The infrared spectrum (KBr) showed no OH or C=O bands. The nmr spectrum (CS_2) showed peaks at 4.2 ppm from TMS (s, 2.2 H) and a complex multiplet at 1.5 (40.0 H).

2-Ethylhexyl 2-Ethylhexoxyacetate (Expt 3). A mixture of 2-ethylhexanol, 40% glyoxal, and *p*-toluenesulfonic acid (amounts given in Table I) was heated at reflux and water was removed azeotropically. During this operation the head temperature was 90° and the kettle was 155°. After all of the water had been removed the temperature had reached 200° and heating and distillation was continued while a mixture of 2-ethylhexene and di-2-ethylhexyl ether (identified by glpc, mass spectrum, and comparison with authentic samples) was isolated overhead. Continued distillation at reduced pressure gave the product, bp 126–130° (1 mm), $n^{22}D$ 1.4381.

Anal. Calcd for $C_{18}H_{30}O_3$: C, 72.00; H, 12.00; mol wt, 294. Found: C, 72.10; H, 11.93; mol wt, 294 (mass spectrum).

***n*-Butyl Butoxyacetate (Expt 1 and 2).** A mixture of 1-butanol, 40% glyoxal, and acid (amounts and type given in Table I) was heated to reflux and water was removed azeotropically (head 96°, kettle 97°). After all of the water had been removed the distillation was continued at atmospheric pressure, allowing the temperature to rise and reach 140°. During this time olefins and di-*n*-butyl ether (identified by comparison of infrared spectrum) distilled. The temperature of the kettle was maintained at 160–170° for 1 hr and then distillation was continued at reduced pressure to recover the product, bp 95° (10 mm), $n^{25}D$ 1.4234 [lit.[8] bp 113–115° (17.5 mm), $n^{25}D$ 1.4160].

1,1′,2,2′-Tetrakis(benzyloxy)ethane. A mixture of benzyl alcohol (4.0 mol, 432.0 g), 40% aqueous glyoxal (1.0 mol, 145.0 g), 500 ml of benzene, and 2.0 g of *p*-toluenesulfonic acid was charged to a flask equipped with an automatic azeotrope head. The mixture was brought to reflux and water was removed. When no more water came off, the benzene and any other low boilers were removed at reduced pressure (150 mm) and the contents of the reaction flask were allowed to stand overnight at room temperature. The resultant solid crystals were filtered (464.0 g) and recrystallized from 500 ml of heptane. Filtration gave 261.8 g of product, mp 71°. Cooling of the mother liquors gave 89.2 g of additional material. The yield was 77%.

Anal. Calcd for $C_{30}H_{30}O_4$: C, 70.30; H, 6.61. Found: C, 79.49; H, 6.57.

The nmr spectrum (CCl_4) showed peaks at 4.55 (s, 7.8 H), 4.65 (s, 2.3 H), and 7.13 ppm (s, 20.0 H).

Acid-Catalyzed Decompositions of Acetals. A. In a typical reaction, the acetal was introduced to a magnetically stirred reaction flask equipped with a thermometer and a short Vigreux column with a take-off head. The appropriate amount of acid (either *p*-toluenesulfonic or sulfuric) was added and the mixture was heated to reflux. The resulting low-boiling azeotrope of water and organic product was removed until no more came off, or until a maximum yield of glycolate was produced (usually 45–60 min of reaction). The mixture was cooled, neutralized with sodium bicarbonate, and distilled. The products were identified either by mass spectra and glpc, or by isolation and identification in the usual manner (C, H analysis, nmr, and comparison with known physical properties).

B. A mixture of acetal (1.0 mol) and water (4.8 mol) was heated under conditions of temperature and acid shown in Table IV. After 4–5 hr, the reaction mixture was neutralized and analyzed by glpc and mass spectroscopy.

Acknowledgment. We thank Mr. B. E. Wilkes for the mass spectra.

Registry No.—Benzyl alcohol, 100-51-6.

References and Notes

(1) (a) Part V: J. M. Kliegman and R. K. Barnes, *J. Org. Chem.*, **38**, 556 (1973). (b) Address correspondence to this author at GAF Corp., 1361 Alps Rd., Wayne, N. J. 07470.

(2) J. M. Kliegman and R. K. Barnes, *Tetrahedron*, **26**, 2555 (1970).

(3) H. Baganz and K. E. Krüger, *Chem. Ber.*, **87**, 1622 (1954).

(4) F. C. Cook, Union Carbide Corp., unpublished results.

(5) M. S. McElvain, *Chem. Rev.*, **45**, 453 (1949).

(6) Melting and boiling points are uncorrected. Infrared, nmr, and mass spectra were recorded on Perkin-Elmer, Varian A-60A, and AIC MS 9 spectrometers. Elemental analyses were performed by the UCC staff.

(7) W. Reppe, H. Friederich, and O. A. Grosskinsky, German Patent 951,925 (Nov 8, 1956); *Chem. Abstr.*, **53**, 2119 (1959).

(8) R. W. MacNamee and L. G. MacDowell, U. S. Patent 2,366,272 (1945).

Thermal Decomposition and Dehydration of Tri-*tert*-butylcarbinol. Competing Free Radical and Carbonium Ion Reactions

John S. Lomas and Jacques-Emile Dubois*

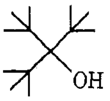
Laboratoire de Chimie Organique Physique de l'Université de Paris VII, associé au Centre National de la Recherche Scientifique, 1, rue Guy de la Brosse, 75005, Paris, France

Received November 26, 1973

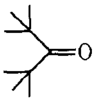
Since its synthesis in 1945, tri-*tert*-butylcarbinol[1] has received little attention, despite widespread interest in steric effects on reactivity. We wish now to report the results of an investigation of the dehydration of this compound in a variety of media, undertaken as part of a continuing study on the reactivity of tertiary alcohols and the synthesis of encumbered olefins.[2-4]

Treatment with hexamethylphosphorus triamide (HMPT) at 215–240° has proved to be a particularly convenient and mild method of dehydrating alcohols (in the sense that little or no rearrangement occurs).[3,5] For secondary alcohols, an E2 mechanism involving alkyl tetramethyldiamidate intermediates has been proposed[5] whereas, for tertiary alcohols and, exceptionally, for di-*tert*-butylcarbinol, a carbonium ion mechanism seems to be operative.[3]

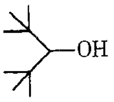
This method fails, however, for the title compound **1**. When samples of **1** in HMPT were heated at temperatures between 180 and 240° (Table I), only hexamethylacetone (**2**) and the corresponding secondary alcohol **3** were obtained, in a ratio which varied from 0.5:1 to 1.2:1 as the temperature was increased. At 240°, alcohol **3** is partially dehydrated with rearrangement to 2,3,4,4-tetramethylpent-1-ene (**4**). Subsequently it was found that alcohol **1** is decomposed when heated *alone* for 5 min at 240°, giving again ketone **2** and alcohol **3** in the ratio 1.5:1. In the presence of α-methylstyrene the product ratio is slightly different (Table II) and two new compounds, identified by nmr, ir, and mass spectroscopy as **5b** and **6**, are obtained in very nearly the same ratio as **2** and **3**. The addition of styrene and of *trans*-β-methylstyrene was also examined; only the corresponding saturated adducts, **5a** and **5c**, could be isolated.



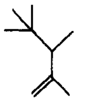
1



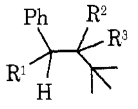
2



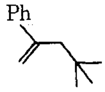
3



4



5a, $R^1 = R^2 = R^3 = H$
b, $R^1 = Me$; $R^2 = R^3 = H$
c, $R^1 = R^2 = H$; $R^3 = Me$



6

Since the same adducts **5** and **6** are formed also in HMPT solution, it is clear that, in HMPT or alone, alcohol **1** reacts by the same *free radical* mechanism. The formation of **2** and **3** would appear to be consistent with the following mechanism for the decomposition of **1**.

$$t\text{-Bu}_3\text{COH} \xrightarrow{\Delta} t\text{-Bu}_2\text{COH}\cdot + t\text{-Bu}\cdot$$

$$2\ t\text{-Bu}_2\text{COH}\cdot \longrightarrow \mathbf{2} + \mathbf{3}$$

$$t\text{-Bu}_2\text{COH}\cdot + t\text{-Bu}\cdot \longrightarrow \mathbf{2} + [C_4H_{10}]$$

$$\text{or}\ t\text{-Bu}_2\text{COH}\cdot + t\text{-Bu}\cdot \longrightarrow \mathbf{3} + [C_4H_8]$$

Table I
Decomposition of 1 in HMPT and DMSO Solutions

Temp, °C	Time, min	HMPT[a] 2	3	4	DMSO[a] 2	3	7	8
180	120	34	62		60	15	3	20
200	60	40	51		69	9	1	4
220	30	44	47					
240	15	45	38	2				

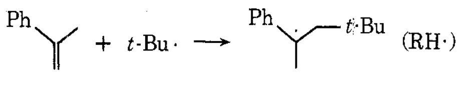
[a] Per cent yields determined by calibration against internal *trans*-decalin.

Table II
Effects of Styrene Additives on the Decomposition of 1

Additive	2:3[a]	2[b]	3[b]	5[b]	6[b]
None	60:40	48	32		
Styrene	73:27	35	16	18	
α-MeS[c]	77:23	51	20	39	14
β-MeS[d]	65:35	38	26	24	

[a] Ratio determined by analytical glpc. [b] Yields obtained by preparative glpc. [c] α-Methylstyrene. [d] *trans*-β-Methylstyrene.

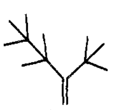
In the presence of α-methylstyrene, for example,

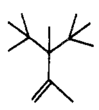


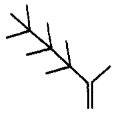
$$t\text{-Bu}_2\text{COH}\cdot + \text{RH}\cdot \longrightarrow \mathbf{2} + \mathbf{5b}$$

$$\text{or } t\text{-Bu}_2\text{COH}\cdot + \text{RH}\cdot \longrightarrow \mathbf{3} + \mathbf{6}$$

For alcohol dehydration in another dipolar aprotic solvent, DMSO, there is evidence for a carbonium ion mechanism,[6] though the way in which the ions are formed is not clear. Attempted dehydration of 1 in DMSO again led to the radical decomposition products in good yields, but in this medium they were accompanied by the expected dehydration products, olefins 7 and 8, in the approximately the same ratio (3 and 20%, respectively, at 180°) as was observed previously[7] in the solvolysis of the *p*-nitrobenzoate (14 and 86%, respectively). At higher temperature the extent of dehydration was smaller.


7


8


9

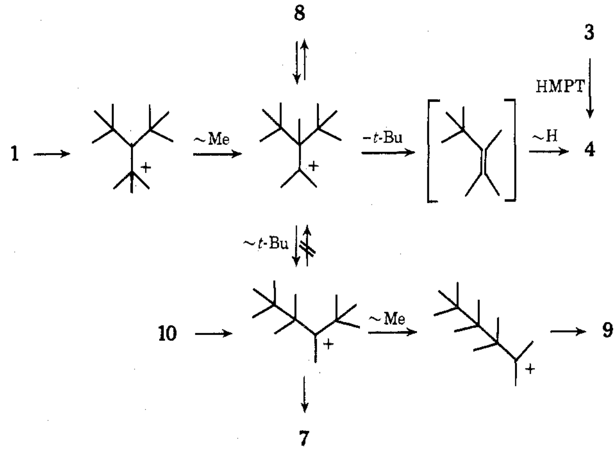
Alcohol 1 therefore reacts by two competing pathways in DMSO. It is evident that the carbonium ion route would be favored by working at even lower temperatures, but the reaction time becomes inconveniently long.

With a view to the isolation of the dehydration products of 1 more conveniently, two other systems which are known to yield carbonium ion intermediates were examined: thionyl chloride-pyridine, which is generally a mild dehydration agent (though it leads to more rearrangement than HMPT),[2,3] and dilute sulfuric acid in anhydrous acetic acid, where extensive carbonium ion rearrangement might be expected.

In the former, the major product 8 (95% of the recovered material) had suffered only the obligatory 1,2-methyl migration which precedes deprotonation of the carbonium ion, the remainder being isomer 7, which is formed by 1,2-methyl migration, 1,2-*tert*-butyl migration, then deprotonation.

Dilute sulfuric acid in acetic acid, on the other hand, gives a complex mixture of products, including 4, 7, 8, and a new isomer, 2,3,3,4,4,5,5-heptamethylhex-1-ene (9) (31, 42, 10, and 7%, respectively, after one alcohol half-life at 25°), in proportions which depend markedly on the duration of the reaction, since olefin 8 undergoes rapid rearrangement to 7 and 9 and fragmentation, principally to 4, in acid media ($k = 1.2 \times 10^{-4}$ sec^{-1} at $H_0 = -1.35$ and 25° whereas for the alcohol under the same conditions $k = 8.3 \times 10^{-5}$ sec^{-1}).

Scheme I



The highly ramified olefin 9 could be obtained pure neither by dehydration of 1 nor by rearrangement of 8. It could, however, be isolated by dehydration of *tert*-butylmethyltriptylcarbinol (10), isomeric with 1. In principle, the carbonium ion generated from 10 can undergo three 1,2-alkyl migrations (see Scheme I) but one of these, 1,2-Me from triptyl, is a degenerate rearrangement[8] and another, 1,2-*t*-Bu from triptyl, is sterically prohibited. Thus, only olefins 7 and 9 are formed in this reaction.

The observation of a free radical mechanism for the thermal decomposition of alcohol 1 requires some comment. It seems reasonable to suggest that relief of steric strain is responsible for the unusual[9] behavior of this compound. The molecular structure of a closely related compound, tri-*tert*-butylmethane,[10] shows marked bond-angle and bond-length deformations due to steric congestion, and molecular mechanics calculations estimate the strain energy to be at least 33.5 kcal/mol. Corresponding effects on the alcohol would be expected to be higher.

Peroxide- and/or radical-induced formation of free radicals from alcohols by hydrogen atom abstraction is a familiar process and the subsequent addition of the alkoxide moiety to olefins is well documented,[11] but, to our knowledge, the free radical decomposition of an alcohol by loss of an alkyl group has not previously been observed.[12]

Experimental Section

Tri-*tert*-butylcarbinol (1) was prepared by the addition of hexamethylacetone to *tert*-butyllithium in ether at −60°. After chromatography on an alumina column in pentane to remove the secondary alcohol 3 and recrystallization from pentane it had mp 113-116° (lit.[1b] mp 113-117°).

Reaction of 1 in HMPT and DMSO. Samples (1 ml) of a solution of 1 (0.25 *M*) and *trans*-decalin (0.16 *M*) in HMPT or DMSO were sealed in Pyrex tubes under argon. After treatment, as indicated in Table I, the contents were analyzed by glpc; product composition was determined by calibration of pure products against *trans*-decalin.

Decomposition of 1 in the Presence of Styrenes. A typical run was as follows. Alcohol 1 (1.0 g, 0.005 mol) and α-methylstyrene (0.59 g, 0.005 mol) were sealed in a Pyrex tube and heated at 235 ± 5° for 10 min. After cooling, the tube was carefully opened and the reaction products were separated by preparative glpc on an Apiezon L column (5% on Chromosorb 60/80, 10 ft × 0.375 in.) at 220° into two fractions (0.72 and 0.55 g, respectively). The first fraction, containing 2, 3, and residual α-methylstyrene, was reinjected 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_2SO_4–HOAc (0.33% v/v) was followed by glpc. Samples (0.2 ml) were quenched in saturated Na_2CO_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_2SO_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_2SO_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.

References and Notes

(1) (a) P. D. Bartlett and A. Schneider, *J. Amer. Chem. Soc.*, **67**, 141 (1945); (b) P. D. Bartlett and E. B. Lefferts, *ibid.*, **77**, 2804 (1955).

(2) J. S. Lomas, D. S. Sagatys, and J. E. Dubois, *Tetrahedron Lett.*, 599 (1971).

(3) J. S. Lomas, D. S. Sagatys, and J. E. Dubois, *Tetrahedron Lett.*, 165 (1972).

(4) J. E. Dubois and J. S. Lomas, *Tetrahedron Lett.*, 1791 (1973).

(5) R. S. Monson, *Tetrahedron Lett.*, 567 (1971); *J. Org. Chem.*, **36**, 3826 (1971).

(6) V. J. Traynelis, W. L. Hergenrother, J. R. Livingston, and J. A. Valicenti, *J. Org. Chem.*, **27**, 2377 (1962).

(7) P. D. Bartlett and T. T. Tidwell, *J. Amer. Chem. Soc.*, **90**, 4421 (1968).

(8) R. E. Leone and P. v. R. Schleyer, *Angew. Chem., Int. Ed. Engl.*, **9**, 860 (1970).

(9) For comparison di-*tert*-butylneopentylcarbinol is dehydrated normally, if slowly, in refluxing HMPT[3] and is recovered almost (5–10% fragmentation) unchanged after heating alone at 240° for 2 hr.

(10) H. B. Burgi and L. S. Bartell, *J. Amer. Chem. Soc.*, **94**, 5236 (1972); L. S. Bartell and H. B. Burgi, *ibid.*, **94**, 5239 (1972).

(11) (a) C. Walling and E. S. Huyser, *Org. React.*, **13**, 91 (1963); (b) W. G. Lloyd, *Chem. Technol.*, 687 (1971).

(12) A referee has suggested that thermal decomposition of **1** could proceed *via* an ionic mechanism analogous to that for alkoxide cleavage: H. D. Zook, J. March, and D. E. Smith, *J. Amer. Chem. Soc.*, **81**, 1617 (1959). However, alkoxide cleavage leads only to ketones and alkanes except when a radical reaction occurs: D. J. Cram, A. Langemann, W. Lwowski, and K. R. Kopecky, *ibid.*, **81**, 5760 (1959).

(13) P. D. Bartlett and M. Stiles, *J. Amer. Chem. Soc.*, **77**, 2806 (1955).

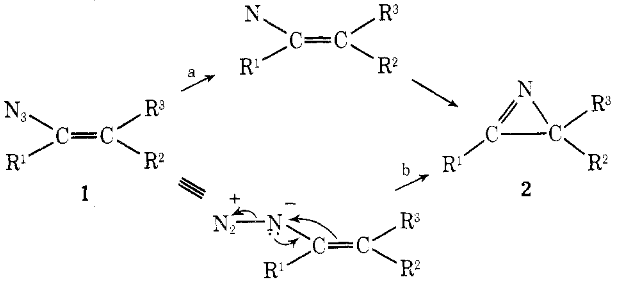
On the Mechanism of the Thermal Decomposition of Vinyl Azides

Gerrit L'abbé* and Georges Mathys

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

Received February 22, 1974

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-