Chemistry of α-Halo Aldehydes. V.[1] Reaction of α-Halo Aldehydes with α-Acetylcyclopentanones in the Presence of Base[2]

Akira Takeda,* Sadao Tsuboi, Fumitaka Sakai, and Mamoru Tanabe

*Department of Synthetics Chemistry, School of Engineering, Okayama University, Tsushima, Okayama, Japan 700*

Received January 31, 1974

Reaction of chloral with 2-acetylcyclopentanone (3a) in the presence of potassium carbonate in tetrahydrofuran spontaneously yielded 2-(2'-chlorovinyl)cyclobutenecarboxylic acid (6a). The pathway, which involves the transient existence of α-(2,2,2-trichloroethylidene)cyclopentanone (4a) followed by the Favorskii-type rearrangement, has been postulated for the formation of 6a. The reaction of chloral with 1-morpholino-1-cyclopentene (8a) gave 2-(2',2',2'-trichloro-1'-hydroxyethyl)cyclopentanone (9a). The dehydration of 9a with H_2SO_4 led to the formation of 2-(2',2'-dichlorovinyl)-2-cyclopentenone (10a). The treatment of 9a with alkali failed to give 6a. The analogous reaction of dichloroacetaldehyde with α-acetylcyclopentanone gave 5-acetyl-7,7-dichloro-5-heptenoic acid (14a). The reaction of acetylcyclohexanone with chloral solely resulted in the recovery of the starting material.

We have been studying the chemical properties of α-(2-haloalkylidene) ketones. In the previous paper,[3] we reported that α-(2,2,2-trichloroethylidene)acetone as well as the related compounds (1) underwent Favorskii-type rearrangement as the vinylogs of α-chloroacetone to give 2,4-pentadienoic acid derivatives (2). As an extension of previ-

$$RCCl_2CH{=}CHCOCH_3 \xrightarrow{\text{HO}^-} RCH{=}CHCH{=}CHCO_2H$$

$$\mathbf{1} \qquad\qquad\qquad \mathbf{2}$$
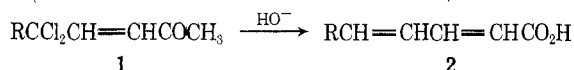
ous works,[1,3] we were interested in investigating the Favorskii-type rearrangement of five- and six-membered ring systems such as α-(2-chloroalkylidene)cyclopentanone (4) and α-(2-chloroalkylidene)cyclohexanone (5) in order to find out a new route leading to ring-contracted cycloalkenecarboxylic acids (6). To obtain halogenated alkyli-

$$\mathbf{4}, n = 3$$
$$\mathbf{5}, n = 4 \qquad\qquad \mathbf{6}$$
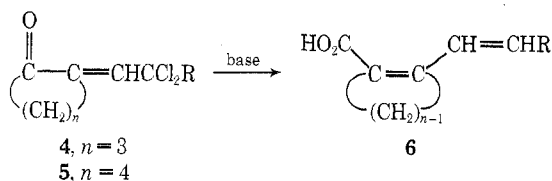
denecycloalkanones 4 and 5, the procedure, which we[3,4] devised for the preparation of halogenated α-alkylideneacetone 1 has been adapted. It involves the reaction of α-halo aldehyde with α-acetylcycloalkanone (3) in the presence of potassium carbonate in tetrahydrofuran (THF). The attempted reaction of α-acetylcyclohexanone, however, failed to afford the desired product (5). Although we were unsuccessful in isolating the intermediate α-alkylidenecyclopentanone 4 in the reaction of α-acetylcyclopentanone with α-chloro aldehydes, there are evidences for the fact that a crossed aldol condensation has preceded, since the final products it gave were apparently those derived by ring cleavage or by ring contraction of the appropriate condensation products. This paper will describe and discuss the results of these reactions. Structures of the products were determined principally based on both spectral data and elemental analysis. Oxidative degradations of the ethylenic products were also carried out in order to substantiate the structural assignments.
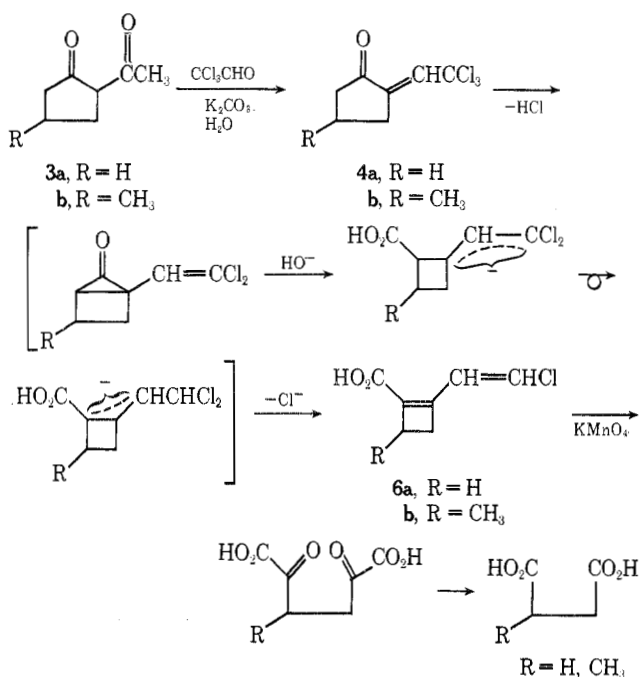
Results and Discussion

It has already been found that the base-catalyzed condensation of chloral with acetylacetone affords α-(2,2,2-trichloroethylidene)acetone in good yield.[4] In contrast, the reaction of α-acetylcyclopentanone (3a) with chloral gave, not the expected α-(2,2,2-trichloroethylidene)cyclopentanone (4a), but 2-(2'-chlorovinyl)cyclobutenecarboxylic acid

(6a) in 32% yield.[5] An absorption band at 1565 cm^{-1} in ir spectrum of 6a[6] and singlet (4 H) at 2.50 ppm in its nmr spectrum strongly indicated the presence of cyclobutene ring.[7] The mass spectrum of 6a showed clear molecular ions at *m/e* 158 with the characteristic chlorine isotope distribution. The fact that Favorskii-type products have never been isolated from the basic treatment of α-chlorocyclopentanones[8] prompted us to examine its generality for other α-acylcyclopentanone and chloro aldehydes. Thus, 2-acetyl-4-methylcyclopentanone (3b) with chloral afforded 2-(2'-chlorovinyl)-4-methylcyclobutenecarboxylic acid (6b) in a 21% yield along with a small amount (yield 4%) of 2-(2',2'-dichlorovinyl)-4-methyl-2-cyclopentenone (10b). The treatment of 6a with diazomethane yielded its methyl ester (7), which gave the correct analysis.[9] Undoubtedly, the cyclopentenone 10b is considered to have been derived from its precursor 4b, which has for the most part undergone Favorskii-type rearrangement to give 6b. The structure of 6 has been further confirmed by its oxidative degradation to succinic acid. For instance, the treatment of 6b with aqueous potassium permanganate gave methylsuccinic acid[10] in a 43% yield. Reflecting the chemical properties of straight-chained analogs like 1,[3] the pathway, which involves the transient existence of α-ethylidenecyclopentanone 4 followed by the Favorskii-type rearrangement, can be reasonably postulated for the formation of 6 as is shown in Scheme I. Compound 4, if generated, however, seems to be labile at the condition concerned, since several reactions attempted for preparing 4 all turned out to be a failure.
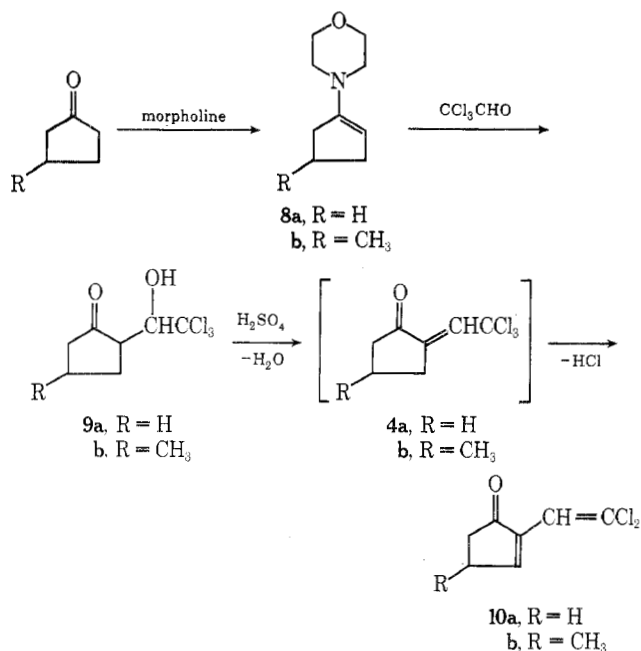
The reaction of chloral with 1-morpholino-1-cyclopentene (8a) and its 4-methyl derivative (8b) gave 2-(2',2',2'-trichloro-1'-hydroxyethyl)cyclopentanone (9a) and its 4-methyl derivative (9b) in 61 and 53% yields, respectively. The dehydration of 9a and 9b with H_2SO_4 caused a concurrent dehydrochlorination to yield 2-(2',2'-dichlorovinyl)-2-cyclopentenone (10a) and its 4-methyl derivative (10b) (Scheme II). The treatment of 9a with SOCl$_2$ afforded 2-(1',2',2',2'-tetrachloroethyl)cyclopentanone (11) in a 13% yield. The dehydrochlorination of compound 11 also failed to give 4a. While α-hydroxy ketones such as 5,5,5-trichloro-4-hydroxy-2-pentanone (chloralacetone) and 5,5-dichloro-4-hydroxy-2-pentanone yielded the appropriate 2,4-pentadienoic acids behaving as precursors of α-(2,2,2-trichloroethylidene)acetone and α-(2,2-dichloroethylidene)acetone,[3] cyclic hydroxy ketones 9a and 9b only gave an intractable, resinous material when they were subjected to the treatment with alkali.

The behavior of dichloroacetaldehyde toward 3a was in a striking contrast to that of chloral. The base-catalyzed con-

Scheme I

3a, R = H
b, R = CH₃

4a, R = H
b, R = CH₃

6a, R = H
b, R = CH₃

R = H, CH₃

Scheme II

8a, R = H
b, R = CH₃

9a, R = H
b, R = CH₃

4a, R = H
b, R = CH₃

10a, R = H
b, R = CH₃

densation of **3a** with dichloroacetaldehyde in THF gave 5-acetyl-7,7-dichloro-5-heptenoic acid (**14a**, yield 36%) in place of Favorskii-type product. When the reaction was conducted in water, the yield was increased to 59%. The acid **14a** was converted to methyl ester **14b** with diazomethane in order to facilitate the purification. The ir band at 1740 cm⁻¹ supported the presence of unconjugated ester carbonyl. The nmr spectrum of **14b** in carbon tetrachloride showed the signal due to one olefinic proton and one C-7 methine proton as a singlet (2 H) at δ 6.70 ppm, and that due to ester methyl protons as a singlet at 3.66 ppm. The signal due to acetyl methyl protons appeared at 2.37 ppm as a singlet. The mass spectrum of **14b** showed a strong peak at *m/e* 217 (M⁺ − Cl). The permanganate oxidation of **14a** yielded glutaric acid in a 54% yield together with a small amount of succinic acid.[11] The reaction sequence for the formation of the acid **14a** is shown in Scheme III, in

Scheme III

3a

12

13

**14a**, R = H
b, R = CH₃

(R = H)

(R = H)
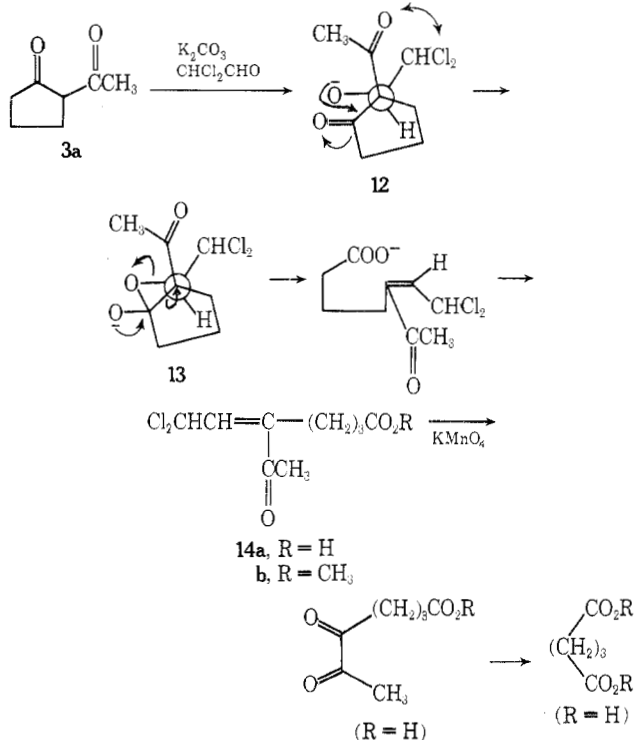
which the condensation product **12** undergoes a retro acetoalkanoate reaction.[12]

The oxy anions **12** and **15**, which are produced primarily in these reactions, are considered to be of erythro forms,

erythro   threo
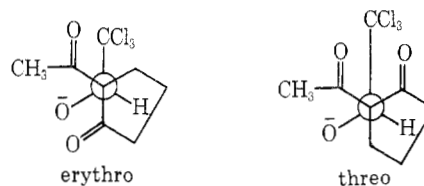
i.e., less hindered, hence more stable ones. Whether electronic or steric, the polychloromethyl group of these intermediates obviously has an effect in determining the product. While the oxy anion of **12** is readily arranged eclipsed to and can attack the ring carbonyl of cyclopentanone to form a possible intermediate **13**, the bulkiness of trichloromethyl group as compared to dichloromethyl group does not allow the oxy anion of **15** to take the same arrangement as **12** at the transition state. It can be arranged eclipsed to acetyl carbonyl more readily to form the intermediate **16**, which is then converted to **6**.

15

16

→ **6**
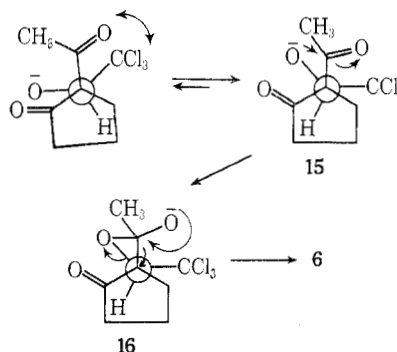
It was rather surprising that the reaction of α-acetylcyclohexanone with chloral resulted in the recovery of the starting material. It may be attributable in part to the hindrance caused by axial hydrogens of acetylcyclohexanone, which disturbs its approach to chloral. As compared to cy-

clohexanone ring, the carbanion of acetylcyclopentanone appears less masked by ring protons.

Experimental Section

Melting points and boiling points are uncorrected. Elemental analyses were carried out by Mr. Eiichiro Amano of our laboratory. The analytical determinations by glpc were performed on a Hitachi Model K-53 gas chromatograph (3 mm o.d. × 1 m, 10% Apiezon grease L on Chromosorb W column); carrier gas, N_2 (0.5 kg/cm^2, 40 ml/min); detector, FID. The preparative glpc was performed on a Yanagimoto Model GCG-550T gas chromatograph (3 mm o.d. × 2.25 m, 10% Apiezon grease L on Chromosorb W column; detector, TCD). Analytical thin layer chromatography (tlc) was done on silica gel GF$_{254}$ (E. Merck AG, Darmstadt) with layers of 0.2-mm thickness. Preparative tlc was done on silica gel PF$_{254}$ (E. Merck AG, Darmstadt) with plates of 20 × 20 cm^2 and 1.0-mm thickness. Mass spectra were run on a Hitachi Model RMS-4 mass spectrometer and nmr spectra were obtained on a Hitachi Model R-24 spectrometer (60 MHz). Commercial grade THF, which was purified by distillation after being treated with Na_2SO_4 overnight, was used.

α-Acetylcyclopentanone (3a) was prepared by the method described in the literature,[13] using 1-morpholino-1-cyclopentene (8a) and acetyl chloride, bp 80–85° (12 mm) [lit.[14] bp 75° (8 mm)]. α-Acetyl-4-methylcyclopentanone (3b) was prepared in a way similar to 3a: yield 64%; bp 61.5° (3 mm); ir (neat) 1738 (C=O), 1705 (C=O), 1650, and 1610 cm^{-1}; nmr (CDCl$_3$) δ 1.11 (d, 3, CH$_3$), 1.96 (s, 3, COCH$_3$), 2.00–3.10 (m, 5, C$_3$, C$_4$, and C$_5$H), and 3.20–3.80 ppm (m, 1, C$_2$H).

2-(2′-Chlorovinyl)cyclobutenecarboxylic Acid (6a). To a mixed solution of 1.3 g (0.01 mol) of 3a and 1.5 g (0.01 mol) of chloral in 10 ml of dry THF was added 1.8 g (0.013 mol) of anhydrous potassium carbonate in several portions. After being stirred at room temperature for 1 hr and then at 32–34° for 5 hr, the mixture was poured into 30 ml of water and acidified with 10% hydrochloric acid. The organic layer was extracted with ether and the ethereal extract was dried over MgSO$_4$. After removal of the solvent, the residue was distilled to give 0.5 g of 6a: yield 32%; bp 116–120° (5 mm); mp 118–119° (benzene); ir (KBr) 2300–3400 (COOH), 1665 (C=O), 1630 (C=C), and 1565 cm^{-1} (cyclobutene C=C); nmr (CDCl$_3$) δ 2.50 (s, 4, cyclobutene ring protons), AB quartet centered at 6.62 and 7.03 (2, J = 14 Hz, –CH=CHCl), 6.50–7.10 ppm (broad s, 1, COOH); mass spectrum (70 eV) m/e (rel intensity) 158 (18, M$^+$, 1 Cl), 123 (100, M$^+$ – Cl).

Anal. Calcd for C$_7$H$_7$ClO$_2$: C, 53.02; H, 4.45. Found: C, 52.84; H, 4.26.

Methyl 2-(2′-Chlorovinyl)cyclobutenecarboxylate (7). To a solution of 0.35 g (0.0022 mol) of 6a in 3 ml of dry ether was added an ethereal solution of diazomethane (*ca.* 0.7 mol/l.) in several portions at −30° until evolution of nitrogen ceased. After the mixture was allowed to stand for 30 min, distillable material (unreacted diazomethane and the solvent) was removed *in vacuo.* Tlc analysis[15] of the residue (0.37 g) showed two spots at R_f values of 0.42 and 0.26, in a ratio of 10:7. The compound with the R_f value of 0.42 was collected by preparative tlc and identified as 7: yield 57%; ir (neat) 1690 (C=O), 1610 (C=C), and 1565 cm^{-1} (cyclobutene C=C); nmr (CDCl$_3$) δ 2.47 (broad s, 4, cyclobutene ring protons), 3.97 (s, 3, COOCH$_3$), AB quartet centered at 6.54 and 6.96 ppm (2, –CH=CHCl); mass spectrum (70 eV) m/e (rel intensity) 172 (36, M$^+$), 137 (85, M$^+$ – Cl), 95 (100), 87 (42), 65 (52), 52 (34), 43 (66).

Anal. Calcd for C$_8$H$_9$ClO$_2$: C, 55.67; H, 5.25. Found: C, 55.55; H, 5.25.

The compound with the R_f value of 0.26 was similarly collected and analyzed: mp 83.5–84.5°; ir (KBr) 1780, 1705, 1632, and 1574 cm^{-1}; nmr (CDCl$_3$) δ 2.28 (s), 2.40–2.88 (m), and 6.79 ppm (s); mass spectrum (70 eV) m/e (rel intensity) 200 (2.4, 1 Cl), 123 (100), 87 (6), 51 (13), 43 (17).

Anal. Found: C, 53.92; H, 3.97.[16]

2-(2′-Chlorovinyl)-4-methylcyclobutenecarboxylic   Acid (6b). To a mixed solution of 4.0 g (0.028 mol) of 3b and 5.3 g (0.036 mol) of chloral in 30 ml of dry THF was added 8.3 g (0.06 mol) of anhydrous potassium carbonate in several portions. After being stirred at room temperature for 1 hr and then at 30–35° for 5 hr, the mixture was poured into 100 ml of water. The organic layer (neutral portion) was extracted with ether and then the ethereal extract was washed with water and dried over MgSO$_4$. After removal of the solvent, the residue was distilled to give 1.2 g of oil, bp 81–115° (0.1 mm). Tlc analysis[17] of this oil showed two spots at R_f values of 0.34 and 0.60, in a ratio of 4:1. The compound with the

R_f value of 0.34 collected by preparative tlc was identified as 6b: yield[18] 21%; mp 59.5–60.5°; ir (KBr) 2000–3450 (COOH), 1675 (C=O), 1645 (C=C), and 1575 cm^{-1} (cyclobutene C=C); nmr (CDCl$_3$) δ 1.19 (d, 3, J = 7.5 Hz, CH$_3$), 1.98–3.02 (m, 3, cyclobutene ring protons), AB quartet centered at 6.57 and 7.00 ppm (2, J = 14 Hz, –CH=CHCl), 6.50–7.40 (broad s, 1, COOH); mass spectrum (70 eV) m/e (rel intensity) 172 (82, M$^+$), 138 (63), 137 (100, M$^+$ – Cl), 109 (64), 102 (52), 81 (54), 79 (54), 71 (50), 53 (59).

Anal. Calcd for C$_8$H$_9$ClO$_2$: C, 55.67; H, 5.25. Found: C, 55.68; H, 5.32.

The compound with the R_f value of 0.60 was similarly collected and identified as 10b: yield 4%; ir (neat) 1710 (C=O), 1620 (C=C), and 1600 cm^{-1} (C=C); nmr (CCl$_4$) δ 1.28 (d, 3, J = 7.5 Hz, CH$_3$), 1.87 (q, 1, J = 18 and 2.5 Hz, C$_5$ H), 3.0 (m, 1, C$_4$ H), 6.55 (s, 1, –CH=CCl$_2$), and 7.93 ppm (d, 1, J = 3 Hz, C$_3$ H); mass spectrum (70 eV) m/e (rel intensity) 190 (20, M$^+$, 2 Cl), 175 (10, M$^+$ – CH$_3$), 155 (100, M$^+$ – Cl), 147 (14), 127 (33), 91 (26), 77 (20).

Anal. Calcd for C$_8$H$_8$Cl$_2$O: C, 50.29; H, 4.22. Found: C, 50.07; H, 4.23.

Oxidation of 6b with Potassium Permanganate. To a solution of 0.494 g (0.0031 mol) of potassium permanganate in 6.6 ml of water was added in one portion a solution of 0.06 g (0.35 mmol) of 6b in aqueous potassium hydroxide (0.057 g of KOH, and 1.4 ml of water) at 35°. After being stirred for 30 min at 75°, the mixture was acidified with dilute sulfuric acid (0.35 ml of concentrated sulfuric acid and 1.07 ml of water) and then heated on a steam bath for 15 min to coagulate the manganese dioxide, which was filtered while hot. The filtrate was evaporated to a volume of about 2 ml. The ethereal extract of the organic layer was washed with brine and dried over MgSO$_4$. After removal of the solvent the residue gave 0.040 g of a solid, which was recrystallized from *n*-hexane, giving 0.020 g (43%) of methylsuccinic acid, mp 107–109° (*n*-hexane) (lit.[10] mp 110–111°). Ir and nmr spectra were identical with those of an authentic sample.[10]

Oxidation of 6a with potassium permanganate was carried out in the same way as that of 6b, and the white crystals obtained was identified as succinic acid by comparison of ir and nmr spectra with those of an authentic sample.

2-(2′,2′,2′-Trichloro-1′-hydroxyethyl)cyclopentanone   (9a). To a solution of 10.7 g (0.07 mol) of 8a in 35 ml of dry chloroform was added a solution of 10.6 g (0.072 mol) of chloral in 15 ml of dry chloroform at room temperature over a 1-hr interval. The mixture was stirred for 1 hr and then 35 ml of 20% HCl was added. After the mixture was refluxed for 5 hr, it was cooled and the organic layer was separated. The aqueous layer was adjusted to a pH of about 6 with a 25% aqueous NaOH and then the organic layer was extracted with chloroform. The combined extract was washed with saturated sodium chloride and dried over MgSO$_4$. Removal of the solvent left a crude crystalline product which gave 9.8 g (61%) of 9a: mp 126–127° (benzene); ir (Nujol) 3400 (OH), 1720 (C=O), 800, and 820 cm^{-1}; nmr (CDCl$_3$) δ 1.90–2.50 (m, 6, C$_3$, C$_4$, C$_5$H), 2.75 (m, 1, C$_2$ H), 3.47 (s, 1, OH), and 4.70 ppm (broad d, 1, J = 1.6 Hz, >CHOH).

Anal. Calcd for C$_7$H$_9$Cl$_3$O$_2$: C, 36.32; H, 3.92. Found: C, 36.11; H, 3.58.

2-(2′,2′,2′-Trichloro-1′-hydroxyethyl)-4-methylcyclopentanone (9b) was prepared from 8b (15.8 g, 0.095 mol) and chloral (14.7 g, 0.1 mol) in the same way as in the preparation of 9a. The crude product was distilled to give 12.1 g (53%) of 9b: bp 120–122° (0.2 mm); ir (neat) 3480 (OH), 1742 (C=O), 1160, 1120, 820, and 740 cm^{-1}; nmr (CDCl$_3$) δ 1.08 and 1.26 (2 d,[19] 3, J = 6.5 Hz, CH$_3$), 1.50–2.70 (m, 5, C$_3$, C$_4$, C$_5$ H), 3.00 (m, 1, C$_2$ H), 3.47 (broad s, 1, OH), 4.71 ppm [broad s, 1, >CH(OH)]; mass spectrum (70 eV) m/e (rel intensity) 244 (0.4, M$^+$, 3 Cl), 209 (21, M$^+$ – 2 Cl), 127 (83), 109 (100), 81 (85).

Anal. Calcd for C$_8$H$_{11}$Cl$_3$O$_2$: C, 39.13; H, 4.52. Found: C, 39.10; H, 4.40.

After a few days, this fraction gave white crystals:[20] mp 98.5–99° (from *n*-hexane); ir (KBr) 3380 (OH), 1726 (C=O), 1160, 1120, 823, 795, and 734 cm^{-1}; nmr (CDCl$_3$) δ 1.08 (d, 3, J = 6.5 Hz, CH$_3$), 1.60–2.70 (m, 5, C$_3$, C$_4$, C$_5$ H), 2.70–3.26 (m, 1, C$_2$ H, J = 5.5 Hz, OH), and 4.71 ppm (q, 1, J = 5.5 and 1.5 Hz, >CHOH).

Anal. Calcd for C$_8$H$_{11}$Cl$_3$O$_2$: C, 39.13; H, 4.52. Found: C, 39.42; H, 4.21.

2-(2′,2′-Dichlorovinyl)-2-cyclopentenone (10a). To 70 ml of concentrated H$_2$SO$_4$ was added 7.0 g (0.03 mol) of 9a at 0–5° with stirring. After being stirred for 20 hr, the mixture was poured into 200 ml of ice water. The organic layer was extracted with ether, washed with water, and dried over MgSO$_4$. Removal of the solvent left 3.9 g of a light brown oil which, on distillation, gave 1.2 g (23%)

of **10a**: bp 75–82° (3 mm); ir (neat) 1710 (C=O), 1620 (C=C), 808, and 790 cm^{-1}; nmr (CCl$_4$) δ 2.25–2.45 (m, 2, C$_5$ H), 2.60–2.84 (m, 2, C$_4$ H), 6.60 (s, 1, CCl$_2$=CH–), and 8.09 ppm (m, 1, C$_3$ H); mass spectrum (70 eV) *m/e* (rel intensity) 176 (65, M$^+$, 2 Cl), 141 (100, M$^+$ – Cl), 120 (51), 113 (58), 99 (43), 85 (39), 77 (54).

Anal. Calcd for C$_7$H$_6$Cl$_2$O: C, 47.49; H, 3.42. Found: C, 47.24; H, 3.59.

Synthesis of 10b from 9b. Hydroxy ketone **9b** was treated with concentrated H$_2$SO$_4$ in a way similar to the case of **10a**. It gave a 43% yield of **10b**. Ir and nmr spectra of this sample were identical with those of **10b** obtained in the preparation of **6b**.

5-Acetyl-7,7-dichloro-5-heptenoic Acid (14a). Procedure A. To a mixed solution of 1.3 g (0.01 mol) of **3a** and 1.7 g (0.015 mol) of freshly distilled dichloroacetaldehyde in 7 ml of dry THF was added 4.1 g (0.03 mol) of anhydrous potassium carbonate in several portions. After the mixture was stirred for 3 hr at room temperature, it was poured into 30 ml of water, washed with ether to remove neutral material, and then acidified with 10% HCl. The organic layer was extracted with ether several times, and the combined ethereal extract was dried over MgSO$_4$. Removal of the solvent left 1.44 g (36%[21]) of a light brown oil (**14a** of *ca.* 60% purity by thin layer chromatography[22]). A pure sample of **14a** was collected by preparative tlc for microanalysis and spectral determinations: R_f 0.30; ir (neat) 2300–3700 (COOH), 1710 (C=O), 1680 (C=O), and 1635 cm^{-1} (C=C); nmr (CDCl$_3$) δ 1.48–2.00 (m, 2, –CH$_2$CH$_2$CH$_2$–), 2.10–2.63 (m, 4, –CH$_2$CH$_2$CH$_2$–), 2.38 (s, 3, COCH$_3$), 6.58 and 6.98 (AB quartet, 2, J = 10 Hz, =CHCHCl$_2$), and 9.56 ppm (broad s, 1, COOH); mass spectrum (70 eV) *m/e* (rel intensity) 202 (98, M$^+$ – HCl, 1 Cl), 185 (39, 1 Cl), 168 (84), 167 (54), 142 (100), 129 (96), 108 (85), 95 (98), 84 (66), 43 (72).

Anal. Calcd for C$_9$H$_{12}$Cl$_2$O$_3$: C, 45.20; H, 5.06. Found: C, 44.99; H, 5.42.

Procedure B. Water was used as solvent. The procedure was analogous to that described in the above experiment. Removal of the solvent from the ethereal extract gave nearly pure **14a**, yield 59%. Spectral data (ir, nmr) were identical with those described above.

Methyl 5-Acetyl-7,7-dichloro-5-heptenoate (14b). Acid **14a** (0.41 g, 0.0017 mol) was esterified with diazomethane in the usual method. The crude product (0.37 g) was microdistilled to give 0.19 g of a clean oil which, on tlc analysis,[15] showed two spots at R_f values of 0.41[23] and 0.51. The compound with the R_f value of 0.51 was collected by preparative tlc and identified as **14b**: yield 28%; ir (neat) 1740 (C=O), 1680 (C=O), and 1640 cm^{-1} (C=C); nmr (CCl$_4$) δ 1.40–1.90 (m, 2, –CH$_2$CH$_2$CH$_2$–), 2.37 (s, 3, COCH$_3$), 2.10–2.60 (m, 4, –CH$_2$CH$_2$CH$_2$–), 3.66 (s, 3, COOCH$_3$), and 6.70 ppm (s, 2, =CHCHCl$_2$); mass spectrum (70 eV) *m/e* (rel intensity) 217 (52, M$^+$ – Cl, 1 Cl), 185 (100, M$^+$ – Cl – CH$_3$OH, 1 Cl), 181 (60, M$^+$ – Cl – HCl), 121 (80), 95 (60), 79 (82), 43 (84).

Anal. Calcd for C$_{10}$H$_{14}$Cl$_2$O$_3$: C, 47.45; H, 5.57. Found: C, 47.08; H, 5.53.

Oxidation of 14a with Potassium Permanganate. To a solution of 0.45 g (0.003 mol) of potassium permanganate in 6.1 ml of water was added in one portion a solution of 0.14 g (0.59 mmol) of **14a** in aqueous potassium hydroxide (0.053 g of KOH and 1.3 ml of water) at 35°. The mixture was stirred at 75° for 30 min, and then a solution of 0.32 ml of concentrated sulfuric acid in 0.98 ml of water was added. The mixture was heated on a steam bath for 15 min to coagulate the manganese dioxide, which was filtered while hot. The filtrate was evaporated to about 2 ml. The ethereal extract of the organic layer was washed with brine and dried over MgSO$_4$. After removal of the solvent the residue gave 0.058 g of white crystals. Tlc analysis[24] of this crystals showed two spots at R_f values of 0.21 and 0.31 in a ratio of 7:12. The compound with the R_f value of 0.21 was collected by preparative tlc and identified as succinic acid by comparison of its ir and nmr spectra with those of an authentic sample: mp 184–186° (lit.[25] mp 185°).

The compound with the R_f value of 0.31 was also collected by preparative tlc and identified as glutaric acid by comparison of its ir and nmr spectra with those of an authentic sample: yield 54%; mp 88–90° (from ether) (lit.[26] mp 89.5–91.5°).

Reaction of 2-Acetylcyclohexanone (15) with Chloral. To a mixed solution of 14.2 g (0.1 mol) of **15** and 14.7 g (0.1 mol) of chlo-

ral in 50 ml of dry THF was added 18.0 g (0.13 mol) of anhydrous potassium carbonate in several portions. The mixture was stirred for 12 hr at room temperature and then poured into 200 ml of water. After the mixture was acidified with 10% HCl, the organic layer was extracted with ether several times. The combined ethereal extract was washed with water and dried over MgSO$_4$. After removal of the solvent, the residue was distilled to give 5.2 g of **15**, bp 62–67° (2 mm) [lit.[27] bp 97–98° (11 mm)], and 1.3 g of a fraction of bp 80–109° (2 mm). Tlc analysis[15] of the last fraction showed several spots and each of the components could not be separated. The same reaction was carried out in the similar way as described above, using dimethylsulfoxide as solvent. However, only the starting material **15** was recovered.

Treatment of 9a with Sodium Methoxide. To a suspension of 2.1 g (0.039 mol) of sodium methoxide in 20 ml of dry ether was added a solution of 1.5 g (0.0065 mol) of **9a** in 12 ml of ether at 0° with stirring. The color of the solution turned to brown during the course of addition, and the temperature rose to 13°. After the complete addition, the mixture was stirred for 30 min at room temperature and then acidified with 10% HCl. The organic layer was extracted with ether, washed with water, and dried over MgSO$_4$. After removal of the solvent, there was obtained the residue (0.21 g) which, on distillation, gave a solid. Its ir spectrum was identical with that of the starting material.

Registry No.—**3a**, 1670-46-8; **3b**, 52034-97-6; **6a**, 52034-99-8; **6b**, 52035-00-4; **7**, 52035-01-5; **8a**, 936-52-7; **8b**, 52124-24-0; **9a**, 52124-25-1; **9b**, 52124-26-2; **10a**, 52124-27-3; **10b**, 52124-28-4; **14a**, 52124-29-5; **14b**, 52124-30-8; **15**, 874-23-7.

References and Notes

(1) Preceding paper: A. Takeda, S. Tsuboi, and Y. Oota, *J. Org. Chem.*, **38**, 4148 (1973).

(2) Preliminary communication: A. Takeda, S. Tsuboi, F. Sakai, and M. Tanabe, *Tetrahedron Lett.*, 4961 (1973). Presented in part at the 27th Annual Meeting of the Chemical Society of Japan, Nagoya, Japan, Oct 12, 1972.

(3) A. Takeda and S. Tsuboi, *J. Org. Chem.*, **38**, 1709 (1973).

(4) This procedure to prepare α-alkylideneacetones from acetylacetone and α-halo aldehydes has been explored by one of us and his collaborator: A. Takeda, and T. Uno, to be published.

(5) A large amount of resinous material was produced. A trace of water in commercial grade THF is both essential and efficient for the reaction to occur.

(6) L. J. Bellamy, "Advances in Infrared Group Frequencies," Methuen, London, 1968, p 24; it is known that the C=C frequency is observed usually at 1566 cm^{-1}.

(7) S. Borcic and J. D. Roberts, *J. Amer. Chem. Soc.*, **87**, 1056 (1965).

(8) A. E. Favorskii and V. N. Bozhovskii, *J. Russ. Phys. Chem. Soc.*, **50**, 582 (1920); *Chem. Abstr.*, **18**, 1476 (1924); M. Mousseron, R. Jacquier, and A. Fontaine, *Bull. Soc. Chim. Fr.*, **19**, 767 (1952).

(9) In addition to compound **7**, a moderate amount of nitrogen-free by-product melting at 83.5–84.5° was isolated. Its ir spectrum showed notable bands at 1780 (lactone C=O), 1705, 1632, and 1574 cm^{-1}. The identification of this material is still being elaborated.

(10) G. B. Brown, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 615.

(11) It may be suggested that a part of **14a** underwent a double bond shift to form 5-acetyl-7,7-dichloro-4-heptenoic acid.

(12) C. R. Hauser, F. W. Swamer, and B. I. Ringler, *J. Amer. Chem. Soc.*, **70**, 4023 (1948); P. J. Hamrick, Jr., C. F. Hauser, and C. R. Hauser, *J. Org. Chem.*, **24**, 583 (1959).

(13) W. Kemp, "Practical Organic Chemistry," McGraw-Hill, New York, N. Y., 1967, p 130.

(14) E. E. Blaise, and A. Koehler, *C. R. Acad. Sci.*, **148**, 1401 (1909).

(15) Developer, *n*-hexane–acetone (3:1 v/v).

(16) Any significant amount of nitrogen was not found.

(17) Developer, *n*-hexane–acetone (5:1 v/v).

(18) Total yield of **6b**. From the aqueous layer, an additional amount of **6b** (0.04 g) was obtained.

(19) This indicates the presence of cis and trans isomers (*ca.* 1:1).

(20) Either of the cis and trans isomers.

(21) Estimated as **14a**.

(22) Developer, *n*-hexane–acetone (2:1 v/v).

(23) This component was proved to be paraffin by ir spectrum.

(24) Developer, benzene–acetic acid–methanol (10:1:1 v/v/v).

(25) B. B. Allen, W. Wyatt, and H. R. Henze, *J. Amer. Chem. Soc.*, **61**, 843 (1939).

(26) J. English, Jr., and J. E. Dayan, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 499.

(27) W. Borsche, *Justus Liebigs Ann. Chem.*, **377**, 87 (1910).