Then, with the assumption that the isotope effects for methyl and methylene groups are the same

$$k_H^m/k_{\gamma\text{-}d_4}^m = (R_D^H)^2 \quad \text{(i)}$$

because there are two deuterated methylene groups not migrating in this part of the reaction of the γ-d_4 compound and

$$k_H^r/k_{\gamma\text{-}d_4}^r = (R_D^H)(R_H^D) \quad \text{(j)}$$

because for ring expansion in the γ-d_4 compound one CD_2 group migrates and one does not migrate. Thus,

$$k_H/k_{\gamma\text{-}d_4} = 1/[(a/(R_D^H)^2) + (b/(R_D^H)(R_H^D))] = (R_D^H)^2R_H^D/(aR_H^D + bR_D^H) \quad \text{(k)}$$

In one assumes that the isotope effects are the same *per D* in methyl and methylene groups, the last equation becomes

$$k_H/k_{\gamma\text{-}d_4} = (R_D^H)^{4/3}(R_H^D)^{2/3}/[a(R_H^D)^{2/3} + b(R_D^H)^{2/3}] \quad \text{(l)}$$

Acid-Catalyzed Decomposition of Trialkyltriazenes: Protected Alkyldiazonium Ions

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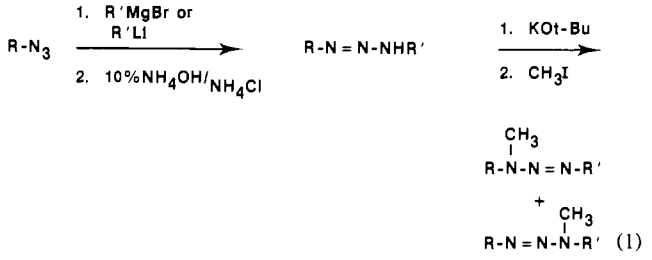
Contribution from the Chemical Carcinogenesis Program, Frederick Cancer Research Center, Frederick, Maryland 21701. *Received June 23, 1980*

Abstract: The acid-catalyzed decomposition of 1,3-di-*n*-butyl-3-methyltriazene and the synthesis and decomposition of 1,3-bis(cyclopropylcarbinyl)-3-methyltriazene are reported. A kinetic study of the acid-catalyzed decomposition of 1,3-di-*n*-butyl-3-methyltriazene indicates that the reaction is subject to general acid catalysis. The rates of reaction have been studied by monitoring the disappearance of a triazene UV absorption band (263 nm). A plot of the buffer concentration vs. k_{obsd} was a straight line, whose slope gave $k_{cat} = 1.84 \times 10^{-2}$ min^{-1} M^{-1}. A linear dependence of the log (k_{obsd}) on pH (6.9-8.4) was observed, along with a solvent isotope effect (k_D/k_H) of 2.05. The products of the decomposition of the butyltriazene (*n*-butyl and *sec*-butyl alcohols and 1- and 2-butene) were accounted for by the intermediacy of a diazonium ion. The mechanism was corroborated by the product analysis of the decomposition of the (cyclopropylcarbinyl)triazene. The alcoholic products isolated were cyclopropylcarbinyl alcohol (48%), cyclobutyl alcohol (48%) and 3-buten-1-ol (4%). This distribution is conclusive evidence that these trialkyltriazenes decompose in aqueous media to produce alkyldiazonium ions or directly to produce carbonium ions in cases where the alkyl group is capable of stabilizing a positive charge.

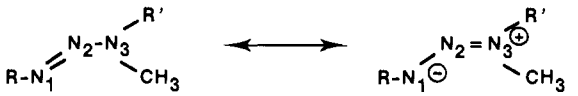
Introduction

The chemistry of trialkyltriazenes is relatively unknown since only a few isolated instances of preparation of these substances exist in the literature.[1-5] We recently reported[6] a general, high-yield synthesis of this class of compounds starting from alkyl azides (eq 1). Some properties of trialkyltriazenes are similar



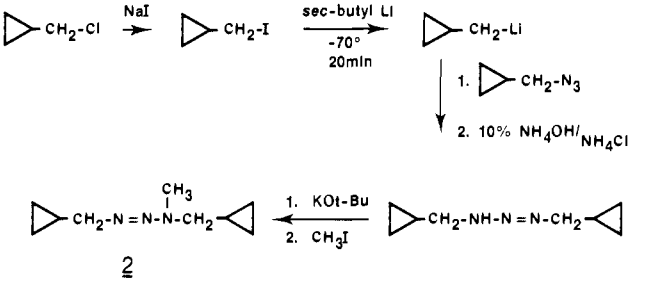
(1)

to their better known analogues, the aryldialkyltriazenes, including a barrier to rotation about the N(2)-N(3) bond,[6]



the magnitude of which was calculated to be around 10.5-11.5 kcal/mol, about 3 kcal/mol lower than that of the aryl analogues. Trialkyltriazenes were also found to be extremely acid sensitive, decomposing rapidly with the evolution of nitrogen. Their lack of reactivity toward alkylating agents such as methyl iodide, dimethyl sulfate, and methyl fluorosulfonate mirror the behavior of 1-phenyl-3,3-dimethyltriazene.

Scheme I



The intermediacy of the alkyldiazonium ion in the acid-catalyzed decomposition of alkylaryltriazenes and in the nitrous acid deamination of primary amines has been the subject of extensive research.[7-10] The decomposition of RNNNHPh in aqueous acids is known to give ROH, N_2, and $PhNH_2$ as products,[8-10] and it is known that the decomposition of alkylphenyltriazenes in HX-H_2O proceeds by an ionic mechanism.[8-10] In the absence of HX, decomposition in media such as H_2O-CH_3OH or H_2O-C_6H_6 was

(1) (a) Gale, D. M.; Middleton, W. J.; Krespan, C. G. *J. Am. Chem. Soc.* **1965**, *87*, 657-658. (b) *Ibid.* **1966**, *88*, 3617-3623.
(2) Atherton, J. H.; Fields, R. *J. Chem. Soc. C* **1968**, 2276-2278.
(3) Makarov, S. P.; Yakubovich, A. Ya.; Englin, M. A.; Nikiforova, T. Ya. *Zh. Obshch. Khim.* **1968**, *38* (4), 709-715.
(4) Kirmse, W.; Baron, W. J.; Seipp, U. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 994-998.
(5) Kirmse, W.; Seipp, U. *Chem. Ber.* **1974**, *107*, (3), 745-758.
(6) Sieh, D. H.; Wilbur, D. J.; Michejda, C. J. *J. Am. Chem. Soc.* **1980**, *102*, 3883-3887.
(7) Zollinger, H. "Azo and Diazo Chemistry"; Interscience: New York, 1961; Chapter 8.
(8) Dimroth, O. *Ber. Dtsch. Chem. Ges.* **1905**, *38*, 670-673.
(9) Lee, C. C.; Ko, E. C. F. *Can. J. Chem.* **1976**, *54*, 3041-3044.
(10) Andakushkin, V. Ya.; Dolgoplosk, B. A.; Radchenko, I. I. *Zh. Obshch. Khim.* **1956**, *26*, 2972-2975.

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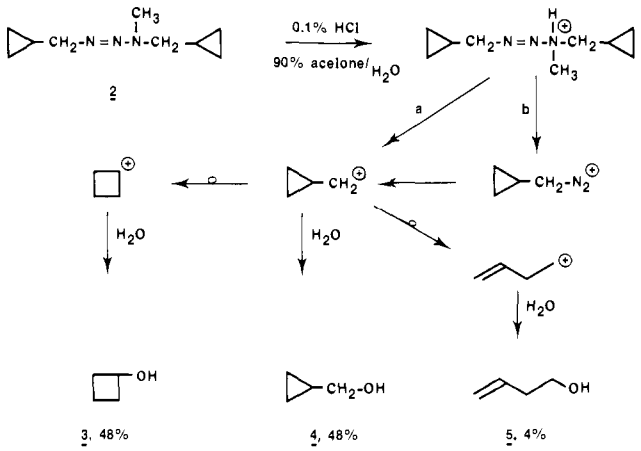
Scheme II



shown to proceed by a similar mechanism and not by involvement of radicals.[11] It was therefore of interest to study the acid-catalyzed decomposition of some selected trialkyltriazenes and compare these results to published data.

Results and Discussion

Synthesis of Trialkyltriazenes. 1,3-Di-*n*-butyl-3-methyltriazene (**1**, eq 1, R = R′ = *n*-butyl) was prepared in a straightforward manner following the procedure discovered in this laboratory.[6] The preparation of 1,3-bis(cyclopropylcarbinyl)-3-methyltriazene (**2**) was more difficult. It was necessary to prepare (cyclopropylcarbinyl)lithium and then react it with cyclopropylcarbinyl azide. The resulting 1,3-bis(cyclopropylcarbinyl)triazene was methylated by the procedure developed previously.[6] As can be seen from Scheme I, the lithiated compound was prepared by an exchange reaction between cyclopropylcarbinyl iodide and *sec*-butyllithium according to the procedure developed by Lansbury et al.[12] The lithium compound was treated with cyclopropylcarbinyl azide at -70 °C. After methylation by the procedure developed previously,[6] triazene **2** was isolated and purified by column chromatograph on alumina. The crude triazene was contaminated with small amounts (<5%) of two other triazenes, probably 1-(cyclopropylcarbinyl)-3-*sec*-butyl-3-methyltriazene and 1-*sec*-butyl-3-(cyclopropylcarbinyl)-3-methyltriazene which were formed because of the incomplete exchange of the *sec*-butyllithium with the cyclopropylcarbinyl iodide. Both of these eluted off the column after the desired triazene.

Acid-Catalyzed Decompositions. The acid-catalyzed decomposition of **1** and **2** was effected at room temperature with 1 equiv of 0.1% HCl in 90% aqueous acetone.[9] When **1** was decomposed according to the above conditions, two alcoholic products (*n*-butyl alcohol (68%), *sec*-butyl alcohol (32%)) were isolated along with the corresponding amine. These products are consistent with the decomposition via the diazonium ion, which can be trapped by solvent to afford *n*-butyl alcohol or can rearrange to the *sec*-butyl cation followed by trapping with solvent.

When **2** was decomposed according to the above conditions, three isomeric alcohols were isolated. These isomeric alcohols are consistent with the mechanism shown in Scheme II. The distribution of products **3**, **4**, and **5** was precisely the same as the distribution found by Roberts and Mazur[13] in the nitrous acid deamination of cyclobutylamine or (cyclopropylcarbinyl)amine. These product analyses lead to the conclusion that trialkyltriazene decomposition proceeds via the alkyldiazonium ion when the alkyl group is a primary one or directly to carbonium ions when the alkyl group is capable of stabilizing a positive charge. Further corroboration of this mechanism followed our observation that when 3-benzyl-1,3-dimethyltriazene was decomposed in presence of benzoic acid, there was a quantitative production of methyl benzoate.

Table I. Observed First-Order Rate Constants for the Disappearance of 1,3-Di-*n*-butyl-3-methyltriazene from pH 6.9 to 8.3 in Water at 22 °C

pH[a]	rate constant k_{obsd},[b] min^{-1}	$t_{1/2}$, min
6.9	$1.37 \pm 0.09 \times 10^{-2}$	49
7.4	$8.08 \pm 0.87 \times 10^{-3}$	86
7.8	$5.27 \pm 0.32 \times 10^{-3}$	129
8.3	$2.87 \pm 0.26 \times 10^{-3}$	243

[a] Disodium hydrogen phosphate-sodium hydrogen phosphate buffer system was used with concentration kept constant at 0.5 M. [b] Average of three determinations.

Table II. Influence of Phosphate Buffer Concentration[a] on the Rate of Decomposition of 1,3-Di-*n*-butyl-3-methyltriazene[b] at pH 7.4 in Water at 22 °C

[buffer], M	rate constant k_{obsd},[c] min^{-1}	$t_{1/2}$, min
0.05	$4.39 \pm 0.36 \times 10^{-4}$	1599
0.10	$1.43 \pm 0.08 \times 10^{-3}$	482
0.25	$3.63 \pm 0.42 \times 10^{-3}$	195
0.50	$8.79 \pm 0.56 \times 10^{-3}$	83

[a] Ionic strength held constant at 0.75 M with KCl. [b] Initial concentration 5×10^{-5}. [c] Average of three determinations.

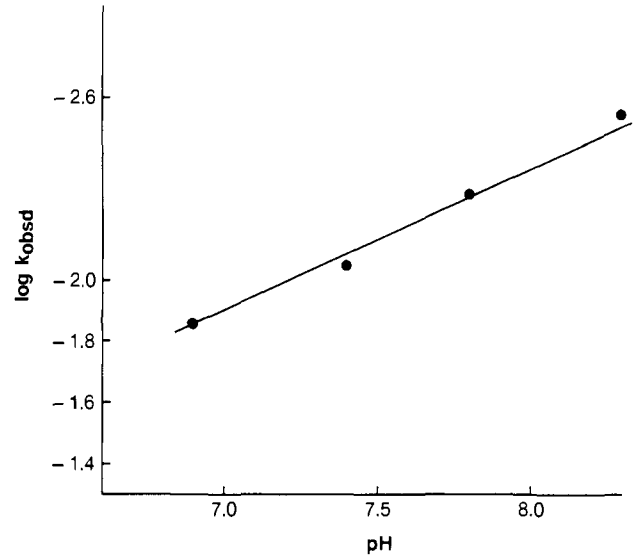


Figure 1. Relationship between the logarithms of the observed first-order rate constants for the disappearance of 1,3-di-*n*-butyl-3-methyltriazene and the pH of the solution.

General Acid Catalysis of 1. The acid-catalyzed decomposition of **1** was followed by monitoring the disappearance of the UV absorption maximum at 263 nm. The observation that **1** decomposed upon standing in a water solution prompted the kinetics to be studied in the pH 6.9–8.3 range. The decomposition of **1** yields *n*-butyl alcohol (UV cutoff at 260 nm) so that an accurate determination of A_∞ was not possible. Nevertheless, the rates of disappearance of the trialkyltriazene can be measured accurately for at least 3 half-lives.

The decomposition reaction of **1** is a first-order process from pH 6.9 to pH 8.3.[14] The rate constants are summarized in Table I. The data indicate that the rate of disappearance of **1** is directly proportional to the acid strength in this pH range. The relationship between the logarithms of the observed first-order rate constants and pH is shown in Figure 1.

The influence of buffer concentration on the rate of decomposition is summarized in Table II. The rate of disappearance

(11) Lee, C. C.; Reichle, R.; Weber, U. *Can J. Chem.* **1978**, *56*, 658–662.
(12) Lansbury, P. T.; Pattison, V. A.; Clement, W. A.; Sider, D. *J. Am. Chem. Soc.* **1964**, *86*, 2247–2251.
(13) Roberts, J. D.; Mazur, R. H. *J. Am. Chem. Soc.* **1951**, *73*, 2509–2520.
(14) At pH above 8.5, the solubility of the triazene in the aqueous medium was drastically reduced, and at pH's below 6.9, the decomposition became too rapid to measure by our techniques.

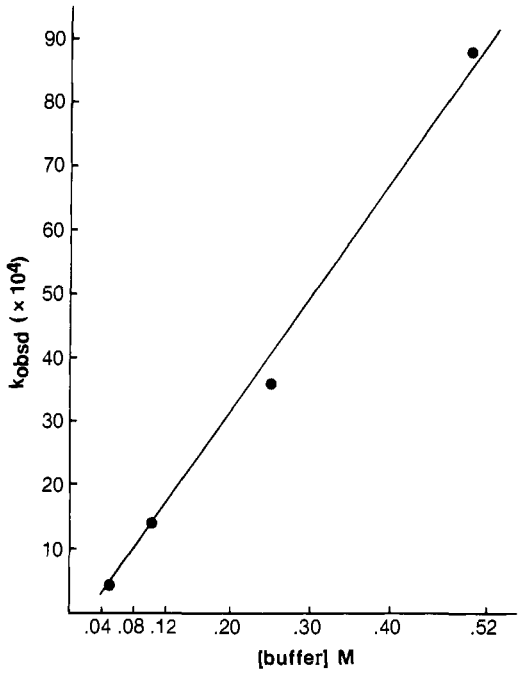
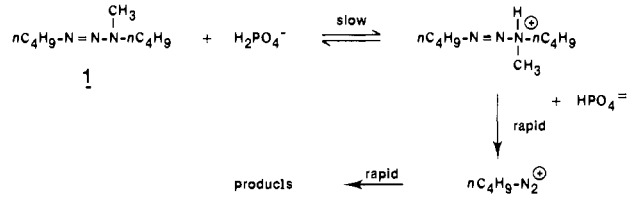


Figure 2. Effect of phosphate buffer concentration on the rate of disappearance of 1,3-di-*n*-butyl-3-methyltriazene at pH 7.4 in water at 22 °C.

Scheme III



of **1** increases with increasing buffer concentration. Figure 2 depicts graphically the linear relationship that exists between these two parameters. The slope provides the catalytic rate constant (k_{cat} = 1.84 × 10^{-2} min^{-1} M^{-1}) and the intercept (k = 5.64 × 10^{-4} min^{-1}) gives the rate constant for H_3O^+ acting as the general acid. These data are consistent with general acid catalysis, and a mechanism can be written that will account for these results (Scheme III).

When the reaction was carried out in 0.5 M phosphate buffer in D_2O (nominal pH meter value of 7.4, I = 0.75 with KCl), the observed rate constant was $k_{obsd}^{D_2O}$ = 1.08 × 10^{-2} min^{-1}. Since the pD value differs from the observed pH reading according to the equation[26] pD = pH_{obsd} + 0.4, the above rate constant has to be compared with the rate obtained at pH 7.8 (H_2O). This value was (Table I) $k_{obsd}^{H_2O}$ = 5.27 × 10^{-3} min^{-1}. Therefore the solvent isotope effect for the reaction was k_D/k_H = 2.05. This value suggests that the concentration of the conjugate acid of the triazene is higher in D_2O than in H_2O, a result consistent with the mechanism in Scheme III.

Formation of the aryl diazonium ion during the acid-catalyzed decoposition of monosubstituted and symmetrically disubstituted diaryltriazenes has been established by several groups[15-19] including Hughes and Ingold.[20,21] The formation of the alkyldiazonium ion in the acid-catalyzed decomposition of alkylaryltriazenes is somewhat more in doubt.[7,9] For these compounds protonation can occur at either the aryl nitrogen, which would decompose via an alkyldiazonium ion, or at the alkyl nitrogen, where decomposition would occur via an aryldiazonium ion. The latter is a much more favorable reaction, on a thermodynamic basis. In our system, with alkyl groups at all three positions, the acid-catalyzed decomposition clearly proceeds through an alkyldiazonium ion intermediate.[27] We can thus regard these compounds as protected alkyldiazonium ions, which can be generated in situ whenever desired by the addition of a proton source. *Warning.* Alkyldiazonium ions are regarded as putative ultimate carcinogens formed during the metabolism of dialkylnitrosamines, which are known to be potent carcinogens. Indeed, we have found[28] that several trialkyltriazenes are very potent, directly acting mutagens in the Ames assay. Thus, trialkyltriazenes must be regarded as likely carcinogens, and proper care should be exercised in handling them.

Experimental Section

Materials. Unless otherwise specified, all materials were reagent grade and used without further purification. *tert*-Butyl alcohol was distilled over BaO and stored over 4-Å molecular seives. Cyclopropylcarbinyl azide and *n*-butyl azide were prepared and purified by the procedure of Boyer and Hamer[22] starting from the respective chlorides. Hexane, pentane, and diethyl ether were dried over sodium shavings before use. The yields reported are isolated yields. Mass spectra were obtained on a Finnigen 3300 mass spectrometer equipped with a Finnigan 6000 data system. The relative intensities have an estimated error of ±3%. High-pressure liquid chromatography (high-pressure LC) was performed on a Laboratory Data Control Constametric II liquid chromatograph equipped with a UV monitor, Model 1203, using a 40 cm × 2 mm i.d. column packed with 18-30-μm basic alumina. Gas chromatography (GLC) was performed on a Perkin-Elmer Sigma II Series gas chromatograph equipped with a 2 m × 2 mm i.d. column packed with 20% Carbowax 20 M on Chromosorb WHP and a nitrogen/phosphorus detector. Both gas and liquid chromatographs were interfaced to a Hewlett-Packard Model 3354 computer through a Hewlett-Packard 18652A A/D converter. The area slice method of peak integration was used. NMR spectra were obtained on a Varian XL-100 spectrometer with a Nicolet TT-100 Fourier transform accessory at a radio frequency of 100 MHz for ^1H. Kinetic measurements were carried out on a Cary 17 UV spectrophotometer. Chemical analyses were performed by Galbraith Laboratories, Inc.

Preparation of 1,3-Bis(cyclopropylcarbinyl)-3-methyltriazene (2). (Cyclopropylcarbinyl)lithium was prepared by the procedure of Lansbury et al.[12] In a typical synthesis, a solution of 10 g (0.11 mol) of cyclopropylcarbinyl chloride and 16.5 g (0.11 mol) of sodium iodide in 150 mL of reagent grade acetone was heated gently at reflux overnight. The solution was then decanted from the inorganic residue; the latter was extracted with petroleum ether and the extract added to the main solution. Solvent was removed by distillation through a Vigreux column, and the product was then distilled under vacuum at 30 °C, the distillate being trapped in a dry ice–acetone cooled flask. Careful distillation of the crude iodide provide 11.5 g (0.063 mol, 57%) of cyclopropylcarbinyl iodide, bp 86–88 °C (140 mmHg). The NMR spectrum and boiling point were consistent with literature values.[12]

In a one-necked round-bottomed flask, which contained 50 mL of pentane that had been flushed with nitrogen and fitted with a rubber septum, was placed 0.01 mol of *sec*-butyllithium (7.7 mL of a 1.3 M solution in cyclohexane, obtained from Aldrich). This magnetically stirred solution was cooled to −70 °C in a dry ice–acetone bath, and to this was added a solution of 2.18 g (0.12 mol) of cyclopropylcarbinyl iodide in 5 mL of dry pentane via a syringe. After being stirred for 2 min, a solution of 1.0 g (0.01 mol) of cyclopropylcarbinyl azide in 5 mL of dry pentane was added via a syringe to the reaction mixture. After an additional 30 min the reaction mixture was hydrolyzed by the addition of 2 mL of 10% NH_4OH/10% NH_4Cl and allowed to gradually warm to room temperature. Workup, following established procedures,[6] afforded the crude 1,3-bis(cyclopropylcarbinyl)triazene. This triazene was used in the next step without purification.

According to the procedure already described,[6] the dialkyltriazene anion–potassium cation complex was allowed to react with methyl iodide to afford the desired trialkyltriazene **2**. In a typical synthesis, 1.53 g (0.01 mol) of the crude dialkyltriazene in 25 mL of *tert*-butyl alcohol was added dropwise under a nitrogen atmosphere to a stirred solution of 1.35 g (0.12 mol) of potassium *tert*-butoxide in 50 mL of *tert*-butyl alcohol. After the addition was completed, 2.82 g (0.02 mol) of methyl iodide in 10 mL of *tert*-butyl alcohol was added dropwise over a period of 15 min,

(15) Griess, P.; Martius, A. C. *Z. Chem.* **1866**, *2*, 132.
(16) Frieswell, R. J.; Grenn, A. G. *J. Chem. Soc.* **1885**, *47*, 917.
(17) Frieswell, R. J.; Grenn, A. G. *J. Chem. Soc.* **1886**, *49*, 746.
(18) Neitzki, R. *Ber. Dtsch. Chem. Ges.* **1877**, *10*, 662.
(19) Suizu, K.; Yokozima, N. *Kogyo Kagaku Zasshi*, **1926**, *19*, 32.
(20) Hughes, E. D.; Ingold, C. K. *Q. Rev., Chem. Soc.*, **1952**, *6*, 34.
(21) Ingold, C. K. "Structure and Mechanism in Organic Chemistry"; Cornell University Press: Ithaca, NY, 1953; p 610.
(22) Boyer, J. H.; Hamer, J. *J. Am. Chem. Soc.* **1955**, *77*, 951–954.

and the resulting mixture was allowed to stir overnight at ambient temperature. The excess *tert*-butyl alcohol was removed at reduced pressure and 100 mL of diethyl ether added immediately. The resulting heterogeneous mixture was filtered to remove excess KI, dried over $MgSO_4$, refiltered, and concentrated at reduced pressure. The crude triazene was purified on an alumina column (eluant hexane–ether, 20:1). Considerable decomposition on the column reduced the overall yield which, starting from the azide, was 55%. High-pressure liquid chromatography using a basic alumina column (solvent hexane) provided a check on the purity of the triazene.

1,3-Bis(cyclopropylcarbinyl)-3-methyltriazene (**2**): ^1H NMR ($CDCl_3$) δ 0.1–1.5 (m, 8 H), 3.02 (s, 3 H), 3.42 (d, 2 H), 3.44 (d, 2 H), 3.61 (m, 2 H); mass spectrum m/z 167 (M^+). Anal. ($C_9H_{17}N_3$): C, H, N.

Preparation of 1,3-Di-*n*-butyl-3-methyltriazene (1). In a typical synthesis, 2.0 g (0.02 mol) of *n*-butyl azide was alkylated by 1.5 equiv of *n*-butyllithium according to the procedure of Lee and Ko[9] and worked up to afford the dialkyltriazene. The crude dialkyltriazene was purified by column chromatography on alumina (elution series for 2 g of crude material; 200 mL of hexane and then 200 mL of hexane–ether, 4:1, for a 1-m column). The unreacted azide eluted off in the initial fraction, and the pure dialkyltriazene appeared after the eluant polarity had been increased.

The triazene **1** was prepared by the standard procedure using 1.57 g (0.01 mol) of the purified 1,3-di-*n*-butyltriazene, 1.34 g (0.012 mol) of potassium *tert*-butoxide, and 2.82 g (0.02 mol) of methyl iodide. After workup, the crude triazene was purified on an alumina column (eluant hexane–ether, 20:1), yield (from the azide) 88%. As before, high-pressure LC using a basic alumina column (eluant hexane) provided a check on the purity.

1,3-Di-*n*-butyl-3-methyltriazine (**1**): ^1H NMR ($CDCl_3$) δ 0.92 (t, 6 H), 1.1–1.8 (m, 9 H), 2.95 (s, 3 H), 3.56 and 3.58 (d, 4 H); mass spectrum, m/z 171 (M^+). Anal. ($C_9H_{21}N_3$): C, H, N.

Acid Catalyzed Decompositions. Both triazenes **1** and **2** were decomposed by the same set of conditions that Lee and Ko[9] used to generate triarylvinyl cations from (triarylvinyl)phenyltriazenes, except that 0.1% HCl was used instead of 0.1% $HClO_4$. In a typical decomposition, 1 equiv of the appropriate triazene was added to 100 mL of 90% aqueous acetone at ambient temperatures. To this was immediately added 1 equiv of 0.1% HCl with stirring. After nitrogen evolution ceased (1–2 min), $MgSO_4$ was added and the resultant heterogeneous mixture filtered. Aliquots (10 μL) of the resultant organic solution were injected directly into the gas chromatograph. GLC with the 20% Carbowax 20 M on Chromosorb WHP column (column temperature 45 °C, injector temperature 150 °C, helium rate 20 mL/min, F.I.D.) afforded good separation of the isomeric alcohols. *sec*-Butyl alcohol (retention time 3.48 min, 32%) and *n*-butyl alcohol (7.94 min, 68%) were characterized from the decomposition of triazene **1** by comparison of retention times with authentic starting materials and comparison of mass spectra by using GC–MS techniques. 3-Buten-1-ol (retention time 10.46 min, 4%), cyclopropylcarbinyl alcohol (16.5 min, 48%) and cyclobutyl alcohol (17.1 min, 48%) were characterized from the decomposition of triazene **2** by the same methods used above.[23] All the yields given are based on an average of three separate runs.

Kinetic Experiments. Solutions of the triazene **1** were prepared in dried reagent grade acetone[24] and stored at −9 °C. These stock solutions were stable for months. An aliquot of the stock solution was placed in a 50-mL volumetric flask and the solvent removed. The appropriate phosphate buffer was then added so as to make the initial concentration about 5×10^{-5} M and the timer was started. The ionic strength was adjusted with KCl. All solutions were thermostated at 22 ± 0.1 °C. For a typical determination, a 3-mL aliquot was withdrawn from the volumetric flask and placed in the spectrophotometer and the wavelength scanned from 360 to 200 nm. At the maximum (263 nm) the time was noted along with the absorbance. Several time points were taken during each experiment. The reactions were followed to a minimum of 3 half-lives. The absorbance after several half-lives (A_∞) was estimated to 0.0.[25] Typical rate data are shown in Tables I and II. All the rate constants presented in the tables are based on an average of triplicate experiments.

Kinetic Solvent Isotope Effect. Solutions of the buffer salts were prepared by the addition of disodium hydrogen phosphate and sodium hydrogen phosphate to 99.8% deuterium oxide. The buffer concentrations were the same as the concentrations used in the experiments with water. The reaction solutions were prepared and studied as described above. The pD was calculated by the method of Glasoe and Long.[26]

Acknowledgment. This work was supported by Contract No. N01-CO-75380 with the National Cancer Institute, NIH, Bethesda, MD 20014.

(23) The separation of the cyclic alcohols was incomplete; therefore, since the area slice method of peak integration was used, the assumption must be made that the peaks are similar in shape.

(24) Since the triazene **1** decomposes in hydroxylic solvents, these solvents can not be used for the kinetic determinations or for storage purposes.

(25) It was impossible to determine A_∞ spectrophotometrically because of the interference of a product of the decomposition (*n*-butyl alcohol) which absorbed in the same region. After 6–10 half-lives, the decomposition mixture was extracted with ether and the ethereal extract injected into the GC (same conditions as described earlier). In all cases no unreacted triazene was detected.

(26) Glasoe, P. K.; Long, F. A. *J. Phys. Chem.* **1960**, *64*, 188–190.

(27) The question of whether an alkyldiazonium ion is a discrete intermediate is probably a function of the alkyl group. While the evidence for simple primary alkyldiazonium ions is strong. the alkyl loss of nitrogen may occur almost synchronously with the formation of diazonium ions substituted by alkyl groups capable of stabilizing a positive charge. Thus, the (cyclopropylcarbinyl)diazonium ion may not be a discrete intermediate; i.e., path a, Scheme II, may be the path of decomposition of the protonated triazene **2** rather than path b, Scheme II. For a discussion of this problem see: (a) Moss, R. A. *Acc. Chem. Res.* **1974**, *7*, 421–427; (b) Moss, R. A.; Shulman, F. C.; Emery, E. M. *J. Am. Chem. Soc.* **1968**, *90*, 2731–2732; (c) Maskill, H.; Southam, R. M.; Whiting, M. C. *Chem. Commun.* **1965**, 496–497.

(28) Sieh, D. H.; Andrews, A. W.; Michejda, C. J. *Mutat. Res.*, in press.