735 cm^{-1}; mass spectrum *m/e* (rel intensity) 203 (1, M − 1), 175 (1), 149 (2.5).

Isomerization of 5 to 6. Into 2.0 ml of methanol containing 0.20 g of sodium 0.07 g of **5** was dissolved and the solution was maintained at 100 °C in a sealed tube for 20 h. The solution was poured into 20 ml of water and acidified with dilute hydrochloric acid, and the oily mixture was extracted with ether (20 ml × 2). The combined extracts were washed with water (30 ml) and dried ($CaCl_2$). To this solution was added ethereal diazomethane solution generated from *N*-nitrosomethylurea until the solution remains yellow colored and the evolution of nitrogen ceases. After standing for 0.5 h at room temperature, a few drops of acetic acid were added to remove excess diazomethane and the solution was washed with saturated aqueous sodium bicarbonate, then with water and dried (Na_2SO_4). After evaporation the crude product was subjected to VPC analysis (Carbowax 20M, capillary tube 45 m × 0.25 mm, 140 °C), which exhibited the presence of **6** as a main component and the ratio over **5** to be 20.

Diimide Reduction of 6. To a stirred suspension of 4.05 g (20.9 mmol) of potassium azodicarboxylate in 20 ml of methanol containing 2.05 g (9.4 mmol) of **6** was added a solution of 3.15 g (52.5 mmol) of acetic acid in 5 ml of methanol during 0.5 h. After stirring was continued for an additional 0.5 h, 30 ml of water was added and the product was extracted with ether (30 ml × 2). The combined extracts were washed with water (30 ml) and dried (Na_2SO_4). After evaporation of solvent, the crude product (1.85 g) was chromatographed on silica gel using ether–petroleum ether (1:20) eluent. By collecting intermediate fractions, 1.433 g (6.51 mmol) of 4-*exo*-carbomethoxy-*endo,endo*-tetracyclo-[6.2.1.1^{3,6}.0^{2,3}]dodecane (**7a**) was isolated (69%): NMR 1.2–1.8 (m), 2.00 (br s), 2.36 (br s) (these signals were not separately recorded and total signal intensity in this region corresponds to 15 protons), 2.60 (br s, 1 H), 3.30 (ddd, 1 H, *J* = 1.5, 5.5, 9.0 Hz), 3.66 ppm (s, 3 H); ir (neat) 3020, 2950, 2885, 1738, 1420, 1355, 1303, 1195, 1173, and 1050 cm^{-1}; mass spectrum *m/e* (rel intensity) 220 (1, M^+), 193 (1.5), 180 (8), 161 (5), 134 (4), 121 (515), 119 (8), 104 (6), 93 (7.5), 91 (7.5), 87 (7.5).

Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15; O, 14.52. Found: C, 76.05; H, 9.28; O, 14.29.

Transformation of 6 to 4-*exo*-Hydroxy-*endo,endo*-tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodecane (7e). To 10 ml of 10% methanolic potassium hydroxide, 1.205 g (5.48 mmol) of **7a** was dissolved and the solution was stirred overnight at room temperature. The reaction mixture was poured into 50 ml of water and acidified with dilute hydrochloric acid, and the product mixture was extracted with ether (30 ml × 3). The combined extracts were washed with water (30 ml) and dried (Na_2SO_4). Evaporation of ether afforded 1.08 g of crude carboxylic acid **7b**. The crude **7b** was heated under reflux with 10 ml of thionyl chloride and 0.50 ml of pyridine for 3 h. Excess thionyl chloride was removed by distillation, and the residue was further distilled under reduced pressure at 100–130 °C (0.1–0.5 mm) by using a Kugelrohr micro distilling apparatus to obtain 1.750 g of pale brown solid. This crude **7c** was used directly without further purification. A chilled stirred mixture of 1.750 g of crude **7c** and 1.583 g (7.78 mmol) of 85% *m*-chloroperbenzoic acid in 20 ml of *n*-hexane (dried over sodium) was treated dropwise with 0.615 g (7.78 mmol) of pyridine in 5 ml of *n*-hexane (5 min). The mixture was allowed to warm to room temperature with stirring and was left stand overnight. The solution was decanted from pyridine hydrochloride and the residue was washed with 5 ml of ether. The combined washings were evaporated and replaced with 30 ml of 10% methanolic potassium hydroxide. The solution was stirred at room temperature for 2 h followed by heating under reflux for 1 h. After cooling to room temperature, the solution was concentrated under reduced pressure, and the residue was treated with 30 ml of ether. The combined extracts were evaporated and the crude mixture was chromatographed on silica gel using ether–petroleum ether (1:5) eluent to isolate 0.165 g (0.93 mmol) of 4-*exo*-hydroxytetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodecane (**7e**) (17% from **7a**). This material was confirmed to be identical with the authentic sample of **7e** by means of NMR, ir, and VPC.

Acknowledgment. We wish to thank Professor T. Fueno for helpful discussions.

Registry No.—**1**, 6675-72-5; **4**, 58240-70-3; **5**, 58240-71-4; **6**, 58267-54-2; **7a**, 58240-72-5; **7b**, 58240-73-6; **7c**, 58240-74-7; **7d**, 58240-75-8; **7e**, 7273-98-5; methyl acrylate, 96-33-3; methyl propiolate, 922-67-8.

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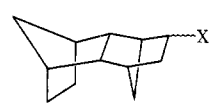
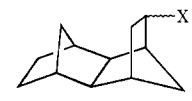


8a



8b

the parent hydrocarbon **7** is thermochemically less stable by 9.05 kcal/mol than its isomer **8** (X = H): E. M. Engler, J. D. Andose, and P. v. R. Schleyer, *ibid.*, **95**, 8005 (1973).

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Propellanes. XI. On the Mechanism of Oxygenation of Cyclopropyllithiums

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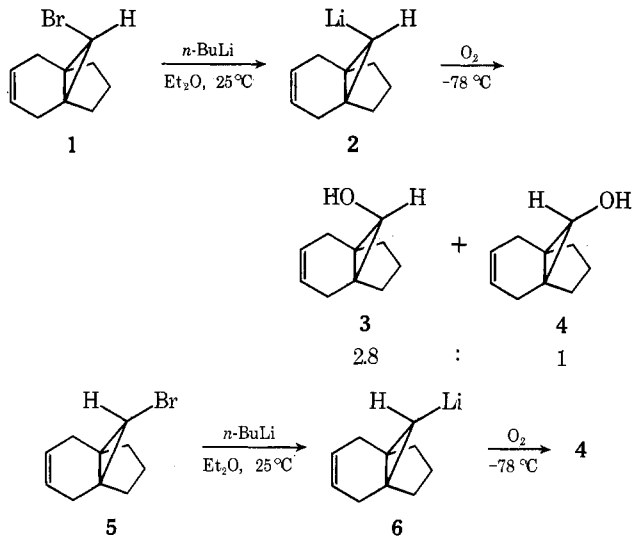
Some time ago, Longone[1] reported that the oxygenation of cyclopropyllithiums to give cyclopropanols was a synthetically useful reaction. However, the stereochemistry, and hence mechanism, of the oxygenation step was not elucidated. We now report results which strongly implicate an electron transfer process to give a superoxide intermediate.

Propellanes **1** and **5** were initially chosen as substrates, owing in part to our need to obtain the corresponding alcohols for another study.[2] We took advantage of the previously demonstrated[3,4] stereoretention of the *n*-BuLi exchange reaction in order to generate **2** and **6**. After cooling to −78 °C, O_2 was bubbled through the solution for ≥1 h. The resultant mixture of cyclopropanol(s) and 1-butanol (a tenfold excess of *n*-BuLi was normally used) was usually acetylated directly, followed by purification and separation of the epimeric acetates; **3** and **4** could then be regenerated by reaction with KOH in aqueous MeOH. A particularly distinguishing feature of **3**, not found for **4**, was an intramolecularly hydrogen-bound hydroxyl absorption in the ir spectrum.

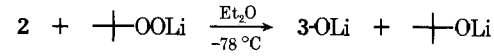
While the exclusive formation of **4** from **5** might lead one to consider direct collapse of **6** with O_2, the epimeric mix-



ture obtained from 1 strongly implies an electron transfer mechanism, which would proceed via an intermediate cyclopropyl radical–lithium superoxide ion pair; the lifetime of this radical pair would allow epimerization at C_{10}.[5] However, one must exclude the possibility that 4 arises via an SN2 displacement[6] by LiO_2^- (formed from the reaction of *n*-BuLi and O_2) on 1. To this end, a fivefold excess of *n*-BuLi and 1 were cooled to −78 °C and O_2 bubbled through; 1 was almost quantitatively recovered. Thus oxygenation of cyclopropyllithiums apparently occurs via the same electron transfer mechanism already observed for simpler alkylmagnesiums.[7]

Since the initial product formed from the collapse of a cyclopropyl radical with superoxide is a hydroperoxide salt, but the isolated product is an alcohol, a step involving the transformation of hydroperoxide to alkoxide salt must occur. This is well known to be the reaction of ROOLi with RLi to give two molecules of ROLi. In the cases we studied, the ratio of *n*-BuLi to cyclopropyllithium was 9:1; thus, assuming that the rates of oxygenation of *n*-BuLi, 2, and 6 are not much different, the secondary reactions of the peroxide salts from 2 and 6 were primarily with *n*-BuLi. If true, the stereochemistry observed was that of the primary step (see Scheme I). Nevertheless, it was of interest to determine the stereochemistry of the secondary step, as follows.

A solution of *t*-BuOOLi in ether, prepared by adding *n*-BuLi to dissolved *t*-BuOOH, was dropped into an ethereal solution of 2 (prepared as above) which was kept at −78 °C. Acetylation and analysis of the products showed that, to within the limits of NMR analysis, only 3-OAc was formed. Thus the carbanionic reduction of lithium hydroperoxides indeed appears to be an SN2 reaction, although an electron transfer process within a cage too tight to allow epimerization is, of course, not excludable.



Finally, within the context of Scheme I, we cannot tell whether 8 is more stable than 7, or whether 8 collapses to 10 more rapidly than 7 does to 9; note that the conversion of 7 to 8 involves more than simply inversion of a cyclopropyl radical.[5]

Experimental Section

10α-Bromotricyclo[4.3.1.0^{1,6}]dec-3-ene (1) and 10β-Bromotricyclo[4.3.1.0^{1,6}]dec-3-ene (5). The reduction of 10,10-dibromotricyclo[4.3.1.0^{1,6}]dec-3-ene[8] was achieved using 1 equiv of *n*-Bu_3SnH.[9] Typically, 5 g of the dibromide was placed in a flask, to which was added 5 g of *n*-Bu_3SnH. The reaction mixture became warm, and was allowed to stand for 2 h. Distillation of one or more such runs led to a ca. 85% yield of monobromides (bp 58–61 °C, 0.6 Torr).

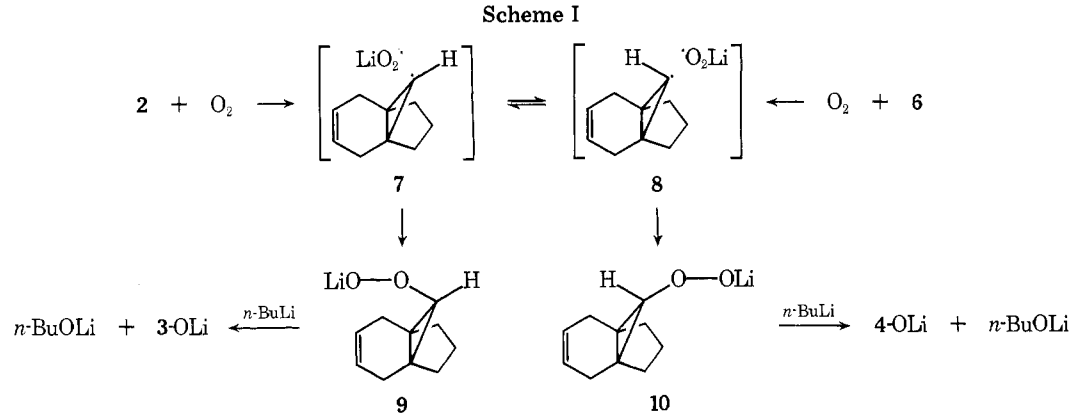
Anal. Calcd for $C_{10}H_{13}Br$: C, 56.36; H, 6.15. Found: C, 56.68; H, 6.23.

GLC analysis (2 m × 0.25 in. column of 20% Carbowax on 80/100 Chromosorb W) showed a 3.3:1 ratio of the isomers. Preparative separation was achieved via chromatography on activity I neutral Woelm alumina. Elution with hexane gave the minor isomer first (which was partly destroyed by the chromatography), followed by the major isomer. The identification of the major isomer as 1, and the minor isomer as 5, was based primarily on the NMR spectrum, and secondarily on the overall self-consistency of the observed chemistry (i.e., overall stereoretention in carbanionic reactions[4] and solvolytic reactivity of 5 but not 1[10]). The NMR of the major isomer (CCl_4) showed peaks at δ 5.44 (narrowly split multiplet, 2 olefinic H), 2.23 (broad s, 4 allylic H), 2.1–1.1 (multiplet, 6 aliphatic H), and 2.85 (s, cyclopropyl H). The minor isomer had peaks at δ 5.40 (narrowly split multiplet, 2 olefinic H), 2.5–1.6 (multiplet, 4 allylic + 6 aliphatic H), 3.16 (s, cyclopropyl H). The key difference between the spectra is that the major isomer shows a singlet for the allylic protons, whereas the minor isomer's allylic protons are broadly split up. Comparison with the NMR of the dibromide,[8] which has a singlet (δ 2.33, CCl_4) for the allylic protons, the NMR of 3-OAc (see below, singlet for allylic protons), and the NMR of 4-OAc (see below, broadly split up pattern for the allylic protons) confirms the identification of the major isomer as 1.

10α-Bromotricyclo[4.3.1.0^{1,6}]decane. To a solution of 100 mg of 1 in 50 ml of Et_2O was added a catalytic amount of 5% Pt/C. Room pressure hydrogenation was complete in less than 1 h. Filtration and evaporation of solvent gave a virtually quantitative yield of the saturated bromide: NMR (CCl_4) δ 2.86 (s, cyclopropyl H), 2.3–0.8 (m, 14 H). Anal. Calcd for $C_{10}H_{15}Br$: 214.03571. Found: 214.03533.

Oxygenation of 1. To a solution of 100 mg (0.47 mmol) of 1 in 10 ml of Et_2O contained in a flame-dried, N_2-swept 50-ml Schlenk flask was added a solution of 4.99 mmol of *n*-BuLi in 3 ml of hexane and 10 ml of Et_2O. The resulting mixture was allowed to stir for 0.75–1 h, after which it was cooled to −78 °C. O_2 was then bubbled into the solution (fritted glass bubbler) for 1 h. This was followed by addition of aqueous NH_4Cl to the reaction mixture (at ≥0 °C). After shaking in a separatory funnel, the layers were sepa-

Scheme I



rated and the aqueous layer further extracted with Et_2O. Combination of the ethereal layers was followed by drying (K_2CO_3) and solvent evaporation.

The crude mixture of **3**, **4**, and *n*-BuOH was then dissolved in ca. 5 ml of dry pyridine, to which was added ca. 1 ml of Ac_2O. The solution was heated to 75° for 1 h, followed by cooling, addition of H_2O, and extraction with Et_2O. The Et_2O extracts were then washed with 1 N HCl until the wash remained acidic. Drying of the ether layer was followed by rotoevaporation using a hot water bath (ca. 75 °C) to evaporate the *n*-BuOAc. The resulting crude oil was analyzed by NMR. The only methine peaks seen proved to be those for **3**-OAc and **4**-OAc in the ratio of 2.8:1. It was assumed that this ratio also applied to the alcohols **3** and **4**.

Separation and purification of **3**-OAc and **4**-OAc was achieved by chromatography on silica gel (of 355 mg of crude material). Both acetates were eluted with 4% Et_2O–96% hexane, with **4**-OAc coming through first. The total isolated yield of cyclopropyl acetates was 38%.

3-OAc: NMR ($CDCl_3$) δ 5.50 (narrowly split multiplet, olefinic H), 3.82 (s, cyclopropyl H), 2.13 (s, 4 allylic H), 2.1–1.2 (m, 6 aliphatic H), 1.90 (s, OAc); ir ($CDCl_3$) 3020 (m), 1740 (s), 1665 (w), 1250 cm^{-1} (s). Anal. Calcd for $C_{12}H_{16}O_2$: 192.1150. Found (70 eV): 192.1160.

4-OAc: NMR ($CDCl_3$) δ 5.50 (narrowly split multiplet, olefinic H), 3.95 (s, cyclopropyl H), 2.8–1.5 (m, 4 allylic + 6 aliphatic H), 2.07 (s, OAc); ir ($CDCl_3$) 3020 (m), 1735 (s), 1654 (w), 1245 cm^{-1} (s). Anal. Calcd for $C_{12}H_{16}O_2$: 192.1150. Found (70 eV): 192.1160.

Oxygenation of 5. In a manner exactly analogous to that described for **1**, 50 mg (0.23 mmol) of **5** was oxygenated and acetylated. To within the error limits of NMR analysis, the only detectable product was 4-OAc.

10α-Hydroxytricyclo[4.3.1.0^{1,6}]dec-3-ene (3). In 1 ml of a 5% KOH in 25% aqueous MeOH solution was dissolved 16 mg of pure **3**-OAc. The mixture was heated for 2 h at 50 °C, followed by dilution with H_2O and extraction with Et_2O. After drying (K_2CO_3), filtering, and evaporating the solvent, ca. 5 mg of solid white product was recovered. The ir ($CDCl_3$) showed peaks at 3590 (sharp, free OH), 3540 (sharp, intramolecularly hydrogen-bound OH), and 3430 cm^{-1} (broad, intermolecularly hydrogen-bound OH).

10β-Hydroxytricyclo[4.3.1.0^{1,6}]dec-3-ene(4). In the manner described above, a 50-mg sample of pure **4**-OAc was hydrolyzed (in 1 ml of the basic solution, and for only 40 min at 50 °C); 13 mg of product was recovered. The ir ($CDCl_3$) showed peaks at 3600 (sharp, free OH) and 3430 cm^{-1} (broad, intermolecularly hydrogen-bound OH).

Oxygenation of 10α-Bromotricyclo[4.3.1.0^{1,6}]decane. A variation of the procedure described above was tried, both to examine the effect on yield and mechanism (if any) of changing solvent. In a dried 100-ml Schlenk flask were placed 0.88 g (4.1 mmol) of 10α-bromotricyclo[4.3.1.0^{1,6}]decane and 6 ml of THF. To the resulting solution was added 26 ml of a 1.6 M hexane solution of *n*-BuLi (42 mmol), under N_2. After stirring for 1 h at room temperature (during which time the solution turned orange) the solution was cooled to −78 °C, and O_2 bubbled in for 1 h. The work-up of the reaction was carried out as described for the oxygenation of **1**. By pumping on the crude product at 1.5 Torr, it was possible to remove the *n*-BuOH; the resulting oil showed singlets at δ 2.98 and 3.17 (for cyclopropyl H) in a ca. 1:1 ratio.

Acetylation of the yellow oil was carried out as before (but at room temperature for 20 h). Chromatography of the products gave 0.34 g (43%) of an inseparable mixture of 10α-acetoxy- and 10β-acetoxytricyclo[4.3.1.0^{1,6}]decane in a 1:1 ratio. Analysis of a GLC-purified sample (20% DEGS on Chromosorb P column) gave the following.

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.18; H, 9.35. Found: C, 74.23; H, 9.23.

Spectral data for the mixture showed NMR peaks (CCl_4) at δ 3.72 (s, cyclopropyl H), 3.63 (s, cyclopropyl H), 2.00 (s, OAc), 1.96 (s, OAc), and 2.3–0.9 (m, aliphatics); ir (CCl_4) peaks at 3020 (w), 1754 (shoulder), 1740 (s), and 1235 cm^{-1} (s).

Catalytic hydrogenation (Et_2O, Pt/C) of a 25-mg sample of a 2.8:1 mixture of **3**-OAc and **4**-OAc served to establish that the peak at δ 3.63 belonged to the 10α-acetoxy- and that at δ 3.72 to the 10β-acetoxytricyclo[4.3.1.0^{1,6}]decane.

Reaction of 10α-Lithiotricyclo[4.3.1.0^{1,6}]dec-3-ene (2) with Lithium *tert*-Butylhydroperoxide. **1** (100 mg) was converted to the corresponding organolithium (**2**) exactly as described for the oxygenation of **1**. Subsequently, an addition funnel above the Schlenk flask containing **2** was charged with 5 mmol of *n*-BuLi in 3 ml of hexane and 5 ml of Et_2O. To this were cautiously added 5 mmol (90 mg) of *t*-BuOOH (previously dried, over K_2CO_3, in pentane) in 5 ml of Et_2O (a syringe was utilized). The resulting ethereal solution of LiOO-*t*-Bu was then added dropwise to the solution of **2** (which had been cooled to −78 °C). Thus the only way **3** and/or **4** could form would be via reaction with *t*-BuOOLi. The work-up and subsequent acetylation of the product mixture was performed as described for the oxygenation of **1**. To within the error of NMR analysis, the only cyclopropyl acetate formed was **3**-OAc.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

Registry No.—**1**, 58191-00-7; **2**, 58191-01-8; **3**, 58191-02-9; **3**-OAc, 58191-03-0; **4**, 58239-38-6; **4**-OAc, 58239-39-7; **5**, 58239-40-0; 10,10-dibromotricyclo[4.3.1.0^{1,6}]dec-3-ene, 38749-47-2; 10α-bromotricyclo[4.3.1.0^{1,6}]decane, 58191-04-1; 10α-acetoxytricyclo[4.3.1.0^{1,6}]decane, 58191-05-2; 10β-acetoxytricyclo[4.3.1.0^{1,6}]decane, 58239-41-1; lithium *tert*-butylhydroperoxide, 14680-31-0.

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(2) The saturated alcohols corresponding to **3** and **4** were also required. In addition to their synthesis via reduction of **3** and **4**, the saturated bromide analogue of **1** was lithiated (*n*-BuLi) in THF and oxygenated to give a ca. 1:1 mixture of the epimeric saturated alcohols. This provides independent evidence for the involvement of electron transfer in the oxygenation. Details are given in the Experimental Section.
(3) (a) A literature precedent for stereoretentive lithiation–deuteration is C. P. Lewis and M. Brookhart, *J. Am. Chem. Soc.*, **97**, 621 (1975); (b) E. Vogel, A. Vogel, H.-K. Kübbeler, and W. Sturm, *Angew. Chem., Int. Ed. Engl.*, **9**, 514 (1970), reported a possible case of nonstereoretention in a lithiation–carboxylation sequence. However, since they started with a mixture of epimers, and the overall yield was low, one cannot be sure that selective loss of one isomer was not occurring.
(4) We have established the overall stereoretention of the lithiation–deuteration and lithiation–carboxylation sequences (using *n*-BuLi). These sequences were carried out on **1**, at room temperature or below, with invariant stereochemical results. In the latter case, the stereochemistry was proven by iodolactonization of the acid. We also showed that loss ot the epimeric acid was not occurring, since when the reaction was carried out with Mg, followed by CO_2, both acids resulted. Details of these experiments will be published soon.
(5) Of course we realize that some or all of the reaction may proceed via a radical chain mechanism, wherein the inversion of the cyclopropyl center (e.g., **7** → **8**) may be more complicated. There seems to be some evidence for cage reactions in oxygenations of Grignards, but other cases definitely involve chains. A good summary of this point is given by G. A. Russell, E. G. Janzen, A. G. Bemis, E. J. Geels, A. J. Moye, S. Mak, and E. T. Strom, "Selective Oxidation Processes", *Adv. Chem. Ser.*, **No. 51** (1965), and by A. G. Bemis, Ph.D. Dissertation, Iowa State University, Ames, Iowa, 1966.
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(10) P. Warner and S. Lu, submitted for publication.

Base-Promoted Elimination Reactions in the 2-Aza-5-norbornene System. Stereospecific Ring Opening of 2-(*p*-Toluenesulfonyl)-*exo*-3-(trichloromethyl)-2-azabicyclo[2.2.1]hept-5-ene by Lithium Alkyls[1]

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Received October 2, 1975

An ongoing interest in aza-aromatic and -antiaromatic character[2] has stimulated our curiosity as to the nature of