J. Org. Chem. 1985, 50, 2736-2739

mp 89-90.5 °C, $[\alpha]^{25}_{D}$ −128.1° (*c* 0.49, EtOH). Anal. Calcd for $C_{12}H_{19}NO_4S$: C, 52.73; H, 7.01; N, 5.12; S, 11.73. Found: C, 52.50; H, 7.08; N, 4.89; S, 11.79.

In a similar experiment (*S*)-**6** was prepared from the silyl acetal (*S*)-**22** in 74% yield: mp 88-90 °C; $[\alpha]^{25}_{D}$ +122.8° (*c* 0.50, EtOH).

(*R*)-4-[(*tert*-Butoxycarbonyl)amino]-4,5-dihydro-2-thiophenecarboxylic Acid [(*R*)-7]. To a stirring, ice-cooled solution containing 20.5 g (75 mmol) of (*R*)-**6** in 240 mL of EtOH was added 100 mL of 1 N LiOH. After being stirred for 1 h the reaction was neutralized with 10 mL of 6 N HCl and the bulk of the EtOH was removed in vacuo. The mixture was diluted with 250 mL each of EtOAc and ether and 30 mL of 2 N HCl, and the organic phase was washed with 2 × 30 mL water and brine, dried, and concentrated to afford 18.0 g (98% yield) of (*R*)-**7** as a white crystalline solid. This material was shown to be a 98.7/1.3 mixture of *R*/*S* isomers. Recrystallization (85 mL of EtOAc/95 mL of hexane) produced 11.24 g of (*R*)-**7** containing no detectable *S* isomer: mp 147 °C dec; $[\alpha]^{25}_{D}$ −140.8° (*c* 0.50, EtOH); NMR δ 1.50 (s, 9 H, *t*-Bu), 3.15 (dd, 1 H, $J_{4,5}$ = 5 Hz and $J_{5,5'}$ = 12 Hz, H-5), 3.65 (dd, 1 H, $J_{4,5'}$ = 12 Hz, H-5′), 5.15 (m, 2 H, H-4 and NH), 6.60 (d, 1 H, $J_{3,4}$ = 3 Hz, H-3), 11.0 (s, 1 H, CO_2H); IR (KBr) 3360, 1700, 1515, 1370, 1250, 1160 cm^{-1}. Anal. Calcd for $C_{10}H_{15}NO_4S$: C, 48.96; H, 6.16; N, 5.71; S, 13.07. Found: C, 48.75; H, 6.16; N, 5.66; S, 12.99.

In a similar experiment (*S*)-**7** was prepared from (*S*)-**6** in 95% yield and shown to be 99.1/0.9 mixture of *S*/*R* isomers by HPLC. After recrystallization this sample contained no detectable *R* isomer: mp 133 °C dec; $[\alpha]^{25}_{D}$ +141.3° (*c* 1.05, EtOH). Anal. Calcd: as above. Found: C, 48.84; H, 6.26; N, 5.46; S, 13.10.

(*R*)-4-Amino-4,5-dihydro-2-thiophenecarboxylic Acid [(*R*)-1]. Dry HCl gas was bubbled into an ice-cooled, stirring solution containing 11.15 g (45.5 mmol) of the recrystallized acid (*R*)-**7** in 400 mL of EtOAc for 4 min. The cooling bath was removed, and stirring was continued for 2 h at which point the reaction was filtered, and the collected solid was washed with EtOAc and ether to produce 6.4 g of the crude hydrochloride of (*R*)-**1**. The filtrate was concentrated to 100 mL in volume and extracted with water, and the aqueous phase was then back-extracted with 3 × 70 mL of ether. The combined organic extracts were dried and concentrated to yield 1.55 (27% yield) of thiophene-2-carboxylic acid. The aqueous wash was combined with the 6.4 g of filtered solid, adjusted to pH 8-9 with NH_4OH, and purified by ion exchange chromatography to afford 4.41 g (63% yield) of analytically pure (*R*)-**1** as a white crystalline solid: mp 202 °C dec; $[\alpha]^{25}_{D}$ −145.9° (*c* 0.5, 0.1 N NaOH). HPLC analysis showed no detectable *S* isomer. Anal. Calcd for $C_5H_7NO_2S$: C, 41.37; H, 4.86; N, 9.65; S, 22.09. Found: C, 41.12; H, 4.86; N, 9.41; S, 22.04.

Employing the same procedure described for the synthesis of (*R*)-**1** with the exception that the product in the filtrate was not recovered, 1.2 g (4.9 mmol) of (*S*)-**7** was converted to 325 mg (46% yield) of (*S*)-**1**: mp 203 °C dec; $[\alpha]^{25}_{D}$ +143.7° (*c* 0.5, 0.1 N NaOH). HPLC analysis detected 0.2% of the *R* isomer. Anal. Calcd: as above. Found: C, 41.53; H, 4.86; N, 9.58; S, 22.01.

Acknowledgment. We are indebted to Mr. Edward Huber for providing the optical rotation data and to Mrs. Charlene Mercer for preparing the manuscript.

Synthesis and Reactions of Tetranitroethylene[1]

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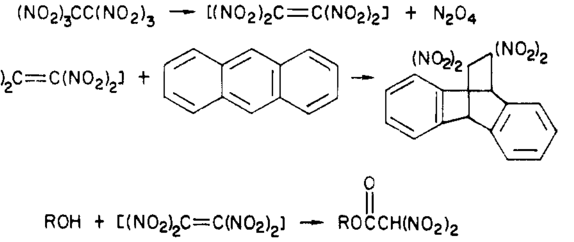
Tetranitroethylene was isolated in 50% yield by flash vacuum pyrolysis of hexanitroethane. Critical for the isolation is a trap temperature such that dinitrogen tetraoxide is not condensed. Tetranitroethylene reacted quantitatively with anthracene to give 11,11,12,12-tetranitro-9,10-dihydro-9,10-ethanoanthracene, and competition experiments with anthracene showed that tetranitroethylene is at least an order of magnitude more reactive than tetracyanoethylene. Tetranitroethylene reacted with cyclopentadiene to give 5,5,6,6-tetranitronorbornene and with ethanol to give ethyl dinitroacetate. Acetylenes and olefins reacted with tetranitroethylene to give 3-nitroisoxazoles and 3-nitro-2-isoxazolines, respectively.

The isolation of tetranitroethylene, expected to be an exceptionally powerful dienophile and electron acceptor, has not been reported. Previously, we found that heating hexanitroethane in refluxing benzene in the presence of a diene or an anthracene derivative gave the products that would be expected from the Diels-Alder reactions of these compounds with tetranitroethylene.[2] The products were rationalized on the basis of the extrusion of dinitrogen tetroxide from hexanitroethane to give tetranitroethylene, as an unstable intermediate, which reacts in situ with these reagents. Similarly, heating hexanitroethane with alcohols gave alkyl dinitroacetates,[3] explainable by the addition of the alcohols to tetranitroethylene followed by loss of the labile nitro groups adjacent to the resulting ether.



Thermolysis of this anthracene adduct of tetranitroethylene resulted in another extrusion of dinitrogen tetroxide to give the corresponding *vic*-dinitro olefin,[4] a stable compound, providing additional evidence for the course of the hexanitroethane reactions. Nevertheless, the existence of tetranitroethylene as a discrete intermediate is not proved by this evidence, and mechanisms involving stepwise reactions of hexanitroethane π complexes or pentanitroethyl radicals are not rigorously excluded.

Heating hexanitroethane in the absence of a trapping agent has been reported to give only simple gaseous decomposition products.[5] The reaction of the ambident NO_2

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(1) This work was supported by the U.S. Army Research Office.

(2) Griffin, T. S.; Baum, K. *J. Org. Chem.* **1980**, *45*, 2880.

(3) Tzeng, D.; Baum, K. *J. Org. Chem.* **1983**, *48*, 5384.

(4) Baum, K.; Griffin, T. S. *J. Org. Chem.* **1981**, *46*, 4811.

radical with olefins is known to give both C–N and C–O products,[6] and readdition to tetranitroethylene by the latter mode would give unstable dinitro–nitrite structures. The decomposition of tetranitroethylene by dinitrogen tetroxide would release more dinitrogen tetroxide, making the decomposition reaction autocatalytic.

$$(NO_2)_2C{=}C(NO_2)_2 + N_2O_4 \rightarrow (O_2N)_3CC(NO_2)_3 + (O_2N)_2C(ONO)C(NO_2)_3 + (O_2N)_2C(ONO)C(NO_2)_2(ONO)$$

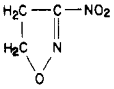
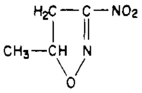
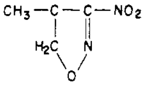
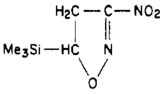
It was apparent, then, that if tetranitroethylene is to be isolated from the thermolysis of hexanitroethane, efficient chemical trapping or physical separation of the nitrogen oxides from the product is needed. Trapping agents generally used for nitrogen oxides such as ureas and polyhydric phenols are unlikely to be compatible with tetranitroethylene, and, indeed, screening experiments in this area were unsuccessful. Subsequently, an investigation of a variety of vacuum thermolysis conditions was carried out, using a dry-ice trap to condense the product. Only decomposition products were obtained. Varying the trapping temperature, however, resulted in the isolation of tetranitroethylene. The key was to select a trap temperature low enough to condense the olefin but not low enough to condense dinitrogen tetroxide.

The optimum conditions for the isolation of tetranitroethylene consisted of passing hexanitroethane vapor at 1 mmHg through a pyrolysis tube heated at 240–270 °C and condensing the product in a 10 °C trap. A greenish yellow solid was collected in the trap. The material was stable at room temperature under continuous pumping and sublimed at about 40 °C (1 mm). Without vacuum to remove small amounts of decomposition products, the material decomposed rapidly to give a dark viscous oil and oxides of nitrogen. When the preparation of tetranitroethylene was carried out with the isolation trap cooled to −15 °C instead of +10 °C, the product isolated was similar to this decomposed material.

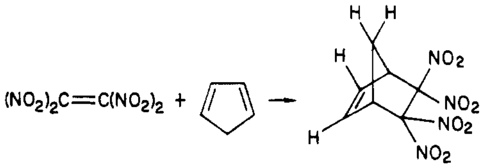
Weighing freshly prepared samples, sealed under vacuum, indicated a 50 ∓ 1% yield of tetranitroethylene. The material reacted instantly at room temperature with a solution of anthracene in benzene to give 11,11,12,12-tetranitro-9,10-dihydro-9,10-ethanoanthracene in 70% yield. Some decomposition was noted during the time interval needed to remove the sample from the vacuum system and to complete the weighing. However, when the tetranitroethylene was not weighed and the anthracene solution was added directly to freshly prepared samples of tetranitroethylene without removing the material from the vacuum system, the yield of the Diels–Alder product was quantitative, based on the weight of the olefin that was obtained in other experiments consistently under the same conditions. The preparation of the Diels–Alder adduct from hexanitroethane, by contrast, was carried out in refluxing benzene.[2]

Tetracyanoethylene has been reported to be the most reactive common dienophile, 2 orders of magnitude above fumaryl chloride and 7 above methyl acrylate in reaction rates with cyclopentadiene.[7] It was of interest, therefore, to compare tetracyanoethylene with tetranitroethylene. Mixtures of the known[2,8] anthracene adducts are readily analyzed by NMR. When a benzene solution of 25% of the theoretical amount of anthracene was added to a neat equimolar mixture of tetracyanoethylene and tetranitroethylene, a 10:1 ratio of the tetranitroethylene adduct of anthracene to that of tetracyanoethylene was obtained. The reactivity ratio is only approximate because the reaction is heterogeneous. A more accurate determination could not be made by predissolving the olefins because tetranitroethylene is unstable in solution.

Table I. Reactions of Tetranitroethylene with Olefins

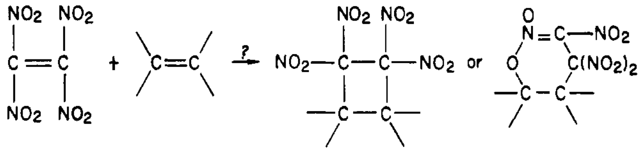
olefin	products	% yield
$CH_2{=}CH_2$	 1	32
$CH_2{=}CHCH_3$	 2 +  3	12 (95:5)
$CH_2{=}CHSiMe_3$	 4	20

The addition of a solution of cyclopentadiene in methylene chloride to tetranitroethylene gave an 85% yield of 5,5,6,6-tetranitronorbornene. This compound was previously[2] obtained in 15% yield by the in situ reaction with hexanitroethane.



A 5% solution of ethanol in benzene reacted with tetranitroethylene at room temperature to give a 72% yield of ethyl dinitroacetate. This material was obtained previously[3] by the reaction of hexanitroethane with refluxing ethanol.

Reactions of tetranitroethylene with simple olefins would be expected to produce cyclobutanes by [2 + 2] cycloaddition or cyclic six-membered nitronate esters by [2 + 4] cycloaddition through the oxygen of one of the nitro groups:



The products obtained, however, were isoxazoline derivatives, as shown in Table I. Ethylene gave 3-nitro-2-isoxazoline (**1**), identical with authentic material prepared from 1-bromo-3-chloropropane and sodium nitrite/alkyl nitrite.[9] The major product from propylene was identified as 3-nitro-5-methyl-2-isoxazoline (**2**) by independently synthesizing the material from 1,3-dibromobutane and sodium nitrite/propyl nitrite. The minor product of the propylene–tetranitroethylene reaction was assigned the isomeric structure 3-nitro-4-methyl-2-isoxazoline (**3**) on the basis of its NMR spectrum. Vinyltrimethylsilane gave 3-nitro-5-(trimethylsilyl)-2-isoxazoline (**4**).

Reactions of acetylenes with tetranitroethylene, summarized in Table II, gave isoxazoles. Acetylene gave 3-nitroisoxazole (**5**), identical with material synthesized by a reported method[10] from propargyl bromide and sodium

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(5) Marshall, H. P.; Borgardt, F. G.; Noble, P., Jr. *J. Phys. Chem.* **1965**, *69*, 25.

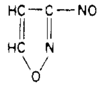
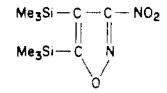
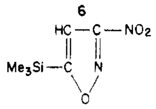
(6) Schechter, H. *Rec. Chem. Prog.* **1964**, *25*, 55.

(7) Sauer, J.; Wiest, H.; Mielert, A. *Chem. Ber.* **1964**, *97*, 3183.

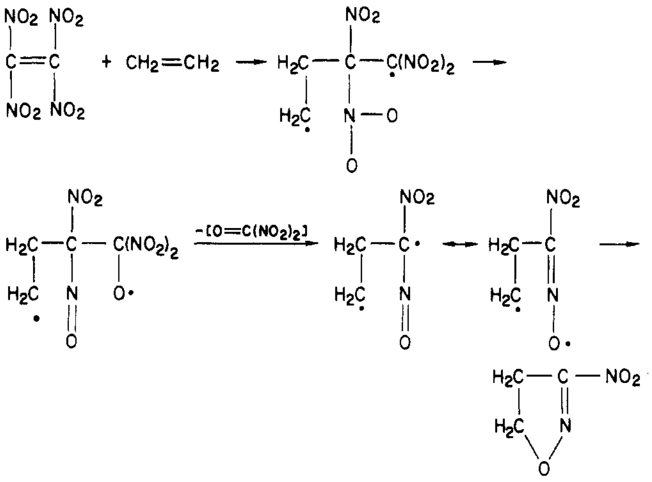
(8) Middleton, W. J.; Heckert, R. E.; Little, E. L.; Krespan, C. G. *J. Am. Chem. Soc.* **1958**, *80*, 2783.

(9) Wade, P. A. *J. Org. Chem.* **1978**, *43*, 2020.

Table II. Reactions of Tetranitroethylene with Acetylenes

acetylene	product	% yield
CH≡CH	 5	37
$Me_3SiC≡CSiMe_3$	 6	24
$HC≡CSiMe_3$	 7	23

Scheme I



nitrite. Bis(trimethylsilyl)acetylene similarly gave 4,5-bis(trimethylsilyl)-3-nitroisoxazole (**6**), and (trimethylsilyl)acetylene gave a product identified as 5-(trimethylsilyl)-3-nitroisoxazole (**7**).

The path by which isoxazolines and isoxazoles are formed from olefins and acetylenes is uncertain, but the products can be rationalized on the basis of diradical mechanisms similar to that shown in Scheme I. In this scheme, the electron-deficient dinitromethyl radical abstracts an oxygen from an adjacent nitro group, and loss of $O=C(NO_2)_2$ and ring closure give the observed product. The order of these steps may be varied. The oxygen-transfer step is reminiscent of that which has been reported for the conversion of *o*-azidonitrobenzenes to furoxanes via *o*-nitro nitrenes.[11]

In summary, tetranitroethylene has been prepared by the flash vacuum pyrolysis of hexanitroethane, using a collection-trap temperature that prevents condensation of N_2O_4. Tetranitroethylene decomposes autocatalytically in the presence of N_2O_4, but it is stable at least to 40 °C if trace amounts of N_2O_4 are removed continually under vacuum. Competition experiments with anthracene indicate that tetranitroethylene is at least an order of magnitude more reactive than tetracyanoethylene. This exceptional electron deficiency is manifested by its unexpected reactions with olefins and acetylenes to give isoxazolines and isoxazoles.

Experimental Section

NMR spectra were obtained with a Varian T-60 spectrometer with tetramethylsilane as an internal reference. Infrared spectra were recorded with a Perkin-Elmer 700 spectrophotometer. Elemental analysis was carried out by Galbraith Laboratories Inc., Knoxville, TN.

Manipulations of tetranitroethylene should be performed behind safety shielding. Dilute methylene chloride solutions of unsaturated compounds did not react violently with tetranitroethylene, but neat materials sometimes exploded on mixing. Additions were carried out safely from beind a shield by syringe through "spaghetti" tubing.

Tetranitroethylene. A flask containing 0.2–0.4 g of hexanitroethane was connected to a 12 mm (i.d.) × 25 cm glass pyrolysis tube wrapped with heating tape. The upper end of the pyrolysis tube was connected to a tared U-tube with stopcocks at each end. The U-tube was immersed in a 10 °C water bath, and the system was evacuated to 1 mmHg. The temperature of the pyrolysis tube was maintained at 260–270 °C, and the flask was heated at 85–90 °C to sublime the hexanitroethane. A greenish yellow solid collected in the U-tube, and weighing the U-tube after sealing the stopcocks consistently gave 50 ± 1% of the theoretical yield of tetranitroethylene. Addition of 0.45 g (2.5 mmol) of anthracene in 50 mL of benzene gave a 70% yield of 11,11,12,12-tetranitro-9,10-dihydro-9,10-ethanoanthracene,[2] based on the weight of the condensate.

In the same way, tetranitroethylene was generated from 0.750 g (2.5 mmol) of hexanitroethane, but the product was not weighed. A solution of 0.45 g (2.5 mmol) of anthracene in 50 mL of benzene was added to the receiver immediately after the generation was complete. The anthracene solution was added through an adapter at the exit of the U-tube, without releasing the vacuum. Isolation[2] gave 0.478 g of 11,11,12,12-tetranitro-9,10-dihydro-9,10-ethanoanthracene, a 99% yield based on the 50% yield of the tetranitroethylene from hexanitroethane.

Relative Reactivity of Tetranitroethylene and Tetracyanoethylene. Tetracyanoethylene (64 mg, 0.5 mmol) was placed in the U-tube of the tetranitroethylene apparatus, and 0.5 mmol of tetranitroethylene was generated (from 300 mg, 1.0 mmol of hexanitroethane) and condensed into the same U-tube. A solution of 22.5 mg (0.125 mmol) of anthracene in 10 mL of benzene was injected into this U-tube, which was still under vacuum, and the mixture was agitated gently at room temperature for 15 min. The insoluble product was collected by filtration, washed twice with 10-mL portions of benzene, and dried under vacuum to give 52.5 mg of white solid. NMR (Me_2SO-d_6) showed that this material was a 14:1 mixture of 11,11,12,12-tetranitro-9,10-dihydro-9,10-ethanoanthracene[2] and 11,11,12,12-tetracyano-9,10-dihydro-9,10-ethanoanthracene,[8] with a total yield of 92%. The mixture was analyzed on the basis of the bridgehead proton signals at δ 6.25 and 5.80, respectively.

5,5,6,6-Tetranitronorbornene. A solution of 0.42 g (6.3 mmol) of cyclopentadiene in 50 mL of methylene chloride was added under vacuum to the freshly prepared tetranitroethylene (1.42 mmol) obtained from 0.85 g (2.82 mmol) of hexanitroethane by the above procedure. Solvent was removed under vacuum. Column chromatography (silica gel, 60:40 hexane–methylene chloride) gave 330 mg (85%) of 5,5,6,6-tetranitronorbornene, identical with an authentic sample.[2]

Ethyl Dinitroacetate. Addition of a 5% solution of ethanol in benzene to freshly prepared tetranitroethylene by the above procedure gave ethyl dinitroacetate (72%), identical with the material that was previously obtained by the in situ method.[3]

3-Nitro-2-isoxazoline (1). A solution of 0.60 g (21.4 mmol) of ethylene in 50 mL of methylene chloride (assayed by NMR) was added to 0.96 mmol of freshly prepared tetranitroethylene by the above procedure. Preparative TLC (silica gel, 9:1 hexane–methylene chloride) gave 35.7 mg (32%) of 3-nitro-2-isoxazoline (1): NMR ($CDCl_3$) δ 3.42 (t, 2 H, J = 11 Hz), 4.82 (t, 2 H, J = 11 Hz); IR 1540, 1365 cm^{-1}.

Anal. Calcd for $C_3H_4N_2O_3$: C, 31.04; H, 3.47; N, 24.13. Found: C, 31.28; H, 3.58; N, 23.85.

3-Nitro-5-methyl-2-isoxazoline (2) and 3-Nitro-4-methyl-2-isoxazoline (3). A solution of 0.60 g (14.3 mmol) of propene in 50 mL of methylene chloride was added to 0.96 mmol of freshly prepared tetranitroethylene by the above procedure. Preparative TLC (silica gel, 9:1 hexane–methylene chloride) gave 15.0 mg (12%) of product identified as a 95:5 mixture of 3-nitro-5-methyl-2-isoxazoline (2) and 3-nitro-4-methyl-2-isoxazoline (3)

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(10) Rossi, S.; Duranti, E. *Tetrahedron Lett.* **1973**, 485.

(11) Noelting, E.; Kohn, A. *Chem.-Ztg.* **1894**, *18*, 1095. Hall, J. H.; Behr, F. E.; Reed, R. L. *J. Am. Chem. Soc.* **1972**, *94*, 4952.

on the basis of the integrals of NMR methyl signals at δ 1.5 and 1.3, respectively. The NMR spectrum of the mixture was otherwise identical with that of authentic 3-nitro-5-methyl-2-isoxazoline.

The 3-nitro-5-methyl-2-isozazoline (**2**) was identified by independent synthesis. A mixture of 10.0 g (46.3 mmol) of 1,3-dibromobutane, 6.4 g (93 mmol) of sodium nitrite, 4.2 g (47.2 mmol) of *n*-propyl nitrite, and 60 mL of dimethyl sulfoxide was stirred for 16 h at room temperature. The resulting solution was added to 50 mL of ice water, and the product was extracted with five 20-mL portions of methylene chloride. The methylene chloride solution was washed with two 20-mL portions of water and was dried over sodium sulfate. Distillation gave 2.30 g (42%) of 3-nitro-5-methyl-2-isoxazoline: bp 92–93 °C (1.2 mm); NMR ($CDCl_3$) δ 1.5 (d, 3 H, J = 6 Hz), 3.2 (d of d, 1 H, J = 9, 16 Hz), 3.3 (d of d, 1 H, J = 10, 16 Hz), 4.8–5.4 (m, 1 H); IR 1535, 1365 cm^{-1}.

Anal. Calcd for $C_4H_6N_2O_3$: C, 36.93; H, 4.65; N, 21.53. Found: C, 37.20; H, 4.61; N, 21.45.

3-Nitro-5-(trimethylsilyl)-2-isoxazoline (4). A solution of 1.80 g (18.0 mmol) of vinyltrimethylsilane in 50 mL of methylene chloride was added to 0.96 mmol of freshly prepared tetranitroethylene by the above procedure. Preparative TLC (silica gel, 9:1 hexane–methylene chloride) gave 36.2 mg (20%) of 3-nitro-5-(trimethylsilyl)-2-isoxazoline (**4**): NMR ($CDCl_3$) δ 0.45 (s, 9 H), 3.35 (d of d, 1 H, J = 14, 16 Hz), 3.50 (d of d, 1 H, J = 12, 14 Hz), 4.72 (d of d, 1 H, J = 12, 16 Hz); IR 1535, 1365 (NO_2), 1265 (Me_3Si) cm^{-1}.

Anal. Calcd for $C_6H_{12}N_2O_3Si$: C, 38.29; H, 6.43; N, 14.88. Found: C, 38.56; H, 6.45; N, 14.78.

3-Nitroisoxazole (5). A solution of 0.6 g (23.1 mmol) of acetylene in 50 mL of methylene chloride was added to 0.96 mmol of freshly prepared tetranitroethylene by the above procedure. Preparative TLC (silica gel, 9:1 hexane–methylene chloride) gave 40.6 mg (37%) of 3-nitro-2-isoxazole (**5**): NMR ($CDCl_3$) δ 6.68 (d, 1 H, J = 2 Hz), 8.37 (d, 1 H, J = 2 Hz); IR 1545, 1360 cm^{-1}. The spectra were identical with those of a sample prepared by a reported method.[10]

3-Nitro-4,5-bis(trimethylsilyl)isoxazole (6). A solution of 1.80 g (10.6 mmol) of bis(trimethylsilyl)acetylene in 50 mL of methylene chloride was added to 0.96 mmol of freshly prepared tetranitroethylene. TLC isolation gave 60 mg (24%) of 3-nitro-4,5-bis(trimethylsilyl)isoxazole (**6**): NMR ($CDCl_3$) δ 0.50 (s, 9 H), 0.62 (s, 9 H); IR 1560, 1320 (NO_2), 1260 (Me_3Si) cm^{-1}.

Anal. Calcd for $C_9H_{18}N_2O_3Si_2$: C, 41.84; H, 7.02; N, 10.84. Found: C, 41.58; H, 7.26; N, 11.07.

3-Nitro-5-(trimethylsilyl)isoxazole (7). A solution of 1.80 g (18.4 mmol) of (trimethylsilyl)acetylene in 50 mL of methylene chloride was added to 0.96 mmol of freshly prepared tetranitroethylene by the above procedure. Preparative TLC (silica gel, 9:1 hexane–methylene chloride) gave 41.0 mg (23%) of 3-nitro-5-(trimethylsilyl)isoxazole (**7**): NMR ($CDCl_3$) δ 0.55 (s, 9 H), 6.75 (s, 1 H); IR 1560, 1320 (NO_2), 1265 (Me_2Si) cm^{-1}.

Anal. Calcd for $C_6H_{10}N_2O_3Si$: C, 38.70; H, 5.42; N, 15.04. Found: C, 38.45; H, 5.40; N, 14.89.

Registry No. **1**, 1121-14-8; **2**, 6497-20-7; **3**, 96914-18-0; **4**, 40393-14-4; **5**, 39485-31-9; **6**, 96914-19-1; **7**, 96914-20-4; $(O_2N)_2C{=}C(NO_2)_2$, 13223-78-4; $CH_2{=}CH_2$, 74-85-1; $CH_2{=}CHCH_3$, 115-07-1; $BrCH_2CH_2CH(Br)CH_3$, 107-80-2; $CH_3CH_2CH_2NO_2$, 543-67-9; $CH_2{=}CHSiMe_3$, 754-05-2; $HC{\equiv}CH$, 74-86-2; $Me_3SiC{\equiv}CSiMe_3$, 14630-40-1; $Me_3SiC{\equiv}CH$, 1066-54-2; $(O_2N)_3CC(NO_2)_3$, 918-37-6; $(NC)_2C{=}C(CN)_2$, 670-54-2; EtOH, 64-17-5; $(O_2N)_2CHCOOEt$, 87711-32-8; anthracene, 120-12-7; 11,11,12,12-tetranitro-9,10-dihydro-9,10-ethanoanthracene, 73804-83-8; 11,11,12,12-tetracyano-9,10-dihydro-9,10-ethanoanthracene, 1625-84-9; 5,5,6,6-tetranitro-2-norbornene, 73804-86-1; cyclopentadiene, 542-92-7.

Reactions of Neopentyl Bromide with Nucleophiles by the $S_{RN}1$ Mechanism

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The photostimulated reaction of neopentyl bromide (1) with benzenethiolate ion gave neopentyl phenyl sulfide in high yields. The photostimulated reaction of 1 with benzeneselenate ion gave neopentyl phenyl selenide, dineopentyl selenide, and diphenyl selenide but in low overall yields. The photostimulated reaction of 1 with diphenylphosphide and diphenylarsenide ions gave good yields of the substitution products. These reactions are slow in the dark and the photostimulated reactions are inhibited by radical scavengers such as di-*tert*-butyl nitroxide. All these results suggest that 1 reacts with these nucleophiles by the $S_{RN}1$ mechanism of nucleophilic substitution.

Nucleophilic substitution by the $S_{RN}1$ mechanism is a well established process.[1] This mechanism has been proposed for aliphatic systems with electron-withdrawing groups,[1a,2] unactivated aromatic systems,[1b–d] vinyl halides,[3] perfluoroalkyl iodides,[4] bridgehead halides,[5] and halocyclopropanes.[6]

Except for aliphatic systems bearing electron-withdrawing groups, all the other systems have the same reactivity pattern in S_N1 or S_N2 processes in that they either react slowly or do not react at all with nucleophiles.

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