2-(4-Isobutylphenyl)propionitrile (6). Tetrakis(tri-*p*-tolyl phosphite)nickel(0) (1.50 g, 1.0 mmol) and tri-*p*-tolyl phosphite (0.30 mL, 1.0 mmol) are dissolved in toluene (30 mL). Zinc chloride (0.06 g, 0.5 mmol) is dissolved in propionitrile (0.5 mL) and then added to the catalyst mixture which is then heated to 88 °C under nitrogen. *p*-Isobutylstyrene **5** (3.45 g, 21.5 mmol) is added by syringe pump; 0.30 g is added initially and the remainder added at 1.33 mL/h. HCN/N_2 is fed at 3 mL/min for 3 h and then 1 mL/min for 3 h. Flash chromatography of the reaction mixture (hexane/ethyl acetate, 90:10, R_f 0.32) results in the isolation of **6** (2.66 g, 14.2 mmol, 68% yield) as a colorless liquid. Anal. Calcd for $C_{13}H_{17}N$: C, 83.37; H, 9.15; N, 7.48. Found: C, 83.31; H, 8.95; H, 7.47. ^1H NMR δ 0.90 (d, J = 7, 6 H); 1.61 (d, J = 7, 3 H), 1.76–1.94 (m, 1 H), 2.47 (d, J = 7, 2 H), 3.86 (q, J = 7, 1 H), 7.14 (d, J = 8, 2 H), 7.25 (d, J = 8, 2 H).

(±)-Naproxen (2). To a stirred mixture of **4** (5.0 g, 23.7 mmol), potassium hydroxide (50 g), and water (30 mL) was added ethylene glycol (70 mL). When the initial exotherm subsided, the mixture was heated in a 125 °C oil bath for 24 h. The mixture was neutralized by slow addition of concentrated hydrochloric acid (100 mL) at 0 °C. The mixture was extracted with ether (3 × 100 mL) and the combined organics were extracted with H_2O (25 mL). Removal of solvent afforded a crude product which was recrystallized from hot toluene to afford **2** (4.62 g, 85%), mp 154–155.5 °C. Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13. Found: C, 73.12; H, 6.30. ^1H NMR δ 1.58 (d, J = 7, 3 H), 3.87 (q, J = 7, 1 H), 3.91 (s, 3 H), 7.09–7.15 (m, 2 H), 7.41 (dd, J = 8, 2, 1 H), 7.66–7.73 (m, 3 H).

Ibuprofen (1). In similar manner, we obtained, after recrystallization from heptane with cooling to −25 °C, **1** (4.50 g, 82%), mp 74 °C. Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.43; H, 8.69. ^1H NMR δ 0.89 (d, J = 7, 6 H), 1.50 (d, J = 7, 3 H), 1.76–1.86 (m, 1 H), 2.44 (d, J = 7, 2 H), 3.70 (q, J = 7, 1 H), 7.09 (d, J = 8, 2 H), 7.21 (d, J = 8, 2 H).

Registry No. (±)-**1**, 58560-75-1; (±)-**2**, 26159-31-9; **3**, 63444-51-9; (±)-**4**, 99148-33-1; **5**, 63444-56-4; (±)-**6**, 99148-34-2; (dmpe)$NiCl_2$, 14726-53-5; CH_2=CHBr, 593-60-2; *p*-BrC_6H_4CH=CH_2, 2039-82-9; (dppp)$NiCl_2$, 15629-92-2; *i*-BuCl, 513-36-0; $((p\text{-}H_3CC_6H_4O)_3P)_4Ni$, 36700-08-0; $(p\text{-}H_3CC_6H_4O)_3P$, 620-42-8; HCN, 74-90-8; $ZnCl_2$, 7646-85-7; 2-bromo-6-methoxynapthalene, 5111-65-9.

Reaction of 5,6-Benzobicyclo[2.2.1]hepta-2,5-diene with Thallium(III) Nitrate

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Thallium(III) nitrate (TTN) is known to be a useful and extremely versatile reagent in organic synthesis, particularly for ring contraction of cyclic alkenes,[2] which are often rapidly converted into the corresponding cyclocarboxaldehyde product. For instance, cyclohexene can be converted to cyclopentanecarboxaldehyde in 85% yield when treated with TTN in methanol followed by acid hydrolysis of the intermediate dimethyl acetal.[3] This rearrangement reaction has been postulated to proceed via the organothallium cation **1** and has been applied to both cycloheptene and cyclobutene systems,[3,4] giving good yields of ring-contracted products. Thus we were surprised to discover that use of this reaction on a bicyclic system produced not ring contraction, but oxidative nitration. In particular, reaction of 5,6-benzobicyclo[2.2.1]hepta-2,5-diene (benzonorbornadiene), **2**, with TTN in methanol did not give rise to the ring-contracted product **3** but afforded good yields of the nitrate ester derivatives **8** and **9**. The stereochemical analysis of these products and the mechanism of their formation are discussed below.

Table I. ^1H NMR Parameters for 8 and 9

	δ_H ($CDCl_3$)		
	8	**9**	
1-H	3.93	3.84	
2-H	4.95	3.46	
3-exo-H	2.27	2.07	
3-endo-H	2.15	1.83	
4-H	3.60	3.44	
7-syn-H	4.91	4.75	
OCH_3		3.29	
	J_{HH}/Hz		
	8	**9**	dihedral angle/deg[a]
$^2J_{3\text{-endo},3\text{-exo}}$	13.5	12.7	
$^3J_{2\text{-endo},3\text{-endo}}$	7.2	7.1	2
$^3J_{2\text{-endo},3\text{-exo}}$	3.2	3.1	121
$^3J_{3\text{-exo},4}$	3.6	3.7	42
$^4J_{3\text{-endo},7\text{-syn}}$	0.97	1.3	

[a] Determined from X-ray crystallographic data; estimated standard deviations 1–2°.

Compound **2** was allowed to react with TTN in methanol followed by treatment with 2 N sulfuric acid. The reaction products were chromatographed on a silica gel column and the racemic nitrate esters **8** and **9** obtained as homogeneous bands.

The ^1H NMR spectrum (Table I) of **8** had four resonance patterns in the aliphatic region. At highest field was the AB portion of an ABX pattern centered at 2.21 ppm and integrating for two protons. Two signals at 3.93 and 3.60 ppm each integrated for one proton. The fourth aliphatic signal integrated for two hydrogens and was centered at 4.93 ppm.

The location of the two ONO_2 groups was immediately evident from the gross features of the ^1H NMR spectrum. The existence of an ABX pattern with a large coupling to the X proton can only be accommodated by three hydrogens located on carbons 2 and 3. The absence of another AB pattern potentially attributable to the hydrogens on C-7 immediately locates the remaining ONO_2 group. Analysis of the ABX pattern resulted in a J(AB) of 13.5 Hz and chemical shifts of 2.15 and 2.27 ppm for the C3 hydrogens. The lowest field resonances are readily assigned to the 2- and 7-hydrogens because of the strongly

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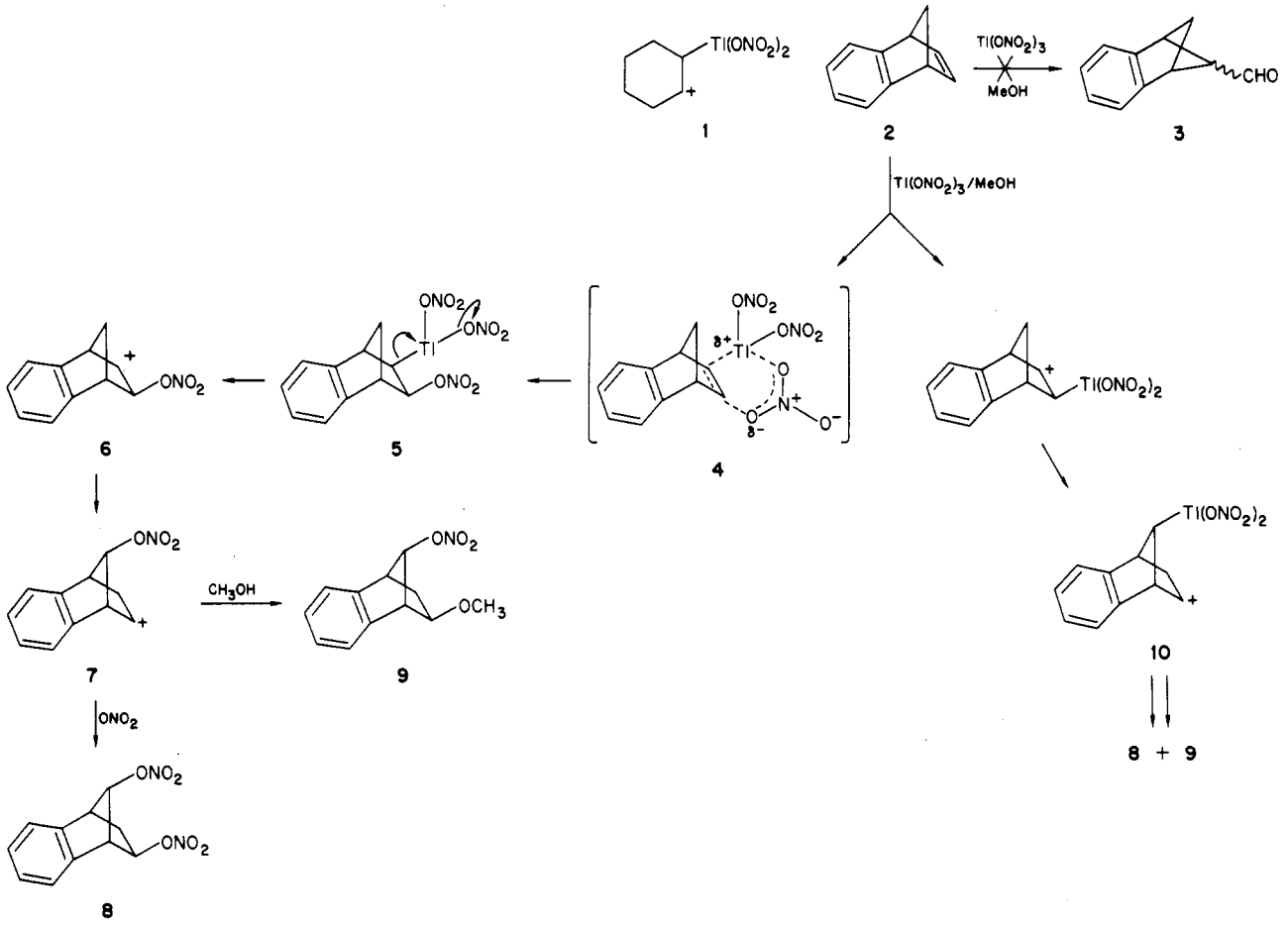
Scheme I



electronegative substituents attached to the respective carbons.

The large couplings (7.2 and 3.2 Hz) from the 3-hydrogens identify the H2 from the overlapping H7 resonance. Further, the 7.2-Hz coupling must be between cis H's. The remaining two signals belong to the bridgehead hydrogens 1 and 4.

It would be expected that the largest vicinal coupling from either bridgehead hydrogen 1 and 4 would be one to an exo hydrogen on 2 or 3, respectively. The dihedral angle is approximately 60° which, according to the Karplus relationship,[5] would have a moderate coupling in the 3–4-Hz range. If the 2-nitrate group was substituted endo, then both bridgehead H's would show this coupling. In fact, only the bridgehead H at 3.60 ppm shows a larger coupling which is to the exo 3 H with the smaller coupling to H2. This establishes the pattern of 4 H to 3-exo to 3-endo to 2-endo, hence requiring that the 2-ONO_2 group be exo. This is confirmed by the absence of a significant coupling between H1 and H2.

The stereochemistry of the 7-nitrate substituent is established by identifying a long range coupling (0.97 Hz) from the 7-syn-H to the 3-endo-H. A four-bond aliphatic coupling of this magnitude would be expected if the two hydrogens and three intervening carbons were in a planar "W" configuration. This is the case with the 7-syn-H and the 3-endo-H, but not with the 7-anti-H. The nitrate group must therefore be anti. The existence of this coupling also directly confirms the 3-endo-H assignment.

An autocorrelated two-dimensional NMR experiment was performed to help make assignments, and a single-crystal structure determination of 8 confirmed the results of the NMR analysis (see supplementary material for details).

The proton NMR spectrum of **9** was similar to the spectrum of 8 but had one more sharp resonance at 3.29 ppm for the methoxy group. The change in substituent of nitrate to OMe moves all the resonances upfield an average of 0.19 ppm, except for the 2-hydrogen which goes upfield 1.49 ppm, establishing the location of the OMe group.

The coupling pattern and values of the protons in **9** are similar to those in 8, indicating the stereochemistry of the two products to be identical.

The ^{13}C NMR spectra of 8 and **9** were assigned by using two-dimensional cross-correlation spectra.

The formation of 8 and **9** in the above reaction most likely involves initial electrophilic attack of the $Tl(ONO_2)_2^+$ species in a cis molecular addition mode, presumably via a concerted or near concerted addition of TTN to **2** through the cyclic intermediate **4**, to give **5**. A similar mechanism previously has been proposed for the addition of thallium(III) acetate to norbornene derivatives and other cyclic olefins.[6,7] Generation of carbocation **6**, followed by rearrangement to **7** and capture of the nucleophile from the exo side, leads to the formation of 8 and **9**. Alternatively, one cannot rule out rearrangement occurring before dethallation to give species **10**, with subsequent formation

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of product(s) (Scheme I). Analysis of the crude reaction mixture also indicated the absence of carbonyl-containing compounds, and no thallium adducts could be detected in, or isolated from, the reaction mixture.

Experimental Section

Melting points were taken on a Koeffler hot-stage microscope and are uncorrected. IR spectra were recorded on a Perkin-Elmer 237 spectrophotometer. NMR spectra were recorded in $CDCl_3$ on a Varian XL-200 spectrometer. ^1H NMR spectra were obtained at 200 MHz, and ^{13}C NMR spectra were obtained at 50.3 MHz. Chemical shifts are reported in parts per million downfield from Me_4Si. Low-resolution mass spectra were performed on an A.E.I. MS9 spectrometer operating at a probe temperature of 250 °C. Microanalyses were conducted by Mr. M. Hart, Department of Chemistry, Manchester University, Manchester, U.K.

5,6-Benzobicyclo[2.2.1]hept-5-ene-2-*exo*,7-*anti*-diyl Dinitrate (8). Addition of thallium(III) nitrate (12.4 g, 0.028 mol) in methanol (30 mL) to a stirred solution of **2** (4.0 g, 0.028 mol) in methanol (30 mL) gave an immediate precipitate of thallium(I) nitrate which was removed by filtration and the filtrate added to a 2 N solution of sulfuric acid (100 mL). The acidic solution was shaken for 5 min and extracted with ether (3 × 50 mL), and the combined ether extracts were washed with saturated $NaHCO_3$ solution (3 × 50 mL). The ether layer was filtered and evaporated to dryness to give a viscous yellow oil (6.75 g), which was subjected to column chromatography through silica gel (35–65 mesh, 100 g) with chloroform as eluent. An initial band was obtained as a gum after evaporation of solvent, which was crystallized from diethyl ether–petroleum ether (bp 30–40 °C) to afford **8** as a white crystalline product (2.83 g, 38%): mp 100–101 °C; ν_{max} (Nujol) 1660, 1638, 1280, 1290, 1300, 1305 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 32.7 (C-3), 44.8 (C-4), 50.0 (C-1), 83.0 (C-2), 88.5 (C-7), 123.7 (C-11), 128.0 (C-9), 128.7 (C-10), 137.1 (C-5), 142.7 (C-6); MS, *m/e* 220 (M - NO_2), 204, 158, 131 (base). Anal. Calcd for $C_{11}H_{10}O_6N_2$: C, 49.62; H, 3.76; N, 10.53. Found: C, 49.71; H, 3.82; N, 10.34.

2-*exo*-Methoxy-5,6-benzobicyclo[2.2.1]hept-5-en-7-*anti*-yl Nitrate (9). A second homogeneous fraction was obtained on further elution of the above silica gel chromarographic column with chloroform, which crystallized from petroleum ether (40–60 °C) and afforded **9** as a white crystalline product (2.72, 41.1%); mp 55–56 °C; IR ν_{max} (Nujol) 1650, 1630, 1295, 1284 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 33.4 (C-3), 44.8 (C-4), 49.9 (C-1), 57.2 (OCH_3), 82.0 (C-2), 89.5 (C-7), 121.8 (C-8), 123.0 (C-11), 127.3 (C-10), 127.7 (C-9), 139.5 (C-5), 143.4 (C-6); MS, *m/e* 204 (M - OCH_3), 189, 129 (base). Anal. Calcd for $C_{12}H_{13}O_4N$: C, 61.30; H, 5.33; N, 5.95. Found: C, 61.52; H, 5.70; N, 5.93.

Crystal Structure Determination of 5,6-Benzobicyclo-[2.2.1]hept-5-ene-2,7-diyl Dinitrate (8). Slow evaporation of a chloroform solution of **8** produced crystals belonging to the monoclinic space group C_{2h}^6—$C2/c$ with a = 24.100 (4) Å, b = 6.990 (2) Å, c = 17.524 (3) Å, and β = 129.07 (2)° at 22 °C and Z = 8. The calculated density is 1.543 g·cm^{-3}. Of the 2621 unique reflections measured with Mo Kα radiation ($2\theta_{max}$ = 55°) on an Enraf-Nonius CAD4/F diffractometer, 2101 having $F_o^2 \geq 3\sigma(F_o^2)$ were included in the final refinement. There was no important absorption or decomposition. In the final full-matrix least-squares refinement cycles the C, N, and O atoms were refined with anisotropic, and the H atoms with isotropic, thermal parameters; final agreement factors R and R_w on F_o are 0.034 and 0.046 for 213 variables. All C–H bond lengths fall in the range 0.91–0.99 Å. The ten largest peaks (height <0.26 e·$Å^{-3}$) in the final difference Fourier map are located at the centers of C–C bonds; the deepest trough (–0.20 e·$Å^{-3}$) is near the center of the aromatic ring. The structure is illustrated in Figure 2 in the supplementary material; H–C–C–H dihedral angles are given in Table I, together with observed hydrogen coupling values from the NMR analysis.

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Registry No. **2**, 4453-90-1; **8**, 98875-84-4; **9**, 98875-85-5; thallium(III) nitrate, 13746-98-0.

Supplementary Material Available: Tables of refined atomic positional and thermal parameters, selected bond lengths and angles, and observed and calculated structure factor amplitudes for **8** and autocorrelated two-dimensional 200-MHz ^1H NMR contour plot of **8** and perspective drawing of the molecular structure of **8** (19 pages). Ordering information is given on any current masthead page.

Indicator Deprotonation in Micelles of a Hydroxyethyl Surfactant

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Functionalized surfactants can generate micelles which are effective nucleophilic or basic reagents.[2-4] In many systems reaction involves attack of an oximate, hydroxamate, alkoxide, or thiolate residue formed by deprotonation of a weak acid, so that reaction rates are pH dependent. The variation of the overall rate constant with pH can be used to calculate an apparent equilibrium constant for deprotonation of the weakly acidic functional group.[3,5]

Deprotonation of indicators in solutions of cationic micelles can be treated quantitatively by calculating the concentration of OH^- bound to the micelle and the distribution of the indicator between the micellar and aqueous pseudophases.[6,7] For a system containing OH^- and surfactant counterion the concentration of micellar bound OH^- can be calculated in terms of the ion-exchange model. This treatment has been applied successfully to deprotonations of areneimidazoles,[8] nitroindoles,[9] and phenols, based on some simplifying assumptions.[10,11] It readily explains how deprotonation of a weakly acidic group at a micellar surface follows not the total concentration of OH^- but that at the surface of the micelle and, for a given [OH^-], decreases with increase of [surfactant] or addition of salt. A similar approach has been applied to micellar rate effects.[4,6,7,13]

The extents of deprotonation of weakly acidic groups of functional micelles seem to follow the total amount of OH^-, as given stoichiometrically,[5] or by the measured pH if buffers are used,[3] whereas the ion-exchange model predicts that the determining factor should be the amount of OH^- at the micellar surface.[6-8] We have investigated

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