July, 1977] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (7), 1831—1835 (1977) 1831

Synthesis of Methyl-substituted 1-Cyclopentene-1-carboxylates and Related Compounds*

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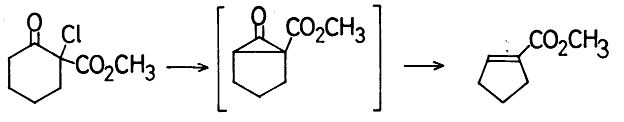
(Received January 20, 1977)

The treatment of methyl-substituted 1-chloro-2-oxo-1-cyclohexanecarboxylic esters (**7a**—**e**) with anhydrous Na_2CO_3 in refluxing xylene gave the corresponding methyl-substituted 1-cyclopentene-1-carboxylic esters (**1a**—**e**). Several intermediates important in the synthesis of natural products, such as 4,4-dimethyl-1-cyclopentene-1-carbaldehyde (**9**), 5-methyl-1-cyclopentene-1-carbaldehyde (**12**), α-(3-methyl-1-cyclopentenyl)propionic acid (**16**), and ethyl 2-methyl-3-oxo-1-cyclopentene-1-carboxylate (**17**), have been prepared starting from esters **1e**, **1d**, **1b**, and **1a**, respectively.

During the course of our work in cyclopentane monoterpene synthesis we required several methyl-substituted 1-cyclopentene-1-carboxylic esters (**1a**—**d**) and/or the corresponding aldehydes (**2**). The synthetic procedures of **1** as well as **2** so far reported appear to be inconvenient because they yield a mixture of structural isomers.[1,2] Recently Büchi *et al.*[3] have reported the dehydrochlorination-decarbonylation of 2-chloro-2-alkyl-1,3-cyclohexanedione to produce 2-alkyl-2-cyclopentene-1-one. The reaction was then extended to other 2-chloro-1,3-dicarbonyl compounds, such as cyclic α-chloro-β-keto aldehydes and α-chloro-β-keto esters. Thus, the dehydrochlorination-decarbonylation of methyl 1-chloro-2-oxo-1-cyclohexanecarboxylate (**3**) with sodium carbonate in hot xylene afforded methyl 1-cyclopentene-1-carboxylate (**5**).[4] Büchi has suggested that the product originates from the cyclopropanone intermediate (**4**) by thermal, nonconcerted elimination of carbon monooxide.



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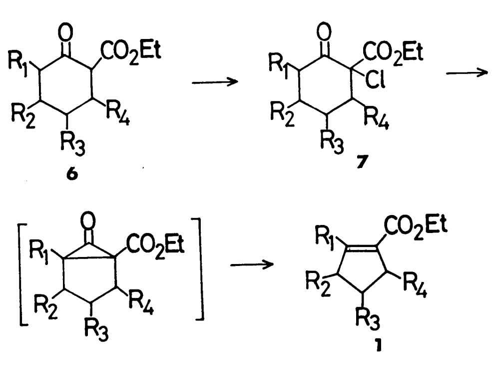
We decided to investigate the dehydrochlorination-decarbonylation of four methyl-substituted 1-chloro-2-oxo-1-cyclohexanecarboxylic esters (**7a**—**d**) in an attempt to devise a straightforward synthesis of the desired esters **1a**—**d**.



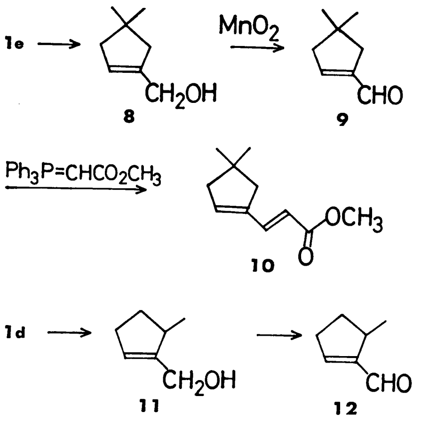
6a, **7a**, **1a**: $R_1=CH_3$, $R_2=R_3=R_4=H$
6b, **7b**, **1b**: $R_2=CH_3$, $R_1=R_3=R_4=H$
6c, **7c**, **1c**: $R_3=CH_3$, $R_1=R_2=R_4=H$
6d, **7d**, **1d**: $R_4=CH_3$, $R_1=R_2=R_3=H$

Four methyl-substituted 2-oxo-1-cyclohexanecarboxylic esters (**6a**—**d**) were chlorinated with *t*-butyl hypochlorite (*t*-BuOCl) under conditions similar to those in the literature[4] to give the corresponding α-chloro-β-keto esters (**7a**—**d**) in good yields (Table 1). The spectral data given in Table 2 support their structure. Both the IR spectra and the NMR spectra of compounds **7a**—**d** clearly show that they are nonenolizable β-keto esters. The NMR signals of the methyl protons of **7d** shifted to a lower field (δ 1.30) as compared with the other isomers, being affected by the neighboring chlorine atom.

These chlorides were treated with anhydrous Na_2CO_3 in refluxing xylene in the presence of glass powder until their exhaustion to give the corresponding 1-cyclopentene-1-carboxylates (**1a**—**d**) in 47—82% yields. The results are listed in Tables 3 and 4.

Starting from appropriate cyclopentenecarboxylates, we also prepared several intermediates such as 4,4-dimethyl-1-cyclopentene-1-carbaldehyde (**9**),[10] 5-methyl-1-cyclopentene-1-carbaldehyde (**12**),[12,13] α-(3-methyl-1-cyclopentenyl)propionic acid (**16**),[14] and ethyl 2-methyl-3-oxo-1-cyclopentene-1-carboxylate (**17**), useful for the synthesis of natural products.

The chlorination of ethyl 5,5-dimethyl-2-oxo-1-cyclohexanecarboxylate (**6e**)[11] with *t*-BuOCl gave ethyl 1-chloro-5,5-dimethyl-2-oxo-1-cyclohexanecarboxylate (**7e**) in a 79% yield. The treatment of **7e** with Na_2CO_3 afforded ethyl 4,4-dimethyl-1-cyclopentene-1-carboxylate (**1e**) in a 76% yield. The reduction of **1e** with $LiAlH_4$ gave 4,4-dimethyl-1-cyclopentenylmethanol (**8**) in a 93% yield. This alcohol was oxidized with active manganese dioxide[15] to the aldehyde **9** in a 33%



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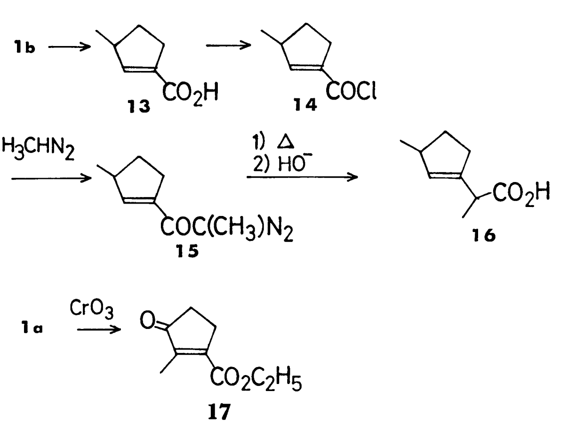
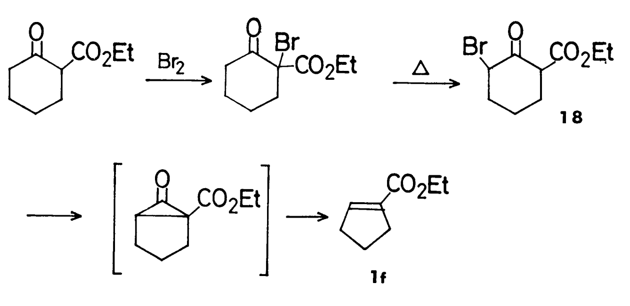
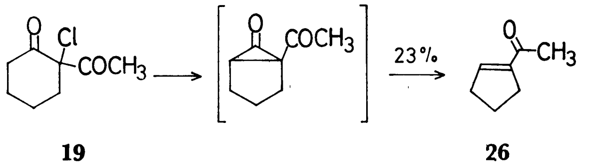
* Presented in part at the 33rd Annual Meeting of the Chemical Society of Japan, Fukuoka, October 1975.

yield. Compound **9** was further converted into methyl *trans*-β-(4,4-dimethyl-1-cyclopentenyl)acrylate (**10**)[10] by the Wittig reaction with Ph_3P=$CHCO_2CH_3$.[16] Ethyl 5-methyl-1-cyclopentene-1-carboxylate (**1d**) was also converted into aldehyde **12** *via* 5-methyl-1-cyclopentenylmethanol (**11**) in a 35% overall yield. Ethyl 3-methyl-1-cyclopentene-1-carboxylate (**1b**) can be used as a starting material to prepare the acid **16**. The reaction of 3-methyl-1-cyclopentene-1-carbonyl chloride (**14**) with diazoethane afforded the corresponding diazo ketone (**15**). The thermal decomposition of **15** and the subsequent hydrolysis of the product gave the acid **16**. Compounds **12** and **16** are important intermediates for the synthesis of iridomyrmecin.[12–14] The oxidation of ethyl 2-methyl-1-cyclopentene-1-carboxylate (**1a**) with CrO_3 in glacial acetic acid gave 2-methyl-3-oxo-1-cyclopentene-1-carboxylate (**17**), the ester of the structural isomer of sarcomycine, in a 20% yield.[17]



Further synthetic application was carried out by the use of ethyl 3-bromo-2-oxo-1-cyclohexanecarboxylate (**18**),[18,19] 2-chloro-2-acetylcyclohexanone (**19**),[20] 2-chloro-2-acetylcyclopentanone (**22**),[21] propyl 1-chloro-2-oxo-1-cyclopentanecarboxylate (**23**), 2-chloro-2-formylcyclohexanone (**24**), and 2-chloro-2-formyl-4,4-dimethylcyclohexanone (**25**) as substrates. The treatment of the bromide **18** with Na_2CO_3 yielded ethyl 1-cyclopentene-1-carboxylate (**1f**), the same product as that from the 2-halogeno derivative, in a 61% yield. While the IR spectrum of **19** obtained by the chlorination of 2-acetylcyclohexanone (**31**)[30] with *t*-BuOCl was identical with that of the literature,[20] the TLC analysis as well as the NMR survey indicated the presence of the 6-chloro isomer (**20**) (**19** : **20**=1 : 4). This mixture of isomers **19** and **20** was used for the next step without separation, since the both compounds should give the same Favorskii-type products, as is shown in the case of **18**. Thus, the reaction of the mixture of isomers **19** and **20** afforded 1-acetyl-1-cyclopentene (**26**) in a 23% yield.[22] The reactions of compounds **22**, **23**, **24**, and **25** failed to afford the anticipated products, instead yielding only tarry material.[21]





19 **26**

Studies of the synthesis of furopelargone[23] from the ester **1b**, that of photocitral[24] from the aldehyde **12**, and that of nepetalic acid[25] from the ester **1d** are now in progress.

Experimental

The melting points and boiling points are uncorrected. The 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 fitted with the following columns (3 mm o.d. × 1 m) A, 10% Apiezon Grease L on Chromosorb W; B, 10% poly(neopentyl 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). The mass spectra were obtained with a Hitachi Model RMS-4 mass spectrometer. The NMR spectra (60 MHz) were recorded with a Hitachi Model R-24 apparatus. The thin-layer chromatograms were prepared with Merck Kieselgel 60 PF_{254} (E. Merck AG, Darmstadt). The column chromatograms were prepared with Wakogel B-5F (Wako Junyaku Kogyo Co., Ltd.).

The following compounds were obtained in ways which have been described in the literature: **6a**,[5] **6b**,[6] **6c**,[7] **6d**,[8] **18**,[19] 2-acetylcyclopentanone (**21**),[28] 2-hydroxymethylenecyclohexanone (**30**),[29] and **31**.[30]

The following are typical runs. The reaction of **6b** illustrates the manner in which the chlorination of **6a**—**d** and the dehydrochlorination-decarbonylation of the chlorides **7a**—**d** were carried out.

Ethyl 1-Chloro-4-methyl-2-oxo-1-cyclohexanecarboxylate (7b). To a stirred solution of 7.4 g (0.04 mol) of ethyl 4-methyl-2-oxo-1-cyclohexanecarboxylate (**6b**)[6] dissolved in 60 ml of methanol was added 4.8 g (0.044 mol) of *t*-BuOCl[31] below 0 °C under nitrogen. After it had been stirred for an additional 1 h at the same temperature, the mixture was kept in a refrigerator for 40 h, and then allowed to stand at room temperature for 4 h. After the evaporation of methanol, the solution was distilled under reduced pressure to give 7.9 g (91%) of **7b**.

Ethyl 3-Methyl-1-cyclopentene-1-carboxylate (1b). Following the procedure reported by Büchi,[4] a flask was charged with 9.3 g (0.088 mol) of crushed, anhydrous Na_2CO_3 and 36 g of glass powder. After the content of the flask had been dried at 160 °C for 2 h *in vacuo*, it was filled up with nitrogen gas. A solution of 16 g (0.073 mol) of the chloride **7b** in 110 ml of xylene was then added to the flask, and the mixture was refluxed with stirring. The reaction was continued for 40 h until the chloride **7b** had been exhausted, as checked by GLPC. The resulting mixture was cooled and filtered. After evaporation of the solvent, it was fractionally distill-

Table 1. Chlorination of ethyl 2-oxo-1-cyclohexanecarboxylates (**6a**—**d**)

Product	Yield (%)	Bp (Torr)	Found (%)		Calcd (%) for $C_{10}H_{15}ClO_3$	
			C	H	C	H
7a[a)]	62	80— 83 (0.05)	54.76	6.82	54.93	6.91
7b[a)]	91	99—100 (0.07)	54.78	6.93	54.93	6.91
7c[a)]	79	80— 81 (0.035)	55.14	6.98	54.93	6.91
7d[b)]	70	100—102 (0.05)	55.10	6.84	54.93	6.91

a) *t*-BuOCl 1.1 times as much as **6** in mol was used. b) *t*-BuOCl 1.6 times as much as **6** in mol was used.

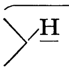
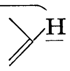
Table 2. Spectral data of ethyl 1-chloro-2-oxo-1-cyclohexanecarboxylates

Compound	NMR (CCl_4, δ)				IR (neat, cm^{-1})
	$C\underline{H}_3$ (ring)	$CO_2CH_2C\underline{H}_3$	$CO_2C\underline{H}_2CH_3$	Ring-proton	
7a	1.04 (d, J=6 Hz, 3H)	1.34 (t, 3H)	4.24 (q, 2H)	1.5—3.0 (m, 7H)	1730
7b	1.05 (d, J=6 Hz, 3H)	1.30 (t, 3H)	4.23 (q, 2H)	1.6—3.0 (m, 7H)	1725, 1750
7c	1.05 (d, J=6 Hz, 3H)	1.31 (t, 3H)	4.25 (q, 2H)	1.6—2.7 (m, 7H)	1725, 1750
7d	1.30 (d, J=6 Hz, 3H)	1.31 (t, 3H)	4.22 (q, 2H)	1.5—3.0 (m, 7H)	1730

Table 3. Dehydrochlorination of 1-chloro-2-oxo-1-cyclohexanecarboxylates (**7a**—**d**)

Substrate	Product	Yield (%)	Found (%)		Calcd (%) for $C_9H_{14}O_2$		MS (70 eV) m/e (rel intensity)
			C	H	C	H	
7a	**1a**	74	69.89	9.17	70.10	9.15	154 (19, M^+), 125 (23), 109 (55), 81 (100)
7b	**1b**	79	69.79	8.79	70.10	9.15	154 (9, M^+), 125 (9), 109 (53), 81 (100)
7c	**1c**	82	69.81	9.15	70.10	9.15	154 (13, M^+), 109 (42), 81 (100)
7d	**1d**	47	70.32	9.15	70.10	9.15	154 (16, M^+), 109 (57), 81 (100)

Table 4. Spectral data of methyl-substituted 1-cyclopentene-1-carboxylates

Compound	NMR (CCl_4, δ)					IR (neat, cm^{-1})	
	$C\underline{H}_3$ (ring)	$CO_2CH_2C\underline{H}_3$	$CO_2C\underline{H}_2CH_3$	Ring-proton		C=O	C=C
							
1a	2.08 (s, 3H)	1.28 (t, 3H)	4.13 (q, 2H)	1.6—2.9 (m, 6H)		1705	1642
1b	1.07 (d, 3H)	1.23 (t, 3H)	4.08 (q, 2H)	1.5—2.9 (m, 5H)	6.50 (s, br, 1H)	1710	1625
1c	1.05 (d, 3H)	1.24 (t, 3H)	4.08 (q, 2H)	1.6—3.0 (m, 5H)	6.56 (s, br, 1H)	1710	1625
1d	1.12 (d, 3H)	1.27 (t, 3H)	4.11 (q, 2H)	2.0—3.2 (m, 5H)	6.59 (s, br, 1H)	1710	1623

ed under diminished pressure to give 8.9 g (79%) of the ester **1b**: bp 93—94 °C/22 Torr.

*Ethyl 5,5-Dimethyl-2-oxo-1-cyclohexanecarboxylate (**6e**).*[11)] This substance was prepared from 4,4-dimethylcyclohexanone (**29**)[27)] in a 24% yield by an adaptation of Snyder's method:[9)] bp 90—110 °C/60 Torr [lit,[11)] bp 75 °C/1Torr]; IR (neat) 1755, 1720, 1668, and 1627 cm^{-1}; NMR ($CDCl_3$) δ 0.98 (s, 6H), 1.30 (t, 3H), 2.20 (s, 2H), 2.28 (m, 4H), and 4.20 ppm (q, 2H).

*Ethyl 1-Chloro-5,5-dimethyl-2-oxo-1-cyclohexanecarboxylate (**7e**).* The ester **6e** (1.22 g, 62 mmol) was chlorinated in 15 ml of methanol with 0.85 g (7.9 mmol) of *t*-BuOCl in the manner used in the preparation of **7b**. The distillation of the residue obtained after working up as usual gave 1.12 g (79%) of the chloride **7e**: bp 115 °C (0.2 mm); IR (neat) 1730 cm^{-1}; NMR (CCl_4) δ 1.07 (s, 3H), 1.14 (s, 3H), 1.33 (t, 3H), 4.22 (q, 2H), and 1.6—3.0 ppm (m, 6H).

Found: C, 56.99; H, 7.20%. Calcd for $C_{11}H_{17}ClO_3$: C, 56.78; H, 7.36%.

*Ethyl 4,4-Dimethyl-1-cyclopentene-1-carboxylate (**1e**).* The dehydrochlorination-decarbonylation of the chloride **7e** (0.512 g, 2.1 mmol) with anhydrous Na_2CO_3 (0.256 g, 2.4 mmol) was carried out in refluxing xylene (4 ml) in the presence of glass powder (1.5 g). The reaction was continued for 28 h at the refluxing temperature until **7e** was exhausted, as checked by GLPC. The resultant mixture was cooled, filtered, and passed through a column of 10 g of dried silica gel. After the removal of xylene, using hexane as the eluant, a colorless eluate was collected with chloroform. The subsequent evaporation of chloroform afforded 267 mg (76%) of a pure ester (**1e**): IR (neat) 1725, and 1630 cm^{-1}; NMR (CCl_4) δ 1.16 (s, 6H), 1.23 (t, 3H), 2.3 (m, 3H), 2.31 (s, 2H), 4.07 (q, 2H), and 6.51 ppm (br, 1H).

*4,4-Dimethyl-1-cyclopentenylmethanol (**8**).* To a stirred suspension of $LiAlH_4$ (77 mg, 2 mmol) in 3 ml of dry ether was added dropwise the ester **1e** (267 mg, 5 mmol) dissolved in 1 ml of dry ether at −76 °C over a period of 0.5 h. After the addition had been completed, the mixture was stirred for an additional 4.5 h at −50——20 °C. To the mixture which had been allowed to warm up to room temperature was added 132 mg (1.5 mmol) of ethyl acetate to decompose the excess of $LiAlH_4$. The resulting mixture was treated with

0.35 ml of saturated aqueous ammonium chloride. The solid residue was washed with ether. The combined ethereal solution was then dried ($MgSO_4$) and evaporated to yield 175 mg (93%) of crude alcohol (**8**): IR (neat) 3360 cm^{-1}; NMR (CCl_4) δ 1.07 (s, 6H), 2.10 (s, 4H), 3.15 (br, s, 1H), 4.00 (s, 2H), and 5.41 ppm (br, s, 1H).

*4,4-Dimethyl-1-cyclopentene-1-carbaldehyde (**9**).* A mixture of 2.0 g of active manganese dioxide,[15] 175 mg (1.39 mmol) of crude alcohol **8**, and 10 ml of petroleum ether (bp 30—44 °C) was stirred for 3.5 h under nitrogen at room temperature, filtered and evaporated to give 168 mg of a crude product. Separation by column chromatography (silica gel) afforded 56 mg (33%) of pure aldehyde (**9**): IR (neat) 1678, and 1617 cm^{-1}; NMR (CCl_4) δ 1.12 (s, 6H), 2.32 (m, 4H), 6.63 (br, s, 1H), and 9.67 ppm (s, 1H).

Methyl trans-*β-(4,4-Dimethyl-1-cyclopentenyl)acrylate (**10**).* A solution of 56 mg (0.45 mmol) of the aldehyde **9** in 1 ml of benzene was added to 196 mg (0.59 mmol) of $Ph_3P{=}CHCO_2CH_3$,[16] after which the mixture was refluxed for 17 h. After working up,[2] 30 mg (37%) of the ester **10** was obtained. The spectral data (IR and NMR) of this product were identical with those of the literature.[10]

*5-Methyl-1-cylopentenylmethanol (**11**).* To a stirred suspension of $LiAlH_4$ (300 mg, 7.9 mmol) in 12 ml of dry ether was added dropwise ethyl 5-methyl-1-cyclopentene-1-carboxylate (**1d**) (937 mg, 6.1 mmol) dissolved in 5 ml of dry ether at −76 °C over a period of 20 minutes. The crude product which was obtained after working up in the manner used in the preparation of the alcohol **8** was subjected to vacuum distillation to yield 257 mg (38%) of pure alcohol (**11**): bp 62—64 °C (10 mm); IR (neat) 3350 cm^{-1}; NMR ($CDCl_3$) δ 1.05 (d, 3H, J=6 Hz), 1.55 (m, 2H), 2.27 (m, 2H), 2.70 (br, m, 1H), 3.60 (br, s, 1H, $-O\underline{H}$), 4.18 (s, 2H, $-C\underline{H}_2OH$), and 5.69 ppm (br, s, 1H).

Found: C, 74.76; H, 10.63%. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78%.

*5-Methyl-1-cyclopentene-1-carbaldehyde (**12**).* A mixture of 3.2 g of active manganese dioxide, 250 mg (2.2 mmol) of the alcohol **11**, and 16 ml of petroleum ether was stirred for 5.5 h under nitrogen at room temperature. The working-up was essentially the same as in the preparation of the aldehyde **9**, yielding 159 mg (65%) of the aldehyde **12**: IR (neat) 1672, and 1610 cm^{-1}; NMR ($CDCl_3$) δ 1.13 (d, 3H, J=6 Hz, $-C\underline{H}_3$), 1.65 (br, m, 2H), 2.50 (br, m, 2H), 3.00 (br, m, 1H), 6.78 (m, 1H, $=\!/^{\underline{H}}$), and 9.75 ppm (s, 1H, $-C\underline{H}O$).

*3-Methyl-1-cyclopentene-1-carboxylic Acid (**13**).* To a solution of potassium hydroxide (67 g, 1.2 mol) in 500 ml of ethanol was added 57 g (0.37 mol) of ethyl 3-methyl-1-cyclopentene-1-carboxylate (**1b**). The soultion was then refluxed for 20 h. After the evaporation of the solvent, enough dilute hydrochloric acid to acidify the mixture was added. The acidic organic layer was then extracted with ether. After being dried with $MgSO_4$, the ethereal solution was evaporated to dryness to give 47 g (quantitative) of the acid **13**: mp 34 °C (lit,[32] mp 35—36 °C); IR (Nujol) 3600—2100, 1675, and 1625 cm^{-1}; NMR (CCl_4) δ 1.11 (d, 3H, J=7 Hz), 1.3—3.1 (m, 5H), and 6.70 ppm (m, 1H).

*3-Methyl-1-cyclopentene-1-carbonyl Chloride (**14**).* This substance was prepared by treating the acid **13** (875 mg, 7 mmol) with $SOCl_2$ (1.05 g, 8.8 mmol) as usual. The subsequent removal of the excess $SOCl_2$ by evaporation gave 838 mg (84%) of the chloride **14**: bp 75—79 °C/31 Torr; IR (neat) 1752, and 1623 cm^{-1}; NMR (CCl_4) δ 1.16 (d, 3H, J=7 Hz), 1.3—3.3 (m, 5H), and 6.96 ppm (m, 1H, $=\!/^{\underline{H}}$).

*α-(3-Methyl-1-cyclopentenyl)propionic Acid (**16**).* The Arndt-Eistert reaction with diazoethane[33] was employed to prepare this compound. The chloride **14** (793 mg, 5.8 mmol) was allowed to react with 15 mmol of diazoethane in 100 ml of ether to give the diazo ketone (**15**): IR (neat) 3400, 2070, 1718, 1621, and 1550 cm^{-1}. This product was then subjected to thermal decomposition, followed by hydrolysis. The subsequent purification of the crude product with TLC [silica gel, benzene–methanol–AcOH (50 : 1 : 1), R_f=0.3] gave 156 mg of the acid **16** (18% yield from **14**): IR (neat) 3600—2400, 1700, and 1628 cm^{-1}; NMR ($CDCl_3$) δ 1.10 (d, 3H), 2.12 (d, 3H), 1.0—3.0 (br, m, 6H), 6.77 (m, 1H), and 7.44 ppm (br, s, 1H, $CO_2\underline{H}$).

*Ethyl 2-Methyl-3-oxo-1-cyclopentene-1-carboxylate (**17**).* To a stirred solution of ethyl 2-methyl-1-cyclopentene-1-carboxylate (**1a**) (1.96 g, 12.7 mmol) in 2.5 ml of glacial acetic acid was added dropwise a solution of chromium trioxide (2.0 g, 20 mmol) in aqueous acetic acid (3.8 ml of AcOH mixed with 1.1 ml of H_2O) over a 1-h period at room temperature. After the completion of the addition, the mixture was stirred for a further 54 h. The resulting mixture was treated with 70 ml of brine and then extracted with ether. The ethereal layer was washed twice with a 5% aqueous sodium hydroxide solution and dried over $MgSO_4$. After the evaporation of the solvent, the residue was subjected to column chromatography (silica gel, hexane : acetone=50 : 1 to 20 : 1), giving 615 mg of the unchanged ester and 418 mg (20%) of the ester **17**: IR (neat) 1712 and 1637 cm^{-1}; NMR (CCl_4) δ 1.33 (t, 3H, $-CO_2-C-C\underline{H}_3$), 1.99 (t, 3H, $=\!\langle^{C\underline{H}_3}$), 2.32 (m, 2H, $=\!\langle^{C\underline{H}_2-}$), 2.65 (m, 2H, $-\underset{\overset{\|}{O}}{C}-C\underline{H}_2-$), 4.25 ppm (q, 2H, $-CO_2-C\underline{H}_2-$); MS (70 eV) *m/e* (rel intensity) 168 (M^+, 31), 140 (30), 123 (33), 112 (55), 95 (25), 67 (100).

*Ethyl 1-Cyclopentene-1-carboxylate (**1f**).* A mixture of 3.27 g (13.1 mmol) of ethyl 3-bromo-2-oxo-1-cyclohexanecarboxylate (**18**),[19] 2.0 g (19 mmol) of anhydrous Na_2CO_3, and 10 g of glass powder was heated in refluxing xylene (20 ml) under an atmosphere of nitrogen for 29 h. The resulting mixture was filtered and passed through a column packed with 6 g of dry silica gel. After the elution of xylene with hexane, 1.12 g (61%) of the product **1f**, was obtained by washing out with chloroform: IR (neat) 1715 and 1630 cm^{-1} [lit,[34] IR (CCl_4) 1710 and 1620 cm^{-1}]; NMR (CCl_4) δ 1.23 (t, 3H), 1.5—2.7 (m, 6H), 4.09 (q, 2H), and 6.63 ppm (br, s, 1H).

*2-Chloro-2-acetylcyclohexanone (**19**) and 6-Chloro-2-acetylcyclohexanone (**20**).* *t*-BuOCl (2.15 g, 19.8 mmol) was stirred into a solution of 2-acetylcyclohexanone (**31**)[30] (2.31 g, 16.5 mmol) in absolute methanol (20 ml) under nitrogen over a 40 minute period, the temperature being kept below −20 °C. The mixture, which was then worked up as usual, yielded 1.77 g (62%) of a mixture of isomers **19** and **20**: bp 85—105 °C (0.3 Torr) [lit,[20] bp 50—51 °C/0.1 Torr]. The preparative TLC of this product (80 mg) afforded 14 mg of the chloride **19** [R_f=0.38; IR (neat) 1724 cm^{-1}; NMR (CCl_4) δ 2.29 (s, 3H, $-\underset{\overset{\|}{O}}{C}-C\underline{H}_3$), 1.5—2.6 ppm (m, 8H, ring proton)], together with 54 mg of the chloride **20** [R_f=0.24; IR(neat) 1720, 1630, and 1585 cm^{-1}; NMR (CCl_4) δ 2.29 (s, 3H, $-\underset{\overset{\|}{O}}{C}-C\underline{H}_3$), 1.5—2.3 (m, 7H), 4.1—4.5 (br, m, 0.6H, $-\underset{\overset{\|}{O}}{C}-C\underline{H}-\underset{\overset{\|}{O}}{C}-$), and 15.02 ppm (s, 0.4H, $-\underset{\overset{|}{O\underline{H}}}{C}=C-$)].

*2-Chloro-2-acetylcyclopentanone (**22**).* The chlorination of 2-acetylcyclopentanone (**21**)[28] with *t*-BuOCl gave this substance in an 80% yield: bp 75—80 °C (0.1 Torr) [lit,[21] bp

92—94 °C/13 Torr]; IR (neat) 1750, 1715, and 1650 cm^{-1}; NMR (CCl_4) δ 2.40 (s, 3H, $-\underset{\underset{O}{\|}}{C}-C\underline{H}_3$), and 1.7—2.7 ppm (m, 6H, ring proton).

Propyl 1-Chloro-2-oxo-1-cyclopentanecarboxylate (23). The chlorination of propyl 2-oxo-1-cyclopentanecarboxylate (**27**) with *t*-BuOCl gave the chloride **23** in an 85% yield: bp 105—110 °C (0.05 Torr); IR (neat) 1755, and 1723 cm^{-1}; NMR (CCl_4) δ 0.77 (t, 3H), 1.72 (m, 2H), 2.0—3.0 (m, 6H), and 4.14 ppm (t, 2H).

2-Chloro-2-formylcylclohexanone (24). The chlorination of 2-hydroxymethylenecyclohexanone (**30**)$^{29)}$ with *t*-BuOCl in chloroform gave this substance in a 70% yield: bp 50—60 °C/5 Torr; IR (neat) 1740 and 1720 cm^{-1}; NMR (CCl_4) δ 1.98 (m, 4H), 2.4—3.3 (m, 2H), and 9.55 ppm (s, 1H, $-C\underline{H}O$).

2-Chloro-2-formyl-4,4-dimethylcyclohexanone (25). The chlorination of 2-hydroxymethylene-4,4-dimethylcyclohexanone (**28**) with *t*-BuOCl in chloroform gave this substance in a 59% yield: bp 74—77 °C/5 Torr; IR (neat) 1740 and 1730 cm^{-1}; NMR (CCl_4) δ 1.08 (s, 3H, $-C\underline{H}_3$), 1.28 (s, 3H, $-C\underline{H}_3$), 1.5—3.0 (m, 6H, ring proton), and 9.37 ppm (s, 1H, $-C\underline{H}O$).

*1-Acetyl-1-cyclopentene (26). Dehydrochlorination-decarbonylation of the Chloride **19**.* The treatment of the crude chloride **19** (554 mg, 3.2 mmol) with 450 mg of anhydrous Na_2CO_3 in refluxing xylene afforded 267 mg of a crude product, which was subsequently purified by preparative TLC (silica gel, hexane : acetone = 10 : 1) to give 79 mg (23%) of the ketone: IR (neat) 1663 and 1616 cm^{-1}; NMR (CCl_4) δ 2.20 (s, 3H, $-\underset{\underset{O}{\|}}{C}-C\underline{H}_3$), 1.7—2.8 (m, 6H, ring proton), and 6.52 ppm (br, s, 1H, $=\!\langle^{\underline{H}}$).

Propyl 2-Oxo-1-cyclopentanecarboxylate (27). This substance was prepared in a 79% yield by the Dieckmann condensation$^{26)}$ of dipropyl adipate: bp 95—100 °C/7 Torr; IR (neat) 1755, 1720, 1658, and 1620 cm^{-1}; NMR (CCl_4) δ 0.95 (t, 3H), 1.65 (m, 2H), 2.14 (m, 6H), 3.00 (m, 1H), and 4.01 ppm (t, 2H).

2-Hydroxymethylene-4,4-dimethylcyclohexanone (28). This substance was prepared in a 45% yield by the formylation of 4,4-dimethylcyclohexanone (**29**)$^{27)}$ in a manner similar to that used in the preparation of 2-hydroxymethylenecyclohexanone (**30**)$^{29)}$: bp 63—65 °C/10 Torr; IR (neat) 2900, 1640, and 1600 cm^{-1}: NMR (CCl_4) δ 1.00 (s, 6H), 1.45 (t, 2H), 2.10 (s, 2H), 2.42 (t, 2H), 8.50 (s, 1H, $=C\underline{H}-OH$), and 14 ppm (br, s, 1H, $=CHO\underline{H}$).

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