Synthesis of 5,5-Dimethyl-4-acetoxy-2-cyclopentenone and 5-Methyl-*t*-5-acetoxymethyl-*r*-4-acetoxy-2-cyclopentenone Intermediates for Illudin M and S

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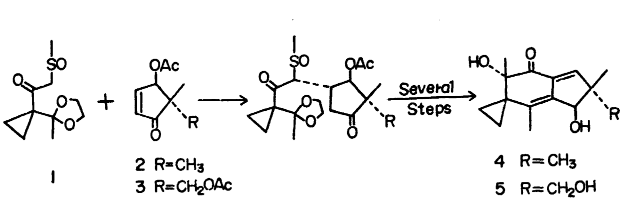
5,5-Dimethyl-4-acetoxy-2-cyclopentenone and 5-methyl-*t*-5-acetoxymethyl-*r*-4-acetoxy-2-cyclopentenone, intermediates for illudin M and S respectively, have been synthesized from ethyl adipate.

In an earlier communication[1] we reported a total synthesis of *dl*-illudin M[2] (**4**) through the Michael reaction between **1** and the cyclopentenone **2**. A total synthesis of illudin S[2,3] (**5**) has also been presented[4] by an analogous route employing **3a** (Scheme 1). In this paper we should like to describe synthesis of these cyclopentenone intermediates **2**[5] and **3a**.



Scheme 1.

At first attempts were made to derive the cyclopentenone **2** from 2,2-dimethylcyclopentanone[6] (**20**). However, **20** had been obtained as a mixture with some other methylated cyclopentanones by methylation of either cyclopentanone or methylcyclopentanone. Thus another route for **20** was desirable.

2-Methyl-2-carbethoxycyclopentanone[7] **6** was reduced by lithium aluminum hydride to give a semicrystalline 2-methyl-2-hydroxymethylcyclopentanol (**18**) in 80% yield, bp 148—153°C/4 mmHg, which was converted into a monotosylate **19** quantitatively. Treatment of one mol of **19** with 1.5 mol of lithium aluminum hydride afforded in 64% yield 2,2-dimethylcyclopentanol[7] (**17**) which furnished on Jones oxidation the desired ketone **20**, bp 139°C, in 70% yield. Alcohol **17** was also prepared by a modified Eschenmoser's method[7] through **8**→**9**→**15**→**16**. Attempted transformation of 2-methyl-2-tosyloxymethylcyclopentanone ethylene ketal (**14**) to **20** with lithium aluminum hydride was unsuccessful, *O*-tosyl bond being cleaved to regenerate **8**. The steric hindrance probably changed the vulnerable point of the tosyloxy group.[8] Bromination of **20** with bromine followed by dehydrobromination with lithium chloride in dimethylformamide gave, in 60% yield (two steps), 5,5-dimethyl-2-cyclopentenone (**22**), bp 150—154°C, which was again brominated with *N*-bromosuccinimide. Subsequent treatment with silver acetate in acetic acid gave 5,5-dimethyl-4-acetoxy-2-cyclopentenone (**2**), bp 92—94°C/10 mmHg, as an oil in 43% yield (from **22**).

The above method for the preparation of acetoxycyclopentenone **2** is advantageous in that diacetoxycyclopentenone **3**, the

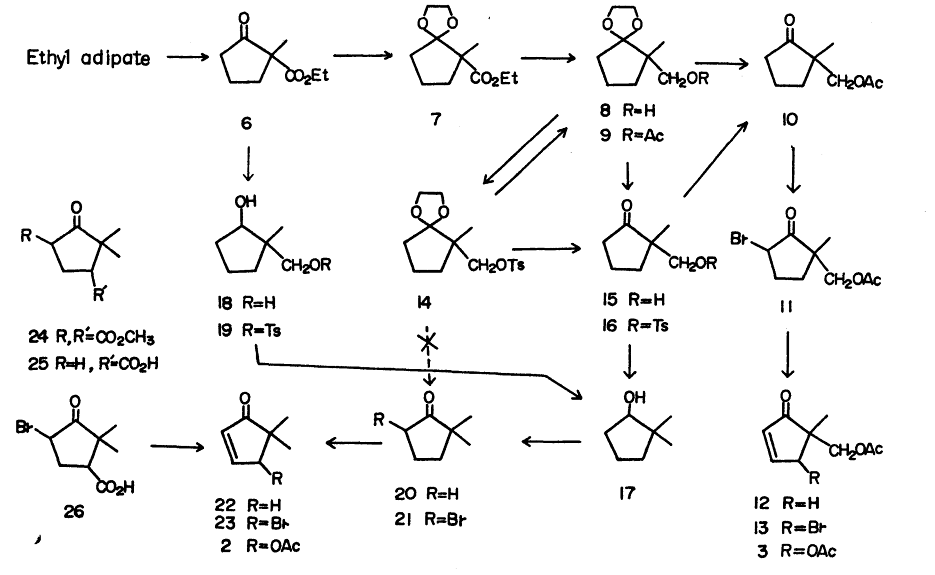


Fig. 1.

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2) T. C. McMorris and A. Anchel, *ibid.*, **87**, 1594 (1965).

3) T. Matsumoto, H. Shirahama, A. Ichihara, Y. Fukuoka, T. Takahashi, Y. Mori, and M. Watanabe, *Tetrahedron*, **21**, 2671 (1965); T. Matsumoto, Y. Fukuoka, A. Ichihara, Y. Mori, H. Shirahama, Y. Takahashi, and M. Watanabe, This Bulletin, **37**, 1716, (1964); K. Nakanishi, M. Ohashi, M. Tada, and Y. Yamada, *Tetrahedron*, **21**, 1231 (1965).

4) T. Matsumoto, H. Shirahama, A. Ichihara, H. Shin, S. Kagawa, F. Sakan, and K. Miyano, *Tetrahedron Lett.*, **1971**, 2049.

5) The synthesis of **2** was partly presented in a preliminary report. T. Matsumoto, H. Shirahama, A. Ichihara, H. Shin, S. Kagawa, N. Ito, T. Hisamitsu, T. Kamada, F. Sakan, K. Saito, S. Nishida, and S. Matsumoto, *Tetrahedron Lett.*, **1968**, 1925.

6) H. O. House and B. M. Trost, *J. Org. Chem.*, **30**, 2502 (1965); F. G. Gault, J. E. Germain, and Jean-Marie Conia, *Bull. Soc. Chim. Fr.*, **1957**, 1064.

7) A. Eschenmoser and A. Frey, *Helv. Chim. Acta*, **35**, 1660 (1952).

8) H. Schmid and P. Karrer, *ibid.*, **32**, 1371 (1949).

intermediate for illudin S, can be prepared through common compounds. However, for the synthesis of illudin M, a simpler method for **2** was desirable. Readily accessible 5,5-dimethyl-2,4-dicarbethoxycyclopentanone **24**[9] was converted by boiling with dilute perchloride acid into 5,5-dimethyl-4-carboxycyclopentanone (**25**), mp 107°C, in 60% yield. Bromination of **25** with bromine afforded, in quantitative yield, 5,5-dimethyl-4-carboxy-2-bromocyclopentanone (**26**), mp 152—154°C, which was converted into **22** by treatment with lithium chloride in dimethylformamide in 43% yield with simultaneous decarboxylation.

The second five membered intermediate 5-methyl-*t*-5-acetoxymethyl-*r*-4-acetoxy-2-cyclopentenone (**3a**) was prepared in a similar way through bromination-dehydrobromination from 2-methyl-2-hydroxymethylcyclopentanone (**10**), bp 83.5°C/4 mmHg, which was obtained through the steps **6**→**7**→**8**[6]→**9**→**10** or **8**→**15**[6]→**10**. Cyclopentenone **12** was then converted into diacetoxycyclopentenone **3**, bp 134—160°C/20 mmHg, (70%), by the same method as employed in the preparation of acetoxycyclopentenone **2** from **22**. Compound **3** thus obtained was a mixture of two configurational isomers with respect to 4-acetoxy and 5-acetoxymethyl groups. The isomers were separated by preparative gas chromatography (3 m DEGS column) to give **3a** and **3b**. Isomer **3b**, which has a shorter retention time, exhibited in its NMR spectrum AB quartet peaks due to the acetoxymethyl group attached to a chiral center at τ 6.23 and 5.77 (J= 12 Hz). The other isomer **3a** showed a smaller difference of chemical shift between the diastereotopic methylene protons (ABq, τ 5.99 and 5.89, J=11 Hz). The larger magnitude of nonequivalence suggested that **3b** might have *cis* arrangement of the acetoxymethyl group to the acetoxy group on cyclopentanone, since in **12** the corresponding methylene protons showed a singlet at τ 6.07.

For the confirmation of stereochemistry, **3b** was converted into diol **18** to observe intramolecular H-bond between the two hydroxyl groups. Treatment of **3b** with sodium borohydride gave a single saturated alcohol **27**[10] which was oxidized with Jones reagent to give rise to 2-methyl-2-acetoxymethyl-3-acetoxycyclopentanone (**28**). Reduction of **3b** with sodium borohydride proceeded stereospecifically[11] and the the attack of the reagent took place from the less hindered site to give an alcohol **27**. The OAc/CH$_2$-OAc *cis* structure of alcohol **27** was deduced because the monoacetate of **27** exhibited in the NMR spectrum a sharp singlet due to methylene protons of acetoxylmethyl group suggesting the presence of the plane of symmetry in the triacetate (monoacetate of **27**). Pentanone **28** was converted into thioketal **29** which was desulfurized with Raney nickel to give diacetate **30**. On the other hand, an isomeric mixture of diol **18** obtained from **6** by reduction with lithium aluminum hydride was separated by chromatography to yield two stereoisomeric diols with the weight ratio of *ca.* 1 : 4. On observation on the IR spectrum of each isomer in highly diluted solution, the major diol **18a** exhibited absorption bands due to hydroxyl group at 3648 and 3590 cm^{-1} ($\Delta\nu$OH=58 cm^{-1}) and the minor one **18b** at 3645 and 3570 cm^{-1} ($\Delta\nu$OH=75 cm^{-1}). Thus the latter should have *cis* configuration with respect to hydroxyl and hydroxymethyl groups. Comparison of the diacetylated *trans* and *cis* diols (**18a** and **b**) with the diol diacetate **30** derived from isomer **3b** revealed that **3b** actually had *cis* configuration.

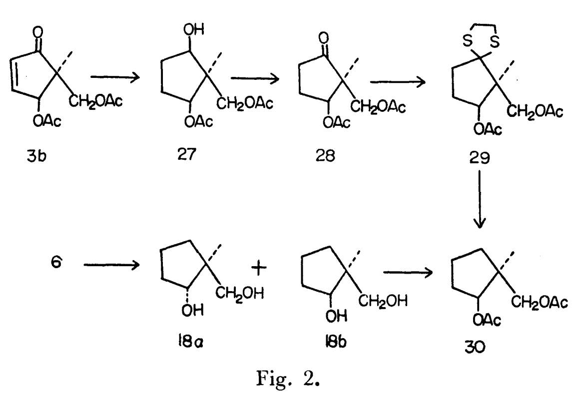

Fig. 2.

Experimental

2-Methyl-2-hydroxymethylcyclopentanol (*18*). To an ice cooled solution of 32 g of lithium aluminum hydride in 1.5 *l* of dry ether was added dropwise a solution of 127 g of 2-methyl-2-carbethoxycyclopentanone (**6**) in 100 m*l* of dry ether over a period of 2 hr with mechanical stirring. The resulting mixture was allowed to stand at room temperature and then refluxed for 5 hr. After the reaction was completed water was added dropwise to the ice cooled reaction mixture to decompose the excess of the reagent. The ethereal solution was washed with saturated salt solution, dried over anhydrous sodium sulfate and distilled to give 78 g (80%) of diol **18**: bp 148—153°C/4 mm; IR (neat) 3330, 1030 cm^{-1}.

Found: C, 64.70; H, 10.70%. Calcd for $C_7H_{14}O_2$: C, 64.58; H, 10.84%.

Chromatographic separation of *cis* and *trans* diols was achieved on a column of silica gel employing a mixture of benzene and ethyl acetate (3 : 2) as a solvent. Crude diol (450 mg) gave 121 mg of *trans* isomer **18a** (later eluted): IR (CCl_4, 0.005 M) 3648, 3590 cm^{-1}; NMR τ ($CDCl_3$) 9.00 (3H, s, CH_3), 6.71 (2H, s, OH), 6.52 (2H, s, CH_2O), 6.10 (1H, m, CHO) and 34 mg of *cis* isomer **18b** (earlier eluted): IR (CCl_4, 0.005 M) 3645, 3570 cm^{-1}; NMR τ ($CDCl_3$) 9.00 (3H, s, CH_3), 6.93 (2H, s, OH), 6.40 and 6.27 (2H, ABq, J=11 Hz, CH_2O), 6.04 (1H, m, CHO).

2-Methyl-2-tosyloxymethylcyclopentanol (*19*). To a solution of 260 g of diol **18** in 1 *l* of dry benzene were added 208 g of pyridine and 500 g of *p*-toluenesulfonyl chloride. After standing overnight at room temperature pyridine hydrochloride formed was removed by filtration. The benzene solution was washed six times with 6 N hydrochloric acid under ice cooling, three times with aqueous sodium carbonate solution, once with saturated salt solution and then dried over anhydrous sodium sulfate. Removal of the solvent left 567 g (quantitative) of tosylate **19**. An analytical sam-

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[9] G. Stork and F. H. Clarke, Jr., *J. Amer. Chem. Soc.*, **83**, 3114 (1961).

[10] In general, the reduction of 2-cyclopentenone with complex hydrides gives saturated alcohol. See H. C. Brown and H. W. Hess, *J. Org. Chem.*, **34**, 2206 (1969).

ple was prepared by chromatography on silica gel: IR (neat) 3500, 3400, 1600, 1360, 1180 cm^{-1}.

Found: C, 58.85; H, 6.91%. Calcd for $C_{14}H_{20}O_4S$: C, 59.13; H, 7.09%.

*2,2-Dimethylcyclopentanol (**17**). A) By Reduction of **19**:* To an ice cooled solution of 57 g of lithium aluminum hydride in 1.8 *l* of dry ether was added dropwise 284 g of of tosylate **19** over a period of 2 hr with mechanical stirring. The resulting solution was allowed to stand at room temperature and then refluxed for 19 hr. After the reaction was completed the excess reagent was decomposed by water under ice cooling. The ethereal solution was washed, dried and distilled to afford 73 g (64%) of dimethylcyclopentanol **17**: bp 59.5—62°C/10 mmHg (lit,[7] 100°C/110 mmHg); IR (neat) 3370, 1380, 1360 cm^{-1}.

*B) By Reduction of **16**:* Tosylate **16** (19.2 g) was reduced by lithium aluminum hydride in dry ether in the same manner as above to yield 5.2 g (71%) of the alcohol **17**.

*2,2-Dimethylcyclopentanone (**20**):* To a solution of 57 g of cyclopentanol **17** in 130 m*l* of acetone was added dropwise the Jones reagent (prepared from 44 g of chromic anhydride in 130 m*l* of water and 38.2 m*l* of concentrated sulfuric acid) over a period of 2 hr with stirring by a mechanical stirrer under ice cooling. The resulting mixture was allowed to be warmed up to room temperature for 1 hr. The reaction mixture was then poured into 1 *l* of water and extracted with ether and the ethereal extract was washed with sodium carbonate solution and saturated salt solution, dried and distilled. 39 g (70%) of fragrant oil **20**, was obtained: bp 139°C; IR (neat) 1740, 1410, 1380, 1360 cm^{-1}.

Found: C, 74.98; H, 10.66%. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78%.

*5,5-Dimethyl-2-cyclopentenone (**22**). A) Preparation from Dimethylcyclopentanone **20**.* To a solution of 11.2 g of **20** in 250 m*l* of chloroform was added dropwise a solution of 16 g of bromine in 100 m*l* of the same solvent with stirring over a period of 5 hr. The reaction mixture was washed with aqueous sodium bicarbonate, then with saturated salt solution and dried. After removal of the solvent the residual bromoketone was dissolved in 130 m*l* of dimethylformamide and 11.4 g of lithium chloride was added. The solution was heated to reflux for 4 hr. The reaction mixture was poured into a large quantity of water and extracted several times with ether. The combined extracts were washed with sodium bicarbonate solution and saturated salt solution, dried and distilled to give 6.6 g (60%) of dimethylcyclopentanone **22**: bp 150—154°C; IR (neat) 3040, 1710, 1590, 1380, 1360, 810 cm^{-1}; NMR τ (CCl_4) 8.97 (6H, s, $2\times CH_3$) 7.53 (2H, t, $J=2$ Hz, CH_2), 4.02 (1H, d ($J=6$ Hz) of t ($J=2$ Hz) =CHCO), 2.53 (1H, d ($J=6$ Hz) of t ($J=3$ Hz), =CH–). Dinitrophenylhydrazone: mp 172—173°C.

Found: C, 53.77; H, 5.10; N, 19.49. Calcd for $C_{13}H_{14}N_4O_4$: C, 53.78; H, 4.86; N, 19.30%.

*B) Preparation from Bromoacid **26**:* A solution of 30 g of bromoacid **26** and 32 g of lithium chloride in 300 m*l* of dimethylformamide was refluxed for 1.5 hr. After cooling the reaction mixture was poured on 1 *l* of ice water and extracted three times with ether. The combined extracts were washed with saturated salt solution and dried. The solvent was removed and the residual oil was distilled, 6.1 g (43%).

*5,5-Dimethyl-4-acetoxy-2-cyclopentenone (**2**).* A solution of 2.2 g of cyclopentanone **22**, 5 g of *N*-bromosuccinimide and 80 mg of benzoyl peroxide in 70 m*l* of CCl_4 was heated to reflux for 2 hr. After reaction was completed the precipitated succinimide was removed by filtration. The filtrate was washed with sodium hydrosulfite, sodium bicarbonate and saturated salt solution, dried and evaporated to leave bromoketone **23** as an oil which was used in the next step without further purification. A sample of **23** was chromatographed (silica gel, benzene) for measuring spectra: IR (neat) 1720, 1585, 835 cm^{-1}; NMR τ (CCl_4) 8.80 (3H, s, CH_3), 8.76 (3H, s, CH_3), 5.02 (1H, d ($J=3$ Hz) of d ($J=1.5$ Hz), BrCH–), 3.78 (1H, d ($J=6$ Hz) of d ($J=1.5$ Hz), =CHCO), 2.42 (1H, d ($J=6$ Hz), of d ($J=3$ Hz), =CH–).

To a solution of crude bromoketone **23** (14 g) from four batches in 80 m*l* of acetic acid which was dried over phosphorus pentoxide, 18.5 g of silver acetate was added. The resulting mixture was heated at 110—115°C for 14 hr with stirring to precipitate silver bromide. The reaction mixture was then diluted with chloroform and filtered. The filtrate was neutralized with aqueous sodium carbonate solution, washed with saturated salt solution and dried. After removal of the solvent the residue was distilled to give 5.7 g of acetoxycyclopentanone **2** (42.5% from **22**): bp 92—94°C/10 mmHg; IR (neat) 3050, 1740, 1725, 1600, 1235 cm^{-1}; NMR τ (CCl_4) 9.05 (3H, s, CH_3), 8.83 (3H, s, CH_3), 7.93 (3H, s, AcO), 4.52 (1H, d ($J=3$ Hz) of d ($J=1$ Hz), AcOCH), 3.78 (1H, d ($J=6$ Hz) of d ($J=1$ Hz), =CHCO), 2.65 (1H, d ($J=6$ Hz) of d ($J=3$ Hz) =CH–).

Found: C, 64.51; H, 7.16%. Calcd for $C_9H_{12}O_3$: 64.27, H, 7.19%.

*5,5-Dimethyl-2,4-dicarbomethoxycyclopentanone (**24**).* This compound was prepared according to the method of Stork and Clarke[9] Two hundred and twenty grams of diester were obtained from 384 g of ethyl 2,3-dicyano-3-methylbutyrate (42% over 4 steps): bp 170—176°C/20 mmHg.

*5,5-Dimethyl-4-carboxycyclopentanone (**25**):* A mixture of 220 g of diester 24 and 1260 m*l* of 20% perchloric acid was refluxed for 7 hr until a homogeneous solution was obtained. The resulting solution was extracted with chloroform. The extract was washed with saturated salt solution and dried over anhydrous sodium sulfate and the solvent was distilled off. The crystalline residue was washed with hexane, 90 g (60%). A sample of product was recrystallized for analysis: mp 107°C; IR (Nujol) 1740, 1710 cm^{-1}; NMR ($CDCl_3$) 8.97 (3H, s, CH_3), 8.75 (3H, s, CH_3), 6.9—8.6 (5H, m, CH_2CH_2CH), -0.13 (1H, bs, CO_2H).

Found: C, 61.69; H, 7.88%. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.75%.

*5,5-Dimethyl-4-carboxy-2-bromocyclopentanone (**26**).* The keto acid **25** (20 g) was dissolved in 200 m*l* of chloroform and 206 g of bromine was added with stirring under ice-cooling over a period of 1 hr. The chloroform solution was washed with water and dried over anhydrous sodium sulfate. Removal of the solvent left crude crystalline bromide (30 g). A small sample was recrystallized for analysis; mp 152—154°C; IR (Nujol) 1740, 1720 cm^{-1}.

Found: C, 40.65; H, 4.65%. Calcd for $C_8H_{11}O_3Br$: C, 40.53; H, 4.68%.

*2-Methyl-2-tosyloxymethylcyclopentanone Ethylene Ketal (**14**).* A solution of 29.2 g of 2-methyl-2-hydroxymethylcyclopentanone ethylene ketal (**8**)[7], 32.9 g of tosyl chloride and 30 g of pyridine in 180 m*l* of benzene was allowed to stand overnight in a refrigerator. The reaction mixture was poured into water and extracted with benzene. The extract was washed with aqueous sodium bicarbonate and saturated salt solution and dried. Evaporation of the solvent left 55 g (quantitative) of crude tosylate **14**. A sample of crude tosylate was recrystallized from carbon tetrachloride; mp 80°C, IR (Nujol) 1360, 1180 cm^{-1}.

Found: C, 59.03; H, 6.70%. Calcd for $C_{16}H_{22}O_5S$: C, 58.88; H, 6.80%.

*Reduction of Tosylate **14** with Lithium Aluminum Hydride.* To an ice-cooled solution of 750 mg of lithium aluminum hydride in 20 m*l* of dry ether was added dropwise with stirring a solution of 2.5 g of the tosylate **14** in 16 m*l* of dry ether. After refluxing for 7 hr the original tosylate was recovered. The recovered tosylate was dissolved in 25 m*l* of tetrahydrofuran and refluxed with 750 mg of lithium aluminum hydride for 24 hr. The product obtained was the original alcohol **8** instead of dimethylcyclopentanone ethylene ketal.

*2-Methyl-2-tosyloxymethylcyclopentanone (**16**). A) By Tosylation of the Ketoalcohol **15**:* The keto alcohol (141 g) was quantitatively converted by treatment with 209 g of tosylchloride and 87 g of pyridine in 500 m*l* of benzene to 310 g of tosylate **16**. A sample of the tosylate was recrystallized from carbon tetrachloride, mp 65—67°C; IR (Nujol) 1750, 1600, 1350, 1160 cm^{-1}.

*B) By Deketalization of Tosylate **14**:* A solution of 2.5 g of ketal **14** and a pinch of *p*-toluenesulfonic acid in 100 m*l* of acetone was refluxed for 3 hr. The reaction mixture was concentrated under reduced pressure to remove most of acetone, and the residue was taken with ether. The ethereal phase was then washed with aqueous sodium bicarbonate solution and saturated salt solution and dried. Evaporation of ether left 1.6 g (74%) of tosylate **16**.

*2-Methyl-2-acetoxymethylcyclopentanone (**10**). A)* To a solution of 48 g of 2-methyl-2-hydroxymethylcyclopentanone ethylene ketal (**8**)[7] and 63 mg of *p*-toluenesulfonic acid in 480 m*l* of dry acetone was refluxed for 4.5 hr. After the reaction mixture was concentrated under reduced pressure at room temperature to remove most of acetone, benzene was added to the residue and the solution was washed with aqueous sodium bicarbonate solution and saturated salt solution and dried. The solvent was evaporated and the residue was distilled to give 26 g (73%) of ketone **15**, bp 93—98°C/6 mmHg, (lit,[6] 103—108°C/12 mmHg). Treatment of 10 g of the above alcohol with acetic anhydride and pyridine by the usual method gave 11.7 g (89%) of acetate **10**: bp 91—93°C/3 mmHg; IR (Neat) 1760, 1230 cm^{-1}.

Found: C, 63.32; H, 8.11%. Calcd for $C_9H_{14}O_3$; C, 63.53; H, 8.23%.

B): Ketal **8** (101 g) was acetylated by the usual method and treated with a pinch of *p*-toluenesulfonic acid in acetone to yield 80.2 g (80%) of acetoxy ketone **10**: bp 125—128°C/25 mmHg.

*5-Methyl-5-acetoxymethyl-2-bromocyclopentanone (**11**).* To a solution of 11 g of the acetoxy ketone **10** in 72 m*l* of chloroform was added dropwise a solution of 3.35 m*l* of bromine in 48 m*l* of the same solvent with stirring. The resulting mixture was washed with sodium bicarbonate solution and saturated salt solution and dried. The solvent was evaporated and the residue was distilled at 110—118°C/7 mmHg to give 145 g (90%) of bromoketone **11**. Formation of two configurational isomers might be expected. However, separation and examination of the ratio were not attempted. A sample of the bromo compound was redistilled and analyzed: IR (neat) 1750, 1735 cm^{-1}.

Found: C, 43.16; H, 5.27%. Calcd for $C_9H_{13}O_3Br$: C, 43.33; H, 5.22%.

*5-Methyl-5-acetoxymethyl-2-cyclopentenone (**12**).* A solution of 13 g of bromo compound **11** and 8.8 g of lithium chloride in 350 m*l* of dimethylformamide was heated at 150—160°C for 4 hr. The reaction mixture was then poured into ice-water and extracted several times with benzene. The combined extracts were washed successively with sodium bicarbonate and saturated salt solution, dried and distilled to yield 5.9 g (66%) of cyclopentenone; bp 94—100°C/4 mmHg, IR (neat) 1745, 1710, 1590, 1240 cm^{-1}; NMR τ (CCl_4) 8.91 (3H, s, CH_3), 8.07 (3H, s CH_3), 7.62 and 7.30 (2H, ABq, (*J*=19 Hz, each peak is split into *J*=2.5 Hz), CH_2) 6.07 (2H, s, CH_2OAc), 3.93 (1H, d (*J*=6 Hz) of t (*J*=2 Hz), =CHCO), 2.37 (1H, d (*J*=6 Hz) of t (*J*=2.5 Hz), =CH–).

Found: C, 64.23; H, 7.33%. Calcd for $C_9H_{12}O_3$: C, 64.28; H, 7.14%.

*5-Methyl-*t*-5-acetoxymethyl-*r*-4-acetoxy-2-cyclopentenone (**3**).* The compound (44.5 g 70%) was prepared from 52.2 g of cyclopentenone **12** by the same treatment as in the conversion of **22** into **2**. Bp 134—160°C/20 mmHg. A sample of ketone **3** was subjected to preparative vpc. A column of DEGS (3 m) was used at 170°C employing helium as a carrier gas (100 m*l*/min). The *cis* isomer **3b** appeared at 52 min (retention time) and the *trans* isomer **3a** at 62 min with a weight ratio of *ca.* 1 : 2.5. *cis*-5-Acetoxymethyl-4-acetoxy isomer (**3b**): IR (neat) 1745, 1725, 1595 and 1235 cm^{-1}; NMR τ (CCl_4) 8.80 (3H, s, CH_3), 8.05 (3H, s, AcO), 7.95 (3H, s, AcO), 6.23 and 5.77 (2H, ABq, *J*=2 Hz), HCOAc), 3.70 (1H, d (*J*=2 Hz) of d (*J*=6 Hz), =CHCO), 2.57 (1H, d (*J*=6 Hz) of d (*J*=3 Hz), -CH=). *trans*-5-Acetoxymethyl-4-acetoxy isomer (**3a**): IR (neat) 1745, 1725, 1595 and 1235 cm^{-1}; NMR τ (CCl_4) 9.05 (3H, s, CH_3), 8.05 (3H, s, AcO), 7.89 (3H, s, AcO), 5.99 and 5.89 (2H, ABq, *J*=11 Hz), 4.22 (1H, d (*J*=3 Hz) of d (*J*=2 Hz), HCOAc), 3.73 (1H, d (*J*=6 Hz) of d (*J*=3 Hz), –CH=), 2.56 (1H, d (*J*=6 Hz) of d (*J*=3 Hz), –CH=).

*2-Methyl-*c*-2-acetoxymethyl-*c*-3-acetoxy-*r*-1-cyclopentanol (**27**).* A sample (940 mg) of cyclopentenone **3b** was dissolved in 25 m*l* of ethanol. The solution was cooled in an ice bath and 315 mg of sodium borohydride was added with stirring. After stirring for 40 min, a small amount of acetic acid was added and the reaction mixture was poured into water and extracted with ethyl acetate. The extract was washed with saturated salt solution and dried. Removal of the solvent left 904 mg of reduced product: IR (neat) 3450, 1740, 1725, 1040 cm^{-1}.

Found: C, 57.18; H, 7.86%. Calcd for $C_{11}H_{18}O_5$: C, 57.38; H, 7.88%.

Treatment of 60 mg of alcohol with acetic anhydride and pyridine by the usual method gave 49 mg of pure triacetate; IR (neat) 1745, 1238, 1038 cm^{-1}; NMR τ (CCl_4) 8.90 (3H, s, CH_3), 8.00 (9H, s, 3×AcO), 5.99 (2H, s, CH_2OAc), 5.10 (2H, m, 2×HCOAc).

*2-Methyl-*r*-2-acetoxymethyl-*c*-3-acetoxycylcopentanone (**28**).* To a solution of 904 mg of alcohol derived from **3a** in 45 m*l* of acetone 0.7 m*l* of Jones reagent was added dropwise over a period of 80 min with ice cooling. After standing at room temperature for 20 min a small amount of ethanol was added and the precipitate was filtered off. The solvent was evaporated and the residue was extracted with ether. The extract was washed with saturated salt solution, sodium bicarbonate solution and then saturated salt solution and dried. Evaporation of the solvent left ketone which was chromatographed on silica gel to give 515 mg of ketone **28**: IR (neat) 1750, 1240, 1050, cm^{-1}; NMR τ(CCl_4) 8.88 (3H, s, CH_3), 8.03 (3H, s, AcO), 8.00 (3H, s, AcO), 5.94 (2H, d (appearance) *J*=2.4 Hz CH_2OAc), 4.87 (1H, m, HCOAc); *m*/*e*; 228 (M^+).

*2-Methyl-*r*-2-acetoxymethyl-*c*-3-acetoxycyclopentanone Ethylene Thioketal (**29**).* To a solution of 200 mg of ketone **28** in 2.7 m*l* of acetic acid, 840 mg of ethanedithiol and then 1.1 m*l* of boron trifluoride etherate were added and stirrred. The reaction mixture was allowed to stand at room temperature for 24 hr and poured into almost the same quantity of water and extracted with ether. The extract was washed with sodium carbonate solution and with saturated salt solution and dried. After evaporation of the solvent, the residual oil was purified by chromatography to give 134 mg of thioketal; IR (neat) 1750 1250, 1045 cm^{-1}; NMR τ (CCl_4) 8.79 (3H, s, CH_3), 8.02, (3H, s, AcO), 7.91 (3H, s, AcO), 6.79 (4H, s, SCH_2CH_2S), 5.45 and 6.14 (4H, ABq, J=11 Hz CH_2OAc), 5.10 (1H, m, HCOAc).

r-*1-Acetoxy-2-methyl-*c*-2-acetoxymethylcyclopentane* (***30***). To solution of 130 mg of thioketal **29** in 40 m*l* of ethanol, 2.5 g of Raney nickel W-2 was added. The reaction mixture was stirred at 85°C to make the solvent reflux for 24 hr. The Raney nickel used was removed through a short column of aluminum oxide and the solvent was evaporated. The residue was dissolved in ether and filtered to remove solid mass and washed with saturated salt solution and dried. After removal of the solvent the residual oil was chromatographed to yield 91 mg of diacetate **30**; IR (neat) 1750, 1245, 1050 cm^{-1}.

Found: C, 61.86; H, 8.18%. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47%.