by addition of 5 g of Na_2CO_3 to remove H_2O. The supernatant liquid was decanted and found to be sufficiently pure for synthesis. The yield of clear colorless liquid was 101 g (85%): ^1H NMR (CCl_4) δ 4.9 (quart., J = 8 Hz); IR (neat) 1400, 1430, 1680 cm^{-1}.

Synthesis of 2-(Trifluoromethyl)-2-propyl Nitrate. Trifluoroacetic anhydride (16 g, 75 mmol) was cooled to 0 °C with stirring under argon, in a 50-mL round-bottomed flask. Nitric acid (4.5 g, 75 mmol) was carefully added over 5 min to avoid excessive heating. After the addition was complete, the mixture was stirred for 20 min at 0 °C, 2-(trifluoromethyl)-2-propanol (6.5 g, 50 mmol) was added, and the reaction mixture was stirred for an additional 30 min. The reaction mixture was diluted with 25 mL of dichloromethane, extracted with 100 mL of ice–water, dried over Na_2CO_3, and distilled at ~400 Torr. The yield of clear, colorless liquid was 5.3 g (62%): bp 60 °C (400 torr); ^1H NMR (CCl_4, 60 MH_z) δ 1.7 (s); IR (neat) 1660 cm^{-1}. The neat compound gave off traces of NO_2 gas after 1 month of storage at room temperature, but its NMR spectrum was unchanged. At low temperatures (0 °C) no decomposition has been observed, even after 1 year.

Reaction of 1,1,1-Trifluoroethyl Nitrate with Piperidine. Piperidine (4.3 g, 50 mmol) was dissolved in 50 mL of diethyl ether and the resultant mixture treated with trifluoroethyl nitrate (9 g, 60 mmol). An exotherm ensued, causing the solvent to reflux. After 1 h, the exotherm had subsided, and a solid had precipitated from the reaction mixture. The solid was isolated by filtration, and the filtrate was freed of acidic and basic compounds by extraction with aqueous base and acid, respectively. The ether layer was found to contain approximately 600 mg (~10% yield) of *N*-nitropiperidine, as determined by IR, NMR, and TLC in comparison with those of an authentic sample. The solid (2.3 g) was unstable, degrading to *N*-nitrosopiperidine on standing. The solid had an NMR spectum identical with that of piperidine·HNO_3, but its IR spectrum was different from that of an authentic sample. On this basis, and due to its tendency to degrade to *N*-nitrosopiperidine, the solid was assumed to be piperidine·HNO_2.

Reaction of 2-(Trifluoroethyl)-2-propyl Nitrate with Secondary Amines. The secondary amine (1 mmol) was mixed neat with 2-(trifluoromethyl)-2-propyl nitrate (250 mg, 1.5 mmol) and kept at 50 °C for 7 days. Volatiles including 2-(trifluoromethyl)-2-propanol were evaporated in vacuo, and the crude product was filtered through a short plug of silica gel to give pure *N*-nitramines. The products were identical with known materials in their spectroscopic and physical properties. The yields were not further optimized (see Table II).

Synthesis of 2,2-Bis(chloromethyl)propane-1,3-diol Dinitrate. Fuming nitric acid (90%) (100 mL) was saturated with $NaNO_3$ at room temperature. Next, 3,3-bis(chloromethyl)oxetane (20 g, 130 mmol) was added. A mild exotherm was observed, and ice cooling was applied. The mixture was stirred at 0–15 °C for 5 h, with gradual warming from 0 to 15 °C over that interval. The reaction mixture was cooled to 0 °C and was carefully treated with 40 mL of 30% fuming H_2SO_4, stirring and adding the acid in 2-mL aliquots. The resulting mixture was warmed to room temperature over 15 min and poured over ice, giving a white solid. The solid was collected by filtration, dissolved in 150 mL of warm carbon tetrachloride, and crystallized to give 25 g (73%) of large, colorless prisms: mp 63 °C; ^1H NMR ($CDCl_3$, Me_4Si) δ 3.7 (s), 4.6 (s); IR (CCl_4 smear) V_{max} 1670, 1300 cm^{-1}. Anal. Calcd for $C_5H_8Cl_2N_2O_6$: C, 22.83; H, 3.07; N, 10.65; Cl, 26.95. Found: C, 22.90; H, 2.98; N, 10.60; Cl, 26.78.

Reaction of 2,2-Bis(chloromethyl)propane-1,3-diol Dinitrate with Secondary Amines. The amine (10 mmol) was mixed with 2,2-bis(chloromethyl)propane-1,3-diol dinitrate (1.3 g, 5 mmol) and the resultant mixture heated in a sealed vial at 55 °C for 3 days. Unreacted nitrate ester was destroyed by adding 5 mL of ethyl alcohol and 2 mL of hydrazine and heating at 80 °C for 1 h. The reaction mixture was partitioned between 100 mL of ether and 100 mL of water. The ether layer was concentrated and chromatographed, eluting chloroform over silica gel, yielding the pure nitramines, which were visualized by UV. The products were chromatographically and spectroscopically identical with known samples of the target compounds (see Table III).

Acknowledgment. We thank Dr. Anthony Matuszko of the Air Force Office of Scientific Research (Contract No. F49620-83-K-0023) for his encouragement and support of this work.

Registry No. $(F_3C)_2CHOH$, 920-66-1; $(F_3C)_2CHONO_2$, 107149-24-6; F_3CCH_2OH, 75-89-8; $F_3CCH_2ONO_2$, 461-38-1; $F_3CC(CH_3)_2OH$, 507-52-8; $F_3CC(CH_3)_2ONO_2$, 107149-25-7; $C_6H_5CH_2NHCH_3$, 103-67-3; $NH(CH_3)_2$, 124-40-3; $H_3CN(NO_2)CH_2C_6H_5$, 36239-05-1; $O_2NN(CH_2CH_3)_2$, 7119-92-8; $O_2NN(CH_3)_2$, 4164-28-7; $C_6H_5CH_2N(NO)CH_3$, 937-40-6; $O_2NOCH_2C(CH_2Cl)_2CH_2ONO_2$, 107149-26-8; piperidine, 110-89-4; morpholine, 110-91-8; pyrrolidine, 123-75-1; *N*-nitropiperidine, 7119-94-0; *N*-nitromorpholine, 4164-32-3; *N*-nitropyrrolidine, 3760-55-2; 3,3-bis(chloromethyl)oxetane, 78-71-7.

Nitroacetylenes: Synthesis of 1-Nitro-2-(trialkylsilyl)acetylenes via Nitrodesilylation of Bis(trialkylsilyl)acetylenes

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Received September 30, 1986

As part of a study to develop a new synthetic route to nitroacetylenes, this report describes a general synthesis of 1-nitro-2-(trialkylsilyl)acetylenes 1. The method in-

$$R_3SiC{\equiv}CNO_2$$
1

volves direct reaction between a nitronium ion source [i.e., nitronium tetrafluoroborate (NTFB), nitronium hexafluorophosphate (NHFP), or nitryl fluoride], bis(trialkylsilyl)acetylene, and a fluoride ion source. Only five nitroacetylenes have been reported previously,[1-6] and all are reported to be thermally unstable. The synthesis routes to known nitroacetylenes are shown in eq 1 and 2.

$$RC{\equiv}CSnMe_3 + N_2O_5 \xrightarrow{\text{inert solvent}} RC{\equiv}CNO_2 \quad (1)$$

R = Ph, Me_3Si, *n*-Pr, *i*-Pr

$$RC{\equiv}CH + NO_2I \rightarrow R(I)C{=}C(H)NO_2 \xrightarrow{\text{base/heat}} RC{\equiv}CNO_2 \quad (2)$$

R = *t*-Bu

We report here a general synthesis method for preparing 1-nitro-2-(trialkylsilyl)acetylenes. This unique one-step procedure allows for the preparation of numerous nitroacetylenes not accessible through the known synthesis methods.

Recently, we reported[7] an improved, one-step synthesis of 1-nitro-2-(trimethylsilyl)acetylene by treating bis(trimethylsilyl)acetylene with NTFB in methylene chloride (eq 3). When freshly triturated NTFB is used, a 70%

$$Me_3SiC{\equiv}CSiMe_3 + NO_2BF_4 \xrightarrow{CH_2Cl_2} Me_3SiC{\equiv}CNO_2 \quad (3)$$

yield of the nitroacetylene is obtained. The effects of alkyl substituents on both the acetylene and silyl substrate, the nitronium ion source, and reaction solvents have been studied. A special feature of this one-step nitrodesilylation reaction is the regioselectivity observed with bis(trialkylsilyl)acetylene substrates, allowing for the preparation of numerous 1-nitro-2-(trialkylsilyl)acetylenes, not easily

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0022-3263/87/1952-2294$01.50/0

Table I. Nitroacetylene Yields

starting material	nitronium salt	nitroacetylene product	yield, %
$Me_3SiC{\equiv}CSiMe_3$	NTFB	$Me_3SiC{\equiv}CNO_2$	70[a]
$Me_3SiC{\equiv}CSiMe_2$-*i*-Pr	NHFP	*i*-$PrMe_2SiC{\equiv}CNO_2$	34[b]
		$Me_3SiC{\equiv}CNO_2$	6[b]
$Me_3SiC{\equiv}CSiMe_2$-*t*-Bu	NHFP	*t*-$BuMe_2SiC{\equiv}CNO_2$	59[a]
		$Me_3SiC{\equiv}CNO_2$	29[a]
$Me_3SiC{\equiv}CSi(i\text{-}Pr)_3$	NHFP	$(i\text{-}Pr)_3SiC{\equiv}CNO_2$	57[a]
		$Me_3SiC{\equiv}CNO_2$	0
$Me_3SiC{\equiv}CCH_3$	NHFP	$CH_3C{\equiv}CNO_2$	*c*,*d*
$Me_3SiC{\equiv}C$-*t*-Bu	NHFP	*t*-$BuC{\equiv}CNO_2$	0
$Me_3SiC{\equiv}CC_6H_5$	NHFP	$C_6H_5C{\equiv}CNO_2$	0
$Me_3SiC{\equiv}C(CH_2)_4C{\equiv}CSiMe_3$	NHFP	$Me_3SiC{\equiv}C(CH_2)_4C{\equiv}CNO_2$	0

[a] Isolated yield. [b] Yield determined from internal standard. [c] Rapidly decomposes. [d] Trace yield, observed by GC/MS.

accessible by known preparative routes.

One aspect of the synthesis study centered on generalizing the reaction of 1-alkyl-substituted silylacetylenes with nitronium ion sources. Purified NTFB in anhydrous acetonitrile or nitromethane and methylene chloride solvents proved to be an effective medium for the nitrodesilylation reaction, giving 1-alkyl-2-nitroacetylene compounds in low yield (Table I). Treatment of 1-phenyl-2-(trimethylsilyl)acetylene with nitronium ion sources failed to yield the desired nitroacetylene product. The nitronium salt, either NTFB or NHFP, must be thoroughly pure as impurities lead to reaction difficulties.

Good to excellent yields of nitroacetylenes were obtained when the R of eq 4 was a trialkylsilyl group. The presence

$$RC{\equiv}CSiMe_3 \xrightarrow[\text{acetonitrile/nitromethane}]{\text{NTFB/NHFP}} RC{\equiv}CNO_2 \quad (4)$$

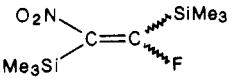
of a silicon atom α to the triple bond provides extra stabilization to the nitronium ion/acetylene transition state. Table I gives the yield of nitroacetylenes from the various bis(trialkylsilyl)acetylene substrates. Note that particularly high yields of the nitroacetylene products were obtained when bis(trialkylsilyl)acetylene substrates were used compared with the low nitroacetylene yields for the monosilylacetylene substrates.

Two products can result from the nitrodesilylation of bis(trialkylsilyl)acetylene substrates: one resulting from replacement of the Me_3Si group, the other from replacement of the more sterically crowded trialkylsilyl group (eq 5). In general, the ease of desilylation, and consequently

$$Me_3SiC{\equiv}CSiRR'R'' \xrightarrow{\text{NHFP/CH}_3\text{CN}} NO_2C{\equiv}CSiRR'R'' + Me_3SiC{\equiv}CNO_2 \quad (5)$$

the relative proportion of the two nitroacetylene products, follow the order generally observed for elimination of trialkylsilyl moieties:[8] $Me_3Si > Me_2$-*i*-$PrSi > Me_2$-*t*-$BuSi > (i\text{-}Pr)_3Si$. This high degree of regioselectivity (entries 2–4) results from the ease of attack by fluoride ion on the trialkylsilyl moiety. The steric crowding encountered in the triisopropylsilyl case results in exclusive fluoride ion assisted displacement of the Me_3Si group, whereas mixtures of nitroacetylenes were obtained when less bulky silyl substituents were studied entries 2 and 3, Table I.

In addition to the target nitroacetylene compounds, two other minor products were isolated from many of these nitrodesilylation reactions. They resulted from cis and trans addition of NO_2F across the triple bond, **2**.



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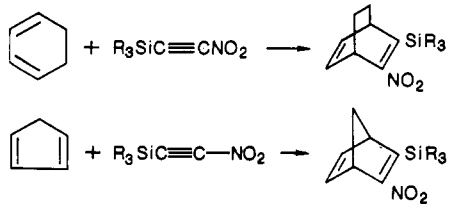
The nitroacetylenes were characterized by a combination of GC/MS and GC/FTIR observations (Tables II and III; see paragraph at end of paper about supplementary material). All nitroacetylenes show the characteristic acetylene stretching frequency band between 2150 and 2250 cm^{-1} in the infrared. Furthermore, in all compounds the characteristic asymmetric and symmetric NO_2 stretching frequencies were observed in the infrared spectra near 1525 and 1350 cm^{-1}, respectively.

The 1-nitro-2-(trialkylsilyl)acetylenes frequently gave a molecular ion ($M^{\bullet+}$) under electron impact mass spectrometry (70 eV). Other characteristic fragmentations are loss of an alkyl group from the silyl moiety ($M - R^+$) and complete loss of the silyl group ($M - SiR_3^+$).[8] The general fragmentation pathways for nitroacetylenes are shown in eq 7. Additional simple fragmentations are observed from the alkyl or other functional groups.

$$R_3SiC{\equiv}CNO_2 \xrightarrow{e^-} \begin{array}{l}[R_3SiC{\equiv}CNO_2]^{\bullet+}\ (M^{\bullet+}) \\ [R_2SiC{\equiv}CNO_2]^+ + R^\bullet\ (M^+ - R) \\ [C{\equiv}CNO_2]^\bullet + R_3Si^+ \\ R_3SiC{\equiv}C^+ + NO_2\ (M^+ - NO_2)\end{array} \quad (7)$$

The nitroacetylenes readily undergo Diels–Alder reactions with various cyclic dienes (eq 8). The structures of



(8)

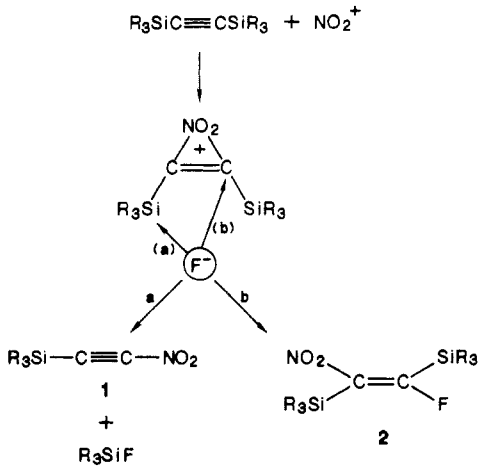
these products were confirmed by a combination of field ionization mass spectrometry, ^1H NMR, infrared, and elemental analysis.

Two possible mechanisms may account for the dramatic differences in the yields of nitroacetylenes formed when bissilyl- and monosilylacetylene substrates are used in the nitrodesilylation reaction. The first results from electrophilic attack of nitronium ion on the triple bond, followed by fluoride attack at silicon or carbon to give silyl fluoride and nitroacetylene or cis/trans fluoronitro olefin products. The second mechanism arises from initial fluoride displacement of the silyl group to give silylfluoride and the acetylide anion, followed by nitronium ion addition to the carbanion (Schemes I and II, respectively). The driving force for either mechanism is the formation of the strong Si–F bond resulting from attack of fluoride ion at silicon.[9]

We postulate that the first mechanism is the most probable. The contrast in reactivity between mono- and bissilylacetylenes is due to the ability of silicon to stabilize the carbonium ion intermediates over that of carbon.[10-13]

(1) Petrov, A. A.; Zavgorodinii, V. S.; Rall, K. B.; Vil'davskaya, A. I.; Bogoradovskii, E. T. *J. Gen. Chem. USSR (Engl. Transl.)* **1978**, *48*, 865.
(2) Jager, V.; Motte, J.-C.; Viehe, H. G. *Chimica* **1975**, *29*, 516.
(3) Jager, V.; Viehe, H. G. *Angew. Chem., Int. Ed. Engl.* **1969**, 273.
(4) Rall, K. B.; Vil'davskaya, A. I.; Petrov, A. A. *Russ. Chem. Rev. (Engl. Transl.)* **1975**, *44*, 373.
(5) Kashin, A. N.; Bumagin, N. A.; Bessonova, M. P.; Beletskaya, I. P.; Reutov, O. A. *J. Org. Chem. USSR (Engl. Transl.)* **1980**, *16*, 1153.
(6) Stevens, T. E.; Emmons, W. D. *J. Am. Chem. Soc.* **1958**, *80*, 338.
(7) Schmitt, R. J.; Bedford, C. D. *Synthesis* **1986**, 493.
(8) Pierce, A. E. *Silylation of Organic Compounds*; Pierce Chemical Co.: Rockford, IL, 1982; pp 1–39.
(9) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem* **1982**, 493.
(10) Weber, W. P. *Silicon Reagents for Organic Synthesis*; *Reactivity and Structure Concepts in Organic Chemistry, 14*; Springer-Verlag: Berlin, 1983; and references therein.

Scheme I. Cyclic Nitronium Ion Intermediate



Scheme II. Acetylide Ion Intermediate

$$Me_3SiC{\equiv}CR + F^- \rightarrow RC{\equiv}C^- + Me_3SiF$$
$$RC{\equiv}C^- + NO_2^+ \rightarrow RC{\equiv}CNO_2$$

Silicon is known to stabilize β-carbonium ions through hyperconjugation significantly better than alkyl groups. A second factor supporting the first mechanism is the observation of the small amounts of NO_2F addition products that would not be expected from the second reaction mechanism. Third, alkyl groups more readily undergo carbonium ion rearrangements, for example, to give a tertiary carbonium ion, than do silicon systems. This propensity of carbonium ions to rearrange may in part explain why we cannot synthesize *tert*-butylnitroacetylene from *tert*-butyl(trimethylsilyl)acetylene. Finally, addition of nitronium ion salts to a lithioacetylene does not give any nitroacetylene product.

Experimental Section

CAUTION! All nitroacetylene compounds are considered toxic and potentially explosive and should be handled with appropriate precautions.

Materials. Nuclear magnetic resonance spectra were recorded on a Varian Associates EM-360 or a JEOL FXQ-90. Infrared spectra were obtained on a Digilab-20 GC/FTIR (HP5980 GC). Mass spectra were obtained on a HP mass selective detector 5790B with gas chromatographic separation on a HP5970 GC. The reaction progress was monitored by gas chromatography using a Varian Model 3700 equipped with a SE-54, 50-m capillary column. High-quality NHFP and NTFB were obtained from Ozark-Mahoning. NHFP was used as obtained. NTFB was purified by triturating with nitromethane, decanting away the residual nitric acid components, and then rotoevaporating the wet NTFB to dryness. This step was repeated several times, resulting in NTFB free of acidic impurities. The silicon compounds were generally obtained from Petrarch Systems, Inc., or from Aldrich Chemical Co.

General Synthesis Procedure for the Synthesis of Nitroacetylenes Using Nitronium Hexafluorophosphate or Nitronium Tetrafluoroborate. NHFP (1 equiv) or purified NTFB (1 equiv) suspended in anhydrous acetonitrile, nitromethane, or nitromethane/methylene chloride was added to 1 equiv of the (trimethylsilyl)acetylene in acetonitrile, nitromethane, or nitromethane/methylene chloride with rapid stirring for 1 h at room temperature. The crude nitroacetylenes were 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, applying suction at the effluent port and rinsing with 100 mL of chloroform. The effluent was typically concentrated to 10 mL in vacuo and quickly utilized in subsequent synthetic transformations. *NOTE*: Do not wash with brine or bicarbonate solutions; they cause rapid decomposition of the nitroacetylenes. Nitroacetylenes will generally decompose rapidly if concentrated and allowed to stand. Decomposition can be slowed by dilution in an inert solvent and storing in a freezer. However, both (triisopropylsilyl)nitroacetylene and (dimethyl-*tert*-butylsilyl)nitroacetylene are stable for a few hours at room temperature when concentrated. The stability of the nitroacetylenes goes up dramatically with increasing size of the silyl group attached to the nitroacetylene. For example, we find no decomposition of (triisopropylsilyl)- or (dimethyl-*tert*-butylsilyl)nitroacetylenes when dissolved in methylene chloride at room temperature over several weeks. Characterization of the new nitroacetylene compounds are shown in Tables II and III (available as supplementary material).

2-Nitro-3-(triisopropylsilyl)bicyclo[2.2.1]hepta-2,5-diene. (Triisopropylsilyl)nitroacetylene (70 mg, 0.4 mmol, with 30 mg of (triisopropylsilyl)acetylene as impurity) was dissolved in 10 mL of CCl_4 and treated 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) 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) 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. 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, by using a vacuum aspirator to hasten 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 the 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 C–H), 2960 (m, C–H), 1520 (s, NO_2), 2360 (s, NO_2) cm^{-1}; ^1H NMR (CCl_4) 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)norbornadiene. 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 (trimethylsilyl)nitroacetylene 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, eluting with chloroform, collecting the R_f 0.7 material. 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 C–H), 2960 (m, C–H), 1505 (s, nitro), 1350 (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, 6.70. Found: C, 56.73; H, 7.43; N, 6.39.

Acknowledgment. We thank Dr. Anthony Matuszko of the Air Force Office of Scientific Research (Contract F49620-83-K-0023) for his encouragement and support of this work.

Registry No. NTFB, 13826-86-3; NHFP, 19200-21-6; $Me_3SiC{\equiv}CSiMe_3$, 14630-40-1; $Me_3SiC{\equiv}CSiMe_2$-*i*-Pr, 107474-00-0; $Me_3SiC{\equiv}CSiMe_2$-*t*-Bu, 107474-01-1; $Me_3SiC{\equiv}CSi(i\text{-}Pr)_3$, 107474-02-2; $Me_3SiC{\equiv}CCH_3$, 6224-91-5; $Me_3SiC{\equiv}$-*t*-Bu, 14630-42-3; $Me_3SiC{\equiv}CC_6H_5$, 2170-06-1; $Me_3SiC{\equiv}C(CH_2)_4C{\equiv}CSiMe_3$, 63873-32-5; *t*-$BuMe_2SiC{\equiv}CNO_2$, 107474-04-4; $Me_3SiC{\equiv}CNO_2$,

(11) Apeloig, Y.; Stanger, A. *J. Am. Chem. Soc.* **1985**, *107*, 2806.
(12) Wierschke, S. G.; Chandrasekhar, J.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1985**, *107*, 1496.
(13) Shiner, V. J., Jr.; Ensiger, M. W.; Kriz, G. S. *J. Am. Chem. Soc.* **1986**, *108*, 842.

67177-80-4; *i*-PrMe$_2$C≡CNO$_2$, 107474-03-3; (*i*-Pr)$_3$SiC≡CNO$_2$, 107474-05-5; CH$_3$C≡CNO$_2$, 107474-06-6; **2**, 107474-09-9; (*i*-Pr)$_3$SiC≡CH, 89343-06-6; cyclopentadiene, 542-92-7; 1,3-cyclohexadiene, 592-57-4; 2-nitro-3-(triisopropylsilyl)norbornadiene, 107474-07-7; 2-nitro-3-(trimethylsilyl)bicyclo[2.2.2]octa-2,5-diene, 107494-77-9; 2-nitro-3-(trimethylsilyl)norbornadiene, 107474-08-8.

Supplementary Material Available: IR spectral data for all new nitroacetylenes (Table II) and MS fragmentation patterns for nitroacetylenes and (trimethylsilyl)acetylenes (Table III) (3 pages). Ordering information is given on any current masthead page.

Synthesis of Monoalkyl Derivatives of 7,7,8,8-Tetracyano-*p*-quinodimethane from 2,5-Dimethoxybenzoic Acid

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Received November 10, 1986

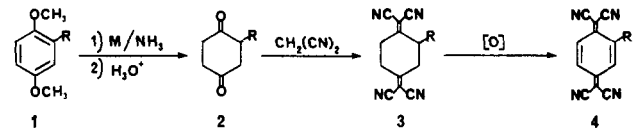
7,7,8,8-Tetracyano-*p*-quinodimethane (TCNQ, **4a**) and its derivatives have received much attention by virtue of their reversible stepwise two-electron redox chemistry,[1,2a] their capacity to form electrically conductive charge-transfer complexes,[2] and the bistable electrical and photochemical switching behavior ascribed to certain metal–TCNQ salts.[3] Although a large number of substituted TCNQ derivatives have been studied in these contexts, the great majority have been di- and tetrasubstituted, with only a few reports of the less symmetrical monosubstituted derivatives.[4]

Syntheses of the monosubstituted TCNQ derivatives **4b–d** (Scheme I) have been reported by others.[4c,d] These all employ a metal–ammonia reduction/hydrolysis sequence, starting from the correspondingly substituted derivatives of 1,4-dimethoxybenzene (**1b–d**), to arrive at the key 1,4-cyclohexanedione intermediates **2b–d**. These cyclohexanediones are then converted to the corresponding TCNQ derivatives **4b–d** by the classical condensation/oxidation sequence of Acker and Hertler.[1] The utility of this general route to 1,4-cyclohexanediones is limited, however, by the availability of starting materials **1** and by the applicability of the metal–ammonia reduction to the chosen substrates. In our efforts to utilize the above procedure, we arrived at a convenient new method for synthesis of 1,4-cyclohexanediones that overcomes these limitations by employing 2,5-dimethoxybenzoic acid (**5**) as a universal starting material.

Results and Discussion

The method of Scheme I was used in our laboratories to prepare the hitherto unknown ethyl derivative of

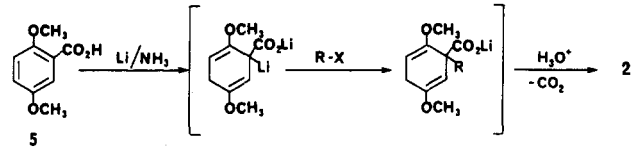
Scheme I



1 **2** **3** **4**

a, R = H **d**, R = $CH_2CH_2CO_2H$ **g**, R = $CH_2C_6H_5$
b, R = CH_3 **e**, R = C_2H_5 **h**, R = $COCH_3$
c, R = CH_2CO_2H **f**, R = *n*-$C_{12}H_{25}$ **i**, R = $CO(CH_2)_{10}CH_3$

Scheme II



5 **2**

TCNQ. To accomplish this, we needed to synthesize 2-ethyl-1,4-dimethoxybenzene (**1e**)[5] by reduction[6] of the commercially available acetyl derivative **1h**. In an analogous attempt to synthesize *n*-dodecyl-TCNQ, we prepared substrate **1f** in two steps from **1a** (acylation with lauroyl chloride[7] to give **1i**, followed by reduction[6]), only to find that the metal–ammonia reduction of **1i** was hampered by solubility problems.

At this point, an examination of the literature on alternate metal–ammonia reduction methods led us to a reductive alkylation process based on 2,5-dimethoxybenzoic acid (**5**).[8] As depicted in Scheme II, it was reasoned that hydrolyses of these reductive alkylation products, with concomitant decarboxylation, would afford 1,4-cyclohexanediones **2** directly. This dione formation had already been observed, as an undesired side reaction, by Hook and Mander.[8a]

In practice, diones **2e–g** were successfully prepared from **5** and an alkyl iodide or bromide, each in a single synthetic operation, and in high yield. Table I summarizes the complete synthesis of monoalkyl-TCNQ derivatives **4e–g** using this method. The overall yields of TCNQ derivatives based on **5** were 20–50%. In the malononitrile condensation step (**2** → **3**), it was found that aqueous THF was a useful solvent system for the β-alanine-catalyzed modification of Andersen and Jorgensen.[4d]

Table II lists the cyclic voltammetric data for the newly synthesized TCNQ derivatives **4e–g** and lists the first and second half-wave reduction potentials of (unsubstituted) TCNQ (**4a**), measured by us and by others,[2a] for reference. The first reduction potentials observed for the new derivatives are consistent with expectations, based on the relative inductive effects of the substituents.

In conclusion, what we have demonstrated here is a route to 1,4-cyclohexanediones involving a common starting material and an alkyl halide, which considerably extends the range of easily accessible monosubstituted TCNQ derivatives.

Experimental Section

Melting points were determined on a Fisher-Johns apparatus and were not corrected. Infrared spectra were recorded on a Nicolet 5DX FTIR spectrophotometer. NMR spectra were re-

(1) Acker, D. S.; Hertler, W. R. *J. Am. Chem. Soc.* **1962**, *84*, 3370.
(2) (a) Wheland, R. C.; Gillson, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 3916. (b) Wheland, R. C. *Ibid.* **1976**, *98*, 3926. (c) Melby, L. R.; Harder, R. J.; Hertler, W. R.; Mahler, W.; Benson, R. E.; Mochel, W. E. *Ibid.* **1962**, *84*, 3374.
(3) Poehler, T. O.; Potember, R. S.; Hoffman, R.; Benson, R. C. *Mol. Cryst. Liq. Cryst.* **1984**, *107*, 91. Kamitsos, E. I.; Risen, W. M., Jr. *Solid State Commun.* **1983**, *45*, 165. Kamitsos, E. I.; Tzinis, C. H.; Risen, W. M., Jr. *Ibid.* **1982**, *42*, 561. Potember, R. S.; Poehler, T. O.; Cowan, D. O.; Bloch, A. N. In *The Physics and Chemistry of Low-Dimensional Solids*; Alcacer, L., Ed.; Reidel: Boston, 1980; pp 419–428.
(4) (a) Uno, M.; Seto, K.; Masuda, M.; Ueda, W.; Takahashi, S. *Tetrahedron Lett.* **1985**, *26*, 1553. (b) Kini, A.; Mays, M.; Cowan, D. *J. Chem. Soc., Chem. Commun.* **1985**, 286. (c) Baghdadchi, J.; Panetta, C. A. *J. Org. Chem.* **1983**, *48*, 3852. (d) Andersen, J. R.; Jorgensen, O. *J. Chem. Soc., Perkin Trans. 1* **1979**, 3095. (e) Wheland, R. C.; Martin, E. L. *J. Org. Chem.* **1975**, *40*, 3101.
(5) (a) Shulgin, A. T. *J. Med. Chem.* **1975**, *18*, 1201. (b) Orlando, C. M., Jr.; Mark, H.; Bose, A. K.; Manhas, M. S. *J. Org. Chem.* **1968**, *33*, 2512. (c) Howe, C. A.; Hamel, C. R.; Stedman, E. D.; Hyman, F. *Ibid.* **1960**, *25*, 1245.
(6) KOH, hydrazine, triethylene glycol, 190 °C; see: Huang-Minlon *J. Am. Chem. Soc.* **1946**, *68*, 2487.
(7) Lauroyl chloride, $AlCl_3$, $CHCl_3$, reflux; see: Morimoto, K.; Furuya, K.; Toriuchi, M. Ger. Offen. DE 3 437 545, 25 April 1985.
(8) (a) Hook, J. M.; Mander, L. N. *J. Org. Chem.* **1980**, *45*, 1722. (b) Hook, J. M.; Mander, L. N.; Urech, R. *Synthesis* **1979**, 374.

0022-3263/87/1952-2297$01.50/0