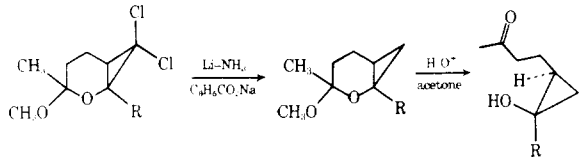
that its rearrangement product (*E*)-3-chloro-3-octene-2,7-dione (**5b**) is also isolated after acetylation.

(10) Since we have demonstrated [A. J. Duggan and S. S. Hall, *J. Org. Chem.*, **40**, 2238 (1975)] that the dichlorocarbene adducts can be reduced to 3-alkoxy-2-oxanorcaranes, this procedure constitutes a synthesis of the *cis*-3-(3-ketobutyl)cyclopropanols as well.



(11) L. Skattebøl, *J. Org. Chem.*, **31**, 1554 (1966).

(12) (a) E. B. Whipple, J. H. Goldstein, and G. R. McClure, *J. Am. Chem. Soc.*, **82**, 3811 (1960); (b) E. B. Whipple, J. H. Goldstein, and L. Mandell, *ibid.*, **82**, 3010 (1960).

(13) (a) R. C. DeSelms and U. T. Kreibich, *J. Am. Chem. Soc.*, **91**, 3659 (1969); (b) T. Ando, H. Yamanaka, and W. Funasaka, *Tetrahedron Lett.*, 2587 (1967); (c) L. Ghosez, P. Laroche, and G. Slinckx, *ibid.*, 2767 (1967); (d) W. F. Sliwinski, T. M. Su, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **94**, 133 (1972), and references cited therein; (e) D. B. Ledlie and W. H. Hearne, *Tetrahedron Lett.*, 4837 (1969).

(14) (a) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965); (b) H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, **87**, 2045 (1965); (c) P. v. R. Schleyer, W. F. Sliwinski, G. W. Van Dine, U. Schöllkopf, J. Paust, and K. Fellenberger, *ibid.*, **94**, 125 (1972), and references cited therein; (d) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Verlag Chemie, Weinheim/Bergstr., Germany, 1970, p 46; (e) C. H. DePuy, L. G. Schnack, J. W. Hausser, and W. Wiedemann, *J. Am. Chem. Soc.*, **87**, 4006 (1965).

(15) The IR spectra were determined with a Beckmann Model IR-9 infrared recording spectrophotometer. The UV spectra were determined with a Carey Model 14 ultraviolet recording spectrophotometer. The NMR spectra were determined at 100 MHz with a Varian Associates Model HA-100 NMR spectrometer, and decoupling was determined with a Varian Associates Model XL-100 NMR spectrometer. The chemical shifts are expressed in δ values (parts per million) relative to a Me_4Si internal standard. The mass spectra were obtained with a Consolidated Electronics Corp. Model 110-21B and a Varian Associates Model CH5 mass spectrometer. Gas chromatographic analyses (GLC) were performed on a Hewlett-Packard Model 402 high-efficiency chromatograph with a flame ionization detector attached to a Hewlett-Packard Model 3380A integrator.

(16) Data on **3a** (crude): IR (film) 3400 (br), 1717 cm^{-1}; NMR (60 MHz, $CDCl_3$) δ 4.00 (1 H, br s, exchanges in D_2O), 3.67 (1 H, d, J = 7.5 Hz), 2.87–2.57 (2 H, m), 2.10 (3 H, s), 2.00–1.37 (3 H, m).

(17) Data on **3b** (crude): IR (film) 3400 (br), 1715 cm^{-1}; NMR (60 MHz, CCl_4) δ 4.16 (1 H, br s, exchanges in D_2O), 2.63 (2 H, superficial t, J = ~7 Hz), 2.17 (3 H, s), 1.58 (3 H, s) superimposed on 2.0–1.4 (3 H, m).

Facile Product Isolation from Organostannane Reductions of Organic Halides

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The reduction of organic halides by organostannanes, first reported by vanderKerk et al.,[2] has subsequently found numerous applications. The reduction product has generally been separated from the organotin halide byproduct by distillation, gas chromatography, selective extraction, column chromatography, sublimation, a combination of some of these techniques, or in an unspecified manner.[3] We would like to report a facile, general method for the isolation of reduction products from the concomitantly formed organotin halide byproducts (eq 1).

$$\text{>C–X} + \text{>Sn–H} \rightarrow \text{>C–H} + \text{>Sn–X} \qquad (1)$$

In general, the reactants and products of the reduction reaction are all soluble in nonpolar organic solvents, and a simple solubility-based separation of the reduction product and the organotin halide cannot be achieved. In contrast to organotin chlorides, bromides, and iodides, trialkyl- and triaryltin fluorides are high melting, nonvolatile, insoluble (in both organic solvents and in water), "polymeric" materials.[4]

The desired separation of reduction product and organotin halide can be accomplished by conversion of the organotin halide (R_3SnX; X = Cl, Br, I) to the insoluble organotin fluoride by simply "extracting" the reduction mixture, dissolved in a nonpolar solvent, with a solution of potassium fluoride in water (eq 2). The original organotin halide is converted to an insoluble (in either the organic or aqueous phase) organotin fluoride which can be readily separated by filtration. The organic layer can be separated and dried and the solvent removed to yield the reduction product.[5]

$$R_3SnX + KF_{aq} \rightarrow R_3SnF\downarrow + KX_{aq} \qquad (2)$$

X = Cl, Br, I

As an example, the reduction of 1,3,5,7-tetrabromoadamantane to adamantane-*1,3,5,7-*d_4 in quantitative (crude) and 92% (isolated) yield is reported below. We suggest that this technique is of general utility and that it markedly facilitates product isolation in organostannane reductions.[6,7]

Experimental Section

Adamantane-*1,3,5,7-*d_4 (**1**) was prepared by the reaction (under nitrogen) of 9.5 g (0.021 mol) of 1,3,5,7-tetrabromoadamantane[8] with 25.0 g (0.086 mol) of tri-*n*-butyltin deuteride[9] in 100 mL of dry benzene at reflux for 24 h. After cooling, the benzene was removed on a rotary evaporator and the resultant residue was dissolved in 100 mL of ether. The ethereal solution was treated with excess KF in water (~10 g in 100 mL). The precipitated tri-*n*-butyltin fluoride was removed by filtration at reduced pressure, and the ether layer of the filtrate was separated and dried ($MgSO_4$). Removal of the solvent yielded 2.90 g (quantitative yield) of crude **1**; subsequent sublimation of the crude product yielded 2.70 g (92%) of **1**, mp 268–269 °C (sealed tube) [lit.[10] mp 269.6–270.8 °C (sealed tube)]. NMR and mass spectral analyses indicated ~95% d_4 incorporation.[11]

Acknowledgment. We thank the National Science Foundation for support of this work (Grant No. CHE77-07808).

Registry No.—**1**, 19215-02-2; 1,3,5,7-tetrabromoadamantane, 7314-86-5; tri-*n*-butyltin deuteride, 6180-99-0; tri-*n*-butyltin fluoride, 1983-10-4.

Supplementary Material Available: A complete list of references to organotin hydride reductions of alkyl halides to late 1977 (3 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Address correspondence to this author at Tulane University.

(2) G. J. M. vanderKerk, J. G. Noltes, and J. G. A. Luitjen, *J. Appl. Chem.*, **7**, 366 (1957).

(3) A complete list of references (ca. 125) is not presented here but is available as supplementary material. See paragraph at the end of paper about supplementary material.

(4) The tin atoms in solid trialkyltin fluorides are pentacoordinate: e.g., the crystal structure of $(CH_3)_3SnF$ consists of planar $(CH_3)_3Sn$ units linked by interspersed (nonequivalent) fluorines $[\cdots(CH_3)_3Sn\cdots F\cdots(CH_3)_3Sn\cdots F)_n\cdots]$: H. C. Clark, R. J. O'Brien, and J. Trotter, *Proc. Chem. Soc., London*, 85 (1963); *J. Chem. Soc.*, 2332 (1964); K. Yasuda, Y. Kawasaki, N. Kasai, and T. Tanaka, *Bull. Chem. Soc. Jpn.*, **38**, 1216 (1965). Similarly, solid dimethyltin difluoride exists as an infinite two-dimensional array of pentacoordinate Sn atoms: E. O. Schlemper and W. C. Hamilton, *Inorg. Chem.*, **5**, 995 (1966).

(5) Organotin halide impurities occurring in preparations of tetraalkyl and tetraaryl organotin compounds have been removed by a similar procedure; see W. P. Neumann, "The Organic Chemistry of Tin", Interscience, New York, 1970, pp 23 and 49.

(6) A similar reaction in which the product was sublimed directly from the reaction mixture yielded only 34% of the theoretical amount of product. It should be noted that substantially higher yields have been reported in similar reactions; e.g., adamantane-d_1 has been isolated in ~90% yield from the reduction of adamantyl bromide with tri-*n*-butyltin deuteride by a sublimation procedure: E. W. Della and H. K. Patney, *Synthesis*, 251 (1976).

(7) An alternate procedure for the reduction of alkyl halides employing lithium aluminum hydride and catalytic amounts of organotin halides has been reported [H. G. Kuivila, *Adv. Organomet. Chem.*, **1**, 47 (1964)], but this modification has not found general use.

(8) H. Stetter and C. Wulff, *Chem. Ber.*, **93**, 1366 (1960).

(9) Alfa Inorganics, Inc., product employed without further purification.

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(10) P. v. R. Schleyer, *J. Am. Chem. Soc.*, **79**, 3292 (1957).
(11) **Note Added in Proof:** A procedure similar to that reported here has appeared since submission of this work (D. Milstein and J. K. Stille, *J. Am. Chem. Soc.*, **100**, 3636 (1978)).

Branching Strategy in Organic Synthesis. A Versatile Ketone to Enone Homologation

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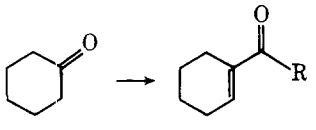
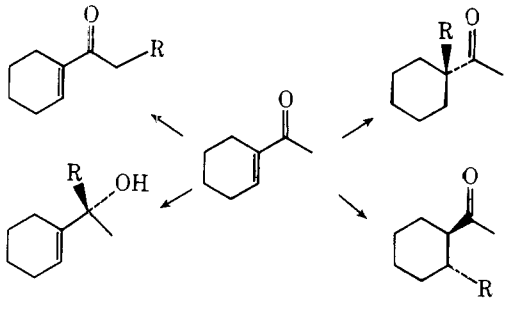
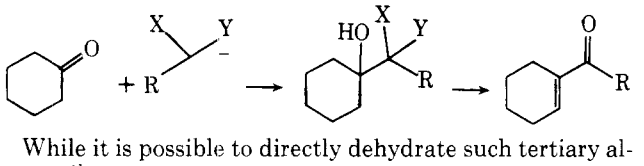
The delineation of new strategies for the construction of carbon–carbon bonds is fundamental to the development of synthetic organic chemistry. We report such a strategy, a simple procedure for the conversion of a ketone to the homologated enone.[1]



We chose ketones to be the starting functionality because of their central role in organic construction. Enones were chosen for the targets because they are activated for branching at four contiguous centers.



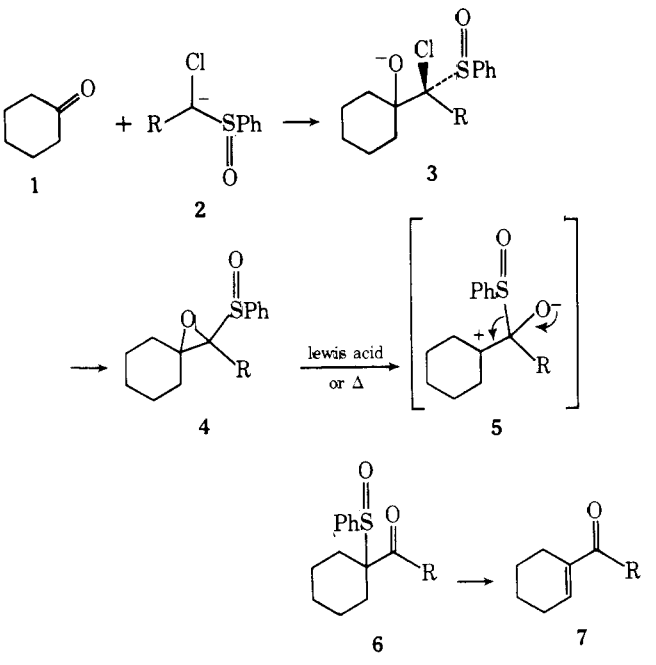
In developing this method, we sought a nucleophilic reagent the condensation of which with a ketone would lead to an adduct that could be readily carried on to the enone. There are two subproblems in the conversion of the adduct to the enone: unmasking of the carbonyl and elimination to introduce the olefin.



While it is possible to directly dehydrate such tertiary alcohols,[1b] we thought it preferable to introduce a group which could undergo elimination under very mild conditions. The phenylsulfinyl group seemed an ideal candidate.[2] The problem then was to exchange phenylsulfinyl for hydroxyl in the course of unmasking the carbonyl. The mechanism we envisioned is outlined in Scheme I.[3]

A search of the literature indicated that chlorosulfoxides are readily available from the corresponding sulfides[4] and that they can be deprotonated[5] and condensed with ketones to give epoxides.[6] There was a report[7] that **4** (R = H) smoothly thermolyzed to **7** (R = H). While this work was in progress an extensive study of this aldehyde synthesis was published.[8]

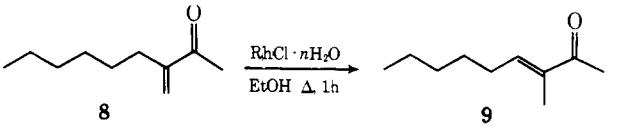
Scheme I



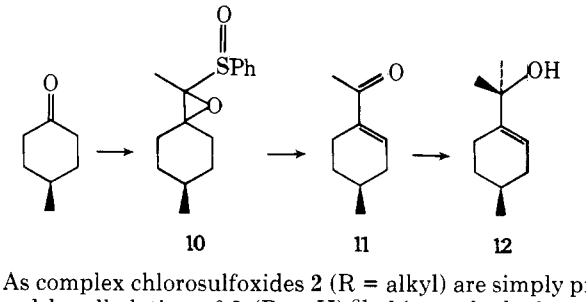
Results and Discussion

We have prepared representative chlorosulfoxides **2** (R = H, Me, Et) and investigated their condensation with typical ketones[9] and the thermolysis of the resultant sulfoxides. The results are summarized in Table I.

Entries 7 and 8 suggest an important consideration. Where two regioisomeric enones could be formed, it would be desirable to cleanly make one or the other. This has been found to be possible. Thus, reluctance to eliminate a methine proton[2] appears to be sufficient to ensure the formation of a single regioisomer (entry 7). Even more significantly, we have found that when a mixture of regioisomers is formed (entry 8), the mixture is cleanly converted to the more substituted isomer by refluxing with a catalytic amount of $RhCl_3 \cdot nH_2O$[17] in 95% ethanol for an hour.[18] Neither the disubstituted enone **8** nor the *Z* isomer of **9** could be detected in the product by NMR.



The synthetic utility of this procedure is illustrated by the preparation of 8-hydroxy-*p*-menth-3-ene (**12**), a component of the essential oil of *Mentha gentilis*.[19] Thus, condensation of **2** (R = Me) with 4-methylcyclohexanone gave the corresponding epoxysulfoxide **10**. Thermolysis of **10** led to the known[20] enone **11**, which on addition of methyllithium gave **12**.



As complex chlorosulfoxides **2** (R = alkyl) are simply prepared by alkylation of **2** (R = H),[21] this method of enone construction should be widely applicable in organic synthesis.

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