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 At several time intervals aliquots were withdrawn from the reaction vessel, cooled to 0°, and analyzed.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 $\Delta S^* = 4.576 \log k_1 (sec^{-1}) - 49.14 - 4.576 \log T + E_a/T$.

Acknowledgment. The authors are indebted to the IWONL (Belgium) for a fellowship to one of them (G. M.).

Registry No.—3, 2032-04-4.

References and Notes

(1) G. Smolinsky and C. A. Pryde in "The Chemistry of the Azido Group," S. Patai, Ed., Interscience, New York, N. Y., 1971, p 555.
(2) G. L'abbé, *Chem. Ind. (London)*, 278 (1971).
(3) G. L'abbé, *Chem. Rev.*, **68**, 345 (1968).
(4) P. A. S. Smith, J. H. Hall, and R. O. Kan, *J. Amer. Chem. Soc.*, **84**, 485 (1962).
(5) (a) L. K. Dyall and J. E. Kemp, *J. Chem. Soc. B*, 976 (1968), and references cited therein; R. A. Abramovitch and E. P. Kyba in "The Chemistry of the Azido Group," S. Patai, Ed., Interscience, New York, N. Y., 1971, p 221. (b) Recently, M. Komatsu, S. Ichijima, Y. Ohshiro, and T. Agawa, *J. Org. Chem.*, **38**, 4341 (1973), favored a nitrene mechanism for the conversion **1** → **2**. However, with the recognition that azirines might exist in (small) equilibrium with vinyl nitrenes, no evidence was advanced by the authors to substantiate their conclusion.
(6) G. Smolinsky, *J. Org. Chem.*, **27**, 3557 (1962).
(7) F. D. Lewis and W. H. Saunders in "Nitrenes," W. Lwowski, Ed., Interscience, New York, N. Y., 1970, p 47.
(8) J. S. Meek and J. S. Fowler, *J. Amer. Chem. Soc.*, **89**, 1967 (1967); *J. Org. Chem.*, **33**, 985 (1968).
(9) J. L. Brewbaker and H. Hart, *J. Amer. Chem. Soc.*, **91**, 711 (1969).
(10) S. Maiorana, *Ann. Chim. (Rome)*, **56**, 1531 (1966); A. N. Nesmeyanov and M. I. Rybinskaya, *Dokl. Akad. Nauk SSSR*, **170** 600 (1966); *Proc. Acad. Sci. USSR*, **170**, 916 (1966); F. W. Fowler, A. Hassner, and L. A. Levy, *J. Amer. Chem. Soc.*, **89**, 2077 (1967); A. Hassner and F. W. Fowler, *J. Org. Chem.*, **33**, 2686 (1968); A. Hassner and F. Boerwinkle, *J. Amer. Chem. Soc.*, **90**, 216 (1968); A. Hassner, G. L'abbé, and M. J. Miller, *J. Amer. Chem. Soc.*, **93**, 981 (1971).

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

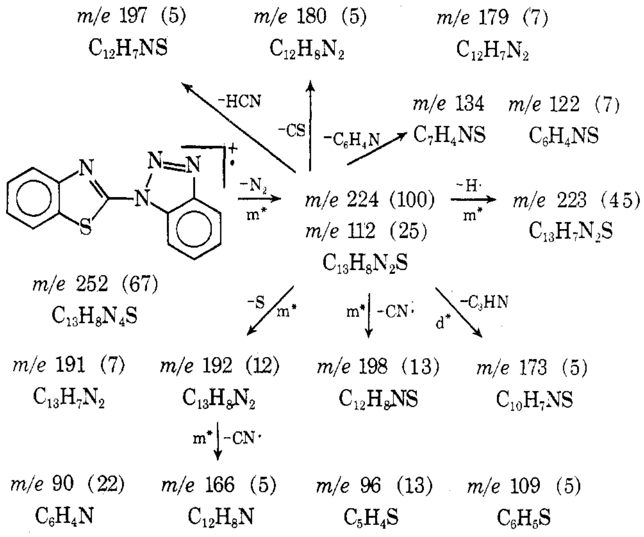
Denis C. K. Lin and Don C. DeJongh*

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

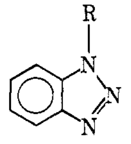
Received February 7, 1974

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 benzothiazoles. 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** 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]

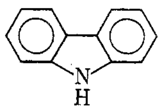
Scheme I[a]



[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.

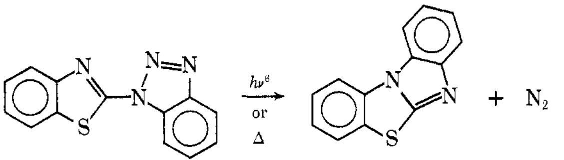


1, R = $-CH_2Ph$
2, R = $-C_6H_5$



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 relatively 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**.



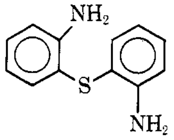
(1)

5 **4**

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 molecular ions of **4**, and that the fragment ions originate from the ion found at *m/e* 224.

Small molecules and radicals are lost from the ion at *m/e* 224, *viz.*, CS, H·, S, CN·, HCN, etc. The loss of C_3HN (possibly propynonitrile) is difficult to explain, but a metastable ion is found to confirm this transition. The major portion of the ion current is composed of ions of *m/e* 252, 224, and 223.

The only pyrolysis of **5** which has previously been reported was done in polyphosphoric acid.[6] In this case, *o,o'*-diaminodiphenyl sulfide (**6**) was the product. The formation of **6** under these conditions would require a process more complicated than a loss of N_2 followed by ring closure to **4**. In our system, compounds are pyrolyzed at short contact times in the gas phase.[7,8] We thought we would be more likely to obtain primary pyrolysis products with this system. Pyrolyses of **5** were performed by sublimation of **5** into a stream of N_2 which passed through an unpacked quartz tube surrounded by a 12-in. furnace. Products were trapped in a series of cooled traps and identified by physical as well as spectroscopic methods.

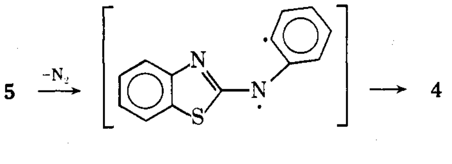


6

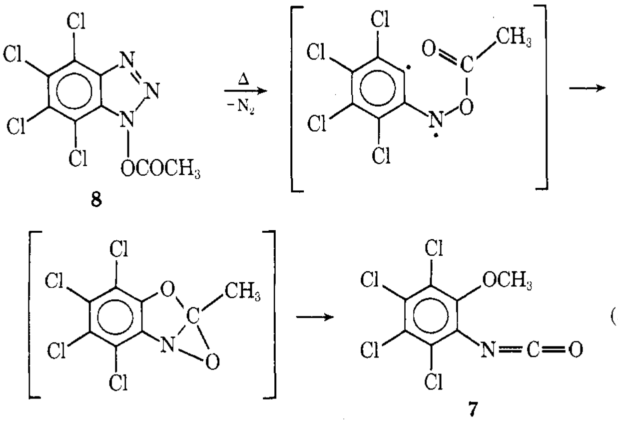
We pyrolyzed **5** at 750°, and, upon working up the trapped materials, we were able to isolate only one product. Comparison of this product with **4** prepared by a published procedure[6] showed that benzimidazo[2,1-*b*]benzothiazole (**4**) was formed in 42–46% yield. Traces of minor products were present but in such minute quantities that they were scarcely detectable and were not characterized.

This facile pyrolytic loss of N_2 is in agreement with the fact that N_2 is readily and exclusively lost from **5** upon photolysis and electron impact. It seems likely that primary pyrolysis products are not observed in the pyrolysis in polyphosphoric acid.

Thus, we find that **5** behaves in a similar manner as **2**: N_2 is lost and the diradical closes to give the final product (eq 2). We have no evidence to confirm whether or not the electronic structures of the intermediate are the same in the pyrolytic and photolytic reactions. The behavior of **1** has been rationalized by proposing that the ground-state diradical formed upon pyrolysis cyclizes, whereas the diradical produced upon irradiation is either an excited singlet or triplet state and abstracts a hydrogen atom intramolecularly or from a solvent cage.[1]



(2)



(3)

An intermediate similar to the one in eq 2 has been proposed to explain the formation upon pyrolysis of 2-methoxy-3,4,5,6-tetrachlorophenyl isocyanate (**7**) from 1-acetoxy-4,5,6,7-tetrachlorobenzotriazole (**8**), eq 3.[9] Labeling with oxygen-18 proved that the carbonyl oxygen ends up attached to the aromatic ring. The formation of **7** requires a methyl migration from the original carbonyl carbon to the final ether oxygen. This experiment provides a close precedent for the intramolecular trapping of the diradical intermediate shown in eq 2.

Experimental Section

Spectra. Infrared spectra were recorded with a Beckman IR-8 spectrometer and a Perkin-Elmer Infracord. Ultraviolet spectra (1-cm path) were determined on a Bausch and Lamb Spectronic 505. Low-resolution mass spectra were obtained from a Hitachi RMU-6D mass spectrometer. Electron-voltage readings were taken directly from the dial since more precise values were not needed. Exact-mass data were obtained from an AEI MS-902 mass spectrometer linked to a PDP-8 computer. All experimental values agreed with the calculated values within ±0.002 mass units. Metastable ions were observed in the low-resolution spectra and, in certain cases, sought with the AEI MS-902 spectrometer operating in the defocused mode.

1-(2-Benzothiazolyl)benzotriazole (5). Compound **5** was prepared from benzotriazole (Aldrich) by the method of Orth and Soedigdo;[10] yield of **5**, 34%; mp 174° (lit.[10] mp 174°). *Anal.*[11] Calcd for $C_{13}H_8N_4S$: C, 61.89; H, 3.19; N, 22.21; S, 12.71. Found: C, 61.68; H, 3.33; N, 22.36; S, 13.05.

Benzimidazo[2,1-*b*]benzothiazole (4). Compound **4** was prepared from **5** (1 g) as described by Hubert,[6] using a 450-W high-pressure Hg lamp: yield 0.17 g (18%); λ_{max} (EtOH) 300, 291, 283, 263 sh, 242, and 222 nm. *Anal.* Calcd for $C_{13}H_8N_2S$, *m/e* 224.0408. Found: 224.0405.

Pyrolysis. The pyrolysis apparatus and procedure have been described previously.[7,8] Sample sizes of 0.71 and 0.83 g of **5** were used. The sample was sublimed ino a stream of N_2 (flow rate 0.20–0.25 l./min; system pressure, 0.5–2.7 Torr). The quartz tube was heated to 750°. The pyrolysis products were condensed in three cold traps in series. The first one was air-cooled while the other two were cooled by liquid N_2. The traps and the quartz tube were washed with acetone and chloroform. The solution was made up to 25 ml in a volumetric flask for analysis. Thin-layer chromatography showed one spot with the same R_f value as compound **4**, prepared as previously described.[6] Gas chromatography, using a 6-ft column of 10% SE-54 on Chromosorb G in a Hewlett-Packard 5752B Research chromatograph with a thermal conductivity detector, with the temperature programmed from 100 to 265° (hold) at 10°/min, showed only one major peak which had a retention time identical with that of compound **4**. There were some other extremely small bumps on the gas chromatogram, but no attempts were made to identify them. The major pyrolysis product was collected and showed identical uv, ir, nmr, and mass spectra as compound **4**. The yields of **4** from **5** were estimated by uv spectroscopy, 42 and 46%.

Acknowledgments. We would like to thank the National Research Council of Canada for financial support. Also, we would like to thank Mr. A. S. Blair for assistance in obtaining the high-resolution mass spectra and Professor D. Gravel for use of photolysis equipment.

Registry No.—**4**, 206-80-4; **5**, 5499-59-2.

References and Notes

(1) K. Tsujimoto, M. Ohashi, and T. Yonezawa, *Bull. Chem. Soc. Jap.* **45**, 515 (1972).
(2) M. S. Gibson, *J. Chem. Soc.*, 1076 (1956).
(3) M. Ohashi, K. Tsujimoto, A. Yoshino, and T. Yonezawa, *Org. Mass Spectrom.*, **4**, 203 (1970).
(4) C. Graebe and F. Ullmann, *Justus Liebigs Ann. Chem.*, **291**, 16 (1896).
(5) E. M. Burgess, R. Carithers, and L. McCullagh, *J. Amer. Chem. Soc.*, **90**, 1923 (1968).
(6) A. J. Hubert, *J. Chem. Soc. C*, 1334 (1969).
(7) D. C. DeJongh, D. C. K. Lin, and M. L. Thomson in "Advances in

Mass Spectrometry," Vol. 6, A. R. West, Ed., Applied Science Publishers, Barking, Essex, England, 1974, Chapter 12.
(8) M. L. Thomson and D. C. DeJongh, *Can. J. Chem.*, **51**, 3313 (1973).
(9) N. J. Leonard and K. Golankiewicz, *J. Org. Chem.* **34**, 359 (1969).
(10) R. E. Orth and S. Soedigdo, *J. Heterocycl. Chem.*, **2**, 486 (1965).
(11) Analyses were performed by Midwest Microlab, Inc., Indianapolis, Ind.

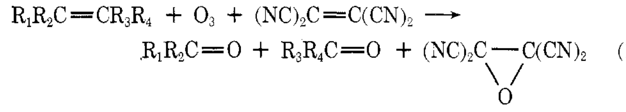
Ozonation of Acetylenes and Related Compounds in the Presence of Tetracyanoethylene and Pinacolone

Nien-chu C. Yang* and Jacqueline Libman

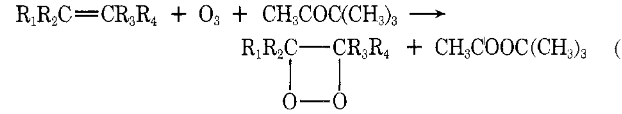
Department of Chemistry, University of Chicago, Chicago, Illinois 60637

Received October 2, 1973

The ozonation of olefins has been a subject of continuing research interest because of its application in degradative and synthetic chemistry.[1,2] Contributions from many laboratories have led to a better understanding of its reaction pathway.[1-3] The ozonation of acetylenes, on the other hand, has received only limited attention.[4-9] The reaction has been suggested to proceed *via* an analogus pathway to the ozonation of olefins.[2,5] Derivatives of carboxylic acids and α-dicarbonyl compounds have been obtained among the reaction products, and α-diketones have been isolated in moderate yields (30–60%) when ozonated acetylenes were reduced immediately with sodium iodide.[5] Contributions from Criegee's laboratory demonstrated that olefins were smoothly cleaved by ozone in the presence of tetracyanoethylene (TCNE) to give carbonyl compounds in good yields (reaction 1).[10] Later work by Story suggested that ozonation of olefins in pinacolone yielded dioxetanes which could give carbonyl compounds upon decomposition (reaction 2).[11] In order to gain more insight into the action of ozone on acetylenes and to devise a more efficient method for the conversion of acetylenes to α-diketones, the ozonation of acetylenes in the presence of TCNE or pinacolone as the *in situ* reducing agents was investigated. In addition, the ozonation of several olefins in the presence of TCNE was also studied.


(1)

$$R_1R_2C{=}CR_3R_4 + O_3 + (NC)_2C{=}C(CN)_2 \longrightarrow R_1R_2C{=}O + R_3R_4C{=}O + (NC)_2C\overset{O}{\frown}C(CN)_2 \quad (1)$$


(2)

$$R_1R_2C{=}CR_3R_4 + O_3 + CH_3COC(CH_3)_3 \longrightarrow R_1R_2C(O)-(O)CR_3R_4 + CH_3COOC(CH_3)_3 \quad (2)$$

Experimental Section

Diphenylacetylene, phenylacetylene, TCNE, 9-bromofluorene, and 2-adamantanone were purchased from Aldrich Chemical Co., 5-decyne and 1-phenyl-1-butyne from Farchan Chemical Co., and pinacolone from Chemical Sample Co. They were used as received. Bis(fluorenylidene) was prepared from 9-bromofluorene[12] and bis(adamantylidene) from 2-adamantanone[13] according to known procedures. Silica gel (Woelm) was purchased from the Waters Associates. Solvents used were reagent grade. Melting points given were not corrected.

General Procedure. Ozone (2%) in oxygen was generated in a laboratory ozonator.[14] The flow rate was approximately 200 ml/min. The reaction mixture was kept at low temperature with a Dry Ice–acetone bath. The temperature given was that of the reaction mixture. The ozonation was continued until the solution turned light blue indicating the presence of unreacted ozone. At this point, the reaction was 80–100% complete depending on the acetylene used. Diphenylacetylene was qualitatively less reactive than the other acetylenes. Since acetylenes are less reactive than olefins, unreacted ozone which passed through the solution to turn an aqueous solution of KI to a brown color was not a good indication for the conclusion of this reaction. TCNE epoxide was readily isolable from the reaction mixture owing to its low solubility (56–66%), and no attempt was made to optimize its yield. Also no attempt was made to demonstrate the presence of *tert*-butyl acetate in the ozonation of acetylenes in pinacolone.

Benzil, benzoic acid, 9-fluorenone, 2-adamantanone, and bis(adamantylidene) epoxide[15] were identified by comparison with the respective authentic sample. Phenylglyoxal, bp 73–77° (5 mm), was identified as 2-phenylquinoxaline, mp 74–76° (lit. mp 76–77°),[16] 1-phenylbuta-1,2-dione as its dioxime, mp 207–210° (lit. mp 215–216°),[17] and deca-5,6-dione as its bis(phenylhydrazone), mp 127–129° (lit. mp 127°).[18]

The procedure is illustrated by the ozonization of 1-phenyl-1-butyne below and the results are summarized in Table I.

Ozonation of 1-Phenyl-1-butyne (1c). A solution of **1c** (1.3 g, 10 mmol) in 20 ml of ethyl acetate containing an equivalent amount of TCNE (1.28 g, 10 mmol) was kept at −78° with a Dry Ice–acetone bath and treated with ozone until the solution turned a light blue color. After the solution had been warmed up to room temperature, TCNE epoxide was removed by filtration (830 mg, 59%). The filtrate was evaporated and the residue was chromatographed on silica gel (activity II). 1-Phenylbuta-1,2-dione (1.14 g) was isolated in 71% yield.

A solution of **1c** (1.3 g, 10 mmol) in pinacolone (10 ml) was cooled to −45° in a Dry Ice–acetone bath and treated with ozone. After the conclusion of the reaction, the solution was evaporated and the residue was chromatographed over silica gel. Benzoic acid (920 mg) was isolated in 75% yield and a fraction (430 mg) containing about 60% of 1-phenylbuta-1,2-dione (by nmr) was also isolated. Pure 1-phenylbuta-1,2-dione may be isolated from that fraction by vpc on a 10% SF-96 on Chromosorb column (5 ft × 0.25 in., 140°).

In a separate experiment, a solution of **1c** (10 mmol) in 20 ml of pinacolone was ozonated under similar conditions. The crude reaction mixture exhibited ir frequencies at 1780 and 1730 cm^{-1}, indicating the presence of acid anhydrides.[19] The mixture was then treated with aniline (980 mg, 10 mmol) and was allowed to remain at 23° for 1 hr. The whole mixture was then chromatographed on silica gel (activity IV). From this chromatography, an earlier fraction containing 1-phenylbuta-1,2-dione (4%), benzanilide [80 mg, 4%, mp 160–162° (lit. mp 161°)],[20] benzoic acid (290 mg, 24%), and propionanilide [536 mg, 36%, mp 105–106° (lit. mp 103°)][20] were isolated.

Another sample of **1c** was ozonated in an equivolume mixture of pinacolone and ethyl acetate at −78° and 9,10-diphenylethynylanthracene was added to the reaction mixture after the ozonation. Chemiluminescence similar to the fluorescence of the fluorescer added was observed when the solution was warmed to room temperature.

Ozonation of Ethylidenecyclohexane. A solution of ethylidenecyclohexane (550 mg, 5 mmol) in ethyl acetate (20 ml) containing an equivalent amount of TCNE (640 mg, 5 mmol) was ozonated at − 78°. After the reaction, vpc analysis of the mixture (20% Carbowax 20M on Chromosorb P, 15 ft × 0.25 in., 120°) revealed the presence of both acetaldehyde and cyclohexanone. The mixture was distilled at 0.5 mm and −20° to give a distillate which was chemiluminescent upon heating and a residue. TCNE epoxide (370 mg, 51%) was isolated from the residue by washing it with dichloromethane. The distillate was redistilled at 5 mm and −20° to give a nonchemiluminescent distillate which contained acetaldehyde but no cyclohexanone by vpc analysis and a chemiluminescent residue which contained no acetaldehyde but cyclohexanone by vpc analysis.

Discussion

Ozonation of acetylenes has been suggested to proceed *via* the following pathways, and the presence of A as an intermediate is supported by spectroscopic evidence at −40°.[6,9]

Our results indicate that ozonation of acetylenes in the presence of TCNE yields α-dicarbonyl compounds in good to excellent yields while the ozonation in the presence of pinacolone yields acid anhydrides or acid derivatives as the major products (Table I). At −78°, acetylenic solutions containing TCNE turn yellow instantaneously when ozonated while those containing pinacolone do not. There-