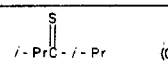
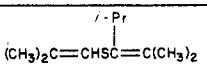
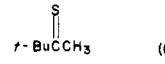
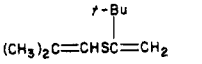
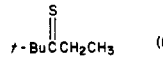
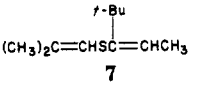
Table I. Yields and Spectral Properties of Divinyl Sulfides

starting thione	product sulfide	% yield[a]	mass spectrum, m/e (relative intensity)	IR,[b] cm^{-1}	NMR,[c] δ
 1	 5	40	186 (M$^+$ + 2, 7.7), 185 (M$^+$ + 1, 12.4), 184 (M$^+$, 69), 141 (15), 97 (63), 55 (100)	1620 (C=C)	1.05 (d, J = 7, 6, i-Pr), 1.75 (s, 3, CH_3), 1.77 (s, 3, CH_3), 1.85 (s, 3, CH_3), 1.95 (s, 3, CH_3), 3.10 (sept, 1, CH), 5.45 (m, 1, C=CH)
 2	 6	31	172 (M$^+$ + 2, 4.9), 171 (M$^+$ + 1, 11.8), 170 (M$^+$, 77), 113 (76), 101 (90), 57 (100)	1600 (C=C)	1.20 (s, 9, t-Bu), 1.80 (br s, 3, CH_3), 1.90 (br s, 3, CH_3), 4.75 (s, 1), 5.15 (s, 1), 5.80 (m, 1)
 3	 7	26	186 (M$^+$ + 2, 5.7), 185 (M$^+$ + 1, 13.1), 184 (M$^+$, 75), 127 (71), 55 (100)	1620 (C=C)	1.15 (s, 9, t-Bu), 1.75 (m, 6), 1.76 (d, J = 6, 3), 5.25 (m, 1), 5.85 (q, J = 6, 1)

[a] Isolated yield, based on total thione used; see text. [b] Neat, NaCl plates. [c] In CCl_4, internal Me_4Si.

Experimental Section

Infrared spectra were recorded on a Beckman IR5A spectrometer, and proton NMR spectra were recorded on a Varian EM-390 spectrometer. Mass spectra were obtained on a Varian MAT 112 GC-mass spectrometer. All commercial reagents were ACS reagent grade and solvents were purified and dried prior to use.

Thiones 1-3 were prepared by reaction of the corresponding commercial carbonyls with liquid H_2S and gaseous HCl according to literature procedures.[6] Vinyl triflate 4 and tetra-n-butylammonium fluoride were prepared as previously reported.[7]

Reaction of Vinyl Triflate 4 with Diisopropyl Thioketone. Formation of Divinyl Sulfide 5. General Procedure. To a flame-dried 100-mL round-bottom flask, equipped with a serum cap, magnetic stirring bar, and an argon inlet and outlet via syringe needles, were added 0.65 g (5 mmol) of diisopropyl thioketone, 1.38 g (5.5 mmol) of silylvinyl triflate 4 and 50 mL of dry glyme. The solution was cooled to -23 °C with a dry ice-CCl_4 slush bath. To the cooled solution was added, all at once via a syringe, 7 mL of a 0.81 M (5.67 mmol) solution of n-Bu_4NF in glyme. The red-orange color of the solution rapidly faded to pale yellow. The solution was stirred at -23 °C for 1 h. At the end of this period the solvent was removed under reduced pressure and the residue was taken up in pentane. The pentane solution was filtered to remove the salts and then concentrated and subjected to medium-pressure LC with a silica gel column. Elution with hexanes gave the product in the lead fraction. Evaporation of the solvent yielded 367 mg (40%) of divinyl sulfide 5 as a colorless liquid.

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Registry No. 1, 13390-86-8; 2, 17380-91-5; 3, 25946-21-8; 4, 73876-87-6; 5, 75961-70-5; 6, 75961-71-6; 7, 75961-72-7.

Improvements in the Hexachloroacetone/Triphenylphosphine Procedure for the Conversion of Allylic Alcohols into Chlorides

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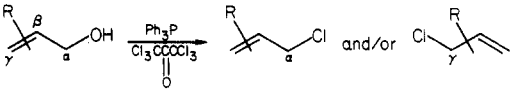
Several procedures have been described for the conversion of allylic alcohols into chlorides with predictable stereo- and regiochemistry, but none is generally applicable to all types of substitution patterns.[2] Recently we reported[3] that the reagent system hexachloroacetone (HCA)/triphenylphosphine provides a partial solution to this synthetic problem: primary and secondary allylic alcohols afford nearly quantitative yields of largely or exclusively unrearranged chloride; the geometry of the β-γ double bond is preserved; inversion of configuration occurs at C_α; the conditions of the reaction, workup, and isolation are exceedingly mild.



Two drawbacks of the procedure are the wasteful use of HCA as solvent as well as reagent and the extensive rearrangement and elimination which occur with tertiary allylic alcohols. We sought a solvent which would address the first problem and, perhaps, alleviate the second. Criteria for selection of a solvent include the following: high boiling point (to allow easy isolation of volatile allylic chlorides); high polarity; inertness to HCA, Ph_3P, and the allylic alcohol. Of the several dipolar aprotic solvents tested, we are pleased to report that sulfolane (tetramethylene sulfone) is a superior medium for this synthesis: reaction occurs rapidly under mild conditions, yields are high, and isolation of the chloride is facile.

Our initial studies were with β-methylallyl alcohol (2-methyl-2-propen-1-ol, 1), a symmetrical molecule (in the absence of an isotopic label) which does not produce a mixture of regioisomers. As shown in Table I, Ph_3P, alcohol 1, and a stoichiometric quantity of HCA in sulfolane give an excellent yield of chloride regardless of the order of mixing of the reagents (runs 3-5). For all of the entries (except runs 4 and 5) HCA in sulfolane was added to a stirred, cooled mixture of the alcohol and triphenylphosphine in the same solvent. Excess HCA (runs 1 and 2) is not beneficial in terms of yield or rate. Significantly, the yield of allylic chloride is not appreciably diminished when even as little as 0.4 equiv of HCA is used (runs 6-9). This suggests that two chlorines are available from HCA, support for which comes from the observation of singlets at δ 6.8 and 6.5, respectively, for pentachloroacetone and *sym*-tetrachloroacetone in the residue from flash distillation; under the conditions of short reaction time and low temperature, more than two chlorines are not used (runs 10 and 11). That the isolated yield of allylic chloride is not even higher is attributed, in part, to its high volatility. Another noteworthy feature is that the persistent forma-

(1) National Science Foundation Undergraduate Research Participant, summer 1980.

(2) R. M. Magid, *Tetrahedron*, **36**, 1901 (1980).

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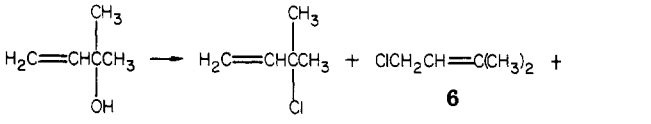
Table I. Reactions of Alcohols with HCA/Ph_3P[a]

run	alcohol	molar quantities × 10^2			molar ratio of HCA/ alcohol	volume of sulfolane, mL	yield of chloride, %[b,c]
		alcohol	HCA	Ph_3P			
1	1	3.40	10.7	2.70	3.15	30	93.7
2	1	2.73	5.23	2.83	1.92	20	85.3
3	1	13.9	13.9	14.5	1.00	40	95.7
4[d]	1	2.37	2.57	2.78	1.08	20	84.3
5[e]	1	2.34	2.52	2.82	1.08	30	93.0
6	1	2.83	2.21	3.02	0.78	20	80.4
7	1	2.30	1.37	2.31	0.60	18	80.1
8	1	2.45	0.967	2.50	0.39	18	76.2
9	1	3.40	1.37	3.66	0.40	20	76.3
10	1	2.50	0.544	2.55	0.22	18	49.5[f]
11	1	3.74	0.718	3.80	0.17	18	36.8[g]
12	2	3.74	3.69	3.79	0.99	20	78.6
13	2	3.14	1.56	3.21	0.50	18	77.7
14	3	3.82	3.81	3.87	1.00	21	72.1
15	4	3.31	3.31	3.34	1.00	18	59[h]

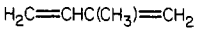
[a] HCA in sulfolane was added to alcohol and Ph_3P in sulfolane at 10 °C, except for runs 4 and 5. [b] Isolated yield based on alcohol, except for run 1 in which Ph_3P was the limiting reagent. [c] The distilled product is cleanly 3-chloro-2-methyl-1-propene (runs 1-11), 1-chlorobutane (runs 12, 13), or 2-chlorobutane (run 14), except where noted. [d] Alcohol 1 added to HCA/Ph_3P in sulfolane. [e] Ph_3P added to alcohol 1/HCA in sulfolane. [f] Distilled product, by NMR and VPC, is ca. 95% chloride and 5% unreacted alcohol. [g] Along with 0.0138 mol of chloride, the distillate contains 0.0056 mol of unreacted alcohol; the pot residue, by NMR, contains both unreacted Ph_3P and alcohol 1. [h] The distilled product, by VPC and NMR, is a mixture (% yield) of chlorides **5** (37%) and **6** (22%) and diene **7** (27%).

tion of CCl_4 in our original procedure[3b] is not a problem in the improved method.

Saturated alcohols 1-butanol (**2**) and 2-butanol (**3**) also react readily and in high yield under the same conditions (runs 12-14); as above, 0.5 equiv of HCA suffices. Especially gratifying is the behavior of tertiary allylic alcohol 2-methyl-3-buten-2-ol (**4**). When HCA was used as both



4 **5** **6**



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reagent and solvent, the yields of products **5**-**7** were 21.2%, 43.2%, and 17.7%, respectively.[3b] Although elimination is still a problem in sulfolane (run 15), the major allylic chloride is now the unrearranged **5**.

(3) (a) R. M. Magid, O. S. Fruchey, and W. L. Johnson, *Tetrahedron Lett.*, 2999 (1977); (b) R. M. Magid, O. S. Fruchey, W. L. Johnson, and T. G. Allen, *J. Org. Chem.*, 44, 359 (1979).

Experimental Section

All ^1H NMR spectra were obtained with a Varian T-60 spectrometer; tetramethylsilane was used as an internal standard. VPC analyses were performed by using a Varian Aerograph Model 920 gas chromatograph with a 9 ft × $^1/_4$ in. column of SE-30 (5%) on 80/100 Chromosorb W. Sulfolane and hexachloroacetone were stored over 4-Å molecular sieves.

General Procedure for Reactions. In a 100-mL, round-bottomed flask equipped with magnetic stirrer were placed ca. 0.03 mol of the alcohol and (usually) a slight excess of Ph_3P in 10-15 mL of sulfolane. To the cooled (10 °C) stirred solution was added HCA in ca. 10 mL of sulfolane dropwise; after an initial temperature rise and formation of a precipitate, the temperature gradually dropped to ambient as the rest of the HCA solution was added. The reaction mixture was allowed to come to room temperature. Immediate flash distillation at 4-5 torr into a dry ice-acetone-cooled receiver gave product which was analyzed by VPC and ^1H NMR; in most instances, the material was exclusively the allylic or saturated chloride.

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Communications

Regiochemical Control in the Conjugate Addition of Dithianylidene Anions: Total Syntheses of (±)-Aromatin and (±)-Confertin

Summary: The lithium anion of the dithiane of (*E*)-2-methyl-2-butenal has been shown to undergo a highly regioselective Michael addition-alkylation sequence. Subsequent stereoselective transformations of the derived adduct have culminated in syntheses of the pseudoguaianolides (±)-aromatin and (±)-confertin.

Sir: Aromatin (**12b**)[1] and confertin (**15**)[2] are representatives of the class of physiologically active pseudoguaianolide sesquiterpenes.[3] The former substance (helenanolide) stereochemically differs from the latter (am-

(1) For a recent synthesis of (±)-aromatin see: Lansbury, P. T.; Hangauer, D. G.; Vacca, J. P. *J. Am. Chem. Soc.* **1980**, *102*, 3964.

(2) For syntheses of confertin see: (a) Marshall, J. A.; Ellison, R. H. *J. Am. Chem. Soc.* **1976**, *98*, 4312. (b) Semmelhack, M. F.; Yamashita, A.; Tomesch, J. C.; Hirotsu, K. *Ibid.* **1978**, *100*, 5565. (c) Wender, P. A.; Eissenstat, M. A.; Filosa, M. P. *Ibid.* **1979**, *101*, 2196. (d) Quallich, G. J.; Schlessinger, R. H. *Ibid.* **1979**, *101*, 7627.

(3) (a) Kupchan, S. M.; Eakin, M. A.; Thomas, A. M. *J. Med. Chem.* **1971**, *14*, 1147. (b) Lee, K. H.; Huang, E. S.; Piantadosi, C.; Pagano, J. S.; Geissman, T. A. *Cancer Res.* **1971**, *31*, 1649. (c) Rodriguez, E.; Towers, G. H. N.; Mitchell, J. C. *Phytochemistry* **1976**, *15*, 1573. (d) Hall, I. H.; Lee, K. H.; Mar, E. C.; Starnes, C. O. *J. Med. Chem.* **1977**, *20*, 333.

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