232°).[13] Chromium(II) acetate[15] in ethyl alcohol smoothly reduced epoxy ketone 7 (70 mg) to an easily separable mixture of hydroxy ketone 8 (42 mg, prisms from chloroform–methanol, mp 235–239°)[13] and canarigenone (19 mg). Selective reduction of ketone 8 (30 mg) in ethyl alcohol with Urushibara[16] nickel-A completed synthesis of periplogenin (**1c**, 26 mg, from methanol, mp 227–234°, lit.[7] mp 138–232°).

The syntheses of canarigenin, periplogenin, and uzarigenin just described should enhance the availability of these three cardenolides for biological evaluation.

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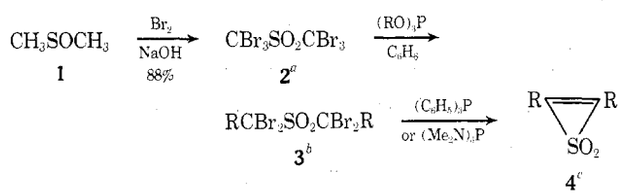
Synthesis of Alkyl-Substituted Thiirene Dioxides

Summary: A new synthesis of dialkylthiirene 1,1-dioxides *via* debromination of bis(α,α-dibromoalkyl) sulfones by means of trisubstituted phosphines is reported.

Sir: Previously the synthesis of the theoretically interesting and synthetically useful diaryl, aryl alkyl, and dialkylthiirene 1,1-dioxides has been described.[1] Unfortunately, derivatives bearing alkyl substituents have been obtained so far only *via* sulfene and diazoalkane intermediates and therefore are not readily available on a large scale either for an extensive study of their properties or as precursors of other useful synthetic intermediates. With this deficiency in mind we now describe a new route to the dialkyl thiirene dioxides **4** which makes these compounds as easily obtainable as the diaryl analogs. Central to the new approach is the 1,3-elimination[2] of bromine from a bis(α,α-dibromoalkyl) sulfone by means of triphenylphosphine or a tris(dialkylamino)phosphine [*e.g.*, **3** → **4**; R = CH_3 (50%); R = CH_3CH_2 (89%)].

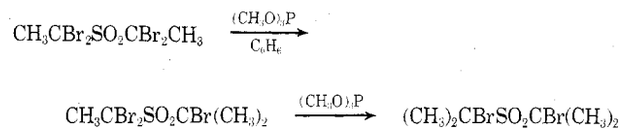
Scheme I



[a] Prepared by a modification of the methods of W. V. Farrar [*J. Chem Soc.*, 508 (1956)] and H. Liebig and H. Pfetzing [German Patent 1,256,216; *Chem. Abstr.*, **69**, 18609 (1968)]. [b] **R** = Et, 70% yield; mp 101.5–102°; nmr ($CDCl_3$) δ 1.42 (t, 3 H), 3.02 (q, 2 H). [c] R = Et, 89% *via* $(Me_2N)_3P$ at −70°; liquid; nmr ($CDCl_3$) δ 1.30 (t, 3 H), 2.75 (q, 2 H). Thermolysis (100°) gave 3-hexyne (90%).

To be useful this method requires a simple synthesis of the tetrabromo sulfones **3**, and such a method has now been developed on the basis of a novel but obscure reaction first described in the patent literature.[3] Adapting Szabo's method for the synthesis of the corresponding tetrachloro analogs, reaction of trimethyl and triethyl phosphite with bis(tribromomethyl) sulfone (**2**) gives sulfone **3** (R = Me or Et). In addition to its importance for the preparation of the vinylene sulfones, this unique method of carbon–carbon bond formation combined with conversion to **4** and subsequent facile thermal cycloelimination of sulfur dioxide represents a useful route to internal acetylenes. Although it was not possible to stop the alkylation of **2** by trimethyl phosphite with the introduction of a single methyl group, it was thereafter possible to introduce selectively the third and fourth methyl groups (Scheme II). Tri- and dibromo sulfones such as **5** and **6** are potentially of interest as precursors of olefins by extension of the present process.

Scheme II



[a] Yield 80%; mp 126–127°; nmr ($CDCl_3$) δ 2.48 (s, 6 H), 3.01 (s, 3 H). [b] Yield 90%; mp 129–130°; nmr ($CDCl_3$) δ 2.30 (s).

This new method can also be applied to the synthesis of cyclopropenones although in the case of the dimethyl derivative the yields obtained so far *via* **7** have been very poor (<2%). On the other hand, treatment of **8**[4] with a 1:1

$CH_3CBr_2COCBr_2CH_3$ (7) $C_6H_5CBr_2COCHBrC_6H_5$ (8)

mixture of tris(dimethylamino)phosphine and triethylamine gave diphenylcyclopropenone in 60% yield. Optimizing the yields in the dialkyl cases would make this a valuable route to the otherwise difficultly accessible aliphatic cyclopropenones.[6] Sample experimental procedures follow.

Preparation of $CH_3CBr_2SO_2CBr_2CH_3$. A solution of 16.6 g of $(MeO)_3P$ in 30 ml of dry benzene was added dropwise (15 min) to a stirred solution of 37.9 g of $CBr_3SO_2CBr_3$ in 125 ml of benzene. The temperature rose to 80°. After 1 hr at room temperature the solution was washed with water and 10% $NaHCO_3$, dried ($MgSO_4$), and concentrated to 50 ml *in vacuo*. Dilution with 300 ml of cold hexane (0°) and recrystallization of the precipitated solid from benzene–hexane (1:2) gave 20 g (70%) of the sulfone, mp 142–143°, nmr ($CDCl_3$) δ 3.15 (s, CH_3).

Preparation of Dimethylthiirene Dioxide. A solution of 8.76 g of **3** (R = Me) in 150 ml of dry CH_2Cl_2 was treated (15 min) at −40 to −30° with 10.48 g of triphenylphosphine in 50 ml of CH_2Cl_2. The solution was warmed to 0° for 1 hr and cooled to −10°; 1.44 g of H_2O was added with stirring. The mixture was allowed to warm to room temperature, the solvent evaporated, and the white solid extracted with six 15-ml portions of H_2O. The combined water extracts were added to 300 ml of CH_2Cl_2; the solution was cooled to 0° and solid $NaHCO_3$ added until gas evolution ceased. Anhydrous $MgSO_4$ was then added (keeping the temperature below 10°) until the drying agent formed a solid mass. The CH_2Cl_2 was decanted and a fresh portion of CH_2Cl_2 (300 ml) used to extract the residue. Evaporation of the combined CH_2Cl_2 solutions gave 1.2 g (50%) of the vinylene sulfone, mp 100.5–101.5° dec (lit.[1] mp 101–101.5° dec).

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(4) The compound reported in the literature[5] as $\alpha,\alpha,\alpha',\alpha'$-tetrabromodibenzyl ketone may in fact be the tribromo derivative **8**. In our hands all attempts to prepare the tetrabromo ketone gave only the tribromo derivative.
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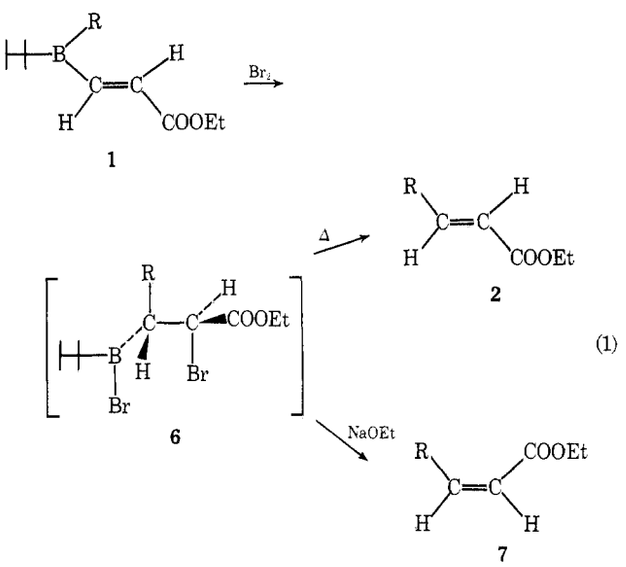
A Novel Stereoselective Synthesis of (*E*)- and (*Z*)-α,β-Unsaturated Carboxylic Esters *via* Hydroboration

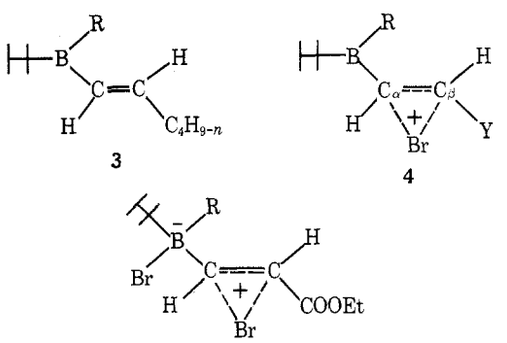
Summary: Treatment of thexylalkyl(β-carbethoxyethenyl)-boranes (1) with 1 equiv of bromine followed by refluxing produces the ethyl esters of (*E*)-3-alkylpropenoic acids (2) in good yields, whereas the bromination of 1 followed by the addition of sodium ethoxide provides the *Z* isomers of **2**.

Sir: We wish to report unique results of the bromination of 2,3-dimethyl-2-butylalkylalkenylboranes (thexylalkylalkenylboranes, 1), which permit a convenient stereoselective synthesis of either (*E*)- or (*Z*)-α,β-unsaturated carboxylic esters with the possibility of incorporating stereochemically defined groups in the β position.



We have recently found that the hydroboration of ethyl propiolate, with 2,3-dimethyl-2-butylmonoalkylboranes (thexylmonoalkylboranes)[1] cleanly produces **1**.[2] Treatment of **1** with 1 equiv of bromine followed by refluxing permits coupling of the alkyl group (R) and the β-carbethoxyethenyl group to form (*E*)-α,β-unsaturated carboxylic acid esters (**2**) in a highly stereoselective manner (>95%). The experimental results are summarized in Table I.

The results are unexpected, since the bromination of alkenylboranes are known to produce the corresponding alkenyl bromides.[3] Indeed, the bromination of **3** produces predominantly a mixture of (*E*)- and (*Z*)-alkenyl bromides. Therefore, the presence of the β-carbethoxy group must be responsible for diverting the course of the reaction.



Y = C_4H_{9}-*n* or COOEt