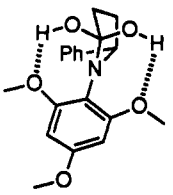


Figure 4. Stabilization of 4 by hydrogen bonding.

ion at m/z 272 were determined to be $C_{19}H_{24}NO_5$ (M + H)$^+$ (calcd 346.1654, obsd 346.1657) and $C_{16}H_{18}NO_3$ (M + H)$^+$ (calcd 272.1287, obsd 272.1299), respectively. The data from these observations clearly indicates that the intermediate is the unprecedented hydrated γ-lactam 4. Hydrate 4 represents a unique and stable hydrated amide bond, commonly postulated in enzymatic hydrolysis of peptides, which to our knowledge has not been reported as a stable isolable entity in a nonenzymatic environment.[8]

The unusual stability of this hydrate appears to be due to the presence of the 2,6-dimethoxy substitution in the *N*-aryl moiety. When 2,6-diethylaniline was substituted for 2,4,6-trimethoxyaniline, the corresponding hydrate was not isolated. This suggests that the methoxy groups are very important for the formation and the stabilization of the hydrate via intramolecular hydrogen bonding as shown in Figure 4. Also, as indicated by following the conversion of 4 to 1 by ^{1}H-NMR, 4 converts exclusively to 1. The corresponding amino acid that would result from the ring opening of the orthoamide was not detected. We were unable to convert 1 to 4 by subjecting 1 to the standard reaction conditions indicating that there is no equilibrium process involved between 1 and 4. We are not certain of the mechanism for the formation of 4, but we believe that the presence of water and/or hydroxide is important,[9] for when the cyclization of the amino ester 5 was affected in anhydrous DMF using NaH as the base, a 64% isolated yield of lactam 1 was obtained, but the presence of hydrate 4 was not detected.

In conclusion, we were able to isolate and assign the structure of the tetrahedral intermediate 4. To our knowledge 4 represents the first isolated stable hydrate reported in a nonenzymatic environment.[8]

Experimental Section

Both ^{1}H- and ^{13}C-NMR spectra were obtained in $CDCl_3$ using TMS as the internal standard. Signals are given in parts per million. All reactions were carried out under a nitrogen atmosphere. For flash column chromatography, silica gel 40-μm (Universal Scientific Inc.) and, for TLC analysis, silica gel GF 250-μm plates (Analtech Inc.) were used.

Procedure for the Alkylation–Acylation of 2,4,6-Trimethoxyaniline with Methyl 4-Bromo-4-phenylbutyrate. A mixture of potassium hydroxide (1.56 mmol) and DMSO (2.5 mL) was stirred for 10 min at ambient temperature. 2,4,6-Trimethoxyaniline (0.39 mmol) was then added, and the reaction mixture was stirred for an additional 1 h at ambient temperature. Methyl 4-bromo-4-phenylbutyrate (0.39 mmols) was then added, and the reaction mixture was heated at 80 °C for 6 h. The reaction mixture was diluted with water (10 mL) and extracted with ether (2 × 10 mL). The ether layer was washed with water (30 mL), and the combined aqueous layers were treated with saturated ammonium chloride solution (30 mL) and extracted with ethyl acetate (3 × 10 mL). The combined organic extracts were washed consecutively with water and brine and concentrated to give the crude hydrate 4 (57 mg, 42% yield): ^{1}H NMR ($CDCl_3$) δ 1.95–2.08 (m, 1 H), 2.24–2.40 (m, 1 H), 2.61–2.88 (m, 2 H), 3.64 (s, 6 H), 3.74 (s, 3 H), 4.25 (dd, J = 4, 10 Hz, 1 H), 6.05 (s, 2 H), 7.07–7.30 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 31.1, 33.3, 55.3, 55.7, 62.6, 91.3, 116.0, 126.9, 127.5, 128.0, 128.3, 142.4, 152.9, 156.8; liquid SIMS m/z 346 (M + H)$^+$, 272, 184, 168; HRMS (SIMS) exact mass calcd for $C_{19}H_{24}NO_5$ (M + H)$^+$ MW 346.1654, found 346.1657.

***N*-(2,4,6-Trimethoxyphenyl)-4-phenyl-4-butanelactam.** The hydrate 4 (57 mg) was either placed in a drying pistol (refluxing 2-propanol) overnight or heated neat at 80 °C under nitrogen overnight to give *N*-(2,4,6-trimethoxyphenyl)-4-phenyl-4-butanelactam as the only product. The crude was purified by silica gel chromatography eluting with ethyl acetate yielding the γ-lactam 1 (38 mg, 70% yield): ^{1}H NMR ($CDCl_3$) δ 2.06–2.23 (m, 1 H), 2.50–2.81 (m, 3 H), 3.64 (s, 3 H), 3.70 (s, 3 H), 3.79 (s, 3 H), 5.12 (t, J = 8 Hz, 1 H), 5.98 (d, J = 2 Hz, 1 H), 6.02 (d, J = 2 Hz, 1 H), 7.14–7.35 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 29.1, 30.6, 55.0, 55.5, 63.9, 90.8, 91.0, 107.8, 127.4, 127.6, 127.9, 141.3, 156.9, 157.5, 160.5, 175.3; liquid SIMS m/z 328 (M + H)$^+$ 184, 168; HRMS (SIMS) exact mass calcd for $C_{19}H_{22}NO_4$ (M + H)$^+$ MW 328.1549, found 328.1554.

Mass Spectrometry. The samples were analyzed by Cs^+ ion liquid secondary ion mass spectrometry (SIMS) obtained on a VG-ZAB-SE double-focusing reverse geometry mass spectrometer operating at an accelerating voltage of 8 kV, using a VG 11-250J data system. The samples were dissolved in DMSO, and glycerol/thioglycerol (1/1) was used as the matrix. The collisionally activated dissociation (CAD) spectra were obtained in the mass-analyzed ion kinetic energy (MIKE) mode. This was done by colliding the precursor ion with helium in the MIKES gas cell to reduce the intensity of the precursor ion beam by approximately 50% and scanning the electrostatic analyzer (ESA) to pass the daughter ions. The CAD MIKE spectrum for each ion was obtained by summing over 30 scans at 5 s/scan. All operations were conducted at room temperature.

Acknowledgment is made to Profs. D. H. R. Barton and R. Breslow and Drs. A. Ganguly, D. Burnett, J. Clader, T. Fevig, and W. Vaccaro for their helpful discussions and to Dr. T. M. Chan and Ms. R. Ostermann for the deuterium exchange NMR data.

Supplementary Material Available: 300-MHz ^{1}H- and ^{13}C-NMR spectra of 1 and 4 (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(8) Cipiciani et al. have reported the formation of a tetrahedral intermediate in the acid hydrolysis of *N*-(trifluoroacetyl)pyrrole. Cipiciani, A.; Linda, P.; Savelli, G. *J. Chem. Soc., Chem. Commun.* **1977**, 857.

(9) In all reactions that yielded the orthoamide 4, commercial reagent-grade potassium hydroxide was used which normally contains ~ 10–15% water.

In Situ Formation of Vinylboranes for Use in Diels–Alder Reactions. An Easy One-Pot Diels–Alder Synthesis of Cyclohexenols

Daniel A. Singleton,* Jose P. Martinez, and Grace M. Ndip

Department of Chemistry, Texas A&M University, College Station, Texas 77843

Received May 1, 1992

Recent reports from this laboratory have detailed the high reactivity and selectivity of vinylboranes as Diels–Alder dienophiles and have described the exceptional physical organic aspects of these reactions.[1] The major limitation on the utility and synthetic appeal of vinylboranes is the difficulty associated with manipulating these highly pyrophoric materials. This is particularly true of the highly volatile vinyldimethylborane, with which standard syringe and septa techniques provide insufficient safeguards. We now report a simple methodology that

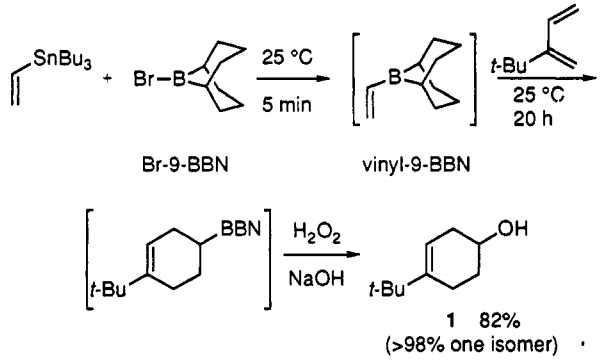
(1) (a) Singleton, D. A.; Martinez, J. P. *J. Am. Chem. Soc.* **1990**, *112*, 7423. (b) Singleton, D. A.; Martinez, J. P. *Tetrahedron Lett.* **1991**, *32*, 7365. (c) Singleton, D. A.; Martinez, J. P.; Watson, J. V. *Tetrahedron Lett.* **1992**, *33*, 1017.

0022-3263/92/1957-5768$03.00/0

avoids the problems of borane synthesis and manipulations, increases the range of vinylboranes available, and significantly eases their application in synthesis. As a result, 3-cyclohexen-1-ols are now essentially as available as 3-cyclohexenecarboxylates from Diels–Alder reactions.

Vinyldialkylboranes have been made by metal–metal exchange of boron halides with vinyltin derivatives, but the isolated yields from these reactions have routinely been low, and complex mixtures have often been produced.[2] The use of tin–boron exchange as the first step in a one-pot process did not seem practical until NMR studies revealed that the reaction of vinyltributyltin with 9-bromo-9-borabicyclo[3.3.1]nonane (Br-9-BBN) to form 9-vinyl-9-borabicyclo[3.3.1]nonane (vinyl-9-BBN) was fast, clean, and quantitative. The same observation was made for the formation of vinyldimethylborane from vinyltributyltin and bromodimethylborane. It appears that many of the low yields and complex mixtures associated with previous syntheses of vinylboranes were the result of insufficient vinyltin being used and difficulties encountered in the isolation of vinylboranes.

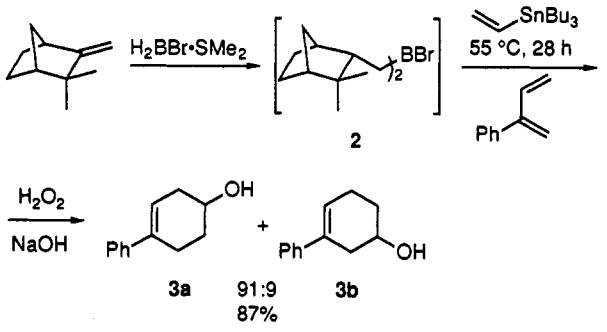
The application of metal–metal exchange to a one-pot Diels–Alder synthesis of 3-cyclohexen-1-ols was then easy. A mixture of 1.5 mmol of the commercial 1.0 M Br-9-BBN in CH_2Cl_2 and 1.9 mmol of vinyltributyltin was stirred at 25 °C for 5 min, and 1.00 mmol of 2-*tert*-butylbutadiene was added. After 20 h at 25 °C, an oxidative workup afforded 82% of 4-*tert*-butyl-3-cyclohexen-1-ol (1) with no detectable formation (>98:2) of the alternative regioisomer. It should be noted that an excess of vinyltributyltin was used to remove adventitious protic acid and that a greater than usual amount of H_2O_2/NaOH was used to allow for reaction with the byproduct bromotributyltin.



Our results are summarized in Table I. All of the major products have been previously prepared, but **1**, **3**, **4**, and **5** were available only through multistep processes.[3] The excellent regioselectivity observed in these reactions (96:4 at worst with vinyl-9-BBN) was similar to that of our previous reactions of isolated vinylboranes,[1c] indicating that the tin plays no role in the cycloaddition step. Tetravinyltin may be used in place of vinyltributyltin, and should be a fairly economical source of vinyl groups for these reactions.[4]

Reactions of vinyldimethylborane may be accomplished with reasonable safety using a stock solution of bromodimethylborane in toluene. Vinyldimethylborane is much more reactive than vinyl-9-BBN with 2,3-dimethylbutadiene, presumably due to an absence of inhibiting steric interactions with the BBN group. We have proposed that these steric interactions are responsible for the high regioselectivity observed with vinyl-9-BBN,[1c] and the lower regioselectivity with vinyldimethylborane is consistent with this proposal. With cyclopentadiene, vinyldimethylborane is comparable in reactivity to vinyl-9-BBN—the apparent rate constant at 25 °C was 6×10^{-5} M^{-1} s^{-1},[5] compared to 6.5×10^{-5} M^{-1} s^{-1} for vinyl-9-BBN[1a]—but more endo stereoselective (84:16 vs 67:33).

An additional reaction may be added to the one-pot process by incorporating an initial hydroboration. The reaction of 2.2 equiv of (+)-camphene with $H_2BBr{\cdot}SMe_2$ at 25 °C affords a solution of the bromodialkylborane **2** contaminated by 10–15% of a presumably isomeric material.[6] Exploratory NMR studies indicated that the tin–boron exchange with **2** was very slow and required heating to 55 °C for several hours. In the preparative reaction, the diene was added before any heating and reacted with the vinylborane as it was formed. Oxidative workup afforded an 87% yield of a 91:9 mixture of **3a** and **3b**. The enantiomeric excess in **3a**, determined after conversion to the corresponding Mosher's ester,[7] was <10%. Higher asymmetric induction may be possible with rationally chosen chiral alkenes. This result opens the way for the exploration of a multitude of vinylboranes, including many nonisolable boranes, by variation of the initial alkene. This variability should also greatly increase the utility of coupling Diels–Alder reactions on vinylboranes with a final carbonylation step.



The Diels–Alder reaction is probably the most important ring-forming reaction in chemistry,[8] and the absence of direct methods for Diels–Alder reactions on vinyl alcohol, ethylene, ketene, and vinylamine is among its most significant limitations. The potential one-pot availability of the equivalent products from commercially available reagents with high selectivity via vinylboranes should find widespread synthetic use.

Experimental Section

All of the major 3-cyclohexenol products have been previously reported.[3] Reactions were carried out in dry glassware under a

(2) (a) Good, C. D.; Ritter, D. M. *J. Am. Chem. Soc.* **1962**, *84*, 1162. (b) Hall, L. W.; Lowman, D. W.; Ellis, P. D.; Odom, J. D. *Inorg. Chem.* **1975**, *14*, 580. (c) Odom, J. D.; Hall, L. W.; Riethmiller, S.; Durig, J. R. *Inorg. Chem.* **1974**, *13*, 170. (d) Brinckman, F. E.; Stone, F. G. A. *J. Am. Chem. Soc.* **1960**, *82*, 6218.

(3) (a) Danheiser, R. L.; Martinez-Davilla, C.; Sard, H. *Tetrahedron* **1981**, *37*, 3943–50. (b) Stolow, R. D.; Bonaventura, M. M.; Larsen, J. W. *J. Org. Chem.* **1963**, *28*, 2862–5. (c) Sood, V. K. *Parfuem. Kosmetik* **1965**, *46*, 351–3. (d) Clarke, T. C.; Bergman, R. G. *J. Am. Chem. Soc.* **1974**, *96*, 7934. Lambert, J. B.; Marko, D. E. *J. Am. Chem. Soc.* **1985**, *107*, 7978.

(4) An NMR study of the reaction of tetravinyltin with four equiv of Br-9-BBN revealed that all four vinyl groups are transferred from tin to boron over the course of 9 h at 25 °C, with the first two vinyl groups being transferred in <30 min.

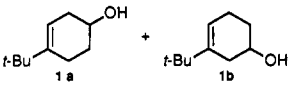
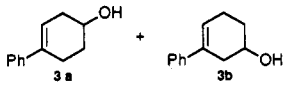
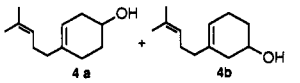
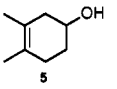
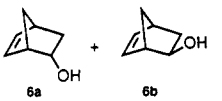
(5) The rate constant with vinyldimethylborane should be considered an approximate estimate due to the slow disproportionation of vinyldimethylborane into trimethylborane and divinylmethylborane (see ref 2a).

(6) A 9:1 mixture of endo and exo isomers was observed in the reduction of camphene with monochloroborane: Izarewicz, I.; Izarewicz, A. *Rocz. Chem.* **1976**, *50*, 1315.

(7) Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543.

(8) By a Chemical Abstracts On-Line search, "Diels–Alder" was an indexing term in over 9500 abstracts. "Diels–Alder" appeared in the title of over 300 articles or patents in the year 1989 alone. The only comparable organic name reaction is "Grignard", which is a more common indexing term but appears in far fewer titles.

Table I. Reaction Conditions, Products, and Yields for Diels–Alder Reactions of Vinylboranes Formed in Situ

diene	vinylborane source[a]	temp, °C/time, h	yield, % (ratio[b])	product(s)
	A	25/20	82 (>98:2)	 1a 1b
	B	55/16	75 (90:10)	
	A	25/16	86 (98:2)	 3a 3b
	B	25/22	84 (84:16)	
	C	55/28	87 (91:9)	
	A	55/36	81 (96:4)	 4a 4b
	D	65/12	92 (61:39)	
	B	100/7	78	 5
	B	25/22	81 (84:16)	 6a 6b

[a] Vinylborane source A: Br-9-BBN, CH_2=$CHSnBu_3$; B: $BrBMe_2$, CH_2=$CHSnBu_3$; C: (+)-camphene, H_2BBr, CH_2=$CHSnBu_3$ (see text); D: Br-9-BBN, $(CH_2$=$CH)_4Sn$. [b] Ratios were determined by ^1H NMR integration of the vinylic protons for 1, 3, and 4 and the carbinyl proton for 6.

nitrogen atmosphere using solvents dried by standard techniques. The heated reactions were carried out in a Schlenck tubes tightly stoppered with a Teflon-lined screw cap and with closed outlets. (*CAUTION*: Proper high-pressure equipment should be used for larger scale reactions.) In a "standard oxidation, extraction, and chromatography", the reaction mixture was cooled to rt and treated successively with 5 mL of THF, 1.5 mL of 3 N NaOH, and (*CAUTION*: slowly) 1.5 mL of 30% H_2O_2, and the mixture was stirred at rt for 2–4 h. The reaction mixture was then extracted with three 10–20-mL portions of ether, and the combined organic layers were rinsed with 10–20 mL of saturated aqueous KF and 10 mL of brine and dried (Na_2SO_4), and the solvent was removed on a rotary evaporator. The residue was chromatographed on a 8-in. × 19-mm silica gel (230–400-mesh Kieselgel 60 from E. Merck) column using the solvent to be named as eluent.

A stock solution of bromodimethylborane was prepared by adding the contents of a 5-g vial (Aldrich) to ~10 mL of toluene under N_2. The solution had a density of 0.948, and analysis by NMR showed that the solution was 31.6% by weight bromodimethylborane, making the solution 2.48 M. *CAUTION*! Solutions containing vinyldimethylborane remain a significant fire hazard if opened to air, even under a flow of nitrogen, and it is important to maintain an inert atmosphere through the first few minutes of the H_2O_2/NaOH oxidation. The progress of these reactions is most easily followed by NMR. This can be accomplished conveniently by sealing a ~75-μL aliquot from the reactions in a nitrogen-flushed capillary made from a disposable pipette and placing the capillary in a regular NMR tube.

4-*tert*-Butyl-3-cyclohexen-1-ol (1):[3b] **Method A.** A mixture of 1.5 mL (1.5 mmol) of 1 M Br-9-BBN in CH_2Cl_2 and 621 mg (1.96 mmol) of vinyltributyltin was stirred at rt for 5 min, treated with 110.2 mg (1.00 mmol) of 2-*tert*-butyl-1,3-butadiene, and stirred at rt for 20 h. A standard oxidation, extraction, and chromatography using 10% EtOAc/petroleum ether as eluent afforded 126 mg (82%) of a >98:2 mixture of **1a** and **1b**.

Method B. A mixture of 600 μL (1.49 mmol) of 2.48 M bromodimethylborane in toluene and 625 mg (1.97 mmol) of vinyltributyltin was prepared at 0 °C, stirred at rt for 20 min, treated with 110.1 mg (1.00 mmol) of 2-*tert*-butyl-1,3-butadiene, and heated to 55 °C for 16 h. A standard oxidation, extraction, and chromatography using 10% EtOAc/petroleum ether as eluent afforded 115.8 mg (75%) of a 90:10 mixture of **1a** and **1b**.

4-Phenyl-3-cyclohexen-1-ol (3a): Method A. A mixture of 1.5 mL (1.5 mmol) of 1 M Br-9-BBN in CH_2Cl_2 (Aldrich) and 701 mg (2.21 mmol) of vinyltributyltin was stirred at rt for 15 min, treated with 133 mg (1.02 mmol) of 2-phenyl-1,3-butadiene, and stirred at rt for 16 h. A standard oxidation, extraction, and chromatography using 20% EtOAc/petroleum ether as eluent afforded 153 mg (86%) of a 98:2 mixture of **3a** and **3b**: mp 79–82 °C (lit.[3a] mp 79–81 °C).

Method B. A mixture of 600 μL (1.49 mmol) of 2.48 M bromodimethylborane in toluene and 585 μL (635 mg, 2.00 mmol) of vinyltributyltin was prepared at 0 °C, stirred at rt for 20 min, treated with 128.6 mg (0.99 mmol) of 2-phenyl-1,3-butadiene, and stirred at rt for 22 h. A standard oxidation, extraction, and chromatography using 20% EtOAc/petroleum ether as eluent afforded 144.7 mg (84%) of a 84:16 mixture of **3a** and **3b**.

Method C. A mixture of 2.0 mL (2.0 mmol) of 1.0 M monobromoborane–dimethyl sulfide complex in CH_2Cl_2 and 670 mg (4.92 mmol) of camphene was stirred at rt for 3 h, and 570 μL (618 mg, 1.95 mmol) of vinyltributyltin was added. After the mixture was stirred at 9 h at rt, 136.1 mg (1.05 mmol) of 2-phenyl-1,3-butadiene was added, and the resulting mixture was heated to 55 °C for 28 h. A standard oxidation, extraction, and chromatography using 20% EtOAc/petroleum ether as eluent afforded 158.1 mg (87%) of a 91:9 mixture of **3a** and **3b**.

4-(5-Methyl-4-pentenyl)-3-cyclohexen-1-ol (4a):[3c] **Method A.** A mixture of 2.0 mL (2.0 mmol) of 1 M Br-9-BBN in CH_2Cl_2 and 775 mg (2.44 mmol) of vinyltributyltin was stirred at rt for 1 h, treated with 152 mg (1.04 mmol, based on 93% purity) of technical-grade myrcene, and heated to 55 °C for 36 h. A standard oxidation, extraction, and chromatography using 15% EtOAc/petroleum ether as eluent afforded 152 mg (81%) of a 96:4 mixture of **4a** and **4b**.

Method B. A mixture of 600 μL (1.49 mmol) of 2.48 M bromodimethylborane in toluene and 200 μL (249 mg, 1.10 mmol) of tetravinyltin was stirred at 0 °C for 15 min, treated with 140.1 mg (0.96 mmol, based on 93% purity) of technical-grade myrcene, and heated to 65 °C for 12 h. A standard oxidation, extraction, and chromatography using 12% EtOAc/petroleum ether as eluent afforded 158.9 mg (92%) of a 61:39 mixture of **4a** and **4b**.

3,4-Dimethyl-3-cyclohexen-1-ol (5). A mixture of 600 μL (1.49 mmol) of 2.48 M bromodimethylborane in toluene and 585 μL (635 mg, 2.00 mmol) of vinyltributyltin was prepared at 0 °C, stirred at rt for 20 min, treated with 85.2 mg (1.036 mmol) of 2,3-dimethyl-1,3-butadiene, and heated to 100 °C for 7 h. A standard oxidation, extraction, and chromatography using 10% EtOAc/petroleum ether as eluent afforded 101.6 mg (78%) of **5**, which exhibited ^1H and ^{13}C NMR spectra identical to that previously reported.[3d]

5-Norbornen-2-ol (6). A mixture of 600 μL (1.49 mmol) of 2.48 M bromodimethylborane in toluene and 585 μL (635 mg, 2.00 mmol) of vinyltributyltin was prepared at 0 °C, stirred at rt for 20 min, treated with 67.2 mg (1.017 mmol) of freshly prepared cyclopentadiene, and stirred at rt for 22 h. A standard oxidation, extraction, and chromatography using 15% EtOAc/petroleum ether as eluent afforded 90.3 mg (81%) of an 84:16 mixture of **6a** and **6b** which exhibited ^1H and ^{13}C NMR spectra identical to commercial material.

Acknowledgment. We thank the Institute of General Medical Sciences of the National Institutes of Health and the Robert A. Welch Foundation for support of this research.

Supplementary Material Available: ^1H and ^{13}C NMR spectra of the reaction of Br-9-BBN in CH_2Cl_2 with vinyltributyltin and spectra of vinyl-9-BBN for comparison (4 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Exclusive Peri-Selective and Regio- and Stereoselective Cycloaddition Reactions of Benzocycloheptadienones

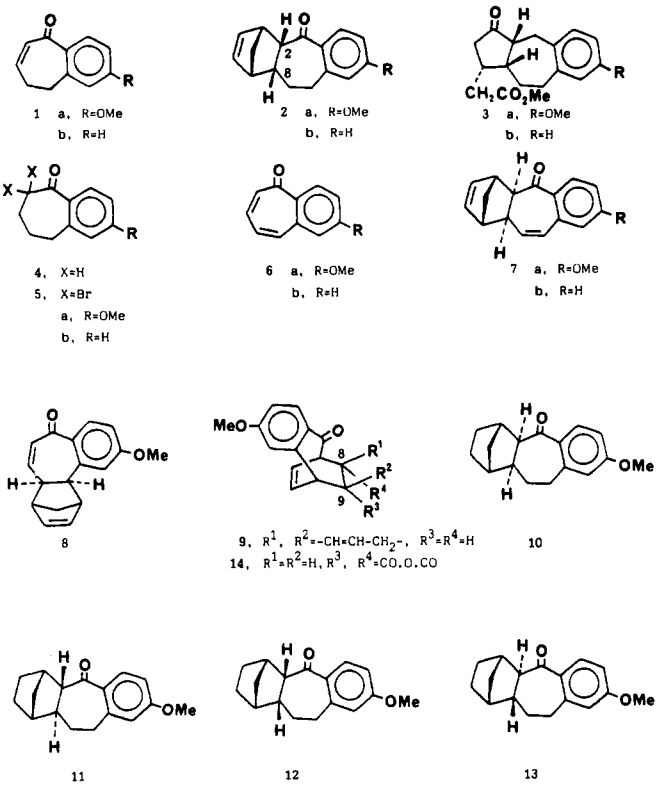
Subrata Sarkar, Goutam Saha, and Subrata Ghosh*

Department of Organic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta - 700 032, India

Received April 10, 1992

Recently we have shown[1] that the Diels–Alder reaction of benzocycloheptenones **1a,b** with cyclopentadiene under Lewis acid catalysis produces exclusively the endo adducts **2a,b**. These adducts have been transformed to the tricyclic keto esters **3a,b** in an effort directed toward the synthesis of diterpenes bearing the linearly arrayed 5-7-6 tricyclic system. As an extension of this work, we became interested in the cycloaddition of benzocycloheptadienones as this would lead to adducts with an additional functionality in the seven-membered ring that might be required for elaboration to natural products. While the cycloaddition behavior of 2,4-cyclohexadienones[2] has been studied extensively, little is known about the cycloaddition characteristics of cycloheptadienones. Earlier it was reported that 2,4-cycloheptadienones[3] exhibited low dienic reactivity with dienophiles. A recent study[4] using eucarvone has shown that 2,4-cycloheptadienone can exhibit both dienic and dienophilic reactivity toward dienes. Herein, we report the results of our investigation on cycloaddition of benzocycloheptadienones. The cycloaddition reactivity of these species differs from the reported cycloaddition behavior of 2,4-cyclohexadienones and 2,4-cycloheptadienones.

Chart I



Results and Discussion

Benzocycloheptadienones **6a,b** were prepared by bromination of the benzosuberones **4a,b** followed by dehydrobromination of the resulting dibromo derivatives **5a,b**. Refluxing a benzene or toluene solution of the dienone **6a** in the presence of cyclopentadiene failed to produce any adduct. On the other hand, when a solution of **6a** in THF was allowed to react with cyclopentadiene in the presence of $BF_3{\cdot}Et_2O$ at 0–5 °C for 20 h, a single crystalline compound, mp 113 °C, was obtained in 75% yield. The structural and stereochemical assignment of this adduct was made by spectral analysis as well as by chemical transformation. On the basis of previous findings[2-4] on cycloaddition behavior of cyclohexadienones and cycloheptadienones, one can expect three exo, endo pairs of adducts, **7**, **8**, and **9** (only the exo isomer is shown). Of these three possibilities, the formation of compound **8** bearing the conjugated enone functionality can be excluded by examination of the ^{13}C NMR spectrum, which showed the presence of four olefinic methines at δ 132.04, 132.68, 133.09, and 136.13, much lower than the chemical shift (δ 150 ppm) for the β-carbon of a cyclic conjugated ketone. The cycloadduct from **6a** was hydrogenated, and the resulting product, on treatment with methanolic sodium methoxide, was found to undergo epimerization. This observation clearly excludes the possibility of formation of the compound **9** and at the same time suggests **7a** to be the structure of the adduct as its hydrogenation product **10** could be epimerized to produce **11**. Thus, during cycloaddition **6a** behaved as a dienophile involving the α,β-double bond. It is interesting to note that 2,4-cyclohexadienone[2a] behaved as a diene in its reaction with cyclopentadiene.

The stereochemical assignment of the cycloadduct **7a** was made by comparison of the coupling constants of the protons at C_2 and C_8 with those reported for the C_2, C_3

(1) (a) Saha, G.; Saha Roy, S.; Ghosh, S. *Tetrahedron* **1990**, *46*, 8229. (b) Ghosh, S.; Saha, S. *Ibid.* **1985**, *41*, 349.
(2) (a) Curtin, D. Y.; Fraser, R. R. *J. Am. Chem. Soc.* **1959**, *81*, 662. (b) Bertrand, M.; Pelerin, G.; Teisseire, P. *Tetrahedron Lett.* **1980**, *21*, 2051, 2055. (c) Auksi, H.; Yates, P. *Can. J. Chem.* **1981**, *59*, 2510. (d) Becker, H.-D.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1983**, *36*, 1361. (e) Schultz, A. G.; Dittami, J. P.; Lavicri, F. P.; Salowey, C.; Sundararam, P.; Szymula, M. B. *J. Org. Chem.* **1984**, *49*, 4429. (f) Yates, P.; Gomes, A.; Bornell, D. J.; Cong, D. D.; Sawyer, J. F. *Can. J. Chem.* **1988**, *67*, 37.
(3) (a) Meinwald, J.; Emerman, S. L.; Yang, N. C.; Buchi, G. *J. Am. Chem. Soc.* **1955**, *77*, 4401. (b) Chapman, O. L.; Pasto, D. J. *Ibid.* **1959**, *81*, 3696.
(4) Guo, M.; Minuti, L.; Taticchi, A.; Wenkert, E. *J. Org. Chem.* **1990**, *55*, 1366.

0022-3263/92/1957-5771$03.00/0