jected at 150° to give **2** (0.36 g, 51%) and **3** (0.15 g, 20%). The components of the second fraction were separated at 190° to give **5b** (0.32 g, 39%) and **6** (0.13 g, 14%). The ir spectra of **5a–c** are consistent with the presence of an aromatic ring and a *tert*-butyl group. Neohexylbenzene (**5a**) has nmr singlet (δ 0.95), 9 H of *tert*-butyl; ABXY multiplet (δ 1.3–2.75), 4 H of –(CH$_2$)$_2$–; singlet (δ 7.12), 5 aromatic H. 2,2-Dimethyl-4-phenylpentane (**5b**) has nmr singlet (δ 0.80), 9 H of *tert*-butyl; doublet (δ 1.22), 3 H of α-methyl; multiplet (δ 1.60), 2 H of saturated methylene; multiplet (δ 2.78), 1 benzylic H; singlet (δ 7.17), 5 aromatic H. 2,2-Dimethyl-3-benzylbutane (**5c**) has nmr doublet (δ 0.72), 3 H of methyl; singlet (δ 0.96), 9 H of *tert*-butyl; multiplet (δ 1.45), 1 β-H; doublet of doublets (δ 2.03), 1 benzylic H; doublet (δ 3.00, both slightly split), 1 benzylic H; singlet (δ 7.14, broad), 5 aromatic H. α-Neopentylstyrene (**6**) has ir doublet (890 and 900 cm⁻¹), C–H out-of-plane deformation (terminal methylene), 1620 cm⁻¹ (phenyl conjugated C=C); nmr singlet (δ 0.77), 9 H of *tert*-butyl; singlet (δ 2.45), 2 H of saturated methylene; multiplets (δ 4.99 and 5.21), 2 olefinic H; multiplet (δ 7.25), 5 aromatic H. The identities of **5a–c** and **6** were confirmed by their synthesis by conventional methods.

Dehydration of 1 by Thionyl Chloride–Pyridine. To alcohol **1** (2.5 g, 0.0125 mol) in pyridine (20 ml) at −50° was added dropwise thionyl chloride (5 ml, 8.2 g, 0.069 mol) with stirring. The reaction mixture was allowed to warm to room temperature during 1 hr and then worked up normally. After evaporation of the solvent there remained 2.1 g (93% yield) of a mixture of **7** (5%) and **8** (95%). 1-*tert*-Butyl-1-triptylethylene (**7**) and 2,3,4,4-tetramethyl-3-*tert*-butylpent-1-ene (**8**) have been described previously;[7] **8** is a solid, mp 152–154° when freshly purified, and has in the ir (CCl$_4$ solution) *doublets* associated with the C–H stretching (3097 and 3106 cm⁻¹) and out-of-plane deformation (890 and 902 cm⁻¹) characteristic of the terminal methylene group.

Dehydration of 1 in Dilute Sulfuric Acid. Dehydration of **1** (0.025 *M* solution) in H$_2$SO$_4$–HOAc (0.33% v/v) was followed by glpc. Samples (0.2 ml) were quenched in saturated Na$_2$CO$_3$ solution and extracted into pentane (0.5 ml). By calibration with an internal standard, *trans*-decalin, both the reaction rate and the evolution of the product composition during the course of dehydration were determined. In addition to the predominant fragmentation product, **4**, three other low molecular weight products were detected. After approximately one half-life of the alcohol the product composition was **4**, 31%; **7**, 42%; **8**, 10%; and **9**, 7%.

Acid-Catalyzed Rearrangement of 8. Olefin **8** (2.1 g, 95% pure) was treated with H$_2$SO$_4$–HOAc (1% v/v, 40 ml) at 20° for 2 hr. After the usual work-up the products were separated by glpc on SE-30 to give a mixture of fragmentation products (0.20 g, 80% olefin **4**), **7** (0.75 g, 34%), and a mixture of **8** and **9** (0.04 g) which could not be separated further: 2,3,4,4-Tetramethylpent-1-ene (**4**) has ir 890, 1637, and 3068 cm⁻¹ (terminal methylene); nmr singlet (δ 0.90), 9 H of *tert*-butyl; doublet (δ 1.00), 3 H of 3-methyl; singlet (δ 1.71, slightly split), 3 H of 2-methyl; quartet (δ 1.98), 1 H; multiplets (δ 4.63 and 4.71), 2 olefinic H.

tert-**Butyl Triptyl Ketone.** Repeated methylation of methyl triptyl ketone in dimethoxyethane with a fourfold excess of NaNH$_2$ and methyl iodide gave, after preparative glpc, 41% yield of the desired ketone, approximately 95% pure.

tert-**Butylmethyltriptylcarbinol (10).** The above ketone (2.1 g, 0.011 mol) was stirred with an ethereal solution of methyllithium (1 *M*, 65 ml, 0.065 mol) overnight. The residual oil, after hydrolysis and evaporation of the solvent, was free of ketone and was used without further purification.[13]

Dehydration of 10. Alcohol **10** (2.0 g, 0.01 mol) was treated with H$_2$SO$_4$–HOAc (0.2 v/v, 25 ml) at 20° for 10 min, after which the reaction was quenched by the addition of water. Olefins **7** and **9** were obtained in yields of 47 (0.85 g) and 17% (0.30 g), respectively, by preparative glpc. 2,3,3,4,4,5,5-Heptamethylhex-1-ene (**9**) is a solid: mp 32°; ir 892, 1620, 3090 cm⁻¹ (terminal methylene); nmr singlet (δ 0.94), 6 H of two 4-methyls; singlet (δ 0.99), 9 H of *tert*-butyl; singlet (δ 1.17), 6 H of two 3-methyls; singlet (δ 1.95, slightly split), 3 H of 2-methyl; singlet (δ 4.87, slightly split), 2 olefinic H.

Registry No.—**1**, 41902-42-5; **2**, 815-24-7; **3**, 14609-79-1; **4**, 50987-59-2; **5a**, 17314-92-0; **5b**, 2319-54-2; **5c**, 50987-60-5; **6**, 7283-47-8; **8**, 38575-30-3; **9**, 50987-61-6; **10**, 51016-45-6.

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On the Mechanism of the Thermal Decomposition of Vinyl Azides

Gerrit L'abbé* and Georges Mathys

Department of Chemistry, Laboratory of Synthetic Organic Chemistry, University of Louvain, Celestijnenlaan 200F, B-3030 Heverlee, Belgium

Although thermal decomposition of vinyl azides (**1**) gives rise to a variety of products depending on substituents, most of them are rationalized by invoking the intermediacy of an azirine (**2**).[1] Two mechanistic pathways are currently given for the transformation **1** → **2**. The vinyl azide can either lose nitrogen to give a vinyl nitrene which then cyclizes to the azirine (path a), or it can decompose with simultaneous ring closure to give **2** directly (path b).
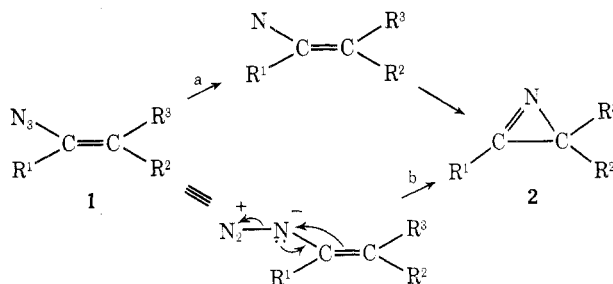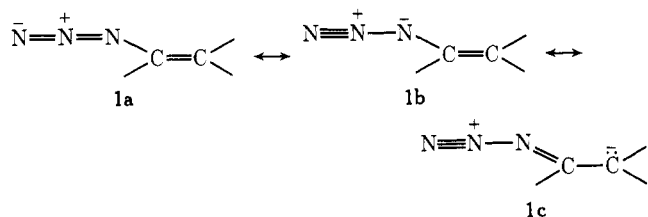

In order to distinguish between the two possible mechanisms, we have investigated the kinetics of the thermal decomposition of several vinyl azides using ir techniques. Thus, toluene solutions of the azides were allowed to decompose at the appropriate temperatures and the rates of decomposition were followed by recording the decrease of the azide absorption band at about 2130 cm⁻¹. By plotting log absorbance *vs.* time, linear plots up to a high degree of conversion (80%) were obtained. The first-order rate constants and the activation parameters are summarized in Table I.

In comparing the thermal stability of vinyl azides with that of other classes of organic azides, it should be kept in mind that the azido group in vinyl azides increases the electron density at the β carbon atom to almost the same extent as an amine function in enamines.[2] This means that canonical structure **1c** contributes appreciably to the overall resonance stabilization of the azide with the result that the order of the N$_2$–N bond which breaks on thermol-
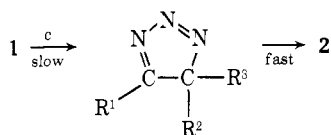
Table I
Rate Constants and Activation Parameters for the Thermal Decomposition of 1 in Toluene

R¹	R²	R³	ν_{as} N₃, cm⁻¹	Temp, °C	10⁵ k_1, sec⁻¹	E_a, kcal mol⁻¹	ΔS^* (at 70°), eu	Registry no.
H	Ph	H	2110	59.5	2.79	26.6	−1.8	18756-03-1
				71.0	10.97			
				84.2	45.45			
				92.0	103.33			
H	p-MeC₆H₄	H	2100	59.5	4.06	26.9	0.0	51201-98-0
				71.0	14.74			
				84.2	71.55			
				92.0	150.31			
H	p-ClC₆H₄	H	2105	59.5	2.96	26.8	−0.7	51201-99-1
				71.0	11.79			
				84.5	49.98			
				92.0	109.51			
H	PhCO	H	2140	42.8	2.26	26.3	+1.2	13850-37-8
				52.4	8.30			
				63.0	29.72			
				71.5	70.93			
H	PhCO	Me	2130	69.5	1.58	27.2	−3.2	24325-94-8
				82.3	6.29			
				90.5	16.03			
				100.0	44.12			
PhCO	H	Ph	2100	69.5	1.98	29.7	+4.5	26309-08-0
				91.5	25.6			
				97.0	43.3			
				103.0	83.6			
MeCO	H	Ph	2110	73.5	1.61	30.5	+5.4	26309-09-1
				82.0	4.89			
				94.0	21.09			
				104.0	58.17			

ysis is less than 1.5. Therefore, comparison should not be made with alkyl azides which only decompose at 180–200°,[3] but with aryl azides where the aryl group has been shown to stabilize a negative charge equally well.[4] For those aryl azides whose pyrolysis proceeds *via* a nitrene intermediate, the energies of activation range from 34 to 40 kcal/mol and the entropies of activation are usually high (*ca.* 18 eu).[5a] Table I now clearly shows that vinyl azides exhibit moderate energies of activation and rather low entropies of activation, inconsistent with a nitrene mechanism.[5b] Instead, the E_a and ΔS^* values are comparable with those recorded for the Curtius rearrangement[3] and for some ortho-substituted aryl azides which manifest neighboring-group participation.[3,5] That vinyl azides decompose with anchimeric assistence is also evident from the low decomposition temperatures compared with the 140–170° decomposition range of ordinary aryl azides.[3]
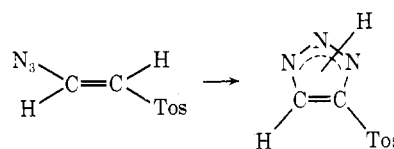
Smolinsky, who first pyrolyzed vinyl azides to azirines,[6] also considered the possibility that 1 would decompose to 2 *via* an unstable isotriazole intermediate (path c). Al-


though this reaction path has not found general acceptance in the literature as a possible mechanistic route,[7] it should be considered for the simple reason that some vinyl azides, which possess an acidic β-H atom, undergo facile base-promoted cyclizations to triazoles.[8]

Table II
Rate Constants and Activation Parameters for the Thermal Decomposition of 3 in Ether (ν_{as} 2080 cm⁻¹)

Temp, °C	10⁵ k_1, sec⁻¹	E_a, kcal mol⁻¹	ΔS^* (at 34°), eu
21.1	4.11	22.6	−3.6
26.1	7.82		
30.4	14.19		
34.3	22.55		

If accumulation of negative charge on the β-carbon atom of vinyl azides would facilitate thermal decomposition by path c, this would be observed in the kinetic data. Introduction of an electron-donating (Me) or an electron-withdrawing aryl substituent (Cl) in the para position of *trans*-β-azidostyrene, however, had almost no effect on the rates of decomposition (see Table I). These findings do not decisively exclude path c because Brewbaker and Hart have shown that thermal decomposition of the corresponding 3-diazo-1-arylpropenes is also not appreciably influenced by para substituents.[9] The latter decompose by a mechanism analogeous to path c, giving pyrazoles *via* isopyrazoles (*e.g.*, 3 → 4).
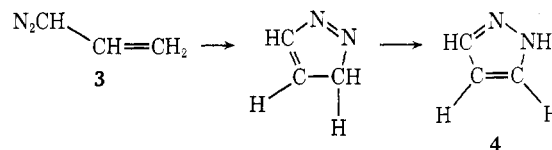
In order to gain some insight into the activation parameters of the reaction 3 → 4, we have undertaken a kinetic study. The results, summarized in Table II, show that 3 decomposes at a much lower temperature than do vinyl azides. This decrease in decomposition temperature is re-

flected in the value of the energy of activation. The entropy of activation is similar to those recorded for vinyl azides in Table I and suggests that path c would not differ from path b in this respect.

Experimental Section

Toluene solutions (*ca.* 0.01 mol/l.) of the vinyl azides (prepared by known procedures[10]) were introduced in a reaction vessel covered with a rubber cap and provided with a capillary needle for nitrogen evolution. The solutions were allowed to come to thermal equilibrium in a thermostat at the appropriate temperature. At several time intervals aliquots were withdrawn from the reaction vessel, cooled to 0°, and analyzed. The decrease of the azide absorption band at *ca.* 2130 cm^{-1} was recorded, using a Perkin-Elmer ir 521 instrument. Graphical representation of log absorbance *vs.* time showed a linear behavior up to 80% conversion. The first-order rate constants (k_1) were determined from the slopes of the linear plots. Measurements were made at several temperatures and the energies of activation were determined graphically from log k_1 *vs.* $1/T$. The entropies of activation were calculated from the rate constants at 70° using the equation $\Delta S^* = 4.576 \log k_1 (\sec^{-1}) - 49.14 - 4.576 \log T + E_a/T$.

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Pyrolysis and Mass Spectrum of 1-(2-Benzothiazolyl)benzotriazole

Denis C. K. Lin and Don C. DeJongh*

Département de chimie, Université de Montréal, C.P. 6128, Montréal 101, Québec, Canada

It has been reported[1] that the photochemical decomposition of 1-benzylbenzotriazole (1) gives a different result from its pyrolytic[2] and mass spectrometric[3] decompositions. The same behavior has been observed from several 1-substituted benzotriazoles. This difference has been accounted for in terms of the electronic structures of the diradical intermediates formed by the loss of N$_2$.[1] On the other hand, 1-phenylbenzotriazole (2) is an exception. Both the pyrolytic[4] and photolytic[5] decompositions of 2

Scheme I[a]
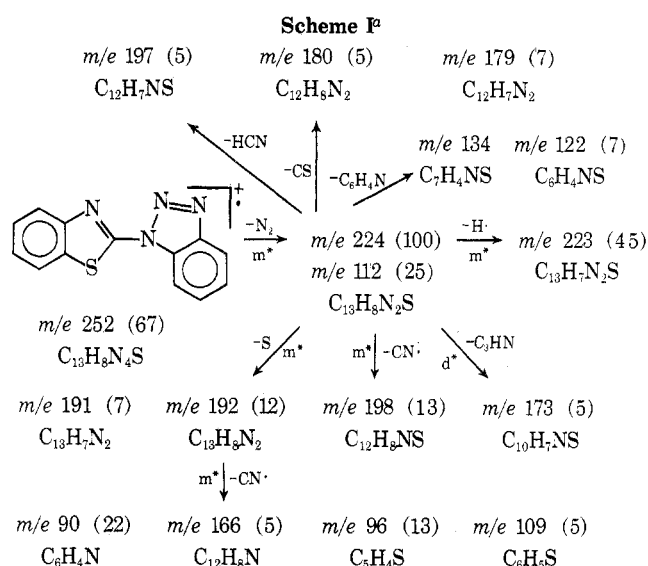

a The elemental compositions are the result of exact-mass measurements. The values in parentheses are relative intensities, and m* denotes the presence of a metastable-ion peak. The symbol d* denotes a metastable-ion peak detected by the operation of the instrument in the defocused mode.

give carbazole (3) almost quantitatively. In fact, the pyrolytic method of Graebe and Ullmann[4] for the preparation of carbazoles from 1-phenylbenzotriazole is of wide application in synthesis. Also, in the 70-eV mass spectrum of 2, the peak at *m/e* 167, from the loss of N$_2$, is the base peak.[3]

1, R = —CH$_2$Ph
2, R = —C$_6$H$_5$
3
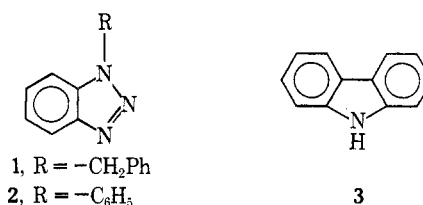
As part of a different study, we recently prepared benzimidazo[2,1-b]benzothiazole (4) from 1-(2-benzothiazolyl)benzotriazole (5), using the photochemical method reported by Hubert (eq 1).[6] Compound 4 is formed in a rel-

5   4
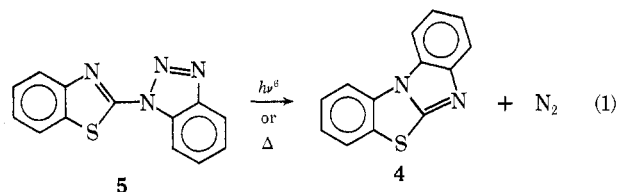
atively good yield, in the order of 20%. During our preparation and characterization of 4, we observed an intense metastable-ion peak in the mass spectrum of 5 for the loss of N$_2$ from the molecular ions. The peak for the (M − N$_2$) ion remains at 8 eV and is the only ion other than the molecular ion found at this ionizing voltage. The photochemical loss of N$_2$ and the loss of N$_2$ observed in the mass spectrum prompted us to study the mass spectrum and pyrolysis of 5 in order to determine whether its behavior resembles the behavior of 1 or that of 2.

The 70-eV mass spectrum of 1-(2-benzothiazolyl)benzotriazole (5) is summarized in Scheme I. At 12 eV, the intensities of the peaks at *m/e* 252 and 224 are approximately equal, and, at 15 eV, the ions found at *m/e* 223, 198, 192, 191, 180, 173, and 134 begin to appear. Since the mass spectrum of 5 is very similar to the mass spectrum of 4, except for the peak at *m/e* 252, we assume that the structure of the ion at *m/e* 224 is the same as that of the