tion of ethylmagnesium bromide. About 35 ml., or approximately enough to react with the acetone present, was added before a self-sustaining reaction set in. The remainder of the acetone–allyl bromide solution was then added without further difficulty.

Structure of 5-Allyl-5-hydroxy-2,4,4-trimethyl-7-octen-3-one (2).—A mixture of 22.7 g. of 2 and 0.2 g. of $Ba(OH)_2$ was heated in a 125–140° oil bath at a pressure of 20 mm. Distillate, b.p. 43–50° (20 mm.), was collected as it formed; 21.1 g. was collected in 90 min. Fractionation of 30.7 g. of such pyrolysate through a spinning-band column at 20 mm. gave (1) 13.6 g., 31–32°, $n^{25}\text{D}$ 1.3992; (2) 3.0 g., 36–51°, $n^{25}\text{D}$ 1.4410; and (3) 10.5 g., 51–53°, $n^{25}\text{D}$ 1.4421. Fractions 2 and 3 were yellow. Fraction 1 was identified as diisopropyl ketone by its characteristic p.m.r. spectrum, fraction 2 by p.m.r. analysis contained 8% diisopropyl ketone, 69% diallyl ketone, and 23% allyl propenyl ketone, and fraction 3 similarly contained 1% diisopropyl ketone, 91% diallyl ketone, and 8% allyl propenyl ketone. Fraction 3 showed a $\lambda_{\max}$ 225 mμ (isooctane); this is consistent with the presence of allyl propenyl ketone rather than dipropenyl ketone since the latter is reported[19] to have a $\lambda_{\max}$ 245, 251 mμ.

Fraction 3 did not give a sharp melting 2,4-dinitrophenylhydrazone or semicarbazone. However, treatment of 3 g. of fraction 3 with 0.5 g. of lithium aluminum hydride in 20 ml. of ether yielded 1.9 g. of diallyl carbinol, b.p. 53–54° (14 mm.), $n^{25}\text{D}$ 1.4490, 3,5-dinitrobenzoate m.p. 60.5–61.5°, m.m.p. 60–61.5° with an authentic sample. The infrared spectrum of this diallyl carbinol was identical with a spectrum of the material independently prepared (see Table II).

It was found that 2 would cleave thermally without base-catalysis, but somewhat more slowly. Compound 2, 11.2 g., was heated in a 130–160° oil bath at a pressure of 15 mm. and distillate, 10.0 g., was collected at 40–65° over a period of 5 hr. Fractionation through the spinning-band column at 15 mm. gave (4) 4.8 g., 24–25°, $n^{25}\text{D}$ 1.3982; (5) 0.8 g., 37–46°, $n^{25}\text{D}$ 1.4362; and (6) 3.5 g., 46–47°, $n^{25}\text{D}$ 1.4420. All fractions were colorless but fractions 5 and 6 yellowed on storage in soft glass containers. By p.m.r. analysis fraction 4 was substantially pure diisopropyl ketone; fractions 5 contained 13% diisopropyl ketone, 84% diallyl ketone, and 3% allyl propenyl ketone; and fraction 6 appeared to be better than 99% diallyl ketone and contained only traces of diisopropyl and allyl propenyl ketone. The $\lambda_{\max}$ at 225 mμ was absent in the ultraviolet spectrum of fraction 6.

Anal. of fraction 6. Calcd. for $C_7H_{10}O$: C, 76.32; H, 9.15. Found: C, 75.86, 76.04; H, 9.18, 9.24.

A 2,4-dinitrophenylhydrazone of fraction 6 was readily obtained, dark red platelets, m.p. 133–135°, from ethanol.

Anal. Calcd. for $C_{13}H_{14}N_4O_4$: C, 53.79; H, 4.86; N, 19.30. Found: C, 53.78, 53.91; H, 5.47, 5.31; N, 19.48, 19.18.

Acknowledgment.—The author wishes to thank Dr. J. C. Westfahl for the determination and interpretation of the p.m.r. spectra and Dr. F. W. Shaver and Dr. J. C. Westfahl for many helpful discussions.

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Rates and Relative Rates of Chloro- and Iododesilylation. Evidence for a Four-Center Transition State

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Recently, the mechanisms of cleavage of carbon–metalloid bonds have received considerable attention.[1-3] The major uncertainty in the description of the activated complex for these reactions involves the significance to be ascribed to four-center interactions. As an approach to this problem we have evaluated the effectiveness of iodine monochloride and chlorine as reagents for desilylation of phenyltrimethylsilane.

The reaction between phenyltrimethylsilane and iodine monochloride in dry acetic acid at 25° yields iodobenzene and hexamethyldisiloxane as the only detectable products in greater than 90% yield.

Observations obtained in a typical kinetic experiment are presented in Table I.

The failure of second- or third-order rate laws to accommodate the data, Table I, and the observations of other kinetic studies[4] of iodination suggested the effective concentration of iodine monochloride was reduced by complex formation.

$$\mathrm{ICl} + \mathrm{Cl}^- \overset{K}{\rightleftharpoons} \mathrm{ICl_2}^-$$

Rate law based on this equilibrium and a second-order rate-determining reaction between iodine monochloride and phenyltrimethylsilane is the following,

$$\mathrm{ICl} + \mathrm{PhSiMe_3} \xrightarrow{k} \text{products}$$

$$\frac{-d[\mathrm{ICl}]}{dt} = \frac{k[\mathrm{PhSiMe_3}][\mathrm{ICl}]}{1 + K[\mathrm{Cl}^-]} \tag{1}$$

where [ICl] is the titrimetric concentration. The calculated second-order rate constants, k, reported in Tables I and II are based on the known value, K = 250 l. mole^{-1}, for the equilibrium constant in acetic acid at 25°.[4] As illustrated in Table I, this rate law provides a good fit of the kinetic observations.[5]

Chlorodetrimethylsilylation by chlorine in 1.5% aqueous acetic acid at 25° was previously examined by Eaborn and Webster.[6] They report the reaction kinetics are satisfied by a second-order rate equation, but their typical data reveal the observed second-order rate constant decreases through the course of an experiment from an initial value of 5.3×10^{-2} to 2.8×10^{-2} l. mole^{-1} sec.$^{-1}$ at 85% reaction. In this study, dry acetic acid was adopted as the solvent for the reaction. It was found that the reaction obeyed second-order kinetics to 70–80% completion. The rate constant observed, 1.57×10^{-2} l. mole^{-1} sec.$^{-1}$, is somewhat less than reported by Eaborn and Webster. Presumably, the removal of water contributes to the reduction of the reaction velocity.[7]

Rate constants for iododesilylation and chlorodesilylation as determined in a series of independent experiments with different samples of phenyltrimethylsilane, iodine monochloride, and chlorine are summarized in Table II.

Comparison of the second-order rate constants indicates chlorodesilylation is eightfold less rapid than iododesilylation under identical conditions.[8] This finding contrasts sharply with the rate ratios observed

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[2] C. Eaborn and D. E. Webster, *J. Chem. Soc.*, 179 (1960); R. W. Bott, C. Eaborn, and J. A. Water, *ibid.*, 681 (1963).

[3] C. Eaborn and D. W. Steward, *Proc. Chem. Soc.*, 59 (1963).

[4] L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **79**, 1412 (1957).

[5] The corresponding third-order rate equation, second-order in iodine monochloride with inhibition by chloride ions, does not accommodate the results.

[6] C. E. Eaborn and D. E. Webster, *J. Chem. Soc.*, 4449 (1957).

[7] L. M. Stock and A. Himoe, *J. Am. Chem. Soc.*, **83**, 1937 (1961).

TABLE I

KINETIC OBSERVATIONS AND DERIVED RATE CONSTANTS FOR IODODETRIMETHYLSILYLATION WITH IODINE MONOCHLORIDE IN ACETIC ACID AT 25°

Observations				Rate constants		
Time, sec.	Titer[a]	[ICl], M	[PhSiMe$_3$], M	k_2,[b] l. mole^{-1} sec.$^{-1}$	k_3,[c] l.^{2} mole^{-2} sec.$^{-1}$	k,[d] l. mole^{-1} sec.$^{-1}$
0.0		0.0216	0.0890			
21	5.355	.0174	.0848	0.119	6.13	0.149
76	4.155	.0135	.0809	.073	4.34	.125
150	3.20	.0104	.0778	.059	4.06	.137
212	2.755	.0089	.0763	.051	3.86	.141
297	2.350	.0076	.0750	.043	3.61	.133
414	1.925	.0062	.0736	.038	3.56	.139

[a] Milliliters of 0.0342 N $Na_2S_2O_3$ required for 5-ml. aliquot. [b] Second-order rate constant. [c] Third-order rate constant, first-order in silane, second-order in iodine monochloride. [d] Second-order rate constant calculated on the basis of equation 1.

TABLE II

RATE CONSTANTS FOR IODODETRIMETHYLSILYLATION (ICl) AND CHLORODETRIMETHYLSILYLATION (Cl_2) IN ACETIC ACID AT 25°

Initial concentration, M			Second-order rate constants, l. mole^{-1} sec.$^{-1}$	
[PhSiMe$_3$]	[ICl]	[Cl$_2$]	k^a	10^2k_2
0.178	0.0216		0.135 ± 0.005	
.178	.00866		.109 ± 0.009	
.100	.0232		.123 ± 0.003	
.089	.0216		.137 ± 0.005	
.0820		0.0397		1.63 ± 0.02
.0954		.0192		1.53 ± 0.06
.0968		.00875		1.54 ± 0.06

[a] Equation 1.

TABLE III

RELATIVE RATES FOR THE SUBSTITUTION OF SILANE AND BENZENE DERIVATIVES

Substrate	Relative rate	
Toluene[a, b]	k_{Cl_2}/k_{Br_2}	200
Phenyltrimethylsilane[c, d]	k_{Cl_2}/k_{Br_2}	1.7 ± 0.4
p-Chlorophenyltrimethylsilane[c, d]	k_{Cl_2}/k_{Br_2}	2.7 ± 0.5
Toluene[e, f]	k_{Cl_2}/k_{ICl}	200
Phenyltrimethylsilane[g]	k_{Cl_2}/k_{ICl}	0.13 ± 0.02

[a] In aqueous acetic acid solvents, reaction of mixed second- and third-order for bromination but second-order for chlorination. [b] See ref. 9. [c] In acetic acid with 1.5% water, reaction of mixed second- and third-order for bromination, but second-order for chlorination. [d] See ref. 6. [e] In trifluoroacetic acid at 25°, reaction is second-order for both iodination and chlorination. [f] See ref. 4, 10. [g] In acetic acid at 25°, second-order rate constants compared.

for electrophilic substitution in benzene. Some pertinent data are summarized in Table III.

Comparisons of the reactivity of the halogens are often complicated by uncertainties in the order of the reactions. The problem is evident for noncatalytic bromination and chlorination in acetic acid media, Table III. It is certain, nevertheless, that chlorine is a much better electrophile than bromine with benzene derivatives.[9] The large difference in the electrophilic reactivity of these halogens is appreciably reduced with phenyltrimethylsilane as a reference substrate. This fact has been most reasonably interpreted to be a consequence of the decreased selectivity of the more nucleophilic silane.[6]

The iodination of benzenes and its derivatives by iodine monochloride is far less rapid than the rates for noncatalytic bromination or chlorination. Because of the slowness of this reaction only a few kinetic observations have been reported. The large relative rate, k_{Cl_2}/k_{ICl} 200, found for the reactions with toluene in trifluoroacetic acid is presumably typical. This relative rate should decrease with the less selective phenyltrimethylsilane as a reference substrate. However, if selectivity effects are dominant the value must remain greater than one. The relative rate for chloro- and iododesilylation, 0.13, indicates other influences are more significant than selective properties of the substrate.

The large variation in the effectiveness of iodine monochloride relative to chlorine in reactions with C–H and C–Si bonds suggests the transition states for the reactions are quite dissimilar. For the C–H bond, the available information for iodination favors the view that the reaction proceeds through an activated complex which approaches the character of a benzenonium ion. This model is inadequate for iododesilylation. The relative rate variation and the polarizability of iodine monochloride prompts the suggestion that iododesilylation occurs with an important additional interaction between silicon and chlorine in a four-center transition state.[1,3] Four-center processes for other desilylations by dipolar or polarizable reagents in nondissociating solvents may be expected to be significant.

Experimental

Materials.—Phenyltrimethylsilane was prepared by the reaction of phenyl Grignard reagent with chlorotrimethylsilane and by the reaction of methyl Grignard reagent with phenyltrichlorosilane. Each product was carefully fractionated to yield material homogeneous to vapor phase chromatography, $n^{25}D$ 1.4880. Iodine monochloride was prepared from the elements and purified by fractionation, b.p. 103–105° at atmospheric pressure. This reagent was prepared and distilled just prior to each kinetic experiment. Chlorine (Matheson, 99.5%) was used without further purification. Acetic acid (Baker and Adamson reagent grade) was distilled in a column packed with glass helices in a dry atmosphere. Other reagents were employed as commercially available.

Kinetic Measurements.—The reaction rates were followed by conventional iodometric procedures.[7] Typical results and a summary of typical observations are reported in Tables I and II.

Reaction Products.—An examination of the products of the reaction was carried out by vapor phase chromatographic analysis. Comparison of the ratios of areas, chlorobenzene to residual phenyltrimethylsilane and iodobenzene to residual phenyltrimethylsilane indicated the reactions to be virtually quantitative.

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(8) Competitive experiments indicated the relative rate k_{Cl_2}/k_{ICl} to be 0.22. The competitive method, however, is not a valid technique for the assessment of the relative rate in this case because of the importance of complexation of ICl as ICl_2^-, the presumed formation of ICl_3, a chlorinating agent, and the possible catalysis of chlorination by ICl. In view of these difficulties the value determined in the competition experiments is useful only as a confirmation of the lesser reactivity of chlorine.

(9) See P. B. D. de la Mare and J. H. Ridd, "Aromatic Substitution," Butterworths Scientific Publications, London, 1959, Chap. 9.

(10) A. Himoe and L. M. Stock, unpublished results.

TABLE IV.—COMPETITIVE EXPERIMENTS OF ICl AND Cl_2 FOR PHENYLTRIMETHYLSILANE IN ACETIC ACID AT 25°

Concentration, 10^3M						
$[PhSiMe_3]_i$	$[Cl_2]_i$	$[ICl]_i$	$[HCl]_f$	$[PhI]_f$	Reaction, %	k_{Cl_2}/k_{ICl}
16.9	69.2	74.6	6.6	5.5	39.1	0.23
12.7	51.9	112	8.8	8.0	69.0	0.21
12.7	104	56	5.1	3.5	40.0	0.21

The response of the detector to the halobenzene and phenyltrimethylsilane was shown to be in accord with the molar concentrations of these substances by the analysis of known mixtures. Chlorobenzene was not detected among the products of the iododesilylation reaction.

Competitive Measurements.—Several competitive experiments were performed to achieve a confirmation of the greater reactivity of iodine monochloride (see ref. 8). An attempt was made to avoid the inhibition of the iododesilylation reaction by hydrogen chloride through the adoption of a short reaction time (about 100 seconds). This approach, however, was not successful. It is pertinent to recognize that a 10% increase in the amount of iodobenzene produced would yield relative rate data in good agreement with the kinetic observations. The results of three experiments are summarized in Table IV.

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The Isolation of a New Diterpene Acid

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A bicyclic diterpene acid has been isolated from the acid fraction of slash pine oleoresin (*Pinus elliotti*). This new acid, termed elliotinoic acid, was isolated by partition chromatography on a silicic acid column by the method described by Loeblich, Baldwin, and Lawrence.[2] Elliotinoic acid collected from the silicic acid column was found to be essentially pure. Several batches of slash pine oleoresin and rosin were examined and elliotinoic acid was present in all samples and was the only acid eluted in fractions 16–21. Elliotinoic acid accounts for about 5% of the acid fraction of slash pine oleoresin. The new acid resisted all efforts to crystallize it and was quite sensitive to oxidation.

Elliotinoic acid was reduced with lithium aluminum hydride to the previously reported elliotinol.[3,4] On analysis by gas–liquid chromatography, elliotinol prepared by the lithium aluminum hydride reduction of elliotinoic acid and a sample of elliotinol isolated from the neutral fraction of slash pine oleoresin were found to have the same emergence time on a silicone (SE-30) column and on mixing in equal parts only one peak was obtained. The infrared spectra, optical rotation, and melting points of the two samples of elliotinol were identical. A mixture melting point of the two samples showed no depression. The elliotinyl *p*-nitrobenzoate derivative prepared from the two samples of elliotinol had identical infrared spectra, optical rotation, and melting points, alone and when mixed.

Elliotinoic acid and elliotinol are present in about equal amounts and together account for about 10% of the slash pine oleoresin. These two compounds are the first bicyclic diterpenes isolated from the oleoresin of the slash pine.

Experimental

Isolation of Elliotinoic Acid from Rosin.—A sample containing 2.50 g. of WW slash rosin in 10 ml. of isooctane was put on a silicic acid column.[2] Fractions (100-ml.) were collected and an aliquot of each was titrated. Elliotinoic acid was eluted in fractions 16–21. These fractions were combined, washed with water, and dried. The solvent was removed under reduced pressure and the dry residue dissolved in isooctane. A sodium hydroxide solution (3 *N*) was added dropwise with constant stirring until there was no further salt precipitation. The sodium elliotinate was filtered and dried under reduced pressure. Snow white plates of sodium elliotinate (0.12 g.) were recrystallized from hot water until the melting point, ultraviolet absorption, and optical rotation were constant: m.p. 387–389° (sealed evacuated tube); $\lambda_{\max}^{\text{alcohol}}$ 233 mμ (ε 27,500); $[\alpha]^{25}\mathrm{D}$ +42° (*c* 0.5, in alcohol).

Anal. Calcd. for $C_{20}H_{29}O_2Na$: C, 74.1; H, 9.0; Na, 7.1; neut. equiv., 324. Found: C, 74.2; H, 8.9; Na, 7.0; neut. equiv., 320.

Sodium elliotinate (0.10 g.) was suspended in ether and acidified with 3 *N* phosphoric acid. The ether solution was washed neutral, dried, and the ether removed. The residue (0.08 g.) was sublimed onto a cold finger at 120° (5 μ). The sublimate was a clear colorless oil; $[\alpha]^{25}\mathrm{D}$ +40° (*c* 1.0, in alcohol); $\lambda_{\max}^{\text{alcohol}}$ 232 mμ (ε 28,900); neut. equiv., 302.

Preparation of Elliotinol from Elliotinoic Acid. A.—An ether solution containing 0.10 g. of sodium elliotinate was added slowly to an excess of lithium aluminum hydride solution. The mixture was allowed to stand overnight and water was added to destroy the excess lithium aluminum hydride. The solution was filtered and the solvent removed under reduced pressure. The oily residue was sublimed at 140° (10 μ) onto a cold finger. The alcohol crystallized in long needles on the bottom of the cold finger; m.p. 14–15°; $\lambda_{\max}^{\text{alcohol}}$ 232 mμ (ε 20,600); $[\alpha]^{25}\mathrm{D}$ +14° (*c* 2.0, in alcohol).

Anal. Calcd. for $C_{20}H_{32}O$: C, 83.3; H, 11.2. Found: C, 83.4; H, 10.9.

B.—Elliotinyl *p*-nitrobenzoate (2.30 g.), prepared from slash pine neutrals,[3] was saponified by refluxing in alcoholic potassium hydroxide. Water was added and the elliotinol extracted with ether. The ether was removed under reduced pressure to leave a yellow viscous oil (1.29 g.). A pentane solution of the oil was put through a short column of silicic acid to give 0.89 g. of a colorless viscous oil. Vacuum sublimation of this oil onto a cold finger gave pure elliotinol with infrared spectrum, optical rotation, and melting point (alone and mixture) identical with the alcohol prepared from elliotinoic acid.

Preparation of Elliotinyl *p*-Nitrobenzoate. A.—A dry pyridine (4 ml.) solution of 0.55 g. of the alcohol obtained by the lithium aluminum hydride reduction of elliotinoic acid was stirred at room temperature with *p*-nitrobenzoyl chloride for 6 hr. The resulting solution was poured over crushed ice and the water decanted. The yellow gummy precipitate crystallized from boiling 95% ethanol; m.p. 116–121°. Two crystallizations from 95% ethanol gave the pure ester; m.p. 128–130°; $[\alpha]^{25}\mathrm{D}$ +74° (*c* 2.0 in alcohol).

Anal. Calcd. for $C_{27}H_{35}O_4N$: C, 74.1; H, 8.0. Found: C, 73.9; H, 8.0.

B.—Slash rosin neutrals (2.3 g.) in 7.0 ml. of pyridine on stirring with *p*-nitrobenzoyl chloride gave 0.63 g. of crude elliotinyl *p*-nitrobenzoate, m.p. 116–122°. Two recrystallizations from 95% ethanol gave 0.45 g. of the pure ester whose infrared spectrum, optical rotation, and melting point (alone and mixture) were identical with the ester of the alcohol prepared by the reduction of elliotinoic acid.

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