Registry No. $PhP(CH_2)_2BH_3$, 35512-87-9; p-$ClC_6H_4P(CH_2)_2BH_3$, 96292-74-9; p-$CH_3C_6H_4P(CH_2)_2BH_3$, 96292-75-0; p-$OCH_3C_6H_4P(CH_2)_2BH_3$, 96292-76-1; p-$N(CH_3)_2C_6H_4P(CH_2)_2BH_3$, 96292-77-2; p-t-$C_4H_9C_6H_4P(CH_2)_2BH_3$, 96292-78-3; m-$OCH_3C_6H_4P(CH_2)_2BH_3$, 96292-79-4; PhBr, 108-86-1; p-ClC_6H_4Br, 106-39-8; p-$CH_3C_6H_4Br$, 106-38-7; p-$OCH_3C_6H_4Br$, 104-92-7; p-$N(CH_3)_2C_6H_4Br$, 586-77-6; p-t-$C_4H_9C_6H_4Br$, 3972-65-4; m-$OCH_3C_6H_4Br$, 2398-37-0; $Cl(CH_3)_2PBH_3$, 54220-72-3.

Comparison of the Ease of Thermolysis of Ortho-Substituted Phenyl Azides Having α,β or β,γ Imine Functions[1]

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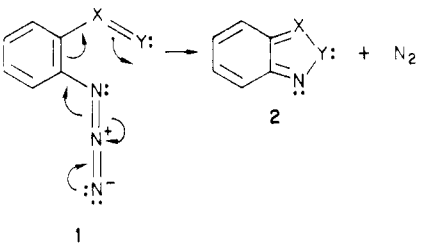
Received May 23, 1984

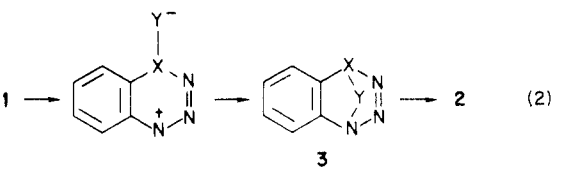
o-Azidobenzaldehyde benzylimine (**7**) thermolyzes 34 times faster than phenyl azide and 1.6 times faster than *p*-chlorobenzaldehyde *o*-azidoanil (**8**), whereas benzaldehyde (*o*-azidobenzyl)imine (**9**) and acetophenone (*o*-azidobenzyl)imines (**10a–e**) show little or no rate enhancement over phenyl azide. An electrocyclic mechanism can account for the rates of **7** and **8** relative to each other but not of **8** relative to phenyl azide; **9** and **10a–e** appear to thermolyze by nitrene formation, even though a mechanism through intramolecular cycloaddition may in principle be available. A mechanism based on electrostatic effects in a dipolar transition state can correlate the effects of different types of α,β-unsaturated ortho substituents.

Phenyl azides without ortho substituents decompose with unimolecular kinetics in the temperature range 140–180 °C to form nitrogen and products derived from further reactions of initially formed nitrene.[2-5] Activation energies are generally high (30–40 kcal/mol). The presence of almost any substituent in an ortho position causes some increase in rate of thermolysis (e.g., the ratio of rates for *o*-tolyl and phenyl azides is 1.27), but where the substituent is α,β-unsaturated, thermolysis is faster still and requires much lower temperatures[2-7] (50–110 °C) and activation energies are lower (ca. 22–27 kcal/mol). These facts were explained for *o*-nitrophenyl azide by the concept of a cyclic transition state for a concerted process in which the nitro group assists in the fragmentation of the azido group.[8-10] Dyall and Kemp[11] generalized this concept as shown in eq 1.



1 2 (1)

An alternative mechanism proposed by Hall, Behr, and Reed in 1974 consists of 1,3-cycloaddition of the azido group to the unsaturated ortho substitutent as a rate-limiting step, followed by extrusion of nitrogen from the resulting heterocycle (eq 2). These two mechanisms have engendered much experimentation and lively debate.[4,15-19]



1 3 2 (2)

A third mechanism has recently been proposed[18] in order to account for the sequence of accelerating effects with different ortho substituents, which has a pronounced gradient: ArN=N > O=N(O) > O=C(R) > R_2C=C(R). This mechanism assumes that conjugative charge separation contributes more to the structure of phenylnitrene than to the corresponding azide. Although it has a close relationship to the electrocyclic mechanism, it differs from it in an important respect, for in the latter mechanism, as viewed by Dyall,[4,14,16,19] "the driving force is provided by the delocalization energy of the new heterocycle which is partly formed in the transition state". In phenylnitrenes with an interactive substituent in the ortho position, a

(1) Taken in part from the doctoral dissertation of S.-S.P.C. and in part from the Senior Honors thesis of G.F.B. Presented in part at the Second Chemical Congress on the North American Continent, Las Vegas, NV, Aug, 1980.

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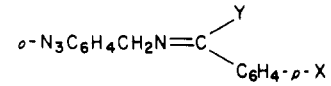
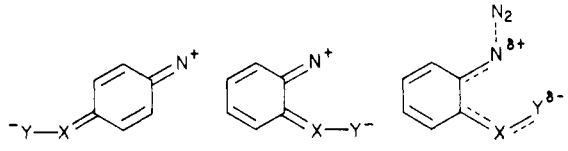
Table I. Imines of 2-Azidobenzylamine



compd	X	Y	mp, °C	T_{dec},[a] °C	time,[b] h	yield, %
9	H	H	49–50		1	84
10a	H	CH_3	84.5–85	155	6.5	76.5
10b	CH_3	CH_3	96–97.5	125	6	28.6
10c	CH_3O	CH_3	90–92	130	18	37
10d	Cl	CH_3	101–102	125	20	53
10e	NO_2	CH_3	129–130	145	12	66

[a] Onset of visible decomposition in the melt. [b] Duration of refluxing in toluene (for **9**, benzene) in the preparation.

substantial lowering of energy can be expected from the proximity of opposite charges (**5**). Dissipation of the



4 **5** **6**

charges occurs as the N–Y bond is formed in the final product (**2**). Rate enhancement would be observed when the transition state (**6**) is far enough along the reaction coordinate to resemble **5** to a substantial degree. However, there is no simple correlation with the bond energies of the N–Y links that are ultimately formed.

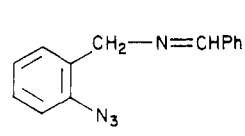
The lowering of the energy of the transition state would be most pronounced with substituents best able to sustain a negative charge on the β atom, Y. The order is thus expected to be that of electronegativity, O= > RN= > R_2C=, and is, in fact, the order observed[4,15,20] with the ortho substituents O=C(R) and R_2C=C(R). (The high rate enhancement by the azo group may also reflect some contribution from the delocalization energy of the incipient heterocycle and thus represent a shift toward the Dyall mechanism, the transition state lying further toward the products.) The steric effects reported by Dickson and Dyall[4,14] are consistent with both the electrocyclic and charge-separation mechanisms. The azo and nitro groups, in which the α atom, N, is also more electronegative than carbon, would have the ability to sustain a negative charge further increased by the inductive effect of X, an expectation that concords with the fact that the accelerating effect of these two groups is greater than that of the carbonyl group. The effect of the azo group, in such compounds as *o*-azidoazobenzene, would be enhanced with respect to the nitro group by the fact that it has no other substituent on the α atom to interfere with the assumption of a coplanar conformation, required for closest approach of charges in **6**.

The imino groups, RN=C(R) and R_2C=N, could not be reliably placed in the sequence of accelerating effects when the research reported here was begun, owing to the absence of kinetic measurements. However, the fact that the isomeric imines *o*-azidobenzaldehyde benzylimine (**7**) (i.e., **1** in which X=Y is CH=NCH_2Ph) and *p*-chlorobenzaldehyde *o*-azidoanil (**8**) (i.e., **1** in which X=Y is N=CHC_6H_4Cl) had been reported[22,23] to require the same temperature for thermolysis was cited in support of the cycloaddition mechanism. Whereas **7** has a lone electron pair on the β atom, which would facilitate the electrocyclic mechanism by conferring aromatic stability on **2**, **8** has none and would show no more acceleration than the vinyl group causes in *o*-azidostyrenes. In contrast, it is an expected consequence of the charge-separation mechanism that **7** would thermolyze faster than **8** and that both would thermolyze faster than phenyl azide but not as fast as *o*-azidophenyl ketones or aldehydes. In this paper, we examine these azides and the homologous nonconjugated imines kinetically in order to distinguish among the three mechanisms.

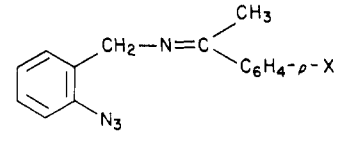
Results and Discussion

Benzaldehyde *o*-azidoanil has been reported[22] to be difficult to purify, a fact that we have confirmed. We therefore used the *p*-chlorobenzylidene analogue (**8**). Both it and **7**, prepared from *o*-azidobenzaldehyde and benzylamine, were obtained crystalline. In many and varied attempts to prepare analogues of **8** derived from ketones, no reaction could be achieved under conditions that did not also bring about decomposition of the azido group.

The isomeric imine system with the double bond of the ortho substituent in the allylic position (**9** and **10a–e**) was



9



10a, X = H
b, X = CH_3
c, X = OCH_3
d, X = Cl
e, X = NO_2

generated from *o*-azidobenzylamine (prepared from *o*-azidobenzyl bromide[24] by the Gabriel phthalimide method) by treatment with benzaldehyde or ketone in boiling benzene or toluene (Table I). Several (*o*-azidobenzyl)-imines having wholly aliphatic alkylidene groups, such as isopropylidene, were also prepared, but since they were oils that were difficult to purify, kinetic measurements were not made with them. However, the relatively high temperatures required for their thermolysis provided qualitative evidence for a lack of an accelerating effect.

(20) *o*-Azidostyrene derivatives show no evidence for an enhanced rate of thermolysis and require temperatures above 180 °C for conveniently fast fragmentation, with formation of indoles and byproducts: Sundberg, R. J.; Russell, H. F.; Ligon, W. V., Jr.; Liu, L.-S. *J. Org. Chem.* **1972**, *37*, 719. Smith, P. A. S.; Rowe, C. D.; Hansen, D. W., Jr. *Tetrahedron Lett.* **1983**, *24*, 5769. A C–C double bond γ–δ to the benzene ring, however, reacts with an *o*-azido substituent to give an observable intermediate resulting from 1,3-dipolar addition, and loss of nitrogen is exceptionally easy.[21]

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Table II. Susceptibility of Phenyl Azides to Thermolysis in Decalin

substituent	apparent T_{dec}, °C[a]	k/k_{Ph}[b,c]	E_a, kcal/mol	$\Delta S^{\ddagger}$,[d] eu
H	~150	1.0[b]	32.6 ± 1.2[e]	−2.3 ± 3.0[e]
$CH_2N{=}CHPh$ (**9**)	~150	0.7[b]	36.3 ± 1.7	8.3 ± 4
$CH_2N{=}C(CH_3)Ph$ (**10a**)	~140	2.7[b], 2.9[c]	35.0 ± 2	−7 ± 3
$CH_2N{=}C(CH_3)C_6H_4CH_3$ (**10b**)	~140	1.8[c], 0.9[c,h]		
$CH_2N{=}C(CH_3)_3C_6H_4OCH_3$ (**10c**)	~140	2.6[c], 1.2[c,h]		
$CH_2N{=}C(CH_3)C_6H_4Cl$ (**10d**)	~140	1.9[c], 0.9[c,h]		
$CH_2N{=}C(CH_3)C_6H_4NO_2$ (**10e**)	~140	2.1[c], 1.0[c,h]		
$CH_2CH{=}CH_2$	~200	<1		
$CH_2CH{=}O$	~180	<1		
$OCH{=}CHCH_3$ (cis)	~155	~1		
$CH{=}NCH_2Ph$ (**7**)	95	34.1[b]	30.0 ± 1.0	0.1 ± 2.5
$N{=}CHC_6H_4$-*p*-Cl (**8**)	100[f]	21.2[b]	27.4 ± 0.4	−7.5 ± 1.0
$C(CH_3){=}O$[e]		287[b]	26.1 ± 1.1[e]	−7.4 ± 4.0[e]
$N{=}NPh$[e]	<50	21, 180[b]	22.7 ± 0.2[e]	−7.3 ± 0.6[e]
$N(O){=}O$[e]	<100	738[b]	25.5 ± 0.6	−6.9 ± 1.8
$OCH_2CH{=}CH_2$[g]	~50	>500[b,g]	21[g]	−16[g]
$C(CH_3){=}CHCH_3$ (**11**)	165	0.5		

[a] Visible gas evolution from solutions. [b] Rate relative to phenyl azide at 393 K. If *o*-tolyl azide is used as the reference compound, the values in this column are reduced by a factor of 1/1.27. [c] Rate relative to phenyl azide at 413 K. [d] Activation entropies are included for reference, since the rates are related to them as well as to the activation energies, but the interpretation of the magnitudes of them is obscure.[4,13,15] However, the very large negative $\Delta S^{\ddagger}$ for *o*-(allyloxy)phenyl azide is an expected consequence of the rate-determining formation of a cyclic intermediate. [e] From Dyall.[4,15] [f] Hall and Kamm[23] noted a decomposition temperature of 130 °C (boiling point of dimethylformamide) for various *N*-benzylidene-*o*-azidoanilines. [g] Smith and Chou.[21] [h] In $CDCl_3$.

The decompositions were followed by volumetric measurement of evolved nitrogen and spectroscopic monitoring (NMR or IR) of the disappearance of the substrate. The results were closely alike, in spite of large differences in the concentration required (at higher concentrations, deviations from first-order kinetics are sometimes encountered, owing to a free-radical chain reaction[4]). Reproducibility was better with the spectroscopic methods. Because most of the rates that have been reported previously were obtained in decalin solution, whereas for the NMR method, the solubility in decalin was too low for some of the substrates, we compared the behavior of **10a** by tandem runs in decalin, Me_2SO, and $CDCl_3$. There was a clear accelerating effect by the more polar solvents: the rate in $CDCl_3$ was just over twice that in decalin, and that in Me_2SO was 2.5 times that in $CDCl_3$. We did not wish to make a major study of solvent effects at this time (there are only fragmentary reports about them in the literature[4,16,25]), but it is clear that they should not be ignored when comparing kinetics from one set of experiments to another.

The rates obeyed first-order kinetics accurately, even through several half-lives. Heats of activation were determined for representative examples. The results are summarized and compared with those of other azides in Table II. The products from **9** were 2-phenylquinazoline (7%) and 2-benzylindazole (68%), and those from **10a–e** were (1-arylethyl)indazoles (31–59%), (1-arylvinyl)-indazoles (8–16%), and 2-aryl-2-methyl-1,2-dihydroquinazolines (8–18%), along with ill-defined material usually produced in arylnitrene reactions. The products from **9** and **10a–e** and other related imines will be described in another paper.

The rate of thermolysis of **7** was about 60% greater than that of **8** (X = *p*-Cl). The rate enhancements with respect to phenyl azide, k/k_{Ph} = 34.1 for **7** and 21.2 for **8**, were substantial, although smaller than those of most other phenyl azides with α,β-unsaturated substituents, such as *o*-nitro (k/k_{Ph} = 738) and *o*-acetyl (k/k_{Ph} = 287).[4] The activation energies are somewhat lower than those of simple phenyl azides but not so low as those characteristic of azides that are generally taken to exemplify assisted fragmentation,[4] and the temperatures required for easily measurable decomposition, 124–167 °C, are high for assisted fragmentation but slightly low compared to those required by simple phenyl azides. These compounds thus show intermediate kinetic characteristics.

The results are consistent with Hall, Behr, and Reed's[12] expectation that **7** should decompose more readily than **8** if an electrocyclic mechanism applied. The difference is also in the direction to be expected if the charge-separation mechanism applies, although its magnitude is too small to be definitive. Perturbation by the *p*-chloro group may be discounted, for it has been shown to have only a small (slightly accelerating) effect in analogous instances.[12,25] However, the fact that **8** decomposes over 20 times as fast as phenyl azide is not consistent with the electrocyclic mechanism, for the ring system that is formed (**2**, X = N; Y = CR_2) is an interrupted 8-π-electron one and does not have the aromatic stabilization postulated[4,14,15,19] to be required for lowering the energy of the transition state for concerted release of nitrogen from the azide.

With **9** and **10a–e**, neither the electrocyclic nor the charge-separation mechanisms should operate. The cycloaddition mechanism should be feasible, however, and provide assistance, and the substituents in **10a–e** should noticeably affect the ease of cycloaddition to the imine bond. However, the rates of thermolysis showed no assistance to fragmentation and little effect by substituents. In fact, **9** decomposed slightly less readily than phenyl azide, notwithstanding the fact that noninteracting substituents generally produce a small rate enhancement. Phenyl azides bearing three other β,γ-unsaturated ortho substituents also show no rate enhancement.[21]

We have additionally investigated (*E*)-1-azido-2-(but-2-en-2-yl)benzene (*o*-azido-α,β-dimethylstyrene) (**11**), prepared from the corresponding bromo compound through the reaction of its Grignard reagent with tosyl azide. It showed no rate enhancement and actually decomposed slightly more slowly than phenyl azide. It is now possible to complete the ranking of ortho substituents according to their accelerating effect: $ArN{=}N > O{=}N(O) > O{=}C(R) > RN{=}C(R) > R_2C{=}N > R_2C{=}C(R) \simeq H \simeq R_2C{=}NCH_2$. This order is implied only by the charge-separation mechanism, which is also the only one of the three hypotheses that is consistent with the new kinetic data. It implies a form of assistance to fragmen-

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Table III. Measured Rates of Thermolysis of Aryl Azides

compd	solv[a]	method[b]	10^{-5} k,[c] s^{-1} (T, °C)
7	$C_{10}H_{18}$	IR	5.95 (109.2), 29.7 (124.4), 82.5 (135.7), 130 (141.9)
8	$C_{18}H_{18}$	IR	4.07 (108.6), 44.5 (136.2), 66.8 (142.1), 140 (149.8)
9	$C_{10}H_{18}$	IR	4.00 (141.7), 11.1 (150.4), 14.6 (154.8), 52.3 (167.0)
10a	$C_{10}H_{18}$	vol	32 (155)
10a	$C_{10}H_{18}$	NMR	5.02 (139.5), 22.3 (155)
10a	$CDCl_3$	NMR	6.29 (137), 11.2 (139.5), 44.2 (155), 148 (177)
10a	Me_2SO	NMR	28.4 (139.5)
10b	$C_{10}H_{18}$	vol	25–41 (155), 22–29 (157.7), 73–76 (166.5)
10b	$CDCl_3$	NMR	6.39 (139.5)
10c	$C_{10}H_{18}$	vol	27 (155), 46 (157.5)
10c	$CDCl_3$	NMR	9.17 (139.5)
10d	$C_{10}H_{18}$	vol	23–40 (155)
10d	$CDCl_3$	NMR	6.80 (139.5)
10e	$C_{10}H_{18}$	vol	28–37 (155), 39 (160)
10e	$CDCl_3$	vol	7.36 (139.5)
11	$C_{10}H_{18}$	vol	24 (164)

[a] $C_{10}H_{18}$ = decalin. [b] Vol = volumetric gas evolution. [c] Determined from the slopes of least-squares analysis of the integrated first-order equation. For the spectroscopic methods, the correlation coefficients were 0.990–0.999.

tation but not a synchronous path.[26]

Experimental Section

Melting points are uncorrected. Elemental analyses were performed by Spang Microanalytical Laboratories. NMR spectra were taken with a Varian Associates T-60 instrument and IR spectra with a Perkin-Elmer Model 247B instrument.

2-Azido-*N*-(4-chlorobenzylidene)aniline (8) was prepared as previously described:[22] mp 52.3–54.3 °C (reported 52 °C); ^1H NMR ($CDCl_3$) δ 7.1–7.2 (4 H), 7.4–7.6 (2 H), 7.8–8.0 (2 H), 8.4 (1 H); IR (KBr pellet) 1625 (N=C), 2060, 2105 cm^{-1} (N_3).

***N*-(2-Azidophenyl)phthalimide.** A mixture of 19.1 g (0.09 mol) of 2-azidobenzyl bromide[24] and 19.0 g (0.10 mol) of potassium phthalimide in 150 mL of dimethylformamide was prepared at room temperature and then heated with vigorous stirring at 80 °C for 12 h; 2-azidobenzyl bromide was no longer detectable by TLC. The cooled mixture was poured into 500 mL of ice/water slush, and the resulting white precipitate was collected, washed with water, and dried in vacuo: 23.7 g (95%), mp 181–182 °C (dec). Recrystallization from chloroform and ether gave 22.5 g (90%): mp 183–184 °C; ^1H NMR ($CDCl_3$) δ 4.87 (s, 2 H), 7.00–7.37 (m, 4 H), 7.53–7.97 (m, 4 H); IR (Nujol) 2100 and 1300 (N_3), 1710 cm^{-1} (C=O). Anal. C, H, N.

2-Azidobenzylamine. A mixture of 17.42 g (0.06 mol) of *N*-(2-azidophenyl)phthalimide, 300 mL of 95% ethanol, and 25 mL of 85% aqueous hydrazine was refluxed under nitrogen for 3 h. The precipitate that formed was dissolved by adding 200 mL of 10% sodium hydroxide solution, the solution was extracted with three 50-mL portions of methylene chloride, and the combined extracts were washed with water and dried over Na_2SO_4. The solvent was removed under aspirator vacuum. Distillation then yielded 7.63 g (86%) of a light yellow oil, bp 75 °C (0.4 mmHg); it absorbed CO_2 readily from air and was therefore stored under nitrogen in a freezer: ^1H NMR δ 1.40 (s, 2 H), 3.73 (s, 2 H), 6.83–7.37 (m, 4 H); IR (neat) 3350 and 3240 (NH_2), 2125 and 1295 cm^{-1} (N_3).

The benzoyl derivative, *N*-(2-azidophenyl)benzamide, was prepared for characterization, using benzoyl chloride and pyridine in benzene: mp 108.5–109.5 °C. Anal. C, H, N.

***N*-Benzylidene-2-azidobenzylamine (9).** A mixture of 0.64 g (4.31 mmol) of 2-azidobenzylamine, 3 mL (28.3 mmol) of benzaldehyde, and 40 mL of benzene was refluxed under N_2, using a Dean–Stark trap to remove water. The benzene was evaporated under aspirator vacuum, and the residual benzaldehyde was removed under oil-pump vacuum, leaving a yellow oil. Crystallization from ether/petroleum ether mixture gave 0.85 g (84%) of a white solid: mp 49–50 °C; ^1H NMR ($CDCl_3$) δ 4.77 (s, 2 H), 7.00–7.57 (m, 7 H), 7.57–7.93 (m, 2 H), 8.33 (s, 1 H); IR (Nujol) 2100 and 1280 (N_3), 1645 cm^{-1} (C=N). Anal. Calcd for $C_{14}H_{12}N_4$: C, 71.17; H, 5.12; N, 23.71. Found: C, 70.97; H, 5.04; N, 23.83.

***N*-(1-Phenylethylidene)-2-azidobenzylamine (10a).** A mixture of 0.449 g (3.03 mmol) of 2-azidobenzylamine, 0.800 g (6.66 mmol) of acetophenone, 45 mL of toluene, and a trace of *p*-toluenesulfonic acid was refluxed under nitrogen, using a Dean–Stark trap. After evaporation of toluene and excess acetophenone, the solid residue was dissolved in 30 mL of methylene chloride and washed with 50 mL of 4 N NaOH and then with water. Evaporation of the solvent from the dried ($MgSO_4$) solution left 0.71 g of solid, which was recrystallized from ether/petroleum ether mixture to obtain 0.58 g (77%) of a white solid: mp 84.5–85 °C; ^1H NMR ($CDCl_3$) δ 2.30 (s, 3 H), 4.63 (s, 2 H), 7.00–7.67 (m, 7 H), 7.67–8.06 (m, 2 H); IR (KBr) 2100 and 1290 (N_3), 1635 cm^{-1} (C=N).

The substituted derivatives **10b–e** were prepared similarly (Table I). Analyses for C, H, and N differed from the theoretical by 0.11% or less. The ^1H NMR spectra were all similar: δ 2.28–2.37 (s, 3 H, CH_3), 4.55–4.63 (s, 2 H, CH_2), plus aromatic CH resonances consistent with the substituents. Infrared spectra (KBr) showed azide stretching at 2100–2110 and 1290–1295 cm^{-1} and C=N stretching at 1635–1640 cm^{-1}.

***N*-(2-Azidobenzylidene)benzylamine (7).** 2-Azidobenzaldehyde was prepared by the method of Schwan and Davis[27] from the reaction of nitrous acid with 2-aminobenzaldoxime, which in turn was obtained by hydrogenating *anti*-2-nitrobenzaldoxime over 5% palladium on carbon in ethanol. The results from seemingly identical experiments were erratic, and the yields from the hydrogenation varied from 9% to 90%.

A mixture of 2.54 g (17.3 mmol) of 2-azidobenzaldehyde, 1.85 g (17.3 mmol) of freshly distilled benzylamine, 7 drops of glacial acetic acid, and 30 mL of ethanol was stirred at room temperature for 30 min. Evaporation of the solvent under oil-pump vacuum left a semisolid mass, which was taken up in ether and filtered from a residual white solid. The deep red filtrate could not be caused to crystallize, but evaporation of the ether left an oil, 3.59 g (88%), which had the expected spectroscopic properties: ^1H NMR ($CDCl_3$) δ 4.7 (s, 2 H), 6.9–7.5 (m, 9 H), 8.7 (s, 1 H); IR (neat) 2100 (N_3), 1640 cm^{-1} (C=N). Anal. Calcd for $C_{14}H_{12}N_4$: C, 71.16; H, 5.12; N, 23.72. Found: C, 71.19; H, 5.13; N, 23.56.

Rate Measurements. Thermolysis was conducted in a glass vessel bearing a thermometer, closed by a rubber septum, and held at a fixed temperature by immersion in the vapors of a vigorously refluxing liquid. The reaction solvent, decalin (15 mL), was placed in the vessel and allowed to come to temperature for 3 h, after which a weighed quantity (ca. 0.7 mmol) of azide was dropped in and stirred briefly with the thermometer (solution took place immediately). Aliquots of the reaction mixture were removed at intervals and chilled. The rates were followed by the decrease in absorbance at the azide stretching frequency in the infrared, using matched cells with decalin in the reference cell. Experiments were carried through several half-lives, and plots of log A vs. time were linear throughout. Alternatively, thermolyses were carried out in $CDCl_3$ solution in sealed NMR tubes, maintained at constant temperature (±0.2 °C) in the same way and containing cyclohexane as an internal standard. The change

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in intensity of a signal characteristic of the substrate was monitored at measured intervals by taking the mean of multiple sweeps (concentrations for NMR kinetics were 0.33–0.50 M).

The results are given in Table III.

For some of the azides, kinetics were also determined by following the volume of nitrogen evolved. This technique allowed more dilute solutions (~0.02 M) to be used than in the NMR method. There was no difference in the rate constants obtained that could not be attributed to solvent effect, and the plots were linear in all cases through one or more half-lives.

(*E*)-1-Bromo-2-(but-2-en-2-yl)benzene.[28] *o*-Bromoacetophenone (91 g) was treated with a small excess of ethylmagnesium bromide; the solvent (ether) was removed, and the residual liquid was boiled with benzene and a trace of iodine until 8.5 mL of water had been collected in a Dean–Stark trap. Distillation of the mixture at 0.1 mmHg yielded 85 g (88%) with a constant boiling point of 70 °C. Its IR spectrum was virtually a band-for-band match with that reported for (*E*)-(but-2-en-2-yl)benzene[29] and was distinctly different from that of the *Z* isomer of the latter and of the structural isomer, (but-1-en-2-yl)benzene. Anal. Calcd for $C_{10}H_{11}Br$: C, 56.60; H, 5.70. Found: C, 56.69; H, 5.55.

(*E*)-1-Azido-2-(but-2-en-2-yl)benzene (11).[28] The foregoing bromo compound (10.0 g) was converted to the Grignard reagent by reaction with magnesium and 100 mL of tetrahydrofuran (THF) and was then added to a solution of *p*-toluenesulfonyl azide in THF at 0 °C, and the mixture was allowed to stand for 12 h. It was then mixed with a solution of 20 g of *p*-toluenesulfonamide and 30 g of NaOH in 200 mL of water and steam-distilled. The distillate was extracted with several portions of ether, and the extracts were dried ($CaCl_2$) and distilled; 4.3 g (52%) of **11**, bp 34–44 °C (0.03 mmHg) was collected: IR (film) 2120, 1290 cm^{-1}, otherwise the same as that of (*E*)-(but-2-en-2-yl)benzene[29] and its *o*-bromo derivative. Anal. Calcd for $C_{10}H_{11}N$: C, 69.34; H, 6.40. Found: C, 69.48; H, 6.42.

Thermolysis[28] of 11. A solution of 1.0 g of **11** in 60 mL of decalin was heated at 175 °C until gas evolution ceased (ca. 1 h); 117 mL was collected (calcd 106 mL). The cooled solution was then extracted with 100 mL of 8% HCl and with concentrated HCl. The concentrated HCl extract was made basic with aqueous NaOH and then extracted with several portions of ether; evaporation of the ether after drying (Na_2SO_4) and treatment with charcoal left 0.40 g (43%) of nearly white solid, which was sublimed at 100 °C (0.01 mmHg) and recrystallized twice from petroleum ether (bp 60–75 °C): 0.20 g (22%); mp 104–107 °C (reported mp 108 °C); IR identical with that of authentic 2,3-dimethylindole.[30]

Registry No. **7**, 96308-06-4; **8**, 959-16-0; **9**, 96308-07-5; **10a**, 96308-08-6; **10b**, 96308-09-7; **10c**, 96308-10-0; **10d**, 96308-11-1; **10e**, 96308-12-2; **11**, 96308-16-6; PhN_3, 622-37-7; *o*-$N_3C_6H_4CH_2CH{=}CH_2$, 78480-04-3; *o*-$N_3C_6H_4CH_2CHO$, 78480-05-4; (*Z*)-*o*-$N_3C_6H_4OCH{=}CHCH_3$, 78480-07-6; PhCHO, 100-52-7; $PhCOCH_3$, 98-86-2; CH_3-*p*-$C_6H_4COCH_3$, 122-00-9; CH_3O-*p*-$C_6H_4COCH_3$, 100-06-1; Cl-*p*-$C_6H_4COCH_3$, 99-91-2; O_2N-*p*-$C_6H_4COCH_3$, 100-19-6; *o*-$N_3C_6H_4CH_2Br$, 31553-17-0; *o*-$N_3C_6H_4CH_2NH_2$, 96308-13-3; CO_2, 124-38-9; *o*-$N_3C_6H_4NHCOPh$, 96308-14-4; PhCOCl, 98-88-4; *o*-$N_3C_6H_4CHO$, 16714-25-3; *o*-$H_2NC_6H_4CH{=}NOH$, 3398-07-0; *anti*-*o*-$O_2NC_6H_4CH{=}NOH$, 4836-00-4; $PhCH_2NH_2$, 100-46-9; (*E*)-*o*-$BrC_6H_4C(CH_3){=}CHCH_3$, 96308-15-5; *o*-$BrC_6H_4COCH_3$, 2142-69-0; *p*-$CH_3C_6H_4SO_2N_3$, 941-55-9; *N*-(2-azidophenyl)-phthalimide, 92159-39-2; potassium phthalimide, 1074-82-4; 2,3-dimethylindole, 91-55-4.

(28) We are indebted to Dr. L. O. Krbechek for this preparation.
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Solution and Flash Vacuum Pyrolysis of Some 2,6-Disubstituted β-Phenethylsulfonyl Azides and of β-Styrenesulfonyl Azide

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Received November 19, 1984

Solution thermolysis of 2,6-dichloro-β-phenethyl- and 2,6-dimethyl-β-phenethylsulfonyl azide leads to the formation of the corresponding 5,8-disubstituted 3,4-dihydro-2,1-benzothiazine 2,2-dioxides resulting from a 1,2-chlorine and -methyl shift, respectively, in the intermediates. No insertion into the phenethyl side chain, or into the side-chain methyl group in the 2,6-dimethyl case, was detected. Attempted cyclization of ethenesulfonanilides to 2,1-benzothiazine 2,2-dioxide failed. The orientation of the dichlorosultam was established unambiguously by its FVP to 4,7-dichloroindoline and by the synthesis of an authentic sample. Solution thermolysis of β-styrenesulfonyl azide gave only hydrogen abstraction (**32**) and solvent insertion (**33**) products, but FVP gave indole, phenylacetonitrile, and phenylacetylene.

The solution and flash vacuum pyrolysis of β-phenethylsulfonyl azide[1] and β-arylpropanesulfonyl azides[2] have been reported. Sultams and ring transformation products were obtained, particularly with the phenethyl compounds. The first step involved the formation of a sulfonylnitrene which then added intramolecularly to give a benzaziridine intermediate. This either gave the expected sultam or underwent ring expansion and subsequent transformations on flash vacuum pyrolysis. It was of interest, therefore, to see what would happen if the position ortho to the ethyl side chain were blocked, since the usual sultam could not then be formed. To this end, we studied the solution and flash vacuum thermolysis of β-2,6-dichlorophenethyl- and β-2,6-dimethylphenethylsulfonyl azides. In no case was any intramolecular C–H insertion by the sulfonylnitrene into the ethyl side chain observed.

The azides were synthesized by standard procedures. The corresponding ethyl bromide **1** was converted to the sodium sulfonate **2** with sodium sulfite and then to the sulfonyl chloride **3** with thionyl chloride and DMF. The

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0022-3263/85/1950-2066$01.50/0