

responding tricyclic halo ketones **6**^{8,16} in ca. 40%.¹⁷ Ring contraction¹⁸ of either **6a** or **6b** was effected by treatment with 40% aqueous KOH (reflux, 18 hr) to yield the crystalline acid **1** (mp 94.0–96.5°) in 75–90% yield. The proton nmr spectrum of the corresponding methyl ester (**1b**) (CH₂N₂, 99%) showed (CDCl₃) δ 3.67 (s, 3, OCH₃), 2.80–3.20 (m, 6, C₁-H, exo C₂-H), and 2.25 ppm (d, 3, J = 12 Hz, endo C₂-H). In the presence of 1 mol equiv of Eu(fod)₃ the 6 H multiplet was resolved into two signals of δ 6.85 (broad t, 3, J = 8 Hz, C₁-H) and 4.40 ppm (broadened d of t, 3, J = 12, 8 Hz, exo C₂-H). The proton noise-decoupled carbon-13 nmr spectrum (CDCl₃, CCl₄) showed signals as singlets at δ 35.7, 39.1, 51.3 and 56.6 ppm downfield from internal TMS.¹⁹ These spectral data uniquely establish the structure assigned to **1**.

(16) Spectral data for **6a**: ir (CCl₄) 1780 cm⁻¹ (C=O); nmr (CCl₄) δ 1.78 (d, 1, endo C₁-H, J = 10 Hz), 2.08 (broad d, 2, endo C_{2,8}-H, J = 12 Hz), 2.35 (m, 3, exo C_{2,8}-H and exo C₁-H), 2.72 (broad d of t, 2, C_{3,5}-H, J = 7, 2 Hz), 3.20 ppm (m, 1, C₁-H). Spectral data for **6b**: ir (CCl₄) 1783 cm⁻¹ (C=O); nmr (CCl₄) similar to that of **6a**; nmr (benzene-*d*₆) δ 1.10 (d, 2, endo C₁-H), 1.23 (broad d, 2, endo C_{2,8}-H, J = 12 Hz) 1.50–1.95 (m, 3, exo C_{2,8}-H and exo C₁-H), 2.12 (broad d of t, C_{3,5}-H, J = 7, 2 Hz), 2.75 ppm (m, 1, C₁-H).

(17) Dry potassium *tert*-butoxide (benzene, 50°, 1 hr) yielded the halo ketones **6** (10–17%).

(18) Cf. P. E. Eaton and T. W. Cole, *J. Amer. Chem. Soc.*, **86**, 962 (1964); J. C. Barborak, L. Watts, and R. Pettit, *ibid.*, **88**, 1328 (1966); N. B. Chapman, J. M. Key, and K. J. Toyne, *J. Org. Chem.*, **35**, 3860 (1970); R. J. Stedman, L. S. Miller, L. D. Davis, and J. R. E. Hoover, *ibid.*, **35**, 4169 (1970).

(19) The carbonyl carbon resonance was not recorded; we express our appreciation to Dr. Barbara Erwin and Mr. Lyle Hassell (Varian Corporation) for running this spectrum for us on a Varian CFT-20 instrument.

(20) National Science Foundation Trainee, 1970–1973.

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Lithium Aluminum Hydride Promoted Ring Contraction of Cyclic Five-Membered α -Sulfonyl Carbanions and Its Application to the Synthesis of 1,2-Dialkylcyclobutenes

Sir:

Synthetic access to 1-substituted and 1,2-disubstituted cyclobutenes has previously depended chiefly upon the availability of 1,3-butadienes capable of photocyclization,¹ acylcyclopropane tosylhydrazones predisposed toward carbenic decomposition with base,² α,β -unsaturated ketones having the propensity for cycloaddition to alkynes from their photoexcited states,³ and cyclopropene 3-carboxylates prone to reductive ring expansion in the presence of LiAlH₄-AlCl₃.⁴ The need

(1) (a) K. J. Crowley, *Proc. Chem. Soc. (London)*, 334 (1962); (b) R. Srinivasan, *J. Amer. Chem. Soc.*, **84**, 4141 (1962); (c) K. J. Crowley, *Tetrahedron*, **21**, 1001 (1965); (d) E. H. White and J. P. Anhalt, *Tetrahedron Lett.*, 3937 (1965).

(2) (a) M. A. Battiste and M. E. Burnes, *Tetrahedron Lett.*, 523 (1966); (b) I. D. R. Stevens, H. M. Frey, and C. L. Bird, *Angew. Chem., Int. Ed. Engl.*, **7**, 646 (1968); (c) C. D. Gutsche and D. Redmore, "Carbocyclic Ring Expansion Reactions," Academic Press, New York, N. Y., 1968, p 111.

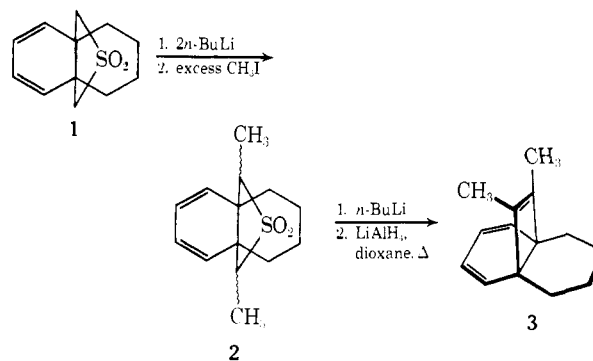
(3) P. E. Eaton, *Accounts Chem. Res.*, **1**, 50 (1968).

(4) W. G. Gensler, J. J. Langone, and M. B. Floyd, *J. Amer. Chem. Soc.*, **93**, 3828 (1971). For examples of other less general but equally inapplicable methods, consult H. H. Freedman and A. M. Frantz, *J. Amer. Chem. Soc.*, **84**, 4165 (1962); R. M. Dodson and A. G. Zielska, *J. Org. Chem.*, **32**, 28 (1967); Y. Hosokawa and I. Moritani, *Tetrahedron Lett.*, 3021 (1969); M. S. Newman and G. Kaugars, *J. Org. Chem.*, **30**, 3295 (1965).

to prepare small ring systems of this type for a mechanistic study underway in these laboratories, coupled with the inadequacy of the existing methods in these specific instances, led to the search for a generally useful new procedure which would complement the earlier approaches. We now describe a novel and versatile scheme which is based on our observation that anions of 2,5-dialkyltetrahydrothiophene dioxides react when heated with lithium aluminum hydride in refluxing dioxane to give 1,2-dialkylcyclobutene derivatives.

The method is illustrated in Scheme I for the conver-

Scheme I



sion of 12-thia[4.4.3]propella-2,4-diene 12,12-dioxide (**1**)⁵ to 11,12-dimethyl[4.4.2]propella-2,4,11-triene (**2**), a polyolefin capable of thermal rearrangement in its own right.⁶ The tricyclic sulfone was dimethylated by sequential treatment with 2 equiv of *n*-butyllithium in tetrahydrofuran at -80° and excess methyl iodide. Without purification, the crude product, which consisted chiefly of **2** (pmr analysis), was dissolved in anhydrous dioxane, treated at 0° with 1 equiv of *n*-butyllithium, and introduced *via* syringe into a refluxing slurry of LiAlH₄ in dioxane. After 6 hr, the triene could be isolated by vacuum distillation in 54% yield (based on **1**), bp 42° (0.15 mm):⁷ $\delta_{\text{TMS}}^{\text{CCl}_4}$ 5.10–5.80 (m, 4), 1.53 (s, 6), and 1.47 (pseudo-s, 8).

This ring contraction leading to 1,2-dimethylcyclobutene derivatives can be realized in good to fair yield with a variety of five-membered ring sulfones and gives every indication of being fully applicable to a broad spectrum of structural types (Table I). Prior treatment of the α,α' -dimethyltetrahydrothiophene dioxide with an organolithium reagent (method A) is not a mandatory prerequisite for successful ring contraction. Cyclobutene formation was also observed to occur merely upon heating of the dimethylated sulfone with LiAlH₄ in dioxane (method B). However, longer reaction times were necessary, the yields were invariably lower (Table I), and less clean products were obtained chiefly as a consequence of significant levels of competitive direct reduction to the sulfide.

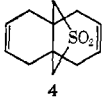
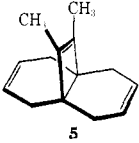
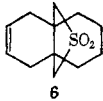
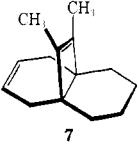

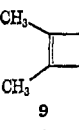
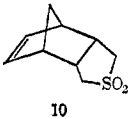
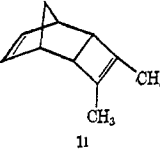
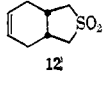
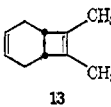
The new synthetic procedure can likewise accommodate conversion of succinic anhydrides to substituted cyclobutene derivatives, a transformation which has not previously been part of synthetic practice. The preparation of hydrocarbon **18** from readily available

(5) L. A. Paquette, R. E. Wingard, Jr., J. C. Philips, G. L. Thompson, L. K. Read, and J. Clardy, *J. Amer. Chem. Soc.*, **93**, 4508 (1971).

(6) L. A. Paquette, R. E. Wingard, Jr., and J. M. Photis, *J. Amer. Chem. Soc.*, in press.

(7) All spectra, as well as the combustion analysis, of this substance were consistent with the assigned structure.

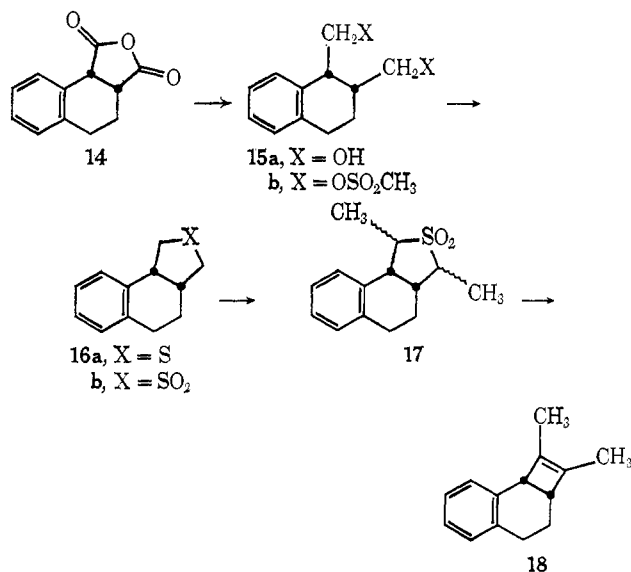
Table I

Sulfone	Product ^a	Method	Reaction time, hr	Isolated overall yield, % ^b
		A B	20 72	62 30
		A B	20 48	67 27
		A	9	20 ^c
		A	15	22
		B	24	18

^a See footnote 7. ^b The per cent yields are not considered maximized. ^c Complications arising from the need to separate product from *n*-hexane (the *n*-BuLi solvent) contributed to the lowered yield.

cis-tetralin-1,2-dicarboxylic anhydride (**14**)⁸ is exemplary (Scheme II). Hydride reduction of **14** under

Scheme II

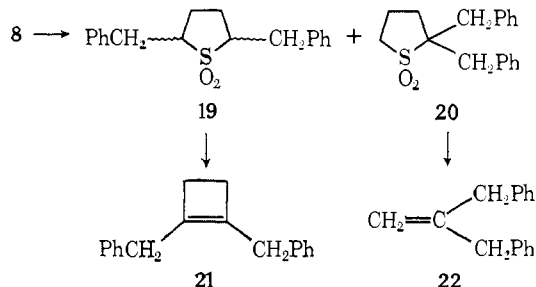


standard conditions gave oily diol **15a**, exposure of which to methanesulfonyl chloride in pyridine resulted in ready formation (75% overall) of the dimesylate **15b**, mp 110–111.5°. The action of anhydrous sodium sulfide in DMSO on **15b** produced **16a** whose direct oxidation with monopero-phthalic acid yielded (80%) the

(8) T. M. Lyssy, *J. Org. Chem.*, **27**, 5 (1962).

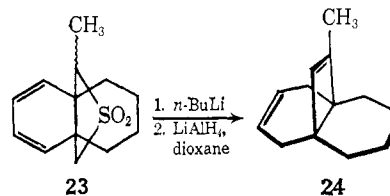
sulfone **16b**, mp 91–93°. When **16b** was subjected to procedure A, **18** was isolated by distillation in 20% yield: $\delta_{TMS}^{CCl_4}$ 6.97 (m, 4), 3.53 (m, 1), 3.06 (m, 1), 2.37–2.70 (m, 2), 1.7–2.2 (m, 2), 1.58 (m, 3), and 1.38 (m, 3).

The variations in yield associated with the title reaction are considered significant and are believed to originate in the varied levels of steric bulk surrounding the sulfone group (which retard reduction to sulfide) and to some extent in the alkylation step. To achieve the requisite 2,5 positional selectivity presumably requires the proper balance of electronic and steric factors in the sulfone, together with suitable reactivity levels in the alkylating agent. 2,2-Disubstitution is the competing process and this reaction channel appears to gain greater importance when benzyl halides are employed. For example, treatment of **8** with 2 equiv each of *n*-butyllithium and benzyl chloride gave a mixture of **19** and **20** which were not isolated but subjected directly



to procedure A. The resulting two products were separated by preparative vpc and identified as **21**⁷ (20.5% isolated; $\delta_{TMS}^{CCl_4}$ 7.12 (m, 10), 3.27 (s, 4), and 2.21 (s, 4)) and **22** (15.4%).⁹ The carbanionic fragmentation of **20** to **22** is precedented.¹⁰

As the level of α substitution on the tetrahydrothiophene dioxide is decreased, there is encountered a parallel lowering in the efficiency of ring contraction. However, this point has not been extensively examined. The conversion of **23**¹¹ to **24** (11.8%) attests to the



feasibility of the method for the preparation of 1-methylcyclobutenes. Under analogous conditions, the parent sulfone (**6**) provided only sulfide.

Dodson and coworkers have demonstrated that *cis*- and *trans*-2,4-diphenylthietane dioxides rearrange stereoselectively to *trans*-1,2-diphenylcyclopropanesulfonic acid when treated with ethylmagnesium bromide.¹² A related process could account for the first step of the present ring contraction. Reductive elimination of the

(9) C. L. Bumgardner and H. Iwerks, *J. Amer. Chem. Soc.*, **88**, 5518 (1966).

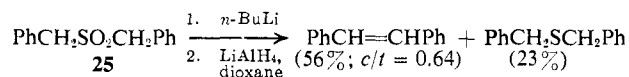
(10) F. Weygand and H. Daniel, *Chem. Ber.*, **94**, 3145 (1961). However, compare T. J. Wallace, J. E. Hofmann, and A. Schreisheim, *J. Amer. Chem. Soc.*, **85**, 2739 (1963).

(11) This sulfone was synthesized by the following sequence of reactions starting with Δ^2 -octalin-9,10-dicarboxylic anhydride: (i) CH_3Li , THF, -78° ; (ii) $LiAlH_4$, THF; (iii) CH_3SO_2Cl , pyridine; (iv) Na_2S in dry HMPA; (v) monopero-phthalic acid oxidation.

(12) R. M. Dodson and G. Klose, *Chem. Ind. (London)*, 1203 (1963); R. M. Dodson, P. D. Hammen, E. H. Jancis, and G. Klose, *J. Org. Chem.*, **36**, 2698 (1971).

sulfonic acid group could complete the conversion to the strained olefin, but such considerations remain to be established by experiment.

Finally, we note the similarities of the present procedure with two other methods capable of supplanting a sulfur atom by a carbon-carbon double bond, namely the Ramberg-Bäcklund¹³ and Stevens rearrangements.¹⁴ The new scheme is clearly superior for the generation of strained tetrasubstituted double bonds, and as illustrated by the behavior of dibenzyl sulfone (**25**) could prove to



be at least equally convenient in a variety of simpler synthetic transformations.¹⁵

(13) L. A. Paquette, "Mechanisms of Molecular Migrations," Vol. I, B. S. Thyagarajan, Ed., Interscience, New York, N. Y., 1968, pp 121-156; L. A. Paquette, *Accounts Chem. Res.*, **1**, 209 (1968); F. G. Bordwell, *ibid.*, **3**, 281 (1970).

(14) For a leading reference, see R. H. Mitchell and V. Boekelheide, *J. Amer. Chem. Soc.*, **96**, 1547 (1974).

(15) This investigation was supported in part by a grant from the National Cancer Institute.

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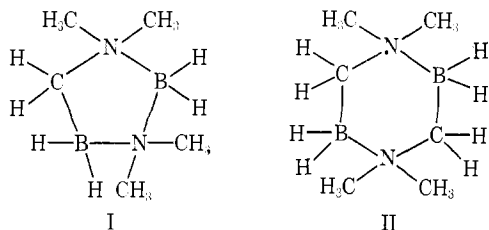
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Synthesis of a New Small Ring Heterocyclic Boron Compound

Sir:

We wish to report the synthesis of a new five-membered boron heterocycle, 1,1,3,3-tetramethyl-1,3-diazonia-2,4-diboracyclopentane, $\text{B}_2\text{C}_3\text{N}_2\text{H}_{18}$ (I). The new compound is isomeric with the cyclic adduct of dimethylaminoborane and dimethylaminomethylborane prepared by Haubold and Schaeffer,¹ and links structurally the four-membered ring systems derived from dimeric aminoboranes to the six-membered heterocycle 1,1,4,4-tetramethyl-1,4-diazonia-2,5-diboracyclohexane, $\text{B}_2\text{C}_6\text{N}_2\text{H}_{20}$ (II).² Compound I was pre-



pared in better than 30% yield from the reaction of bis(trimethylamine)boronium iodide with a Na-K alloy in 1,2-dimethoxyethane. Its reactivity appears to be similar to II.

The compound is a liquid immiscible with water but soluble in most organic solvents. It shows no sign of decomposition after 3 weeks at room temperature in an inert atmosphere or in CH_2Cl_2 solution. Methylene chloride solutions of I show little degradation after 24-hr contact with water but are rapidly decomposed on contact with strong aqueous hydrochloric acid and so-

(1) W. Haubold and R. Schaeffer, *Chem. Ber.*, **104**, 513 (1971).

(2) N. E. Miller and E. L. Muetterties, *Inorg. Chem.*, **3**, 1196 (1964).

dium hydroxide solutions. The compound reacts readily with bromine or iodine.

To synthesize I, 7.16 g of $[(\text{CH}_3)_3\text{N}]_2\text{BH}_2\text{I}$ and 2.29 g of Na-K alloy (25% Na) were slurried with 50-75 ml of 1,2-dimethoxyethane. The mixture was gently refluxed over an oil bath for 2 hr, when gas evolution ceased abruptly. After filtration the clear colorless solution was then concentrated by vacuum evaporation to about 5 ml, and the remaining liquid was fractionated by repeated evaporation and passage through a -23° trap, until the proton nmr spectrum showed that all the solvent had been removed from the product, which tended to collect in the -23° trap.

Since the compound has a vapor pressure of about 1 mm at 25° removal of solvent by trap-to-trap fractionation entails a concomitant not insignificant loss of product. Nevertheless, a total of 0.5 g, 30% yield of analytically pure I was obtained.

Anal. Calcd for $\text{B}_2\text{C}_3\text{N}_2\text{H}_{18}$: C, 46.98; H, 14.19; N, 21.91; B, 16.91. Found: C, 47.07; H, 14.12; N, 21.77; B, 16.85.³

The ir spectrum from 4000 to 600 cm^{-1} , obtained as a thin film between NaCl plates, gave the following bands in cm^{-1} : 3000 ms, 2940 s bd, 2415 s, 2340 s bm, 2265 ms, 1463 s bd, 1402 w, 1360 vw, 1290 m, 945 m bd, 878 w, 830 w bd, 791 ms, 720 vw.

The proton nmr spectrum in methylene chloride, referred to internal tetramethylsilane, shows two broad incompletely resolved peaks and a shoulder. The width at one-half the peak height for the absorption at -2.64 ppm is 5 Hz and the width at one-half the peak height of the absorption at -2.40 ppm is 9 Hz. The shoulder appears to be centered at -2.23 ppm and is assigned to the methylene carbon in position five of the ring based on position and relative intensity to the other two peaks.

Based on peak broadness we assign the absorption at -2.64 ppm to the methyl groups attached to the nitrogen in position one of the ring and the absorption at -2.40 ppm to the methyl groups attached to the nitrogen in position three of the ring.

The mass spectrum was obtained at 70 V and showed the presence of a molecular ion at m/e 128, as expected for the heaviest isotopic variant of $\text{B}_2\text{C}_3\text{N}_2\text{H}_{18}$ and no peaks at higher masses. As is the case for trimethylamine-borane, loss of one and more protons occurs easily on electron impact so that the pattern of molecular ion fragments becomes complex in the mass region immediately below the parent peak. Table I

Table I. Mass Spectrum of $\text{B}_2\text{C}_3\text{N}_2\text{H}_{18}$

m/e	Relative intensity, %	Species	Abundance, %
128	5.7	$\text{B}_2\text{C}_3\text{N}_2\text{H}_{18}^+$	6.3
127	34.6	$\text{B}_2\text{C}_3\text{N}_2\text{H}_{17}^+$	52
126	27.2	$\text{B}_2\text{C}_3\text{N}_2\text{H}_{16}^+$	17
125	20.0	$\text{B}_2\text{C}_3\text{N}_2\text{H}_{15}^+$	21
124	8.7	$\text{B}_2\text{C}_3\text{N}_2\text{H}_{14}^+$	3.0
123	2.7		
122	1.2		

shows the fragmentation pattern and the relative abundance of species calculated on the basis of statistical

(3) Analysis was done by Galbraith Laboratories, Inc., Knoxville, Tenn.