# Synthesis of Ketene Diphenyl Acetals via Decarboxylation of β-Lactones Derived from the Lithium α,α-Diphenoxy-α-lithioacetate Synthon

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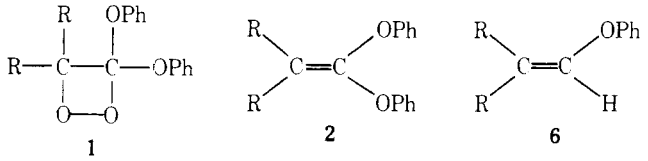
The enol carboxylate of diphenoxyacetic acid has been generated quantitatively by α-lithiation with lithium diisopropylamide in THF at −78 °C as confirmed by deuteration with deuterium oxide. Condensation of this new enolate carboxylate synthon with ketones and aldehydes affords the corresponding labile β-hydroxy acids, characterized through their methyl esters by reaction with diazomethane. β-Lactonization of the crude unstable β-hydroxy acids with benzenesulfonyl chloride and subsequent thermal decarboxylation provided a convenient and general entry into the corresponding ketene diphenyl acetals, which are difficult to prepare by other methods. In this way the diphenyl acetals of dimethyl-, tetramethylene-, phenyl-, methylphenyl-, and diphenylketenes have been prepared in 50% overall yield starting from the respective carbonyl electrophiles and the enol carboxylate.

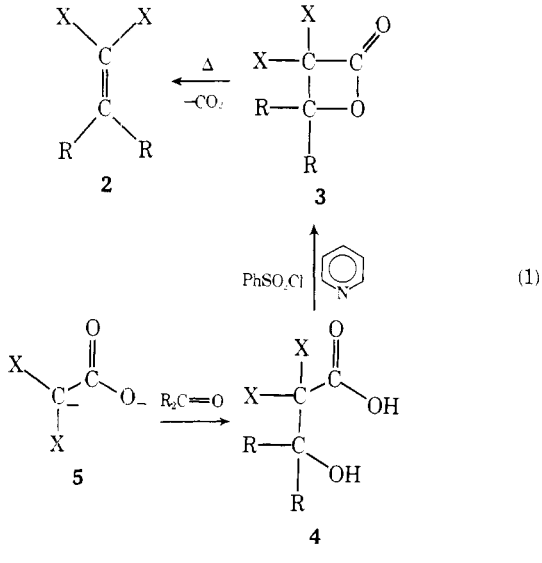
In view of our interest in "high energy" molecules such as the 1,2-dioxetanes,[2] we were interested in elucidating the mechanism of chemi-energization of electronic excitation by 3,3-diphenoxy-1,2-dioxetanes **1**. These dioxetanes should be readily available by singlet oxygenation of the respective ketene diphenyl acetals, **2**,[3] provided the latter are conveniently



**1** **2** **6**

accessible. Unfortunately, no general methods appear to be published for such ketene acetals. The corresponding ketene dialkyl acetals can be prepared by the McElvain method;[4] however, even for these a multistep process is required and the overall yields are usually low. Our attempts to adapt this method to the ketene diaryl acetals **2** met with failure, leading to intractable products. In view of the labile nature of these ketene acetals, we required a mild synthesis of **2**.

Some time ago[5] we showed that double bonds can be generated mildly and stereospecifically by thermal decarboxylation of the β-lactones **3** derived from the respective β-hydroxy acids **4**. The latter were readily prepared by condensation of the enolate carboxylates **5** with ketones (eq 1). More recently



(1)

we applied this synthetic methodology successfully to the preparation of aryl enol ethers **6**. Since the generation of α-alkoxy and α-aryloxy substituted enolate carboxylates **5** from the respective carboxylic acids with lithium diisopropylamide (LDA) was unproblematic,[6,7] we decided to generate the diphenoxy enolate carboxylate **5** (X = PhO) in this way and condense it subsequently with ketones to the respective α,α-diphenoxy-β-hydroxy acids **4** (X = PhO). Dehydrative cyclization to the β-lactones **3** (X = PhO) followed by thermal decarboxylation was expected to afford the desired ketene acetals **2** (X = PhO). Presently we describe our results on this useful method for the preparation of ketene diphenyl acetals **2**, demonstrating its convenience and generality.

## Results and Discussion

**1. Generation of Lithium α-Lithiodiphenoxyacetate (5a).** As described previously for α-phenoxyacetic acid,[7a] on treatment of diphenoxyacetic acid with LDA in THF at −78 °C the respective enolate carboxylate **5a** (X = PhO) was formed in over 95% as confirmed by deuteration with $D_2O$. *n*-BuLi could be used directly instead of LDA, but no excess could be tolerated due to carbonyl addition.

When attempting to condense the useful enolate carboxylate **5a** with acetone to afford the β-hydroxy acid **4** (X = PhO), a number of difficulties were encountered. At the low temperature (−78 °C) required to preserve **5a**, apparently most of it had precipitated from the solution. However, this problem could be readily circumvented by carrying out the lithiation in the presence of an ~10% excess of hexamethylphosphoramide (HMPA).[8] In this case a clear, yellow, and stable solution of the enolate carboxylate **5a** could be obtained and preserved for short periods of time at −78 °C. The detailed procedure is described in the Experimental Section.

**2. Condensation of Enolate Carboxylate 5a with Carbonyl Electrophiles.** The condensation of the enolate carboxylate **5a** with carbonyl electrophiles proceeded smoothly as evidenced by the immediate discharge of the yellow enolate color. The desired crude β-hydroxy-α,α-diphenoxy acids **4** (X = PhO) were obtained in quite high yield (~80–90%); however, about 5–10% starting material (diphenoxyacetic acid) was usually present as detected by $^1H$ NMR. Unfortunately, in their free state these β-hydroxy acids **4** deteriorated quickly on standing even at 0 °C by liberating phenol. Presumably, the mild carboxylic acid is acidic enough to promote hydrolysis of the acetal funtionality. Therefore, it seemed advisable to esterify these sensitive substances with diazomethane directly after acidic workup to afford the corresponding methyl α,α-diphenoxy-β-hydroxy esters **7** (X = PhO). Even these were relatively sensitive substances and deteriorated on standing at room temperature and on attempted purification by molecular distillation or silica gel chromatography. It was, therefore, not possible to prepare analytical samples, but the IR and $^1H$ NMR data and crude yields are summarized in Table I. Exceptions are the β-hydroxy ester **7a**, which crystallized after workup and thus could be rigorously charac-

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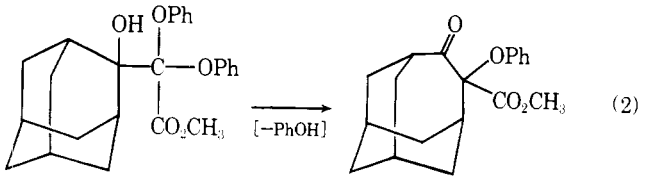
**Table I. Yields, Physical Constants, and Spectral Data for the Methyl α,α-Diphenoxy-β-hydroxycarboxylates 7**

| | $R^1$ | $R^2$ | yield, % | physical constants | type | $^1H$ NMR, δ | no. of H | multiplicity | IR C=O, $cm^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| **7a** | $CH_3$ | $CH_3$ | 80 | mp 103 °C[a] (benzene–hexane) | $R^1 + R^2$ | 1.38 | 6 | s | 1750 |
| | | | | | $OCH_3$ | 3.60 | 3 | s | |
| | | | | | OH | ? | 1 | s | |
| | | | | | $C_6H_5$ | 6.8–7.2 | 10 | m | |
| **7b** | $+CH_2+_4$ | | 82 | *b* | $R^1 + R^2$ | 1.5–2.3 | 8 | m | 1750 |
| | | | | | $OCH_3$ | 3.30 | 3 | s | |
| | | | | | OH | 5.8 | 1 | s | |
| | | | | | $C_6H_5$ | 6.7–7.4 | 10 | m | |
| **7c** | H | Ph | 79 | mp 45–46 °C[a] | $R^1$ | 5.10 | 1 | s | 1755 |
| | | | | | $OCH_3$ | 3.30 | 3 | s | |
| | | | | | OH | 2.7 | 1 | s | |
| | | | | | $C_6H_5$ | 6.7–7.4 | 15 | m | |
| **7d** | $CH_3$ | Ph | 40[c] | *b* | $R^1$ | 1.65 | 3 | s | 1755 |
| | | | | | $OCH_3$ | 3.25 | 3 | s | |
| | | | | | OH | 3.35 | 1 | s | |
| | | | | | $C_6H_5$ | 6.6–7.5 | 15 | m | |
| **7e** | Ph | Ph | 80 | *b* | $OCH_3$ | 3.30 | 3 | s | 1755 |
| | | | | | OH | 2.8 | 1 | s | |
| | | | | | $C_6H_5$ | 6.8–7.5 | 20 | m | |

[a] Satisfactory elemental analysis. [b] Sticky semisolid which resisted crystallization and decomposed on attempted distillation. [c] About 50% unreacted starting material was recovered on several attempts.

terized (cf. Table I), and **7c**, which crystallized into a waxy solid after molecular distillation.

An unexpected result was obtained with adamantanone as electrophile. After acidic workup and esterification with diazomethane, a substance was isolated which analyzed for $C_{19}H_{22}O_4$, corresponding to the expected β-hydroxy ester minus phenol. Mass spectral analysis confirmed the *m/e* 314 as parent ion. The IR lacked the OH band, but possessed a strong C=O absorption at 1750 $cm^{-1}$. The NMR exhibited the adamantyl protons as a broad band at δ 1.5–2.3, the methoxy protons as a sharp singlet at δ 3.40, and the phenyl protons as a multiplet at δ 6.5–7.2 in the expected ratio 14:3:5. On the basis of these data, the rearranged structure **8** (eq 2)




(2)

**8**

was assigned. It is still ambiguous whether the rearrangement takes place at the hydroxy ester **7** or the hydroxy acid **4** stage.

**3. β-Lactonization.** For the β-lactonization step the crude free acids were employed directly without purification in view of their labile nature. The results are summarized in Table II. The crude yield of the β-lactones **3** (X = PhO) was usually high (~80%), but it proved exceedingly difficult to purify these substances, especially for those bearing phenyl substituents at the β carbon, i.e., **3c–e.** In these cases the β-lactones decarboxylated on attempted purification at room temperature, leading to the desired ketene acetals **2** (X = PhO). As is observed usually for β-lactones, on attempted silica gel chromatography decarboxylation takes place already at subambient temperatures. Thus, unless the β-lactones readily crystallized, e.g., the dimethyl **3a** and tetramethylene **3b** derivatives, it was impossible to obtain analytically pure samples. All β-lactones showed the expected carbonyl band at 1840–1850 $cm^{-1}$, ~20 $cm^{-1}$ higher than regular β-lactones due to the inductive effect of the α-phenoxy substituents.

**4. Decarboxylation.** The ease of decarboxylation is quite dependent on substituents. As already pointed out in the previous section, the aryl-substituted derivatives **3c–e** expelled carbon dioxide already at room temperature during purification, while the dialkyl-substituted derivatives **3a** and **3b** required heating at 150 °C or higher. In fact, the dimethyl derivative **3a** sublimed at atmospheric pressure on heating with only partial decarboxylation. However, in all cases the desired ketene acetals **2** (X = PhO) were formed in high yield, better than 70% isolated product. The results are given in Table III. Even the crude product after subliming directly out of the reaction vessel was already quite pure as evidenced by IR and NMR. Either molecular distillation or fractional recrystallization afforded analytically pure ketene acetals **2.**

The C=C stretching vibrations in these ketene acetals deserve some discussion. As expected, they are at quite high energy, occurring in the carbonyl region; however, they can

**Table II. Yields, Physical Constants, and Spectral Data for the β-Lactones 3**

| | $R^1$ | $R^2$ | yield, % | physical constants | type | $^1H$ NMR, δ | no. of H | multiplicity | IR C=O, $cm^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| **3a** | $CH_3$ | $CH_3$ | 83 | mp 94–95 °C[a] (hexane) | $R^1 + R^2$ | 1.50 | 6 | s | 1840 |
| | | | | | $C_6H_5$ | 6.6–7.2 | 10 | m | |
| **3b** | $+CH_2+_4$ | | 80 | mp 79–80 °C[a] (methanol) | $R^1 + R^2$ | 1.6–2.9 | 8 | m | 1850 |
| | | | | | $C_6H_5$ | 6.8–7.4 | 10 | m | |
| **3c** | H | Ph | 75 | *b* | $R^1$ | 5.95 | 1 | s | 1850 |
| | | | | | $C_6H_5$ | 6.6–7.2 | 15 | m | |
| **3d** | $CH_3$ | Ph | 80 | *b* | | *b* | | | 1850 |
| **3e** | Ph | Ph | 78 | *b* | $C_6H_5$ | 6.6–7.8 | 20 | m | 1850 |

[a] Satisfactory elementary analysis. [b] Too unstable to be fully characterized.

Table III. Yields, Physical Constants, and Spectral Data for the Ketene Diphenyl Acetals 2

| | $R^1$ | $R^2$ | Yield, % | physical constants | type | $^1H$ NMR, $\delta$ | no. of H | multiplicity | IR C=C, $cm^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| **2a** | $CH_3$ | $CH_3$ | 95 | mp 41–42 °C[a] (subl) | $R^1 + R^2$ | 1.70 | 6 | s | 1710 |
| | | | | | $C_6H_5$ | 6.6–7.2 | 10 | m | |
| **2b** | $+CH_2+_4$ | | 90 | mp 52 °C[a] (subl) | $R^1 + R^2$ | 1.4–1.8 | 4 | m | 1725 |
| | | | | | | 2.0–2.4 | 4 | m | |
| | | | | | $C_6H_5$ | 6.6–7.2 | 10 | m | |
| **2c** | H | Ph | 70 | oil[a] | $R^1$ | 5.45 | 1 | s | 1675 |
| | | | | | $C_6H_5$ | 6.6–7.4 | 15 | m | |
| **2d** | $CH_3$ | Ph | 60 | *b* | $R^1$ | 2.10 | 3 | s | 1680 |
| | | | | | $C_6H_5$ | 6.6–7.5 | 15 | m | |
| **2e** | Ph | Ph | 80 | mp 113 °C[a] (hexane) | $C_6H_5$ | 6.6–7.4 | 20 | m | 1655 |

[a] Satisfactory elemental analyses. [b] Decomposed on attempted purification by fractional distillation.

be readily distinguished from carbonyl bands in view of their much lower intensity. It is interesting to observe (cf. Table III) that the unstrained and unconjugated ketene acetal double bond absorbs at 1710 $cm^{-1}$, as in the dimethyl derivative **2a.** However, when enclosing it in the strained five-membered ring, as in the tetramethylene derivative **2b,** this band suffers a hypsochromic shift to 1725 $cm^{-1}$, while phenyl conjugation results in a bathochromic shift to 1675–1680 $cm^{-1}$ for the monophenyl derivatives **2c** and **2d** and to 1655 $cm^{-1}$ for the diphenyl derivative **2e.**

One can forgo the β-lactone isolation step and dehydrocarbonate (loss of $H_2CO_3$)[5] the crude β-hydroxy acids **4** (X = PhO). In this case the pyridine–benzenesulfonyl chloride–hydroxy acid mixture is run at elevated temperature(~60–80 °C), leading to the desired ketene acetal in ~30–40% yield. In fact, since the β-hydroxy acids **4** are not isolated in view of their labile nature, this one-step dehydrocarbonation procedure presents a convenient and facile method for the preparation of ketene diphenyl acetals **2.** The β-lactone unit serves thus as a way to fix double bonds, and this synthetic methodology should prove useful for preparing other functionalized double bonds.

## Experimental Section

Boiling points and melting points are uncorrected. Infrared spectra were taken on a Perkin-Elmer Infracord 237B and NMR spectra on a Hitachi Perkin-Elmer R-24B spectrometer. Commercial reagents and solvents were purified to match reported physical and spectral data. Known compounds used in this research were prepared and purified according to literature procedures and will not be reproduced here. The elemental analyses were performed by the Atlanta Analytical Laboratories, Atlanta, Ga. 30366, or Galbraith Laboratories, Knoxville, Tenn. 37921.

**1. General Method for the Preparation of Lithium α,α-Diphenoxy-α-lithioacetates 5.** A 50-mL, two-neck, round-bottom flask provided with a spin bar, a rubber septum, and nitrogen inlet and outlet tubes was flame-dried while passing a vivid stream of dry nitrogen gas. Into the flask were syringed anhydrous tetrahydrofuran (THF) and the required amount of diisopropylamine to make a 1.0 M solution. While stirring magnetically, a stoichiometric amount (based on the amine) of *n*-BuLi in hexane was syringed dropwise into the −78 °C cooled solution (dry ice–acetone bath). After 5 min, the reaction mixture was allowed to warm up to room temperature, stirred for ~10 min, and cooled again to −78 °C, and one-fourth of a stoichiometric amount (based on the amine) of a ~1.0 M solution of diphenoxyacetic acid in anhydrous THF, containing 10% hexamethylphosphoramide (HMPA), was syringed slowly into the cooled reaction mixture and allowed to stir at −78 °C for 15 min. A clear yellow solution of the enol carboxylate **5** resulted, ready for use. α-Deuteration with deuterium oxide confirmed better than 95% α-lithiation.

**2. General Method for the Preparation of α,α-Diphenoxy-β-hydroxy Acids 4.** Into the solution of the enol carboxylate **5** as prepared above, contained in the same reaction flask, was syringed a twofold excess (based on **5**) of the ketone or aldehyde as an ~3.0 M solution in THF at −78 °C while stirring magnetically. After stirring at −78 °C for 30 min, the reaction mixture was worked up by pouring it onto 2–3 volumes of ice, transferring to a separatory funnel, and extracting with 2 × 10 mL of ether to remove neutral components. The aqueous layer was cooled with ice below 10 °C, acidified with 10% HCl to pH ~3 while ice cooling, immediately extracted with 5 × 15 mL of ether, quickly dried over anhydrous $MgSO_4$ (~15–30 min), and rotoevaporated (~30 °C/25 mm) to afford the crude β-hydroxy acids **4** as yellow oils. No further purification of the β-hydroxy acids **4** was attempted because these labile substances immediately released phenol by autohydrolysis of the acid-sensitive diphenyl acetal functionality. In fact, these crude β-hydroxy acids cannot be stored and must be used immediately after isolation.

For characterization, 2.0 mmol of the crude β-hydroxy acid in 10 mL of methanol was treated with an excess of diazomethane solution in ether until persistence of a yellow color. The solvents were rotoevaporated first at ~30 °C/25 mm and subsequently at ~30 °C/1.0 mm, and the crude β-hydroxy esters were purified by silica gel chromatography eluting with $CH_2Cl_2$. The results are summarized in Table I.

**3. General Method of β-Lactonization.** The crude α,α-diphenoxy-β-hydroxycarboxylic acid **4** (2.0 mmol), dissolved in 15 mL of dry pyridine, was placed into a 50-mL stoppered Erlenmeyer flask. After cooling of the contents to ~0 °C with an ice bath, 12 mmol of benzenesulfonyl chloride was added. The reaction mixture was stored overnight in a refrigerator, and afterwards it was poured onto 3–4 volumes of crushed ice and extracted with 4 × 15 mL of ether. The combined ether extracts were washed with 2 × 20 mL of saturated $Na_2CO_3$ and 1 × 20 mL of water and dried over anhydrous $MgSO_4$. The solvent was rotoevaporated, first at ~30 °C/25 mm and subsequently at 30 °C/1.0 mm, and the crude β-lactone recrystallized from the appropriate solvent. The results are given in Table II.

**4. General Method of Decarboxylation.** The β-lactone **3** (2 mmol) was placed into a 10-mL, one-neck, round-bottom flask provided with nitrogen inlet and outlet tubes. The contents were heated at the minimum temperature for decarboxylation in an oil bath until cessation of $CO_2$ evolution. After cooling to room temperature, the crude ketene acetals **2** were sublimed at reduced pressure. The results are collected in Table III.

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**Registry No.**—**2a,** 68438-61-9; **2b,** 68423-80-3; **2c,** 68423-81-4; **2d,** 68423-82-5; **2e,** 68423-83-6; **3a,** 68423-75-6; **3b,** 68423-76-7; **3c,** 68423-77-8; **3d,** 68423-78-9; **3e,** 68423-79-0; **4a,** 68423-84-7; **4b,** 68423-85-8; **4c,** 68423-86-9; **4d,** 68423-87-0; **4e,** 68423-88-1; **5,** 68423-89-2; **7a,** 68423-70-1; **7b,** 68423-71-2; **7c,** 68423-72-3; **7d,** 68423-73-4; **7e,** 68423-74-5; **8,** 68438-60-8; acetone, 67-64-1; cyclopentanone, 120-92-3; benzaldehyde, 100-52-7; acetophenone, 98-86-2; benzophenone, 119-61-9; diphenoxyacetic acid, 729-89-5; adamantanone, 700-58-3.

### References and Notes

(1) NIH Career Development Awardee, 1975–1980.
(2) W. Adam, *Adv. Hetocycl. Chem.*, **21**, 437 (1977).
(3) J. Bollyky, *J. Am. Chem. Soc.*, **92**, 3230 (1970).
(4) D. Borrmann in "Houben-Weyl, Methoden der Organischen Chemie", Vol. 7/4, Thieme Verlag, Stuttgart, Germany, 1968, pp 340–355.
(5) W. Adam, J. Baeza, and J.-C. Liu, *J. Am. Chem. Soc.*, **94**, 2000 (1972).
(6) W. Adam, L. A. Arias Encarnación, and H.-H. Fick, unpublished results.
(7) (a) W. Adam and H.-H. Fick, *J. Org. Chem.*, **43**, 772 (1978); (b) R. Bonjouklian and B. Ganem, *Tetrahedron Lett.*, 2835 (1977); (c) G. Caron and J. Lessard, *Can. J. Chem.*, **51**, 981 (1973).
(8) (a) P. L. Creger, *J. Org. Chem.*, **37**, 1907 (1972); (b) P. E. Pfeffer and L. S. Silbert, *ibid.*, **35**, 2621 (1970); (c) P. L. Creger, *J. Am. Chem. Soc.*, **89**, 2500 (1967).


# Hexachloroacetone/Triphenylphosphine: A Mild Reagent for the Regioselective and Stereospecific Production of Allylic Chlorides from the Alcohols


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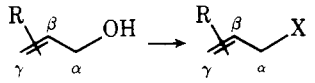
Allylic alcohols **1–16** react with hexachloroacetone/triphenylphosphine in less than 20 min at 10–15 °C to produce excellent yields of the corresponding chlorides. Isolation is accomplished simply by flash distillation. The conversion occurs with total preservation of double bond geometry and with >99% inversion of configuration for optically active alcohol **8**. All of the primary and secondary alcohols give predominantly the unrearranged chloride, the $\alpha/\gamma$ attack ratio being >90:<10 for all but **9**, **12**, **13**, and **14**; only the tertiary alcohols give mostly rearranged product. With more highly substituted systems, elimination to diene becomes an important side reaction.


The synthesis of an allylic halide from its alcohol presents regio- and stereochemical problems not encountered with saturated compounds:



(1) The transformation should be regiospecific, leading exclusively to the $\alpha$-substituted (or $\gamma$-substituted) product.

(2) The conditions must be such that stereochemistry at the $\beta,\gamma$ double bond is not lost.

(3) The synthesis should produce high optical yields when the $\alpha$ carbon is chiral.

(4) The conditions of reaction, workup, and isolation must be mild enough that neither allylic rearrangement of the product nor solvolysis/elimination occurs.

Numerous methods (of variable generality) have been developed, among which are the following: (a) reaction with conventional halide-producing reagents like $SOCl_2$[1] or $PX_3$;[2] (b) formation of a sulfonate ester[3,4] or other reactive group[5] followed by displacement with halide ion in an aprotic solvent; and (c) reaction with dimethyl sulfide and an *N*-halosuccinimide.[2b,4c,6]

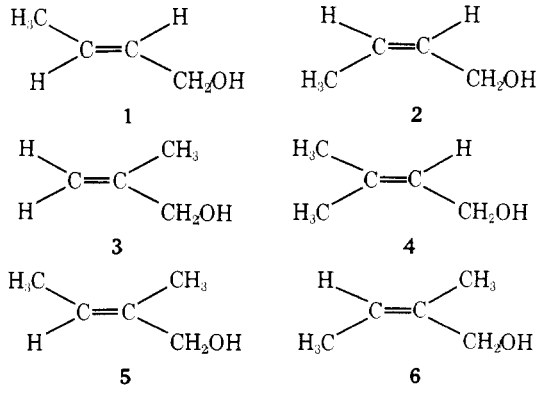
The reagent system triphenylphosphine/carbon tetrachloride and its several variants[7] have proved very versatile for the conversion of alcohols and carboxylic acids into halides,[8] the dehydration of amides and oximes to nitriles,[9] the dihalomethylenation of carbonyl groups,[10] and condensations leading to esters, amides, and peptides.[11] Application of this method to the production of allylic halides seemed most promising in light of the report by Snyder[12] that $Ph_3P/CCl_4$ transforms 2-buten-1-ol exclusively into unrearranged chloride and that only 11% of rearranged material is formed from 3-buten-2-ol. Similarly high regioselectivity has been reported for other allylic alcohols in their reactions with $Ph_3P/CX_4$.[13,3c] Nevertheless, one's enthusiasm is tempered by the fact that low-boiling allylic chlorides such as 1-chloro-2-butene (bp 85 °C (*E*), bp 84 °C (*Z*)) and 3-chloro-1-butene (bp 65 °C) are only with difficulty separable from reagent $CCl_4$ (bp 77 °C) and product $CHCl_3$ (bp 62 °C); similar isolation troubles have been noted by others.[2g,3c,14]

In connection with our study of the stereochemistry of the $S_N2'$ reaction,[15] we needed an efficient synthesis of (*S*)-(+)- or (*R*)-(−)-3-chloro-(*Z*)-1-butene-*1-d* with high optical purity and with preservation of double bond geometry. It occurred to us that we could avoid the isolation problems noted above and yet retain the excellent regioselectivity of the $Ph_3P/CCl_4$ method by replacing $CCl_4$ with a higher boiling source of positive halogen. The generally accepted mechanism[7a,16] for the $Ph_3P/CCl_4$ reaction is outlined in Scheme I. All that remain in dispute are the relative importance of paths (a) and (b) and the precise nature of the final step.[17] Since the rate-determining step appears to be the initial abstraction of "$Cl^+$" by $Ph_3P$, the rate ought to be increased dramatically if a better leaving group than $Cl_3C:^-$ were involved. The desire for a less volatile reagent having a superior leaving group led quite naturally to an investigation of hexachloroacetone (HCA)[19] as a replacement for $CCl_4$. We have, in fact, found that $Ph_3P$/HCA provides very mild conditions for the production of allylic chlorides in excellent yields with very high regio- and stereoselectivity and with great ease of purification.[20]

## Results and Discussion

We have examined the behavior of a variety of primary, secondary, and tertiary allylic alcohols (Charts I, II, and III,

Chart I

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