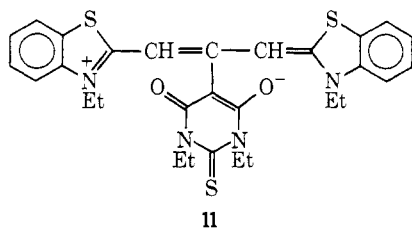


Table I. Visible Absorption Maxima of $R_1^+C\equiv CCH=R_2 ClO_4^-$

Dye	R_1	R_2	λ_{max} (CH_3CN), ^a nm	$\epsilon_{max}^a \times 10^{-4}$
6			568 (601)	8.8 (15.2)
7			539 (581)	21.2 (31.8)
8			513 (541)	8.3 (15.2)
9			473 (513)	14.0 (21.0)
10			513 (553)	9.9 (15.7)

^a The value for the corresponding carbocyanine is shown in parentheses.

give meso-substituted carbocyanines. Addition of weaker acids such as aryl thiols is catalyzed by base. The addition of 1,3-diethyl-2-thiobarbituric acid to give dyes such as **11** exemplifies a general route for the preparation of allolopolar cyanines.^{4b}



Further studies of this interesting new class of compounds are in progress.

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Tricyclo[3.1.1.0^{3,6}]heptane-6-carboxylic Acid¹

Sir:

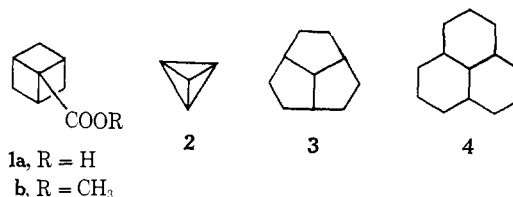
We wish to report the synthesis of tricyclo[3.1.1.0^{3,6}]heptane-6-carboxylic acid (**1**), the first known example of this ring system in which the three alternate carbon atoms of a cyclohexane ring are bonded to a single bridging carbon unit. Other members of this general family of molecules involving the symmetrical bridging of a ring perimeter by a single carbon atom include the elusive tetrahedrane² (**2**) and the well-documented triquinacene³ (**3**) and phenalene⁴ (**4**) systems. Al-

(1) Financial support of this research by the Robert A. Welch Foundation is gratefully acknowledged.

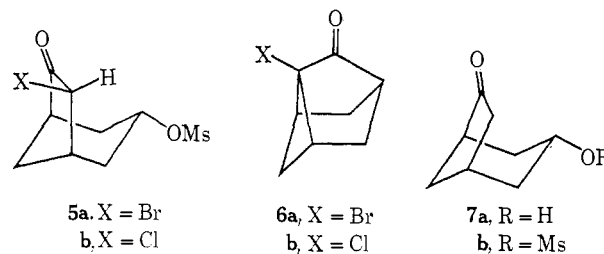
(2) P. B. Shevlin and A. P. Wolff, *J. Amer. Chem. Soc.*, **92**, 406 (1970).

(3) (a) R. B. Woodward, T. Fukunaga, and R. C. Kelly, *J. Amer. Chem. Soc.*, **86**, 3162, (1964); (b) R. Russo, Y. Lambert, and P. Deslongchamps, *Can. J. Chem.*, **49**, 531 (1971).

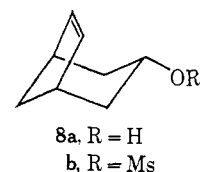
(4) (a) H. C. Brown and W. C. Dickinson, *J. Amer. Chem. Soc.*, **91**, 1226 (1969); (b) H. C. Brown and E. Negishi, *ibid.*, **89**, 5478 (1967).



ternatively, acid **1** can be envisioned as a trisnoradamantane derivative. Our synthetic approach involved formation of the first four-membered ring of acid **1** by intramolecular ring closure⁵ of 7-halobicyclo[3.2.1]octanone **5** to give the 6-halotricyclo[3.2.1.0^{3,6}]octanone intermediate **6**. The two remaining four-membered rings were generated by a base induced semibenzilic acid ring contraction of **6** to yield acid **1**.



The previously reported^{5,6} *exo*-bicyclo[3.2.1]octan-3-ol-6-one (**7a**) was converted⁷ into the crystalline *exo*-mesylate **7b** (70%)⁸ and then into a *single* 7-bromo derivative **5a** (mp 77.5–79.2°, 96%)^{8,9} by treatment with bromine in $CHCl_3$. Alternatively, a *single* 7-chlorobicyclo[3.2.1]octanone **5b** (mp 75.8–79.5°)^{8,10} was obtained in 84% yield by chromyl chloride¹¹ oxidation of *exo*-bicyclo[3.2.1]oct-5-en-3-yl mesylate (**8a**)⁸ which was prepared from the known¹² alcohol **8b** (88%). The



halogen atom in both bicyclo ketones, **5**, is assigned as *exo* on the basis of the observed coupling constant for the C-7 proton ($J = 2-3$ Hz).^{13,14} Treatment of the bicyclic halo ketones, **5**, with sodium hexamethyldisilazane¹⁵ (benzene, 70°, 10 min) furnished the cor-

(5) S. A. Monti and S.-S. Yuan, *Tetrahedron Lett.*, 3627 (1969).

(6) This procedure⁵ yields **7a** of ca. 70% isomeric purity: J. M. Harless, unpublished observations.

(7) R. K. Crossland and K. L. Servis, *J. Org. Chem.*, **35**, 3195 (1970).

(8) All new compounds gave satisfactory spectral and combustion analysis data.

(9) Spectral data for **5a**: ir ($CHCl_3$) 1755 (C=O); 1362, 1338, and 1182 cm^{-1} (OSO_2CH_3); nmr ($CDCl_3$) δ 1.85–2.90 (m, 8), 3.10 (s, 3, $-CH_3$), 4.53 (d, 1, *endo* C-H, $J = 2-3$ Hz), 4.78 ppm (sept, 1, *exo* C-H, $J = 11, 6$ Hz).

(10) Spectra. data for **5b**: ir ($CHCl_3$) 1758 (C=O); 1360, 1340, and 1180 cm^{-1} (OSO_2CH_3); nmr ($CDCl_3$) δ 1.57–2.90 (m, 8), 3.00 (s, 3, $-CH_3$), 4.07 (d, 1, *endo* C-H, $J = 2-3$ Hz), 4.70 ppm (sept, 1, *endo* C-H, $J = 12, 6$ Hz).

(11) K. B. Sharpless and A. Y. Teranishi, *J. Org. Chem.*, **38**, 185 (1973).

(12) N. A. LeBel and R. J. Maxwell, *J. Amer. Chem. Soc.*, **91**, 2307 (1969).

(13) Pyrrolidine catalyzed isomerization of **5b** yielded the *endo* 7-chloro derivative, δ 4.33 ppm (d, 1, *exo* C-H, $J = 6$ Hz).

(14) For a study on the stereoselectivity of chromyl chloride oxidations, see F. W. Bachelor and U. O. Cherigan, *Tetrahedron Lett.*, 3291 (1973).

(15) U. Wannagat and H. Niederprüm, *Chem. Ber.*, **94**, 1540 (1961).

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 6H 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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Received April 1, 1974

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.

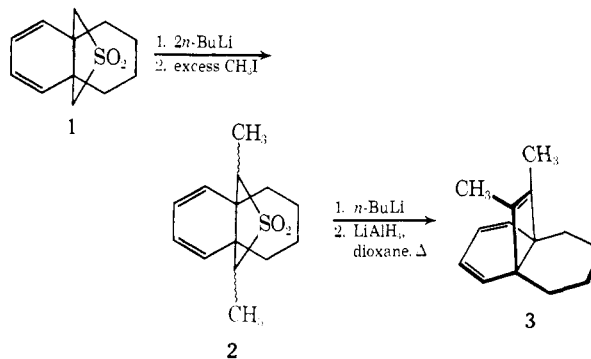
(3) P. E. Eaton, *Accounts Chem. Res.*, **1**, 50 (1968).

(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 (**3**), 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.