of the disposal of such environmentally harmful substances as PCB's and dioxins.

## Experimental Section

All the aromatic compounds described in the text were commercially available materials used without further purification; 2-propanol was distilled from sodium metal. The instrumentation used included an HFT-80 ($^1$H) and a NT-300 ($^{13}$C) NMR spectrometer, a Hewlett Packard 5980-A mass spectrometer, a Waters Associates HPLC Instrument, Model 600A (refractive index detector, $^1/_4$ in. × 30 cm column, 10% (V/V) ethyl accetate–hexanes, 2.0 mL/min flow rate), and a Varian Aerograph 1400 GC instrument with a 10-ft column containing 15% Carbowax 20 M on Chromosorb W.

**Preparation of Raney Nickel.** Aqueous sodium hydroxide (30 g, 150 mL) was cooled in ice in a 500-mL beaker, stirred magnetically while 5 g of nickel–aluminum alloy (50/50 from Alfa) was added in several small portions, and gradually warmed to 100 °C as required to maintain the hydrogen evolution. The nickel was then allowed to settle, and the liquid was decanted. After being washed with 5% fresh sodium hydroxide and finally distilled water until neutral, the nickel suspension was filtered with a sintered glass funnel and then finally washed with 100 mL of 2-propanol. (*Caution*! The catalyst must be kept moist since it is highly pyrophoric!) The catalyst was transferred with small amounts of dry 2-propanol to a glass-stoppered bottle.

**Reduction of 5-Phenyladamantan-2-one.** This compound[10] (20.0 mg, 0.088 mmol) in 5.0 mL of dry 2-propanol was mixed with 400 mg of the Raney nickel and refluxed for 3 days with continuous magnetic stirring. The mixture was filtered, the residue washed twice with 2-propanol (20 mL) and the solvent removed in vacuo to yield 20.4 mg (98%) of a crude product that was purified by crystallization from hexanes: mp 142–5 °C; mass spectrum, *m/z* 234; $^1$H NMR ($CDCl_3$ at $\delta$ 7.25) $\delta$ 0.8–2.0 (b m with a sharp peak at $\delta$ 1.5, 25 H), 3.8 (b s, 1 H); $^{13}$C NMR ($CDCl_3$ at $\delta$ 77.000) $\delta$ 74.660, 74.166, 47.888, 48.435, 38.550 (2 C), 34.877 (2 C), 30.873 (2 C), 33.105 (2 C), 35.272 (2 C), 39.512 (2 C), 36.278 (2 C), 27.606, 28.084, 33.966, 33.714, 26.355 (2 C), 26.052 (2 C), 27.239 (3 C), 26.864 (2 C), 26.905. HPLC showed it to be a mixture of the (*E*)- and (*Z*)-alcohols in the ratio of 57:43.

**General Procedure.** To Raney nickel (2 g) in 2-propanol (5 mL) in a 25-mL round-bottomed flask equipped with a condenser and a mercury bubbler (to minimize the slow loss of volatile components) was slowly added a solution of 500 mg of the compound of interest in 10 mL of 2-propanol at room temperature or at 0 °C as required. The reaction mixture was brought to reflux and was followed by G.C. When the reaction was over or nearly so, the solution was decanted and a sample of the product was isolated by GC for characterization and comparison with the authentic compound.

**Acknowledgment.** We are pleased to acknowledge NSF support for this work.

**Registry No.** 1, 84454-65-9; 5-phenyladamantan-2-one, 38584-33-7; *syn*-5-phenyladamantan-2-ol, 93965-96-9; *anti*-5-phenyladamantan-2-ol, 94062-20-1; *syn*-5-cyclohexyladamantan-2-ol, 93943-16-9; *anti*-5-cyclohexyladamantan-2-ol, 94061-41-3; *tert*-butylbenzene, 98-06-6; *tert*-butylcyclohexane, 3178-22-1; naphthalene, 91-20-3; tetralin, 119-64-2; *cis*-decalin, 493-01-6; *trans*-decalin, 493-02-7; pyridine, 110-86-1; piperidine, 110-89-4; furan, 110-00-9; THF, 109-99-9; anisole, 100-66-3; cyclohexyl methyl ether, 931-56-6; 1-methyl-1-phenylcyclopropane, 2214-14-4; 2-phenylbutane, 135-98-8; 2-cyclohexylbutane, 7058-01-7; *syn*-5-(1-methycycloprop-1-yl)adamantan-2-ol, 93943-17-0; *anti*-5-(1-methylcycloprop-1-yl)adamantan-2-ol, 94061-42-4; 2,2-dimethyl-1,3-dioxolane, 2916-31-6; bromobenzene, 108-86-1; chlorobenzene, 108-90-7; $\alpha,\alpha,\alpha$-trifluorotoluene, 98-08-8; nitrobenzene, 98-95-3; aniline, 62-53-3; cyclohexylamine, 108-91-8; cyclohexylisopropylamine, 1195-42-2; acetone, 67-64-1; isopropylideneaniline, 1124-52-3; Raney nickel, 7440-02-0; 2-propanol, 67-63-0.

(10) Geluk, H. W. *Synthesis* **1972**, 374.

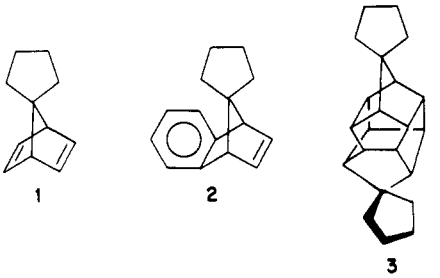
# Heptacyclo[5.5.1.1$^{4,10}$.0$^{2,6}$.0$^{3,11}$.0$^{5,9}$.0$^{8,12}$]tetradecane-13,14-bis(spiro-1′-cyclopentane): A New $C_{22}H_{28}$ Nonacyclic Cage Hydrocarbon. Improved Synthesis of Bicyclo[2.2.1]hepta-2,5-diene-7-spiro-1′-cyclopentane

Alan P. Marchand* and An-hsiang Wu

*Department of Chemistry, North Texas State University, Denton, Texas 76203-5068*

*Received July 30, 1984*

Recent interest in the synthesis and chemistry of new, substituted hepatacyclo[5.5.1.1$^{4,10}$.0$^{2,6}$.0$^{3,11}$.0$^{5,9}$.0$^{8,12}$]tetradecanes[1-3] prompts us to report our findings on the course of the iron carbonyl promoted cyclodimerization of bicyclo[2.2.1]hepta-2,5-diene-7-spiro-1′-cyclopentane (1). The



1 2 3

thermal and photochemical reactions of $Fe(CO)_5$ with norbornadiene and with simple, 7-substituted norbornadienes normally result in the formation of a mixture of several dimeric and trimeric products, some of which are ketonic.[4,5] However, 2,3-benzobicyclo[2.2.1]hepta-2,5-diene-7-spiro-1′-cyclopentane (**2**) has been reported to be nearly inert toward iron pentacarbonyl.[6] This observation suggested to us that the course of the reaction of **1** with $Fe(CO)_5$ might be relatively uncomplicated, affording the corresponding cage dimer **3** as the major (or even sole) reaction product.

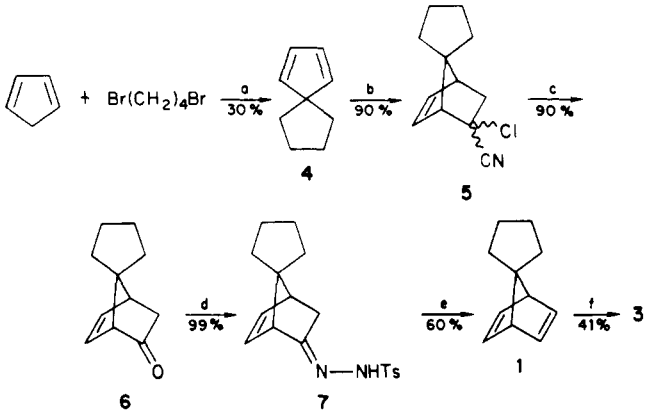
Since the yields of cage dimers produced via reaction of 7-substituted norbornadienes with $Fe(CO)_5$ are often low (i.e., on the order of 15%),[3,4] it was deemed desirable to have several grams of **1** on hand for the attempted cyclodimerization reaction. A multistep synthesis of **1** has been reported by Wilcox and Whitney;[7] however, their eight-step synthesis (starting with cyclopentadiene) affords **1** in only 2% overall yield. Accordingly, we sought to devise a new synthesis which might be capable of producing **1** in fewer steps and in greater overall yield.

Our improved, five-step synthesis of **1** is shown in Scheme I. Spirononadiene **4** is a critical intermediate both in the Wilcox–Whitney synthesis[7] and in the present synthesis of **1**. This compound is thermally labile, and it readily undergoes [1,5]sigmatropic rearrangement.[8] To avoid thermal rearrangement of **4**, this compound was purified by vacuum distillation (0.02 mm), and the distillate was collected and maintained at −78 °C. Diels–Alder addition of **4** to $\alpha$-chloroacrylonitrile was performed in a

(1) Hollowood, M. A.; McKervey, M. A.; Hamilton, R.; Rooney, J. J. *J. Org. Chem.* **1980**, *45*, 4954.
(2) Ealick, S. E.; van der Helm, D.; Hayes, B. R.; Marchand, A. P. *Acta Crystallogr., Sect. B* **1978**, *B34*, 3219.
(3) Marchand, A. P.; Earlywine, A. D. *J. Org. Chem.* **1984**, *49*, 1660.
(4) Marchand, A. P.; Hayes, B. R. *Tetrahedron Lett.* **1977**, 1027.
(5) Weissberger, E.; Laszlo, P. *Acc. Chem. Res.* **1976**, *9*, 209.
(6) Mantzaris, J.; Weissberger, E. *J. Am. Chem. Soc.* **1974**, *96*, 1873, 1880.
(7) Wilcox, C. F.; Whitney, G. C. *J. Org. Chem.* **1967**, *32*, 3348.
(8) Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Verlag Chemie: Weinheim/Bergstr., West Germany, and Academic Press: New York, 1970; pp 114–140.

0022-3263/85/1950-0396$01.50/0 

Scheme I[a]




[a] (a) $NaNH_2$, THF; (b) $H_2C{=}C(Cl)CN$, 70 °C, 60 h; (c) KOH, aqueous $Me_2S{=}O$, 25 °C, 24 h; (d) $H_2N$-NHTs, EtOH, 60 °C; (e) $LiN(i\text{-}Pr)_2$, dry THF, −78 °C; (f) $Fe(CO)_5$, 140 °C, 72 h.

sealed tube at 70 °C, affording the corresponding adduct **5** in excellent yield (90%).[9] Base-promoted hydrolysis of **5** afforded the corresponding ketone **6** in 90% yield. Conversion of ketone **6** into the corresponding tosylhydrazone **7** followed by Bamford–Stevens rearrangement[10] afforded **1**. The overall yield of **1**, produced via the five-step sequence shown in Scheme I (starting with cyclopentadiene), is 15%; this represents a significantly improved synthesis of **1** as compared with the Wilcox–Whitney synthesis.

Iron carbonyl promoted cyclodimerization of **1** proceeded smoothly at 140 °C, affording **3** as the sole reaction product in 41% yield. To our knowledge, this is the most efficient reaction observed to date between a 7-substituted norbornadiene and $Fe(CO)_5$ that results in the formation of a cage dimer. Compound **3** possesses unusual symmetry properties: it is a dendroasymmetric molecule with a perpendibiplanar structure belonging to point group $D_{2d}$.[3,11]

## Experimental Section

Melting points and boiling points are uncorrected. Proton NMR spectra (60 MHz) were obtained on a Hitachi-Perkin-Elmer Model R-24B NMR spectrometer. $^1H$ NMR spectra (90 MHz) and $^{13}C$ NMR spectra were recorded on a JEOL FX-90Q NMR spectrometer. In all cases, signals are reported in parts per million ($\delta$) downfield from internal tetramethylsilane. Infrared spectra were obtained on a Perkin-Elmer Model 1330 infrared spectrophotometer. Mass spectra were obtained on a Hewlett-Packard Model 5960A GC/MS system operating at 70 eV. Elemental microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN, and by Midwest Microlab, Ltd., Indianapolis, IN.

**5-Chloro-5-cyanobicyclo[2.2.1]hept-2-ene-7-spiro-1′-cyclopentane (5).** A mixture of spiro[4.4]nona-1,3-diene[12] (39.0 g, 0.32 mol) and freshly distilled $\alpha$-chloroacrylonitrile (28.7 g, 0.33 mol) was heated in a sealed tube at 70 °C for 60 h to afford a brown oil. This material was distilled in vacuo to afford **5** as a colorless liquid (61.2 g, 90%), bp 92–93.5 °C (0.2 mm). A single epimer of **5** was isolated by careful column chromatography on silica gel (Davisil 62, pentane eluent); the stereochemistry at C-5 in this epimer was not determined; $^1H$ NMR ($CDCl_3$) $\delta$ 1.85 (m, 8 H), 2.73 (m, 1 H), 2.85 (m, 1 H), 3.04 (m, 1 H), 3.08 (m, 1 H), 6.16 (m, 1 H), 6.35 (m, 1 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 24.07 (t), 25.75 (t), 32.58 (t), 33.66 (t), 44.71 (t), 50.13 (d), 57.12 (s), 61.45 (d), 70.39 (s), 126.66 (s), 134.21 (d), 138.92 (d); IR (neat) 3050 (m), 2940 (s), 2860 (s), 2210 (m), 1440 (s), 1320 (m), 1140 (m), 1060 (m), 1000 (m), 950 (m), 870 (m), 840 (m), 720 $cm^{-1}$ (s).

Anal. Calcd for $C_{12}H_{14}ClN$: C, 69.46; H, 6.80. Found: C, 69.22; H, 6.73.

**Bicyclo[2.2.1]hept-5-en-2-one-7-spiro-1′-cyclopentane (6).** To a solution of **5** (10.5 g, 51 mmol) in dimethyl sulfoxide (50 mL) under nitrogen atmosphere in a 500-mL, round-bottomed flask was added a solution of potassium hydroxide (8.0 g, 120 mmol) in water (3 mL). The resulting mixture was stirred continuously under nitrogen at room temperature for 24 h, at which time the reaction mixture was steam distilled. The distillate was extracted with ether (3 × 100 mL), dried (anhydrous magnesium sulfate), and filtered, and the filtrate was concentrated in vacuo. The residue was distilled in vacuo to afford pure **6** (7.43 g, 90%) as a colorless oil: bp 43.5–44.5 °C (0.2 mm); $^1H$ NMR ($CDCl_3$) $\delta$ 1.32–1.59 (complex, m, 9 H), 1.78 (d, $J$ = 2.8 Hz, 1 H), 2.40 (m, 1 H), 2.50 (br s, 1 H), 5.73 (m, 1 H), 6.25 (dd, $J_1$ = 2.8 Hz, $J_2$ = 5.6 Hz, 1 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 24.66 (t), 25.37 (t), 31.60 (t), 31.97 (t), 36.69 (t), 49.20 (d), 64.04 (d), 71.43 (s), 130.03 (d), 143.80 (d), 212.26 (s); IR (neat) 3450 (m), 3050 (m), 2940 (m), 2860 (m), 1725 (s), 1440 (m), 1410 (m), 1320 (m), 1260 (m), 1140 (m), 1110 (m), 1050 (m), 720 (m); mass spectrum (70 eV), $m/e$ (relative intensity) 163.2 (13.3), 162.2 ($M^+$, 100.0), 161.2 (7.9), 147.2 (12.5), 134.1 (14.9), 133.1 (40.6), 121.1 (9.9), 120.1 (15.8), 119.1 (15.2), 106.1 (7.5), 105.1 (17.8), 95.1 (8.3), 94.1 (53.3), 93.1 (30.9), 92.1 (7.9), 91.1 (49.9), 81.1 (17.4), 80.1 (29.7), 79.1 (64.0), 77.1 (27.5), 67.0 (23.6). Comound **6** was further characterized via the tosylhydrazone derivative (vide infra).

**Bicyclo[2.2.1]hept-5-en-2-one-7-spiro-1′-cyclopentane Tosylhydrazone (7).** A mixture of **6** (7.43 g, 45 mmol), (*p*-tolylsulfonyl)hydrazide (9.32 g, 50 mmol), and absolute ethanol (15 mL) maintained under a nitrogen atmosphere was heated overnight at 60 °C with stirring. The corresponding tosylhydrazone (**7**, 14.7 g, 99%) which had precipitated during the time of reaction was collected from the cooled reaction mixture via suction filtration. The material thus collected was recrystallized from absolute ethanol, thereby affording pure **7** as a colorless microcrystalline solid: mp 157.5–158.5 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 1.0–1.8 (m, 8 H), 1.9–2.3 (m, 2 H), 2.5 (br s, 3 H), 2.8 (m, 1 H), 3.0 (m, 1 H), 6.1 (m, 1 H), 6.35 (m, 1 H), 7.4 (*AB*, $J_{AB}$ = 8 Hz, 2 H), 7.9 (*AB*, $J_{AB}$ = 8 Hz, 2 H), ca. 7.6 (br s, NH, obscured by AB pattern of aromatic protons, 1 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 21.25 (t), 24.78 (t), 25.16 (t), 25.43 (t), 31.06 (q), 31.28 (t), 49.70 (d), 57.56 (d), 70.77 (s), 127.54 (d), 129.26 (d), 132.26 (d), 135.45 (s), 140.44 (d), 143.47 (s), 167.63 (s); IR (KBr) 3180 (s), 2920 (s), 2850 (s), 2240 (m), 1900 (m), 1775 (m), 1640 (s), 1580 (s), 1375 (s), 1320 (s), 1150 (s), 1080 (m), 1000 (m), 900 (s), 810 (m), 725 $cm^{-1}$ (s).

Anal. Calcd for $C_{18}H_{22}N_2O_2S$: C, 65.43;, H, 6.71. Found: C, 65.49; H, 6.83.

**Bicyclo[2.2.1]hepta-1-3-diene-7-spiro-1′-cyclopentane (1).** To a stirred solution of lithium diisopropylamide [prepared from diisopropylamine (14.58 g, 144 mmol) and *n*-butyllithium (74.9 mL of a 1.2 M solution in hexane)] in dry tetrahydrofuran (20 mL) under nitrogen atmosphere at −78 °C was added dropwise during 20 min a solution of **7** (11.7 g, 35.4 mmol) in dry tetrahydrofuran (10 mL). The reaction mixture was stirred for an additional 10 min at −78 °C after the addition of **7** had been completed, at which time the external cold bath was removed. The reaction mixture was allowed to warm slowly to ambient temperature; stirring was continued overnight under nitrogen atmosphere at room temperature. The resulting brown mixture was diluted with pentane (150 mL) and washed successively with brine (5 × 50 mL) and then with 1 M aqueous sodium dihydrogen phosphate solution (2 × 30 mL). The organic layer was dried (anhydrous magnesium sulfate) and filtered, and the filtrate was then concentrated in vacuo, affording a brown, oily residue. The crude product was purified by column chromatography on silica gel (pentane eluent); pure **1** (3.11 g, 60%) was thereby obtained as a colorless oil: bp 90 °C (15 mm); $^1H$ NMR ($CDCl_3$) $\delta$ 1.5 (m, 8 H), 3.1 (m, 2 H), 6.5 (m, 4 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 24.99 (t), 33.94 (t), 58.42 (d), 96.18 (s), 142.61 (d); IR (neat) 3050 (w), 2910 (m), 2850 (m), 1450 (m), 1370 (m), 1259 (m); mass spectrum (70 eV), $m/e$ (relative intensity) 147.2 (0.4), 146.2 ($M^+$, 4.3), 145.2 (3.2), 132.1 (1.1), 131.1 (10.6), 129.1 (2.8), 128.1 (2.8), 118.1 (19.6), 117.1 (100.0), 115.1 (26.6), 105.1 (22.8), 104.1 (64.5), 103.2 (15.8), 92.1

(9) The use of $\alpha$-chloroacrylonitrile as a ketene equivalent in Diels–Alder reactions is well documented; see: Ranganathan, S.; Ranganathan, D.; Mehrotra, A. K. *Synthesis* **1977**, 289.

(10) For a review, see: Shapiro, R. H. *Org. React. (N.Y.)* **1976**, *23*, 405.

(11) McCasland, G. E.; Horvat, R.; Roth, M. R. *J. Am. Chem. Soc.* **1959**, *81*, 2399.

(12) Wilcox, C. F.; Craig, R. R. *J. Am. Chem. Soc.* **1961**, *83*, 3866.

(15.8), 91.1 (59.9), 78.1 (37.9), 77.1 (23.6), 68.1 (11.1).

Anal. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.37; H, 9.59.

**Heptacyclo[5.5.1.1$^{4,10}$.0$^{2,6}$.0$^{3,11}$.0$^{5,9}$.0$^{8,12}$]tetradecane-13,14-bis(spiro-1′-cyclopentane) (3).** A mixture of 1 (28.0 g, 19.1 mmol) and iron pentacarbonyl (9.38 g, 47.9 mmol) was heated with stirring under nitrogen atmosphere at 140 °C for 72 h. The reaction mixture was then allowed to cool slowly to room temperature, whereupon a solution of ferric trichloride hexahydrate (13.5 g, 50 mmol) in acetone (50 mL) was added. The resulting mixture was stirred at room temperature for 1 week to decompose any unreacted iron pentacarbonyl and Fe(0) complexes that might be present.[3,13] The resulting black mixture was diluted with brine (100 mL) and extracted with pentane (3 × 50 mL). The combined organic layers were then washed with brine (3 × 30 mL), dried (anhydrous magnesium sulfate), and filtered, and the filtrate was concentrated in vacuo, affording a dark yellow oil. Recrystallization of this oil from acetone afforded a light yellow solid; this material was further purified by careful chromatography on silica gel (pentane eluent) to afford **3** (1.15 g, 41%) as a colorless microcrystalline solid: mp 115–116 °C; $^1$H NMR ($CDCl_3$) $\delta$ 2.53 (s, 8 H), 2.01 (s, 4 H), 1.53 (s, 16 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 25.53 (t), 33.23 (t), 52.51 (d), 58.58 (d), 67.09 (s); IR (KBr) 2940 (s), 2850 (s), 1450 (m), 1370 cm$^{-1}$ (m); mass spectrum (70 eV), *m/e* (relative intensity) 294.2 (3.0), 293.2 (24.1), 292.3 ($M^+$, 100.0), 264.3 (10.8), 263.2 (30.3), 250.3 (7.3), 197.2 (4.0), 184.1 (3.1), 183.1 (3.1), 169.2 (3.1), 159.1 (4.8), 155.1 (3.4), 145.2 (3.5), 143.1 (4.9), 131.1 (6.1), 117.1 (8.9), 91.1 (19.0), 67.0 (9.0).

Anal. Calcd for $C_{22}H_{28}$: C, 90.35; H, 9.65. Found: C, 90.26; H, 9.74.

**Acknowledgment.** Financial support of our study by the Naval Air Systems Command (Grant No. N60530-83-M-435A), the Air Force Office of Scientific Research, Air Force Systems Command (Grant No. AFOSR-84-0085), the Robert A. Welch Foundation (Grant No. B-963), and the North Texas State University Faculty Research Committee is gratefully acknowledged.

**Registry No.** 1, 6572-54-9; 3, 94111-39-4; 4, 766-29-0; 5, 94111-36-1; 6, 94111-37-2; 7, 94111-38-3; Br-$(CH_2)_4$-Br, 110-52-1; $H_2C$=C(Cl)CN, 920-37-6; 1,3-cyclopentadiene, 542-92-7.

(13) Shvo, Y.; Hazum, E. *J. Chem. Soc., Chem. Commun.* **1974**, 336.

## 1,3-Dipole Cycloaddition of Azides with Nitroso Compounds: ESR Studies

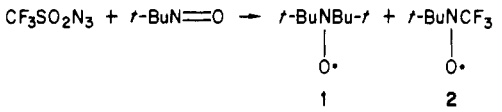
Nobumasa Kamigata,* Osamu Kawakita, Akira Izuoka, and Michio Kobayashi

*Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Fukazawa, Setagaya-ku, Tokyo 158, Japan*

*Received June 12, 1984*

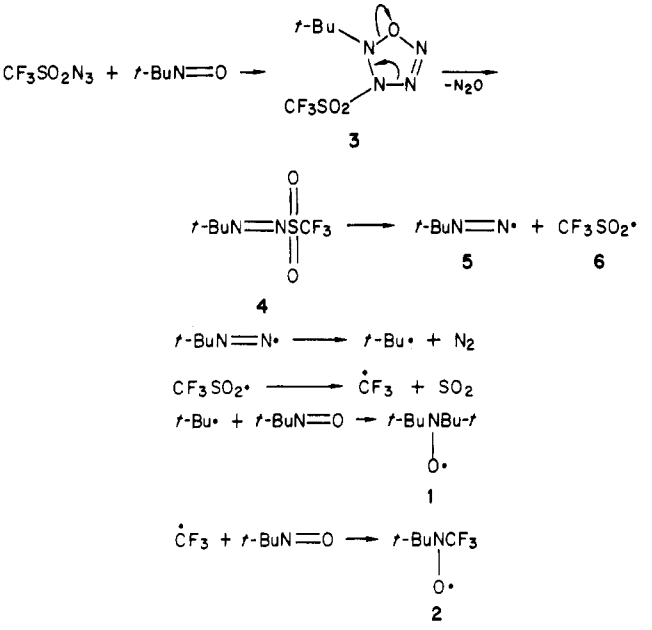
Attention in the chemistry of organic azides continues to be strong because of their utilities for heterocycle synthesis and interests in the reaction mechanisms.[1] 1,3-Dipole cycloaddition of azides to carbon–carbon double[2] or triple[3] bonds and thiocarbonyl[4] and sulfoxide[5] groups is well known. However, there has been no report on the reaction of azides with the nitroso group. We describe here the ESR studies of the reactions of organic azides with some nitroso compounds.

When a solution of trifluoromethanesulfonyl azide and 2-nitroso-2-methylpropane in benzene was degassed and placed in an ESR spectrometer at room temperature, a stable triplet and a stable triplet of quartet ESR signals were observed. The former signal was assigned as di-*tert*-butyl nitroxide radical (1) by its hyperfine splitting




constants and $g$ value ($A_N$ = 15.6 G, $g$ = 2.0060).[6] The latter one was assigned as *tert*-butyl trifluoromethyl nitroxide (2) based on the hyperfine splitting constants and $g$ value ($A_N$ = 12.1 G, $A_F$ = 12.7 G, $g$ = 2.0065). This observation shows that trifluoromethanesulfonyl azide reacts with 2-nitroso-2-methylpropane at room temperature and that the product formed by the reaction decomposes homolytically, giving trifluoromethyl and *tert*-butyl radicals, both of which are spin trapped by 2-nitroso-2-methylpropane. The 1,3-dipole reaction of trifluoromethanesulfonyl azide with 2-nitroso-2-methylpropane may form oxatetrazolidine **3** similar to the 1,3-dipole reactions of azide with the sulfoxide[5] or thiocarbonyl[4] group (Scheme I). The cycloadduct **3** will easily lose nitrous oxide at room temperature, affording *tert*-butylazo trifluoromethyl sulfone (**4**). Since azo sulfones homolytically cleave at the S–N bond,[7] **4** will cleave homolytically giving *tert*-butyldiazenyl radical **5** and trifluoromethanesulfonyl radical (**6**). The radicals **5** and **6** will easily release nitrogen and sulfur dioxide, affording *tert*-butyl radical and trifluoromethyl radicals, respectively. These two radicals are spin trapped by 2-nitroso-2-methylpropane to give nitroxide radicals **1** and **2**, both of which are detected by ESR. GC–mass spectral analysis of the gasous products of this reaction supported the reaction mechanism proposed in Scheme I. Two peaks observed by GC were determined

**Scheme I**




(1) Patai, S., Ed. "The Chemistry of the Azido Group"; Interscience Publishers: New York, 1971. Peterson, W. P., Jr. *Rev. Silicon, Germanium, Tin, Lead Compds.* **1974**, *1*, 193.
(2) Huisgen, R.; Szeimies, G.; Mobius, L. *Chem. Ber.* **1966**, *99*, 475.
(3) Grünanger, P.; Finziand, P. V.; Scotti, C. *Chem. Ber.* **1965**, *98*, 623.
(4) Schönberg, A.; Urban, W. *J. Chem. Soc.* **1935**, 530.
(5) Horner, L.; Christmann, A. *Chem. Ber.* **1963**, *96*, 388.
(6) Kamigata, N.; Kobayashi, M. *Sulfur Rep.* **1982**, *2*, 87. Kobayashi, M.; Minato, H.; Kojima, M.; Kamigata, N. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2501. Kice, J. L.; Gabrielsen, R. S. *J. Org. Chem.* **1970**, *35*, 1004.
(7) Perkins, M. J.; Ward, P. *J. Chem. Soc. B* **1970**, 395. Kobayashi, M.; Gotoh, M.; Minato, H. *J. Org. Chem.* **1975**, *40*, 140.

0022-3263/85/1950-0398$01.50/0 