4-chloro-2-methylbenzenamine, 95-69-2; ethyl 4-aminobenzoate, 94-09-7; *s*-trioxane, 110-88-3; 3,4-dihydro-3-(1-methylethyl)-6-bromo-8-methyl-1*H*-2,1,3-benzothiazine 2,2-dioxide, 69706-01-0; 1-acetyl-3,4-dihydro-8-methyl-3-(1-methylethyl)-1*H*-2,1,3-benzothiadiazine 2,2-dioxide, 69706-02-1; 3,4-dihydro-3-(1-methylethyl)-6-nitro-8-methyl-1*H*-2,1,3-benzothiadiazine 2,2-dioxide, 69706-03-2.

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Synthesis and Structure of Substituted Bicyclo[4.2.1]nona-2,4-dienes[1]

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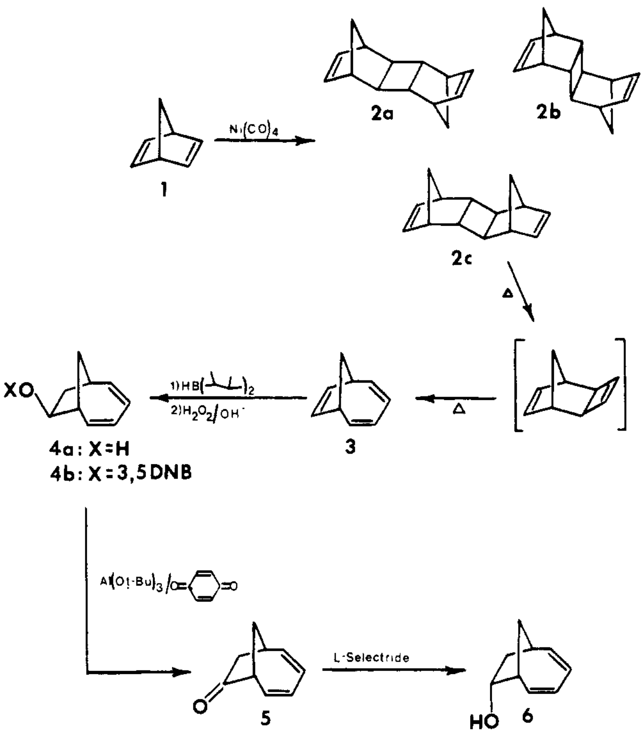
Previous work[2,3] has shown that certain rigid molecules lend themselves to complete structure elucidation by shift reagent techniques. These particular determinations were more readily performed than analysis by the more generally applicable but more operationally difficult method of X-ray diffraction. It was apparent to us that the conformationally rigid compounds **4a** and **5**, which served as intermediates in Masamune's total synthesis of methymycin,[4] and the endo alcohol **6**, also first synthesized by the Masamune group,[5] should be suitable candidates for complete structure determination by shift reagent methods. Moreover, we felt that these compounds, because of their high strain energy and the spatial proximity of the diene moiety to C-7, might show interesting chemical properties.

Although **4a** and **6** had been previously distinguished by determining the relative change in chemical shift of the two methylene bridge protons as a function of concentration of Eu(fod)$_3$,[5] this report details the complete structure assignment for **4a** and **6** and the partial assignment for **5** made possible by straightforward correlation between observed and calculated pseudo-contact shifts.[6] Use of Pr(fod)$_3$, which usually shifts proton resonances upfield with respect to tetramethylsilane, gave optimum separation of peaks. In addition, complete experimental details for the synthesis of **4a**, **5**, and **6** as well as the precursorial triene **3** are presented for the first time.

Synthesis

Heating a mixture of **1** in benzene at 64–65 °C in the presence of Ni(CO)$_4$[7,8] yielded, after 2 days, a ~5:1 mixture of **2c** and **2b** in 60% yield but none of the difficulty pyrolyzable **2a**.[7] Since zero-valent cobalt compounds as used by Arnold[9] promote formation of **2a** almost to the exclusion of the other two trans dimers, the use of Ni(CO)$_4$ offers a real advantage. While the mechanism of the dimerization is not well understood, it seems reasonable to assume that the d orbitals of nickel interact with the π electron system of **1** to promote a reaction which is thermally disallowed in the absence of the metal.[10] The reaction, in our hands, did not involve a strictly catalytic interaction of Ni(CO)$_4$ with substrate, since an essentially stoichiometric amount of nickel compound was required. Moreover, it was observed that a shiny, metallic coating formed on the walls of the reaction apparatus as the reaction proceeded. Interestingly the reaction occurred at 65–70 °C but not at 50 °C.[11]

Scheme I



Pyrolysis of the dimer mixture at 400–430 °C gave **3** in 85% yield. This yield is higher than those reported previously,[5,7] and, more important, purification involved simple distillation only. Treatment of **3** with bis(3-methyl-2-butyl)borane[12a,b] followed by standard alkaline oxidative workup afforded **4a** in 61% yield. Oxidation to **5** in 75% yield required use of a modified Oppenauer oxidation[13a,b] since attempts using Cr(VI) under various conditions failed to produce ketone in significant amounts. Finally stereoselective reduction of **5** to give **6** (70%) was achieved using lithium tri-*sec*-butylborohydride.[14]

Shift Reagent Studies

The unshifted proton NMR spectra of **4a**, **5**, and **6** were complex and not resolved due to overlapping of peaks in the methylene and diene proton regions. Use of Pr(fod)$_3$ as a shift reagent produced shifts to high field resulting in well-resolved spectra, while use of Eu(fod)$_3$, with its downfield shifts, was unsuccessful. The chemical shift of the various proton peaks was plotted vs. ρ, the ratio of concentration of shift reagent to substrate. These plots were essentially linear for **4a** and **6** in the range $\rho = 0$ to 0.4, whereas the plots for **5** were linear only in the range of $\rho = 0$ to 0.2. The observed lanthanide induced shifts, LIS, were taken as the slopes of the linear portion of the plots as determined by least squares, and the positions of peaks in the absence of shift reagent were given by the intercepts.

The calculated LIS values were obtained and compared with those observed using the PDIGM[15] approach as adapted for the IBM 1130 computer.[16] The minimum agreement or R factor, obtained by this approach for each molecule, is associated with the optimum geometry for the lanthanide atom with respect to the protons. Table I gives parameters relating to the optimum geometry for lanthanide complexes of **4a**, **5**, and **6**. The R factors are sufficiently low as to place confidence in the results. To test the sensitivity of the method, calculations were run using the observed LIS values for exo alcohol with the coordinates for the protons of endo and vice versa,

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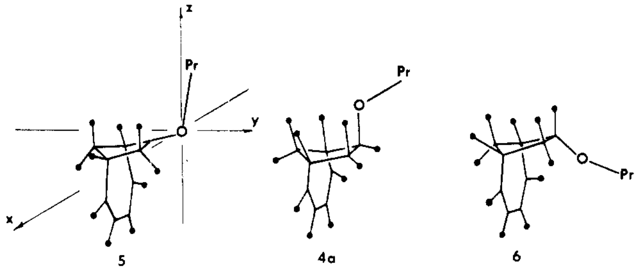
Table I. Lathanide-Substrate Structural Parameters

compd	d^a	w,[b] deg	ϕ,[c] deg	R, %
4a	2.7	63	109	5.33
5	3.9	15	150	3.78
6	2.7	95	129	7.27

[a] Ln–O distance, Å. [b] The angle between the z axis and the Ln–O vector; [c] The angle between the x axis and the projection of the Ln–O vector on the xy plane.



5 4a 6

Figure 1. Structures for the Pr(fod)$_3$ complexes of **5**, **4a**, and **6** depicting the optimum position of the Pr atom with respect to each H atom. The origin is at the O atom in each of the three complexes.

and R factors of 19.1 and 19.5%, respectively, were obtained. Figure 1 shows structures for the Pr(fod)$_3$ complexes depicting the optimum position of the lanthanide atom with respect to the protons of substrate as indicated by LIS calculations.

Experimental Section

General. Melting points were determined on a Fisher-Johns apparatus and are uncorrected. UV spectra were recorded on a Cary 17 spectrophotometer, and IR spectra were obtained from Perkin-Elmer 137 and 457 instruments. A JEOLCO C60HL spectrometer was used to record NMR spectra and was operated in the external lock mode. GLC analyses were carried out on a Carle 800 chromatograph fitted with a thermal conductivity detector using a 6 ft × 0.0625 in. stainless steel column containing 8% SF-96. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Nickel carbonyl was obtained from Matheson Gas Products. Borane in tetrahydrofuran (THF) was supplied by Alfa Products and lithium tri-*sec*-butylborohydride in THF was purchased from Aldrich Chemical Co. Tetrahydrofuran was refluxed over and distilled from LiAlH$_4$ immediately before use. Silica gel (60–200 mesh) for column chromatography was obtained from Sargent-Welch Scientific Co. Organic extracts were dried over MgSO$_4$.

Lanthanide Shift Experiments. For each compound a series of at least nine solutions (CDCl$_3$ solvent dried over 4A molecular sieves) was prepared by means of continuous dilution whereby substrate concentration was constant at 0.5 M and concentration of Pr(fod)$_3$ varied from 0.0 to 0.2 M. Tetramethylsilane (ca. 5%) was added as an internal standard. Obtained from Aldrich Chemical Company, Inc., Pr(fod)$_3$ was heated at 100 °C under reduced pressure before use.

Dimerization of Bicyclo[2.2.1]hepta-2,5-diene. A three-necked 1000-mL round-bottom flask fitted with magnetic stirring bar, pressure-equalizing dropping funnel, reflux condenser, and an adapter, which was connected to both an aspirator and a mercury bubbler, was charged with 90.6 g (0.99 mol) of 1 and 400 mL of dry benzene. The apparatus was flushed with argon three times before 39.3 g (0.23 mol) of Ni(CO)$_4$ was introduced dropwise over a 5-min period. The mixture was stirred under argon for 20 h at 65–70 °C, and then 13.1 g (0.08 mol) of Ni(CO)$_4$ was added rapidly. Stirring at 70 °C continued for 20 h with concomitant formation of a shiny metallic coating on the walls of the apparatus. Finally, solvent and any unreacted starting material were removed under aspirator pressure before the remaining residue was treated with 200 mL of 1 N HNO$_3$ to remove traces of Ni(CO)$_4$. The acidified, gummy mixture which resulted was extracted with 1:1 pentane–ether (800 mL) and the extract was washed with 100 mL of 5% NaOH solution and two 100-mL portions of brine. Drying and concentration under reduced pressure produced 62.0 g of a pale yellow oil. Distillation gave 54.8 g (60%) of a clear, colorless oil which solidified upon cooling to ice-bath temperature: bp 90–110 °C (0.25 mm); IR (CCl$_4$) 1570, 1550, and 710 cm^{-1} (the last peak is characteristic of norbornenes[17]); NMR (CCl$_4$) δ 5.99 and 6.34 (multiplets corresponding to the two different HC=CH of exo, trans, endo) and 6.46 (m, HC=CH, endo, trans, endo) indicating a ratio of isomers of 4.7:1; GLC (120 °C) two peaks, retention time (min) 10.5 and 12.0 in the ratio 4.8:1.

Bicyclo[4.2.1]nona-2,4,7-triene (3). A 27 × 1 cm Pyrex column was filled with glass beads (3-mm diameter) and attached to a three-necked 100-mL round-bottom flask. Affixed to the top of the column through a rubber septum were a 10 mL syringe, a glass tube (2-mm diameter) for introducing N$_2$, and an Omega Engineering iron-constantan thermocouple (inserted into a 12 in. stainless steel sheath). The tip of the thermocouple was positioned in the middle of the column which was wrapped with heating tape and then asbestos tape along its entire length. As the column was heated to 400–430 °C, 120 mL of a mixture of **2b** and **2c** was allowed to flow through under N$_2$ at a rate of 0.16 mL/min. The pyrolysate was collected at −80 °C, allowed to warm to room temperature, and then quickly subjected to rotary evaporation to remove cyclopentadiene. Distillation of the remaining liquid gave 60 g (85%) of a clear, colorless oil: bp 52 °C (14 mm) [lit.[7] bp 81 °C (105 mm)]; UV (pentane) 260 nm (ϵ 4400); IR (thin film) 3050, 3020, 730 cm^{-1}; NMR (CDCl$_3$) δ 1.30 (d, 1 H), 1.92 (5 multiplets, 1 H), 3.11 (broad t, 2 H), 5.25 (broad s, 2 H), 6.00 and 5.80 (overlapping multiplets, 4 H, –C=CC=C–) consistent with Cannell.[7]

***exo*-Bicyclo[4.2.1]nona-2,4-dien-7-ol (4a).** Using the hydroboration procedure of Kono and Hooz,[12a] 115 mL (0.11 mol) of a 0.96 M solution of BH$_3$ in THF was cooled to 0 °C under N$_2$. To the stirred solution was added a solution of 15.4 g (0.22 mol) of 2-methyl-2-butene in 40 mL of dry THF. The temperature was maintained at 0–10 °C for 2 h, and then 11.8 g (0.10 mol) of 3 in 20 mL of dry THF was added taking care to maintain the reaction temperature below 20 °C. After addition was complete, the reaction mixture was stirred at room temperature for 1 h. Subsequently, the mixture was cooled and 34 mL (0.10 mol) of 3 M NaOH solution was added. Next, 36 mL (0.3 mol) of 30% H$_2$O$_2$ solution was introduced at such a rate that the reaction temperature remained at 30–35 °C. Finally, after being stirred at room temperature for 2 h, the mixture was extracted with 100 mL of ether. The extract was washed with brine and H$_2$O, dried, and concentrated under reduced pressure. Distillation produced two fractions: the first essentially pure 3-methyl-2-butanol and the second, weighing 8.1 g (61%), a clear, colorless oil which solidified upon cooling [mp 26 °C; bp 70–98 °C (0.3 mm) [lit.[4] bp 78–81 °C (0.3 mm)]; UV (pentane) 257 nm (ϵ 2500); IR (thin film) 3300 (broad), 1015 cm^{-1}; NMR, see Table I].

***exo*-Bicyclo[4.2.1]nona-2,4-dien-7-yl 3,5-Dinitrobenzoate (4b).** A solution of 1.0 g (7.4 mmol) of **4a** in 25 mL of dry pyridine (distilled from BaO) was cooled to 5 °C as 3.5 g (15 mmol) of 3,5-dinitrobenzoyl chloride was added along with an additional 25 mL of pyridine. The reaction mixture was stirred at 4 °C for 80 h in a sealed container and then diluted with 100 mL of cold 1% aqueous H$_2$SO$_4$. Extraction of the mixture with 100 mL of ether followed by washing with H$_2$O and saturated NaHCO$_3$ solution yielded, upon drying and evaporation of ether, 2.7 g of dark-brown, viscous oil which solidified upon prolonged cooling. Crystallization from hexane gave 2.2 g (89%) of yellow, granular solid: mp 105–108 °C; IR (KBr disk) 1730 (C=O), 1540 and 1350 (NO$_2$), 1280 cm^{-1} (C–O); NMR (CDCl$_3$) δ 1.4–3.1 (complex multiplet, 7 H), 5.1–6.3 (complex multiplet, 4 H, C=CC=C), 9.1 (m, 3 H, aromatic hydrogens). Recrystallization from ethanol produced an analytical sample: mp 107.5–108.5 °C. Anal. Calcd for C$_{16}$H$_{14}$N$_2$O$_6$: C, 58.18; H, 4.27; N, 8.48; O, 29.07. Found: C, 58.31; H, 4.41; N, 8.27; O, 29.01.

Bicyclo[4.2.1]nona-2,4-dien-7-one (5). Using a procedure modified from those of Wiberg[13a] and Bly and Bly,[13b] we heated to reflux temperature for 23 h a mixture of 10.8 g (79.5 mmol) of **4a**, 34.8 g (322 mmol) of p-benzoquinone (recrystallized from hexane), and 19.8 g (80.5 mmol) of aluminum *tert*-butoxide in 500 mL of dry ether. The resulting mixture was treated with 50 mL of 3 M HCl solution and then filtered through a pad of filter aid. The filter cake was washed with 250 mL of ether, and the combined filtrate was separated. After washing the ether phase twice with 100 mL of 3 N HCl solution, five times with 150 mL of 5% NaOH solution, and finally with brine, we dried and then concentrated the mixture under reduced pressure to give 8.94 g of dark-yellow oil. Distillation afforded 8.10 g (75%) of a light-yellow oil: bp 70 °C (0.3 mm) [lit.[4] bp 67–68° (0.7 mm)]; UV (pentane) 258 nm (ϵ 3800); IR (thin film) 3045, 1745 (C=O), 1597 cm^{-1}; NMR, see Table I. A 2,4-dinitrophenylhydrazone was made: mp 171.5–173.5 °C (from EtOH). Anal. Calcd for C$_{15}$H$_{14}$N$_4$O$_4$: C, 57.32; H, 4.49; N, 17.83; O, 21.36. Found: C, 57.39; H, 4.50; N, 17.85; O, 21.26.

***endo*-Bicyclo[4.2.1]nona-2,4-diene-7-ol (6).** A 50-ml, three-necked flask was flushed with argon before introduction of 16.0 mL (16 mmol) of a 1 M solution of lithium tri-*sec*-butylborohydride[14] (L-Selectride) in THF. While the solution was cooled to −80 °C, 2.0

g (15 mmol) of **5**, dissolved in 8 mL of dry THF, were added dropwise with stirring over 10 min. The solution was maintained at −80 °C for 30 min and then allowed to warm to 0 °C over a 90-min period. Then 8 mL (24 mmol) of 3 M NaOH solution was introduced. While the resulting alkaline mixture was maintained at 0–5 °C, 9 mL (100 mmol) of 30% H_2O_2 solution was carefully added (severe foaming occurred). The green solution which remained was stirred at 25 °C for 1 h before 100 mL of a saturated solution of K_2CO_3 was added. Extraction with ether (100 mL) was followed by washing with H_2O and brine. Drying and evaporation of solvent produced 2.84 g of cloudy, viscous oil which was chromatographed on 80 g of silica gel ($CHCl_3$ eluting solvent). Evaporation of solvent from appropriate fractions gave 1.41 g (70%) of a pale-yellow, clear oil: UV (pentane) 260 nm (ϵ 810); IR[18] (thin film) 3450 (broad), 3030, 2980, 1595, 1090 cm^{-1}; NMR, see Table I. Distillation afforded an analytical sample. Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88; O, 11.75. Found: C, 79.60; H, 9.09; O, 11.31.

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Registry No.—**1**, 121-46-0; **2b**, 1624-13-1; **2c**, 2957-68-8; **3**, 5240-87-9; **4a**, 69631-83-0; **4b**, 69631-84-1; **5**, 69124-20-5; **5**•DNP, 69124-21-6; **6**, 69631-85-2.

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Micellar Catalysis in the Oximation Reaction of Aliphatic and Cyclanic Ketones. Hydrophobic Interactions

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Micellar catalysis has been the object of numerous studies[1-5] which have explained this phenomenon in terms of the free energy of the reaction. The increase in the reaction rate is due to a decrease in the value of $\Delta G^{\ddagger}$ because of a variation in the enthalpy and the entropy of activation caused by hydrophobic interactions.[6] This has been postulated for several reactions including the hydrolyses of esters[7,8] and Schiff bases[9] and solvolysis reactions.[10]

In contrast, micellar catalysis of additions of nucleophiles to carbonyl groups has received little attention. We have previously studied[11] the oximation of cyclohexanone and 4-*tert*-butylcyclohexanone under identical conditions in the presence of sodium lauryl sulfate and found that the catalytic effect is greater for the more hydrophobic 4-*tert*-butylcyclohexanone.

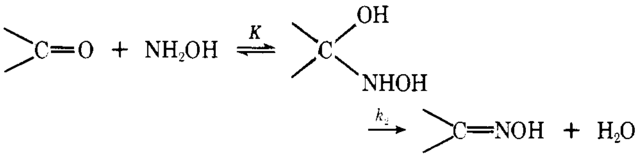
It might be reasonably supposed that the amphipathic substrate is solubilized in the interior of the micelle. This more intimate association of the substrate and the micelle allows a better stabilization of the transition state by the negative charges on the micelle and gives a greater catalysis.

We wished to examine this hypothesis by a study of several other ketones differing in the length and the nature of their hydrocarbon chain.

Experimental Section

The reaction which was examined is the oximation of ketones which occurs in two steps (addition of hydroxylamine and dehydration of the carbinolamine), either of which may be rate determining depending on whether the reaction is run in a acidic or basic medium. The catalytic effects of surfactants in acid were not significant,[11] probably because of the slight change of structure between the transition state and the initial ketone.[12,13]

In basic solution, the effects were much more pronounced than in acid solution. The reaction kinetics were followed spectrophotometrically by monitoring the appearance of the product oxime at 220 nm.



Under conditions where the kinetics are pseudo-first-order, the experimentally observed rate constant, k_{exptl},[11] is given by the expression

$$k_{\text{exptl}} = Kk_2 \frac{[\mathrm{NH_2OH}][\mathrm{H^+}]}{1 + [\mathrm{NH_2OH}]K} \tag{1}$$

Inversion of this equation gives the following relationship

$$\frac{1}{k_{\text{exptl}}} = \frac{1}{k_2K[\mathrm{H^+}]} \cdot \frac{1}{[\mathrm{NH_2OH}]} + \frac{1}{k_2[\mathrm{H^+}]} \tag{2}$$

In principle, utilization of this linear relationship allows the extraction of both k_2 (the second-order rate constant for dehydration of the carbinolamine) and K (the pH-independent equilibrium constant for the ketone–carbinolamine interconversion) by varying the concentration of hydroxylamine. In practice, we were only able to separate these kinetic constants for acetone and 2-butanone, as we were limited to nonsaturating concentrations of hydroxylamine by its solubility.

We define k^0 as the experimental rate constant in aqueous solution and k^{ψ} as the experimental rate constant in the presence of micelles. Each rate constant is the mean of at least three runs and we estimate the precision to be ±3%.

The ketones were commercial products purified by recrystallization or spinning band distillation. The concentration varied between 10^{-4} and 10^{-3} M and that of hydroxylamine hydrochloride was generally about 0.2 M. This large excess is necessary in order for the reaction to proceed to completion and for pseudo-first-order kinetics to be observed.[13] The ionic strength was maintained constant at 0.5 M by the addition of NaCl and kinetic measurements were made at $T = 30 \pm 0.1$ °C at pH 8.5 (borax buffer). This pH value was chosen so as to obtain convenient reaction rates with the ketones we used.

The experimental curves, showing the variation of the rate constant with pH for cycloheptanone with hydroxylamine in the presence of surfactant, are given in Figure 1. It can be readily seen that sodium lauryl sulfate (NaLS) catalyzes the reaction in both neutral and basic solutions. Consequently, we chose to study this anionic surfactant.

The commercial product is recrystallized according to the method of Duynstee and Grunwald.[14] The concentration of surfactant in the reaction medium was 0.1 M, substantially larger than the critical micelle concentration (8.1×10^{-3}M),[1] and on the plateau of saturation for all of the compounds. We also demonstrated that the surfactant

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