The Allylic Rearrangement. III.[1,2] A Favorskii-Type Rearrangement of the Vinylogs of α-Chloroacetones

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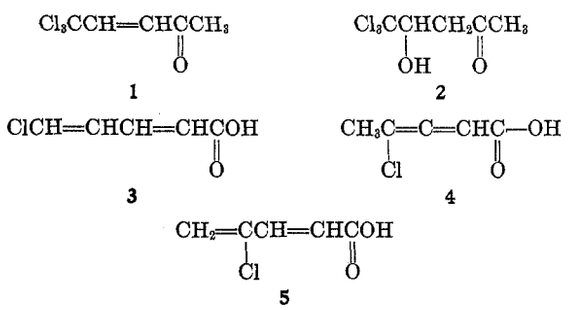
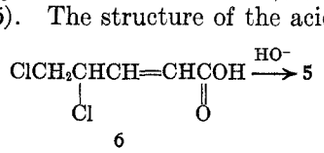
A Favorskii-type rearrangement of the vinylogs of α-chloroacetones is described. The alkaline hydrolysis of 5,5,5-trichloro-3-penten-2-one (1) or its precursor, 5,5,5-trichloro-4-hydroxy-2-pentanone (2), gave 5-chloro-2,4-pentadienoic acid (3) in a 27–29% yield. The treatment of 1 with methanolic sodium methoxide gave the mixture of the methyl ester (10) of 3 and the methyl ester (14) of 5,5-dichloro-4-pentenoic acid (13). The alkaline hydrolysis of 5,5-dichloro-3-penten-2-one (7), 5,5-dichloro-3-hexen-2-one (8), and 5,5-dichloro-4-hydroxypentan-2-one (9) also gave the corresponding unsaturated acids. The reactions carried out in protic solvents tend to afford 4-pentenoic acid derivatives predominantly rather than 2,4-pentadienoic acid derivatives. It is assumed that the pathway of the formation of 3 from the starting material 1 involves a Favorskii-type rearrangement initiated by loss of chlorine at C-5 from the enolate anion of 1 to give a dipolar ion intermediate.

It has long since been known that the alkaline hydrolysis of 5,5,5-trichloro-3-penten-2-one (1)[3] or 5,5,5-trichloro-4-hydroxy-2-pentanone (2)[4] gives a carboxylic acid (3) with the composition of $C_5H_5O_2Cl$, mp 171–172°. Uschakow[4] once assigned the structure of 4-chloro-2,3-pentadienoic acid (4) and/or 4-chloro-2,4-pentadienoic acid (5) to the acid. On the other hand,



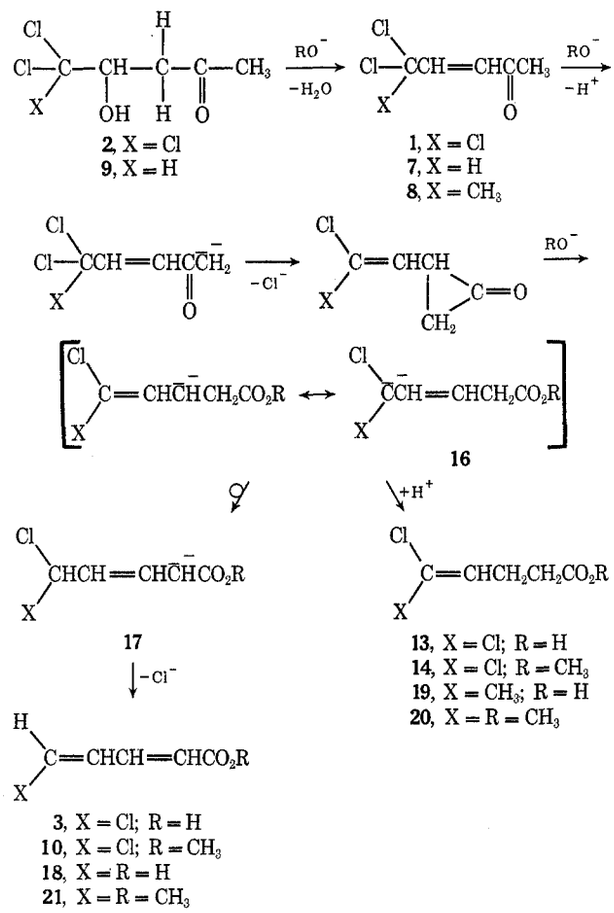
Muskat has later shown that the latter structural assignment of Uschakow was not correct, as he obtained the real acid 5, which melted at about 94°,[5] by the alkaline dehydrochlorination of 4,5-dichloro-2-pentenoic acid (6). The structure of the acid 3 had been



left ambiguous thereafter. In the course of our study on the reactions of the pentenone 1,[2,6] we became interested in reexamining the structure of the acid 3 and have identified it as 5-chloro-2,4-pentadienoic acid.

We assumed the pathway of the formation of 3 from the starting material 1 to involve a Favorskii-type rearrangement initiated by loss of chlorine at C-5 from the enolate anion[7] of 1 as shown in Scheme I. To ensure the validity of this assumption, we carried out the alkaline hydrolysis of a number of substrates with the structures of the vinylog of α-chloroacetones such as 5,5-dichloro-3-penten-2-one (7) and 5,5-dichloro-3-hexen-2-one (8) or the precursor of 7, 5,5-dichloro-4-hydroxypentan-2-one (9). These compounds also afforded the unsaturated carboxylic acids, whose formation can be well explained by the proposed mechanism. This paper describes the structural identification of the acid 3 and the related compounds and discusses the reaction mechanisms of their formation.

SCHEME I



Results and Discussion

By the alkaline hydrolysis of either 1 or 2, we obtained the acid, mp 170°, in a 19–29% yield, which was

(1) Presented in part at the 24th Annual Meeting of the Chemical Society of Japan, Osaka, Japan, April 1, 1971.

(2) Preceding paper: A. Takeda, S. Tsuboi, T. Moriwake, and E. Hirata, *Bull. Chem. Soc. Jap.*, **45**, 3685 (1972).

(3) I. Salkind, *J. Russ. Phys. Chem. Soc.*, **30**, 906 (1898).

(4) S. P. Uschakow, *ibid.*, **29**, 113 (1897).

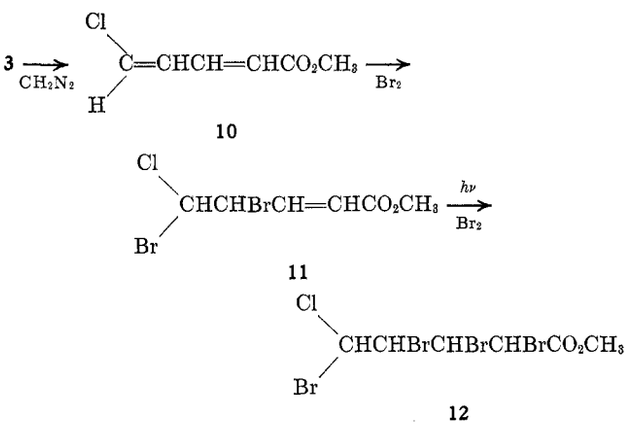
(5) I. E. Muskat and B. C. Becker, *J. Amer. Chem. Soc.*, **52**, 812 (1930). Owing to its ease of polymerization it was not possible for these authors to get a sharp melting point.

(6) A. Takeda and S. Tsuboi, *J. Org. Chem.*, **35**, 2690 (1970).

(7) It appears that Favorskii rearrangements generally involve ionization of halide ion from the initially formed enolate ion to give a dipolar ion intermediate, which then collapses to a cyclopropanone: F. G. Bordwell, R. G. Scamehorn, and W. R. Springer, *J. Amer. Chem. Soc.*, **91**, 2087 (1969); F. G. Bordwell and R. G. Scamehorn, *ibid.*, **93**, 3410 (1971). Applied to compound 1 this mechanism predicts the formation of dipolar ion $Cl_2C{=}CH{-}{}^{+}CHCO\bar{C}H_2^{-}$, which then gives the cyclopropanone shown in Scheme I.

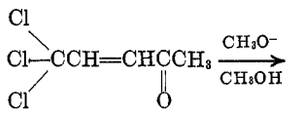
believed to be the same one as that described by Uschakow.[4] The mass spectrum of this product as well as its analyses supported the composition $C_5H_5O_2Cl$. The ir spectrum (KBr) of the acid **3** exhibited absorptions at 3060 (>C=CH), 3000–2500 (carboxy), 1690 and 1670 (conjugated carboxy C=O), 1655 (shoulder, C=C), 1620 (C=C), 1002 and 950 (trans HC=CH), 840 (cis HC=CH), and 710 cm^{-1} (CCl). The allenic structure can be ruled out from the possible structures of **3** because no notable absorption was observed in the region of 1950 cm^{-1}. Since the nmr spectrum [d, $(CD_3)_2CO$] showed signals due to four vicinally coupled protons attached to the individual carbon atoms, 5-chloro-2,4-pentadienoic acid has now been assigned to this product (**3**).[8] The geometry of the acid **3**, trans-2:cis-4, is estimated by the coupling constants observed of four protons[9] and also by the ir absorptions in the region of 800–1000 cm^{-1}.[10] No additional peaks ascribable to other isomers were observed.

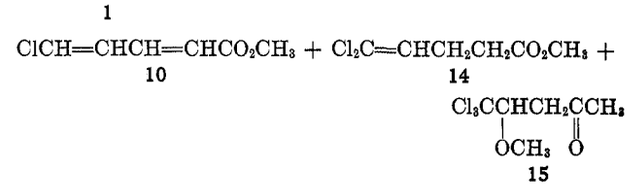
The acid **3** was converted to the methyl ester **10** with diazomethane quantitatively. One mole of the ester **10** took 2 mol of bromine in two steps. In addition to the acid **3**, 5,5-dichloro-4-pentenoic acid (**13**, 19%)



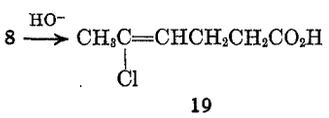
that Uschakow[4] did not allude to was obtained in the alkaline hydrolysis of **1**. The acid **13** was converted to the methyl ester **14**. The nmr spectrum of **14** in carbon tetrachloride showed one olefinic proton as a triplet at δ 5.89 ppm, methyl ester protons as a singlet at 3.64 ppm, and methylene protons as a multiplet centered at 2.41 ppm. The mass spectrum of **14** showed strong molecular ions at *m/e* 182 with the characteristic chlorine isotope distribution.

The treatment of **1** with methanolic sodium methoxide at 20–25° for 10 min gave the mixture of esters **10** and **14** and 5,5,5-trichloro-4-methoxypentan-2-one (**15**).[2] Only the ester **10** was isolated when **1** was treated with sodium methoxide in ether. The derivation of **13** and **14** in hydroxylic solvents can be explained by assuming a delocalized anion **16**, which, in protic solvents, is thought to give protonated products

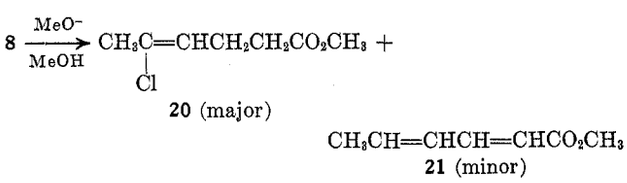




partly and isomerized products partly. The latter products probably underwent a dehydrochlorination to give **3** and **10**. This mechanism is further substantiated by the reaction of dichloro ketones **7**, **8**, and **9** with base. By treatment with aqueous sodium hydroxide, both **7** and **9** were converted to *trans*-2,4-pentadienoic acid (**18**)[11] in a 25% yield. The alkaline hydrolysis of the ketone **8** afforded 5-chloro-4-hexenoic acid (**19**)[12] exclusively in a 27% yield. The ir bands



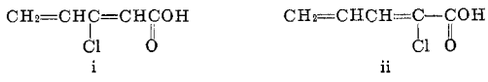
at 1700 (acid C=O) and 1660–1630 cm^{-1} (C=C) indicated the α,β-saturated structure of **19**. The unusually high δ value of its methylene protons (broad singlet, 2.42 ppm) is due to deshielding effects of the acid group and the vinyl group. The transformation of an intermediate **16** to **17** appears to be more favored when the substituent X is chlorine or hydrogen, since ketones **1**, **2**, **7**, and **9** afforded 2,4-pentadienoic acid derivatives as main products in protic solvents, whereas the ketone **8** gave 4-hexenoic acid derivatives as main products in protic solvents. When **8** was treated with sodium methoxide in dry methanol, the methyl ester **20**[13a] of the acid **19** was produced as the major component



along with methyl sorbate (**21**)[13b] as the minor component. The ester **20** was transformed to methyl sorbate (**21**) by the action of sodium methoxide in ether, though in a low yield (6%). This fact presents additional evidence to support the proposed mechanism of the Favorskii-type rearrangement reported here. The reaction sequence of **20** is given in Scheme II.

The effect of aprotic solvents on the product distribution has been further investigated. Table I summarizes the results of the reactions which were carried out in aprotic solvents such as ether, benzene, and *n*-hexane, and also those in protic solvents. There is an indication that the reactions in protic solvents afford more 4-alkenoic acid as compared to those in aprotic

(8) Two monochloropentadienoic acid structures, i and ii, have two geminate protons. Compound ii has been derived by Corre, *et al.*, by the



reaction of 2,3,3-trichloropropenal with vinylmagnesium chloride: M. L. Corre and E. Levas, *C. R. Acad. Sci., Ser. C*, **260**, 3414 (1965); lit. mp 118–119°.

(9) Y. Leraux and E. Vauthier, *C. R. Acad. Sci., Ser. C*, **271**, 1333 (1970).

(10) (a) L. Crombie, *J. Chem. Soc.*, 1007 (1955); (b) J. L. H. Allan, G. D. Meakins, and M. C. Whiting, *ibid.*, 1874 (1955).

(11) H. O. House and G. H. Rasmusson, *J. Org. Chem.*, **26**, 4278 (1961). The geometry of **18**, trans-2, is estimated by the coupling constant ($J_{2,3}$ = 14.8 Hz).

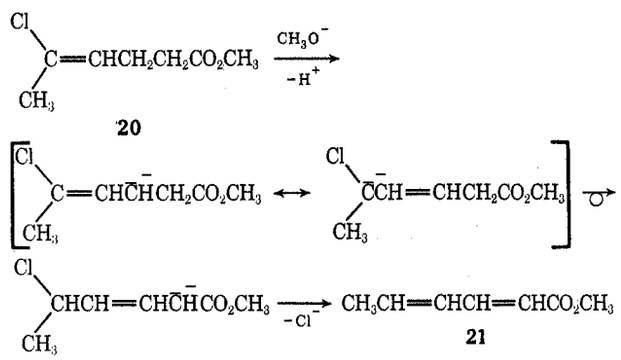
(12) Cis,trans mixture (3:7, or 7:3). Glpc analysis of its methyl ester (**20**) showed the presence of two components, which differed slightly in ir spectra at *ca.* 1340 and 790–800 cm^{-1}.

(13) (a) Cis,trans mixture (1:6 or 6:1). (b) The ir and nmr data indicate the geometry of this product to be trans-2:trans-4.[10]

TABLE I
REARRANGEMENT PRODUCTS FROM THE REACTION OF KETONES WITH BASE IN VARIOUS SOLVENTS

Ketone, $CXCl_2CH{=}CHCOCH_3$ or $XCCl_2CH(OH)CH_2COCH_3$ Compd	X	Base (RO^-) R	Solvent	Yield of rearrangement products, % $XCCl{=}CHCH_2CH_2CO_2R$	$XCH{=}CHCH{=}CHCO_2R$
1	Cl	H	Water	19 (13)	29 (3)
1	Cl	CH_3	Methanol	4 (14)	32 (10)
2	Cl	H	Water	0	27 (3)
1	Cl	CH_3	Ether	0	10 (10)
9	H	H	Water	0	25 (18)
7	H	H	Water	0	25 (18)
8	CH_3	H	Water	27 (19)	0
8	CH_3	CH_3	Methanol	34 (20)	17 (21)
8	CH_3	CH_3	Ether	5 (20)	9 (21)
8	CH_3	CH_3	Benzene	16 (20)	39 (21)
8	CH_3	CH_3	*n*-Hexane	1 (20)	21 (21)

SCHEME II



solvents, probably as a result of protonation of the intermediate **16**.

Experimental Section

The melting points and boiling points are uncorrected. Elemental analyses were carried out by Mr. Eiichiro Amano of our laboratory and microanalysis of chlorine content is due to Mr. Tsunekazu Kirido of Kuraray Co. Ltd., Kurashiki, Japan. Analytical determinations by glpc were performed on a Hitachi Model K-53 gas chromatograph fitted with the following columns (3 mm o.d. × 1 m): A, 10% Apiezon grease L on Chromosorb W; B, 10% polyneopentyl glycol succinate on Chromosorb W; C, 10% SE-30 on Chromosorb W. The preparative isolations by glpc were performed on a Yanagimoto Model GCG-550T gas chromatograph (3 mm o.d. × 2.25 m, 10% Apiezon Grease L on Chromosorb W). Mass spectra were obtained with a Hitachi Model RMS-4 mass spectrometer. We are indebted to Mr. Hiroshi Ooyama, Hokko Chemical Industry Co., Ltd., and Mr. Heizan Kawamoto and Miss Hiromi Ootani for nmr (60 MHz) measurements. Microanalyses and spectral measurements of liquid substances were performed on the samples collected by glpc or tlc.

5,5,5-Trichloro-4-hydroxy-2-pentanone (**2**)[6,14] and 5,5,5-trichloro-3-penten-2-one (**1**)[3,6] were prepared in ways similar to those described in the literature. Sorbic acid of commercial grade was purified by recrystallization from hot water, mp 133–134° (lit.[15] mp 134°). 2,4-Pentadienoic acid was prepared by the method described in the literature,[11] mp 69–70° (lit.[11] mp 71.5–72.5°).

5-Chloro-2,4-pentadienoic Acid (3).—To 165 ml of 12% sodium hydroxide cooled in an ice bath was added with stirring 102 g (0.50 mol) of **2** in one portion. When most of **2** came to solution the ice bath was removed. After the reaction mixture was allowed to come to room temperature, 165 ml of 12% sodium hydroxide was added. After the temperature was decreased to room temperature an additional amount (165 ml) of 12% sodium hydroxide was added. The mixture was heated for several minutes at 50–60°, treated with activated charcoal, and finally acidified with dilute hydrochloric acid to pH 2. The solid was collected, thoroughly washed with water, and air dried to give 18 g (yield 27%) of crude **3**. Recrystallization from chloroform gave 9 g (14%) of **3**: mp 170°; ir (KBr) 3060 (C=CH), 3000–2500 (COOH), 1690 (acid C=O), 1670 (acid C=O), 1620 (C=C), 1330, 1002, 952, 833, 710 cm^{-1}; nmr [$(CD_3)_2CO$] δ 6.02 (d, 1, J = 14.3 Hz, $-CH{=}CHCO_2H$), 6.82 (d, 1, J = 11.4 Hz, $ClCH{=}CH-$), 6.95 (dd, 1, J = 11.4 and 10.4 Hz, $ClCH{=}CH-$), 7.37 ppm (dd, 1, J = 10.4 and 14.3 Hz, $-CH{=}CHCO_2H$); mass spectrum (70 eV m/e (rel intensity) 132 (23, M^+, 1 Cl), 115 (5), 97 (100), 89 (7), 87 (21), 79 (8), 69 (24), 61 (10), 51 (77), 50 (27), 49 (9), 44 (13), 43 (9), 41 (60), 39 (19), 38 (14), 36 (42).

Anal. Calcd for $C_5H_5ClO_2$: C, 45.30; H, 3.80; Cl, 26.71. Found: C, 45.28; H, 3.92; Cl, 26.82.

Methyl 5-Chloro-2,4-pentadienoate (10).—Acid **3** (4.4 g, 0.033 mol) was esterified with diazomethane as usual to give 4.5 g (94%) of **10**: bp 66° (5 mm); mp 43–43.5° (*n*-hexane); ir (neat) 3060 (C=CH), 2960, 1720 (ester C=O), 1630 (C=C), 1585 (C=C), 1440, 1320, 995, 840, 730 cm^{-1} (CCl_4); nmr (CCl_4) δ 3.69 (s, 3, CO_2CH_3), 5.87 (d, 1, J = 14 Hz, $=CHCO_2CH_3$), 6.28–6.90 (m, 1, $-CH{=}CHCO_2CH_3$), 6.48 (d, 1, $ClCH{=}CH-$), 7.19 ppm (m, 1, $ClCH{=}CH-$).

Anal. Calcd for $C_6H_7ClO_2$: C, 49.17; H, 4.81. Found: C, 49.10; H, 4.82.

Alkaline Hydrolysis of 1.—Similar treatment of **1** (3.2 g, 0.016 mol) with 36 ml of 12% aqueous sodium hydroxide gave 0.34 g of crude **3**, as in the case of compound **2**. The extraction of the filtrate with ether gave 0.79 g of light brown needles. Tlc analysis of this product showed two spots, but the separation of these components by tlc was not successful. The esterification of the solid with diazomethane afforded a light brown oil. Glpc analysis (column A, 120°, carrier gas N_2, 0.5 kg/cm^2, 42 ml/min) showed two peaks, with retention times of 7.8 and 9.6 min, respectively, and in an area ratio of 34:66. Components 1 and 2 were collected by preparative glpc and identified as **10** (yield 29%[16]) and methyl 5,5-dichloro-4-pentenoate (**14**) (yield 19%), respectively, by comparison of ir spectrum and retention time with those of authentic samples.[17]

Reaction of 1 with Sodium Methoxide in Dry Methanol.—To a stirred solution of 17.3 g (0.32 mol) of sodium methoxide in 60 ml of dry methanol was added dropwise a solution of 10 g (0.054 mol) of **1** in 20 ml of dry methanol, at 20–25° for a period of 15 min. The mixture was stirred for 10 min and poured into a large excess of water. The organic layer was extracted with ether. The ethereal extracts, treated with activated charcoal, were washed with water and dried over $MgSO_4$. Removal of the solvent left 5.5 g of a clean oil. Glpc analysis (column C, 130°, carrier gas N_2, 0.5 kg/cm^2, 42 ml/min) of this oil showed four peaks. The peaks, retention times (min), and integrated percentages are as follows: 1, 1.8, 46%; 2, 2.7, 7%; 3, 3.2, 6%; 4, 3.8, 38%. Each component was collected by preparative glpc. Component 1, which solidified in a few minutes after separation, was identified as ester **10**, mp 41.5–42° after one recrystallization from *n*-hexane, yield 32%.

Component 2 was identified as **14**: yield 4%; ir (neat) 1735 (ester C=O), 1620 (C=C), 1438, 1175, 890 cm^{-1}; nmr (CCl_4) δ 2.41 (m, 4, $-CH_2CH_2CO_2CH_3$), 3.64 (s, 3, $-CO_2CH_3$), 5.89 ppm

(14) H. Gault and G. Mennicken, *C. R. Acad. Sci. Ser. C*, **229**, 1239 (1949).

(15) C. F. H. Allen and J. Van Allan, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 783.

(16) Total yield of **3**.

(17) For spectral data of compound **14** see the next section.

(t, 1, J = 8 Hz, =CH–); mass spectrum (70 eV) m/e (rel intensity) 182 (52, M^+, 2 Cl), 151 (70, 2 Cl), 147 (100, 1 Cl), 124 (87), 122 (95), 115 (53), 109 (84), 105 (41), 87 (75), 59 (65), 51 (61), 43 (40).

Anal. Calcd for $C_6H_8Cl_2O_2$: C, 39.37; H, 4.40. Found: C, 39.50; H, 4.54.

Component **4** was identified as **15** by comparison of ir and retention time with those of the authentic sample,[2] yield 18%.

Reaction of 1 with Sodium Methoxide in Dry Ether.—To a solution of 5 g (0.027 mol) of **1** in 30 ml of dry ether, 2.9 g (0.053 mol) of sodium methoxide was added slowly at −60 to −50°. The mixture was stirred for 30 min at −60 to −50° and then for 20 min at −40 to −30°. The mixture was poured into ice water and acidified with dilute hydrochloric acid. The organic layer was extracted with ether several times. The extracts were dried over Na_2SO_4. Removal of the solvent left a deep brown oil which, on distillation, gave 0.4 g (10%) of a clean oil, bp 65–68° (6 mm). It was identified as **10** by comparison of retention time and ir spectrum with those of the sample synthesized in the previous section.

Methyl 4,5-Dibromo-5-chloro-2-pentenoate (**11**).—To a solution of 6.3 g (0.043 mol) of **10** in 30 ml of dry carbon tetrachloride was added 6.9 g (0.043 mol) of bromine at 20°. After the mixture had been stirred for 2 hr, it was allowed to stand overnight at room temperature. Removal of the solvent left a brown oil which, on distillation, gave 10.6 g (81%) of **11**: bp 125–133° (5 mm); ir (neat) 3030, 1725 (ester C=O), 1655 (C=C), 1440, 1290, 980, 735 cm^{-1} (CCl); nmr (CCl_4) δ 3.77 (s, 3, CO_2CH_3), 4.95 (m, 1, –CHBrCH=), 5.88 (d, 1, J = 5.9 Hz, ClBrCH), 6.10 (d, 1, J = 13 Hz, $=CHCO_2CH_3$), 6.98 (m, 1, $-CH=CHCO_2CH_3$); mass spectrum (70 eV) m/e (rel intensity) 274 (0.4, $M^+ - CH_3OH$), 244 (1), 225 (24), 189 (14), 165 (6), 145 (13), 115 (58), 111 (100), 87 (85), 59 (65), 51 (73).

Anal. Calcd for $C_6H_7Br_2ClO_2$: C, 23.52; H, 2.30. Found: C, 23.30; H, 2.57.

Methyl 2,3,4,5-Tetrabromo-5-chloropentanoate (**12**).—To a solution of 2 g (0.014 mol) of **10** in 20 ml of dry carbon tetrachloride was added 4.6 g (0.029 mol) of bromine at 0°. The mixture was stirred at room temperature for 2 days under the irradiation of the ultraviolet lamp. Removal of the solvent left a yellow oil which, on distillation under an atmosphere of nitrogen, yielded 2.2 g (35%) of **12**: bp 153–154° (3 mm); mp 133–135° (*n*-hexane); ir (Nujol) 1750 cm^{-1} (ester C=O).

Anal. Calcd for $C_6H_7Br_4ClO_2$: C, 15.43; H, 1.51. Found: C, 15.73; H, 1.69.

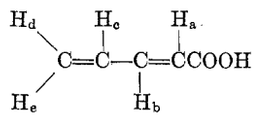
5,5-Dichloro-4-hydroxypentan-2-one (**9**).—This material was prepared by the literature procedure for the synthesis of chloral-acetone (**2**)[14] with a slight modification. A mixed solution of 22.8 g (0.17 mol) of ethyl acetoacetate in dilute aqueous potassium hydroxide prepared from 12 g (0.21 mol) of potassium hydroxide and 460 ml of water was stirred at room temperature for 1 day. After the mixture was acidified with 10% hydrochloric acid, a solution of 18.4 g (0.16 mol) of dichloroacetaldehyde in 28 ml of water was added. The mixture was stirred for 3 days. The pH of the solution was adjusted to 5 by adding 10% hydrochloric acid when necessary. After evaporation of two-thirds of the water, the residual oil was extracted with ether and the extract was dried over Na_2SO_4. Removal of the solvent left a clean oil which, on distillation, gave 14.2 g (52%) of **9**: bp 121–123° (0.1 mm); ir (neat) 3400 (OH), 1710 (C=O), 1425, 1370, 1090, 755, 735, 705 cm^{-1}; nmr ($CDCl_3$) δ 2.26 (s, 3, $COCH_3$), 2.92 (d, 2, J = 5.5 Hz, $-CH_2COCH_3$), 3.58 (s, 1, OH), 4.42 (dt, 1, J = 4 and 5.5 Hz, >CHOH), 5.85 (d, 1, J = 4 Hz, $-CHCl_2$).

Anal. Calcd for $C_5H_8Cl_2O_2$: C, 35.11; H, 4.71. Found: C, 34.83; H, 4.80.

5,5-Dichloro-3-penten-2-one (**7**).—To 17 ml of concentrated sulfuric acid was added 1.7 g (0.01 mol) of **9** at room temperature. The mixture was allowed to stand for 2.5 hr and poured onto cracked ice. The organic layer was extracted with ether several times and the combined extracts were dried over Na_2SO_4. Removal of the solvent left a pale brown oil, which on distillation under an atmosphere of nitrogen gave 1.0 g (65%) of a clean oil (**7**): bp 91–92° (17 mm), ir (neat) 3030, 1710–1660 (C=O), 1640 (C=C), 730 cm^{-1}; nmr (CCl_4) δ 2.3 (s, 3, $COCH_3$), 6.22 (d, 1, J = 15.8 Hz, $=CHCOCH_3$), 6.23 (d, 1, J = 6.4 Hz, $-CHCl_2$), 6.78 ppm (dd, 1, J = 6.4 and 15.8 Hz, $CHCl_2CH=$); mass spectrum (70 eV) m/e (rel intensity) 152 (13, M^+, 2 Cl), 137 (100, $M^+ - CH_3$, 2 Cl), 117 (9, $M^+ - Cl$, 1 Cl), 109 (48, $M^+ - CH_3CO$, 2 Cl).

Anal. Calcd for $C_5H_6Cl_2O$: C, 39.25; H, 3.95. Found: C, 39.62; H, 3.85.

trans-**2,4-Pentadienoic Acid** (**18**). **A. From 9.**—Hydroxypentanone **9** (2.1 g, 0.012 mol) was added to 4.4 ml of 10% sodium hydroxide at room temperature. The mixture was heated at 60° for 5 min, and then was treated with activated charcoal. The filtrate was acidified with 10% hydrochloric acid. The organic layer was extracted with ether several times and the extracts were dried over Na_2SO_4. Removal of the solvent left 0.3 g (25%) of light brown needles (**18**), mp 68–70° (from ether) (lit.[11] mp 71.5–72.5°). Ir and nmr spectra were identical with that of an authentic sample:[11] ir (Nujol) 2900–2500 (COOH),



1690 (C=O), 1630, and 1600 cm^{-1} (C=C); nmr ($CDCl_3$) δ 5.60 (dd, 1, J = 1.6 and 17.2 Hz, H_e), 5.69 (dd, 1, J = 1.6 and 9.4 Hz, H_d), 5.90 (d, 1, J = 14.8 Hz, H_a), 6.50 (dt, 1, J = 9.6 and 17.2 Hz, H_c), 7.38 ppm (dd, 1, J = 9.6 and 14.8 Hz, H_b).

B. From 7.—Pentenone **7** (2.5 g, 0.016 mol) was added to 26 ml of 15% sodium hydroxide and the mixture was stirred for 5 min. After being washed with ether and treated with activated charcoal, the aqueous layer (pH 11) was acidified with 10% hydrochloric acid. The acidic material was extracted with ether three times and the ethereal extracts were dried over Na_2SO_4. Removal of the solvent left 0.7 g of pale brown needles. The fractionation of this product by means of preparative tlc[18] gave 0.4 g (25%) of pale yellow needles of **18**, mp 68–70°. The ir and nmr spectra were identical with those of a pure sample obtained from **9**.

5,5-Dichloro-3-hexen-2-one (**8**).[19]—To a mixed solution of 12.1 g (0.095 mol) of freshly distilled 2,2-dichloropropanal[20] and acetylacetone (10 g, 0.1 mol) in 50 ml of dry THF was added 20.7 g (0.15 mol) of anhydrous potassium carbonate in several portions. After being stirred at room temperature for 1 day, the mixture was poured into 150 ml of water and acidified with 10% hydrochloric acid. The organic layer was extracted with ether and the ethereal extracts were washed with water and dried over Na_2SO_4. Removal of the solvent left a pale brown oil which, on distillation, gave 8.2 g (52%) of **8**: bp 77–80° (6 mm); ir (neat) 1710 and 1685 (conjugated C=O), 1638 (conjugated C=C), 1365, 1285, 1260, 1080, 980, 700, 685 cm^{-1} (CCl); nmr (CCl_4) δ 2.30 (s, 6, 2 CH_3), AB quartet centered at 6.30 and 6.88 ppm (2, J = 15 Hz, $-CH=CHCOCH_3$).

Anal. Calcd for $C_6H_8Cl_2O$: C, 43.15; H, 4.83. Found: C, 43.18; H, 4.97.

5-Chloro-4-hexenoic Acid (**19**).—To 36 ml of 15% sodium hydroxide was added the ketone **8** (4.2 g, 0.027 mol), with stirring at 50°. After being stirred at 70–75° for 4 min, the mixture was cooled, washed with ether to remove neutral materials, and acidified with 10% hydrochloric acid. The organic layer was extracted with ether several times, and the ethereal extracts were dried over $MgSO_4$. The solvent was removed *in vacuo*, and the residue, on distillation, gave 1.1 g (27%) of **19**: bp 105–108° (3 mm); ir (neat) 2650 (COOH), 1700 (C=O), 1660–1630 cm^{-1} (shoulder, C=C); nmr ($CDCl_3$) δ 2.09 (s, 3, $CH_3CCl=$), 2.42 (broad s, 4, $-CH_2CH_2-$), 5.50 (broad t, 1, J = 4 Hz, =CH–), 11.30 ppm (s, 1, COOH); mass spectrum (70 eV) m/e (rel intensity) 148 (64, M^+, 1 Cl), 131 (7, $M^+ - CH_3$), 113 (100, $M^+ - Cl$), 102 (70), 95 (56), 91 (70), 89 (83), 71 (72), 67 (71), 60 (62), 53 (71).

Anal. Calcd for $C_6H_9ClO_2$: C, 48.50; H, 6.10. Found: C, 48.61; H, 6.28.

Methyl 5-Chloro-4-hexenoate (**20**).—Esterification of **19** with diazomethane afforded the ester **20**, bp 55° (5 mm). Glpc analysis (column A, 120°, carrier gas, N_2, 0.5 kg/cm^2, 42 ml/min) showed two peaks. The peaks, retention times (min), and integrated percentages are as follows: 1, 4.2, 70%; 2, 4.9, 30%.

(18) Conditions of preparative tlc: support, silica gel G (E. Merk AG, Darmstadt), 0.8 mm; developer, benzene–acetic acid–methanol (10:1:1 v/v); R_f 0.67.

(19) This procedure to prepare 3-alken-2-one from acetylacetone and α-halogenoaldehydes has been explored by one of us (A. T.) recently: A. Takeda and T. Uno, to be published.

(20) 2,2-Dichloropropanal was prepared by the chlorination of propanal with chlorine by the method of Dick: C. R. Dick, *J. Org. Chem.*, **27**, 272 (1962).

Component 1 was collected by preparative glpc and identified as *trans*-**20** (or *cis*-**20**): ir (neat) 1740 (ester C=O), 1660 (C=C), 1440, 1366, 1175, 1110, 1040, 990, 830, 790 cm^{-1}; nmr (CCl_4) δ 2.08 (s, 3, CH_2CCl=), 2.33 (broad s, 4, $-CH_2CH_2$), 3.62 (s, 3, $-CO_2CH_3$), 5.51 ppm (broad s, 1, -CH=); mass spectrum (70 eV) *m/e* (rel intensity) 162 (19, M^+, 1 Cl), 131 (76), 127 (100, $M^+ - Cl$), 105 (61), 104 (60), 103 (68), 102 (75), 95 (57), 89 (72), 85 (68), 74 (61), 67 (63), 59 (50), 53 (61).

Anal. Calcd for $C_7H_{11}ClO_2$: C, 51.70; H, 6.82. Found: C, 51.58; H, 6.72.

Component 2, collected similarly, was identified as *cis*-**20** (or *trans*-**20**): ir (neat) 1740 (ester C=O), 1660 (C=C), 1440, 1366, 1340, 1175, 1110, 1080, 1035, 990, 860, 830, 800 $cm.^{-1}$ The nmr (CCl_4) and mass spectrum (70 eV) of this component were like those of component 1.

Anal. Calcd for $C_7H_{11}ClO_2$: C, 51.70; H, 6.82. Found: C, 51.43; H, 6.60.

Reaction of 8 with Sodium Methoxide in Dry Methanol.—To a stirred solution of 5.9 g (0.11 mol) of sodium methoxide in 25 ml of dry methanol was added dropwise at 34–45° a solution of **8** (3 g, 0.018 mol) in 6 ml of dry methanol, for a period of 10 min. The mixture was stirred for additional 15 min, and poured into a large amount of water. The organic layer was extracted with ether, washed with water, and dried over $MgSO_4$. Removal of the solvent left 1.4 g of a light yellow, clean oil, bp 75–78° (12 mm). Glpc analysis (column B, 120°, carrier gas N_2, 0.5 kg/cm^2, 42 ml/min) of this oil showed three peaks. The peaks, retention times (min), and integrated percentages are as follows: 1, 3.2, 28%; 2, 4.7, 60%; 3, 6.2, 11%. Component 1 was collected by preparative glpc and identified as methyl sorbate (**21**) by comparison of the infrared spectrum and retention time with those of methyl sorbate prepared by the esterification of sorbic acid with diazomethane: yield 17%; ir (neat) 1723 (ester C=O), 1650 (C=C), 1623 (C=C), 1010 cm^{-1} (=CH);[10] nmr (CCl_4) δ 1.85 (d, 3, J = 5.5 Hz, $-CH_3$), 3.67 (s, 3, $-CO_2CH_3$), 5.69 (d, 1, J = 16 Hz, C-2 H), 6.20 (m, 2, C-4 H and C-5 H), 7.16 ppm (m, 1, C-3 H).[9]

Components 2 and 3 were collected and identified as *trans*-**20** (or *cis*-**20**) (yield 29%) and *cis*-**20** (or *trans*-**20**) (yield 5%), respectively, by comparison of ir spectra and retention times with those of an authentic sample.

Reaction of 8 with Sodium Methoxide in Aprotic Solvents (Ether, Benzene, and *n*-Hexane).—To a suspension of 0.76 g (0.014 mol) of sodium methoxide in 10 ml of aprotic solvent was added 0.88 g (0.0048 mol) of **8** in several portions during the course of 5 min, at 0° with stirring. After the mixture was stirred at 0–10° for a further 30 min, it was worked up in the usual manner. The composition of the products was determined by glpc (column B, 120°, carrier gas N_2, 0.5 kg/cm^2, 42 ml/min).

Transformation of the Ester 20 to the Ester 21 with Sodium Methoxide.—To a mixture of sodium methoxide (0.14 g, 0.0025 mol) and dry ether (1 ml) was added a solution of **20** (0.082 g, 0.0005 mol) in dry ether (1 ml) at 0°. The mixture was stirred for 30 min and filtered. Removal of the solvent gave 0.04 g of a clean oil. Glpc analysis (column A, 120°, carrier gas N_2, 0.5 kg/cm^2, 42 ml/min) indicated this oil to contain three components, which were identified by the comparison of the retention times with those of the authentic samples. Peaks, compounds, retention times (min), and the integrated peak areas are as follows: 1, **21**,[21] 3.3, 9%; 2, *trans*-**20** (or *cis*-**20**), 4.2, 61%; 3, *cis*-**20** (*trans*-**20**), 5.1, 30%.

Registry No.—**1**, 1552-26-7; **2**, 1552-33-6; **3**, 22970-18-9; **7**, 38666-05-6; **8**, 38666-06-7; **9**, 38666-07-8; **10**, 38666-08-9; **11**, 38666-09-0; **12**, 38666-10-3; **14**, 38666-11-4; **18**, 21651-12-7; **19**, 38666-13-6; (*Z*)-**20**, 38666-14-7; (*E*)-**20**, 38666-15-8; **21**, 1515-80-6; ethyl acetoacetate, 141-97-9; dichloroacetaldehyde, 79-02-7; acetylacetone, 123-54-6; 2,2-dichloropropanol, 27313-32-2.

(21) Yield 6%.

Determination of Stereochemistry in Vinyl Phosphorylated Species by Nuclear Magnetic Resonance Shift Reagents. Revised Mechanistic Pathways for the Perkow Reaction[1]

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The application of lanthanide induced shifts employing Eu(DPM)$_3$ [and, to a minor extent, Pr(DPM)$_3$], to the nmr spectra of di-, tri-, and tetrasubstituted vinyl phosphates, phosphonates, and phosphinates is described. Vicinal cis protons or methyl groups undergo greater shifts than the corresponding trans groups. On this basis, *E* and *Z* stereochemical assignments can be made for such groups. The major isomers in the *gem*-phenyl vinyl phosphorylated compounds featuring vicinal phenyl, methyl, bromine, or chlorine groups are shown to be *Z*, reversing our previous assignments. Confirmation of this assignment is found by a positive nuclear Overhauser effect from phenyl to vicinal proton on the major (*Z*) isomer of diethyl 1-phenyl-2-chlorovinylphosphate. Available stereochemical data, including these revised results and the tendency toward smaller *Z*/*E* ratios in Perkow reactions involving alkyl diphenylphosphinites, compared with trialkyl phosphites, are evaluated on the basis of variations of the carbonyl addition mechanism previously proposed. The Perkow reactions of α,α-dibromo ketones and α-bromo-α-phenyl ketones, which give only *Z* vinyl phosphorylated products, may occur *via* halogen attack. The importance of considering the magnitude of k_2 Br/Cl ratios for pairs of bromo and chloro ketones, as well as *E*,*Z* stereochemistry of the products, in evaluating the various mechanistic pathways for the Perkow reaction, is stressed.

We have recently reported the determination of the relative stereochemistry of the *E* and *Z* isomeric vinyl phosphates arising from the Perkow reaction of α-halo ketones with trialkyl phosphites,[2,3] Of the various methods used,[2] the most reliable *seemed* to be the use of nmr additive increments as developed by Simon and Sternhell[4] and modified by Tobey.[5] This method correctly assigns *E* and *Z* stereochemistry to isomeric di- and trisubstituted olefins in a large number of cases.

We now find that in the case of trisubstituted *gem*-phenyl vinyl phosphates (and the related phosphinates and phosphonates[6]) the *E* and *Z* assignments by

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