pure 7 is easily obtained by distillation away from the higher boiling aldol-derived product, 8. Compound 8 has been prepared independently by the reaction of Tf_2O, 1, and dehydrated aldol product of cyclohexanone.[9]

By changing the solvent to carbon tetrachloride we have been able to nearly eliminate formation of 8 and increase the isolated yield of 7 to 86%, a modest improvement over the reaction using 1[5] (Table I). A solvent change to pentane gives similar results as methylene chloride, indicating the change in solvent polarity for carbon tetrachloride is not the key to nearly eliminating the diene triflate 8.

The polymer-bound base 6 is easily regenerated using diisopropylamine/benzene in combination with other organic washes. The beads do become slightly discolored after several uses, but elemental analysis verifies they are unchanged in their chemical makeup. This latter statement is also supported by the fact that through five regeneration cycles, 6 produces consistent yields of vinyl triflate. Mechanical damage to the beads does occur through stirring, but this fact does not seem to effect the efficiency of the polymer-bound base.

The polymer-bound base also works on more sterically hindered ketones (Table I, entries 2 and 3), only requiring somewhat more forcing reaction conditions relative to cyclohexanone, but improved yields are obtained. However, it should be pointed out that given a common substrate, the polymer-bound base appears to react ever bit as fast as 1 in vinyl triflate syntheses. When a ketone, in which a kinetic and thermodynamic vinyl triflate are possible (entry 3) is used, *both* 1 and 6 give predominately the thermodynamic vinyl triflate (90%) and only minor amounts of the kinetic vinyl triflate.

Use of aldehydes in the synthesis of vinyl triflates has been carried out quite successfully with 1 as the base with Tf_2O.[5] We find that when the polymer-bound base is utilized with identical reaction conditions (heptanal, Tf_2O, refluxing 1,2-dichloroethane, 2 h) almost 25% of the product is the diene triflate and the remainder is the expected (*Z*)- and (*E*)-vinyl triflate. Lower reaction temperatures, changes in solvent (CCl_4, CH_2Cl_2), and variation of concentrations (both heptanal and equivalents of 6) have no beneficial effect; in fact, the yield of vinyl triflate decreases.

In summary, an expensive and very useful base, 2,6-di-*tert*-butylpyridine, has been quantitatively incorporated into polymer beads and then shown to be 100% reusable through several cycles of use. In addition, the polymer-bound base 6 gives improved yields of vinyl triflates from ketones when compared to 1 and has the distinct advantage of easy removal at the completion of the reaction. Current efforts are directed at understanding the role of 6 in catalyzing the aldol reaction and surveying the polymer-bound base's full synthetic utility.

Experimental Section

General. All manipulations of compounds and solvents were carried out by using standard Schlenk techniques. Solvents were degassed and purified by distillation under nitrogen from standard drying agents.[12] Spectroscopic measurements utilized the following instrumentation: ^1H NMR, Varian XL 300; ^{13}C NMR, Varian XL 300 (at 75.4 MHz). NMR chemical shifts are reported in δ vs Me_4Si, assigning the $CDCl_3$ resonance in ^{13}C spectra to be at 77.00 ppm. The chloromethylated polystyrene beads (S-X1) were purchased from Bio-Rad Laboratories and used as received. Elemental analyses were performed by Atlantic Microlab, Atlanta, GA.

Preparation of Polymer-Bound 2,6-Di-*tert*-butylpyridine 6. To a chilled (−78 °C) tetrahydrofuran (THF) (40 mL) solution containing 1[13] (3.70 g, 18 mmol) was added *sec*-BuLi (17.0 mL, 1.1 M in cyclohexane) dropwise via syringe. The mixture was stirred at −78 °C for 10 min and then removed from the cold bath. After the mixture became homogeneous, it was cannulated into a chilled (−78 °C) THF slurry containing the chloromethylated polystyrene beads (3.00 g, 3.90 mequiv/g, Bio-Beads S-X1, Bio-Rad Laboratories). Stirring was continued for 30 min at −78 °C, then the cooling was removed, and the mixture was allowed to warm to ambient temperature over a 2-h time period. Methanol (35 mL) was added to the mixture and stirred for 30 min. The solvents were decanted away from the beads and washed with a benzene/methanol (150 mL, 1/1, v/v) solution for 15 min. This solution was decanted off, and the beads were washed with methanol (100 mL) and then dried under reduced pressure at 65 °C for 24 h to yield 4.9 g (100%) of 6. Nitrogen Anal. Calcd: 3.29%. Found: 3.27%.

Vinyl Triflate Preparations. A Schlenk flask was charged with carbon tetrachloride (8 mL), 6 (3.0 mmol, 1.30 g), the appropriate ketone (3.0 mmol), and Tf_2O (3.0 mmol, 0.50 mL), in that order. The mixture was allowed to react for the specified temperature and time given in Table I. After the reaction was complete, the mixture was diluted with pentanes (30 mL), and the organic solvents were decanted away from the beads. The product mixture was washed with water (50 mL) and then brine (25 mL). The organic layer was filtered through basic alumina with a final elution of pentanes/ethyl acetate (50 mL; 9/1, v/v). The solvents were removed, and the vinyl triflate was purified by a bulb-to-bulb transfer at reduced pressure (see Table I for yields and product distributions).

Regeneration of 6. The protonated polymer was treated with a diisopropylamine/benzene solution (15 mL; 1/4, v/v) for 15 min with stirring. The diisopropylamine/benzene solution was removed by cannulation and then the beads were treated with an additional diisopropylamine/THF solution (15 mL; 1/9, v/v) for 15 min with stirring. The solution was removed by cannulation, and the beads were treated with THF (15 mL) for 10 min with stirring, then transferred to a glass-frit (medium porosity), washed with dichloromethane (100 mL) and then methanol (100 mL), and finally dried under reduced pressure at 65 °C for 12 h.

Acknowledgment. M.E.W. is grateful to the Office of the Vice President for Research at Utah State University for generously funding this work.

Registry No. 6, 38222-83-2; 7, 28075-50-5; 8, 110315-54-3; $(H_3C)_2CHC(OTf)=C(CH_3)_2$, 52149-35-6; $(H_3C)_2CHCOCH(CH_3)_2$, 565-80-0; cyclohexanone, 108-94-1; 2-methylcyclohexanone, 583-60-8; 2-methyl-1-cyclohexenyl triflate, 32363-21-6; 6-methyl-2-cyclohexenyl triflate, 76605-82-8.

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Hexacyclo[6.6.1.$0^{2,7}$.$0^{3,12}$.$0^{6,11}$.$0^{9,14}$]pentadecane and Pentacyclo[8.4.0.$0^{3,8}$.$0^{4,14}$.$0^{7,11}$]tetradecane Systems from Decahydro[1,4;5,8]dimethanoanthracene-11,12-dione

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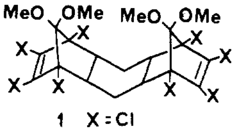
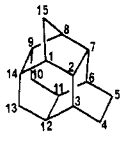
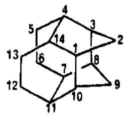
The 2:1 Diels–Alder adduct of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene and 1,4-cyclohexadiene[1,2] is a versatile starting material for a wide variety of novel polycyclic caged systems. Even though its endo,syn,endo stereostructure is clearly evident from its ^{1}H NMR spectrum, as suggested by Fray and Bratby,[2] its inertness toward the intramolecular [2 + 2] photocycloaddition coupled with the fact that 1,4-benzoquinone with tetrachlorodimethoxycyclopentadiene gives an endo,anti,endo 2:1 adduct raises some ambiguity.[3,4] In a continuation of our interest in the synthesis of polycyclic cage compounds,[5] in this paper we describe the synthesis of two new, novel systems **2** and **3** mentioned in the title[6] starting from the bisadduct **1**. The strategy described here, in addition to generation of these new systems, provides unambiguous chemical confirmation to the endo,syn,endo stereostructure of the bisadduct **1**.



1 X=Cl
5 X=H

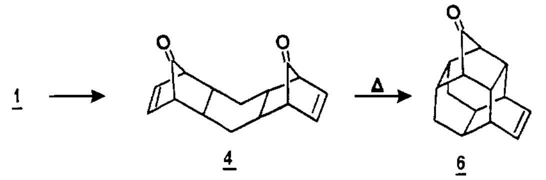


2



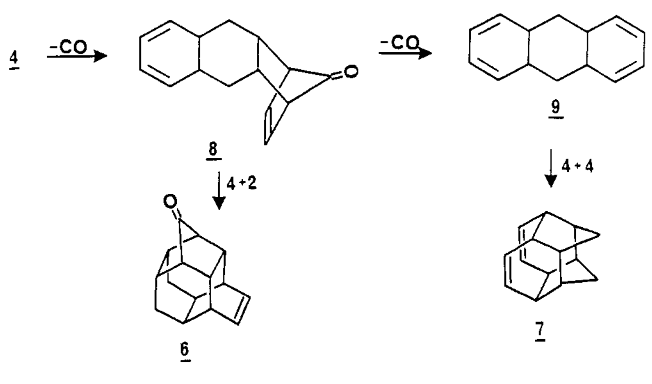
3

The requisite dione **4** was obtained from the abundantly available bisadduct **1**. Reductive dechlorination using excess sodium–EtOH in liquid ammonia furnished the bis(ketal) **5** in over 80% yield. Hydrolysis of the ketal groups with aqueous sulfuric acid produced cleanly the dione **4**. The structure of **4** rests on its parentage and spectral characteristics (see the Experimental Section).

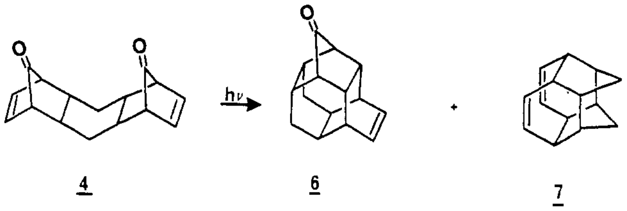


Thermal activation of the dione **4**, either in neat form or in solution (toluene, sealed tube) at 200 °C for 5 or 10 min followed by purification over a silica gel column, furnished the hexacyclic ketone **6** (mp 140–43 °C) in over 80% yield. The structure of **6** and its inherent symmetry were clearly revealed from its spectral characteristics. The eight-line ^{13}C NMR spectrum [δ 212.2 (s), 135.2 (d), 44.8 (d), 34.9 (d), 30.5 (d), 29.1 (d), 26.5 (d), 24.9 (t)] with one carbonyl carbon and one olefinic carbon clearly established the destruction of one of the two symmetries present in the starting dione **4**. In addition, the IR spectrum [ν_{max} 1770 cm^{-1}] established the presence of a norbornan-7-one type carbonyl, and in the ^{1}H NMR spectrum, the appearance of an olefinic proton signal at δ 6.38 as dd, typical of a bicyclo[2.2.2]oct-2-ene system, and AB pattern for the methylene at δ 2.04 and 1.27 in addition to the other expected signals clearly established the structure of **6**.

Scheme I



On the other hand, irradiation of a 0.1% benzene solution (N_2 purged) of dione **4**, in a quartz immersion vessel with a 450-W Hanovia medium-pressure mercury vapor lamp for 30 min, furnished two products, **7** (50%) and **6** (15%), in addition to starting material. While the structure of the minor product can be obtained directly from the spectral and chromatographic comparison with the sample obtained in the thermolysis, the structure of the major product is derived from its spectral data. The IR spectrum clearly indicated the absence of the carbonyl, and the four-line ^{13}C NMR spectrum [δ 131.2 (d), 45.7 (d), 38.3 (d), 28.3 (t)] with one olefinic signal (for four carbons) clearly indicated the maintenance of the twofold symmetry. In addition, in the ^{1}H NMR spectrum the olefinic signal at δ 5.75 (dd) for the four olefinic protons and mechanistic considerations clearly justify the pentacyclic structure for the product. The importance of the polarity of the solvent in photolysis is worth mentioning; in ether diene **7** is formed in lesser yield when compared with that formed in hexane, whereas in acetone diene **7** is not formed at all.



One probable way of explaining the formation of **6** and **7** from the dione **4** is depicted in Scheme I. Thermal decarbonylation of the dione **4** first generates the trienone **8**, which undergoes further rapid intramolecular [4 + 2] Diels–Alder reaction to form the hexacyclic system **6**, whereas in the photolysis double decarbonylation leads to the tetrene **9**, which undergoes further a symmetry-allowed [4 + 4] cycloaddition to furnish the diene **7**. Further work is in progress to identify the actual intermediates involved in the photolysis.[7]

In conclusion, we have described here the synthesis of two new polycyclic cage systems. The formation of these

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(3) Intramolecular [2 + 2] photocycloaddition was observed in a different derivative of the same system in the laboratories of Prof. G. Mehta. We thank Prof. Mehta for exchanging his results prior to publication.

(4) Since the 1:1 adduct is known to be endo, the seven-line ^{13}C NMR spectrum [(67.89 MHz, $CDCl_3$) δ 129.6 (s), 112.3 (s), 78.4 (s), 52.8 (q), 51.6 (q), 45.6 (d), 18.6 (t)] for the bisadduct **1** rules out all other possibilities except the endo,syn,endo and endo,anti,endo stereostructures.

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(6) To our knowledge these systems are not known. However, compound **3** can be found in the computer-generated list of various intermediates in the formation of diamantane, the $C_{14}H_{20}$ stabilomer. See: Gund, T. M.; Schleyer, P. v. R.; Gund, P. H.; Wipke, W. T. *J. Am. Chem. Soc.* **1975**, *97*, 743.

(7) Since the submission of this paper, an efficient, two-step intramolecular [4 + 4] cycloaddition to cycloocta-1,5-dienes was reported: Wender, P. A.; Correia, R. D. *J. Am. Chem. Soc.* **1987**, *109*, 2523.

J. Org. Chem. **1987**, *52*, 5039–5041

systems from the dione 4 unambiguously establishes the endo,syn,endo stereostructure of the bisadduct 1. We are now looking into the different conditions of photolysis to achieve intramolecular [2 + 2] photocycloaddition of the bisadduct 1 and the analogues 4 and 5 to lead to a bishomo–seco heptaprismane derivative and related polycycles.

Experimental Section

IR spectra were recorded on a Perkin-Elmer 781 spectrophotometer. ^{1}H NMR (270, 90, 60 MHz) and ^{13}C NMR (67.89, 22.5 MHz) were recorded on Brucker WH 270, JEOL FX 90Q, and Varian T 60 spectrometers. Chemical shifts and splittings are reported in standard fashion (δ) with reference to internal tetramethylsilane; "st" indicates additional fine structure. Melting points are uncorrected. Elemental analyses were carried out on a Carlo Erba 1106 instrument. Acme 60–120-mesh silica gel was used for column chromatography. Acme silica gel G (containing 13% calcium sulfate as binder) was used for TLC. Liquid ammonia was obtained from the Mysore Ammonia Co. in cylinders and was dried over sodium and distilled directly into the reaction flask prior to use. THF was distilled over sodium benzophenone ketyl. The bisadduct 1 was prepared according to the literature procedure[2] from freshly prepared 1,4-cyclohexadiene (from benzene) and 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene (from hexachlorocyclopentadiene).

1,4,4a,5,8,8a,9,9a,10,10a-Decahydro-11,11,12,12-tetramethoxy-1,4;5,8-dimethanoanthracene (5). Freshly distilled ammonia (300 mL) was placed in a 500-mL round-bottom flask containing a magnetic stirring bar. A solution of the bisadduct 1[2] (1.8 g, 3 mmol) in dry tetrahydrofuran (20 mL) and dry ethanol (2 mL) was carefully added. Sodium (1.38 g, 0.06 mol) was added to this magnetically stirred solution in small pieces over a period of 30 min, and the resultant mixture was stirred for an additional 1 h and quenched with solid ammonium chloride. Ammonia was evaporated over a period of 4 h, and the residue was taken up in 50 mL of water and extracted with methylene chloride (4 × 30 mL). The extract was washed with brine, dried over anhydrous Na_2SO_4, and concentrated. Purification of the residue by passing through a silica gel (20 g) column using methylene chloride as eluent furnished 800 mg (81%) of the dechlorinated bis(ketal) 5: mp 237–40 °C; IR ($CHCl_3$) ν_{max} 1125, 1100, 1060 cm^{-1}; ^{1}H NMR (60 MHz, CCl_4) δ 5.87 (4 H, t, J = 2.2 Hz), 3.1 (3 H, s), 3.0 (3 H, s), 2.54 (4 H, m), 1.8–2.35 (4 H, m), 1.22 (2 H, m), 0.4 (2 H, m). Anal. Calcd for $C_{20}H_{28}O_4$: C, 72.26; H, 8.49. Found: C, 72.35; H, 8.54.

1,4,4a,5,8,8a,9,9a,10,10a-Decahydro-1,4;5,8-dimethanoanthracene-11,12-dione (4). A solution of the bis(ketal) 5 (300 mg, 0.91 mmol) in methylene chloride (20 mL) was placed in a 100-mL round-bottom flask followed by the addition of 20% aqueous sulfuric acid (20 mL). The two layers were vigorously stirred for 16 h at room temperature. The organic layer was separated and the aqueous layer extracted with methylene chloride (2 × 10 mL). The combined organic layer was washed with saturated aqueous sodium bicarbonate solution followed by brine and dried over anhydrous Na_2SO_4. Evaporation of the solvent furnished 200 mg (92%) of crystalline dione 4, which was recrystallized from a mixture of benzene–ethanol: mp 178–180 °C; IR ($CHCl_3$) ν_{max} 1785, 1765 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.43 (4 H, t, J = 3 Hz), 2.85 (4 H, br s), 2.22–2.35 (4 H, m), 1.5 (2 H, td, J = 13, 4 Hz), 0.62 (2 H, q, J = 13 Hz). Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.71, H, 6.67.

Hexacyclo[6.6.1.0^{2,7}.0^{3,12}.0^{6,11}.0^{9,14}]pentadec-4-en-15-one (6). The dione 4 (200 mg, 0.85 mmol) was placed in a 25-mL round-bottom flask filled with nitrogen. The flask was immersed in an oil bath, preheated and equilibrated to 200 °C, for 5 min. The pyrolysate was cooled, taken in benzene, and purified by passing through a silica gel (10 g) column. Alternatively, the pyrolysis can also be carried out in toluene solution (5 mL) in a sealed tube at the same temperature for 10 min. The hexacyclic ketone 6 (140 mg, 79.5%) was further purified by a bulb-to-bulb distillation: mp 140–143 °C; IR (melt) ν_{max} 3060, 1770 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 6.38 (2 H, dd, J = 4.5, 3 Hz), 2.34 (2 H, br s), 2.28 (2 H, br s), 2.04 (2 H, d, J = 13.5 Hz), 1.89 (2 H, s), 1.74 (2 H, s), 1.63 (2 H, br s), 1.27 (2 H, d, J = 13.5 Hz); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 212.2 (s), 135.2 (d), 44.8 (d), 34.9 (d), 30.5 (d), 29.1 (d), 26.5 (d), 24.9 (t); mass spectrum, *m/e* 212, 184, 142, 130, 93, 77. Anal. Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.59. Found: C, 83.62; H, 7.65.

Pentacyclo[8.4.0.0^{3,8}.0^{4,14}.0^{7,11}]tetradeca-5,12-diene (7). A benzene solution (500 mL) of the dione 4 (500 mg, 2.12 mmol) was carefully purged with a slow stream of nitrogen for 15 min. The solution was then irradiated with a Hanovia 450-W medium-pressure mercury vapor lamp in a quartz immersion vessel. After being irradiated for 30 min, solvent was evaporated and placed on a silica gel (20 g) column. Elution with hexane furnished 180 mg (50%) of the crystalline diene 7: mp 240 °C (hexane); IR ($CHCl_3$) ν_{max} 1600 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$) δ 5.75 (4 H, dd, J = 5, 2.5 Hz), 2.7–2.4 (4 H, br s), 2.2 (4 H, br s), 1.8 (2 H, d, J = 11 Hz), 0.85 (2 H, d with st, J = 11 Hz); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 131.2 (d), 45.7 (d), 38.3 (d), 28.3 (t). Further elution of the column with benzene furnished 60 mg (15%) of the hexacyclic ketone 6, which was characterized by spectral comparison with the sample obtained in the previous experiment. Final elution of the column with chloroform furnished 140 mg of the starting dione 4.

Acknowledgment. We thank Prof. V. Ramamurthy of our department for providing the photochemical facilities.

Registry No. 1, 110507-79-4; 4, 110419-02-8; 5, 110419-03-9; 6, 110419-04-0; 7, 110433-13-1.

Micelle-Based Nucleophile Selectivity: Alkoxymercuration in Aqueous Sodium Dodecyl Sulfate

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Olefin hydroxymercuration and alkoxymercuration have become important parts of standard synthetic methodology in the last 2 decades. Their success depends on the electrophilicity of mercuric ions toward olefins, on the efficiency of mercurinium ion trapping by water or alcohol, and on the clean manipulation of the resulting alkyl mercurial. While mercury-mediated hydration of olefins in mixed THF/water solvent works well for a wide range of simple olefins,[1] we have previously described[2] the benefits of conducting the mercuration of dienes in aqueous sodium dodecyl sulfate (SDS) solution. We now report the ability of SDS micelles to enhance ether production via olefin alkoxymercuration. In many respects, this process compares favorably with both alkoxymercuration in alcohol solvent[3] and with olefin mercuration in the presence of stoichiometric amounts of alcohol in inert solvent. Our SDS-mediated process also provides new insight into the potential use of aqueous micelles to control the selectivity of organic reactions. The chemistry that is the basis of this work is summarized in eq 1.

$$C_6H_{13}CH{=}CH_2 + Hg^{2+} \xrightarrow[\text{2. NaBH}_4]{\text{1. H}_2\text{O/ROH}} C_6H_{13}CH(OH)CH_3 + C_6H_{13}CH(OR)CH_3 \quad (1)$$

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