drying the combined extracts ($MgSO_4$), and evaporation produced an oil. The pmr spectrum of this oil exhibited $\delta_{TMS}^{CCl_4}$ 0.88 (t, 3.0), 1.62 (sextet, 2.5, J = 7 Hz), 3.95 (apparent quartet, 2.0, J = 6 Hz), 7.15 (broad singlet, 5.0), which is consistent with that expected for *n*-propyl phenyl phosphate. For *n*-propyl diphenyl phosphate, the pmr spectrum was $\delta_{TMS}^{CCl_4}$ 0.88 (t, 2.9), 1.68 (sextet, 2.2, J = 7 Hz), 4.12 (apparent quartet, resolvable into overlapping triplets centered at 4.07 and 4.20 each with J = 6 Hz, 1.9), 7.23 (multiplet, 10.0).

Registry No.—**1**, 27460-01-1; **2**, 27460-02-2; potassium *tert*-butoxide, 865-47-4; methyl diphenyl phosphate, 115-89-9.

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α-Chlorodicyclopropyl Sulfone. Its Synthesis and Behavior toward Bases[1]

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In 1940, Ramberg and Bäcklund demonstrated that exposure of acylic α-halo sulfones to the action of 2 *N* potassium hydroxide resulted in the production of alkenes with the concomitant ejection of hydrogen halide and sulfur dioxide.[3] Significantly, the new double bond unequivocally supplanted the sulfonyl group in each example studied. These findings, in conjunction with more recent mechanistic studies,[4] have resulted in broad application of the Ramberg–Bäcklund reaction to the preparation of many olefins, both cyclic and acyclic, which would be difficult to prepare by other methods.[5]

In the present instance, we felt that the α-halo sulfone rearrangement could offer an attractive opportunity for facile synthesis of bicyclopropylidene (**1**).

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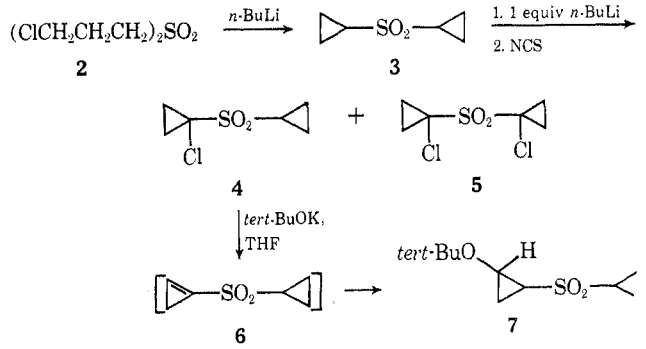
Hopefully, the approach would be entirely general in nature, in constrast to the limited number of highly specific methods known to date for this class of compounds.[6]

The scheme began with the *n*-butyllithium-induced cyclization of readily available γ,γ′-dichlorodipropyl sulfone (**2**) to give dicyclopropyl sulfone (**3**) in 85% yield. The nmr spectrum ($CDCl_3$) featured a multiplet of area 2 at δ 2.50 attributable to the α-sulfonyl protons and a second multiplet of area 8 centered at δ 1.08 for the remaining cyclopropyl hydrogens. Chlorination of sulfone **3** could be effected by initial treatment with slightly more than 1 equiv of *n*-butyllithium, followed by inverse addition of the α-sulfonyl carbanion



solution to excess *N*-chlorosuccinimide. Under these somewhat limiting conditions, the α,α′-dichloro derivative was produced in low (6%) yield. The nmr spectrum of this substance in deuteriochloroform was devoid of peaks in the δ 2.5–3.5 region; rather, two multiplets of equal area were displayed at approximately δ 1.97 and 1.56 for the two nonequivalent sets of ring protons. As expected, this method of chlorination also did give rise to the desired α-chloro sulfone (**4**) in fair (27%) yield. Its nmr spectrum in $CDCl_3$ displayed multiplets centered at δ 2.70 (1 H), 1.76 (2 H), 1.47 (2 H), and 1.18 (4 H), in full agreement with the structural assignment.

At the outset, sulfone **4** was found to be quite stable to the "normal" conditions of the α-halo sulfone rearrangement. Thus, **4** could be recovered intact from prolonged exposure to refluxing solutions of aqueous potassium hydroxide (1.2 *N*, 24 hr) and methanolic sodium methoxide (7 hr). Furthermore, it was noted that addition of *n*-butyllithium to dimethyl ether solutions of **4** at −20°, followed by controlled removal of low boiling components, afforded no volatile product other than solvent. In the presence of powdered potassium *tert*-butoxide in tetrahydrofuran at room temperature, however, **4** reacted readily to give not **1** but β-*tert*-butoxydicyclopropyl sulfone (**7**). The presence in **7** of the indicated β substituent is clearly revealed by the combination of a one-proton multiplet at δ 3.81, a two-proton multiplet at 2.20–2.70, a five-proton multiplet in the 0.80–1.70 region, and a sharp singlet (9 H) at 1.30.

It follows from these observations that **4** is particularly resistant to the α-halo sulfone rearrangement. Instead, potassium *tert*-butoxide is seen to promote dehydrochlorination to cyclopropene **6** and subsequent Michael addition of liberated *tert*-butyl alcohol to this reactive intermediate.[7] The inability of **4** to undergo

(1) This is paper XVI in the series entitled "α-Halo Sulfones." For the previous paper, see L. A. Paquette and R. W. Houser, *J. Amer. Chem. Soc.*, **93**, 944 (1971).

(2) NDEA Fellow, 1967–1970.

(3) L. Ramberg and B. Bäcklund, *Ark. Kemi, Mineral. Geol.*, **13A**, 27 (1940); *Chem. Abstr.*, **34**, 4725 (1940).

(4) For comprehensive reviews of this subject, see (a) L. A. Paquette, *Accounts Chem. Res.*, **1**, 209 (1968); (b) L. A. Paquette, *Mech. Mol. Migr.*, **1**, 121 (1968); (c) F. G. Bordwell, "Organosulfur Chemistry," M. J. Janssen, Ed., Interscience, New York, N. Y., 1967, Chapter 16.

(5) (a) L. A. Paquette, *J. Amer. Chem. Soc.*, **86**, 4383 (1964); (b) N. P. Neureiter, *J. Org. Chem.*, **30**, 1313 (1965); (c) L. A. Paquette and J. C. Philips, *Tetrahedron Lett.*, 4645 (1967); (d) E. J. Corey and E. Block, *J. Org. Chem.*, **34**, 1233 (1969); (e) L. A. Paquette and R. W. Houser, *J. Amer. Chem. Soc.*, **91**, 3870 (1969); (f) L. A. Paquette and J. C. Philips, *Chem. Commun.*, 680 (1969); (g) L. A. Paquette and J. C. Philips, *J. Amer. Chem. Soc.*, **91**, 3973 (1969); (h) R. E. Wingard and R. W. Houser, *ibid.*, in press.

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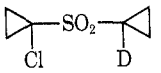
(7) A number of reports have appeared in which dehydrohalogenation of halo- and dihalocyclopropanes to cyclopropene intermediates has been achieved in somewhat analogous fashion: (a) T. C. Shields and P. D. Gardner, *J. Amer. Chem. Soc.*, **89**, 5425 (1967); (b) S. W. Tobey and R. West, *ibid.*, **88**, 2478 (1966); (c) K. B. Wiberg, R. K. Barnes, and J. Albin, *ibid.*, **79**, 4994 (1957); (d) T. C. Shields, B. A. Loving, and P. D. Gardner, *Chem. Commun.*, 556 (1967).

transposition to bicyclopropylidine (**1**) cannot be rationalized on the basis of an insufficient concentration of α-sulfonyl carbanion. Evidence is available that cyclopropyl sulfones possess acidity nearly equal to that of related acyclic structures.[8] In the present work, **4** was found to undergo ready hydrogen–deuterium exchange in $NaOCH_3$–CH_3OD to give **8**.



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This is tantamount to surmising that the energy barrier is encountered in the requisite intramolecular nucleophilic displacement of chloride ion. This conclusion would seem warranted in view of the established unreactivity of cyclopropyl halides and sulfonate esters toward displacement reactions, due to the adverse hybridization characteristics of external bonds attached to three-membered rings[9] (I strain).[10] A consequence of this conclusion is that molecules such as α-chlorocyclohexyl cyclopropyl sulfone might be expected to afford the corresponding methylenecyclopropane when treated with base because the I strain factor has now been eliminated. This point remains to be tested.

Experimental Section

Dicyclopropyl Sulfone (3).—A 1.6 *M* hexane solution of *n*-butyllithium (130 ml, 0.21 mol) was added dropwise under a nitrogen atmosphere to a solution of 20.0 g (0.092 mol) of γ,γ'-dichlorodipropyl sulfone (**2**)[11] in 250 ml of anhydrous tetrahydrofuran. After stirring the yellow solution at room temperature for 1 hr, the solvent was removed *in vacuo* and the residue was taken up in 100 ml of water and 100 ml of methylene chloride. The water phase was extracted with methylene chloride (two 50-ml portions) and the combined organic layers were dried, filtered, and evaporated. Crystallization of the residual oil from ethanol at $-10°$ afforded 11.1 g (84.5%) of **3** as white crystals: mp 69–70°; $\nu_{max}^{CHCl_3}$ 1323, 1287, and 1135 cm^{-1}.

Anal. Calcd for $C_6H_{10}O_2S$: C, 49.29; H, 6.89; S, 21.93. Found: C, 49.25; H, 6.92; S, 21.71.

Chlorination of 3.—To a solution of 2.0 g (13.7 mmol) of **3** in 150 ml of anhydrous tetrahydrofuran at room temperature under a nitrogen atmosphere was added 9.5 ml (15.0 mmol) of 1.6 *M* *n*-butyllithium in hexane. After 15 min, this solution was added dropwise to a stirred slurry of 10.0 g (75.0 mmol) of *N*-chlorosuccinimide in 250 ml of tetrahydrofuran cooled to 0° under a nitrogen atmosphere. The mixture was stirred at room temperature for 2 hr, filtered, and concentrated *in vacuo*. The resultant semisolid was triturated with 100 ml of methylene chloride and filtered. The filtrate was washed with 10% sodium hydroxide solution (three 100-ml portions) and water, dried, and evaporated to give an oil which was chromatographed on silica gel. Elution with ether–petroleum ether mixtures of increasing polarity caused **5** to be eluted first, 180 mg (6.1%). This dichloro sulfone was obtained as colorless crystals: mp 76–77°, from ether–petroleum ether; $\nu_{max}^{CHCl_3}$ 1325 and 1120 cm^{-1}.

Anal. Calcd for $C_6H_8Cl_2O_2S$: C, 33.47; H, 3.75; S, 14.91. Found: C, 33.43; H, 3.81; S, 14.83.

The less rapidly eluted product was identified as **4**, 660 mg (26.8%). Molecular distillation of the initial oil at 70° (0.05 mm) afforded a crystalline distillate, recrystallization of which from ethyl acetate–hexane afforded a white solid: mp 46–47°; $\nu_{max}^{CHCl_3}$ 1323, 1300, and 1130 cm^{-1}.

Anal. Calcd for $C_6H_9ClO_2S$: C, 39.89; H, 5.02; S, 17.75. Found: C, 39.89; H, 5.04; S, 17.25.

Continued elution afforded 330 mg (16.5%) of recovered **3**.

β-*tert*-Butoxydicyclopropyl Sulfone (7).—To a solution of 1.13 g (6.25 mmol) of **4** in 4 ml of anhydrous tetrahydrofuran cooled to 0° under a nitrogen atmosphere was added 2.0 g (18.0 mmol) of powdered potassium *tert*-butoxide in small portions. The resulting mixture was stirred at ambient temperature for 3 hr and then concentrated by distillation with the aid of a nitrogen stream. The distillate was collected in a trap cooled in Dry Ice–acetone, analyzed by gas chromatography, and found to contain only tetrahydrofuran and *tert*-butyl alcohol. The residue was treated with 25 ml of water and 25 ml of ether. The ether layer was separated, dried, and evaporated. Molecular distillation of the resultant oil at 95–98° (0.05 mm) gave 1.12 g (82.3%) of **7** as a colorless liquid: $\nu_{max}^{CHCl_3}$ 1315, 1295, and 1140 cm^{-1}.

Anal. Calcd for $C_{10}H_{18}O_3S$: C, 55.01; H, 8.31; S, 14.69. Found: C, 55.24; H, 8.49; S, 14.59.

Deuterium Exchange of 4.—A solution of 205 mg (1.4 mmol) of **4** and sodium methoxide (prepared from 206 mg of Na) in 5 ml of CH_3OD was heated at reflux for 6 hr, cooled, and quenched by the addition of 1 ml of deuterioacetic acid. The solvent was removed *in vacuo* and the residue was taken up in 25 ml of methylene chloride and 25 ml of water. The organic layer was dried, filtered, and evaporated to yield 150 mg of **8**: $\delta_{TMS}^{CDCl_3}$ 1.76 (m, 2 H), 1.47 (m, 2 H), 1.18 (m, 4 H), and no visible absorption at 2.70.

Registry No.—**4**, 27531-50-6; **5**, 27531-51-7; **7**, 27531-52-8.

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