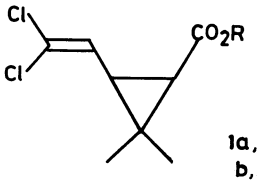
A Convenient Synthesis of 4-(2,2-Dichloroethenyl)-5,5-dimethyltetrahydro-2-furanone Derivatives, a Key Intermediate of Permethrinic Acid[1)]

Sadao Tsuboi, Eiichiro Amano, and Akira Takeda*
Department of Synthetic Chemistry, School of Engineering, Okayama University, Tsushima, Okayama 700
(Received September 5, 1983)

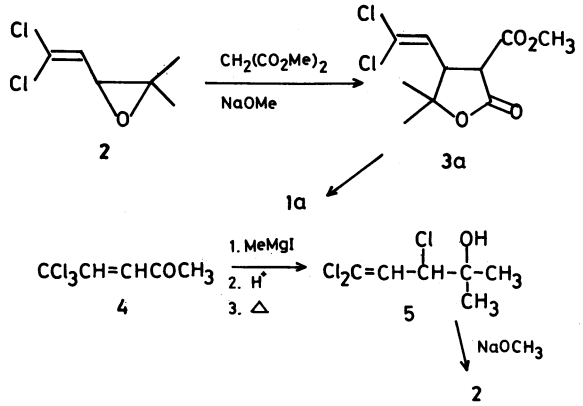
A key intermediate of 2-(2,2-dichloroethenyl)-3,3-dimethylcyclopropanecarboxylic acid, 3-alkoxycarbonyl-(or acyl)-4-(2,2-dichloroethenyl)-5,5-dimethyltetrahydro-2-furanone was prepared by the base-catalyzed condensation of 2-methyl-3,5,5-trichloro-4-penten-2-ol with acetate derivatives such as malonic esters, acetoacetic esters, and benzoylacetate. The reactivity of 3-acetyl-4-(2,2-dichloroethenyl)-5,5-dimethyltetrahydro-2-furanone to an excess amount of thionyl chloride in ethanol was also examined. An analog, 5-butyl-4-(2,2-dichloroethenyl)-3-ethoxycarbonyl-5-methyltetrahydro-2-furanone was also prepared in 31% yield.

A large number of synthetic methods of permethrinic acid [2-(2,2-dichloroethenyl)-3,3-dimethylcyclopropanecarboxylic acid] (**1a**, R=H), the acid moiety of the insecticide Permethrin (NRDC 143)[2b)], have been reported since the first synthesis by Farkas *et al.*[2,3)] Klemmensen *et al.*[4)] have reported a convenient synthesis of ethyl ester **1b** (R=Et) of permethrinic acid



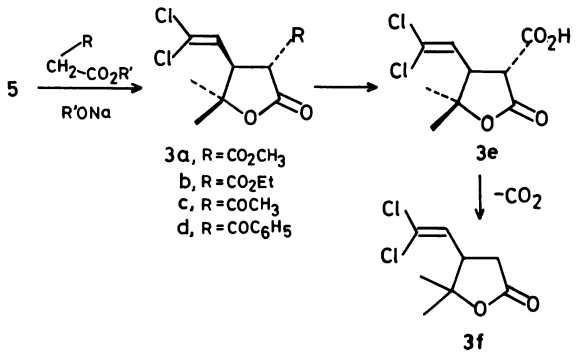
1a, R = H
b, R = Et

from 4-(2,2-dichloroethenyl)-3-methoxycarbonyl-5,5-dimethyltetrahydro-2-furanone (**3a**), which was derived from the reaction of 1,1-dichloro-3,4-epoxy-4-methyl-1-pentene (**2**)[5)] with dimethyl malonate in the presence of base. We had reported a facile synthesis of **2** by dehydrochlorination of 3,5,5-trichloro-2-methyl-4-penten-2-ol (**5**),[5)] which was readily prepared by the Grignard reaction of 5,5,5-trichloro-3-penten-2-one (**4**)[6)] with methylmagnesium iodide.



Recently we found that the chlorohydrin **5** reacts with methyl sodiomalonate to give the lactone **3a**. As an extension of the previous work[5,6)] and to establish the generality of this reaction we investigated in detail the base-catalyzed condensation of **5** with acetate derivatives such as malonic esters and acetoacetic esters. This paper will describe and discuss the results of these reactions.

Chlorohydrin **5** reacted with sodiomalonic esters at room temperature to give the lactones **3a** and **3b** in 30%

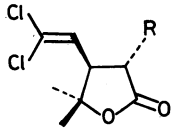


(52%)[7)] and 41% (49%)[7)] yields, respectively. Hydrolyses of **3a** and **3b** gave the corresponding lactone acid **3e**, which released carbon dioxide to yield **3f**[4)] when heated. Reaction of methyl acetoacetate with **5** in the presence of sodium methoxide gave 3-acetyl-4-(2,2-dichloroethenyl)-5,5-dimethyltetrahydro-2-furanone (**3c**) in 50% yield. However, the reaction of ethyl benzoylacetate with **5** in the presence of sodium ethoxide afforded only the poor yield (7%, 24%[7)]) of 3-benzoyl-4-(2,2-dichloroethenyl)-5,5-dimethyltetrahydro-2-furanone (**3d**) along with a mixture of unidentified products and the starting materials. The lactones **3c** and **3d** can be easily converted to **3f** by the deacylation with sodium ethoxide or aqueous sodium hydroxide.[8,9)]

Lactones **3** obtained in the present reactions were characterized by analytical and spectroscopic data, and by comparison with literature data[4)] in the case of the known lactones (**3a** and **3f**). The physical properties and analyses of lactones **3** are listed in Table 1. IR spectra of **3** showed characteristic strong peaks at around 1770 cm^{-1} due to the carbonyl groups of lactone rings. When the olefinic proton of **3a** at the ^1H NMR measurement was irradiated, the coupling constant between C_3–H and C_4–H was observed to be 12.1 Hz. This suggests that the configuration between R and dichloroethenyl group is *trans*.[10)] The best evidence that the lactones **3** have no isomers comes from the clear ^{13}C-NMR spectra which were summarized in Table 2. The signals due to lactone carbonyls exhibit upfieid-shifts of *ca.* 8 ppm from that of unsubstituted γ-butyrolactone.[11)]

Conversion of lactone **3c** to chloroester **6** was attempted by means of the procedure used for the ring opening of pyrocin (**7**).[8)] Treatment of **3c** with a ten-

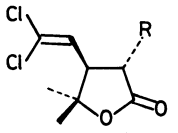
TABLE 1. PHYSICAL PROPERTIES AND ANALYSES OF LACTONES **3**



3

Compd	R	Bp θ_b/°C (Torr) [Mp θ_m/°C]	Found (Calcd) (%) C	Found (Calcd) (%) H	IR ν/cm^{-1}	^{1}H NMR δ
3b	CO_2Et		47.07 (47.00)	5.14 (5.02)	1775 1735 1620	1.32(t, 3, J=8 Hz, OCH_2CH_3), 1.32(s, 3, C_5-CH_3), 1.55(s, 3, C_5-CH_3), 3.54(d, 1, J=12 Hz, C_3-H), 3.84(dd, 1, J=10 and 12 Hz, C_4-H), 4.30(q, 2, J=8 Hz, OCH_2CH_3), 5.80(d, 1, J=10 Hz, =CH-)
3c	$COCH_3$	112(0.07)	57.27 (57.40)	4.66 (4.82)	1765 1735 1645 1625	1.31(s, 3, C_5-CH_3), 1.50(s, 3, C_5-CH_3), 3.60—3.96(m, 2, C_3-H, C_4-H), 5.70(d, 1, J=8 Hz, =CH-)
3d	COC_6H_5	180—210(0.1)	57.45 (57.53)	4.58 (4.51)	1780 1680 1625 1600	1.41(s, 3, C_5-CH_3), 1.60(s, 3, C_5-CH_3), 4.0—4.4(m, 1, C_4-H), 4.62(d, 1, J=10 Hz, C_3-H), 5.82(d, 1, J=10 Hz, =CH-), 7.2—8.2 (m, 5, C_6H_5)
3e	CO_2H	[128—129]	42.85 (42.71)	4.16 (3.98)	2650 1800 1625	1.34(s, 3, CH_3), 1.55(s, 3, CH_3), 3.57(d, 1, J=12 Hz, C_3-H), 3.80(dd, 1, J=8 and 12 Hz, C_4-H), 5.77(d, 1, J=8 Hz, =CH-), 7.46 (s, 1, CO_2H)

TABLE 2. ^{13}C NMR SPECTRA OF LACTONES **3**[a)]

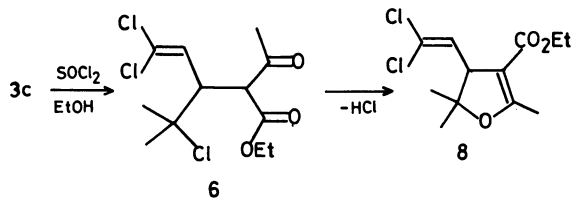


3

Compd	R	^{13}C NMR (δ) C_2	C_3	C_4	C_5	Cl_2C=	CH=	CH_3	CH_3	—R—
3a	CO_2CH_3	169.2	50.0	52.0	85.4	126.1	124.2	23.1	27.3	53.2 (q), 167.1 (s)
3c[b)]	$COCH_3$	169.6 (58.0)	58.7 (47.9)	47.4 (85.7)	85.1	125.5	124.8 (124.9)	23.7	27.6	30.1 (q), 199.0 (s) (29.5)
3d	COC_6H_5	169.7	53.9	48.5	85.3	128.3	124.5	23.9	27.6	128.8 (d), 129.5 (d), 134.2 (d), 135.7 (s), 193.5 (s)
3e	CO_2H	169.7*	50.0	51.9	86.1	126.8	124.1	23.3	27.6	170.2* (s)
3f	H	169.8	34.5	46.0	86.3	124.1	126.4	22.8	27.7	

a) Measured in $CDCl_3$. Assignments are consistent with the multiplicities observed in off-resonance decoupled spectra unless otherwise indicated. b) Signals in parenthesis seem to be those of an enol isomer (22%). * Assignment may be interchangeable.

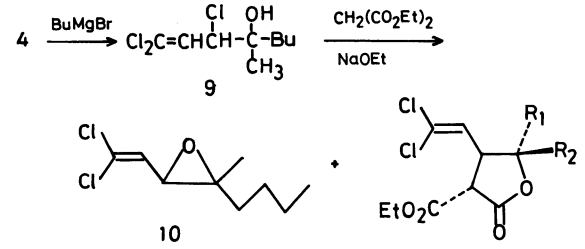
fold excess of thionyl chloride in ethanol resulted in the formation of 4-(2,2-dichloroethenyl)-3-ethoxycarbonyl-2,5,5-trimethyl-4,5-dihydrofuran (**8**) in 79% yield. Dihydrofuran **8** is thought to have been derived from **6** by the spontaneous dehydrochlorination.



6 **8**

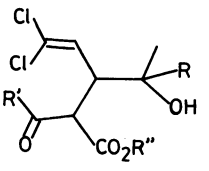
An analog of the lactone **3** was prepared by the adaptation of the method described above. Reaction of **4** with butylmagnesium bromide gave 1,1,3-trichloro-4-methyl-1-octen-4-ol (**9**) in 64% yield. ^{1}H NMR analysis showed that the alcohol **9** exists in two diastereomeric forms, *dl-erythro* and *dl-threo* (3 : 2). Condensation of **9** with diethyl sodiomalonate afforded the dehydrochlorination product of **9**, 1,1-dichloro-3,4-epoxy-4-methyl-1-octene (**10**) (30% yield) and a 3 : 2 diastereomeric mixture of 5-butyl-4-(2,2-dichloroethenyl)-3-ethoxycarbonyl-5-methyltetrahydro-2-furanones (**11a, b**) [31% (45%)[12)] yield]. The epoxide **10**, which was identified by the independent synthesis from **9**, was a mixture of *cis* and *trans* isomers (2 : 3). It has been shown in the previous paper that the *erythro* alcohol is cyclized to the *trans* epoxide and the *threo* alcohol to the *cis* epoxide, respectively.[5)] The stereochemistry of **11a** and **11b** was determined by a detailed study of their proton and ^{13}C NMR spectra. The chemical shift of

methyl carbon of C_5 in **11b** was considerably upfieid from that of methyl carbon of C_5 in **11a**.[13] In addition, the chemical shift of C_1 of butyl group in **11a** was upfield from that of C_1 of butyl group in **11b**. This showed that the methyl group of C_5 and dichloroethenyl group in **11b** was *cis*.[13] This was further confirmed by the observation of 18% NOE between the olefin proton and the methyl protons of C_5 in **11b**.



11a, $R_1=CH_3$; $R_2=Bu$
b, $R_1=Bu$; $R_2=CH_3$

The reaction mechanism on the present reaction is discussed as follows. In the reaction of chlorohydrin **5** with malonic ester and acylacetate under the basic conditions, one can imagine that the initially formed product would be most likely epoxide **2**, which is subsequently attacked by the carbanion of esters to afford the corresponding lactones **3**. This prospect seemed to be valid because both reactions of sodiomalonate with chlorohydrin **5** and with epoxide **2**[4,14] yielded the lactones **3**. However, attempted reactions of acetoacetic esters with **2** resulted in the recovery of the starting materials, while the reactions of acetoacetic esters with **5** gave lactones **3** in reasonable yields, as described above. A number of experiments between acetoacetic esters and **2** were conducted under various conditions, using alcohols, tetrahydrofuran (THF), and *N,N*-dimethylformamide (DMF) as a solvent, in the presence of equimolar or excess amount of base (NaOR and NaH), but the desired product **3** could not be isolated. This result strongly suggests that the present reaction between **5** and acetate derivatives proceeds *via* not the epoxide **2** but an S_N2 substitution product **12** as an intermediate.



12, $R=CH_3$, Bu; $R'=CH_3$, C_6H_5; $R''=CH_3$, C_2H_5

Experimental

The melting points and boiling points are uncorrected. Elemental analyses were carrried out by Mr. Eiichiro Amano. Analytical determinations by GLPC were performed on a Hitachi Model K-53 gas chromatograph filled with 10% Apiezon Grease L on Chromosorb W (3 mm o.d. × 1 m). High-performance liquid chromatography (HPLC) was performed with Yanagimoto components consisting of a PN-101 pump and R-203 differential refractometer. Infrared spectra were determined with a JASCO A-102 diffraction grating infrared spectrophotometer. ^1H NMR spectra (60 MHz) were recorded with a Hitachi Model R-24 apparatus. ^{13}C NMR spectra were obtained with a JEOL LTD, JNM-FX100 apparatus. Chemical shifts were measured using TMS as an internal standard and are given in terms of δ (ppm).

The synthesis of *2-methyl-3,5,5-trichloro-4-penten-2-ol (5)* was described in the previous paper.[5]

4-(2,2-Dichloroethenyl)-3-methoxycarbonyl-5,5-dimethyltetrahydro-2-furanone (3a). Sodium (0.2 g, 8.8 mmol) was dissolved in 50 ml of dry methanol. To the solution was added 1.16g (8.8mmol) of dimethyl malonate. After the mixture was stirred at room temperature for 1 h, **5** (1.62 g, 8 mmol) was added. The mixture was stirred for 1 d, and then condensed *in vacuo*. The residual oil was poured into water, acidified with 10% HCl, and the organic material was extracted with ether. The ethereal layer was washed with water and dried over $MgSO_4$. Removal of the solvent gave a mixture of an oil and crystals. The filtration afforded 0.638 g (30%, 52%[7]) of **3a**: mp 102—103 °C (lit,[4] mp 100—102 °C). IR and ^1H NMR data were identical with those of the authentic sample.[4] The filtrate (1.09 g) was a mixture of **5** and dimethyl malonate (1:1 1.09g by ^1H NMR).

4-(2,2-Dichloroethenyl)-5,5-dimethyl-3-ethoxycarbonyltetrahydro-2-furanone (3b) was prepared in 41% (49%)[8] yield from 0.813 g (4 mmol) of **5** and 0.705 g (4.4 mmol) of diethyl malonate, as described above. The physical properties and analytical data are shown in Table 1.

4-(2,2-Dichloroethenyl)-5,5-dimethyl-2-oxotetrahydro-3-furancarboxylic Acid (3e). The mixed solution of 0.5 g (1.87 mmol) of **3a** and 40 ml of 2 M NaOH (1 M=1 mol dm^{-3}) was stirred at room temperature for 16 h. The mixture was extracted with ether. The organic layer, after being dried over $MgSO_4$, was condensed to leave 0.421 g (89%) of **3e**: mp 128—129 °C (from benzene). The physical data and analyses are shown in Table 1.

3-Acetyl-4-(2,2-dichloroethenyl)-5,5-dimethyltetrahydro-2-furanone (3c). Sodium (0.247 g, 10.7 mmol) was dissolved in 20 ml of dry methanol. Methyl acetoacetate (1.24 g, 10.7 mmol) was added, and the mixture was stirred at 50 °C for 1 h. To the solution was added slowly 2.14 g (10.7 mmol) of **5** under reflux. The mixture was stirred at the reflux temperature for 24 h. After being cooled, the mixture was condensed *in vacuo*, and neutralized with 50% CH_3CO_2H. The organic layer was extracted with ether, and dried over $MgSO_4$. After removal of the solvent, the residual oil was distilled *in vacuo*. The first fraction (1.2 g) was distilled at 110 °C/24 Torr (1 Torr≈ 133.322 Pa). GLPC analysis showed it consists of a 1:1 mixture of the starting materials. The second fraction was collected at 112 °C/0.07 Torr to give 1.33 g (50%, 76%[7]) of **3c**: on TLC analysis (silica gel, 3:1 hexane:acetone), one spot at R_f 0.35. Spectral data and analysis are shown in Table 1.

3-Benzoyl-4-(2,2-dichloroethenyl)-5,5-dimethyltetrahydro-2-furanone (3d). From a mixture of **5** (2.03 g, 10 mmol), ethyl benzoylacetate (1.92 g, 10 mmol), sodium (0.23 g, 10 mmol), and dry ethanol (20 ml), 3.2 g of an oil was obtained by the same treatment as described in the preparation of **3c**. The distillation gave 1.95 g of the first fraction at bp 125 °C/15 Torr, consisting of a 71:29 mixture of ethyl benzoylacetate and **5**, and 0.377 g of the second fraction distilling at bp 180—210 °C/0.1 Torr. TLC analysis (silica gel, 3:1 hexane:acetone) of the second fraction gave two spots at R_f 0.45 and 0.33. The component at R_f 0.33 was collected by preparative TLC to give 0.206 g (7%, 24%[7]) of **3d**. Physical properties and analyses are shown in Tables 1 and 2.

4-(2,2-Dichloroethenyl)-3-ethoxycarbonyl-2,5,5-trimethyl-4,5-dihydrofuran (8). To a solution of **3c** (0.502 g, 2 mmol) in 20 ml of dry ethanol was slowly added 1.4 ml (20 mmol) of thionyl chloride. The solution was heated at 70 °C for 6 h. After being cooled, the mixture was condensed *in vacuo* to give 0.56 g (79%) of **8**: one spot at R_f 0.79 on TLC analysis (silica gel, 3:1 hexane: acetone); IR (neat) 1705 (ester C=O), 1645, 1625 cm^{-1} (C=C); NMR ($CDCl_3$) δ=1.08 (t, 3H,

$OCH_2C\underline{H}_3$), 1.12 (s, 3H, C_5-CH_3), 1.22 (s, 3H, C_5-CH_3), 1.98 (s, 3H, =C-CH_3), 3.57 (d, 1H, J=10 Hz, C_4-H), 3.92 (q, 2H, $OC\underline{H}_2CH_3$), 5.49 (d, 1H, J=10 Hz, =C$\underline{H}$). Found: C, 51.77; H, 5.85%. Calcd for $C_{12}H_{16}Cl_2O_3$: C, 51.63; H, 5.78%.

Reaction of **2** *with Acetoacetic Esters in the Presence of Base.* Reactions of **2** with sodioacetoacetic esters prepared by dissolving acetoacetic esters in the solvents in the presence of NaOR or NaH were carried out under following conditions: (a) **2** (0.5 g, 2.9 mmol), methyl acetoacetate (0.349 g, 2.9 mmol), $NaOCH_3$ (5.0 mmol), MeOH (4.5 ml), at room temperature for 2.5 h and at reflux temperature for 1 h; (b) **2** (1.0 g, 5.9 mmol), ethyl acetoacetate (0.858 g, 6.6 mmol), EtOH (7 ml), at room temperature for 12 h, and at reflux temperature for 6 h; (c) **2** (1.0 g, 5.9 mmol), methyl acetoacetate (0.767 g, 6.6 mmol), NaH (7.2 mmol), THF (10 ml), at room temperature for 22 h and at reflux temperature for 20 min; (d) **2** (1.0 g, 5.9 mmol), methyl acetoacetate (1.56 g, 12 mmol), NaH (18 mmol), THF (5 ml), at reflux temperature for 16 h; (e) **2** (1.0 g, 5.9 mmol), ethyl acetoacetate (0.858 g, 6.6 mmol), NaH (7.9 mmol), DMF (6 ml), at 70—75 °C for 10 h. After the usual work-up, the starting materials were recovered for all procedures.

The Epimeric Mixture (3:2 erythro: threo*) of 1,1,3-Trichloro-4-methyl-1-octen-4-ol (**9**).* An ethereal solution of *n*-BuMgBr (0.10 mol) in dry ether (50 ml) was added dropwise to a solution of **4** (15 g, 0.08 mol) in 50 ml of dry ether at −30 °C during a period of 2 h. After being stirred at −20 — −10 °C for an additional 4 h, the mixture was acidified with 10% HCl. The usual work-up gave an oil, which was distilled to give 12.5 g of **9**, yield 64%: bp 95—102 °C (2 mm); IR (neat) 3350 (OH), 1620 (C=C), 872, 746 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.90 (broad t, 3H, $C\underline{H}_3(CH_2)_3$), 1.21—1.71 (m, 9H, $CH_3(C\underline{H}_2)_3C$-$C\underline{H}_3$), 3.74 (broad s, 1H, OH), 4.67 (d, 1H, J=10 Hz, $\rangle$CHCl), 6.16 (d, 0.6H, J=10 Hz, *erythro* =CH-), 6.18 (d, 0.4H, J=10 Hz, *threo* =CH-). Found: C, 43.83; H, 5.92%. Calcd for $C_9H_{15}Cl_3O$: C, 44.02; H, 6.16%.

The Epimeric Mixture (2:3 cis: trans*) of 1,1-Dichloro-3,4-epoxy-4-methyloctene (**10**).* To a stirred solution of **9** (4.9 g, 0.02 mol) in 40 ml of dry ether was added sodium methoxide (2.38 g, 44 mmol) in several portions at −5 °C. The mixture was stirred at room temperature for 6 h, and then acidified with 10% HCl with cooling. The organic layer was extracted with ether, and the ethereal extract was dried over $MgSO_4$. After removal of the solvent, the residual oil was distilled to give 2.5 g of **10**, yield 60%: bp 124—129 °C (20 mm); IR (neat) 1614 (C=C), 930, 895, 860 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.9 (broad t, 3H, $C\underline{H}_3(CH_2)_3$), 1.28 (s, 1.8H, *trans* O-C-CH_3), 1.34 (s, 1.2 H, *cis* O-C-CH_3), 1.1—1.7 (m, 6H, $CH_3(C\underline{H}_2)_3$), 3.44 (d, 1H, J=8 Hz, $\rangle$C$\underline{H}$-CH=), 5.75 (d, 1H, J=8 Hz, =CH-). Found: C, 51.46; H, 6.48%. Calcd for $C_9H_{14}Cl_2O$: C, 51.69; H, 6.75%.

Reaction of **9** *with Diethyl Malonate in the Presence of Sodium Ethoxide.* A mixture of chlorohydrin **9** (2.76 g, 11.2 mmol) and diethyl sodiomalonate prepared from sodium (0.284 g, 12.3 mg-atom) and diethyl malonate (1.97 g, 12.3 mmol) in dry ethanol (10 ml) was heated at reflux temperature for 24 h. After removal of the solvent, the residue was poured into water. The mixture was acidified with dilute acetic acid and the organic layer was extracted with ether. The ethereal layer was washed with water, and dried over $MgSO_4$. After removal of the solvent, the residual oil was distilled *in vacuo*. The first fraction at bp 140 °C/2 Torr. gave 1.4 g of **10** (28% yield) and diethyl malonate (47:53 by ^1H NMR). Column chromatography (silica gel, 3:1 hexane: acetone) of the residual oil (1.74 g) gave 42 mg (2%) of **10**, 0.168 g of diethyl malonate, and 1.12 g (31%, 45%[12]) of a diastereomeric mixture of *5-butyl-4-(2,2-dichloroethenyl)-3-ethoxycarbonyl-5-methyltetrahydro-2-furanone (**11**)* as an oil. HPLC analysis (Yanapak SA-I, 6×250 mm; 10:1 hexane: ethyl acetate, 1.7 ml/min) showed two peaks at retention times (integrated percentages) of 10.8 (60%) and 15.2 min (40%). Each component was isolated by preparative HPLC. The first fraction yielded t-*5-butyl*-t-*4-(2,2-dichloroethenyl)*-r-*3-ethoxycarbonyl*-c-*5-methyltetrahydro-2-furanone (**11a**)*: an oil; IR (neat) 1790 (lactone C=O), 1742 (ester C=O), 1626 (C=C); ^1H NMR ($CDCl_3$) δ=0.92 (broad t, 3H, $C\underline{H}_3(CH_2)_3$-), 1.32 (t, J=7.5 Hz, 3H, $CO_2CH_2C\underline{H}_3$), 1.52 (s, 3H, C_5-CH_3), 1.1—1.6 (m, 6H, $CH_3(C\underline{H}_2)_3$-), 3.56 (d, J=12 Hz, 1H, C_3-H), 3.87 (q, J=10 and 12Hz, 1H, C_4-H), 4.30 (q, J=7 Hz, 2H, $CO_2C\underline{H}_2CH_3$), 5.85 (d, J=10 Hz, 1H, -CH=): ^{13}C NMR ($CDCl_3$) δ=13.9 (q, $\underline{C}H_3$-$(CH_2)_3$-), 14.0 (q, $CO_2CH_2\underline{C}H_3$), 23.0 (t, $CH_3\underline{C}H_2CH_2CH_2$), 25.0 (q, C_5-CH_3), 25.4 (t, $CH_3CH_2\underline{C}H_2CH_2$-), 36.3 (t, CH_3CH_2-$CH_2\underline{C}H_2$-), 50.8 (d, C_4), 52.3 (d, C_3), 62.4 (t, $CO_2\underline{C}H_2CH_3$), 87.4 (s, C_5), 124.0 (d, -CH=), 125.9 (s, $Cl_2\underline{C}$=), 166.5 (s, $\underline{C}O_2Et$), 169.3 (s, lactone C=O). Found: C, 52.19; H, 6.33%. Calcd for $C_{14}H_{20}Cl_2O_4$: C, 52.02; H, 6.24%. The second fraction gave c-*5-butyl*-t-*4-(2,2-dichloroethenyl)*-r-*3-ethoxycarbonyl*-t-*5-methyltetrahydro-2-furanone (**11b**)*: an oil; IR (neat) 1788 (lactone C=O), 1740 (ester C=O), 1625 (C=C); ^1H NMR ($CDCl_3$) δ=0.94 (broad t, 3H, $C\underline{H}_3(CH_2)_3$-), 1.32 (s, 3H, C_5-CH_3), 1.34 (t, J=7 Hz, 3H, $CO_2CH_2C\underline{H}_3$), 1.1—1.6 (m, 6H, $CH_3(C\underline{H}_2)_3$-), 3.56 (d, J=12 Hz, 1H, C_3-H), 3.91 (q, J=10 and 12 Hz, 1H, C_4-H), 4.31 (q, J=7 Hz, 2H, $CO_2C\underline{H}_2CH_3$), 5.85 (d, J=10 Hz, 1H, -CH=); ^{13}C NMR ($CDCl_3$) δ=13.8 (q, $\underline{C}H_3(CH_2)_3$-), 14.0 (q, $CO_2CH_2\underline{C}H_3$), 21.6 (q, C_5-$\underline{C}H_3$), 22.7 (t, $CH_3\underline{C}H_2CH_2CH_2$-), 25.3 (t, $CH_3CH_2\underline{C}H_2CH_2$-), 39.8 (t, $CH_3CH_2CH_2\underline{C}H_2$-), 48.3 (d, C_4), 52.1 (d, C_3), 62.4 (t, $CO_2\underline{C}H_2CH_3$), 87.2 (s, C_5), 124.4 (d, -CH=), 125.8 (s, Cl_2C=), 166.4 (s, $\underline{C}O_2Et$), 169.1 (s, lactone C=O). Found: C, 52.24; H, 6.27%. Calcd for $C_{14}H_{20}Cl_2O_4$: C, 52 .02; H, 6.24%.

References

1) Presented in part at the 38th National Meeting of the Chemical Society of Japan, Nagoya, October 1978, Lecture No. 2K28.

2) For early syntheses, see: a) J. Farkas, P. Kouriim, and F. Sorm, *Chem. Listy*, **52**, 688 (1958); b) M. Elliott, A. W. Farnham, H. F. Janes, P. H. Needham, E. A. Pulman, and J. H. Stevenson, *Nature (London)*, **246**, 169 (1973); c) K. Kondo and K. Matsui, Japan. Kokai, 51—41316 (1976).

3) For reviews, see: a) M. Elliot, "Synthetic Pyrethroids," ed by American Chemical Society, ACS Symp. Ser. (1977), P. 42; b) H. Yoshioka and S. Miyamoto, *Kagaku To Seibutsu*, **14**, 427, 549 (1976).

4) P. D. Klemmensen, H. Kolind-Andersen, H. B. Madsen, and A. Svendsen, *J. Org. Chem.*, **44**, 416 (1979).

5) A. Takeda, S Tsuboi, T. Moriwake, and E. Hirata, *Bull. Chem. Soc. Jpn.*, **45**, 3685 (1972).

6) S. Tsuboi, T. Uno, and A. Takeda, *Chem. Lett.*, **1978**, 1325.

7) Estimated from the consumed **5**.

8) A. Takeda, T. Sakai, S. Shinohara, and S. Tsuboi, *Bull. Chem. Soc. Jpn.*, **50**, 1133 (1977).

9) A. Takeda, S. Tsuboi, and T. Sakai, *J. Org. Chem.*, **39**, 2601 (1974).

10) M. Petrzilka, D. Felix, and A. Eschenmoser, *Helv. Chim. Acta*, **56**, 2950 (1973).

11) J. B. Stothers and P. C. Lanterour, *Can. J. Chem.*, **42**, 1563 (1964).

12) Estimated from the consumed diethyl malonate.

13) The chemical shifts of sterically perturbed carbon atoms are generally found at higher magnetic fields than for similar carbons which are not spatially crowded: D. M. Grant and B. V. Cheney, *J. Am. Chem. Soc.*, **89**, 5315 (1967); D. E. Dorman, M. Jautelat, and J. D. Roberts, *J. Org. Chem.*, **36**, 2757 (1971).

14) We reinvestigated the reaction of **2** with methyl malonate in the presence of sodium methoxide to give **3a** in 76% yield.