to give 70 mg (90%) of the acetoxy ketone **5**: IR (CCl_4) 2964, 2894, 1739, 1725, 1440, 1365, 1234, 1089 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.84–2.04 (m, 4 H), 2.05 (s, 3 H), 2.27–2.36 (m, 2 H), 2.45–2.55 (m, 2 H), 5.12 (quintet, 1 H); ^{13}C NMR δ 21.08, 30.30, 37.13, 68.50, 170.24, 209.50; CI mass spectrum, *m/e* (%) (M + 1), 157 (4), 97 (18).

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Registry No. 1, 112067-98-8; 2, 112067-99-9; 3, 112021-68-8; 4, 41043-90-7; 5, 41043-88-3; diethyl 2,2-cyclopropanedicarboxylate, 1559-02-0; bicyclo[3.1.0]hexan-2-one, 4160-49-0; bicyclo[4.1.0]-heptan-2-one, 5771-58-4; tricyclo[3.3.0.$0^{2,8}$]octan-3-one, 20826-85-1; (1α,6β,7α)-10-methyl-6-(trimethylacetoxy)tricyclo[5.3.0.$0^{2,10}$]-dec-3-en-9-one, 112021-61-1; diethyl(2-acetoxyethyl)malonate, 110281-43-1; 1,4-diacetoxycycloheptene, 112021-62-2; 1-acetoxy-3-(acetoxymethyl)cyclohexene, 112021-63-3; (1α,5α,8α)-3,8-diacetoxybicyclo[3.3.0]oct-2-ene, 112021-64-4; (1α,5α,6α)-5,8-diacetoxybicyclo[4.3.0]non-7-ene, 112021-65-5; 4-(trimethylacetoxy)-3aα,4α,5,6-tetrahydroazulen-2(3*H*)-one, 112021-66-6; 1-methyl-4-(trimethylacetoxy)-3aα,4α,5,6-tetrahydroazulen-2-(3*H*)-one, 112021-67-7.

Synthesis of 8,8,11,11-Tetranitropentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane

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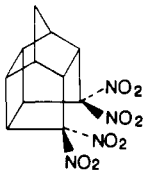
There is considerable current interest in the synthesis and chemistry of polynitropolycyclic "cage" molecules.[1] As part of a program that is involved with the synthesis of novel, substituted pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecanes,[2] we have synthesized the title compound, 1. Compound

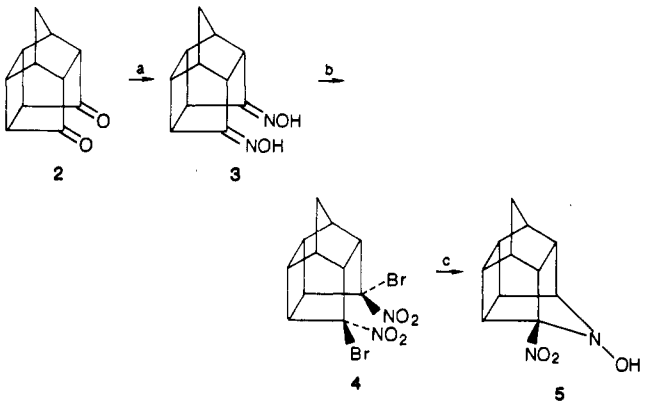


1

1 is of interest as a new, strained energetic material. Strain in this compound potentially can arise from the following sources: (i) deformations of the carbon–carbon framework bonds that are associated with the norbornyl moiety and the cyclobutane ring in 1 and (ii) nonbonded interactions that may occur between the *endo*-8- and *endo*-11-nitro groups in 1.

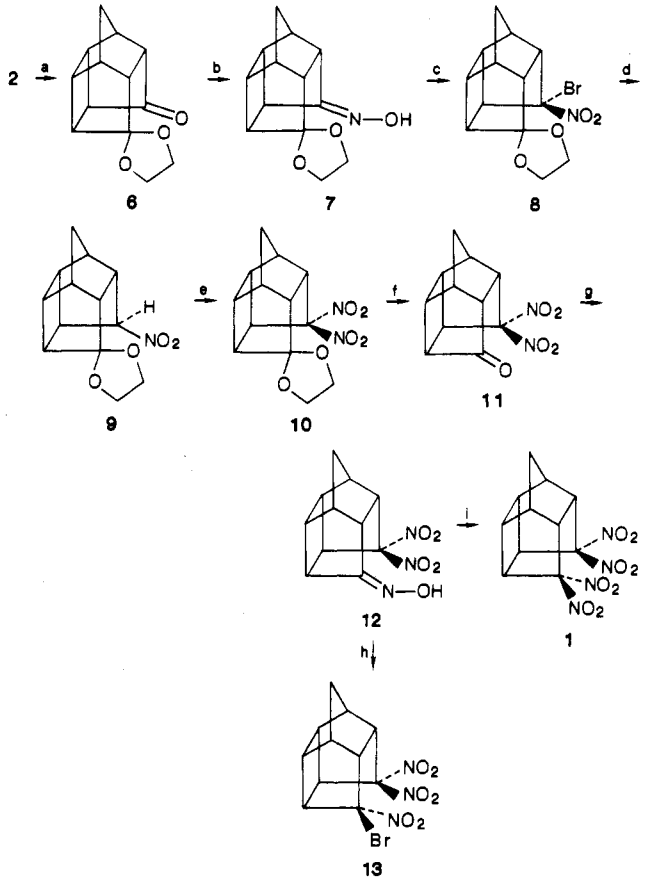
Our initial attempt to synthesize 1 from the readily available cage diketone 2[3] is summarized in Scheme I.

Scheme I[a]



[a] (a) NH_2OH·HCl, NaOAc, EtOH (87%); (b) NBS, $NaHCO_3$, dioxane, room temperature, 48 h (49%); (c) $NaBH_4$, 60% aqueous EtOH, room temperature, 45 min (28%).

Scheme II[a]



[a] (a) $HOCH_2CH_2OH$, TsOH, benzene, Dean–Stark tube (92%); (b) NH_2OH·HCl, NaOAc, EtOH, room temperature, overnight (79%); (c) Br_2, $NaHCO_3$, DMF, 0 °C, and then O_3, CH_2Cl_2, 0 °C (80%); (d) $NaBH_4$, 60% aqueous EtOH, room temperature, 0.5 h (97%); (e) $K_3Fe(CN)_6$, $NaNO_2$, aqueous MeOH, NaOH, room temperature, 0.5 h (73%); (f) concentrated H_2SO_4, CH_2Cl_2, room temperature, overnight (73%); (g) NH_2OH·HCl, NaOAc, EtOH, room temperature, overnight (89%); (h) NBS, $NaHCO_3$, 5% aqueous dioxane, room temperature, 72 h (65.7%); (i) 98% red HNO_3, NH_4NO_3, CH_2Cl_2, reflux 1 h, then 30% H_2O_2, reflux 1 h (31%, 64% based on recovered 11).

Conversion of 2 to the corresponding *exo,exo*-8,11-dibromo-*endo,endo*-8,11-dinitro derivative, 4, was straightforward. Subsequent reaction of 4 with sodium borohydride in methanol was expected to result simply in reduction of the carbon–bromine bonds.[4] However, this

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0022-3263/88/1953-0443$01.50/0

reaction instead unexpectedly afforded *N*-hydroxy-3-nitro-4-azahexacyclo[5.4.1.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$.$0^{8,11}$]dodecane (**5**).[5]

Accordingly, an alternative method was developed for the synthesis of **1** (Scheme II). The readily available cage monoketal **6**[6] was converted into the corresponding oxime, **7**, by using the procedure described by Corey and co-workers.[7] Bromination of oxime **7**[8] followed by ozonolysis of the resulting geminal bromo nitroso derivative afforded **8**. Reduction of **8** with sodium borohydride in ethanol proceeded smoothly to afford exclusively *endo*-8-nitropentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecan-8-one ethylene ketal (**9**).

Further nitration of **9** was performed by using the method described by Kornblum and co-workers.[9] Hydrolysis of the resulting dinitro ketal, **10**, was effected by stirring with concentrated sulfuric acid at room temperature,[10] thereby affording the corresponding dinitro ketone, **11**. Oxidative nitration of the oxime **12** derived from **11** was carried out by using 98% red fuming nitric acid[11] in refluxing methylene chloride; this reaction afforded **1** in 64% yield based on recovered **11**.

Reaction of oxime **12** with *N*-bromosuccinimide afforded *exo*-8-bromo-*endo*-8,11,11-trinitropentacyclo-[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane (**13**, 65.7%). However, repeated attempts to reduce the carbon–bromine bond in **13** failed to afford the corresponding 8,11,11-trinitro compound.

Experimental Section

Melting points are uncorrected. The high-resolution mass spectrum of **5** was obtained by the Midwest Center for Mass Spectrometry. Department of Chemistry, University of Nebraska-Lincoln, Lincoln, NE.

***exo*,*exo*-8,11-Dibromo-*endo*,*endo*-8,11-dinitropentacyclo-[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane (4).** To a suspension of dioxime **3**[12] (2.50 g, 12.3 mmol) and sodium bicarbonate (12.5 g, excess) in 5% aqueous dioxane (200 mL) was added *N*-bromosuccinimide (11.12 g, 62.50 mmol), and the resulting mixture was stirred at room temperature for 48 h. To the reaction mixture was then added 0.5 N aqueous sodium hydroxide solution (150 mL), and the resulting mixture was extracted with methylene chloride (3 × 50 mL). The combined organic layers were washed successively with 0.5 N aqueous sodium hydroxide solution (3 × 50 mL), water (100 mL), and brine (100 mL). The organic layer was dried (anhydrous magnesium sulfate) and filtered, and the filtrate was concentrated in vacuo. The solid residue was purified via column chromatography [silica gel stationary phase, 2:1 methylene chloride–ligroin (bp 60–80 °C) mixed solvent as eluent]. Pure **4** (1.9 g, 49%) was thereby obtained as a colorless microcrystalline solid: mp 220–221 °C; IR (KBr) 1550 (s), 1340 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 1.53 (*AB*, J_{AB} = 11.7 Hz, 1 H), 2.03 (*AB*, J_{AB} = 11.7 Hz, 1 H), 2.9–3.6 (m, 8 H); ^{13}C NMR ($CDCl_3$) δ 31.24 (t), 39.50 (d), 45.94 (d), 49.84 (d), 52.64 (d), 95.62 (s). Anal. Calcd for $C_{11}H_{10}Br_2N_2O_4$: C, 33.53; H, 2.56. Found: C, 33.80; H, 2.81.

Reaction of 4 with Sodium Borohydride. A solution of **4** (788 mg, 2.00 mmol) in absolute ethanol (300 mL) was cooled by application of an external ice bath for 20 min. To the cooled solution was added a solution of sodium borohydride (0.76 g, 21 mmol) in 60% aqueous ethanol (30 mL). The ice bath was removed after all of the sodium borohydride solution had been added, and the reaction mixture was stirred at room temperature for 1 h. The reaction was quenched by adjusting the pH of the solution to 4–5 via gradual addition of dilute aqueous acetic acid solution. The resulting mixture was concentrated in vacuo. The residue was suspended in water (50 mL) and extracted with methylene chloride (3 × 40 mL). The combined organic extracts were washed sequentially with saturated sodium bicarbonate solution (30 mL) and water (2 × 40 mL). The organic layer was dried (anhydrous magnesium sulfate) and filtered, and the filtrate was concentrated in vacuo to afford a solid (0.40 g). This material was further purified via column chromatography (silica gel stationary phase, 2:1 hexane–ethyl acetate mixed solvent as eluent), thereby affording **5** as a colorless solid (122 mg, 28%). Recrystallization of this solid from hexane afforded pure **5** (ca. 1:1 mixture of epimers) as colorless cubes: mp 133.5–134.0 °C; IR (KBr) 3250 (br s), 1535 (s), 1370 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 1.48 (*AB*, J_{AB} = 10.8 Hz, 1 H), 1.67 (*AB*, J_{AB} = 10.8 Hz, 1 H), 1.72 (*AB*, J_{AB} = 10.8 Hz, 1 H), 2.04 (*AB*, J_{AB} = 10.8 hz, 1 H), 2.50–3.20 (m, 12 H), 3.30–3.50 (m, 4 H), 3.78 (m, 1 H), 3.91 (t, J = 4.6 Hz, 1 H), 6.57 (br s, 1 H), 6.65 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ 38.77 (d), 39.22 (t), 41.68 (d), 43.17 (t), 43.49 (d), 43.50 (d), 44.35 (d), 45.31 (d), 45.86 (d), 46.03 (d), 46.33 (d), 46.34 (d), 46.66 (2 C, d), 47.98 (d), 55.42 (d), 55.62 (d), 56.20 (d), 71.64 (d), 72.48 (d), 115.84 (s), 117.03 (s). Anal. Calcd for $C_{11}H_{12}N_2O_3$: M_r 220.0848. Found (high-resolution mass spectrometry): M_r 220.0853.

8-Oximinopentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecan-11-one Ethylene Ketal (7).[7] To a suspension of **6**[6] (5.68 g, 25.8 mmol) in absolute ethanol (150 mL) was added hydroxylamine hydrochloride (6.95 g, 100 mmol) and sodium acetate (16.4 g, 200 mmol). The resulting mixture was stirred at room temperature under nitrogen overnight. The reaction mixture was then concentrated in vacuo, and the residue was diluted with water (50 mL). The resulting aqueous suspension was filtered, and the residue was recrystallized from ethanol. Compound **7** (4.8 g, 79%) was thereby obtained as colorless needles: mp 160–161 °C; IR (KBr) 3343 (br, vs), 1547 cm^{-1} (s). This material was used as obtained without further purification.

***exo*-11-Bromo-*endo*-11-nitropentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]-undecan-8-one Ethylene Ketal (8).**[8] A mixture of oxime **7** (0.58 g, 2.5 mmol), sodium bicarbonate (0.52 g, 5.2 mmol), water (25 mL), and dimethylformamide (DMF, 5 mL) was cooled to 0 °C via application of an external ice bath. Bromine (0.39 g, 2.5 mmol) was added, and the resulting mixture was stirred at 0 °C for 1 h. The reaction mixture was then extracted with methylene chloride (3 × 25 mL). The combined organic extracts were washed sequentially with cold, saturated, aqueous sodium thiosulfate solution (50 mL) and with cold water (50 mL). The organic layer was then dried (anhydrous magnesium sulfate) and filtered. Ozone was passed through the cooled (0 °C) filtrate (blue solution) until the blue color had faded to yellow. The reaction mixture was then concentrated in vacuo, and the solid residue was recrystallized from 95% aqueous ethanol. Pure **8** (1.2 g, 80%) was thereby obtained as colorless prisms: mp 137–138 °C; IR (KBr) 1530 (s), 1330 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.25 (*AB*, J_{AB} = 10.7 Hz, 1 H), 1.80 (*AB*, J_{AB} = 10.7 Hz, 1 H), 2.30 (m, 1 H), 2.55–3.09 (m, 4 H), 3.15–3.30 (m, 2 H), 3.8 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 32.95 (t), 37.39 (d), 39.54 (d), 39.81 (d), 43.58 (d), 45.27 (d), 47.33 (d), 47.94 (d), 51.09 (d), 61.60 (t), 64.60 (t), 96.88 (s), 112.17 (s); mass spectrum (70 eV), *m/e* (relative intensity) (no molecular ion), 141 (100.0). Anal. Calcd for $C_{13}H_{14}BrNO_4$: C, 47.58; H, 4.30. Found: C, 47.65; H, 4.21.

***endo*-11-Nitropentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecan-8-one Ethylene Ketal (9).** Compound **8** (1.05 g, 3.20 mmol) was suspended in ethanol (200 mL), and a solution of sodium borohydride (480 mg, 12.6 mmol) in 60% aqueous ethanol (25 mL) was added dropwise with stirring at room temperature. The resulting mixture was stirred at room temperature for 0.5 h after the addition of sodium borohydride had been completed. The reduction was quenched via addition of dilute aqueous acetic acid solution until the reaction mixture had been rendered acidic to litmus. The resulting mixture was then concentrated in vacuo. The residue was diluted with water (100 mL), and the aqueous suspension was extracted with methylene chloride (3 × 150 mL). The combined extracts were washed sequentially with water (75 mL) and with brine (75 mL). The organic layer was dried (an-

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hydrous magnesium sulfate) and filtered, and the filtrate was concentrated in vacuo, thereby affording a yellow oil. Upon trituration with ether, this oil solidified; recrystallization of the resulting solid from ethanol afforded pure **9** (0.77 g, 97%) as colorless prisms: mp 144–145 °C; IR (KBr) 1530 (s), 1350 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.25 (*AB*, J_{AB} = 10.7 Hz, 1 H), 1.75 (*AB*, J_{AB} = 10.7 Hz, 1 H), 2.25 (m, 1 H), 2.45–2.80 (m, 5 H), 3.15 (m, 1 H), 3.30 (m, 1 H), 3.80 (m, 4 H), 4.20 (t, J = 4.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 35.15 (t), 35.60 (d), 38.64 (d), 39.78 (d), 39.96 (d), 43.90 (d), 44.65 (d), 44.79 (d), 46.29 (d), 62.99 (t), 65.42 (t), 82.33 (d), 114.68 (s); mass spectrum (70 eV), *m/e* (relative intensity) 249 (molecular ion, 3.4), 203 (100.0). Anal. Calcd for $C_{13}H_{15}NO_4$: C, 62.64; H, 6.06. Found: C, 62.61; H, 6.09.

11,11-Dinitropentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8-one Ethylene Ketal (10).[9] To a stirred solution of sodium hydroxide (0.80 g, 20 mmol) in 40% aqueous methanol (36 mL) was added **9** (0.775 g, 3.11 mmol) under nitrogen. The resulting mixture was stirred until a clear solution was obtained. This solution was then added dropwise to a rapidly stirred mixture of potassium ferricyanide (8.00 g, 24.2 mmol), sodium nitrite (4.00 g, 57.9 mmol), water (50 mL), and ether (50 mL). Stirring was continued for 30 min after the addition had been completed. The layers were separated, and the aqueous layer was extracted with methylene chloride (2 × 50 mL). The combined organic layers were washed seuentially with water (2 × 100 mL) and with brine (100 mL). The organic layer was dried (anhydrous magnesium sulfate) and filtered, and the filtrate was concentrated in vacuo. Compound **10** (870 mg, 95%) was thereby obtained; when recrystallized from 1:1 ether–hexane mixed solvent, this material afforded pure **10** (668 mg, 73%) as a colorless microcrystalline solid: mp 160.0–160.5 °C; IR (KBr) 1575 (s), 1350 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 1.38 (*AB*, J_{AB} = 10.6 Hz, 1 H), 1.85 (*AB*, J_{AB} = 10.6 Hz, 1 H), 2.4–2.5 (m, 2 H), 2.65–2.80 (m, 3 H), 2.95 (m, 1 H), 3.45 (m, 1 H), 3.75–3.95 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 35.09 (t), 38.69 (d), 39.07 (d), 39.58 (d), 41.13 (d), 44.61 (d), 45.47 (d), 47.94 (d), 48.73 (d), 63.25 (t), 65.85 (t), 113.74 (s), 124.1 (s); mass spectrum (70 eV), *m/e* (relative intensity) (no molecular ion), 284 (6.3), 248 (15.0), 129 (100.0). Anal. Calcd for $C_{13}H_{14}N_2O_6$: C, 53.06; H, 4.80. Found: C, 53.37; H, 4.89.

11,11-Dinitropentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8-one (11).[10] To a mixture of **10** (8.00 g, 27.2 mmol) and methylene chloride (500 mL) was added concentrated sulfuric acid (50 mL), and the resulting mixture was stirred overnight at room temperature. The reaction mixture was then poured over crushed ice (500 g). Solid sodium bicarbonate was added cautiously with effective stirring until evolution of carbon dioxide had ceased. The resulting mixture was diluted with water (300 mL). The layers were separated, and the aqueous layer was extracted with methylene chloride (3 × 100 mL). The combined organic layers were washed sequentially with 10% aqueous sodium bicarbonate solution (2 × 100 mL) and with water (100 mL). The organic layer was dried (anhydrous magnesium sulfate) and filtered, and the filtrate was concentrated in vacuo, thereby affording **11** (4.94 g, 73%). Recrystallization of this material from ethanol afforded pure **11** as a colorless microcrystalline solid: mp 217–218 °C; IR (KBr) 1730 (s), 1560 (s), 1355 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 1.75 (*AB*, J_{AB} = 10.7 Hz, 1 H), 2.05 (*AB*, J_{AB} = 10.7 Hz, 1 H), 3.00 (m, 4 H), 3.05 (m, 1 H), 3.40 (m, 1 H), 3.60 (m, 1 H), 3.80 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 36.81 (d), 37.72 (t), 40.31 (d), 40.85 (d), 42.25 (d), 43.57 (d), 45.82 (d), 50.78 (d), 53.05 (d), 122.48 (s), 208.29 (s); mass spectrum (70 eV), *m/e* (relative intensity) 250 (molecular ion, 8.6), 204 (4.3), 128 (100.0). Anal. Calcd for $C_{11}H_{10}N_2O_5$: C, 52.80; H, 4.03. Found: C, 52.80; H, 4.06.

11,11-Dinitropentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8-one Oxime (12).[7] To a solution of **11** (11.9 g, 47.6 mmol) in absolute ethanol (250 mL) was added hydroxylamine hydrochloride (14.0 g, 202 mmol) and sodium acetate (20.0 g, 244 mmol), and the resulting mixture was refluxed for 48 h. The reaction mixture was then concentrated by distillation at atmospheric pressure. After most of the ethanol (ca. 200 mL) had been thus removed, cold water (500 mL) was added to the residue. The resulting suspension was filtered, and the residue was recrystallized from ethanol. Pure **12** (11.2 g, 89%) was thereby obtained as a colorless microcrystalline solid: mp 178–180 °C; IR (KBr) 3425 (br s), 1571 (s), 1372 cm^{-1} (m). This material was used as obtained without further purification.

***exo*-8-Bromo-*endo*-8,11,11-trinitropentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (13).** Cage oxime **12** (9.0 g, 34 mmol) was suspended in 5% aqueous dioxane (600 mL). *N*-Bromosuccinimide (15.0 g, 84.2 mmol) and sodium bicarbonate (30.0 g, 357 mmol) were then added, and the resulting mixture was stirred at room temperature for 72 h. Potassium hydroxide pellets (10 g) were added, and the resulting mixture was stirred at room temperature for 15 min. The reaction mixture was extracted with methylene chloride (3 × 150 mL), and the combined organic layers were washed with 10% aqueous potassium hydroxide solution until the washings became colorless. The organic layer was then washed with water (2 × 100 mL), dried (anhydrous magnesium sulfate), and filtered, and the filtrate was concentrated in vacuo. The residue thereby obtained was recrystallized from 1:1 ethanol–diethyl ether mixed solvent. Pure **13** (8.05 g, 65.7%) was thereby obtained as colorless needles: mp 177–178 °C: IR (KBr) 1565 (s), 1350 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 1.45 (*AB*, J_{AB} = 11.7 Hz, 1 H), 1.94 (*AB*, J_{AB} = 11.7 Hz, 1 H), 2.66 (m, 1 H), 3.12 (m, 2 H), 3.45–3.55 (m, 3 H), 3.75 (m, 1 H), 4.0 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 33.00 (t), 40.89 (d), 41.18 (d), 41.20 (d), 44.62 (d), 45.78 (d), 49.25 (d), 52.67 (d), 94.38 (s), 122.50 (s); mass spectrum (70 eV), *m/e* (relative intensity) (no molecular ion), 279 (5.7), 149 (100.0). Anal. Calcd for $C_{11}H_{10}BrN_3O_6$: C, 36.69; H, 2.79. Found: C, 36.69; H, 2.91.

8,8,11,11-Tetranitropentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (1). Red nitric acid (98%) was prepared[11] via distillation at atmospheric pressure of a mixture of 90% nitric acid (100 mL) and 98% sulfuric acid (100 mL). The first 50 mL of distillate was mixed with 98% sulfuric acid (50 mL) and redistilled at atmospheric pressure. The red distillate thereby obtained was used immediately; any material remaining was diluted with water and discarded. To a refluxing solution of **12** (1.5 g, 5.66 mmol) in methylene chloride (75 mL) under nitrogen was added a solution of 98% red nitric acid (20 mL, excess), urea (150 mg, 2.50 mmol), and ammonium nitrate (150 mg, 2.00 mmol) in methylene chloride (50 mL). A deep green color developed initially; the color of the reaction mixture changed to brown as more acid was added. After the addition had been completed, the reaction mixture was refluxed for 1 h, at which time 30% aqueous hydrogen peroxide solution (30 mL, excess) was added cautiously to the refluxing mixture. The reaction mixture was thereby rendered colorless. The resulting mixture was refluxed for an additional 1 h and then allowed to cool to room temperature. The cooled reaction mixture was washed with ice water (3 × 75 mL), dried (anhydrous magnesium sulfate), and filtered, and the filtrate was concentrated in vacuo. The resulting solid residue was purified via column chromatography (silica gel stationary phase, 1:3 methylene chloride–hexane mixed solvent as eluent). The first fraction thereby collected afforded pure **1** (564 mg, 1.73 mmol): mp 198.0–198.5 °C; IR (KBr) 1590 (s), 1360 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 1.49 (*AB*, J_{AB} = 12 Hz, 1 H), 1.99 (*AB*, J_{AB} = 12 Hz, 1 H), 2.69 (m, 2 H), 3.09 (m, 2 H), 3.12 (m, 2 H), 4.09 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 34.01 (t), 39.08 (d), 41.04 (d), 45.39 (d), 48.90 (d), 122.32 (s); mass spectrum (70 eV), *m/e* (relative intensity) (no molecular ion), 204 (100.0). Anal. Calcd for $C_{11}H_{10}N_4O_8$: C, 40.50; H, 3.09. Found: C, 40.52; H, 3.69.

Continued elution of the chromatography column afforded a second fraction, which proved to contain the dinitro ketone **11** derived from oxime **12** (737 mg, 2.95 mmol). Compound **11** thereby obtained could be recycled by using the procedure described above. The total yield of **1** obtained in this reaction was 31% (64% based on recovered **11**).

The structure of **1** has been further confirmed via single-crystal X-ray structural analysis. Details of the structure thereby determined will be published elsewhere.[13]

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Group Transfers. 2. Solvolysis of Isopropyl Arenesulfonates in Sulfolane[1]

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An attempt was made to study near identity replacements of one isopropyl arenesulfonate with another arenesulfonate anion. Such results would have paralleled the analogous studies of methyl transfers between arenesulfonates,[2] except with an alkyl group more able to tolerate a positive charge in the transition state. This attempt, however, failed. The isopropyl esters in tetrahydrothiophene 1,1-dioxide (sulfolane) are not stable enough to observe any significant displacement; they lose arenesulfonic acid too rapidly. At 100 °C overnight isopropyl tosylate from the *p*-nitrophenylsulfonate ester and tosylate anion could not be detected even with an initial 56-fold excess of the nitro ester, which was itself over 90% solvolyzed. At 60 °C the same mixture showed barely detectable tosyl ester formation. At 40 °C the level of tosylate ester that was formed reached only 20% of the maximum possible value before declining from its own solvolysis.

Although sulfolane is widely used as a solvent for nucleophilic substitution reactions, yet save for one report on dehydration of some terpenediols,[3] a search of the literature turned up no studies of eliminations in sulfolane. We therefore decided it was worthwhile to study our elimination reaction and have found it to be an ordinary solvolysis. When 1,8-bis(dimethylamino)naphthalene (Proton sponge, Aldrich) is added to suppress readdition of the sulfonic acids to the propene product, the reactions (followed by reverse-phase HPLC analysis of the sulfonic esters) follow a first-order course with the first-order rate constant not affected, within experimental error, by reduction of the Proton Sponge concentration by a factor of 2.

The table gives these first-order rate constants for several different arenesulfonates. The rate constants fit the Hammett equation with $\rho = +1.71$. This is hardly more than the ρ value of +1.46 reported by Jaffe[4] from the data of Robertson[5] for the solvolysis of isopropyl arenesulfonates in ethanol, and not much less than those reported by Kevill[6] for adamantyl arenesulfonates, $\rho = 1.76$ for 1-adamantyl, and 1.86 for 2-adamantyl.

We had anticipated a much higher ρ value, perhaps close to that for the complete conversion of an arenesulfonate ester to the anion, such as the value of 2.9 reported for the equilibrium constant for methylarenesulfonate exchange with 3,4-dichlorobenzenesulfonate ion, or the value 3.2 for phenacylarenesulfonates equilibrating with benzenesulfonate.

Table I. Solvolysis Rates of Isopropyl Arenesulfonates in Sulfolane

parasubstit	concn of ester, M	concn of Proton Sponge, M	10^5K, min^{-1}
H	0.0108	0.0116	4.83[a,b]
H	0.0132	0.0055	4.85[c]
CH_3	0.00945	0.0103	2.57[a,b,d]
Cl	0.00980	0.0118	15.6[a,e]
NO_2	0.0103	0.0109	117[a,e]

[a] Average of 2 runs. [b] Reaction followed for 2 half-lives. [c] Reaction followed for 1 half-life. [d] Decreasing Proton Sponge concentration by 50% produces no decrease in rate measured over the first 25% of reaction. [e] Reaction followed for 3 half-lives.

If the equilibrium ρ for loss of arenesulfonates from the isopropyl esters is about the same as that for loss of arenesulfonates from methyl esters, then we might conclude that the transition state has less sulfonate anion character (1.7/2.9 = 59%) than it does in the methyl transfer between arenesulfonates (about 1.88/2.9 = 65%).[2] However, this unexpected conclusion is probably in error for several reasons.

First, it is possible that the starting isopropyl esters may already have more ionic character than the methyl esters, and the equilibrium ρ would therefore be less than that for the methyl esters.

Second, our treatment of substituent effects in methyl transfers[7] is based upon reactions of the charge type of reaction (1). However, the present reaction has for the

$$X^- + MeY \rightarrow XMe + Y^- \quad (1)$$

rate-determining step presumably an ionization reaction giving an intimate carbonium, arenesulfonate ion pair. Previous assumptions about work-terms for such a charge-creating reaction are certainly incorrect, thus the basis of the interpretation of ρ is less secure. As an example, the descriptions of the transition state for the Menschutkin reaction are very different from reactions of type (1). Thus, Arnett and Reich determined a slope of $\Delta G^{\ddagger}$ vs $\Delta G°$ of 0.26 for the reaction of methyl iodide with substituted pyridines,[8] i.e., less than 30% of the charge is developed, as measured in this way. The solvolysis of methyl iodide in water as described by Kurz and Kurz[9] turned out to be complicated; most of the activation energy is required to reorganize the solvent structure.

In the transition state for a charge-creating reaction, the positive and negative charges are separated by only a short distance. Thus although the value of ρ for departure of arenesulfonates depends on the charge on the sulfonate ion, it is reduced by the positive charge only a little farther away.

The effect of a charge change on ρ is attenuated by about a factor of 2 for each extra bond interposed. So if the full charge were developed on both the sulfonate and the alkyl group in the transition state without any dimensional change, ρ would be reduced below that for complete ion separation by a factor of $1 - {}^1/_2 = {}^1/_2$, where the negative term arises because the effect of the developing positive charge is opposite in sign to that of the negative charge

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