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(6) W. Adam, L. A. Arias Encarnación, and H.-H. Fick, unpublished results.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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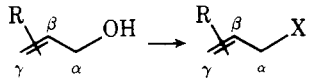
Allylic alcohols **1–16** react with hexachloroacetone/triphenylphosphine in less than 20 min at 10–15 °C to produce excellent yields of the corresponding chlorides. Isolation is accomplished simply by flash distillation. The conversion occurs with total preservation of double bond geometry and with >99% inversion of configuration for optically active alcohol **8**. All of the primary and secondary alcohols give predominantly the unrearranged chloride, the α/γ 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 α-substituted (or γ-substituted) product.

(2) The conditions must be such that stereochemistry at the β,γ double bond is not lost.

(3) The synthesis should produce high optical yields when the α 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]

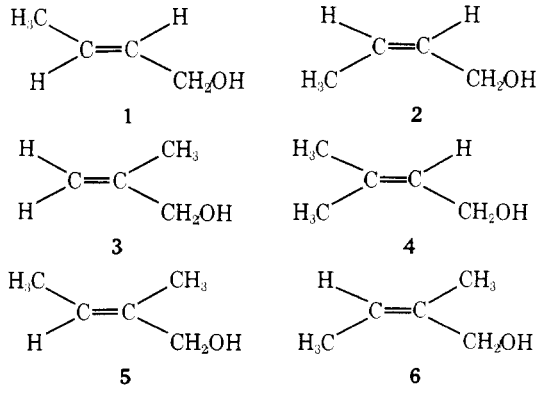
The reagent system triphenylphosphine/carbon tetrachloride and its several variants[7] have proved very versatile for the conversion of alcohols and carboxylic acids into halides,[8] the dehydration of amides and oximes to nitriles,[9] the dihalomethylenation of carbonyl groups,[10] and condensations 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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Scheme I

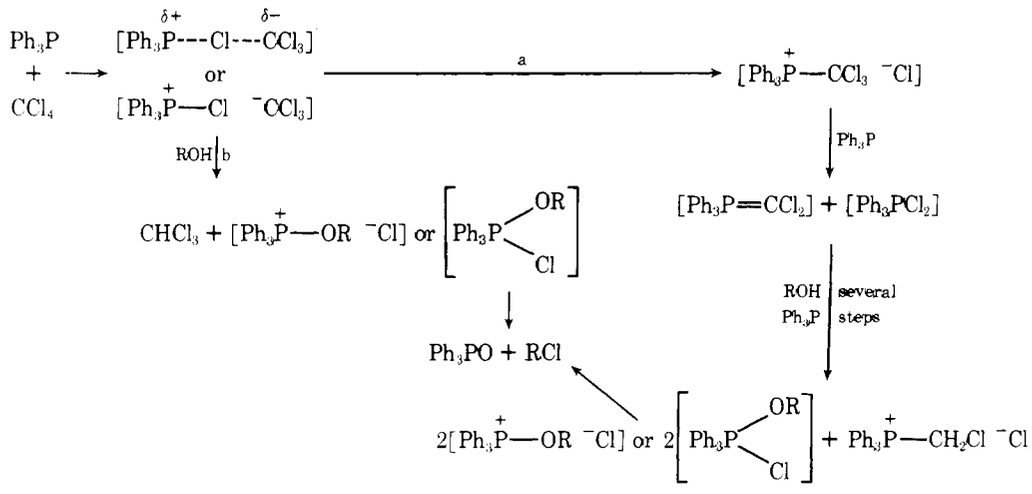


Chart II

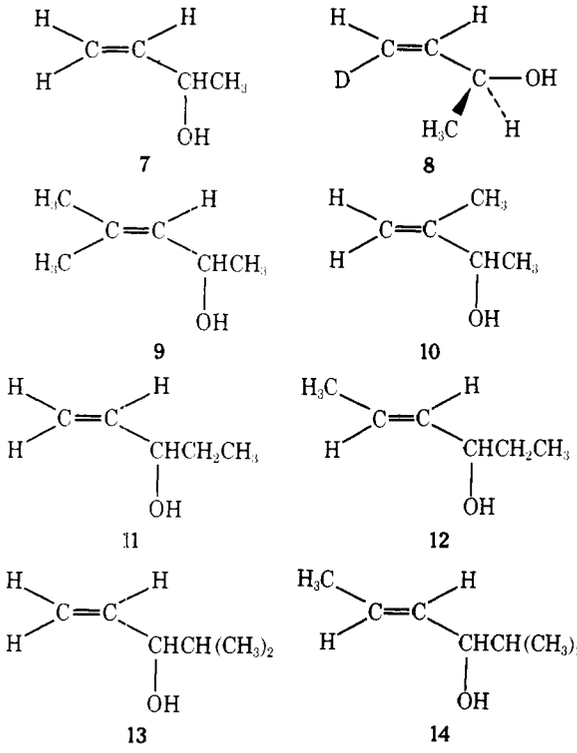
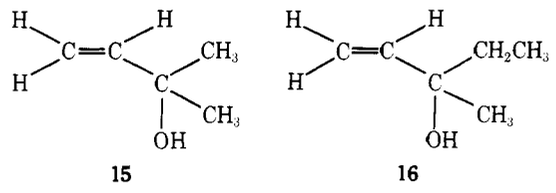


Chart III



respectively) with Ph_3P/HCA. Reaction of the alcohol in HCA solution with a small excess of Ph_3P is rapid (less than 20 min at 10–15 °C) and exothermic. Flash distillation at ambient temperature produces, in most instances, allylic chlorides as the only volatile products (accompanied by small amounts of CCl_4 in the cases of compounds **1–8**). Significantly, the high-boiling reagent HCA (bp 202 °C) and product pentachloroacetone (bp 192 °C) are left behind.

Table I is a display of the relevant data whose salient features are:

(1) The regioselectivity is very high. For primary alcohols **1, 2,** and **4–6,** the product is essentially the unrearranged chloride. For secondary alcohols **7–14,** the unrearranged chloride again predominates, although γ substituents and/or increased hindrance at C_α (**9, 12, 13,** and **14**) allow substantial quantities of rearranged product to form. Rearrangement dominates the product mixture only for tertiary alcohols **15** and **16.**

(2) Pairs of allylic isomers (**1, 2,** and **7; 4** and **15; 5, 6,** and **10**) give distinctly different chloride products, thereby demonstrating that the reaction does not proceed via a free allylic cation.

(3) Double bond geometry is quantitatively preserved (**1, 2, 5, 6, 8, 12,** and **14**) in the unrearranged chloride.

(4) Reaction of optically active alcohol **8** occurs with essentially 100% inversion of configuration.

(5) Contamination by elimination products (dienes) is a problem only with the more reactive systems; in some cases (**9** and **12**), elimination occurs only during VPC analysis.

(6) The absolute yields are very high and in many cases the crude flash distillate can be used without further purification.

(7) The reaction conditions are much milder than in the Ph_3P/CCl_4 procedure which, typically, is run at room temperature for 1–2 days or at 60–80 °C for several hours.

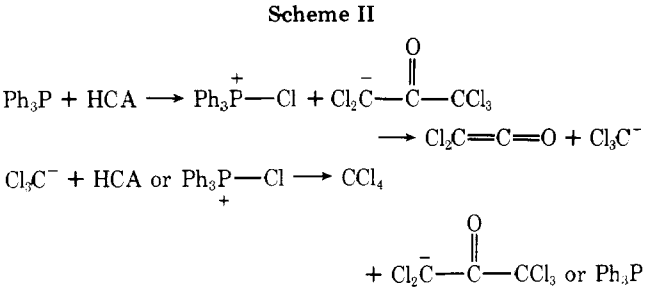
The impetus for this study, it may be recalled, was the annoying contamination of the allylic chlorides by CCl_4 and $CHCl_3$ in the Snyder procedure.[12] It is, therefore, of some concern that the reaction of Ph_3P/HCA with primary alcohols **1–6** and secondary systems **7** and **8** leads to small amounts of CCl_4 in the flash distillate. We have made the useful observation that the extent of CCl_4 production can be lessened by altering the order of mixing of the reagents (see alcohol **3** in the Experimental Section) but we have been unable to eliminate it entirely. The origin of this byproduct is unclear, although it seems certain that it arises either from reaction of Cl_3C^- with a source of "Cl^+" or from Cl^- with "Cl_3C^+". Several possible mechanisms are ruled out by the observation that Ph_3P plus HCA in the absence of alcohol produces no CCl_4, nor is there any reaction of HCA with NaCl (with or without alcohol's being present). The reasonable mechanisms in Schemes II and III have also been excluded as follows. Scheme II does not explain why an alcohol must be present; furthermore, we have been unable to trap dichloroketene when the reaction was performed in the presence of excess cyclopentadiene. Scheme III is negated by the observation that although a dilute solution of sodium 2-methyl-2-propen-1-olate in the corresponding alcohol does react with HCA producing the ester shown plus the bisallylic carbonate, the other product (in high yield) is $CHCl_3$ and not CCl_4; clearly Cl_3C^- is formed

Table I. Reactions of Allylic Alcohols with HCA/Ph_3P

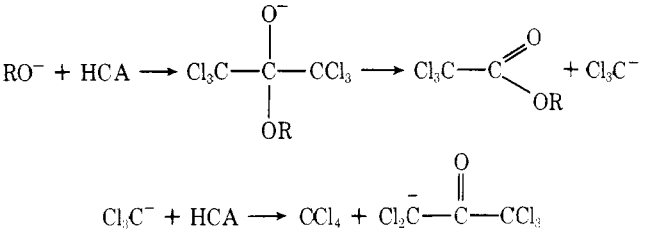
compd	registry no.	percent yield based on allylic alcohol[a] allylic chloride[b] α	γ	diene	ratio of chlorides, %[b] α	γ
1[c]	504-61-0	99.3[d,t]	0.7[u]		99.3	0.7
2[c,e]	4088-60-2	98.0[e]	0.5		99.5	0.5
3[c]	513-42-8	93.4[f,v]			*f*	
4[c]	556-82-1	91.3[w]			100	0
5[c]	497-02-9	98.5[d,x]			100	0
6[c,g]	19319-26-7	100[h]			100	0
7[c]	598-32-3	94.0	6.0[d]		94.0	6.0
8[c]	29453-55-2	94.0[i,y]	6.0[d,z]		94.0	6.0
9	4325-82-0	*j*			82[k]	18[k,d]
10	10473-14-0	92.1[aa]	3.2[l]		96.6	3.4
11	616-25-1	80.3[bb]	6.5[d,cc]	12.1[m,dd]	92.5	7.5
12	29478-27-1	80.6[n]			~67[n,d]	~33[n,d]
13	4798-45-2	27[ee]	15[ff]	61[o,gg]	64	36[d]
14	4798-60-1	*n*		*p*	~62[n,d]	~38[n,d]
15	115-18-4	21.2[hh]	43.2	17.7[q,ii]	32.9	67.1
16	918-85-4	7.1[jj]	14.6[r]	46.8[s]	32.7	67.3

[a] Absolute yields, as determined by quantitative VPC analysis of the flash distilled mixture. [b] Unrearranged chloride is designated α and its allylic isomer γ. [c] CCl_4 produced in reaction, see Experimental Section. [d] Exclusively *E* isomer. [e] A 94/6 (VPC) mixture of *Z* and *E* isomers. [f] Ratio of regioisomers not determined. [g] An 87/13 (NMR) mixture of *Z* and *E* isomers. [h] An 86/14 (VPC) mixture of *Z* and *E* isomers. [i] Exclusively *Z* isomer with >99% inverted configuration at the chiral center. [j] Yield not determined owing to instability of allylic chlorides toward VPC. [k] Determined by NMR integration of crude flash distillate. [l] A 2/1 mixture of *E* and *Z* isomers. [m] (*E*)-1,3-Pentadiene. [n] Product ratio determined by NMR integration; VPC analysis fails, owing to interconversion of α and γ isomers and elimination. [o] 4-Methyl-1,3-pentadiene. [p] An 89/11 mixture of (*E*)-2-methyl-2,4-hexadiene and (*E*)-5-methyl-1,3-hexadiene. [q] 2-Methyl-1,3-butadiene. [r] A 50/50 *Z*/*E* mixture. [s] A 21/79 mixture of 2-ethyl-1,3-butadiene and 3-methyl-1,3-pentadiene (*Z* and *E* isomers). [t] Registry no. 4894-61-5. [u] Registry no. 563-52-0. [v] Registry no. 563-47-3. [w] Registry no. 503-60-6. [x] Registry no. 23009-73-6. [y] Registry no. 29333-33-3. [z] Registry no. 68317-97-5. [aa] Registry no. 5166-35-8. [bb] Registry no. 24356-00-1. [cc] Registry no. 6261-25-2. [dd] Registry no. 2004-70-8. [ee] Registry no. 68317-98-6. [ff] Registry no. 58649-23-3. [gg] Registry no. 926-56-7. [hh] Registry no. 2190-48-9. [ii] Registry no. 78-79-5. [jj] Registry no. 1937-02-6.

Scheme II



Scheme III



but is protonated by alcohol faster than it can react with HCA. Furthermore, Scheme III requires the consumption of a quantity of alcohol equal to the quantity of CCl_4 produced, in disagreement with the nearly quantitative yields of allylic chloride (Table I). Since all three components (alcohol, Ph_3P, and HCA) are needed for CCl_4 to be formed, a variant of Scheme III would have Cl_3C^- attacking $[Ph_3P^+–Cl]$; this is, again, discredited by the high yields of allylic chloride.

Experimental Section

All ^1H-NMR spectra were obtained with a Varian T-60 spectrometer; tetramethylsilane (Me_4Si) was used as internal standard; chemical shifts are recorded in δ units, ppm downfield from Me_4Si. The ^{13}C-NMR spectra were obtained on a Nicolet TT-14 spectrometer and are recorded in δ units, ppm downfield from Me_4Si. A Rudolph MP7A41 photoelectric polarimeter was used for optical rotations. Mass spectra were recorded on a Hewlett-Packard HP-5982A GC–mass spectrometer. Analytical VPC work was accomplished using a Hewlett-Packard Model 5750 gas chromatograph with the following columns: A, 10 ft × ⅛ in. Carbowax 20M (10%) on Chromosorb W; B, 10 ft × ⅛ in. β,β′-oxydipropionitrile (5%) on Chromosorb W; C, 10 ft × ⅛ in. SE-30 (10%) on Chromosorb W. Preparative VPC separations were achieved with a Varian Aerograph Model 920 gas chromatograph and a 6 ft × ¼ in. column of SE-30 (10%) on Chromosorb W, unless otherwise noted.

General Procedure for Reaction of Allylic Alcohols. In a 100-mL round-bottomed flask equipped with magnetic stirrer, the allylic alcohol was dissolved in HCA. The clear solution was cooled to 0 °C and a slight excess (typically 10%) of Ph_3P was added in small portions over 10–20 min. The exothermic reaction was maintained at or below 15 °C by external cooling and by controlling the rate of addition. When the addition of Ph_3P was complete, the mixture was allowed to warm to room temperature over 10 min during which time a thick slurry formed. Immediate flash distillation (1–3 torr, ambient temperature) into a dry ice–acetone cooled receiver gave volatile material which was analyzed by VPC. In some instances, preparative VPC was used to separate the products.

(*E*)-2-Buten-1-ol (1). Reaction of 3.58 g (0.0496 mol) of commercial crotyl alcohol (Chemical Samples Co.) in 17 mL of HCA with 13.5 g (0.0515 mol) of Ph_3P gave 4.8 g of volatile products which analyzed (VPC, column B[21]) for 4.46 g (99.3%) of (*E*)-1-chloro-2-butene, 0.03 g (0.7%) of 3-chloro-1-butene, and 0.3 g of CCl_4; (*Z*)-1-chloro-2-butene could not be detected. ^1H NMR (CCl_4) of the major component: δ 1.76 (d, 3, J = 5 Hz, CH_3), 3.91 (dd, 2, J = 5, 2 Hz, CH_2), and 5.30–5.95 (m, 2, vinyl).

(*Z*)-2-Buten-1-ol (2). Reduction of 2-butyn-1-ol (Farchan Division, Story Chemical Co.) by Zn/Cu[22] in ethanol[23,3d] gave a 94/6 mixture (VPC, Column A) of (*Z*)- and (*E*)-2-buten-1-ol. Reaction of 1.45 g (0.0201 mol) of this mixture in 15 mL of HCA with 7.0 g (0.027 mol) of Ph_3P gave 2.25 g of volatile material which analyzed (VPC, column B[21]) for 1.78 g (98.0%) of a 94/6 mixture of (*Z*)- and (*E*)-1-chloro-2-butene, 0.01 g (0.5%) of 3-chloro-1-butene, and 0.46 g of CCl_4. ^1H NMR (CCl_4) of the major isomer: δ 1.72 (d, 3, J = 5 Hz, CH_3), 4.03 (d, 2, J = 6 Hz, CH_2), and 5.35–5.85 (m, 2, vinyl).

2-Methyl-2-propen-1-ol (3). Reaction of 7.2 g (0.10 mol) of commercial alcohol (Aldrich Chemical Co.) in 40 mL of HCA with 28 g (0.11 mol) of Ph_3P gave 10.36 g of volatile material which analyzed (VPC, column C) for 8.46 g (93.4%) of 3-chloro-2-methyl-1-propene

and 1.90 g of CCl_4. ^1H NMR (CCl_4): δ 1.83 (d, 3, J = 1 Hz, CH_3), 3.97 (s, 2, CH_2), and 4.90 and 5.07 (m, 1 each, vinyl). The yield of CCl_4 was decreased when the order of mixing of reagents was changed; addition of 6.00 g (0.0832 mol) of alcohol to 23 g (0.088 mol) of Ph_3P in 35 mL of HCA produced 7.39 g (98.0%) of allylic chloride and only 0.23 g of CCl_4.

3-Methyl-2-buten-1-ol (4). Reaction of 1.70 g (0.0197 mol) of commercial alcohol (Aldrich Chemical Co.) in 15 mL of HCA with 5.5 g (0.021 mol) of Ph_3P gave 5.21 g of volatile material which analyzed (VPC, column C) for 1.88 g (91.3%) of 1-chloro-3-methyl-2-butene, 2.95 g of CCl_4, and 0.4 g of $CHCl_3$. ^1H NMR (CCl_4): δ 1.7 (bs, 6, CH_3's), 3.97 (d, 2, J = 8 Hz, CH_2), and 5.40 (t with fine splitting, 1, J = 8 Hz, vinyl).

(*E*)-2-Methyl-2-buten-1-ol (5). Reduction of tiglic acid (Aldrich Chemical Co.) by $LiAlH_4$[13c,24] produced alcohol **5**, 3.00 g (0.0348 mol) of which in 17 mL of HCA was treated with 10.1 g (0.0385 mol) of Ph_3P. Flash distillation gave 5.83 g of material which analyzed (VPC, column C) for 3.59 g (98.5%) of (*E*)-1-chloro-2-methyl-2-butene and 2.24 g of CCl_4. ^1H NMR (CCl_4): δ 1.63 (d, 3, J = 8 Hz, terminal CH_3), 1.70 (s, 3, internal CH_3), 3.93 (bs, 2, CH_2), and 5.55 (q with fine splitting, 1, J = 7 Hz, vinyl).

(*Z*)-2-Methyl-2-buten-1-ol (6). Angelic acid was prepared by carbonation[25a] of the lithium reagent produced from (*Z*)-2-bromo-2-butene (Chemical Samples Co.) with *t*-BuLi.[25b] Reduction by $LiAlH_4$[13c,24] gave the desired alcohol as a mixture of (*Z*)-**6** and (*E*)-**5** (87/13 by NMR integration, 86/14 by VPC, column C). Reaction of 0.39 g (4.5 mmol) of this mixture in 12 mL of HCA with 4 g (15 mmol) of Ph_3P produced 0.73 g of volatile product which analyzed (VPC, column C) for 0.47 g (100%) of an 86/14 mixture of (*Z*)- and (*E*)-1-chloro-2-methyl-2-butene and 0.26 g of CCl_4. ^1H NMR (CCl_4) of the major component in the mixture: δ 1.65 (d, 3, J = 6 Hz, terminal CH_3), 1.77 (bs, 3, internal CH_3), 4.00 (s, 2, CH_2), and 5.42 (q with fine splitting, 1, J = 7 Hz, vinyl).

3-Buten-2-ol (7). Reaction of 0.84 g (0.0116 mol) of commercial alcohol (Aldrich Chemical Co.) in 8 mL of HCA with 4.6 g (0.0175 mol) of Ph_3P gave 1.1 g of volatile material which analyzed (VPC, column B[21]) for 1.02 g (94.0%) of 3-chloro-1-butene, 0.066 g (6.0%) of (*E*)-1-chloro-2-butene, and 0.011 g of CCl_4.

(*S,Z*)-(+)-3-Buten-2-ol-*4-d* (8). The optically active alcohol, 1.09 g (0.015 mol), α^{30}_D +21.04° (neat, l = 1), 76.2% optically pure,[15,26] in 20 mL of HCA was treated with 4 g (0.015 mol) of Ph_3P. Purification by preparative VPC gave (*R*)-(−)-3-chloro-(*Z*)-1-butene-*1-d*, α^{24}_D −46.13° (neat, l = 1), 75.5% optically pure.[15,26] Similarly, a sample of (*R*)-(−)-alcohol, α^{24}_D −9.2° (neat, l = 1), 33.3% optically pure, gave (*S*)-(+)-chloride, α^{24}_D +20.2° (neat, l = 1), 33.1% optically pure.

4-Methyl-3-penten-2-ol (9). Reaction of 5.0 g (0.050 mol) of the commercial alcohol (Chemical Samples Co.) in 25 mL of HCA with 14.5 g (0.055 mol) of Ph_3P gave a volatile product that was unstable to VPC analysis; under all conditions investigated, substantial elimination to dienes occurred. NMR analysis of the crude flash distillate showed no dienes and revealed an 82/18 mixture of 4-chloro-2-methyl-2-pentene and 4-chloro-4-methyl-2-pentene (presumably *E*). ^1H NMR (CCl_4) of the major component: δ 1.50 (d, 3, J = 6 Hz, –CHC**H**$_3$), 1.70 (bs, 6, allylic CH_3's), 4.62 (dq, 1, J = 10, 6 Hz, –C**H**Cl–), and 5.22 (dq, 1, J = 10, 1 Hz, vinyl). ^1H NMR (CCl_4) of the minor component (mostly obscured by the allylic isomer): δ ca. 1.6–1.7 (9, methyls) and 5.60 (m, 2, vinyl).

3-Methyl-3-buten-2-ol (10). The commercial alcohol (Polysciences, Inc.) was purified by preparative VPC (10 ft × ⅛ in. Carbowax 20M (20%) on Chromosorb W). Reaction of 3.0 g (0.035 mol) of purified material in 18 mL of HCA with 10 g (0.038 mol) of Ph_3P gave 3.49 g of volatile product which analyzed (VPC, column C) for 3.37 g (92.1%) of 3-chloro-2-methyl-1-butene, 0.080 g (2.1%) of (*E*)-1-chloro-2-methyl-2-butene, and 0.042 g (1.1%) of (*Z*)-1-chloro-2-methyl-2-butene. ^1H NMR (CCl_4) of the major component: δ 1.60 (d, 3, J = 7 Hz, –CHC**H**$_3$), 1.87 (d, 3, J = 1 Hz, allylic CH_3), 4.50 (q, 1, J = 7 Hz, –C**H**Cl–), and 4.83 and 5.02 (m, 1 each, vinyl).

1-Penten-3-ol (11). Reaction of 4.37 g (0.0507 mol) of the commercial alcohol (Chemical Samples Co.) in 17 mL of HCA with 13.5 g (0.0515 mol) of Ph_3P gave 5.1 g of volatile material which analyzed (VPC, column C) for 4.33 g (80.3%) of 3-chloro-1-pentene, 0.35 g (6.5%) of (*E*)-1-chloro-2-pentene, and 0.42 g (12.1%) of (*E*)-1,3-pentadiene. Preparative VPC led to separation of the three components. ^1H NMR (CCl_4) of the major allylic chloride: δ 0.97 (t, 3, J = 7 Hz, CH_3), 1.82 (qd, 2, J = 7, 7 Hz, CH_2), 4.19 (dt, 1, J = 7, 7 Hz, CH), 5.07 (dd, 1, J = 9, 3 Hz, *Z*-terminal vinyl), 5.17 (dd, 1, J = 17, 3 Hz, *E*-terminal vinyl), and 5.88 (ddd, 1, J = 17, 9, 7 Hz, internal vinyl). ^1H NMR (CCl_4) of the minor allylic chloride: δ 1.00 (t, 3, J = 6 Hz, CH_3), 2.07 (m, 2, –C**H**$_2$CH$_3$), 3.93 (d, 2, J = 6 Hz, –C**H**$_2$Cl), and 5.4–5.9 (m, 2, vinyl). ^1H NMR (CCl_4) of the diene: δ 1.75 (d, 3, J = 6 Hz, CH_3), 4.7–5.2 (m, 2, terminal vinyl), and 5.4–6.2 (m, 3, internal vinyl).

(*E*)-4-Hexen-3-ol (12). Reaction of 5.0 g (0.050 mol) of the commercial alcohol (Chemical Samples Co.) in 20 mL of HCA with 13.5 g (0.0515 mol) of Ph_3P gave a distillate which, according to its NMR spectrum, was a mixture of allylic chlorides, 4.76 g (80.6%). VPC analysis (column C) failed to separate the chlorides and led to substantial amounts of elimination. Preparative VPC allowed separation of the chloride and diene fractions. NMR analysis of the chloride mixture revealed an approximately 67/33 ratio of (*E*)-4-chloro-2-hexene and (*E*)-2-chloro-3-hexene. ^1H NMR (CCl_4) of the major component: δ 0.98 (t, 3, J = 6 Hz, –CH_2C**H**$_3$), 1.73 (d, 3, J = 6 Hz, allylic CH_3), ca. 1.9 (obscured, CH_2), 4.15 (dt, 1, J = 6, 6 Hz, CH), and 5.3–5.9 (m, obscured, vinyl). ^1H NMR (CCl_4) of the minor component: δ 0.98 (t, 3, J = 6 Hz, –CH_2C**H**$_3$), 1.58 (d, 3, J = 7 Hz, –CHC**H**$_3$), ca. 1.9 (obscured, CH_2), 4.42 (m, partly obscured, CH), and 5.3–5.9 (m, obscured, vinyl). ^1H NMR (CCl_4) of the diene fraction suggested an 80/20 mixture of (*E,E*)-2,4-hexadiene and (*E*)-1,3-hexadiene. ^1H NMR (CCl_4) of the diene mixture: δ 1.00 (t, J = 7 Hz, CH_3 in minor component), 1.70 (d, J = 8 Hz, CH_3's in major component), and 5.0–6.2 (vinyl).

4-Methyl-1-penten-3-ol (13). Reaction of 1.0 g (0.010 mol) of the commercial alcohol (Chemical Samples Co.) in 5 mL of HCA with 2.7 g (0.0103 mol) of Ph_3P gave 1.0 g of a volatile material which analyzed (VPC, column C) for 0.32 g (27%) of 3-chloro-4-methyl-1-pentene, 0.18 g (15%) of (*E*)-1-chloro-4-methyl-2-pentene, and 0.50 g (61%) of 4-methyl-1,3-pentadiene. Preparative VPC led to separation of the three components. ^1H NMR (CCl_4) of the major allylic chloride: δ 1.00 (d, 6, J = 6 Hz, CH_3's), 1.93 (m, 1, –C**H**$(CH_3)_2$), 4.13 (dd, 1, J = 8, 5 Hz, –CHCl–), 5.12 (dd, 1, J = 10, 2 Hz, *Z*-terminal vinyl), 5.21 (dd, 1, J = 17, 2 Hz, *E*-terminal vinyl), and 5.88 (ddd, 1, J = 17, 10, 7 Hz, internal vinyl). ^1H NMR (CCl_4) of the minor allylic chloride: δ 1.02 (d, 6, J = 6 Hz, CH_3's), 2.32 (m, 1, CH), 3.93 (d, 2, J = 6 Hz, CH_2), and 5.23–5.93 (m, 2, an AB coupling pattern with J = 16 Hz is discernible, vinyl). ^1H NMR (CCl_4) of the diene: δ 1.70 (bs, 6, CH_3's), 4.83 (bd, 1, J = 10 Hz, *Z*-terminal vinyl), 4.88 (bd, 1, J = 17 Hz, *E*-terminal vinyl), 5.70 (bd, 1, J = 10 Hz, H on C_3), and 6.41 (ddd, 1, J = 17, 10, 10 Hz, H on C_2).

2-Methyl-4-hexen-3-ol (14). Reaction of 5.0 g (0.044 mol) of the commercial alcohol (Chemical Samples Co.) in 21 mL of HCA with 12.0 g (0.0458 mol) of Ph_3P gave 4.34 g of a volatile material whose ^1H NMR spectrum revealed a mixture of two allylic chlorides (major, 62/38 ratio) and dienes (minor). VPC analysis (column C) failed to resolve the chloride mixture. Preparative VPC allowed separation into a chloride fraction and a diene fraction. The chlorides proved to be a mixture (changed from the original 62/38 ratio) of (*E*)-4-chloro-5-methyl-2-hexene and (*E*)-2-chloro-5-methyl-3-hexene. ^1H NMR (CCl_4) of the major component: δ 1.02 (d, 6, J = 7 Hz, –CH(C**H**$_3)_2$), 1.75 (bd, 3, J = 5 Hz, allylic CH_3), 1.87 (m, 1, –C**H**$(CH_3)_2$), 4.10 (bt, 1, J = 5 Hz, –CHCl–), and 5.2–6.0 (m, 2, vinyl). ^1H NMR (CCl_4) of the minor component: δ 1.02 (d, 6, J = 7 Hz, –CH(C**H**$_3)_2$), 1.55 (d, 3, J = 7 Hz, –CHClC**H**$_3$), 2.32 (m, 1, –C**H**$(CH_3)_2$), 4.38 (qd, 1, J = 6, 6 Hz, –CHCl–), and 5.2–6.0 (m, 2, vinyl). The diene fraction proved to be an 89/11 mixture of (*E*)-2-methyl-2,4-hexadiene and (*E*)-5-methyl-1,3-hexadiene. ^1H NMR (CCl_4) of the diene mixture: δ 1.0 (d, J = 7 Hz, –CH(C**H**$_3)_2$ in minor component), 1.7 (bs, CH_3's in major component), and 5.2–6.4 (m, vinyl).

2-Methyl-3-buten-2-ol (15). Reaction of 4.28 g (0.050 mol) of the commercial alcohol (Aldrich Chemical Co.) in 15 mL of HCA with 13.5 g (0.0515 mol) of Ph_3P gave 4.0 g of a volatile mixture which analyzed (VPC, column C) for 1.10 g (21.2%) of 3-chloro-3-methyl-1-butene, 2.26 g (43.2%) of 1-chloro-3-methyl-2-butene, and 0.604 g (17.7%) of 2-methyl-1,3-butadiene. Preparative VPC led to separation of the three components. ^1H NMR (CCl_4) of the minor allylic chloride: δ 1.67 (s, 6, CH_3's), 4.98 (dd, 1, J = 10, 2 Hz, *Z*-terminal vinyl), 5.20 (dd, 1, J = 16, 2 Hz, *E*-terminal vinyl), and 6.09 (dd, 1, J = 17, 10 Hz, internal vinyl). ^1H NMR (CCl_4) of the major allylic chloride identical to that of the sole product from alcohol 4. ^1H NMR (CCl_4) of the diene: δ 1.83 (bs, 3, CH_3), 4.95 (bs, 2, H's on C_1), 5.01 (dd, 1, J = 10, 1 Hz, *Z*-vinyl H on C_4), 5.12 (dd, 1, J = 17, 1 Hz, *E*-vinyl H on C_4), and 6.39 (ddm, 1, J = 17, 10 Hz, internal vinyl).

3-Methyl-1-penten-3-ol (16). Reaction of 10 g (0.10 mol) of the commercial alcohol (Chemical Samples Co.) in 29 mL of HCA with 27 g (0.103 mol) of Ph_3P gave 6.4 g of a volatile mixture. VPC analysis (column C) revealed the presence of 0.832 g (7.1%) of 3-chloro-3-methyl-1-pentene, 1.73 g (14.6%) of 1-chloro-3-methyl-2-pentene (as a 50/50 *Z/E* mixture), 0.79 g (9.6%) of 2-ethyl-1,3-butadiene, and 3.05 g (37.2%) of 3-methyl-1,3-pentadiene (as a mixture of *Z* and *E* isomers). Preparative VPC led to separation of the components. ^1H NMR (CCl_4) of the minor allylic chloride: δ 0.98 (t, 3, J = 8 Hz, –CH_2C**H**$_3$), 1.60 (s, 3, CH_3), ca. 1.8 (m, 2, CH_2), 5.03 (dd, 1, J = 10, 2

Hz, *Z*-terminal H), 5.19 (dd, 1, J = 17, 2 Hz, *E*-terminal H), and 5.94 (dd, 1, J = 17, 10 Hz, internal vinyl). ^{1}H NMR (CCl_4) of the major allylic chloride: δ 1.02 (t, 3, J = 7 Hz, $-CH_2CH_3$), 1.72 (s, 3, allylic CH_3), 2.13 (m, 2, $-CH_2CH_3$), 3.98 (d, 2, J = 8 Hz, $-CH_2Cl$), and 5.4 (m, 1, vinyl). ^{1}H NMR (CCl_4) of the minor diene: δ 1.07 (t, 3, J = 7 Hz, CH_3), 2.17 (q, 2, J = 7 Hz, CH_2), 4.88 (bs, 2, H's on C_1), 4.92 (dd, 1, J = 10, 2 Hz, *Z*-vinyl H on C_4), 5.09 (dd, 1, J = 17, 2 Hz, *E*-vinyl H on C_4), and 6.28 (dd, 1, J = 17, 10 Hz, internal vinyl). ^{1}H NMR (CCl_4) of the major diene: δ 1.68 (s, 3, internal CH_3), 1.7 (d, 3, terminal CH_3), 4.82 (bd, 1, J = 10 Hz, *Z*-vinyl H on C_1), 4.96 (bd, 1, J = 17 Hz, *E*-vinyl H on C_1), ca. 5.3 (m, 1, H on C_4), and 6.28 (dd, 1, J = 17, 10 Hz, H on C_2).

Reaction of 2-Methyl-2-propen-1-olate with HCA. To 12.7 g (0.176 mol) of 2-methyl-2-propen-1-ol in a 100-mL, round-bottomed flask was added 0.202 g (0.0088 g-atom) of Na. The solution was cooled in ice and 46.5 g (0.176 mol) of HCA was added over 20 min. The resulting yellow slurry was warmed to room temperature and flash distilled (1 torr, ambient temperature, 1 h) yielding 15.44 g of volatile material which analyzed (VPC, column C) for 14.28 g (0.120 mol) of $CHCl_3$ and 1.16 g of di-2-methyl-2-propen-1-yl carbonate; CCl_4 was absent. The residue was distilled at 58 °C/0.75 torr yielding 30.2 g of clear liquid which proved to be a mixture of the bisallylic carbonate and HCA. ^{1}H NMR (CCl_4) of the carbonate: δ 1.78 (bs, 3, CH_3), 4.48 (bs, 2, CH_2), and 4.92 and 5.05 (m, 1 each, vinyl). ^{13}C NMR ($CDCl_3$) of the carbonate: δ 18.9 ($-CH_3$), 70.7 ($-CH_2-$), 113.1 ($=CH_2$), 139.2 (methine), and 154.7 (carbonyl). Mass spectrum obscured by cracking pattern for HCA although a peak at m/e 55 (2-methylallyl) can be discerned. ^{13}C NMR ($CDCl_3$) of HCA δ 90.0 ($-CCl_3$) and 175.2 (carbonyl); mass spectrum (70 eV) m/e 262 (P, 0.07), 264 (0.24), 266 (0.10), 268 (0.03); 227 (P − Cl, 0.97), 229 (1.6), 231 (0.83), 233 (0.34), 235 (0.10); 117 (CCl_3, 100), 119 (96.0), 121 (34.5), 123 (4.1); many other peaks which are characteristic of the fragments from HCA. In a similar experiment, 2-methyl-2-propen-1-yl trichloroacetate was isolated; mass spectrum (70 eV) m/e 216 (P, 25), 218 (24), 220 (8), 222 (1); 181 (P − Cl, 4), 183 (3); 117 (CCl_3, 100), 119 (95), 121 (32); many other peaks expected for fragmentation of this ester.

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Registry No.—(*Z*)-1-Chloro-2-butene, 4628-21-1; (*Z*)-1-chloro-2-methyl-2-butene, 23009-74-7; (*R,Z*)-(−)-3-butene-2-ol-*4-d*, 68366-29-0; (*S*)-(+)-3-chloro-(*Z*)-1-butene-*1-d*, 68317-99-7; 4-chloro-2-methyl-2-pentene, 21971-94-8; (*E*)-4-chloro-4-methyl-2-pentene, 68318-00-3; (*E*)-4-chloro-2-hexene, 68318-01-4; (*E*)-2-chloro-3-hexene, 68318-02-5; (*E*)-4-chloro-5-methyl-2-hexene, 68318-03-6; (*E*)-2-chloro-5-methyl-3-hexene, 68318-04-7; (*E*)-2-methyl-2,4-hexadiene, 32763-68-1; (*E*)-5-methyl-1,3-hexadiene, 32763-70-5; (*Z*)-1-chloro-3-methyl-2-pentene, 53309-82-3; (*E*)-1-chloro-3-methyl-2-pentene, 53309-84-5; 2-ethyl-1,3-butadiene, 3404-63-5; (*E*)-3-methyl-1,3-pentadiene, 2787-43-1; di-(*Z*)-methyl-2-propen-1-yl carbonate, 64057-79-0; 2-methyl-2-propen-1-yl trichloroacetate, 17542-18-6; HCA, 116-16-5; (*E,E*)-2,4-hexadiene, 5194-51-4; (*E*)-1,3-hexadiene, 20237-34-7; (*Z*)-3-methyl-1,3-pentadiene, 2787-45-3; sodium 2-methyl-2-propen-1-olate, 39863-43-9; Ph_3P, 603-35-0; 2-butyn-1-ol, 764-01-2; tiglic acid, 80-59-1; angelic acid, 565-63-9; (*Z*)-2-lithio-2-butene, 28944-85-6.

References and Notes

(1) (a) W. G. Young, F. F. Caserio, Jr., and D. D. Brandon, Jr., *J. Am. Chem. Soc.*, **82,** 6163 (1960); (b) W. S. Johnson, T. Li, C. A. Harbert, W. R. Bartlett, T. R. Herrin, B. Staskun, and D. H. Rich, *ibid.*, **92,** 4461 (1970); (c) E. Meléndez and M. Pardo, *Bull. Soc. Chim. Fr.*, 632 (1974).
(2) (a) E. J. Corey, D. E. Cane, and L. Libit, *J. Am. Chem. Soc.*, **93,** 7016 (1971); (b) B. M. Trost, D. F. Taber, and J. B. Alper, *Tetrahedron Lett.*, 3857 (1976); (c) D. F. Taber, *J. Am. Chem. Soc.*, **99,** 3513 (1977); (d) P. A. Grieco and Y. Masaki, *J. Org. Chem.*, **39,** 2135 (1974); (e) J. H. Babler, *ibid.*, **41,** 1262 (1976); (f) A. G. Anderson, Jr., N. E. T. Owen, F. J. Freenor, and D. Erickson, *Synthesis*, 398 (1976); (g) J. A. Katzenellenbogen and A. L. Crumrine, *J. Am. Chem. Soc.*, **98,** 4925 (1976).
(3) (a) E. W. Collington and A. I. Meyers, *J. Org. Chem.*, **36,** 3044 (1971); (b) A. I. Meyers and E. W. Collington, *Tetrahedron*, **27,** 5979 (1971); (c) C. Georgoulis and G. Ville, *Bull. Soc. Chim. Fr.*, 607 (1975); (d) S. J. Cristol and C. S. Ilenda, *Tetrahedron Lett.*, 3681 (1976).
(4) (a) G. Stork, P. A. Grieco, and M. Gregson, *Tetrahedron Lett.*, 1393 (1969); (b) Y. Bensimon and E. Ucciani, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **276,** 683 (1973); (c) C. Chuit, G. Cahiez, J. Normant, and J. Villieras, *Tetrahedron*, **32,** 1675 (1976); (d) R. F. Borch, A. J. Evans, and J. J. Wade, *J. Am. Chem. Soc.*, **99,** 1612 (1977).
(5) S. Czernecki and C. Georgoulis, *Bull. Soc. Chim. Fr.*, 405 (1975).
(6) E. J. Corey, C. U. Kim, and M. Takeda, *Tetrahedron Lett.*, 4339 (1972).
(7) Reviews: (a) R. Appel, *Angew. Chem., Int. Ed. Engl.*, **14,** 801 (1975); (b) J. I. G. Cadogan and R. K. Mackie, *Chem. Soc. Rev.*, **3,** 87 (1974).
(8) (a) I. M. Downie, J. B. Lee, and M. F. S. Matough, *J. Chem. Soc., Chem. Commun.*, 1350 (1968); (b) J. B. Lee, *J. Am. Chem. Soc.*, **88,** 3440 (1966); (c) S. L. Regen and D. P. Lee, *J. Org. Chem.*, **40,** 1669 (1975); (d) P. Hodge and G. Richardson, *J. Chem. Soc., Chem. Commun.*, 622 (1975); (e) P. J. Kocienski, G. Cernigliaro, and G. Feldstein, *J. Org. Chem.*, **42,** 353 (1977); (f) J. D. Morrison, J. E. Tomaszewski, H. S. Mosher, J. Dale, D. Miller, and R. L. Elsenbaumer, *J. Am. Chem. Soc.*, **99,** 3167 (1977).
(9) (a) E. Yamato and S. Sugasawa, *Tetrahedron Lett.*, 4283 (1970); (b) C. R. Harrison, P. Hodge, and W. J. Rogers, *Synthesis*, 41 (1977).
(10) (a) N. S. Isaacs and D. Kirkpatrick, *J. Chem. Soc., Chem. Commun.*, 443 (1972); (b) E. J. Corey and P. L. Fuchs, *Tetrahedron Lett.*, 3769 (1972); (c) G. H. Posner, G. L. Loomis, and H. Sawaya, *ibid.*, 1373 (1975); (d) W. G. Salmond, *ibid.*, 1239 (1977); (e) C. Gadreau and A. Foucaud, *Bull. Soc. Chim. Fr.*, 2068 (1976).
(11) (a) L. E. Barstow and V. J. Hruby, *J. Org. Chem.*, **36,** 1305 (1971); (b) R. Appel and L. Willms, *J. Chem. Res. (S)*, 84 (1977).
(12) E. I. Snyder, *J. Org. Chem.*, **37,** 1466 (1972).
(13) (a) E. H. Axelrod, G. M. Milne, and E. E. van Tamelen, *J. Am. Chem. Soc.*, **92,** 2139 (1970); (b) G. Stork, M. E. Jung, E. Colvin, and Y. Noel, *ibid.*, **96,** 3684 (1974); (c) H. L. Goering and S. L. Trenbeath, *ibid.*, **98,** 5016 (1976); (d) S. J. Cristol, R. M. Strom, and D. P. Stull, *J. Org. Chem.*, **43,** 1150 (1978).
(14) (a) B. Stephenson, G. Solladié, and H. S. Mosher, *J. Am. Chem. Soc.*, **94,** 4184 (1972); (b) H. S. Mosher, *Tetrahedron*, **30,** 1733 (1974).
(15) R. M. Magid and O. S. Fruchey, *J. Am. Chem. Soc.*, **99,** 8368 (1977).
(16) (a) R. Appel, F. Knoll, W. Michel, W. Morbach, H-D. Wihler, and H. Veltmann, *Chem. Ber.*, **109,** 58 (1976); (b) R. Appel and H-D. Wihler, *ibid.*, **109,** 3446 (1976); (c) R. Appel and H. Veltmann, *Tetrahedron Lett.*, 399 (1977); (d) R. Appel and H. Schöler, *Chem. Ber.*, **110,** 2382 (1977); (e) R. Appel, R. Milker, and I. Ruppert, *ibid.*, **110,** 2385 (1977); (f) R. Appel and W. Morbach, *Synthesis*, 699 (1977); (g) L. A. Jones, C. E. Sumner, Jr., B. Franzus, T. T-S. Huang, and E. I. Snyder, Abstracts, 173rd National Meeting of the American Chemical Society, New Orleans, LA, March 1977, ORGN 192; we thank Professor Franzus for making his results available to us before publication; (h) I. Tömösközi, L. Gruber, and L. Radics, *Tetrahedron Lett.*, 2473 (1975); (i) B. Castro, Y. Chapleur, and B. Gross, *ibid.*, 2313 (1974).
(17) The facts that the chloride is formed with essentially complete inversion of configuration,[18,13d] that neopentyl[18c,14] (and other systems[13d,18b]) gives mostly unrearranged products, and that attack by added nucleophiles does not occur[18c] all argue for either a concerted breakdown into RCl + Ph_3PO or for reaction via a tight ion pair.
(18) (a) R. G. Weiss and E. I. Snyder, *J. Chem. Soc., Chem. Commun.*, 1358 (1968); (b) R. G. Weiss and E. I. Snyder, *J. Org. Chem.*, **35,** 1627 (1970); (c) R. G. Weiss and E. I. Snyder, *ibid.*, **36,** 403 (1971).
(19) HCA is a useful reagent for the chlorination of enamines: (a) F. M. Laskovics and E. M. Schulman, *Tetrahedron Lett.*, 759 (1977); (b) F. M. Laskovics and E. M. Schulman, *J. Am. Chem. Soc.*, **99,** 6672 (1977).
(20) A preliminary account of this work has appeared: R. M. Magid, O. S. Fruchey, and W. L. Johnson, *Tetrahedron Lett.*, 2999 (1977).
(21) (a) L. J. Brubacher, L. Treindl, and R. E. Robertson, *J. Am. Chem. Soc.*, **90,** 4611 (1968); (b) R. M. Magid and R. D. Gandour, *J. Org. Chem.*, **35,** 269 (1970).
(22) R. T. Rawson and I. T. Harrison, *J. Org. Chem.*, **35,** 2057 (1970).
(23) R. G. Bergman, *J. Am. Chem. Soc.*, **91,** 7405 (1969).
(24) R. M. Magid, E. C. Nieh, and R. D. Gandour, *J. Org. Chem.*, **36,** 2099 (1971).
(25) (a) H. O. House and G. H. Rasmusson, *J. Org. Chem.*, **26,** 4278 (1961); (b) H. Neumann and D. Seebach, *Tetrahedron Lett.*, 4839 (1976).
(26) R. M. Magid and E. C. Nieh, *J. Org. Chem.*, **36,** 2105 (1971).