
5, $R^3 = CH_3$
6, $R^4 = CH_3$
7, $R^2 = R^3 = CH_3$
8, $R^2 = R^4 = CH_3$
9, $R^2 = C_6H_5$
10, $R^3 = R^4 = CH_3$
11, $R^2 = R^3 = R^4 = CH_3$



12, $n = 2$
13, $n = 3$



14, $n = 2$
15, $n = 3$

Although azides of the type shown with Y absent have been extensively investigated, little has been published on the other types. In this paper, we report some experiments with a group of *o*-allyloxyphenyl azides which belong to the type shown in equation 1 with (Y) equal to OCH_2.

Results and Discussion

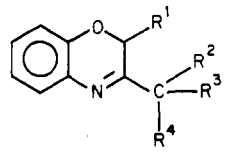
When our investigation had been substantially underway, a paper appeared by Fusco, Garanti, and Zecchi[6] of a parallel nature. Our methods of preparation of the three azides in which our work overlapped (1–3) were the same. In addition, we have prepared 12 other allylic *o*-azidophenyl ethers (4–15, Chart I), the behavior of which gives further insight into the product-determining factors and their implications regarding stereochemistry and the mechanism of fragmentation of triazolines.

All of the foregoing azides were prepared by alkylating the sodium salt of *o*-azidophenol with the appropriate halide or tosylate. In two instances, this required preparation of an intermediate cis allylic alcohol from a propargylic alcohol by partial hydrogenation of the triple bond. Published methods,[7] which used a methanol solution with 5% palladium on barium sulfate, consistently gave products with ca. 15% of the unwanted stereoisomer, but when we included a small amount of potassium hydroxide, the cis isomers wer produced essentially stereochemically pure.

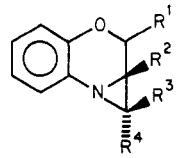
Each azide was thermolyzed by refluxing dilute solutions in toluene under a nitrogen atmosphere for 12–16 h, a time generously larger than required for complete disappearance of the azide. Thermolysis was reasonably rapid even at the lower temperature of boiling benzene, the medium used by Fusco and co-workers, showing that a path other than fragmentation of the azido group to a nitrene is involved.

Fusco and co-workers were able to detect buildup of an intermediate triazoline spectroscopically when a solution of **2** was held at 35 °C for a long time, and we observed complete conversion of **14** to triazoline by allowing its solution to stand at 35 °C for 3 weeks. Subsequent thermolysis of it in refluxing toluene gave the same products as direct thermolysis of **14**. Azide **1**, however, slowly lost nitrogen at 35 °C over 1 week without formation of a detectable concentration of triazoline. In the case of the other azides, we did not try to detect intermediate triazolines, but it is reasonable to assume that they were involved. Triazolines are known to form slowly by intermolecular 1,3-cycloaddition with azides and alkenes,[8-10] but they cannot always be isolated, owing to the ease with which they extrude molecular nitrogen to form imines and/or aziridines.[10] The bicyclic triazoline system derived intramolecularly from *o*-(allyloxy)phenyl azides is not intrinsically strained in the absence of hindering substituents.

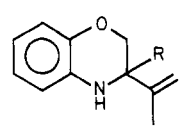
Chart II



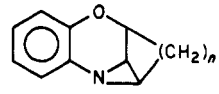
16[a]



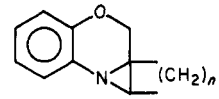
17[a]



18, R = H
19, R = CH_3



20a, $n = 2$
b, $n = 3$



21a, $n = 2$
b, $n = 3$

[a] For **16** and **17**: **a**, $R^1 = R^2 = R^3 = R^4 = H$; **b**, $R^2 = CH_3$; **c**, $R^3 = Ph$; **d**, $R^4 = Ph$; **e**, $R^3 = CH_3$; **f**, $R^4 = CH_3$; **g**, $R^2 = R^3 = CH_3$; **h**, $R^2 = R^4 = CH_3$; **i**, $R^2 = Ph$; **j**, $R^3 = R^4 = CH_3$; **k**, $R^2 = R^3 = R^4 = CH_3$.

To support this interpretation, we made a simple determination of the kinetics of disappearance of **1** over a span of 23 °C. A first-order rate law was followed, and an activation energy of 21 kcal/mol and an activation entropy of -16 eu were calcuated from the results. The former value is far too low for simple fragmentation of an azido group to a nitrene but is consistent with an intramolecular cycloaddition or fragmentation of a triazoline in the rate-limiting step. (The formation from **14** of a triazoline stable at 35 °C, however, implies that in that case the rate-limiting step is fragmentation of the triazoline.)

The products of thermolysis of the azides were examined spectroscopically after removing the solvent and passing the residue through a column of silica gel to remove minor impurities, and the components of the resulting mixtures were isolated in pure form by chromatography (gravity column or thin layer) or distillation whenever feasible. The expected products of triazoline decomposition,[11] imines in the form of benzoxazines **16** and/or aziridine (**17**, **20**, **21**; see Chart II) were found, although rearrangement in some cases accompanied their formation. The structures of these products were assigned on the basis of their IR and NMR spectra.

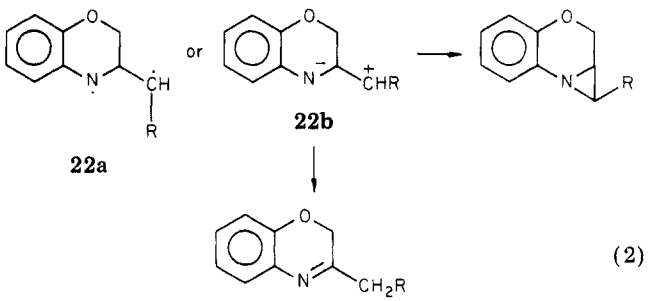
Many of the component products were oils, and it was not feasible to isolate them quantitatively. However, the

(6) R. Fusco, L. Garanti, and G. Zecchi, *J. Org. Chem.*, **40**, 1906 (1975).
(7) L. F. Hatch and H. E. Alexander, *J. Am. Chem. Soc.*, **72**, 5643 (1950).
(8) (a) G. L'abbé, *Chem. Rev.*, **69**, 345 (1969); (b) W. Broeck, N. Overbergh, D. Samyn, G. Smets, and G. L'abbé, *Tetrahedron*, **27**, 3527 (1971).
(9) (a) R Huisgen, R. Grashey, and J. Sauer in "The Chemistry of Alkenes", S. Patai, Ed., Wiley, New York, 1964, 806 ff; (b) T. Sheradsky in "The Chemistry of the Azido Group", S. Patai, Ed., Wiley, New York, 1971, Chapter 6.
(10) (a) W. L. F. Armarego, "Stereochemistry of Heterocyclic Compounds", Wiley, New York, 1977, Part 1, Chapter 2; (b) O. C. Dermer and G. E. Ham, "Ethylene Imine and Other Aziridines", Academic Press, New York, 1969.
(11) H. C. Van der Plas, "Ring Transformations of Heterocycles", Vol. 1, Academic Press, New York, 1973, pp 347–351.

mixtures of isomers were first obtained pure, and in nearly every instance, their NMR spectra were entirely accounted for by those of the isolated components. The results are summarized in Table I.

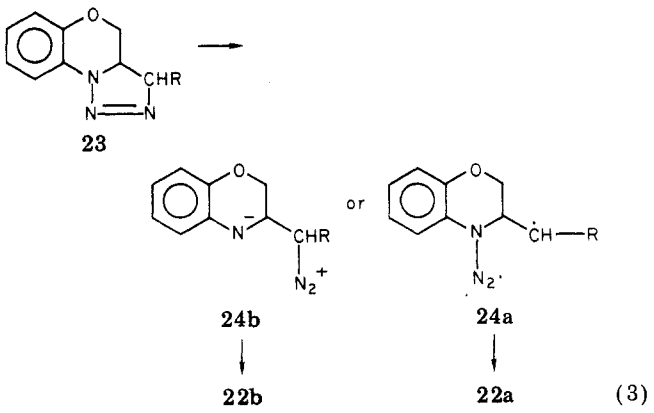
Our results with azides 1–3 were in reasonable agreement with those of Fusco and co-workers,[6] even though our thermolyses were at the temperature of boiling toluene rather than benzene. The only significant difference is that we were able to identify a small amount of the imine isomer (i.e., benzoxazine) **16** arising from 3. However, changing the solvent to much more polar 1-butanol or *N,N*-dimethylacetamide significantly shifted the product composition toward imine **16**.

Azide 4, the geometrical isomer of **3**, gave the same products in the same proportion, a fact that implies either a common intermediate or thermodynamic control of the composition of the products. The latter explanation can be rejected, however, because the major component, the aziridine **17d**, is obviously the less stable, owing to the strain in the three-membered ring. The common intermediate cannot be a triazoline, for cycloaddition of azides to alkenes is stereospecific and would in this instance produce stereochemically different triazolines.[10a] We therefore deduce that the common intermediate is the zwitterion **22** (R = Ph; eq 2) or the corresponding diradical.



(2)

These species would logically be formed by homolytic[8b] or heterolytic opening of the triazoline ring[12,13] (eq 3). The



(3)

diazo structure, **24**, does not qualify as the common intermediate in this case, since it would retain the stereochemistry of the original azide and the triazoline.[9,14] This interpretation is also consistent with the fact that the aziridine formed apparently has the more stable *trans* geometry of substitution on the three-membered ring (the NMR coupling constant for the vicinal aziridine hydrogens is only 3.5 Hz). We deduce that the distribution of product between **16d** and **17d** is kinetically controlled, but the stereochemistry of **17d** approximates the thermodynamic condition, owing to the possibility of free rotation about the exocyclic bond of **22** before ring closure.

Table I. Thermolysis of Allylic *o*-Azidophenyl Ethers in Toluene

azide	yield of products, %	composition of product,[a] % 16	*cis*-17	*trans*-17	other
1	100	27	73		*b*
2	90	0	100		
3	95	7	0	93	
4	94.5	6	0	94	
5	95	35	24	41	
6	100	28	25	47	
7	79	0	50	50	
8	24	0	74[c,d]	26[c,d]	
9	91	10	90		
10	98	31	61		8 (**18**)
11	85	0	0		100 (**19**)
12	86	0	100[e]	0	
13	65	0	100[f]	0	
14	94	0	100[g]	0	
15	76	0	100[h]	0	

[a] As assayed by NMR spectroscopy. [b] In butan-1-ol, ratio 42:58; in dimethylacetamide, ratio 49:51. [c] After correction for the 13% of **7** present in the sample of **8**. [d] **17g** has the methyl groups cis; **17h** has them trans. [e] **20a**. [f] **20b**. [g] **21a**. [h] **21b**.

Table II. Effect of Solvent on Distribution of Products from 5 and 6

azide	solvent (dielectric constant at 25 °C, D)	normalized product ratios, % 16e	cis (17e)	trans (17f)
5	decalin (2.18)	19	28	53
	toluene (2.38)	35	24	41
	1-butanol (17.1)	56	17	27
	Me_2NAc (37.8)	54	17	29
6	decalin	18	29	53
	toluene	28	25	47
	1-butanol	50	18	32
	Me_2NAc	53	14	33

Azides **5** and **6** are another pair of geometrical isomers. The ratio of products, imine and *cis*- and *trans*-aziridine, was essentially the same in toluene, but we were not sure if the small differences were within experimental error. The amount of imine (3-ethyl-2*H*-1,4-benzoxazine) was much larger than from the phenyl analogues **3** and **4**, reflecting more rapid rearrangement of the less stable carbonium ion (**22**, R = CH_3). We considered that the rate at which the **22b** collapsed to aziridine would be sensitive to the polarity of the solvent, and we therefore repeated the thermolyses in a solvent of lower polarity (decalin) and two of greater polarity (1-butanol and dimethylacetamide), all at the same temperature. The results, presented in Table II, show that polarity favors the formation of imine over aziridine, presumably by stabilizing the zwitterion somewhat and allowing more time for migration of H. The ratios of *cis*- and *trans*-aziridine, however, varied little, as is to be expected. The close agreement of the product distributions from **5** and **6** in all four solvents strongly supports the concept of a common intermediate, in which stereochemical differentiation is lost. The sensitivity of the ratios to solvent polarity implies that it is the zwitterion, **22b**, rather than **22a**.

In the geometrically isomeric pair of azides **7** and **8**, a new factor is introduced: there is no hydrogen at the site from which migration must occur if an imine is to be formed. Accordingly, we were not surprised to find that no detectable imine (i.e., benzoxazine) was formed. The

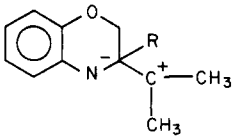
(12) A. L. Logothetis, *J. Am. Chem. Soc.*, **87**, 749 (1965).
(13) P. Scheiner, *J. Org. Chem.*, **32**, 2022 (1967).
(14) A. Padwa, *Angew. Chem., Int. Ed. Engl.*, **15**, 123 (1976).

ratios of *cis*-aziridine (**17g**) to *trans*-aziridine (**17h**) were distinctly different, 1:1 and 3:1, respectively. We believe this difference to be significant, in spite of a lower than usual yield of products from **8** and the fact that a correction had to be made for the presence of 13% of **7** in our sample of **8**.

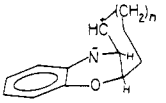
Since steric repulsions in **17g** and **17h** are much the same, as determined from molecular models, the ratio of products from **7** appears to be close to the thermodynamic ratio, consistent with formation from the zwitterion analogue of **22b**. In the case of **8**, the diazonium zwitterion **24b** could give rise to **17g** by an S_N2i process (loss of N_2 concerted with ring closure), whereas the diazonium zwitterion from **7** would give rise to **17h** by such a process. However, the transition state for S_N2i cyclization of the intermediate from **7** would have increased steric repulsions, whereas that from **8** would actually slightly release steric interactions. Accordingly, we suggest that thermolysis of **7** leads to products entirely through the carbonium zwitterion (**22b**) but that thermolysis of **8** involves competition between that path and the S_N2i process, resulting in a preponderance of *cis*-aziridine **17g**. If the two paths were followed to approximately the same extent, the ratio of products would be close to that observed.

In azide **9**, prepared from β-phenylallyl bromide made from α-methylstyrene, a phenyl group replaces the hydrogen that must migrate in order for imine to be formed. The product was a mixture of aziridine with the imine (benzoxazine) resulting from migration of phenyl (**16i**) in a ratio of 9:1. This result should be compared with that form **1**, in which the imine arises by migration of H. The ratio of aziridine to imine, <3:1, is consistent with the generally higher propensity of hydrogen to migrate compared to phenyl.

Azide **10**, prepared from 1-bromo-3-methyl-2-butene obtained by addition of hydrogen bromide to isoprene, would be expected to generate a species (**25**, R = H) analogous to **22** in which the cation or radical is tertiary. Thermolysis produced the expected aziridine and imine as the major products, accompanied by a new type of product, 3-isopropenylbenzomorpholine (**18**); the ratio was 61:31:8. Formation of **18** requires a 1,4-migration of a hydrogen from a methyl group, but the process is not necessarily intramolecular and could involve abstraction of H from the methyl group of one molecule of **25** by the nitrogen of another. Such a process requires an appreciable lifetime for **25**, a condition that would be favored by the fact that the carbonium ion is tertiary, reducing the driving force for migration of a hydrogen to it.



(or diradical)
25



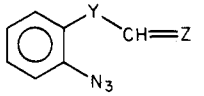
26a, $n = 0$
b, $n = 1$

Azide **11** differs from **10** in that an additional methyl group replaces the hydrogen that migrates to form the imine from **10**. It yielded only a single product, 3-isopropenyl-3-methylbenzomorpholine (**19**), corresponding to the minor product, **18**, from **10**. The low migratory aptitude of methyl in **25** (R = CH_3) has clearly repressed formation of the imine. The lack of aziridine is probably caused by steric repulsion resulting from the larger number of substituents that would be on the aziridine ring. The otherwise poorly favored transfer of hydrogen from a terminal methyl group is thus enabled to become dominant.

Azides **12** and **13**, bearing cycloalkenyl groups, gave aziridines **20a** and **20b** in good yield as the only detectable simple products. Molecular models reveal that if the ring junctures are all cis, there is sensibly no more strain in these molecules than in the simpler aziridines **17** and that the cycloalkane rings are almost perpendicular to the oxazine ring. The lack of imine in the products is consistent with the geometry of the intermediate zwitterions, **26**, in which the carbonium carbon is favorably oriented for ring closure to the nitrogen but unfavorably oriented for generation of an imine, which would require coplanarity of the carbonium carbon with the nitrogen and carbons 2 and 3 of the oxazine ring (the cycloalkane ring would conformationally resist the necessary rotation). It is unlikely that significant amounts of benzoxazines, if formed, would have been destroyed, for the conditions used were as mild as those that were withstood by all the other benzoxazines.

Azides **14** and **15**, prepared from the cycloalkenylmethyl tosylates, were examined in order to investigate the generality of this method of synthesizing polycyclic aziridines. Aziridines **21a,b** were the only products, and their formation can be accounted for by essentially the same arguments as apply to azides **12** and **13**.

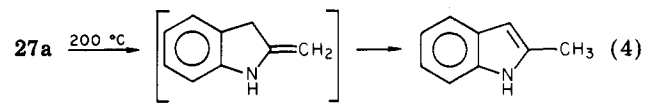
We wished to compare the behavior of the foregoing compounds, in which the substituent ortho to the azido group has a homoallylic bond pattern, to the analogous compounds with an allylic system of bonds, **27**. Prepa-



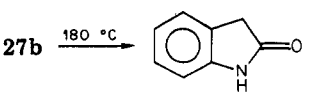
27a, Y = CH_2; Z = CH_2
b, Y = CH_2; Z = O
c, Y = O; Z = CH_3CH=

rative difficulties limited the comparison to three examples, **27a–c**. Azide **27a** was prepared from *o*-allylaniline obtained by rearrangement of *N*-allylaniline, **27b** was prepared from 2-(*o*-azidophenyl)ethanol by Moffatt oxidation, and **27c** was prepared by base-catalyzed isomerization of *o*-(allyloxy)-aniline to *o*-(*cis*-propenyloxy)aniline and conversion to the azide by diazotization and coupling with sodium azide.

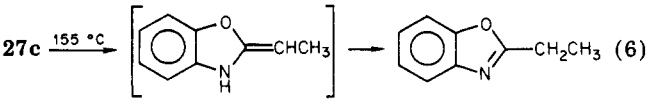
All three azides were inert to fragmentation under the conditions that had been successful with the azides with a homoallylic substituent, and temperatures of 155–200 °C were required, typical of azides that fragment directly to nitrenes without anchimeric assistance, such as phenyl azide.[3] The products, 2-methylindole (82%) from **27a**, oxindole (85%) from **27b**, and 2-ethylbenzoxazole (81%) from **27c**, could all be derived from nitrene insertion reactions at the β positions of the substituent, followed by tautomerization in the case of **27a** and **27c** (eq 4–6).



(4)



(5)



(6)

Although the products can also be formulated as arising by initial cycloaddition, such a process would be deterred by the location of the double bond, which leads to fused-ring triazolines with greater strain than those arising from

azides 1 to 15. Furthermore, the formation of 2-methylindole from **27a** would require two shifts of hydrogen following fragmentation of the triazoline to a zwitterion, compared to only one following direct insertion. The absence of detectable amounts of aziridines or products with six-membered heterocyclic rings should also be noted.

We conclude that an unconjugated double bond in an ortho substituent does not enhance the susceptibility of aryl azides to thermolysis unless it is so situated (homoallylic structure) as to favor intramolecular cycloaddition to form an intermediate triazoline, but where the ortho substituent has an allylic bond structure, thermolysis is not enhanced, and the products are most simply accounted for by nitrene insertion into C–H bonds.

Where a triazoline is involved, the rate-limiting step may be either its formation or its fragmentation. Opening of the triazoline ring heterolytically to zwitterions as represented by **22b** and **24b** rationally accounts for the product-determining process, but it is less clear how homolytic opening to a spin-coupled diradical[8b,15] analogue of **24**, as has been proposed on the basis of insensitivity of the rate to the polarity of the medium, can do so. The observations could be reconciled by the hypothesis that ring opening is homolytic, but the resulting diradical becomes a zwitterion such as **24** before the product-determining stage, or that ring opening is heterolytic with an early transition state, in which polarity would not yet be strongly developed.

Experimental Section

All melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer grating spectrometer, Model 237B. A Varian T-60 or T-60A nuclear magnetic resonance spectrometer was used for ^{1}H NMR spectra with tetramethylsilane as an internal standard, and a JEOL FX-90Q instrument was used for ^{13}C NMR spectra. Eastman chromagram sheets, Type 6060, and preparative precoated alumina plates (alumina GF, 1 mm) made by Analtech Inc. were used for thin-layer chromatography. Column chromatography was performed with Woelm neutral alumina or silica gel. Elemental analyses were performed by Spang Microanalytical Laboratory and Galbraith Laboratories. Some liquid azides were not analyzed because they were insufficiently stable for transportation to an analytical laboratory without some deterioration, but were characterized spectroscopically.

***cis*-Cinnamyl Alcohol.** 3-Phenyl-2-propyn-1-ol[7] was hydrogenated at 2.5 psi of H_2 by a modification of a method reported by Tedeschi and Clark[16] using a mixture of 6.1 g (0.046 mol) of 3-phenyl-2-propyn-1-ol, 0.09 g of potassium hydroxide powder, 100 mL of methanol, and 0.05 g of 5% Pd/$BaSO_4$ (Sigma Chemical Co.). The distilled product (5.1 g, 68% had a boiling point of 74 °C (0.1 mm) [lit.[7] 114–115 °C (3 mm)]. Vaporphase chromatography (10% FFAP on Chromosorb W 60/80, 170–190 °C, temperature program 4 °C/min) showed one peak (lower retention time than *trans*-cinnamyl alcohol).

1-Azido-2-[(3-phenyl-2-propenyl)oxy]benzene (4). A solution of 5.0 g (0.037 mol) of *cis*-cinnamyl alcohol and 7.83 g (0.041 mol) of *p*-toluenesulfonyl chloride in 100 mL of ether was cooled to −20 °C under nitrogen. Freshly powdered sodium hydroxide (5.6 g) was added in portions over a period of 30 min. The milky mixture was stirred at −20 °C for another 2 h and was then poured into ice water. The ether solution was separated, washed with cold water, and dried with anhydrous sodium sulfate. The solution was kept at 0 °C until used for the next reaction.

Procedure A. A solution of 5.0 g (0.037 mol) of 2-azidophenol in 20 mL of dry tetrahydrofuran was added dropwise to a suspension of 0.98 g (0.040 mol) of sodium hydride powder (Alfa Products) in tetrahydrofuran at room temperature under nitrogen. After being stirred for 20 min, the solution turned dark green; the tosylate solution prepared earlier was then added in one portion. The mixture was stirred at 0 °C for 2 h and then at room temperature for 6 h. The slurry was filtered and the filtrate was evaporated to dryness in vacuo. The residue was mixed with water and extracted with chloroform. The extract was washed with water, 10% sodium hydroxide solution, water, and saturated sodium chloride solution and then dried (Na_2SO_4). After the removal of solvent, the residue was passed through a column of 25 g of silica gel (activity grade III) with cyclohexane/methylene chloride (100:1) as eluant to give 3.4 g (37%) of **4** as a light yellow oil: ^{1}H NMR ($CDCl_3$) δ 4.70–4.90 (dd, J = 6.5, 1.5 Hz, 2 H, OCH_2), 5.70–6.17 (dt, J = 11, 1.5 Hz, 1 H, C**H**=CHPh), 6.50–7.47 (m, 10 H, C_6H_5C**H**=C + C_6H_4); IR (neat) 2100 (N_3), 1645 (*cis*-CH=CH), 1020 (CO) cm^{-1}.

Anal. Calcd for $C_{15}H_{13}N_3O$: C, 71.68; H, 5.22; N, 16.72. Found: C, 71.92; H, 5.08; N, 16.85.

Thermolysis of 4. Procedure B. A solution of 0.25 g (0.001 mol) of **4** in 25 mL of toluene was bubbled with nitrogen for 15 min and then refluxed for 12 h under nitrogen. After removal of the solvent, the residue was passed through a column of 20 g of silica gel (activity grade III) with ether/triethylamine (10:1) as the eluant to give 0.21 g (94.5%) of a light yellow oil. Its ^{1}H NMR indicated the presence of *trans*-1-phenyl-1,1a-dihydro-2*H*-azirino[2,1-*c*][1,4]benzoxazine (**17d**) and 3-benzyl-2*H*-1,4-benzoxazine (**16d**) in a ratio of 94:6. These were separated by chromatography on 20 g of silica gel (activity grade III) with ether/triethylamine (15:1) as eluant. Their ^{1}H NMR and IR spectra were identical with those of samples obtained from **3** as reported by Fusco, Garanti, and Zecchi.[6]

1-Azido-2-[((*E*)-2-butenyl)oxy]benzene (5). Procedure C. To a solution of 2.70 g (0.020 mol) of 2-azidophenol in 30 mL of ethanol was added a solution of 1.2 g of sodium hydroxide in mL of water (dark green solution). Crotyl bromide (4.05 g, 0.030 mol); Columbia Organic Chemicals Co.) was added dropwise. After the mixture was stirred at room temperature for 19 h, the solvent was evaporated, water was added, and the mixture was extracted with ether. The extract was washed with 10% sodium sulfate, the solvent was evaporated, and the residue was passed through a column of 20 g of silica gel (activity grade III) with cyclohexane/dichloromethane (100:1) as the eluant to give 2.80 g (74%) of **5** as a light yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.60–1.87 (m, 3 H, CH=C**H**CH_3), 4.33–4.60 (m, 2 H, OCH_2), 5.57–5.87 (m, 2 H, C**H**=CH), 6.63–7.10 (m, 4H, C_6H_4); IR (neat) 2120 and 1310 (N_3), 1676 and 970 (*trans*-CH=CH), 1245 (CO) cm^{-1}.

Thermolysis of 5. By procedure B, 0.24 g of **5** gave 0.20 g (95%) of a light yellow oil. Three components were separated by chromatography. The compound eluted first was assigned the structure 3-ethyl-2*H*-1,4-benzoxazine (**16e**): ^{1}H NMR ($CDCl_3$) δ 1.20 (t, J = 7 Hz, 3 H, CH_3CH_2), 2.37 (q, J = 7 Hz, 2 H, CH_3CH_2), 4.50 (s, 2 H, OCH_2), 6.60–7.37 (m, 4 H, C_6H_4); IR (neat) 1650 (C=N) cm^{-1}.

Anal. Calcd for $C_{10}H_{11}NO$: C, 74.51; H, 6.88; N, 8.69. Found: C, 74.54; H, 6.79; N, 8.51.

The second component was *trans*-1-methyl-1,1a-dihydro-2*H*-azirino[2,1-*c*][1,4]benzoxazine (trans isomer, **17e**): ^{1}H NMR ($CDCl_3$) δ 1.40 (d, J = 6 Hz, 3 H, CH_3), 2.25 (m, 1 H, aziridine CH), 2.53 (m, 1 H, aziridine CH), 4.18 (d, J = 3 Hz, 2 H, OCH_2), 6.60–7.40 (m, 4 H, C_6H_4).

Anal. Calcd for $C_{10}H_{11}NO$: C, 74.51; H, 6.88; N, 8.69. Found: C, 74.38; H, 6.92; N, 8.84.

The third component *cis*-1-methyl-1,1a-dihydro-2*H*-azirino-[2,1-*c*][1,4]benzoxazine (cis isomer, **17f**): ^{1}H NMR ($CDCl_3$) δ 1.04 (d, J = 6 Hz, 3 H, CH_3), 2.43–2.95 (m, 2 H, aziridine CH's), 3.50–3.90 (dd, J = 11, 6 Hz, 1 H, OCH), 4.33–4.77 (dd, J = 11, 6 Hz, 1 H, OCH), 6.70–7.10 (m, 4 H, C_6H_4).

Anal. Calcd for $C_{10}H_{11}NO$: C, 74.51; H, 6.88; N, 8.69. Found: C, 74.36; H, 6.82; N, 8.55.

Decoupling by irradiation at the OCH_2 signals showed N = 3.4 Hz for the aziridine CH=CH of **17e** and 5.6 Hz in the case of **17f**, thereby establishing the configurational assignments.[17] The ^{1}H NMR of the mixture before chromatography indicated the ratio

(15) R. Huisgen, G. Szeimies and L. Möbius, *Chem. Ber.*, **99**, 475 (1966).

(16) (a) B. J. Tedeschi and G. Clark, Jr., *J. Org. Chem.*, **27**, 4323 (1962); (b) L. F. Hatch and S. S. Nesbitt, *J. Am. Chem. Soc.*, **72**, 727 (1950).

(17) T. J. Batterham, "NMR Spectra of Simple Heterocycles", Wiley, New York, 1973.

of the components to be 35:41:24. When thermolysis was carried out in other solvents at the temperature of boiling toluene, the product ratios were those recorded in Table II.

(*Z*)-2-Buten-1-ol. When the literature procedure was followed,[16b] a mixture of *Z* and *E* isomers was obtained, the highest ratio being 88:12. A modification of the method of Tedeschi and Clark[16a] gave the desired product. Freshly ground potassium hydroxide (0.5 g) was dissolved in 14.0 g (0.20 mol) of 2-butyn-1-ol (Farchan Reseach Laboratories) with heating. Methanol (100 mL) and 5% palladium on barium sulfate (0.2 g, Sigma Chemical Co.) were added, and the mixture was hydrogenated at 17 psi of H_2. The mixture was filtered through Celite and most of the solvent was removed by vacuum distillation through a column packed with glass helices. The residue was distilled in vacuo (>1 mm) at room temperature and condensed in a trap cooled with dry ice. Another fractional distillation at 50 °C (35 mm) [lit.[16b] bp 64–65 °C (60 mm)] gave 6.3 g (44%) of a colorless liquid. GC analysis (10% FFAP on Chromosorb W 60/80, 81 °C) indicated >95% of the desired isomer: ^{1}H NMR ($CDCl_3$) δ 1.48 (s, 1 H), 1.66–1.71 (m, 3 H), 4.20–4.25 (m, 2 H), 5.56 and 5.70 (m, 2 H); IR (neat) 3300 (OH), 1665 and 978 (*cis*-CH=CH), 1030 (CO) cm^{-1}.

1-Azido-2-[((*Z*)-2-butenyl)oxy]benzene (6). By procedure A, 3.6 g (0.05 mol) of (*Z*)-2-buten-1-ol, 10.5 g (0.055 mol) of *p*-toluenesulfonyl chloride and 5.4 g (0.040 mol) of 2-azidophenol gave 4.8 g (51%) of **6**: ^{1}H NMR ($CDCl_3$) δ 1.60–1.87 (m, 3 H, CH_3), 4.50–4.75 (m, 2 H, OCH_2), 5.57–5.87 (m, 2 H, CH=CH), 6.73–7.10 (m, 4 H, C_6H_4); IR (neat) 2110 and 1300 (N_3) and 1668 (*cis*-CH=CH) cm^{-1}. Ultimate analysis was not attempted.

Thermolysis of 6. By procedure B, 0.33 g of **6** gave 0.28 g of a light yellow oil. ^{1}H NMR and GC indicated the same three components as obtained from thermolysis of **5**, but in the ratio 28:47:25. Thermolysis at 110–120 °C in other solvents gave the ratio recorded in Table II.

1-Azido-2-[((*E*)-2-methyl-2-butenyl)oxy]benzene (7). (*E*)-2-Methyl-2-buten-1-ol was prepared in 60% yield from tiglic acid (Aldrich Chemical Co.) by reduction with lithium aluminum hydride: bp 66–68 °C (33 mm) (lit.[18] bp 137–138 °C); ^{1}H NMR ($CDCl_3$) δ 1.47–1.80 (m, 6 H)8 2.50 (s, 1 H), 3.93 (s, 2 H), 5.17–5.67 (m, 1 H). IR (neat) 3300 (OH), 1975 (C=C), 1010 (CO) cm^{-1}. It was converted to **7** by essentially the same procedure as described for the preparation of **4**. Oily **7** was obtained in 47% yield: ^{1}H NMR ($CDCl_3$) δ 1.47–1.87 (m, 6 H, $2CH_3$), 4.37 (s, 2 H, OCH_2), 5.33–5.80 (m, 1 H, C=CH), 6.67–7.03 (m, 4 H, C_6H_4); IR (neat) 2110 and 1300 (N_3), 1675 (C=C) cm^{-1}.

Anal. Calcd for $C_{11}H_{13}N_3$: C, 65.00; H, 6.45; N, 20.68. Found: C, 65.04; H, 6.46; N, 20.66.

Thermolysis of 7. By procedure B, two compounds were isolated in a total yield of 0.29 g (79%). The first component was *trans*-1,1a-dimethyl-1,1a-dihydro-2*H*-azirino[2,1-*c*][1,4]benzoxazine (*trans*-**17g**): ^{1}H NMR ($CDCl_3$) δ 1.30 (s, 3 H, CH_3), 1.33 (d, *J* = 6.5 Hz, 3 H, *endo*-CH_3), 2.43 (q, *J* = 6.5 Hz, 1 H, aziridine CH), 3.95 (AB q, *J* = 9 Hz, 2 H, OCH_2), 6.60–7.33 (m, 4 H, C_6H_4).

Anal. Calcd for $C_{11}H_{13}NO$: C, 75.39; H, 7.48; N, 7.99. Found: C, 75.46; H, 7.55; N, 8.05.

The second component was *cis*-1,1a-dimethyl-1,1a-dihydro-2*H*-azirino[2,1-*c*][1,14]benzoxazine (*cis*-**17g**): ^{1}H NMR ($CDCl_3$): δ 1.02 (d, *J* = 6.5 Hz, 3 H, *exo*-CH_3), 1.40 (s, 3 H, CH_3), 2.43 (q, *J* = 6.5 Hz, 1 H, aziridine CH), 3.67 (d, *J* = 12 Hz, 1 H, OCH), 4.20 (d, *J* = 12 Hz, 1 H, OCH), 6.67–7.10 (m, 4 H, C_6H_4).

Anal. Calcd for $C_{11}H_{13}NO$: C, 75.39; H 7.48; N, 7.99. Found: C, 75.38; H, 7.54; N, 8.03.

The NMR spectrum of the mixture before separation corresponded to a 1:1 ratio of the two components.

1-Azido-2-[((*Z*)-2-methyl-2-butenyl)oxy]benzene (8). 3,4-Epoxy-3-methyl-1-butene was prepared from isoprene[19,20] via isoprene bromohydrin; bp 70 °C (25 mm). Distillation from sodium hydroxide pellets gave 3,4-epoxy-3-methyl-1-butene: bp 70–75 °C; ^{1}H NMR ($CDCl_3$) δ 1.43 (s, 3 H), 2.60–2.87 (m, 2 H), 5.00–5.87 (m, 3 H). Reduction with diisobutylaluminum hydride essentially according to the procedure of Lenox and Katzenellenbogen[21] gave (*Z*)-2-methyl-2-buten-1-ol, bp 61–63 °C (25 mm). From ^{1}H NMR (after addition of D_2O), the ratio of (*Z*)- to (*E*)-2-methyl-2-buten-1-ol was found to be 85:15 (lit.[21] 95:5). The spectrum of the pure *Z* isomer was deduced from the spectra of this mixture and of pure (*E*) isomer obtained previously: ^{1}H NMR ($CDCl_3$) δ 1.50–1.90 (m, 6 H), 2.20 (t, *J* = 5.5 Hz, 1 H, OH), 4.15 (d, *J* = 5.5 Hz, 2 H, OCH_2, changed to a singlet on addition of D_2O), 5.37 (q, *J* = 6 Hz, 1 H).

The foregoing alcohol was converted to **8** in the manner used to prepare **4**. A 24% yield of an 87:13 mixture of *Z* and *E* isomers **8** and **7** was obtained: ^{1}H NMR ($CDCl_3$) δ 1.52–2.00 (m, 6 H), 4.58 (br s, 2 H), 5.50 (q, *J* = 7 Hz, 1 H), 6.72.12 (m, 4 H); IR (neat) 2090 and 1310 (N_3) cm^{-1}.

Anal. Calcd for $C_{11}H_{13}NO$: C, 65.00; H, 6.45; N, 20.58. Found: C, 65.01; H, 6.51; N, 20.54.

Thermolysis of 8. By procedure B, a 0.15 g of **8** (containiing 13% of **7**) afforded 0.04 g (24%) of an oil. The ^{1}H NMR indicated the presence of the same pair of aziridines obtained from **7**; the cis/trans ratio was 72.5:27.5. Correction for the presence of the 13% of **7** in the substrate gave the modified ratio 74:26 for pure **8**.

1-Azido-2-[(2-phenyl-2-propenyl)oxy]benzene (*9*). By procedure A, 1.78 g (0.009 mol) of α-(bromomethyl)sytrene[22] was converted to 0.42 g (19%) of a light yellow oil: ^{1}H NMR ($CDCl_3$) δ 4.90 (br s, 2 H, OCH_2), 5.47–5.57 (m, 2 H, $C=CH_2$), 6.8 (m, 4 H, C_6H_4), 7.2–7.5 (m, 5 H, C_6H_5); IR (neat) 2100 and 1300 (N_3), 1640 and 910 ($C=CH_2$), 1025 (CO) cm^{-1}. Ultimate analysis was not attempted.

Thermolysis of 9. Thermolysis of 0.26 g of **9** by procedure B gave 0.21 g (91%) of a light yellow oil, separated by column chromatography into two components, both oils. The first was 1a-phenyl-1,1a-dihydro-2*H*-azirino[2,1-*c*][1,4]benzoxazine (**17i**): ^{1}H NMR ($CDCl_3$) δ 2.52–2.65 (AB, q, *J* ≃ 0.5 Hz, 2 H, aziridine CH_2), 4.17 (d, *J* = 11 Hz, 1 H, OCH), 4.47 (d, *J* = 11 Hz, 1 H, OCH), 6.67–7.52 (m, 9 H, C_6H_4 + C_6H_5).

Anal. Calcd for $C_{15}H_{13}NO$: C, 80.68; H, 5.87; N, 6.28. Found: C, 80.69; H, 5.68; N, 6.41.

The second product was 3-benzyl-2*H*-1,4-benzoxazine (**16i**): ^{1}H NMR ($CDCl_3$) δ 3.72 (s, 2 H, $PhCH_2$), 4.40 (s, 2 H, OCH_2) and 6.63–7.60 (m, 9 H, C_6H_4 + C_6H_5); IR (neat) 1645 (C=N) cm^{-1}.

Anal. Calcd for $C_{15}H_{13}NO$: C, 80.68; H, 5.87; N, 6.28. Found: C, 80.92; H, 5.60; N, 6.55.

The ^{1}H NMR of the unseparated mixture corresponded to a ratio of **17**/**16** of 91:9.

1-Azido-2-[(3-methyl-2-butenyl)oxy]benzene (10). 4-Bromo-2-methyl-2-butene,[23] obtained by the reaction of isoprene with HBr, was converted by procedure C into **10** in 69% yield, light yellow oil: ^{1}H NMR ($CDCl_3$) δ 1.73 (m, 6 H, $2CH_3$), 4.53 (d, *J* = 7 Hz, 2 H, OCH_2), 5.50 (t, *J* = 7 Hz, 1 H, C=CH), 6.70-7.20 (m, 4 H, C_6H_4); IR (neat) 2120 and 1315 (N_3), 1675 (C=C) and 1000 (CO) cm^{-1}. Ultimate analysis was not attempted.

Thermolysis of 10. By procedure A, 0.44 g of **10** gave rise to 0.38 g (98%) of a light yellow oil, which was separated into three components. The first was 3-isopropyl-2*H*-1,4-benzoxazine (**16j**): ^{1}H NMR ($CDCl_3$) δ 1.22 (d, *J* = 7 Hz, 6 H, $2CH_3$), 2.60 (septet, *J* = 7 Hz, 1 H, $CH(CH_3)_2$), 4.50 (s, 2 H, OCH_2), 6.63–7.33 (m, 4 H, C_6H_4); IR (neat) 1645 (C=N) cm^{-1}.

Anal. Calcd for $C_{11}H_{13}NO$: C, 75.39; H, 7.48; N, 7.99. Found: C, 75.31; H, 7.51; N, 7.82.

The second component was 3-isopropenyl-3,4-dihydro-2*H*-benzoxazine (**18**): ^{1}H NMR ($CDCl_3$) δ 1.50 (d, *J* < 1 Hz, 1 H, NCH), 1.80 (d, *J* < 1 Hz, 3 H, $C=CCH_3$), 3.60–4.33 (m, 3 H, OCH_2 + NH), 5.00 (m. 2 H, $C=CH_2$), 6.37–6.83 (m, 4 H, C_6H_4); IR (neat) 3300 (NH); 1640 (C=C) cm^{-1}.

Anal. Calcd for $C_{11}H_{13}NO$: C, 75.39; H, 7.48; N, 7.99. Found: C, 75.52; H, 7.64; N, 8.21.

The third component was 1,1-dimethyl-1,1a-dihydro-2*H*-azirino[2,1-*c*][1,4]benzoxazine (**17j**): ^{1}H NMR ($CDCl_3$) δ 1.00 (s, 3 H, CH_3), 1.40 (s, 3 H, CH_3), 2.57 (t, *J* = 7 Hz, 1 H, aziridine CH), 3.50–3.90 (dd, *J* = 12, 7 Hz, 1 H, OCH), 4.33–4.67 (dd, *J* = 12,

(18) L. F. Hatch and P. R. Noyes, *J. Am. Chem. Soc.*, **79**, 345 (1957).
(19) E. J. Reist, I. C. Junga, and B. R. Baker, *J. Org. Chem.*, **25**, 1673 (1960).
(20) G. Eletti-Bianchi, F. Centini, and L. Re, *J. Org. Chem.*, **41**, 1648 (1976).
(21) R. S. Lenox and J. A. Katzenellenbogen, *J. Am. Chem. Soc.*, **95**, 957 (1973).
(22) S. F. Reed, Jr., *J. Org. Chem.*, **30**, 3258 (1965).
(23) A. A. Stotskii, A. S. Enin, N. V. Bukhvalova, S. L. Gorbunova, and N. M. Stoskaya, *J. Org. Chem.* USSR (*Engl. Transl.*), **7**, 2162 (1971).

7 Hz, 1 H, OCH), 6.63–7.20 (m, 4 H, C_6H_4).

Anal. Calcd for $C_{11}H_{13}NO$: C, 75.39; H, 7.48; N, 7.99. Found: C, 75.37; H, 7.42; N, 7.91.

The ^1H NMR spectrum of the unseparated mixture corresponded to a ratio of **16j/18/17j** of 31:8:61.

1-Azido-2-[(2,3-dimethyl-2-butenyl)oxy]benzene (11). By procedure C, 3.26 g of 1-bromo-2,3-dimethyl-2-butene (prepared[24] from 2,3-dimethyl-1,3-butadiene) was converted to 2.0 g (60%) of **11**, a light yellow oil: ^1H NMR ($CDCl_3$) δ 1.73 (m, 9 H, $3CH_3$)8 4.57 (s, 2 H, OCH_2), 6.70–7.10 (m, 4 H, C_6H_4); IR (neat) 2110 and 1300 (N_3) cm^{-1}. Ultimate analysis was not attempted.

Thermolysis of 11. By procedure B, 0.22 g of **11** gave rise to 0.16 g (85%) of 3-isopropenyl-3-methyl-3,4-dihydro-2*H*-1,4-benzoxazine (**19**): mp 64–65 °C (from petroleum ether); ^1H NMR ($CDCl_3$) δ 1.30 (s, 3 H, CH_3), 1.85 (s, 3 H, C=CCH_3), 3.63 (s, 1 H, NH), 3.85 (d, J = 10 Hz, 1 H, OCH), 4.18 (d, J = 10 Hz, 1 H, OCH), 4.90–5.10 (m, 2 H, C=CH_2), 6.43–7.00 (m, 4 H, C_6H_4); IR (Nujol) 3350 (NH), 1640 (C=C) cm^{-1}.

Anal. Calcd for $C_{12}H_{15}NO$: C, 76.27; H, 8.90; N, 5.34. Found: C, 76.51; H, 8.75; N, 5.43.

1-Azido-2-[(3-cyclopentenyl)oxy]benzene (12). 3-bromocyclopentene,[25] obtained from cyclopentadiene and HBr, was converted by procedure A into **12**, a yellow oil, in 45% yield: ^1H NMR ($CDCl_3$) δ 1.90–3.00 (m, 4 H, $(CH_2)_2$), 5.53–5.57 (m, 1 H, OCH), 5.83–6.37 (m, 2 H, CH=CH), 6.70–7.27 (m, 4 H, C_6H_4); IR (neat) 2110 and 1300 (N_3), 1235 and 1025 (CO) cm^{-1}.

Thermolysis of 12. By procedure B, 0.38 g of **12** yielded 0.28 g (86%) of **20a** (a white solid, mp 84–85 °C) after recrystallization from petroleum ether: ^1H NMR ($CDCl_3$) δ 0.78–2.78 (m, 4 H, $(CH_2)_2$), 2.85–3.17 (m, 2 H, aziridine CHCH), 4.82–5.12 (m, 1 H, OCH), 6.43–7.27 (m, 4 H, C_6H_4). It decomposed readily on exposure to the atmosphere.

Anal. Calcd for $C_{11}H_{11}NO$: C, 76.27; H, 6.40; N, 8.09. Found: C, 76.32; H, 6.34; N, 7.96.

1-Azido-2-[(3-cyclohexenyl)oxy]benzene (13). By procedure A, 3-bromocyclohexene[26] was converted in 17% yield to **13**, an oil, which was purified by bulb-to-bulb distillation at 0.01 mm pressure and a pot temperature 100 °C, with substantial loss: ^1H NMR ($CDCl_3$) δ 1.47–2.33 (, 6 H, $(CH_2)_3$), 4.57–4.90 (m, 1 H, CH), 5.87 (m, 2 H, CH=CH), 6.73–7.07 (m, 4 H, C_6H_4); IR (neat) 2110 and 1325 (N_3), 1650 (C=C), 1235 and 1025 (CO) cm^{-1}. Ultimate analysis was not attempted.

Thermolysis of 13. By procedure B, 0.29 g of **13** gave rise to 0.16 g (65%) of **20b**: mp 40–41 °C (from petroleum ether; ^1H NMR ($CDCl_3$) δ 0.80–2.10 (m, 6 H, $(CH_2)_3$), 2.43–2.70 (m, 1 H, aziridine CH), 2.77–3.03 (m, 1 H, aziridine CH), 4.67–5.00 (m, 1 H, OCH), 6.63–7.23 (m, 4 H, C_6H_4).

Anal. Calcd for $C_{12}H_{13}NO$: C, 76.97; H, 7.00; N, 7.48. Found: C, 76.79; H, 7.03; N, 7.26.

1-Azido-2-[(1-cyclopentenyl)methoxy]benzene (14). By procedure A, (1-cyclopentenyl)methanol,[27] obtained from cyclopentene-1-carbaldehyde,[28] was converted to **14**, an oil, in 22% yield: ^1H NMR ($CDCl_3$) δ 1.60–2.60 (m, 6 H, $(CH_2)_3$), 4.53 (s, 2 H, OCH_2), 5.70 (br s, 1 H, C=CH), 6.60–7.17 (m, 4 H, C_6H_4); IR (neat) 2075 and 1315 (N_3), 1660 (C=C) cm^{-1}. Ultimate analysis was not attempted.

Thermolysis of 14. Thermolysis of 0.19 g of **14** by procedure B gave 0.16 g (94%) of an oily racemate of (3a*R**,10a*S**)- and (3a*S**,10a*R**)-1,2,3,10a-tetrahydro-4*H*-cyclopent[2,3]azirino[2,1-*c*][1,4]benzoxazine (racemic **21a**): ^1H NMR ($CDCl_3$) δ 1.33–2.23 (m, 6 H, $(CH_2)_3$), 2.63 (br s, 1 H, aziridine CH), 4.27 (s, 2 H, OCH_2), 6.60–7.30 (m, 4 H, C_6H_4); ^{13}C NMR ($CDCl_3$) δ 20.3, 28.1, 29.0, 52.6, 54.2, 63.7, 117.2, 121.8, 124.6, 126.5, 137.4, 149.6.

Anal. Calcd for $C_{12}H_{13}NO$: C, 76.97; H, 7.00; N, 7.48. Found: C, 76.94; H, 7.04; N, 7.57.

When a solution of **14** in deuteriochloroform was kept at 35 °C for 3 weeks, the spectrum of **14** changed to one identifiable as the isomeric triazoline; no residual **14** could be detected: ^1H NMR ($CDCl_3$) δ 0.88–2.38 (m, 6 H, $(CH_2)_3$), 3.53 (d, J = 10 Hz, 1 H, OCH), 4.12 (d, J = 10 Hz, 1 H, OCH), 5.2 (m, 1 H, N=NCH), 6.70–7.68 (m, 4 H, C_6H_4).

1-Azido-2-[(1-cyclohexenyl)methoxy]benzene (15). (1-Cyclohexene)methanol[29,30] was prepared from cyclohexanecarboxylic acid (Aldrich Chemical Co.) by Hell–Volhard–Zelinsky bromination, esterification, dehydrobromination with 2,6-lutidine, and reduction with lithium aluminum hydride. By procedure A, it was converted to **15**, an oil, in 15% yield: ^1H NMR ($CDCl_3$) δ 1.43–2.27 (m, 8 H, $(CH_2)_4$), 4.37 (s, 2 H, OCH_2), 5.77 (br s, 1 H, C=CH), 6.67–7.07 (m, 4 H, C_6H_4); IR (neat) 2080 and 1310 (N_3), 1675 (C=C) cm^{-1}.

Anal. Calcd for $C_{13}H_{15}N_3O$: C, 68.10; H, 6.59; N, 18.33. Found: C, 68.17; H, 6.58; N, 18.22.

Thermolysis of 15. By procedure B, 0.36 g of **15** afforded 0.24 g (76%) of (5a*R**,9a*S**)- and (5a*S**,9a*R**)-5a,6,8,9-tetrahydro-7H,10--benz[2,3]azirino[2,1-*c*][1,4]benzoxazine (racemic **21b**). An analytical sample was obtained by bulb-to-bulb distillation at 90 °C (0.01 mm): ^1H NMR ($CDCl_3$) δ 0.87–2.10 (m, 8 H, $(CH_2)_4$), 2.40–2.60 (m, 1 H, aziridine CH), 3.89 (d, J = 11.6 Hz, 1 H, OCH), 4.05 (d, J = 11.6 Hz, 1 H, OCH) 6.53–7.27 (m, 4 H, C_6h_4).

Anal. Calcd for $C_{13}N_{15}NO$: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.61; H, 7.59; N, 6.94.

***o*-Allylaniline.** A mixture of 5.9 g (0.044 mol) of *N*-allylaniline, 6.04 g (0.044 mol) of anhydrous zinc chloride powder (treated with thionyl chloride, filtered, washed with anhydrous ether, and dried in a desiccator), and 20 mL of *p*-xylene was refluxed under nitrogen for 8 h. After cooling to room temperature, the liquid was decanted, 150 mL of 40% aqueous sodium hydroxide was added to the solid mass, and the mixture was heated to dissolve the solid and extracted with three 50-mL portions of ether. The extract was washed with water and saturated sodium chloride solution and dried (Na_2SO_4). Fractional distillation gave 3.65 g (64%) [bp 60–62 °C (0.05 mm), lit.[32] bp 119–122.5 °C (28 mm) of crude product. Purification by silica gel column chromatography with benzene/cyclohexane (1:2) as the eluant gave 2.36 g (40%) of product: ^1H NMR ($CDCl_3$) δ 3.23 (m, 2 H), 3.53 (br s, 2 H, exchangeable with D_2O), 4.80–5.23 (m, 2 H), 5.57–6.20 (m, 1 H), 6.47–7.17 (m, 4 H); IR (neat) 3410 and 3330 (NH_2), 1625 (C=C) cm^{-1}.

***o*-Azidoallylbenzene (27a).** To a solution of 1.33 g (0.01 mol) of 2-allylaniline in 60 mL of 2 N hydrochloric acid cooled at −5 °C was added dropwise a solution of 0.76 g (0.011 mol) of sodium nitrite in 5 mL of water, while the temperature of the reaction mixture was kept between −5 and 0 °C. After 30 min with stirring, a solution of 0.76 g (0.012 mol) of sodium azide in 5 mL of water was added, and stirring was continued for 1 h. The mixture was then saturated with potassium hyddroxide and extracted with methylene chloride. The extract was washed with water and dried (Na_2SO_4), the solvent was removed, and the residue was passed through a column of 40 g of silica gel (activity grade III) with benzene/cyclohexane (1:4) as the eluant to give 0.87 g (55%) of **27a**: ^1H NMR ($CDCl_3$) δ 3.23–3.50 (m, 2 H, CH_2C=C), 4.80–5.23 (m, 2 H, C=CH), 5.60–6.33 (m, 1 H, C**H**=CH_2) and 6.83–7.30 (m, 4 H); IR (neat) 2100 and 1285 (N_3), 1645 (C=C) cm^{-1}. Ultimate analysis was not attempted.

Thermolysis of 27a. A solution of 0.30 g (1.89 mmol) of **27a** in 30 mL of decalin was refluxed under nitrogen for 2 h. After the removal of the solvent under vacuum, the residue was purified by preparative TLC on an alumina plate with benzene/cyclohexane (1:1) as the eluant to give 0.20 g (82%) of 2-methylindole (mp 58–59 °C, recrystallized from petroleum ether), identical in ^1H NMR and IR with an authentic sample.[33]

2-(*o*-Azidophenyl)ethanol. In a manner similar to the preparation of **27a**, 6.85 g of 2-(2-aminopheny6)ethanol (Aldrich Chemical Co.) gave 7.40 g (76%) of a low-melting yellow solid

(24) E. H. Farmer and F. C. B. Marshall, *J. Chem. Soc.*, 129 (1931).
(25) R. B. Moffett, "Organic Syntheses", Collect Vol. IV, Wiley, New York, 1963, p 238.
(26) L. F. Hatch and G. Bachman, *Chem. Ber.*, **97**, 132 (1964).
(27) P. R. Pal, C. G. Skinner, R. L. Dennis, and W. Shive, *J. Am. Chem. Soc.*, **78**, 5116 (1956).
(28) J. B. Brown, H. B. Henbest, and E. R. H. Jones, *J. Chem. Soc.*, 3634 (1950).
(29) L. Field and P. M. Giles, Jr., *J. Med. Chem.*, **13**, 317 (1970).
(30) J. H.-H. Chan and B. Rickborn, *J. Am. Chem. Soc.*, **90**, 6406 (1968).
(31) H. Oehme and R. Thamm, *J. Prakt. Chem.*, **315**, 526 (1973).
(32) C. D. Hurd and W. W. Jenkins, *J. Org. Chem.*, **22**, 1418 (1957).
(33) (a) C. J. Fouchert and J. R. Campbell, "Aldrich Library of NMR Spectra", Vol. 8, Aldrich Chemical Co., Milwaukee, WI, 1974, No. 51B; (b) "Aldrich Library of IR Spectra", Vol. 2, Aldrich Chemical Co. Milwaukee, Wi, 1974, No. 1079B; (c) C. J. Fouchert, *ibid.*, 2nd ed., No. 1079B.

(treatment with charcoal was substituted for chromatography). An analytical sample obtained by recrystallization from petroleum ether/carbon tetrachloride (10:1) had the following: mp 46–47 °C; ^{1}H NMR ($CDCl_3$) 1.80 (s, 1 H), 2.83 (t, J = 6.4 Hz, 2 H), 3.77 (t, J = 6.4 Hz, 2 H), 6.90–7.20 (m, 4 H); IR (neat) 3320 (OH), 2100 and 1300 (N_3) cm^{-1}.

Anal. Calcd for $C_8H_9N_3O$: C, 58.87; H, 5.56; N, 25.75. Found: C, 58.45; H, 5.51; N, 25.72.

(*o*-Azidophenyl)acetaldehyde (27). To a solution of 3.26 g (0.02 mol) of 2-(2-azidophenyl)ethanol in 20 mL of anhydrous dimethyl sulfoxide was added a mixture of 30 mL of benzene, 1.61 mL (0.02 mol) of pyridine, and 077 mL (0.01 mol) of trifluoroacetic acid. With stirring, 6.0 g (0.03 mol) of dicyclohexylcarbodiimide was added in one portion; heat was evolved immediately. The mixture was stirred at 50 °C for 30 min, 100 mL of water was added to precipitate dicyclohexylurea, and the mixture was filtered. The filtrate was extracted with 50 mL of ether, and the extract was washed with 5% sodium bicarbonate solution and water and was dried ($NaSO_4$). After the removal of solvent, the residue was passed through a column of 30 g of silica gel (activity grade III) with benzene/cyclohexane (1:2) as the eluant to give 1.61 g (50%) of oil: ^{1}H NMR ($CDCl_3$) δ 3.66 (d, J = 2 Hz, 2 H, CH_2CHO), 6.80–7.57 (m, 4 H), 9.70 (t, J = 2 Hz, 1 H, CH_2CHO); IR (neat) 2120 and 1290 (N_3), 1735 (C=O) cm^{-1}. Its 2,4-dinitrophenylhydrazone had a melting point of 150–150.5 °C (from ethanol).

Anal. Calcd for $C_{14}H_{11}N_7O_4$: C, 49.27; H, 3.25; N, 28.73. Found: C, 49.22; H, 3.37; N, 28.77.

Thermolysis of 27b. A mixture of 0.20 g (1.24 mmol) of **27b** and 20 mL of decalin was heated under nitrogen in an oil bath at 190–200 °C for 2 h. After removal of the solvent in vacuo, the residue was purified on a preparative alumina TLC plate with benzene/ethyl acetate (10:1) as the eluant to give 0.14 g (85%) of oxindole, mp 126–127 °C. Its ^{1}H NMR and IR spectral data were identical with reported data.[34]

***o*-[((*Z*)-1-Propenyl)oxy]aniline.** Paralleling published methods,[35,36] 4.48 g (0.04 mol) of potassium *tert*-butoxide was added in small portions to a solution of 2.90 g (0.019 mol) of 2-[(2-propenyl)oxy]aniline[37] in 40 mL of dimethyl sulfoxide at room temperature under nitrogen. The mixture was stirred for 1 h, poured into ice–water, and extracted with methylene chloride. The extract was washed with water and dried (Na_2SO_4). Fractional distillation gave 1.53 g (53%) of the desired product: bp 55–58 °C (0.25 mm); ^{1}H NMR ($CDCl_3$) δ 1.57–1.87 (dd, J = 6.8, 1.6 Hz, 3 H), 3.77 (br s, 2 H), 4.83 (quintet, 1 H)8 6.17–6.43 (dq, J = 6.0, 1.6 Hz, 1 H), 6.50–7.00 (m, 4 H); IR (neat) 3450 and 3350 (NH_2), 1675 (OCH=CH) cm^{-1}.

Anal. Calcd for $C_9H_{11}NO$: C, 72.45; H, 7.43; N, 9.39. Found: C, 72.40; H, 7.51; N, 9.60.

1-Azido-2-[((*Z*)-1-propenyl)oxy]benzene (27c). In a manner analogous to the preparation of **27a**, 1.51 g of 2-(*Z*)-propenyloxy]aniline gave 0.77 g (50%) of **27c** (chromatography on alumina rather than silica gel): ^{1}H NMR ($CDCl_3$) δ 1.57–1.83 (dd, J = 6.8, 1.6 Hz, 3 H, CH=CHCH$_3$), 4.87 (m, 1 H, CH=CHCH$_3$), 6.00–6.23 (dq, J = 6.0, 1.6 Hz, 1 H, CH=CHCH$_3$) 6.57–7.03 (m, 4 H); IR (neat) 2100 and 1300 (N_3), 1675 (OC=C) cm^{-1}. Ultimate analysis was not attempted.

Thermolysis of 27c. A solution of 0.15 g (0.84 mmol) of **27c** in 0.5 mL of deuteriochloroform was sealed in an NMR tube and heated at 150 °C for 10 h. After the removal of the solvent and bulb-to-bulb distillation, 0.10 g (81%) of 2-ethylbenzoxazole [lit.[38] bp 210 °C, 84 °C (3 torr)][38,39] was obtained: ^{1}H NMR ($CDCl_3$) δ 1.50 (t, J = 7 Hz, 3 H), 3.1 (q, J = 7 Hz, 2 H), 7.2–7.5 (m, 4 H) ppm. The IR (neat) spectrum matches that reported[39] for a solution in CCl_4, except for minor shifts due to the difference in solvents.

Kinetics of Thermolysis of 1. Solutions of **1** in deuteriochloroform containing cyclohexane as an internal standard was sealed shut and then heated in a constant-temperature bath. At intervals, the tubes were removed and quenched at room temperature. The rate was followed by comparing the integrated intensity of the signals of the ethylenic hydrogens to that of the cyclohexane. A computer-calculated least-squares fit of the data gave $k = 6.7 \times 10^{-5}$ s^{-1} at 56.2 °C, 1.9×10^{-4} s^{-1} 65.2 °C, and 5.6×10^{-4} s^{-1} at 79.2 °C.

Registry No. **1**, 55000-07-2; **2**, 55000-08-3; **3**, 78479-77-3; **4**, 78479-78-4; **5**, 78479-79-5; **6**, 78479-80-8; **7**, 78479-81-9; **8**, 78479-82-0; **9**, 78479-83-1; **10**, 78479-84-2; **11**, 78479-85-3; **12**, 78479-86-4; **13**, 58432-19-2; **14**, 78479-87-5; **15**, 78479-88-6; **16a**, 55000-20-9; **16b/16e**, 78479-89-7; **16d/16i**, 78479-90-0; **16j**, 78479-91-1; **17a**, 55000-17-4; **17b**, 55000-18-5; **17d**, 78479-92-2; **17e**, 78479-93-3; **17f**, 78479-94-4; **17g**, 78479-95-5; **17h**, 78479-96-6; **17i**, 78479-97-7; **17j**, 78479-98-8; **18**, 78479-99-9; **19**, 78480-00-9; **20a**, 78480-01-0; **20b**, 58432-23-8; **21a**, 78480-02-1; **21b**, 78480-03-2; **27a**, 78480-04-3; **27b**, 78480-05-4; **27b** 2,4-dinitrophenylhydrazone, 78480-06-5; **27c**, 78480-07-6; *cis*-cinnamyl alcohol, 4510-34-3; 3-phenyl-2-propyn-1-ol, 1504-58-1; 2-azidophenol, 24541-44-4; *cis*-cinnamyl alcohol tosylate, 78480-08-7; (*E*)-crotyl bromide, 29576-14-5; (*Z*)-2-buten-1-ol, 4088-60-2; 2-butyn-1-ol, 764-01-2; (*E*)-2-methyl-2-buten-1-ol, 497-02-9; tiglic acid, 80-59-1; isoprene, 78-79-5; 3,4-epoxy-3-methyl-1-butene, 1838-94-4; (*Z*)-2-methyl-2-buten-1-ol, 19319-26-7; α-(bromomethyl)styrene, 3360-54-1; 4-bromo-2-methyl-2-butene, 870-63-3; 1-bromo-2,3-dimethyl-2-butene, 5072-70-8; 3-bromocyclopentene, 36291-48-2; 3-bromocyclohexene, 1521-51-3; (1-cyclopentenyl)methanol, 1120-80-5; (1-cyclohexene)methanol, 4845-04-9; *o*-allylaniline, 32704-22-6; *N*-allylaniline, 589-09-3; 2-methylindole, 95-20-5; 2-(*o*-azidophenyl)-ethanol, 31590-12-2; 2-(2-aminophenyl)ethanol, 5339-85-5; oxindole, 59-48-3; *o*-[((*Z*)-1-propenyl)oxy]aniline, 78480-09-8; 2-[(2-propenyl)-oxy]aniline, 27096-64-6; 2-ethylbenzoxazole, 6797-13-3.

(34) Reference 33a, Vol. 7, No. 90C; ref 33b, No 953E.
(35) C. C. Price and W. H. Snyder, *J. Am. Chem. Soc.*, **83**, 1773 (1961).
(36) J. A. Wojtowicz and R. J. Polak, *J. Org. Chem.*, **38**, 2061 (1973).
(37) B. D. Tiffany, *J. Am. Chem. Soc.*, **70**, 592 (1948).
(38) S. Skraup and M. Moser, *Ber. Dtsch. Chem. Ges.*, **55**, 1080 (1922).
(39) V. I. Cohen and S. Pourabass, *J. Heterocycl. Chem.*, **14**, 1321 (1977).