Reactions of 1-Nitro-2-(trialkylsilyl)acetylenes

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The chemistry of nitroacetylenes has been relatively unexplored owing to the lack of stable nitroacetylene derivatives. Our discovery of methods to prepare stable nitroacetylenes allows us the opportunity to investigate their chemistry. We report here on the reactions of (trialkylsilyl)nitroacetylenes in Diels–Alder, 1,3-cycloaddition reactions, and the thermolysis of nitroacetylene adducts.

We recently reported a new, practical, and convenient synthesis route for the preparation of the little studied nitroacetylenes. Our synthesis provides directly 1-nitro-2-(trialkylsilyl)acetylenes from the easily available 1-(trimethylsilyl)-2-(trialkylsilyl)acetylenes[1] where R = CH_3, $CH(CH_3)_2$, or $C(CH_3)_3$. Only a few nitroacetylenes were

$$(CH_3)_3SiC{\equiv}CSiR_3 \xrightarrow[CH_3NO_2]{NO_2PF_6} R_3SiC{\equiv}CNO_2$$

reported previously.[2] Our earlier work has resulted in the synthesis of several new nitroacetylenes whose properties and reactivity have not been fully explored.

Most nitroacetylenes are unstable, decomposing rapidly at room temperature or upon concentration. However, the trialkylsilyl-substituted nitroacetylenes are stable at room temperature in dilute solutions for extended periods of time. We have observed that the stability of silylnitroacetylenes depends directly on the size of the alkyl groups attached to the silicon; e.g., 1-nitro-2-(triisopropylsilyl)-acetylene does not decompose upon standing at room temperature as a neat material for several hours and is much more stable toward decomposition than 1-nitro-2-(dimethyl-*tert*-butylsilyl)acetylene, which in turn is much more stable than 1-nitro-2-(trimethylsilyl)acetylene. Presumably, this increased stability is mainly the result of steric hindrance whereby the extra bulk from the triisopropylsilyl group blocks attack at the 2-position by nuclophiles. Without the large steric bulk, even such weak nucleophiles as the oxygen of the nitro group of the nitroacetylene can react to cause the decomposition of nitroacetylenes. These stable nitroacetylenes make possible the study of reactions which were previously impossible. In this paper we report on (trialkylsilyl)nitroacetylenes in electrocyclic and 1,3-cycloaddition reactions and in thermal reactions.

Results and Discussion

A priori the nitroacetylenes are powerful dienophiles for 2 + 4 electrocyclic addition reactions. Previous studies showed that 1-*tert*-butyl-2-nitroacetylene, 1-*n*-propyl-2-nitroacetylene, and 1-isopropyl-2-nitroacetylene react only with cyclopentadiene and fail to react with other reactive dienes such as 2,3-dimethylbuta-1,3-diene, cyclohexa-1,3-diene, cycloheptadiene, cyclooctatetrene, and furan.[3,4] The failure to isolate reaction adducts with other dienes likely was due to the rapid decomposition of aliphatic nitroacetylenes rather than an inherent lack of reactivity. Nitroacetylenes are also known to react with enamines and ynamines.[5]

Having a synthetic route to a number of stable nitroacetylenes, we have begun studies of their reactivity in 2 + 4 electrocyclic and 1,3-dipolar cycloaddition reactions. 1-Nitro-2-(trimethylsilyl)acetylene easily undergoes 2 + 4 electrocyclic addition reactions with a much wider range of substrates than was observed for aliphatic nitroacetylenes, including cyclopentadiene, cyclohexa-1,3-diene, and furan (Scheme I).

The reduced yields observed with cyclohexa-1,3-diene and furan reflect the relative reactivity of dienes toward electrocyclic reactions, indicating that cyclopentadiene > cyclohexa-1,3-diene ≈ furan in 2 + 4 cycloaddition reactions with nitroacetylenes. The remainder of the nitroacetylene compound was consumed through a series of acetylene polymerization reactions that are still under investigation. 1-Nitro-2-(triisopropylsilyl)acetylene also undergoes cycloaddition with cyclopentadiene.

1-Nitro-2-(trimethylsilyl)acetylene reacts with trimethylsilyl azide and diazomethane, yielding 4-nitro-5-(trimethylsilyl)triazole and 4-nitro-5-(trimethylsilyl)-pyrazole, respectively. 4-Nitro-5-(trimethylsilyl)triazole would be favored over the other isomer owing to stabilizing hydrogen bonding between the nitro group and the acidic proton of the triazole ring. 4-Nitro-5-(trimethylsilyl)-pyrazole would be the expected product from the reaction of diazomethane and a nitroacetylene owing to the orientation effect due to the increased negative charge at the methylene group from the dipolar canonical form of diazomethane, $^-CH_2{-}N{=}N^+$, and the electron deficiency of the carbon α to the nitro group. The synthesis of the

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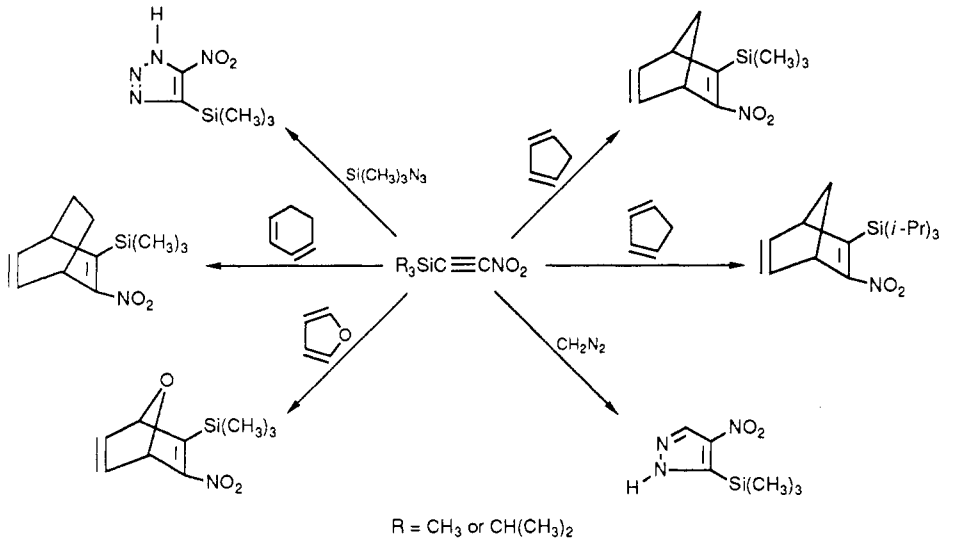
(5) Jager, V.; Viehe, H. G. *Angew. Chem., Int. Ed. Engl.* **1970**, 795.

0022-3263/90/1955-1916$02.50/0

Scheme I. Reactions of Nitroacetylenes



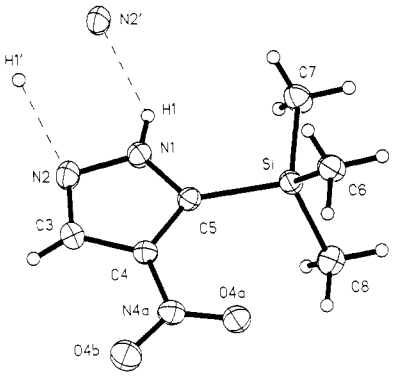


Figure 1. Thermal ellipsoid plot of 4-nitro-5-(trimethylsilyl)-pyrazole with ellipsoids drawn at the 20% probability level. Dashed lines indicate a pair of hydrogen bonds to atoms in a molecule related by an inversion center.

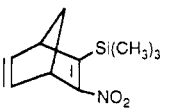
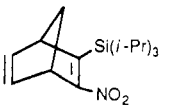
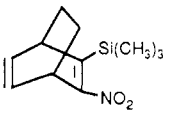
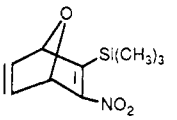
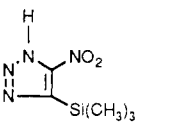
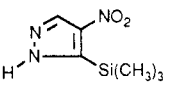
nitrotriazole is significant, since nitrotriazoles cannot be prepared by the direct nitration of triazole.[6]

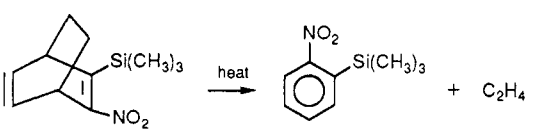
1-Nitro-2-(trimethylsilyl)acetylene decomposes slowly in solution, so it was difficult to calculate yields accurately or to quantitatively rank the reactivity of the different dienes (Table I). We found no evidence of double addition of the diene to the acetylene via the nitroolefin intermediate, even though an excess of diene was used in all cases. All these reactions were run at room temperature, clearly indicating the high reactivity of nitroacetylenes in 2 + 4 or 2 + 3 electrocyclic reactions.

Structure of 4-Nitro-5-(trimethylsilyl)pyrazole. Unambiguous assignment of the structure of 4-nitro-5-(trimethylsilyl)pyrazole was not possible from NMR and IR data alone, so X-ray crystallography was performed. The X-ray structure of 4-nitro-5-(trimethylsilyl)pyrazole (Figure 1) shows clearly that the silyl group is α to a diazomethane nitrogen rather than to the carbon atom. Both models were tested against the X-ray data, with the α-nitrogen model giving a significantly better diffraction R factor. In addition, the α-model exhibits strong NH–N hydrogen bonding between molecules in the crystal (Figure 1).

Thermal Reactions of Nitroacetylene Adducts. Pyrolysis of the cycloadduct of 1,3-cyclohexadiene and 1-nitro-2-(trimethylsilyl)acetylene results in the synthesis of *o*-nitro(trimethylsilyl)benzene with ethylene as the side product. 1-Nitro-2-(trimethylsilyl)arenes can be directly synthesized, but the ortho product is usually a minor reaction product.[7] None of the other cycloadducts shown in Table I undergo such thermal cycloreversion. We failed to effect such a cycloreversion from the ostensibly exo-

Table I. Cycloaddition Reactions of 1-Nitro-2-(trimethylsilyl)acetylenes

diene or 4-electron dipole	adduct	yield, %
		50
		75
		27
		21
$Si(CH_3)_3N_3$		21
CH_2N_2		30



(6) Boyer, J. H. *Nitroazoles; Organic Nitro Chemistry*; Feuer, H., Ed.; VCH Publishers Inc.: Deerfield Beach, FL, 1986; Vol. 1, p 268.

(7) Weber, W. P. *Silicon Reagents for Organic Synthesis: Reactivity and Structure Concepts in Organic Chemistry No. 14*; Springer-Verlag: Berlin, 1983; pp 121–122 and references therein.

thermic rearrangement of furan adduct to give phenolic isomers. Even in the presence of catalysts such as BF_3–etherate or trifluoromethane sulfonic acid, no cycloreversion (or reverse cycloaddition) was observed.

Interestingly, pyrolysis of neat 1-nitro-2-(triisopropylsilyl)acetylene resulted in the loss of NO_2 and coupling of the resulting acetylenic radical to give 1,4-bis(triisopropylsilyl)butadiyne.

$$(i\text{-}Pr)_3SiC{\equiv}CNO_2 \xrightarrow{heat} (i\text{-}Pr)_3SiC{\equiv}CC{\equiv}CSi(i\text{-}Pr)_3$$

This result was quite unexpected, and we speculate that it occurs only because the stability of the $i\text{-}Pr_3SiC{\equiv}C$ radical is great enough for dimerization yet is resistant to oxidation or other possible decomposition reactions. We previously observed that 1-nitro-2-(triisopropylsilyl)-acetylene is the most stable nitroacetylene yet prepared, presumably owing to inductive electron donation and the steric hindrance of the triisopropylsilyl group.

Experimental Section

Caution. All nitroacetylenes are considered to be toxic and potentially explosive and should be handled with appropriate precaution.

Materials. NMR spectra were recorded on a Varian Associates EM-360 or a JEOL FXQ-90 spectrometer. Infrared spectra were obtained on a Digilab-20 GC/FTIR (HP5980 GC) and on a Perkin-Elmer 1420 ratio recording infrared spectrometer. High-quality nitronium hexafluorophosphate (NHFP) and nitronium tetrafluoroborate (NTFB) were obtained from Ozark-Mahoning. NHFP was used as obtained, requiring no further purification. NTFB was purified by triturating with dry nitromethane, decanting away the residual nitric acid components, and then rotoevaporating the wet NTFB to dryness. This step was repeated several times and yielded NTFB free of acidic impurities. The silicon compounds were obtained from Aldrich Chemical Co. or Petrarch Systems, Inc., or synthesized by the addition of a trialkylsilyl chloride to a lithium (trimethylsilyl)acetylide. X-ray crystallography was done at the Structure of Matter Laboratory at NRL.

General Synthetic Procedure for the Synthesis of Nitroacetylenes. NHFP (1 equiv) or purified NTFB (1 equiv) were suspended in anhydrous acetonitrile, nitromethane, or nitromethane/methylene chloride and added to 1 equiv of the 1-(trimethylsilyl)-2-(trialkylsilyl)acetylene and stirred rapidly for 1 h at room temperature. The crude nitroacetylene was purified by simple column chromatography using a silica gel column and chloroform as the eluting solvent. The reaction mixture was quickly passed through a chloroform-saturated plug of silica gel, with suction applied at the effluent port, and the plug was rinsed with 100 mL of chloroform. The effluent was typically concentrated to 10 mL in vacuo and quickly utilized in subsequent synthetic transformations. Caution: Washing with brine or bicarbonate solutions causes rapid decomposition of the nitroacetylenes. Nitroacetylenes will generally decompose if concentrated and allowed to stand, even in a refrigerator. Decomposition can be slowed by dilution in an inert solvent and storage in a freezer. However, both 1-nitro-2-(triisopropylsilyl)acetylene and 1-(dimethyl-*tert*-butylsilyl)-2-nitroacetylene are stable for a few hours at room temperature even when concentrated. Spectral details are available from ref 1.

4-Nitro-5-(trimethylsilyl)pyrazole. Bis(trimethylsilyl)-acetylene (2 g, 12 mmol) was dissolved in a mixture of 30 mL of CH_3NO_2 and 10 mL of $CHCl_3$. Nitronium tetrafluoroborate (1.4 g, 10.5 mmol) was added, and the reaction mixture was stirred with cooling in a 15 °C water bath for 1 h under argon. The reaction mixture was then quickly washed through a 2-in. plug of silica gel, eluting with 150 mL of $CHCl_3$, such that the exposure to silica gel was limited to ≤30 s. The reaction mixture was concentrated to 50 mL and was treated with 100 mL of 0.15 M ethereal diazomethane. A strong exotherm was noticeable even at low concentrations. The reaction mixture was allowed to stand at room temperature overnight. The reaction mixture was concentrated and chromatographed, eluting with 1:1 $CHCl_3$/EtOAc over silica gel, collecting the R_f = 0.5 material. This material was crystallized from hexane/chloroform to give 500 mg (~30%, based on approximately 5 mmol of 1-nitro-2-(trimethylsilyl)acetylene): mp 110–112 °C; IR (KBr) 3250, 1500, 1430, 1400, 1300 cm^{-1}; ^1H NMR ($CDCl_3$, CH_2Cl_2–$CHCl_3$ standard) δ 11.75 (br s, 1 H NH), 8.25 (s, 1 H, aromatic CH), 0.3 (s, 9 H, CH_3). Structure was confirmed by X-ray crystallography.

4-Nitro-5-(trimethylsilyl)-1,2,3-triazole. The 1-nitro-2-(trimethylsilyl)acetylene obtained from the reaction of 10 mmol of bis(trimethylsilyl)acetylene was concentrated to 10 mL on a rotary evaporator and treated with 3.45 g (30 mmol) of azidotrimethylsilane. This mixture was allowed to stand at room temperature for 24 h, concentrated in vacuo, mixed with 25 mL of ethanol, then heated to reflux to desilylate the heteroatom, reconcentrated in vacuo, and eluted through a short plug of silica gel with 80:20 $CHCl_3$/EtOAc. The crude effluent was recrystallized from hot $CHCl_3$ by precipitation with CCl_4 to give 400 mg (21%) of fibrous crystals: mp 180 °C, explodes at 220 °C; IR (KBr) 3150 (s, NH), 2900 (w, CH), 1540 (s, N=N), 1510 (s, C=C), 1430 (s); ^1H NMR ($CDCl_3$, TMS) δ 0.3 (s, 9 H), the NH proton was not visible in this NMR experiment). Anal. Calcd for $C_5H_{10}N_4O_2Si$: C, 32.26; H, 5.38; N, 30.11. Found C, 32.23, H, 4.99, N, 30.11.

2-Nitro-3-(trimethylsilyl)-7-oxabicyclo[2.2.1]hepta-2,5-diene. The 1-nitro-2-(trimethylsilyl)acetylene obtained from the reaction of 10 mmol of bis(trimethylsilyl)acetylene was concentrated to 10 mL on a rotary evaporator and was treated with 40 mL of furan at room temperature for 3 days. The reaction mixture was concentrated in vacuo and chromatographed over SiO_2, eluting with $CHCl_3$ on a 3-in. column. The bicyclic adduct was isolated as a yellow oil with a yield of 450 mg (21%) based on the starting bis(trimethylsilyl)acetylene. The pure product decomposed slowly on standing, giving a black precipitate: IR (neat smear) 3040 (w, vinyl CH), 2970 (m, CH), 1510 (s, nitro), 1350 (s, nitro), 850 (s, SiC) cm^{-1}; ^1H NMR (CCl_4 internal $CHCl_3$ reference) δ 0.14 (s, 9 H, $SiCH_3$), 5.41 (t, 1 H, CH), 5.57 (t, 1 H, CH), 6.91 (dd, 1 H), 7.21 (dd, 1 H). The product was not stable enough for an elemental analysis.

Thermolysis of 2-Nitro-3-(trimethylsilyl)bicyclo[2.2.2]-octa-2,5-diene To Give *o*-(Trimethylsilyl)nitrobenzene. 2-Nitro-3-(trimethylsilyl)bicyclo[2.2.2]octa-2,5-diene (50 mg) was dissolved in 100 mg of decalin and heated in a sealed tube at 200 °C for 4 h. The resulting black solution was chromatographed over silica gel, eluting with 50:50 $CHCl_3$/hexane. The sole fluorescent product (R_f = 0.5) was isolated as a clear oil in a yield of 37 mg (80%). The spectral properties match those of *o*-(trimethylsilyl)nitrobenzene, as reported in the literature.[8]

Thermolysis of 1-Nitro-2-(triisopropylsilyl)acetylene To Give 1,4-Bis(triisopropylsilyl)buta-1,3-diyne. 1-Nitro-2-(triisopropylsilyl)acetylene (100 mg, 0.44 mmol) was heated briefly to ~200 °C in a test tube with a hot air gun with no effort made to exclude air. A violent decomposition was observed, with loss of NO_2 as evidenced by red gas evolution. The residue remaining after this decomposition was chromatographed, eluting hexane over SiO_2, collecting the major fraction, $R_f \sim 0.3$. Concentration of this fraction yielded crystals (40 mg, 50% yield): ^1H NMR (CCl_4/$CHCl_3$) δ 1.1 (br s, CH, CH_3); IR (NaCl, CCl_4 smear) 2970, 2900, 2090 cm^{-1}.

2-Nitro-3-(triisopropylsilyl)bicyclo[2.2.1]hepta-2,5-diene. 1-Nitro-2-(triisopropylsilyl)acetylene (70 mg, 0.4 mmol, with 30 mg of 1-(triisopropylsilyl)-2-(trimethylsilyl)acetylene as impurity) was dissolved in 10 mL of CCl_4 and stirred with cyclopentadiene (300 mg, 5 mmol). This mixture was stirred for 3 days at room temperature, concentrated, and chromatographed over silica gel, eluting with 90% heptane/10% dichloromethane to give 70 mg (75%) of the expected adduct, an oil: ^1H NMR (CCl_4/$CHCl_3$) δ 1.07 (d, 18 H, CH_3), 1.32 (m, 3 H, CH), 2.15 (m, 2 H, CH_2), 4.10 (m, 2 H, CH), and 6.90 (m, 2 H, CH); IR (neat smear) 2925, 2850, 1500, 1465, 1340 cm^{-1}. Anal. Calcd for $C_{16}H_{27}NO_2Si$: C, 65.90; H, 9.35; N, 4.82. Found: C, 65.41; H, 9.54; N, 4.73.

2-Nitro-3-(trimethylsilyl)bicyclo[2.2.2]octa-2,5-diene. Nitronium fluoroborate (1.3 g, 10 mmol) was suspended in 10 mL of nitromethane and stirred under argon at 0 °C with ice cooling.

(8) Benkeser, R. A.; Brumfield, P. E. *J. Am. Chem. Soc.* **1951**, *73*, 4770.

Bis(trimethylsilyl)acetylene (1.7 g, 10 mmol) was then added, and the reaction became homogeneous and amber in color. The entire reaction was filtered through a 3-in. × 1-in. plug of chloroform-saturated silica gel and was eluted with 150 mL of chloroform; a vacuum aspirator was used to hasten the elution rate. The product was concentrated to 10 mL, treated with 1,3-cyclohexadiene (2 g, 25 mmol), and allowed to stand at room temperature overnight. The reaction mixture was then chromatographed over silica gel, eluting with 1:1 hexane/chloroform, collecting the R_f 0.5 material. Concentration of effluent in vacuo yielded 600 mg (27% overall from bis(trimethylsilyl)acetylene) of yellow crystals: mp 53–55 °C; IR (CCl_4 smear) 3085 (w vinyl CH), 2960 (m, CH), 1520 (s, NO_2), 1360 (s, NO_2) cm^{-1}; ^1H NMR ($CCl_4/CHCl_3$) δ 1.4 (m, 4 H, CH_2), 4.1 (m, 1 H, CH), 4.6 (m, 1 H CH), 6.3–6.6 (m, 2 H, CH). Anal. Calcd for $C_{11}H_{17}NO_2Si$: C 59.19; H, 7.62; N, 6.28. Found: C, 59.14, H, 7.45, N, 6.28.

2-Nitro-3-(trimethylsilyl)bicyclo[2.2.1]hepta-2,5-diene. The reaction of nitronium fluoroborate and bis(trimethylsilyl)acetylene was carried out exactly as described in the previous sequence involving cyclohexadiene. The resulting 10 mL of solution containing 1-nitro-2-(trimethylsilyl)acetylene was treated with 5 mL of cyclopentadiene and was stored under argon for 15 h. The reaction mixture was concentrated and chromatographed over silica gel and eluted with chloroform and the R_f = 0.7 material was collected. The effluent was concentrated and distilled in vacuo to give 1.0 g (50%) of yellow oil: bp 44 °C (0.1 Torr); IR (neat smear) 3080 (w, vinyl CH), 2960 (m, CH), 1505 (s, nitro), 1530 (s, nitro) cm^{-1}; ^1H NMR (CCl_4) δ 2.2 (m, 2 H, CH_2), 4.0 (m, 2 H, CH), 6.8 (m, 1 H, CH), 7.1 (m, 1 H, CH). Anal. Calcd for $C_{10}H_{15}NO_2Si$: C, 57.42; H, 7.18; N, 6.7. Found: C, 56.73; H, 7.43; N, 6.39.

X-ray Diffraction Analysis of 4-Nitro-5-(trimethylsilyl)pyrazole. $C_6H_{11}N_3O_2Si$, FW = 185.3, triclinic space group $P\bar{1}$, a = 6.573 (1) Å, b = 6.875 (1) Å, c = 12.138 (1) Å, α = 90.04 (1), β = 97.36 (1), γ = 116.63 (1)°, Vol. = 485.2 (1) Å^3, Z = 2, ρ_{calc} = 1.268 g/cm^3, λ(Cu kα) = 1.541 78 Å, μ = 19.1 cm^{-1}, $F(000)$ = 196, T = 295 K.

A clear colorless 0.15 × 0.17 × 0.32 mm crystal was used for data collection on an automated Nicolet R3m/V diffractometer with incident beam monochromator. Lattice parameters were determined from 25 centered reflections within $60 \le 2\theta \le 76°$. The data collection range of hkl was: $-7 \le h \le 6$, $0 \le k \le 7$, $-13 \le l \le 13$, $\sin(\theta)/\lambda)_{max}$ = 0.56 Å^{-1}. Three standards were monitored every 60 reflections and exhibited a maximum random variation of 3.5% during data collection. A total of 1659 reflections were measured in the $\theta/2\theta$ mode with a scan, width from $[2\theta(K_{\alpha 1}) - 1.0]$ to $[2\theta(K_{\alpha 2}) + 1.0]°$; scan rate was a function of count rate (8 deg/min minimum, 30 deg/min maximum). There were 1462 unique reflections, R_{int} = 0.024 from merging equivalent reflections, and 1394 were observed with $F_o > 3\sigma(F_o)$. Data corrected for Lorentz, polarization and absorption effects, max and min transmission 0.91 and 0.59.

The structure was solved by direct methods with the aid of program SHELXTL.[9] The minimized full-matrix least-squares function was $\sum w(|F_o| - |F_c|)^2$ where $w = 1/[\sigma^2(|F_o|) + g(F_o)^2]$. In this work g = 0.00025. The secondary extinction parameter was p = 0.036 (6) in $F_c^* = F_c/[1.0 + 0.002(p)F_o^2/\sin(2\theta)]^{0.25}$. There were 196 parameters refined: atom coordinates, anisotropic thermal parameters for all non-H atoms, and isotropic thermal parameters for the hydrogens, methyl hydrogens used riding model in SHELXTL, H riding on C, C–H = 0.96 Å, U(H) = 1.2 U_{eq}(C). The final residuals were R = 0.039 and R_w = 0.060 with an error for observations of unit weight of 2.90, N_o/N_v = 11.0. The largest shift to error ratio in the final refinement cycle was 0.076 and final difference Fourier excursions were 0.21 and −0.19 e Å^{-3}. Atomic scattering factors are from the *International Tables for X-ray Crystallography* (1974). Tables of atomic coordinates, bond distances and angles, and anisotropic thermal parameters are available as supplementary material.

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Registry No. $Si(CH_3)_3N_3$, 4648-54-8; 4-nitro-5-(trimethylsilyl)pyrazole, 36960-51-7; 4-nitro-5-(trimethylsilyl)-1,2,3-triazole, 122202-89-5; 2-nitro-3-(trimethylsilyl)-7-oxabicyclo[2.2.1]hepta-2,5-diene, 125251-41-4; 2-nitro-3-(trimethylsilyl)bicyclo[2.2.1]-octa-2,5-diene, 107494-77-9; 2-nitro-3-(triisopropylsilyl)bicyclo-[2.2.1]hepta-2,5-diene, 107474-07-7; 2-nitro-3-(trimethylsilyl)bicyclo[2.2.1]hepta-2,5-diene, 107474-08-8; bis(trimethylsilyl)-acetylene, 14630-40-1; furan, 110-00-9; cyclopentadiene, 542-92-7; 1,3-cyclohexadiene, 592-57-4; *o*-(trimethylsilyl)nitrobenzene, 15290-22-9; 1-nitro-2-(triisopropylsilyl)acetylene, 107474-05-5; 1,4-bis(triisopropylsilyl)buta-1,3-diene, 125251-42-5.

Supplementary Material Available: X-ray crystal structure data for 4-nitro-5-(trimethylsilyl)pyrazole (2 pages); tables of structure factors for 4-nitro-5-(trimethylsilyl)pyrazole (6 pages). Ordering information is given on any current masthead page.

(9) Sheldrick, G. M. SHELXTL80: *An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data*; Univ. of Göttingen: Federal Republic of Germany.

Studies of the Total Synthesis of Fredericamycin A. Preparation of Key Partial Structures and Development of an Intermolecular Alkyne–Chromium Carbene Complex Benzannulation Cyclization Approach to the ABCD(E) Ring System

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A study illustrating factors effecting the cyclization mode and regioselectivity of the alkyne–chromium carbene complex benzannulation cyclization reaction is detailed in development of a synthetic approach to the fredericamycin A ABCD(E) ring system.

Fredericamycin A (1, NSC-305263), a quinone antitumor antibiotic[2] isolated from *Streptomyces griseus*[3] bearing a unique spiro[4.4]nonene central to its structure, has been shown to possess potent in vitro cytotoxic activity and

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