meter, and all ^{11}B NMR chemical shifts are reported relative to BF_3-OEt_2 with low field assigned as positive.

Preparation of Standard Solution of Di-*s*-butoxyborane. An oven-dried, 500-m*l* round-bottomed flask with a sidearm, equipped with a condenser leading to a mercury bubbler was flushed with dry nitrogen and maintained under a static pressure of nitrogen. To this flask were added 40.0 m*l* of 10 M borane-methyl sulfide (400 mmol) and 86.8 m*l* of THF. The temperature of mixture was kept at 25°C by using a water bath. *s*-Butyl alcohol (59.3g, 800 mmol) was added dropwise to the borane solution with stirring. After the complete addition, the stirring was continued for an additional 3 h to ensure the hydrogen evolution. The ^{11}B NMR spectrum of the reaction mixture showed the formation of a > 99% pure di-*s*-butoxyborane, indicating a doublet at δ26.66 ($J_{B\text{-}H}$ = 159.8 Hz). The resulting di-*s*-butoxyborane solution in THF was 2.01 M in hydride content. No significant change in ^{11}B NMR spectra was observed when a solution of di-*s*-butoxyborane was kept at room temperature under a static pressure of nitrogen for 5 days.

General Procedure for Determination of Rate and Stoichiometry. To a 100-m*l* flask fitted with a sidearm and capped by a rubber septum was added 9.95 m*l* of a solution of di-*s*-butoxyborane in THF (20 mmol in hydride). The flask was immersed in a water bath at 25°C. The reaction mixture was diluted with 10.05 m*l* of THF containing 5 mmol of the compound to be reduced. In the case of reaction in the presence of a catalytic amount of lithium tetra-*s*-butoxyborate, 0.5 mmol of the borate (1.0 m*l*) was added instead of the same volume of THF. This makes the mixture 1 M in hydride and 0.25 M in the compound under investigation. At different time intervals, 2 m*l* of samples were withdrawn and quenched in a glycerine-water-methanol hydrolyzing mixture. The hydrgen evolved was measured volumetrically. The reaction was stopped when two or more analyses indicated that no more hydride was taken up. For the reaction of compounds with active hydrogen, the reaction flask was attached to a gas meter to measure the evolved hydrogen.

The reaction of caproaldehyde with di-*s*-butoxyborane is described as a representative. After a 0.5-h reaction time at 25°C, hydrolysis of a 2-m*l* aliquot of the reaction mixture indicated 3.75 mmol of residual hydride, which means that 0.25 mmol of hydride per mmol of caproaldehyde had been consumed. After 72 h, the analysis showed 3.00 mmol of residual hydride, which indicated that the compound had been reduced to the corresponding alcohol. These results are summarized in Table 3-a.

In the case of reaction with di-*s*-butoxyborane in the presence of 2.5 mole % of lithium tetra-*s*-butoxyborate, the hydrolysis of the reaction mixture indicated that 1.00 mmol of hydride was used for reduction at 0.5 h and no more hydride was consumed at 3 h. That means that the reaction was completed within 0.5 h under these conditions. These results are summarized in Table 3-b.

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A Facile Synthesis of Propellanes via Dianion Chemistry

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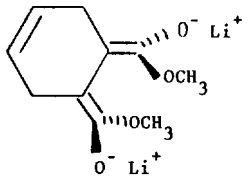
A dianion-mediated dialkylation reaction provides a variety of propellanes. 12-Thia[4.4.3] propel-3-ene, 3-(N-benzyl)-2,4-dioxotricyclo[3.3.3.0] decane and 3-(N-benzyl)-2,4-dioxotricyclo[3.3.2.0] nonane were prepared by this dianion ring annulation methodology.

Introduction

In the related study of ring annulation using dianion chemistry,[1,2] we would like to report a facile preparation of propellanes. It was postulated that a vicinal ester dianion 1, generated from vicinal a diester might be a legitimate in-

termediate if a disubstituted alkane (C_2-C_5) could be found to act as an electrophile in the dianion ring annulation reaction.



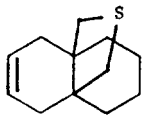
1

Additional credence to this approach was gleaned from the anticipated stability of the dianion generated from the vicinal diester, because it was postulated that the conjugation of the enolates would stabilize the developing charge.

One final bonus of this reaction offered was the expected formation of only cis-vicinal diester. The dienolate being presumably planar to permit conjugation, implied that once the first alkylation has occured, the second displacement would proceed form the same face, since the formation of the trans ring junction would require the alkano group to twist between the two ester residues.

Results and Discussion

An interesting target for our initial efforts was 12-thia [4.4.3] propell-3-ene (**2**), which a synthetic precursor of valerane (**3**), a non-isoprenoid sesquiterpene.[3]



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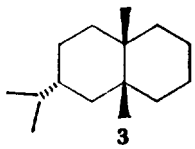
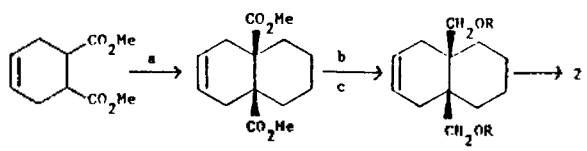


3

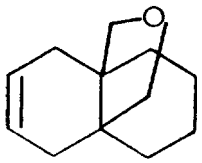
When 1.5 equivalents of 1,4-dibromobutane were added to the cooled, bright red THF solution of the dienolate of **4**, the bicyclic diester, **5**, was obtained in 75% yield. As expected, exhaustive characterization revealed that only the cis-diester had been formed. The diester, **5**, was reduced with lithium aluminum hydride and treatment of the resulting diol, **6**, with methanesulfonyl chloride in pyridine gave the dimesylate, **7**, in high yield. Heating **7** in dry hexamethylphosphoramide(HMPA) with anhydrous sodium sulfide led to sulfide, **2**, in 93% yield. Paquette[4] reported that the use of dry HMPA is essential to the success of this twofold S_N2 displacement cyclization. In its absence, the capability of sulfide ion to attack at the neopentyl centers is greatly diminished and little or no **2** is produced. Clearly, the high cation-solvating capacity of HMPA, which greatly reduces the effective size of the nucleophile relative to its bulk in other (especially protic) media, causes a marked acceleration of the desired chemical change.



4 **5** **6** (R=H) **7** (R=Ms)

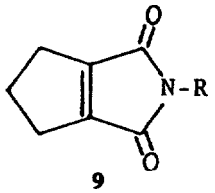
(a) 1,4-dibromobutane, 2.5 eq. of LDA, THF, -78°C. (b) $LiAlH_4$, THF (c) MsCl, Pyridine, 0°C. (d) Na_2S, HMPA

Also, the reaction temperature was essential to make sulfide, **2**, otherwise ether, **8**, was formed at room temperature.[2]



8

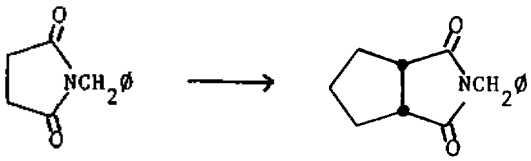
Kasugai[5] reported that N-substituted-Δ-^{1} cyclopentene-1,2-dicarboxylic imides, 9, have fungicidal and herbicidal activities.



9

R: halo, lower alkyl, lower alkoxy, cyano, aralkyloxy, haloaralkyloxy, aralkylthio, haloaralkylthio, phenylnaphthyl.

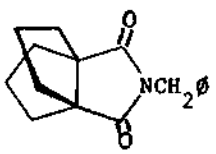
We thought that this compound **9** was a good target molecule to demonstrate the dianion methodology. N-Benzylsuccinimide was chosen as a starting material and reacted with 2.5 equivalents of lithium diisopropyl amide to give a reddish black color of the dienolate which reacted with 1,3-dibromopropane to result in cis-3-(N-benzyl)-2,4-dioxobicyclo[3.3.0]-heptane, **10**.



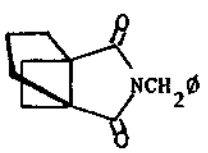
10

In order to introduce the 1,2-double bond in **10**, Wilkening's[1a] method was used. The dienolate of **10** was reacted with 1.1 equivalents of iodine by the established method, but the reaction did not result in formation of the double bond.

In an attempt to test whether the dienolate of **10** was formed, we prepared the propellane of this compound. We have made 5-5-5(**11**) and 5-5-4(**12**) propellanes in 24% and 25% respectively.



11



12

Even though we did not get the target molecule, **9**, this work demonstrates that the dianion reaction could introduce propellane in a convenient way.

Experimental

General. Reported boiling points and melting points are

uncorrected. All NMR spectra were recorded on a Bruker 250 MHz FT-NMR, with the chemical shifts reported in parts per million relative to TMS. $CDCl_3$ was used as a solvent and an internal standard. Mass spectra were obtained using a VG MM16 mass spectrometer and accurate mass data were obtained using a VG 7070 high resolution mass spectrometer. Infrared spectra were recorded using a Beckmann IR-5 spectrometer with absorption frequencies being reported in reciprocal centimeters. GLC analysis were performed using a Varian Aerograph series 2700 gas chromatograph equipped with 11' × 1/4", 10% OV-17 column.

Cis-9,10-Bis (carboxymethyl)-Δ^2-decalin,(**5**). A solution of 150 m*l* of dry THF, 75 m*l* of 2.7 M n-buthyllithium, and 26.1 m*l* of diisopropylamine was stirred under nitrogen at -78°C for 15 min, then 13.5 g(0.0682 mole) of the 4,5-dimethyl cyclohexene dicarboxylate was injected via a syringe and the bright red solution was stirred for an additional 10 min. At this time 22 g(1.5 eq.) of 1,4-dibromobutane in 30 m*l* dry THF was added to the reaction mixture. This resulted in a lightening of the color of the reaction to a pale yellow. After stirring for 3 h at room temperature, the reaction was quenched by pouring it into excess dilute HCl. The phases were separated and the aqueous phase was extracted three times with 50 m*l* portions of methylene chloride. The combined organic layer was dried, evaporated and distilled (0.4 mmHg). Collection at 115-120°C gave 12.9 g of a clear, colorless liquid (75% yield).

^{1}H NMR: δ5.57(2H,s); 3.63(6H,s); 2.5-1.3(12H, m).
^{13}C NMR: δ176.2(s), 123.0(d), 51.3(q), 45.6(s), 32.9(t), 21.8(t).
MS: 252(M^+), 220, 192, 133 (base), 91, 79.
HRMS: Calcd for $C_{14}H_{20}O_4$: 252.1360. Observed: 252.1356.
IR: 2874,1715(C=O), 1429, 1299, 1149, 1079, 1020, 760, 680, 649 cm^{-1}.

Cis-9,10-Bis (hydroxymethyl)-Δ^2-decalin, (**6**). A solution of 12.9 g (0.0512 mole) of **5** in 20 m*l* of dry THF was slowly added (exothermic) to a stirred mixture of 4 g(0.1 mole) of $LiAlH_4$ and 100 m*l* of dry THF. After 10 h stirring at rt, the reaction mixture was hydrolyzed by slowly adding 60 m*l* of ether and 20 m*l* of water. The inorganic salts were filtered off and the ether layer was washed with 5% aqueous HCl followed by saturated brine. Evaporation gave 9.79 g of white solid (98% yield).

mp: 143-145°C (without recrystallization). (ref. 147-149°C).[4]
^{1}H NMR: δ5.56(2H,s); 3.68(2H,d,J=10Hz); 3.56(2H,d, J = 10Hz); 3.12(2H,br s); 2.04(4H, br s); 1.73-1.35(8H,m).
^{13}C NMR(pyridine + $CDCl_3$): δ123.8(d), 65.9(t), 38.1(t), 30.7(t), 29.6(t), 20.3(t).
MS: 178(M^+-H_2O), 160, 147, 105, 91(base), 79,67,41.
HRMS: Calcd for $C_{12}H_{18}O$: 178.1356. Observed: 178.1355.
IR: 3226(-OH),2899,1471,1087,1058,1020,1000,980, 658cm^{-1}.

Cis-9,10-Bis(methanesulfonyloxymethyl)-Δ^2-decalin,(**7**). To an ice-cold stirred solution of 12.5 m*l*(0.162 mole) of methanesulfonyl chloride in 20 m*l* of pyridine was added dropwise a solution of 9.5 g(0.048 mole) of **6** in 40 m*l* of pyridine at 0-5°C. After an additional 2 h stirring in the cold ice bath, the reaction mixture was poured into ice-5% HCl solution and extracted with three 50 m*l* portions of chloroform, washed with 5% aqueous sodium bicarbonate, saturated brine and dried over anhydrous magnesium sulfate. Evaporation gave 16.7 g of a white solid (98% yield).

mp: 121-123°C (from methanol). (ref. 124.5-125.5°C).[4]
^{1}H NMR: δ5.59(2H,s); 4.29(2H,d,J=10Hz); 4.13(2H, d,J=10Hz); 3.01(6H,s); 2.21(2H,br d,J=17Hz); 2.02(2H,br d,J=17Hz); 1.58-1.52(8H,m).
^{13}C NMR: δ123.3(d), 72.8(t), 37.8(s), 37.2(q), 30.6(t), 28.5(t), 20.2(t).
MS: 178(M^+-Ms_2O), 160,147,123,105,91(base),79,67,41.
HRMS: Calcd for $C_{12}H_{18}O$: 178.1356. Observed: 178.1355.
IR: 2890,1468,1340(asymmetric SO_2 stretching), 1180(symmetric SO_2 stretching) 943,850,763,670 Cm^{-1}.

12-Thia[4.4.3]propell-3-ene,(**2**). The dimesylate(15.4 g; 0.0438 mole), (**7**), was mixed with 12 g(0.15 mole) of sodium sulfide (sodium sulfided·9 hydrate was treated with benzene azeotrope to remove water) and 150 m*l* of dry HMPA, and heated to 120°C for 24 h. The brownish-colored contents were cooled to rt and treated with 150 m*l* of water, extracted with ether. The ether layer was washed with water, saturated brine, dried over magnesium sulfate and reduced in volume to give 7.9 g of a white solid (93% yield).

mp: 84-86°C (from methanol). (ref. 85-87°C).[4]
^{1}H NMR: δ5.51(2H,s); 2.81(2H,br s); 2.68(2H,br s); 2.11(2H,d,J=7Hz); 1.97(2H,d,J=7Hz); 1.59-1.33(8H,m).
^{13}C NMR: δ123.5(d), 44.3(s), 41.2(t), 32.5(t), 31.0(t), 21.6(t).
MS: 194(M^+), 147,133,119,105,91(base), 79,67,41.
HRMS: Calcd for $C_{12}H_{18}S$: 194.1129. Observed: 194.1161.
IR: 2890,1453,734,661 Cm^{-1}

Cis-3-(N-Benzyl)-2,4-dioxobicyclo[3.30]heptane,(**10**). A solution of 5.0 g(0.0 26 mole) of N-benzylsuccinimide in 40 m*l* of dry THF was added to a stirred solution of 2.5 equivalents of lithium diisopropylamide at -78°C. The reaction mixture was stirred for 10 min at -78°C and then 4 m*l* (1.5 eq.) of 1,3-dibromo-propane was added and stirred overnight at rt. 100 m*l* of 5% aqueous HCl solution was added to the reaction mixture and extracted with three 60 m*l* portions of ether, washed with 5% sodium bicarbonate, saturated and reduced in volume. After separation of 1,3-dibromopropane by a silica gel column using ether as an eluent 3.64 g of liquid was obtained (60% yield).

^{1}H NMR: δ7.31-7.26(5H,m); 4.6(2H,s); 3.13(2H,br d,J=8.9Hz); 2.15-1.60(4H,m); 1.19 (2H,m).
^{13}C NMR: δ 180.0(s),136.0(s),128.6(d),128.5(d),127.8(d), 45.1(d),42.3(t),30.4(t),24.7(t).
MS: 229(M^+, base),201,172,158,145,132,104,91,67,51.
HRMS: Calcd for $C_{14}H_{15}NO_2$: 229.1103. Observed: 229.1101.
IR: 2915,1695(C=O),1389,1340,1176,697cm^{-1}.

3-(N-Benzyl)-2,4-dioxotricyclo[3.3.3.0]decane, (**11**). To a

stirred solution of 2.5 equivalents of LDA in 30mL of dry THF was added 0.33 g(0.0014 mole) of **10** in 5 mL of dry THF at −78°C under nitrogen. After 10 min, 0.22 mL(1.5 eq.) of 1,3-dibromopropane was added to the reaction mixture and stirred overnight at rt. Work-up as usual gave 0.093 g of liquid(24% yield).

^{1}H NMR: δ7.27(5H,br s); 4.60(2H,s); 2.06(4H,m); 1.70(4H,m); 1.50(4H,m).

^{13}C NMR: δ181.7(s),136.3(s),128.6(d),128.2(d),127.7(d), 63.4(s),42.4(t),36.4(t),27.4(t).

MS: 269(M$^+$, base),241,229,213,200,185,172,145,132, 109,91,79,66.

HRMS: Calcd for $C_{17}H_{19}NO_2$: 269.1413. Observed: 269.1403.

IR: 2941,1709(C=O),1399,1353,1147,969,701.

3-(N-Benzyl)-2,4-dioxotricyclo[3.3.2.0]nonane, **12**. 1,2-Dibromoethane(0.9 mL, 1.5 eq.) was used instead of 1,3-dibromopropane as the synthesis of **11** (25% yield).

^{1}H NMR: δ7.6-7.25(5H,m); 4.63(2H,s); 2.32-1.53 (10H,m).

MS: 255(M+,base),227,199,171,150,136,123,108, 91,79,65.

HRMS: Calcd for $C_{16}H_{17}NO_2$: 255,1259, Observed: 255.1254.

Acknowledgements. The partial support of the Montana Agricultural Experiment Station is gratefully acknowledged. One of the authors(J.-G. Jun) wishes to dedicate this work to Professor Nung Min Yoon on the occasion of his 60th birthday.

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Reaction of Thexylbromoborane-Methyl Sulfide in Methylene Chloride with Selected Organic Compounds Containing Representative Functional Groups†

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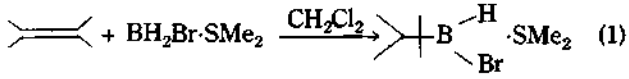
The approximate rate and stoichiometry of the reaction of excess thexylbromoborane-methyl sulfide, ThxBHBr·SMe$_2$, with selected organic compounds containing representative functional groups under standardized conditions (methylene chloride, 0°C) were studied in order to characterize the reducing characteristics of the reagent for selective reductions. The selectivity of the reagent was also compared to the selectivity of thexylchloroborane-methyl sulfide. Thexylbromoborane appears to be a much milder and hence more selective reducing agent than thexylchloroborane. The reagent tolerates many organic functionalities. Thus, the reagent shows very little reactivity or no reactivity toward acid chlorides, esters, epoxides, amides, nitro compounds including simple olefins. However, this reagent can reduce aldehydes, ketones, carboxylic acids, nitriles, and sulfoxides. Especially the reagent reduces carboxylic acids including α,β-unsaturated ones and nitriles to the corresponding aldehydes. In addition to that, thexylbromoborane shows good stereoselectivity toward cyclic ketones, much better than the chloro-derivative.

Thexylchloroborane-methyl sulfide has appeared to be a fascinating reducing agent for the selective reduction of organic functionalities[1], especially for the direct reduction of carboxylic acids to the corresponding aldehydes[2]. It is believed that this unique reducing characteristics is due to the introduction of chlorine atom to thexylborane[3], which provides such fascinating selectivity and specificity. This intrigued us. Consequently, we prepared thexylbromoborane-methyl sulfide, which is analogous to the chloro-derivative in structure but different in electronic and steric effect, and explored the reducing characteristics of the reagent systematically.

Thexybromoborane-methyl sulfide can be prepared readily from the addition of 2,3-dimethyl-2-butene (tetramethylethylene) to monobromoborane-methyl sulfide in methylene chloride (eq.1).



(1)

The reagent, ThxBHBr·SMe$_2$, in methylene chloride is very stable and no disproportionation or loss of hydride is ob-

† Dicated to Professor Nung Min Yoon on the occasion of his 60th birthday.