quentially with water (200 mL), 50% aqueous EtOH (200 mL), and acetone (200 mL). After drying, the isolated solid (17.3 g) contained 90% $Ba_2(S_P)$-ATP-α-S[13] by weight (20 mmol, 53% yield from AMPS), no detectable (R_P)-ATP-α-S, and <3% ATP (determined by HPLC and ^{31}P NMR);[13] ^{31}P NMR δ -43.5 (d, P_α), +5.8 (d, P_γ), +22.3 (dd, P_β); $J_{P_\alpha-P_\beta}$ = 27.2 Hz, $J_{P_\beta-P_\gamma}$ = 20.0 Hz (Figure 1).

Registry No. (S_P)-ATP-α-S, 58976-48-0; (S_P)-ATP-α-S·2Ba, 88157-74-8; AMPS, 19341-57-2; adenosine, 58-61-7; PEP, 138-08-9; ATP, 56-65-5; PK, 9001-59-6; AK, 9013-02-9.

(13) The $Ba_2(S_P)$-ATP-α-S was solubilized for analysis by stirring with 2 equiv of $(NH_4)_2SO_4$ (pH 8.0, 4 °C, 1 h). The $BaSO_4$ was removed by centrifugation.

Synthesis of 4-Alkenoic and 4-Alkynoic Esters via Alkylation of O-Silylated Ketene Acetals

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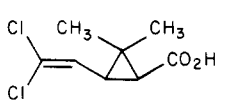
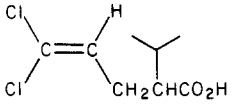
In recent years considerable interest has been shown in insecticidal esters derived from 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylic acid (1). Cleavage of the



1



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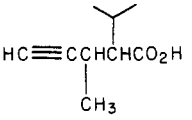


3

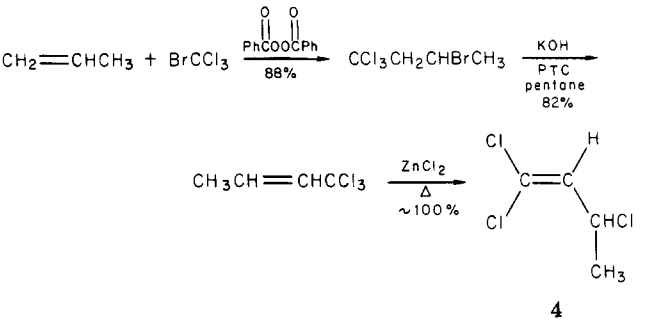
C_2–C_3 bond in 1 yields 5,5-dichloro-2-(1-methylethyl)-4-pentenoic acid (2). In this paper we report the synthesis, by direct allylation of O-silylated ketene acetals, of several esters of acids related to 2 but bearing one or two alkyl groups at C_3. We also report the synthesis of an ester of the 4-alkynoic acid 3 using a similar procedure.[1]

The alkylation of O-silylated ketene acetals has been shown to proceed efficiently with halides that can readily form a stablized carbonium ion in the presence of the Lewis acid catalyst. Thus, *tert*-butyl,[2] secondary benzyl,[3] prenyl,[3] methoxymethyl,[3] and 2-norbornyl halides[4] all give good yields when condensed with O-silylated ketene acetals at room temperature in the presence of a Lewis acid catalyst. However, primary and secondary halides do not undergo reaction with these ketene acetals even under forcing conditions.[5] The success of the alkylation procedure is thus quite dependent upon the halide.

It has been found that 1,1-dichloroallyl halides (with at least one alkyl substituent at C_3) will react smoothly under Lewis acid catalysis with O-silyated ketene acetals to give esters of the desired acid (Table I). The O-silylated ketene acetals were prepared from known or commercially available esters by using published procedures.[6]

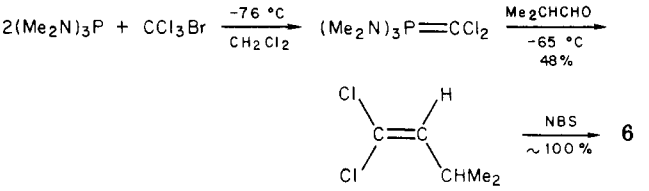
(1) Biological activity of certain esters of these acids will be reported elsewhere.
(2) Reetz, M. T.; Schwellnus, K. *Tetrahedron Lett.* **1978**, 1455.
(3) Paterson, I. *Tetrahedron Lett.* **1979**, 1519.
(4) Reetz, M. T.; Sauerwald, M.; Walz, P. *Tetrahedron Lett.* **1981**, *22*, 1101.
(5) Under the conditions reported in this paper, isopropyl iodide would not react with the ketene acetals.

Scheme I



4

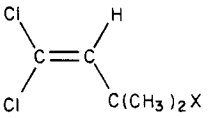
Scheme II



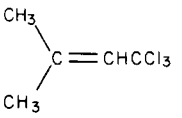
The 1,1,3-trichloro-1-butene (4) required in the synthesis of several of the esters in Table I was prepared as shown in Scheme I.

The use of KOH/pentane with a phase-transfer catalyst for the dehydrobromination of 1,1,1-trichloro-3-bromobutane resulted in twice the yield of 1,1,1-trichloro-2-butene reported in the literature.[7] The latter compound was quantitatively isomerized at room temperature to the desired allylic halide 4 by using a catalytic amount of zinc chloride.

The halide 5 required in the synthesis of several of the desired esters is reported to have been synthesized by refluxing 1,1,1,3-tetrachloro-3-methylbutane with anhydrous ferric chloride in benzene.[8] We found that these conditions did not produce 5 but gave a mixture of 4,4,4-trichloro-2-methyl-1-butene, 1,1,1-trichloro-3-methyl-2-butene, and starting material.



5, X = Cl
6, X = Br



7

A possible precursor to 5 is 7, which has reportedly been synthesized by dehydrohalogenation of 1,1,1-trichloro-3-bromo-3-methylbutane with KOH/ethanol at 0 °C.[7] We found that these conditions gave a mixture of 7 and 4,4,4-trichloro-2-methyl-1-butene. This mixture could not be readily separated by fractional distillation.

The allylic bromide 6 was synthesized as shown in Scheme II. The 1,1,3-trichloro-1-pentene shown in Table I was synthesized by a variation of Scheme I in which 1-butene and carbon tetrachloride were the starting materials.

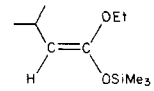
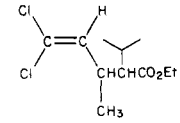
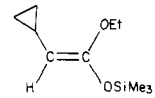
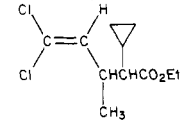
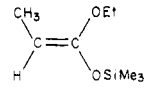
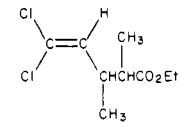
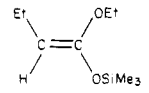
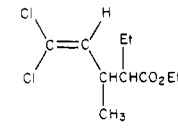
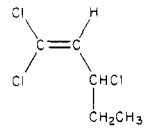
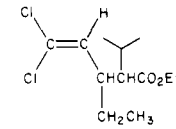
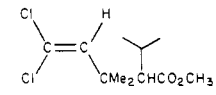
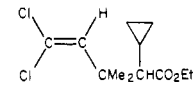
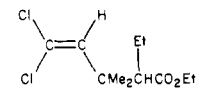
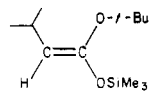
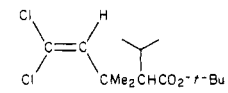
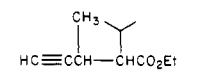
The synthesis of 1,1-dichloro-3-methyl-1-butene was accomplished via a slight modification of a literature procedure for preparing 1,1-dihaloalkenes.[9]

It has also been found that secondary propargyl halides will alkylate O-silylated ketene acetals. This provides a

(6) Ainsworth, C.; Chen, F.; Kuo, Y. N. *J. Organomet. Chem.* **1972**, *46*, 59.
(7) Nesmeyanov, A. N.; Freidlina, R. K.; Zakharkin, L. I.; Belayvskii, A. B. *Zh. Obschi. Khim.* **1956**, *26*, 1070; *Chem. Abstr.* **1956**, *50*, 16658*i*.
(8) Topchiev, A. V.; Bogomolova, N. T.; Gol'dfarb, Y. Y. *Dokl. Akad. Nauk. SSSR* **1956**, *107*, 420; *Chem. Abstr.* **1956**, *50*, 14503*e*.
(9) Salmond, W. G. *Tetrahedron Lett.* **1977**, 1241.

0022-3263/84/1949-0706$01.50/0

Table I. Esters Prepared by Allylation of Ketene Acetals

halide	ketene acetal	product	isolated yield,[a] %
4	 8	 11	62
4	 9	 12	30
4		 13	50
4	 10	 14	48
	8	 15	58
6	8	 16	69
6	9	 17	51
6	10	 18	67
6		 19	89[b]
	8	 20	39

[a] No effort was made to optimize yields. [b] The *tert*-butyl ester partially pyrolyzed to the acid during vacuum distillation.

convient synthesis of 4-alkenoic esters as demonstrated by the synthesis of **20** (Table I).

Due to the steric hinderance about the ester function and the lability of the dichlorovinyl moiety, the saponification of the ethyl esters to the desired acids did not always proceed without difficulty. Thus, the methyl ester **16** could not be saponified even by prolonged refluxing with 4 N NaOH in ethanol–water. More stringent conditions resulted in the decomposition of **16**. The problem was solved by preparing the O-silylated ketene acetal of *tert*-butyl-3-methylbutyrate, alkylation with **6**, and thermolysis to the desired acid.

In summary, it has been found that esters of 5,5-dihalo-4-alkenoic acids with at least one alkyl substituent at C_3 may be prepared by condensing the appropriate allyl halide with an O-silylated ketene acetal under Lewis acid catalysis. Under identical conditions, propargyl halides and O-silylated ketene acetals give esters of 4-alkynoic acids. The mild reaction conditions required in the alkylation and the structural variation possible in the O-silylated ketene acetals make possible the synthesis of highly hindered esters with relatively labile moieties using this method.

Experimental Section

General Procedures. Melting points were determined with a Thomas-Hoover capillary apparatus and are uncorrected. Infared spectra were recorded on a Perkin-Elmer Model 197 or Beckman AccuLab 2 spectrometer. NMR spectra were obtained with a Varian EM 360L spectrometer with Me_4Si as an internal

standard. Elemental analyses were obtained by the Union Carbide Technical Center Analytical Group.

Ethyl 5,5-Dichloro-3-methyl-2-(1-methylethyl)-4-pentenoate (11). This procedure is representative of that used to prepare all of the esters in Table I. A mixture of 30.36 g (0.15 mol) of 1-[(trimethylsilyl)oxy]-1-ethoxy-3-methyl-1-butene, 23.9 g (0.15 mol) of 1,1,3-trichloro-1-butene (vide infra), and ~0.50 g of anhydrous zinc chloride in 100 mL of methylene chloride was stirred at room temperature under nitrogen. The reaction was monitored by observing the gradual disappearance of the ketene acetal C=C peak at 1675 cm^{-1} and the appearance of an ester C=O at 1720 cm^{-1}. After 3 days the reaction appeared complete, and the solution was washed with 5% $NaHCO_3$ and then with water and dried ($MgSO_4$). The solvent was removed under reduced pressure and the residue vacuum distilled through a Vigreux column to give 23.41 g (62%) of 11 as a clear colorless liquid: bp 64–68 °C (0.30 mm); NMR ($CDCl_3$) δ 0.71–1.21 (m, 9 H, isopropyl and C_3-Me), 1.30 (t, J = 5 Hz, 3 H, ester CH_3), 1.5–2.4 (m, 2 H, isopropyl CH and C_3-CH), 1.62–3.30 (m, 1 H, $CHCO_2$), 4.20 (q, J = 4, 2 H, ester CH_2), 5.7 and 6.25 (dd, J = 10 Hz, 1 H, olefinic).

1,1,3-Trichloro-1-butene. A mixture of 159.25 g (2.45 mol) of powdered KOH and ~1 g of dicyclohexyl-18-crown-6 in pentane was heated to reflux, and 393.16 g (1.64 mol) of 1,1,1-trichloro-3-bromobutane[10] were added dropwise. The mixture was refluxed overnight during which the white suspension of KOH disappeared and was replaced by a dark precipitate. The pentane was washed with water, dried ($MgSO_4$), and fractionally distilled through a Vigreux column to give 217.17 g (83%) of 1,1,1-trichloro-2-butene: bp 79–84 °C (100 mm); NMR ($CDCl_3$) δ 1.85 (d, J = 5 Hz, 3 H, CH_3), 6.20 (m, 2 H, olefinic).

The 1,1,1-trichloro-2-butene (146.07 g, 0.92 mol) was stirred at room temperature under N_2 with 5.8 g of anhydrous zinc chloride for 16 h. The light yellow liquid was decanted from the zinc chloride to give 134.51 g (92%) of 1,1,3-trichloro-1-butene, which was used without purification: NMR ($CDCl_3$) δ 1.65 (d, J = 7 Hz, 3 H, CH_3), 4.85 (m, 1 H, allylic CH), 6.05 (d, J = 10 Hz, 1 H, olefinic).

1,1,3-Trichloro-1-pentene. To a solution of 66.0 g (1.0 mol) of 85% KOH in 500 mL of anhydrous ethanol stirred under N_2 and cooled with a salt–ice bath was added, dropwise, 209.9 g (1.0 mol) of 1,1,1,3-tetrachloropentane.[11] During the addition the temperature was maintained between +3 and +8 °C. The mixture was stirred in the salt–ice bath for 5 h after the addition was complete, then diluted with 2 L of ice water, and extracted with hexane (3 × 400 mL), and the combined hexane extracts were washed with water and dried ($MgSO_4$); the hexane was distilled off at atmospheric pressure. The residue was vacuum distilled through a Vigreux column to give 115.7 g (67%) of 1,1,1-trichloro-2-pentene: bp 88–91 °C (55 mm); NMR ($CDCl_3$); δ 1.00 (t, J = 7 Hz, 3 H, CH_3), 1.52–2.47 (m, 2 H, CH_2), 5.83–6.61 (m, 2 H, olefinic).

The 1,1,1-trichloro-2-pentene (91.0 g, 0.52 mol) was added dropwise to 2.1 g (0.015 mol) of anhydrous zinc chloride with stirring under N_2, with a surrounding ice bath to keep the temperature <5 °C. The mixture was stirred for 1 h at ~30 °C, an additional 0.5 g of $ZnCl_2$ added, and the mixture allowed to stir overnight at room temperature. The 1,1,3-trichloro-1-pentene (90.5 g) was used without purification: NMR ($CDCl_3$) δ 1.02 (t, J = 7 Hz, 3 H, CH_3), 1.58–2.20 (m, 2 H, CH_2), 4.30–4.87 (m, 1 H, allylic CH), 6.00 (d, J = 10 Hz, 1 H, olefinic).

1,1-Dichloro-3-bromo-3-methyl-1-butene (6). A solution of 39.66 g (0.200 mol) of bromotrichloromethane in 100 mL of CH_2Cl_2 was cooled[12] to −65 °C and 81.61 g (0.50 mol) of hexamethylphosphorus triamide in 100 mL of CH_2Cl_2 added dropwise. Care was taken to maintain the reaction temperature at −65 °C during this addition and for 30 min after completion of the addition. The isobutyraldehyde (14.42 g, 0.200 mol) was added in 50 mL of CH_2Cl_2 while maintaining the −65 °C temperature. The mixture was brought to room temperature by being allowed to stand overnight. The mixture was poured into ice water, and the CH_2Cl_2 was separated, washed with 5% HCl and then water, and dried ($MgSO_4$), and the solution was distilled through a Vigreux column to give 13.44 g (48%) of 1,1-dichloro-3-methyl-1-butene: bp 68 °C (145 mm); NMR ($CDCl_3$) δ 1.00 (d, J = 6 Hz, 6 H, CH_3's), 2.30–3.00 (m, 1 H, allylic CH),5.70 (d, J = 9 Hz, 1 H, olefinic). This material was converted to the desired allyl bromide by refluxing for 30 min with 1.1 equiv of *N*-bromosuccinimide in carbon tetrachloride containing 100 mg of dibenzoyl peroxide: NMR ($CDCl_3$) δ 2.05 (s, 6 H, CH_3's), 6.25 (s, 1 H, olefinic).

Ethyl 5,5-dichloro-3-methyl-2-cyclopropyl-4-pentenoate (12): bp 82–85 °C (0.60 mm); NMR ($CDCl_3$) δ 0.05–0.82 (m, 5 H, cyclopropyl), 0.98 and 1.08 (dd, 3 H, C_3-Me), 1.23 (t, J = 7 Hz, 3 H, ester CH_3), 1.42–1.88 (m, 1 H, C_3-CH), 2.72–3.21 (m, 1 H, C_2-CH), 4.11 (q, J = 8 Hz, 2 H, ester CH_2), 5.73 and 5.96 (dd, J = 10 Hz, 1 H, olefinic); IR (film) 2970, 1730, 1620, 1450, 1370, 1300, 1250, 1180, 1155, 1030, 900, 870, 850, 830 cm^{-1}. Anal. Calcd for $C_{11}H_{16}Cl_2O_2$: C, 52.60; H, 6.42. Found: C, 52.45; H, 6.31.

Ethyl 5,5-dichloro-2,3-dimethyl-4-pentenoate (13): bp 68–72 °C (1.4 mm); NMR ($CDCl_3$) δ 1.10 (t, J = 7 Hz, 3 H, ester CH_3), 1.15 and 1.35 (dd, 3 H, C_3-Me), 1.05 and 1.25 (dd, 3 H, C_2-Me), 2.0–3.1 (m, 2 H, C_3- and C_4-CH), 4.18 (q, J = 8 Hz, 2 H, ester CH_2), 5.76 and 5.92 (dd, J = 9 Hz, 1 H, olefinic), IR (film) 2980, 2890, 1730, 1620, 1455, 1380, 1260, 1240, 1180, 1130, 1100, 1070, 10040, 915, 890, 860, 830 cm^{-1}. Anal. Calcd for $C_9H_{14}Cl_2O_2$: C, 48.02; H, 6.27. Found: C, 47.84; H, 6.17.

Ethyl 5,5-dichloro-2-ethyl-3-methyl-4-pentenoate (14): bp 92 °C (2.0 mm); NMR ($CDCl_3$) δ 1.03 (t, J = 6 Hz, 3 H, C_2-ethyl), 1.05 and 1.15 (dd, 3 H, C_3-Me), 1.30 (t, J = 7 Hz, 3 H, ester CH_3), 1.53 (m, 2 H, C_2-ethyl), 2.23 (m, 1 H, C_3-CH), 2.81 (m, 1 H, C_2-CH), 4.20 (q, J = 7 Hz, 2 H, ester CH_2), 5.72 and 6.02 (dd, J = 10 Hz, 1 H, olefinic); IR (CH_2Cl_2) 2970, 2950, 2890, 1725, 1625, 1470, 1450, 1380, 1230, 1190, 1155, 1100, 10030, 890, 850 cm^{-1}. Anal. Calcd for $C_{10}H_{16}Cl_2O_2$: C, 50.22; H, 6.74. Found: C, 49.93; H, 6.72.

Ethyl 5,5-dichloro-3-ethyl-2-(1-methylethyl)-4-pentenoate (15): bp 87–91 °C (0.70 mm); NMR ($CDCl_3$) δ 0.60–1.11 (m, 9 H, isopropyl Me's and C_3-ethyl), 1.30 (t, J = 6 Hz, 3 H, ester CH_3), 1.68–2.50 (m, 4 H, isopropyl CH, C_3-CH, C_3-ethyl), 2.50–3.20 (m, 1 H, C_2-CH), 4.20 (q, J = 7 Hz, 2 H, ester CH_2), 5.60 and 6.20 (dd, J = 10 Hz, 1 H, olefinic); IR (film) 2970, 2945, 2880, 1730, 1620, 1460, 1380, 1230, 1180, 1150, 1125, 1030, 915, 900, 870, 850, 775 cm^{-1}. Anal. Calcd for $C_{12}H_{20}Cl_2O_2$: C, 53.94; H, 7.55. Found: C, 53.82; H, 7.47.

Methyl 5,5-dichloro-3,3-dimethyl-2-(1-methylethyl)-4-pentenoate (16): bp 77–84 °C (1.0 mm); NMR ($CDCl_3$) δ 0.90 and 1.05 (dd overlapping, J = 6 Hz, 6 H, isopropyl Me's), 1.29 (s, 6 H, C_3-Me's), 1.74–2.40 (m, 1 H, isopropyl CH), 2.58 (d, J = 7 Hz, 1 H, C_2-CH), 3.71 (s, 3 H, ester Me), 6.12 (s, 1 H, olefinic); IR (film) 2960, 2870, 1725, 1610, 1455, 1430, 1385, 1365, 1350, 1275, 1245, 1190, 1140, 1020, 1005, 910, 870, 790, 715, 660 cm^{-1}. Anal. Calcd for $C_{11}H_{18}Cl_2O_2$: C, 52.19; H, 7.17. Found: C, 52.03; H, 6.95.

Ethyl 5,5-dichloro-2-cyclopropyl-3,3-dimethyl-4-pentenoate (17): bp 80–85 °C (0.10 mm); NMR ($CDCl_3$) δ 0.05–0.83 (m, 5 H, cyclopropyl), 1.26 (t, J = 7 Hz, 3 H, ester Me), 1.30 (s, 6 H, C_3-Me's), 1.71 (d, J = 9 Hz, 1 H, C_2-H), 4.10 (q, J = 7 Hz, 2 H, ester CH_2), 6.15 (s, 1 H, olefinic); IR (CH_2Cl_2) 3090, 2060, 2990, 2920, 1725, 1610, 1460, 1450, 1890, 1370, 1330, 1260, 1190, 1150, 1040, 920, 900 cm^{-1}. Anal. Calcd for $C_{12}H_{18}Cl_2O_2$: C, 54.35; H, 6.84. Found: C, 54.27; H, 6.80.

Ethyl 5,5-dichloro-3,3-dimethyl-2-ethyl-4-pentenoate (18): bp 90–94 °C (2.0 mm); NMR ($CDCl_3$) δ 0.88 (t, J = 6 Hz, 3 H, C_2-ethyl), 1.30 (s, 6 H, C_3-Me's), 1.30 (t, J = 6 Hz, 3 H, ester Me), 1.30–2.00 (m, 2 H, C_2-ethyl), 2.10–2.65 (m, 1 H, C_2-CH), 4.20 (q, J = 8 Hz, 2 H, ester CH_2), 6.08 (s, 1 H, olefinic); IR (CCl_4) 2970, 2930, 2870, 1720, 1610, 1450, 1390, 1370, 1345, 1250, 1180, 1140, 1095, 1040, 1020, 840, 700, 630 cm^{-1}. Anal. Calcd for $C_{11}H_{18}Cl_2O_2$: C, 52.19; H, 7.17. Found: C, 51.98; H, 7.02.

***tert*-Butyl 5,5-dichloro-3,3-dimethyl-2-(1-methylethyl)-4-pentenoate (19):** bp 112–114 °C (0.4 mm); NMR ($CDCl_3$) δ 0.98 (dd, 6 H, isopropyl Me's), 1.29 (s, 6 H, C_3-Me's), 1.49 (s, 9 H, ester *t*-Bu), 1.71–2.55 (m, 2 H, C_2-CH and isopropyl CH), 6.10 (s, 1 H, olefinic); IR (CCl_4) 2960, 2870, 1710, 1610, 1450, 1365, 1310, 1250, 1195, 1165, 1140, 1050, 970, 920, 890, 850 cm^{-1}. Anal. Calcd for $C_{14}H_{24}Cl_2O_2$: C, 56.95; H, 8.19. Found: C, 56.81; H, 7.98.

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(12) Contrary to the general procedure given in ref 9, failure to maintain the temperature at −65 °C resulted in a much lower yield of the dihalo olefin.

Ethyl 3-methyl-2-(1-methylethyl)-4-pentynoate (20): bp 70–74 °C (7.0 mm); NMR ($CDCl_3$) δ 0.90 and 1.00 (dd, 6 H, isopropyl Me's), 1.10 and 1.28 (dd, 3 H, C_3-Me), 1.30 (t, J = 6 Hz, 3 H, ester Me), 1.97–2.53 (m, 3 H, isopropyl CH, C_3-CH, alkynyl CH), 2.53–3.20 (m, 1 H, C_2-CH), 4.20 (q, J = 7 Hz, 2 H, ester CH_2); IR (film) 3230, 2920, 1730, 1460, 1370, 1300, 1250, 1200, 1170, 1070 cm^{-1}. Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.96. Found: C, 72.38; H, 9.83.

Registry No. **4**, 13279-86-2; **5**, 88302-98-1; **6**, 88302-99-2; **8**, 63547-55-7; **9**, 88303-00-8; **10**, 65946-52-3; **11**, 83190-45-8; **12**, 88303-01-9; **13**, 88303-02-0; **14**, 88303-03-1; **15**, 88303-04-2; **16**, 88303-05-3; **17**, 88303-09-7; **18**, 88303-10-0; **19**, 88303-06-4; **20**, 88303-11-1; $Cl_2C{=}CHCH(CH_3)_2$, 32363-91-0; $CH_3CH{=}C(OEt)Si(CH_3)_3$, 80675-53-2; $Cl_2C{=}CHCHClCH_2CH_3$, 88303-07-5; $HC{\equiv}CCHClCH_3$, 21020-24-6; $(CH_3)_2CHCH{=}C(OC(CH_3)_3)Si(CH_3)_3$, 88303-08-6; hexamethylphosphorous triamide, 1608-26-0; bromotrichloromethane, 75-62-7; isobutyraldehyde, 78-84-2; 1,1,1,3-tetrachloropentane, 19967-19-2.

Acid-Catalyzed Isomerization of Cycloartane Triterpene Alcohols. The Formation of Cucurbitane- and Lanostane-Type Isomers

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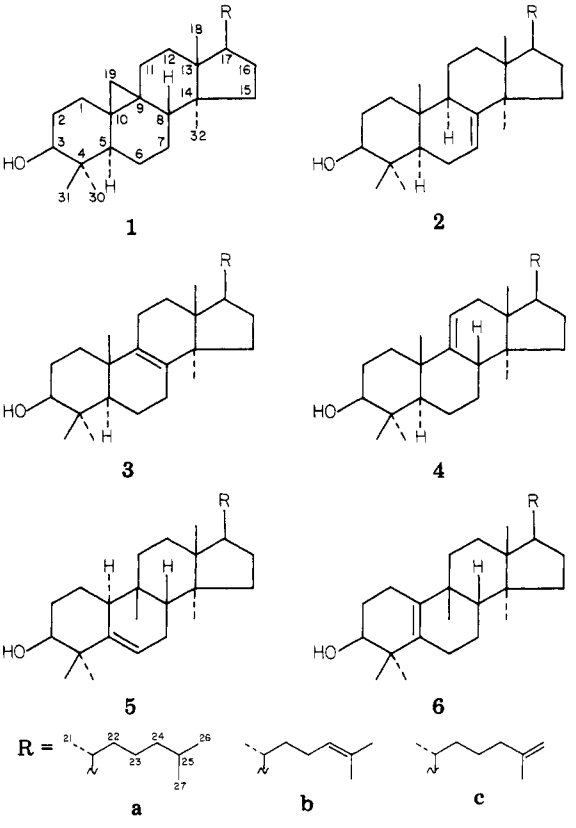
Cycloartane (9β,19-cyclolanostane) triterpene alcohols, for example, cycloartenol (9β,19-cyclo-5α-lanost-24-en-3β-ol, **1b**), contain a cyclopropane ring and are considered to be intermediates of sterol biosynthesis in photosynthetic eucaryotes.[1] The cyclopropane ring has olefinic properties and, upon treatment with acidic reagents, gives ring-opened products. The cyclopropane–alkene isomerization has been explained by invoking the formation of either of two types of protonated cyclopropanes, edge-protonated and corner-protonated, and subsequent C,C-bond fission with the elimination of a proton.[2] The acid-catalyzed isomerization of cycloartanol (9β,19-cyclo-5α-lanostan-3β-ol, **1a**) with gaseous hydrogen chloride in chloroform has been shown to afford three isomers of the lanostane-type, 5α-lanost-7-en-3β-ol (**2a**), 5α-lanost-8-en-3β-ol (**3a**), and, mainly, 5α-lanost-9(11)-en-3β-ol (**4a**).[3] However, Markovnikov cleavage might conceivably give rise to another type of isomerized triterpene, i.e., a cucurbitane [19(10→9β) abeolanostane]-type isomer, which would be generated by C_{10}–C_{19} bond cleavage, in addition to the lanostane-type isomers. We have, therefore, undertaken a detailed investigation of the isomerization of two cyclopropanes, **1a** and **1b**.

The isomerization was performed with three Brønsted acids: hydrochloric acid, sulfuric acid, and *p*-toluenesulfonic acid, while chloroform, isopropyl alcohol, and glacial acetic acid were used as the solvent. The results of the isomerization of **1a** are summarized in Table I. The treatment of **1a** with gaseous HCl in $CHCl_3$ at 0 °C for 1 h yielded only three lanostane-type isomers, **2a**, **3a**, and **4a**; this finding is consistent with the previous observations.[3] However, when **1a** was treated with hydrochloric acid in *i*-PrOH at 80 °C for 1 h, there were obtained very small amounts of two cucurbitane-type isomers, 10α-cucurbit-5-en-3β-ol (**5a**) and cucurbit-5(10)-en-3β-ol (**6a**), together with the three lanostane-type isomers, the dehydration products, and a substantial amount of the starting material. The formation of the two cucurbitane-type isomers was also observed in the isomerization with H_2SO_4 and *p*-$MePhSO_3H$ in *i*-PrOH. The exposure of **1a** to H_2SO_4 for 3 h resulted largely in the recovery of the starting material; after 12 h, the amount of the recovered starting material was considerably decreased, and increasing amounts of lanostane- and cucurbitane-type isomers and also of the dehydration products were obtained. After an extension of the reaction time to 24 h, although the starting material almost disappeared, the amounts of isomerized triterpene alcohols were found to be virtually unchanged or to have undergone a significant loss in the case of a cucurbitane-type isomer **6a**, with the amounts of the dehydration products increased appreciably. In AcOH as the solvent, the cyclopropane ring opening proceeded more smoothly than in *i*-PrOH, giving three lanostane-type isomers, **2a**, **3a**, and **4a**, and much larger amounts of the dehydration products, but we could identify no cucurbitane-type isomers, **5a** or **6a**, or only trace amounts of them.



Isomerization of cycloartenol (**1b**), with a catalytic amount of H_2SO_4 in *i*-PrOH for 12 h, gave the following isomerized lanostane- and cucurbitane-type isomers: 5α-lanosta-7,24-dien-3β-ol (**2b**, 7%), lanosterol (5α-lanosta-8,24-dien-3β-ol, **3b**, 7%), parkeol [5α-lanosta-9(11),24-dien-3β-ol, **4b**, 30%], 5α-lanosta-7,25-dien-3β-ol (**2c**, 2%), 5α-lanosta-8,25-dien-3β-ol (**3c**, 2%), 5α-lanosta-9(11),25-dien-3β-ol (**4c**, 4%), anhydrolitsomentol (**5b**, 7%), cucurbita-5(10),24-dien-3β-ol (**6b**, 16%), 10α-cucurbita-5,25-

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