CH_3OD was passed once through the focal point of the laser jet (flow 0.60 mL/min, 100-μm capillary, 3.0 W over all UV lines). The solvent was evaporated and the ^1H NMR spectrum (250 MHz, $CDCl_3$) revealed ethane **3** and ether **5** in a ratio of 72:28. For the ether **5** the integration of the signals at 3.26 ppm (OCH_3) and at 5.20 ppm (CH) gave a 3:1 ratio within the error limits.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for generous financial support.

Registry No. 1, 1733-63-7; benzhydryl, 4471-17-4; benzhydryl cation, 709-82-0.

Thermal and Photochemical Decomposition of *N*-[2-(3,3-Dimethyl-1-butynyl)-2,5,5-trimethyl-1-pyrrolidinyl]nitrene

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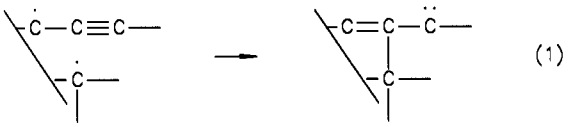
Contribution from the Laboratories of The Rockefeller University, New York, New York 10021-6399. *Received January 31, 1992*

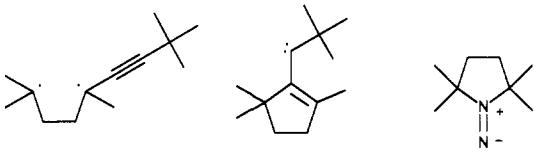
Abstract: Oxidation of *N*-aminopyrrolidine **5** with *tert*-butyl hypochlorite at −130 °C yields the 1,1-disubstituted diazene **4**, which is stable in dimethyl ether solution at this temperature. Thermal (−90 °C) or photochemical (−130 °C, λ > 330 nm) decomposition of **4** furnishes singlet alkyl propargyl biradical **1**, which undergoes fragmentation to **16**, cyclization to **17**, and disproportionation to **18** and **19** (Table I). The absence of products attributable to the cyclization of **1** to vinyl carbene **2** (cf. eq 1) is interpreted as evidence that cyclization according to eq 1, when observed, occurs directly from the triplet biradical in competition with intersystem crossing.

Alkyl propargyl biradicals can cyclize (eq 1) to vinyl carbenes whose subsequent fate depends on their specific structure. There



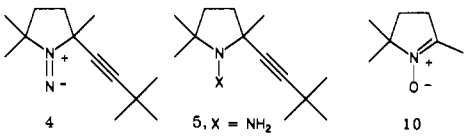
(1)

are now examples of this process in 1,4 biradicals created by several different photochemical routes,[1] along with evidence suggesting that the biradical cyclizes specifically from its triplet state in competition with the intersystem crossing to the singlet that precedes its other possible reactions.[1,2] In the present work, we have prepared the simple alkyl propargyl biradical **1** specifically in its singlet state in order to examine products formed under such defined conditions of biradical spin. We were particularly interested in learning whether products resulting from cyclization of **1** to carbene **2** according to eq 1 were formed under these conditions.

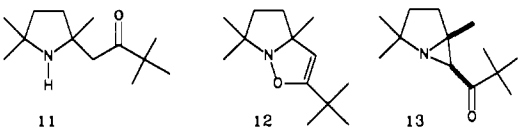


1 2 3

For this study we required a precursor that would reliably furnish **1** in its singlet state. The 1,1-disubstituted diazene **3** and diazenes from related pyrrolidines thermally decompose to hydrocarbon products at −20 °C and also decompose on direct irradiation at −78 °C, where they are thermally stable. These two reactions, which have been the object of careful study, lead to a very similar distribution of products, and both processes are believed to involve singlet 1,4 biradicals.[3] With this earlier work in mind, we chose 1,1-disubstituted diazene **4** as a suitable precursor for **1**, in part because it offers these two independent routes, by way of both **4**(S_0) and **4**(S_1), to singlet **1** under mild conditions. We have prepared and purified diazene **4**, decomposed it thermally at −90 °C and by direct irradiation at −130 °C, and identified the products formed in these reactions. Our results are reported below.



4 5, X = NH_2 6, X = OH 7, X = H 8, X = $OCOCH_3$ 9, X = NO 10



11 12 13

Preparative Chemistry. The relatively stable precursor for **4** was hydrazine **5**. The earlier preparation of **3**[3] provided a model for the synthesis of **4**, but two steps in this sequence required modification to avoid undesirable attack on the triple bond. Addition of (*tert*-butylethynyl)magnesium chloride to nitrone **10**[3] furnished hydroxylamine **6**. Attempts to reduce **6** to the secondary amine **7** with zinc dust in acetic acid[3] failed. Concomitant hydration of the triple bond took place under these conditions, and the product obtained was amino ketone **11**. Treatment of **6** with zinc dust in methanol containing a drop of concentrated hydrochloric acid gave instead the cyclization product **12**. This result suggests that in hot acetic acid **12** is also formed and that subsequent reduction of the N–O bond under these more vigorous conditions then leads to **11**. Isoxazoline **12** was thermally unstable,

(1) Rathjen, H.-J.; Margaretha, P.; Wolff, S.; Agosta, W. C. *J. Am. Chem. Soc.* **1991**, *113*, 3904. This report contains complete references to earlier work.
(2) Saba, S.; Wolff, S.; Schröder, C.; Margaretha, P.; Agosta, W. C. *J. Am. Chem. Soc.* **1983**, *105*, 6902.
(3) Schultz, P. G.; Dervan, P. B. *J. Am. Chem. Soc.* **1982**, *104*, 6660 and earlier papers cited therein.

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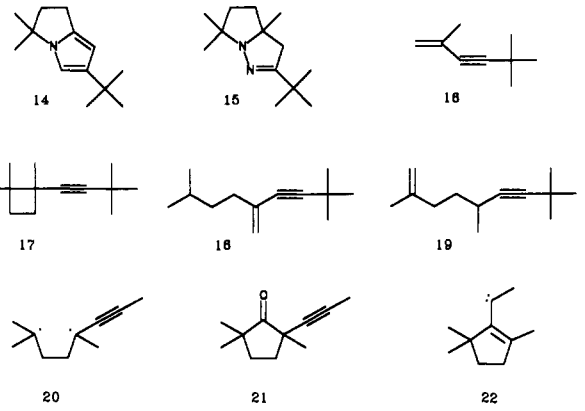
Table I. Hydrocarbon Decomposition Products from **4**

conditions of decomposition	relative yield of product, %			
	16	**17**	**18**	**19**
thermal	14	81	<1	5
photochemical	20	78	<1	2

and attempts to purify it by preparative gas chromatography led to its transformation into a 5:1 mixture of acyl aziridine **13** and pyrrole **14**. These thermal transformations are examples of two reactions of isoxazolines that were first described some years ago.[4,5] The stereochemistry indicated for **13** is that expected on the basis of an earlier example of this rearrangement.[5] In both the previous and current examples, a single isomer of the relevant aziridine was isolated.



Conversion of **6** into acetate **8** prior to reduction prevented attack on the acetylene, and zinc dust in acetic acid reduced **8** to **7** as desired. A more convenient procedure, however, was to reduce **6** directly to **7** by means of titanium trichloride in aqueous sodium acetate. Our procedure was based on conditions reported for the reduction of nitrosamines and hydrazines in buffered solution.[6] Nitrosation[3] of **7** with sodium nitrite in dilute hydrochloric acid then furnished the corresponding nitrosamine **9**. Exposure of **9** to zinc in hot acetic acid[3] led to involvement of the triple bond, as well as overreduction, and yielded a 2:1 mixture of pyrazoline **15** and pyrrolidine **7**.[7] A second titanium reagent offered a satisfactory alternative procedure. The brownish-black solution formed on treatment of titanium tetrachloride with magnesium powder in ether–dichloromethane, which is thought to contain a Ti(*II*) species,[8] smoothly reduced **9** to **5** in good yield. Hydrazine **5** could be purified by column chromatography over neutral alumina.

1,1-Disubstituted Diazene 4 and Its Decomposition Products. Oxidation of **5** by *tert*-butyl hydrochlorite in a mixture of pentane and dimethyl ether (5:1), containing triethylamine to neutralize acid formed in the reaction, afforded the very reactive diazene **4**, which was purified directly by chromatography over deactivated basic alumina.[3] Elution with pentane–dimethyl ether removed impurities, and then purified **4** could be eluted from the column with dimethyl ether. Both oxidation and column chromatography were carried out at −130 °C. The pink solution of the diazene in dimethyl ether was stable at this temperature and could be stored frozen in liquid nitrogen after chromatography.

The color of the diazene solution disappeared over ~2 h at −90 °C, and these conditions provided convenient, mild thermal decomposition of **4** for preparative purposes. Volatile products were isolated by preparative gas chromatography after the decolorized solution was warmed to room temperature and solvent dimethyl ether was vented. Under these conditions, products **16–19** were obtained in a total yield of ~85%; relative yields are recorded in Table I. NMR and IR spectra of these hydrocarbons and their molecular ions on high-resolution MS were compatible with the assigned structures. Enyne **16** was identical with a sample prepared by reaction of (*tert*-butylethynyl)magnesium chloride with acetone followed by dehydration by thionyl chloride and pyridine; its proton NMR spectrum was in agreement with that on record for unpurified **16**.[9]

Diazene **4** also decomposed smoothly on irradiation ($\lambda > 330$ nm) in dimethyl ether solution at −130 °C. Products, formed in ~94% yield, were the same as from thermal decomposition, and their relative yields are included in Table I. In both the thermal and photochemical reactions, the very minor disproportionation products **18** and **19** were formed in a ratio of ~1:6. These isomers were not separated in either case, but their ratio could be determined from NMR spectra of their mixture.

Discussion. Alkynyl-substituted diazene **4** was considerably more reactive than its tetramethyl analogue **3**. Although **3** is stable at −78 °C,[3] **4** decomposed slowly above −100 °C. For both **3** and **4**, thermal and photochemical decomposition furnish a quite similar distribution of products. However, **4** gives mostly cyclobutane **17**, while the paths followed by **3** are fragmentation (54%), cyclization to the cyclobutane (44%), and disproportionation (2%).[10]

The most significant observation in this study is that products attributable to the cyclization of biradical **1** to vinyl carbene **2** are completely absent. This is the first alkyl propargyl biradical that we have examined that completely fails to cyclize to the carbene.[1] It is also the only such biradical that was created specifically in its singlet state. The behavior of **1** may be contrasted with that of the related biradical **20**, which is presumed to be an intermediate formed largely in its triplet state[11] on direct photolysis of **21**.[12] The photoproducts from **21** included hydrocarbons derivable from vinyl carbene **22** as well as the normal fragmentation and coupling products of biradical **20**. The present findings provide a new line of evidence consistent with our earlier suggestion[1,2] that conversion of alkyl propargyl biradicals to vinyl carbenes (eq 1) takes place directly from the triplet state. As we have noted before,[1,2] the rate-controlling step in normal reactions of triplet biradicals is intersystem crossing, and it appears that spin-allowed closure of alkyl propargyl biradicals to the triplet carbene (eq 1) competes successfully with this intersystem crossing. In contrast, closure from the singlet biradical to the singlet carbene cannot compete with fragmentation, coupling, and disproportionation, all of which are rapid and highly exothermic.

Experimental Section

Materials and Equipment. These have been described previously,[13] with the exception of the apparatus for preparation and purification of **4** at −130 °C, which is described in a later paragraph.

1-Hydroxy-2-(3,3-dimethyl-1-butynyl)-2,5,5-trimethylpyrrolidine (6). 3,3-Dimethyl-1-butyne (4.6 mL, 37.3 mmol) was added to a 3.2 M

(4) Grigg, R. *Chem. Commun.* **1966**, 607. Acheson, R. M.; Bailey, A. S.; Selby, I. A. *Ibid.* **1966**, 835. Baldwin, J. E.; Pudussery, R. G.; Qureshi, A. K.; Sklarz, B. *J. Am. Chem. Soc.* **1968**, *90*, 5325. Adachi, I.; Harada, K.; Kano, H. *Tetrahedron Lett.* **1969**, 4875.

(5) Padwa, A.; Dean, D.; Oine, T. *J. Am. Chem. Soc.* **1975**, *97*, 2822.

(6) Lunn, G.; Sansone, E. B.; Keefer, L. K. *J. Org. Chem.* **1984**, *49*, 3470. Titanium trichloride has been used previously for reduction of hydroxamic acids (*N*-acyl hydroxylamines) to amides, although the mechanism proposed would not apply to the reduction of simple hydroxylamines: Mattingly, P. G.; Miller, M. J. *J. Org. Chem.* **1980**, *45*, 410.

(7) For earlier examples of addition of amines and hydrazines to triple bonds under similar conditions, see: Kruse, C. W.; Kleinschmidt, R. F. *J. Am. Chem. Soc.* **1961**, *83*, 213. Darbinyan, E. G.; Saakyan, A. A.; Eliazyan, M. A.; Matsoyan, S. G. *Arm. Khim. Zh.* **1970**, *23*, 61.

(8) Entwistle, I. D.; Johnstone, R. A. W.; Wilby, A. H. *Tetrahedron* **1982**, *38*, 419.

(9) Macomber, R. S. *J. Org. Chem.* **1973**, *38*, 816.

(10) This is the distribution for direct irradiation at −78 °C. The product distribution for thermolysis is quite similar (ref 3).

(11) Such fully substituted ketones typically undergo some α-cleavage directly from S_1 in competition with intersystem crossing. Thus, some **20**(S_1) could be formed directly, as well as on intersystem crossing from **20**(T_1): Yang, N. C.; Feit, E. D. *J. Am. Chem. Soc.* **1968**, *90*, 504. Dalton, J. C.; Pond, D. M.; Weiss, D. S.; Lewis, F. D.; Turro, N. J. *J. Am. Chem. Soc.* **1970**, *92*, 2564. Yang, N. C.; Feit, E. D.; Hui, M. H.; Turro, N. J.; Dalton, J. C. *J. Am. Chem. Soc.* **1970**, *92*, 6974.

(12) Rudolph, A.; Margaretha, P.; Agosta, W. C. *Helv. Chim. Acta* **1987**, *70*, 339. Attempted triplet-sensitized photolysis of **21** in acetone was unsuccessful owing to competitive processes.

(13) Rao, V. B.; George, C. F.; Wolff, S.; Agosta, W. C. *J. Am. Chem. Soc.* **1985**, *107*, 5732. Matlin, A. R.; George, C. F.; Wolff, S.; Agosta, W. C. *Ibid.* **1986**, *108*, 3385.

solution of methylmagnesium bromide (10.5 mL, 33.6 mmol) in ether at reflux, and the mixture was stirred and heated for 3 h. To this mixture was added dropwise 2,2,5-trimethylpyrroline oxide[3] (3.112 g, 24.5 mmol) in THF (10 mL), and the mixture was refluxed for an additional 18 h. The solution was cooled to 0 °C and neutralized with NH_4Cl (3.4 g, 63.6 mmol) in water (15 mL). The ethereal layer was washed with brine, and the aqueous layers were combined and extracted six times with ether. The ethereal extracts were combined with the first ether layer and dried over $MgSO_4$. Solvent was removed in vacuo to provide the crude hydroxylamine as a yellow oil which darkened rapidly (3.051 g, 60%): IR 3375 (br), 2950, 2910, 2848, 1450, 1355, 1270, 1198, 1155, 735 cm^{-1}; ^1H NMR (60 MHz) δ 1.11 (s, 3 H), 1.18 (s, 3 H), 1.23 (s, 9 H), 1.40 (s, 3 H), 1.53–2.07 (m, 5 H). This material was reduced to **7** without further purification.

2-(3,3-Dimethyl-1-butynyl)-2,5,5-trimethylpyrrolidine (7). A. To a thick suspension of $TiCl_3$ (3 g, 19.4 mmol) and NaOAc (16.4 g, 200 mmol) in H_2O (45 mL), stirred under nitrogen, was added hydroxylamine **6** (895 mg, 4.28 mmol) in one portion. After 2 h, NaOH (~1 g) was carefully added, and the mixture was stirred for 0.5 h. The blue mixture was extracted with Et_2O (4×), and the combined extracts were dried over $MgSO_4$ and $NaHCO_3$ (4:1). After filtration and removal of solvent, the amine was obtained as a light yellow oil (687 mg) of 88% purity (73% yield). Portions of **7** were combined and distilled bulb-to-bulb (65 °C, 0.05 Torr) to give a colorless oil: IR 3410, 3240, 2975, 2890, 2200 (w), 1455, 1365, 1270, 1165 cm^{-1}; ^1H NMR (300 MHz) δ 1.14 (s, 3 H), 1.18 (s, 9 H), 1.31 (s, 3 H), 1.38 (s, 3 H), 1.53–1.83 (m, 3 H), 1.87–1.99 (m, 1 H), 2.00–2.09 (m, 1 H). Anal. ($C_{13}H_{23}N$) C, H, N.

B. Hydroxylamine **6** (840 mg) was dissolved in CH_2Cl_2 (2 mL) and treated with 1 equiv of HCl and then acetic anhydride (4 mL), and the mixture was stirred at room temperature overnight. The mixture was transferred to a separatory funnel, diluted with CH_2Cl_2 (10 mL) and water (10 mL), and carefully neutralized with solid Na_2CO_3. The organic layer was removed and the aqueous portion extracted (3×) with CH_2Cl_2. The combined organic layers were washed with saturated $NaHCO_3$ and with brine and dried over $MgSO_4$. Filtration and removal of the solvent yielded the crude *N*-acetoxypyrrolidine **8** as a brown oil (0.936 g): IR 2955, 1748, 1360, 1195, 1000 cm^{-1}; ^1H NMR (60 MHz) δ 1.30 (s, 12 H), 1.38 (s, 3 H), 1.44 (s, 3 H), 1.83–2.07 (m, 4 H), 2.18 (s, 3 H). The crude acetate was dissolved in AcOH (5 mL) and heated to 65 °C, and zinc dust (800 mg, 12.2 mmol) was added in four portions over 2 h. After a total of 7.5 h, the reaction mixture was cooled to room temperature, diluted with water (5 mL), and filtered. The flask and filtercake were washed with several milliliters of 3 M HCl, and the combined filtrates were washed once with CH_2Cl_2. The acidic aqueous layer was made basic with 50% aqueous NaOH and extracted with CH_2Cl_2 (5×). The initial organic wash was back-washed with 3 M HCl (3×), and these aqueous layers were neutralized and extracted with CH_2Cl_2 (3×). The combined basic organic extracts were washed once with saturated aqueous $NaHCO_3$ and dried over $MgSO_4$, filtered, and concentrated. The product was distilled bulb-to-bulb (65 °C, 0.05 Torr) to yield amine **7** as a colorless oil (0.530 g, 67%).

1-Nitroso-2-(3,3-dimethyl-1-butynyl)-2,5,5-trimethylpyrrolidine (9). To a mixture of pyrrolidine **7** (3.847 g, 19.9 mmol) in 0.45 M HCl (45 mL), magnetically stirred and heated to 60 °C, was added $NaNO_2$ (2.760 g, 40 mmol) in H_2O (10 mL). After 6 h an additional portion of $NaNO_2$ (2.848 g, 41 mmol) in H_2O (10 mL) was added. After stirring at 60 °C for 64 h, the mixture was cooled and extracted with ether (3×). The combined extracts were washed with 3 M HCl and brine and dried over $MgSO_4$. After filtration and removal of solvent in vacuo, the product was distilled bulb-to-bulb (95 °C, 0.05 Torr) to give a light yellow solid (4.070 g, 92%): mp 31.5–32.5 °C; IR 2960, 2880, 2805, 1450, 1425, 1355, 1320, 1305, 1270, 1190, 1165, 1140 cm^{-1}; ^1H NMR (300 MHz) δ 1.15 (s, 9 H), 1.18 (s, 9 H), 1.38 (s, 3 H), 1.53 (s, 3 H), 1.57 (s, 3 H), 1.59 (s, 3 H), 1.63 (s, 3 H), 1.74–1.81 (m, 1 H), 1.85 (s, 3 H), 1.88–2.28 (m, 7 H); ^{13}C NMR (75 MHz) δ 91.92, 90.32, 80.41, 78.27, 65.89, 65.33, 62.21, 59.16, 38.94, 38.48, 37.87, 36.62, 30.86, 30.83, 29.57, 29.12, 28.58, 25.78, 25.62, 23.91. Anal. ($C_{13}H_{22}N_2O$) C, H, N.

1-Amino-2-(3,3-dimethyl-1-butynyl)-2,5,5-trimethylpyrrolidine (5). To a solution of $TiCl_4$ (0.250 mL, 2.28 mmol) in ether (2 mL) and CH_2Cl_2 (8 mL) was added magnesium (59 mg, 2.43 mmol) as a 50-mesh powder. The mixture was stirred for 2 h, at which time a solution of nitrosamine **9** (99.5 mg, 0.448 mmol) in ether (2 mL) was added dropwise. After 4 h, the reaction was made acidic with 1 M HCl (4 mL). The mixture was transferred to a separatory funnel and made very basic with 50% aqueous NaOH, and the ethereal layer was removed. The aqueous portion was extracted with ether (3×), and the combined ethereal layers were dried over $MgSO_4$ and $NaHCO_3$, filtered, and concentrated to yield the hydrazine as a crude oil (68.8 mg, 74%). This was purified by chromatography over neutral alumina: IR 3350, 3200, 2960, 2925, 2890, 2855, 2200 (w), 1450, 1355, 1265, 1195, 1135, 1068, 900 cm^{-1}; ^1H NMR (60 MHz) δ 1.20 (s, 3 H), 1.30 (s, 12 H), 1.37 (s, 3 H), 1.60–1.97 (m, 4 H), 2.50–3.00 (br s, 2 H). Anal. ($C_{13}H_{24}N_2$) C, H, N.

Reduction of 6 with Zinc in Acetic Acid. 2-(2-Oxo-3,3-dimethylbutyl)-2,5,5-trimethylpyrrolidine (11). Hydroxylamine **6** (93 mg) was dissolved in AcOH (1 mL), treated with 1 equiv of HCl, and heated to 70 °C. Zinc dust (94 mg, 1.44 mmol) was added, and the mixture was stirred at 70–80 °C for 15 h. The reaction mixture was cooled to room temperature, diluted with water and EtOAc, and filtered through Celite. The filtrate was made basic, the aqueous layer was washed with $CHCl_3$ (3×), and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated to furnish the crude amino ketone **11** (78 mg, 70%). This was purified by vapor-phase chromatography (QF-1, 155 °C, 60 mL/min): IR 3380, 2960, 2870, 1705, 1475, 1460, 1390, 1365, 1055, 998 cm^{-1}; ^1H NMR (60 MHz) δ 1.13 (s, 12 H), 1.22 (s, 6 H), 1.65–1.97 (m, 5 H), 2.67 (s, 2 H). Anal. ($C_{13}H_{25}NO$) C, H, N.

Reduction of 6 with Zinc in Acidified Methanol. 3-(1,1-Dimethylethyl)-5,8,8-trimethyl-1-aza-2-oxa-3-bicyclo[3.3.0]octene (12). Hydroxylamine **6** (84 mg) was dissolved in methanol (1 mL), and zinc dust (30 mg) and concentrated HCl (1 drop) were added. The mixture was heated briefly at 50 °C and agitated and then allowed to stand for 2 h at room temperature. The solution was filtered through Celite and concentrated. The residue was dissolved in CH_2Cl_2, neutralized with K_2CO_3, filtered, and concentrated to give **12** as a yellow oil: IR 2965, 2860, 1665, 1460, 1363, 1280, 1200, 1158, 1118, 1052, 738 cm^{-1}; ^1H NMR (60 MHz) δ 1.15 (s, 12 H), 1.25 (s, 3 H), 1.38 (s, 3 H), 1.60–1.83 (m, 4 H), 4.22 (s, 1 H); ^{13}C NMR (75 MHz) δ 23.28, 27.51, 28.14, 30.21, 31.18, 36.20, 38.06, 68.80, 97.10, 97.27, 162.44.

Attempted purification of this material by vapor-phase chromatography (QF-1, 150 °C, 60 mL/min) yielded **13** and **14** in a 5:1 ratio. Data for **13**: IR 2960, 2930, 2865, 1705, 1465, 1455, 1385, 1375, 1360, 1237, 1208, 1077, 995 cm^{-1}; ^1H NMR (60 MHz) δ 1.18 (s, 15 H), 1.22 (s, 3 H), 1.38–2.28 (m, 4 H), 2.66 (s, 1 H); ^{13}C NMR (75 MHz) δ 16.35, 25.33, 26.23, 28.86, 33.45, 33.96, 42.01, 43.85, 55.22, 65.07, 209.97; MS *m/z* 209.1839 (M^+, calcd for $C_{13}H_{23}NO$ 209.1780). Data for **14**: IR 2955, 2855, 1494, 1470, 1450, 1410, 1365, 1355, 1247, 1220, 1170, 778, 768 cm^{-1}; ^1H NMR (60 MHz) δ 1.26 (s, 9 H), 1.41 (s, 6 H), 2.25 (m, 2 H), 2.80 (m, 2 H), 5.67 (br s, 1 H), 6.31 (d, 1 H); ^{13}C NMR (75 MHz) δ 23.26, 28.02, 31.12, 32.06, 42.70, 60.10, 96.14, 105.30, 134.83, 139.97; MS *m/z* 191.1686 (M^+, calcd for $C_{13}H_{21}N$ 191.1674). Anal. ($C_{13}H_{21}N$) C, H, N.

Reduction of Nitrosamine 9 with Zinc in Acetic Acid. 3-(1,1-Dimethylethyl)-5,8,8-trimethyl-1,2-diaza-2-bicyclo[3.3.0]octene (15). Nitrosamine **9a** (98 mg, 0.441 mmol) was dissolved in AcOH (5 mL) and brought to 100 °C, and zinc dust (102 mg, 1.56 mmol) was added. After 75 min at this temperature, an additional portion of zinc dust (98 mg, 1.50 mmol) was added. After an additional 2 h at 100–103 °C, the reaction mixture was cooled to room temperature and filtered. The flask and filtercake were washed well with water and CH_2Cl_2. The combined filtrate was made basic with 50% aqueous NaOH, and the organic layer was removed. The aqueous portion was washed with CH_2Cl_2 (2×), and the combined organic layers were washed with saturated aqueous $NaHCO_3$ and with brine and dried over $MgSO_4$. After filtration and concentration, the residue (67 mg) was found to be a 2:1 mixture of **15** and **7**. Pyrazoline **15** was isolated by preparative vapor-phase chromatography (QF-1, 135 °C, 60 mL/min): IR 2960, 2860, 1470, 1452, 1360, 1270, 1165 cm^{-1}; ^1H NMR (60 MHz) δ 1.27 (s, 12 H), 1.40 (s, 6 H), 1.73 (m, 4 H), 2.51 (d, J = 16.5 Hz, 1 H), 2.75 (d, J = 16.5 Hz, 1 H); ^{13}C NMR (75 MHz) δ 25.40, 28.26, 29.72, 30.06, 33.81, 37.37, 39.01, 47.36, 63.87, 70.48, 162.23. Anal. ($C_{13}H_{24}N_2$) C, H, N.

Apparatus and Procedure for Preparation of Diazene 4. Solutions of purified diazene were prepared in an apparatus consisting of three components, a preparation flask, a chromatography chamber, and a receiver, joined by small ground-glass joints. The preparation flask was built from a three-neck flask and was fitted with a gas inlet adapter with a stopcock, an inlet covered with a rubber septum, and a pressure equalizing tube connected to the chromatography chamber. The bottom of the preparation flask was fitted with a glass frit above the joint by which it was connected to the chromatography chamber. By controlling the gas pressure and stopcock positions, the contents of the preparation flask could be maintained above the frit or forced down into the chromatography chamber. The ground-glass joints between the components were lubricated with a film of Teflon administered as an aerosol (Fluoroglide CP, Chemplast, Inc.). The apparatus was assembled hot and flushed with nitrogen. The chromatography chamber was charged with a thin layer of sand, followed by basic alumina (ICN, Activity IV), and topped with a layer of sand. The entire apparatus was cooled in a bath of freezing pentane slush (−130 °C), and the preparation flask was charged with a small amount of sand to cover the glass frit, about 0.5 mL of dimethyl ether, and 4 mL of pentane. This solvent mixture was deaerated

for 10 min and then passed into the chromatography chamber to wet the alumina. The reaction flask was then charged with 0.5 mL of dimethyl ether and 2 mL of pentane. The hydrazine (0.1–0.5 mmol) was added in 0.5 mL of pentane, followed by 1.5 equiv of triethylamine. The solution was deaerated for 10 min. Then *tert*-butyl hypochlorite (1.1 equiv) was slowly added, and the apparatus was agitated following the addition of each drop of oxidant. The reaction was allowed to proceed for 1 h, and the reaction mixture was then passed into the chromatography chamber. Elution from the column was assisted with nitrogen pressure. The column was washed once with 5 mL of 4:1 pentane–dimethyl ether and once with 5 mL of 1:1 pentane–dimethyl ether. Pure dimethyl ether was passed through the column until the pink diazene band was near the bottom of the alumina column. The chromatography was halted and the receiver was changed. The elution was continued with dimethyl ether until the entire pink band had been collected in the fresh receiver. The apparatus was then removed from the frozen pentane bath, and the receiver was immediately immersed in liquid nitrogen to freeze its contents. The receiver was carefully disconnected from the chromatography chamber and topped with a gas inlet adapter.

Decomposition of Diazene. Purified solutions of diazene in dimethyl ether or dimethyl ether–pentane mixtures were irradiated at −130 °C with a 450-W Hanovia medium-pressure mercury lamp or with a 150-W compact arc xenon lamp with an elliptical reflector. All reactions were analyzed after they were warmed to room temperature and the volatile solvents vented. (The reaction chemistry of the 1,1-disubstituted diazene does not appear to be affected by the presence of impurities resulting from its preparation. Preliminary qualitative results were therefore obtainable from the study of crude, unchromatographed diazene preparations. These solutions were prepared in the cells to be used for irradiation.) Thermal decomposition (in a pentane bath held at −90 °C by the addition of liquid nitrogen) and direct irradiation (−130 °C, $\lambda > 330$ nm) of **4** yielded products **16–19** (Table I). Data for **16**: IR 3098, 2971, 2865, 2220, 1616, 1476, 1456, 1372, 1362, 1307, 1240, 1204, 894 cm^{-1}; ^1H NMR (300 MHz) δ 1.24 (s, 9 H), 1.86 (t, J = 1 Hz, 3 H), 5.11–5.13 (m, 1 H), 5.17, 5.19 (m, 1 H); MS m/z 122.1114 (M^+, calcd for C_9H_{14} 122.1092). Data for **17**: IR 2968, 2900, 2866, 1475, 1464, 1455, 1382, 1371, 1361, 1296, 1263, 1204, 1145, 1104, 996, 987 cm^{-1}; ^1H NMR (500 MHz) δ 0.95 (s, 3 H), 1.17 (s, 3 H), 1.19 (s, 9 H), 1.20 (s, 3 H), 1.59–1.75 (m, 3 H), 2.04–2.11 (m, 1 H); MS m/z 178.1698 (M^+, calcd for $C_{13}H_{22}$ 178.1720). Anal. ($C_{13}H_{22}$) C, H. Data for **18** and **19** (purified mixture): IR 3075, 2969, 2931, 2869, 1649, 1456, 1375, 1362, 1334, 1265, 1205, 890 cm^{-1}; ^1H NMR (normalized on singlet at δ 1.19 [*tert*-butyl protons of **19**] = 9 H) (500 MHz) δ 0.89 (d, J = 6.5 Hz, 0.9 H), 1.12 (d, J = 6.9 Hz, 3 H), 1.19 (s, 9 H), 1.24 (s, 1.3 H), 1.35–1.42 (m, 0.3 H), 1.46–1.54 (m, 2 H), 1.73 (s, 3 H), 1.81–1.82 (m, 0.1 H), 2.03–2.21 (m, 2.3 H), 2.33–2.42 (m, 1 H), 4.68–4.72 (m, 2 H), 5.10–5.12 (m, 0.1 H), 5.17–5.19 (m, 0.1 H); MS m/z 178.1728 (M^+, calcd for $C_{13}H_{22}$ 178.1720).

Reaction of (3,3-Dimethyl-1-butynyl)magnesium Bromide with Acetone and Dehydration. 2,5,5-Trimethyl-1-hexen-3-yne (16). (3,3-Dimethyl-1-butynyl)magnesium bromide, prepared as described above from 3,3-dimethyl-1-butyne (500 mg), was allowed to react with acetone (550 mg) in the usual manner. Workup with ether and acid gave crude 2,5,5-trimethyl-3-hexyn-2-ol. This was treated directly with thionyl chloride (1.15 g) in pyridine (4 mL) at 0 °C, followed by warming to room temperature over 3 h. The reaction mixture was worked up with pentane and water, and preparative vapor-phase chromatography gave authentic **16**, the properties of which were essentially identical with those given above. The NMR spectrum was in good agreement with that previously recorded for unpurified **16**.[9]

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Stabilization Energy of Polyenyl Radicals: *all-trans*-Nonatetraenyl Radical by Thermal Rearrangement of a Semirigid {4-1-2} Heptaene. Model for Thermal Lability of β-Carotene

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Abstract: Evaluation of the stabilization energy of the nonatetraenyl radical directly from the enthalpy of activation of the thermal anti–syn rearrangement of a semirigid nonaene having a symmetrical distribution {4-1-4} of double bonds is thwarted by insolubility. Indirect comparison of the enthalpy of activation of an unsymmetrical {4-1-2} heptaene with that of an already determined symmetrical {2-1-2} pentaene leads to an inferred enthalpy of activation of 24.5 kcal/mol for the {4-1-4} nonaene. Perhaps the point of greatest theoretical interest is the rapidity with which successive increments in stabilization energies (SE_n) decrease with increasing number of double bonds in the conjugated polyenyl radicals. Values of SE_n for n = 1 (allyl), 2 (pentadienyl), 3 (heptatrienyl), and 4 (nonatetraenyl) are 13.5, 16.9, 19.2, and 20.7 kcal/mol, respectively.

In an initial paper,[1] stabilization enthalpies of the pentadienyl and heptatrienyl radicals have been estimated from activation parameters for the thermal anti–syn isomerization about the central double bond of a {1-1-1} hexatriene $\mathbf{1}_{1.1.1}$, a {2-1-2} decapentaene $\mathbf{2}_{2.1.2}$, and a {3-1-3} tetradecaheptaene $\mathbf{3}_{3.1.3}$ (see Table III). In a second paper,[2] solvent friction has been tentatively recognized as a small factor, which may serve as a warning against uncritical transfer to the gas phase of data acquired in solution. In the present paper, determination of the stabilization enthalpy of the nonatetraenyl radical extends the series far enough to permit the tentative conclusions that the experimental enthalpies of activation agree best with the theoretical values of Saïd, Maynau, Malrieu, and Garcia Bach[3] and that *all-trans*-β-carotene (11 double bonds) should rearrange slowly at physiological temperature

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