Acta Chemica Scandinavica B 30 (1976) 613—618

The Preparation of 4-Hydroxy-5,6-dihydro-2-pyrones and Their Conversion to Kawa-lactones as well as to Other Precursors of Naturally Occurring 2-Pyrones

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The dianion of ethyl acetoacetate was reacted with a series of aldehydes to give aldol-type products, which after hydrolysis and acidification readily lactonized to 4-hydroxy-5,6-dihydro-2-pyrones. Some of the lactones were methylated to give the Kawa-lactones kawain, marindinin, methysticin, and 5,6-dihydroyangonin. Furthermore, synthetic precursors (and in one case possibly a biogenetic precursor) to radicinin, pestalotin, a pestalotin-related metabolite, and nectriapyrone were prepared.

2-Pyrones constitute an important sub-group of the acetogenins, examples being the Kawa-lactones[1] [*e.g.* kawain (*2a*) and methysticin (*2e*)] and the gibberellin synergist pestalotin (*5*).[2,3]

The Kawa-lactones have earlier been prepared according to the following procedures: Reformatsky-type reactions from 4-bromo-3-methoxycrotonic esters,[4] conjugate addition of methanol to 5-hydroxy-2-alkynoic esters,[5] or by $TiCl_4$-promoted addition of diketene to aldehydes.[6] Recently Seebach and Meyer [7] have published an elegant synthesis of pestalotin (*5*) by acetoacetate dianion addition to an aldehyde, and Carlson and Oyler [8] have reported on the synthesis of the same compound using the propiolic acid dianion as an acyl equivalent.

We here report on the synthesis of some naturally occurring 5,6-dihydro-2-pyrones and their synthetic precursors by modifying the method of Seebach and Meyer,[7] by which the dianion of ethyl acetoacetate reacts with an aldehyde to give an aldol-type product, which upon hydrolysis and acidification readily lactonizes to a 4-hydroxy-5,6-dihydro-2-pyrone (*1*).*

We have found it to be very important that the hydrolysis of the aldol product first formed is carried out at low temperature (0 °C) in order to avoid decarboxylation and retroaldol processes. Following the original procedure,[7] the formation of by-products made isolation difficult. This is shown by the reaction of 4-methoxycinnamaldehyde with ethyl acetoacetate giving a mixture of about equal amounts of the expected dihydropyrone and of 6-(4-methoxyphenyl)-3,5-hexadien-2-one (NMR evidence), only the latter compound being readily isolated. Ether extraction of the alkaline hydrolysate before acidification greatly facilitates the work-up. Taking these precautions, we have prepared compounds *1a*–*1i* and the 7,8-dihydro derivative of *1a*, mostly in good yields, the purity of the crude products usually being good enough for preparative purposes. The NMR-data recorded in Table 1 give evidence for correct structure assignments and reveal that the synthesized 4-hydroxy-5,6-dihydro-2-pyrones exist fully enolized when dissolved in DMSO.

O-Methylation of the appropriate 4-hydroxy-5,6-dihydro-2-pyrones to the naturally occurring compounds *2a*, *2d*, *2e*, and marindinin (7,8-dihydro derivative of *2a*) gave some difficulties, when the phenyl substituent of *1* carried alkoxy groups. While *1a* was smoothly methylated under standard conditions (di-

* *Added in proof. Cf.* also D. Seebach and H. Meyer *Ger. Offenlegungsschrift* P 2400429.3 of 17.7.75.

Table 1. ^{1}H NMR shifts (in ppm downfield from internal TMS) and coupling constants (in Hz) of 4-hydroxy-5,6-dihydro-2-pyrones. Solvent: DMSO-d_6. Observed multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. The assignments are made in accordance with Achenbach and Regel.[18]

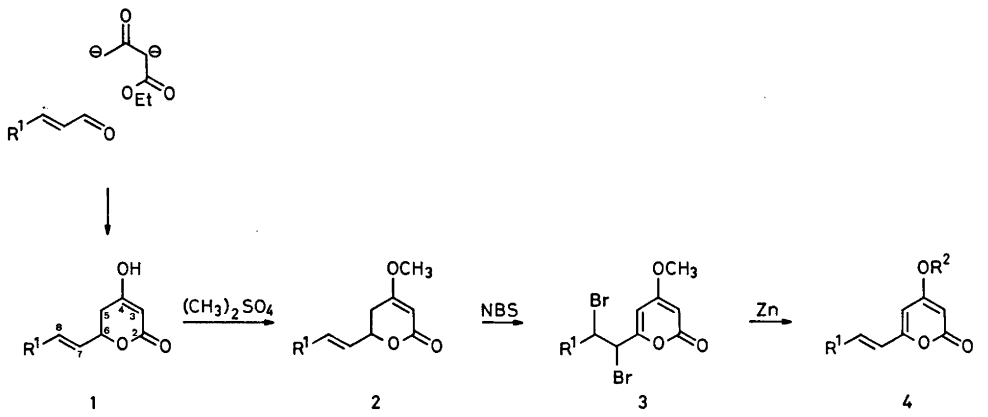
Compound	3-H [a]	5-H	5-H [b]	6-H	7-H [a,c,d]	8-H [c]	R
1a	5.00 s	2.54 s	2.66 d	4.80–5.20 m	6.25 q	6.70 d	7.10–7.50 (aromatic H)
1b	5.08 s	2.56 s	2.68 d	4.87–5.35 m	6.38 q	7.05 d	6.75–7.85 (aromatic H) 3.86 s (OCH_3)
1c	5.05 s	2.55 s	2.66 d	4.90–5.35 m	6.37 q	6.75 q	6.70–7.50 (aromatic H) 3.79 s (OCH_3)
1d	4.96 s	2.50 s	2.63 d	4.65–5.10 m	6.16 q	6.65 q	6.80–7.50 (aromatic H) 3.72 s (OCH_3)
1e	4.97 s	2.50 s	2.62 d	4.80–5.30 m	6.15 q	6.60 d	6.80–7.20 (aromatic H) 5.98 s (OCH_2O)
1f	5.03 s	2.55 s	2.68 d	4.80–5.30 m	6.35 q	covered by aromatic H	6.80–7.30 (aromatic H) 3.72 s (OCH_3) 3.82 s (OCH_3)
1g	5.10 s	2.54 s	2.68 d	4.80–5.25 m	6.27 q	6.67 d	6.40–7.25 (aromatic H) 3.78 s (OCH_3) 3.80 s (OCH_3)
7,8-dihydro derivative of *1a*	5.00 s	2.36 s	*ca.* 2.5	4.5–5.9 m	1.70–2.18 m	2.34–2.92 m	7.25 (aromatic H)
1h	4.85 s	2.45 s	2.58 d	4.70–5.10 m	5.55 q	5.75 m	1.75 d (*J* 5)
1i	4.92 s	2.38 s	2.53 d	4.50–5.00 m	5.48 q	5.86 m	0.87 t (*J* 6.5) 1.30 m (*J* 6.5) 2.00 q (*J* 6.5)
9	1.67 s	2.1–3.1 complex		4.69 q [e]	1.67 s	5.61 q (*J* 6)	1.60 (C-9 CH_3, only one component of d visible)

[a] For compound *9* the value indicates the shift of the methyl group at the given position. [b] $J_{5,6}$ is in the range of 1–2 Hz. [c] $J_{7,8}$ is for all 5,8-unsaturated compounds except for *9* in the range of 15–16 Hz. [d] $J_{6,7}$ is for all 7,8-unsaturated compounds except for *9* in the range of 4–6 Hz. [e] $J_{5ax,6ax}$ = 12 Hz, $J_{5eq,6ax}$ = 5 Hz.

methyl sulfate and potassium carbonate in refluxing acetone) to give kawain (*2a*) (55 % over-all yield from cinnamaldehyde), there was extensive decomposition of the other compounds. When the reaction was performed at room temperature according to Isawa and Mukaiyama,[6] marindinin (7,8-dihydro derivative of *2a*) was obtained in good yield from the corresponding 4-hydroxy-5,6-dihydro-2-pyrone, but *1d* still gave extensive decomposition. Treatment of compounds *1d* and *1e* with diazomethane afforded 5,6-dihydroyangonin (*2d*, 14 % yield) and methysticin (*2e*, 38 % yield), respectively.

The purpose of synthesizing compounds *1b*, *1c*, *1f*, and *1g* was to investigate a possible connection between the substitution pattern of alkoxy groups on the aromatic nucleus and the yield of methylated product. Methylation of the just-mentioned 4-hydroxy derivatives resulted in extensive decomposition of *1f* and *1g*, whereas it was possible to isolate *2b* and *2c* in moderate yields.

The acetoacetate dianion synthesis was also applied to the synthesis of 4-hydroxy-6-(1-propenyl)-2-pyrone (*4b*) a synthetic [9] and possibly biogenetic [10] precursor of radicinin. The two syntheses of *4b* published proceed *via* demethylation of *4a* and involve several steps from either the difficultly accessible tetraacetic acid lactone [9] or from triacetic acid lactone.[11] 4-Hydroxy-6-(1-propenyl)-5,6-dihydro-2-pyrone (*1h*) was prepared in 75 % yield from crotonaldehyde and methylated with dimethyl sulfate and potassium carbonate in refluxing acetone to give *2h* in 82 % yield. Allylic bromination of the methylated product was expected to give either a 5-bromo or a 6-bromo derivative if not the fully unsaturated pyrone derivative. Surprisingly, the only compound which could be isolated was the dibromo derivative (*3a*). The yield isolated was 36 or



a: R^1 = phenyl
b: R^1 = 2-methoxyphenyl
c: R^1 = 3-methoxyphenyl
d: R^1 = 4-methoxyphenyl
e: R^1 = 3,4-methylenedioxyphenyl
f: R^1 = 2,3-dimethoxyphenyl
g: R^1 = 3,4-dimethoxyphenyl
h: R^1 = methyl
i: R^1 = propyl

a: R^1 = methyl

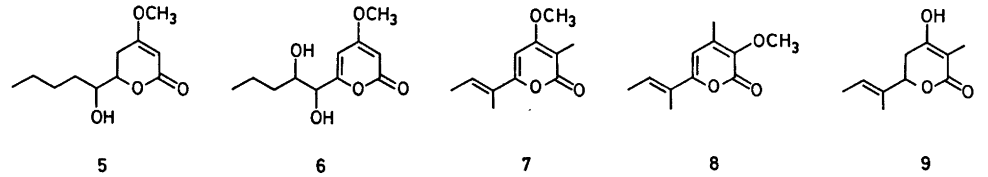
a: R^1 = methyl, R^2 = methyl
b: R^1 = methyl, R^2 = hydrogen

42 %, when one equivalent or two equivalents of *N*-bromosuccinimide, respectively, were used. Dehalogenation with zinc of the dibromo derivative gave 4-methoxy-6-(1-propenyl)-2-pyrone (*4a*) in 93 % yield. Even though the yield in synthesizing *3a* is low, we believe that *4a*, and therefore also *4b*, can be synthesized more easily by our method than by the two above-mentioned.[9,11] Furthermore, the conversion of *2h* to *4a* can be effected without isolation of the intermediate dibromo derivative. The reaction of *2h* to give *3a* is highly unexpected and is accompanied by minor brominated products, which contain vinylic protons in the side chain (NMR evidence). Therefore, we believe that the reaction is best explained by assuming allylic bromination at the 5 as well as the 6 position of the ring followed by two allylic rearrangements giving rise to the more stable pyrone *3a*.

The 6-(1-pentenyl) derivative (*1i*) is of interest seen in the light of the recent isolation of the *Penicillium* metabolite (*6*) [12] and represents an alternative synthon for the synthesis of pestalotin (*5*). Synthetic approaches to *6* with the aim of establishing the relative configuration as well as to *5* are in progress.

Recently, an antibiotic monoterpenoid, nectriapyrone, has been isolated from *Gyrostroma missouriensis* Seeler.[13] Nectriapyrone has been assigned structure *7*, but structure *8* cannot be completely ruled out. We believe that *7* is obtainable from *9*, which is prepared by reacting tiglic aldehyde with the dianion of ethyl 2-methylacetoacetate. Work is in progress for synthesizing *7*.*

* *Added in proof.* Nectriapyrone (*7*) has now been synthesized: T. Reffstrup and P.M. Boll *Tetrahedron Lett.* (1976) 1903.



5 6 7 8 9

EXPERIMENTAL

All m.p.'s are uncorrected. ^{1}H NMR spectra were recorded on a JEOL C-60 HL spectrometer. UV spectra were recorded on a Beckman ACTA III spectrophotometer. For explanation of NMR data *cf.* Table 1. Microanalyses were performed at the Microanalytical Department of the University of Copenhagen. The progression of the methylation reactions were monitored conveniently by TLC with ether or ether/light petroleum as eluent.

General procedure for preparation of 6-substituted 4-hydroxy-5,6-dihydro-2-pyrones (1). The dianion of ethyl acetoacetate (2.6 g, 0.02 mol) is prepared in 50 ml of tetrahydrofuran with sodium hydride (0.02 mol) and butyllithium (0.02 mol) according to the method of Huckin and Weiler.[14] The aldehyde (0.01 mol) is added dropwise (solid aldehydes are dissolved in tetrahydrofuran prior to addition) to the stirred reaction mixture maintained at 0 °C. The stirring is continued for another 10 min and the mixture is then added dropwise to 300 ml of ice water. The strongly alkaline solution is stirred at room temperature for 3.5 h, after which time it is extracted with ether (3 × 75 ml). Cooling of the aqueous phase and careful acidification to pH 1 with conc. HCl under simultaneous addition of ice result normally in the precipitation of crystalline material. If the pyrone separates as oily drops, the aqueous phase is extracted with CH_2Cl_2 to give, after drying and evaporation of solvent, crystalline material.

The compounds synthesized in this manner are quite pure, and give after trituration with ether, often satisfactory elemental analyses. Comparison of NMR spectra of the isolated products and the recrystallized products confirms the statement that the products can be considered as "practical grades" and that they can be used directly for synthetic purposes.

4-Hydroxy-6-(α-trans-styryl)-5,6-dihydro-2-pyrone (1a). Reaction of cinnamaldehyde (2.64 g, 0.02 mol) gave 3.68 g (85 %) of very light yellow crystals, m.p. 109–111 °C (decomp.), which upon recrystallisation from ether/methanol afforded colourless crystals with m.p. 128–130 °C (decomp.) (lit.[5] m.p. 142–144 °C)* UV 256 nm (ε 17 500), 263 nm (ε 17 200) (lit.[5] UV 247–248 nm (ε 29 000)*. (Found: C 72.65; H 5.66. Calc. for $C_{13}H_{12}O_3$: C 72.71; H 5.59).

4-Hydroxy-6-(α-trans-2-methoxystyryl)-5,6-dihydro-2-pyrone (1b). 2-Methoxycinnamaldehyde (5.99 g, 0.044 mol) was reacted to give 7.00 g (76 %) of a light yellow powder, m.p. 109–112 °C (decomp.). On recrystallisation from ether/methanol colourless crystals of m.p. 130–132.5 °C (decomp.) were obtained (Anal. $C_{14}H_{14}O_4$: C, H, O).

* The reported data are more in agreement with those found for kawain.[1]

4-Hydroxy-6-(α-trans-3-methoxystyryl)-5,6-dihydro-2-pyrone (1c). 3-Methoxycinnamaldehyde (5.0 g, 0.034 mol) gave upon reaction 4.47 g (59 %) of a yellow powder, m.p. 106–110 °C (decomp.). Recrystallisation from ether/methanol raised the m.p. to 129–133 °C (decomp.) (Found: C 68.10; H 5.80. Calc. for $C_{14}H_{14}O_4$: C 68.28; H 5.73).

4-Hydroxy-6-(α-trans-4-methoxystyryl)-5,6-dihydro-2-pyrone (1d). 4-Methoxycinnamaldehyde (3.53 g, 0.022 mol) afforded on reaction 3.96 (74 %) of powderlike yellow crystals, m.p. 117–120 °C (decomp.), which upon recrystallisation from ether/methanol gave colourless crystals with m.p. 128–130 °C (decomp.) (Found: C 68.40; H 5.95. Calc. for $C_{14}H_{14}O_4$: C 68.28; H 5.73).

4-Hydroxy-6-(α-trans-3,4-methylenedioxystyryl)-5,6-dihydro-2-pyrone (1e). Reaction of 3,4-methylenedioxycinnamaldehyde (3.90 g, 0.022 mol) afforded 4.78 g (74 %) of a reddish powder, m.p. 119–122 °C, shrinking at 115 °C (decomp.). Recrystallisation from ether/light petroleum gave not quite colourless crystals of m.p. 128–132 °C (decomp.) (Found: C 64.45, H 4.88. Calc. for $C_{14}H_{12}O_5$: C 64.61; H 4.64).

4-Hydroxy-6-(α-trans-2,3-dimethoxystyryl)-5,6-dihydro-2-pyrone (1f). When 2,3-dimethoxycinnamaldehyde (1.26 g, 0.008 mol) was reacted 1.02 g (56 %) of yellow powder, m.p. 110–114 °C (decomp.), was obtained. Recrystallisation from ether/methanol resulted in colourless crystals, m.p. 119–122 °C (decomp.) (Found: C 64.55; H 5.74. Calc. for $C_{15}H_{16}O_5$: C 65.21; H 5.84).

4-Hydroxy-6-(α-trans-3,4-dimethoxystyryl)-5,6-dihydro-2-pyrone (1g). 3,4-Dimethoxycinnamaldehyde (2.16 g, 0.011 mol) afforded upon reaction 1.16 g (37 %) of colourless crystals, m.p. 112–114 °C (decomp.). On recrystallisation from ether/methanol the m.p. was raised to 130–135 °C (decomp.) (Found: C 64.50; H 5.68. Calc. for $C_{15}H_{16}O_5$: C 65.27; H 5.84).

4-Hydroxy-6-phenylethyl-5,6-dihydro-2-pyrone. 3-Phenylpropanal (9.0 g, 0.067 mol) was reacted to give 12.46 g (85 %) of the title compound, m.p. 98–100 °C (decomp.). Trituration with ether afforded analytically pure title compound with m.p. 121–123 °C (decomp.) (Found: C 71.40; H 6.53. Calc. for $C_{13}H_{14}O_3$: C 71.54; H 6.47).

4-Hydroxy-6-(trans-1-propenyl)-5,6-dihydro-2-pyrone (1h). Crotonaldehyde (0.70 g, 0.01 mol) was reacted to give 1.16 g (75 %) of colourless crystals, m.p. 101–103 °C (decomp.). Recrystallisation from ether/methanol afforded 0.75 g of the title compound, m.p. 110–112 °C (decomp.) (Found: C 62.05; H 6.59. Calc. for $C_8H_{10}O_3$: C 62.32; H 6.54).

4-Hydroxy-6-(trans-1-pentenyl)-5,6-dihydro-2-pyrone (1i). *trans*-2-Hexenal (9.8 g, 0.1 mol) gave upon reaction 16.17 g (89 %) of yellow crystals melting at 71–75 °C (decomp.). Recrystallized from ether/light petroleum the m.p. of the title compound was 86–87 °C

(decomp.) (Found: C 65.70; H 7.89. Calc. for $C_{10}H_{14}O_3$: C 65.91; H 7.74).

*4-Hydroxy-3-methyl-6-(*trans*-1-methyl-1-propenyl)-5,6-dihydro-2-pyrone* (*9*). Ethyl 2-methylacetoacetate (5.76 g, 0.04 mol) was converted to the dianion,[14] and to the reaction mixture was added tiglic aldehyde (3.36 g, 0.04 mol). When worked up following the general procedure 5.60 g (77 %) of colourless crystals of m.p. 134–139 °C (decomp.) were isolated. After trituration with ether the title compound melted at 140–141 °C (decomp.) (Found: C 65.70; H 7.60. Calc. for $C_{10}H_{14}O_3$: C 65.91; H 7.74).

6-(4-Methoxyphenyl)-3,5-hexadien-2-one. This synthesis was carried out following the procedure of Seebach and Meyer,[7] but with the purpose of synthesizing a dihydropyrone: To 0.03 mol of the dianion of ethyl acetoacetate in 50 ml of tetrahydrofuran[14] maintained at 0 °C was added solid 4-methoxycinnamaldehyde (2.43 g, 0.015 mol) in one portion. After solution the mixture was stirred for another 10 min and then poured into 300 ml of water at room temp. and stirred for 3.5 h. The mixture was acidified with conc. HCl to pH 1 and the solid formed was filtered off. Yield: 3.37 g, m.p. 108–115 °C. NMR spectra indicated that the crude product was a mixture of 55 % of the dihydropyrone (*1d*) and 45 % of the title compound. Three recrystallisations from ether/methanol afforded the title compound in low yield, m.p. 107–108 °C (lit.[15] m.p. 107–108.5 °C) NMR ($CDCl_3$) 2.50 (s, 3 H), 3.72 (s, 3 H), 6.18 (d, 1 H), 6.57 (d, 1 H), 6.75–7.60 (complex, 6 H).

(R,S)-*Kawain* (*2a*). A solution of *1a* (0.432 g, 0.002 mol) in dry acetone (10 ml) was mixed with dimethyl sulfate (0.315 g, 0.0025 mol) and anhydrous potassium carbonate (1 g). The mixture was refluxed for 7 h, cooled, filtered and the solid washed with dry acetone. Evaporation of the combined filtrate and washings gave a residue, which on trituration with ether deposited slightly yellow crystals (300 mg, 65 %), m.p. 136–138 °C. Recrystallisation from ether/methanol gave colourless crystals with m.p. 144–145 °C (lit.[16] m.p. 142–144 °C) UV 244 nm (ε 24 800) (lit.[17] 245 nm (ε 25 700). The NMR spectrum was in accord with that published.[18]

(R,S)-*Methysticin* (*2e*). Compound *1e* (0.520 g, 0.002 mol) dissolved in methanol/ether was reacted with excess of diazomethane. On evaporation of solvent 0.52 g of a yellow oil was obtained. It could not be induced to crystallize and was thus separated by preparative TLC (silica gel, ether as eluent). The fraction with $R_F = ca.$ 0.5 was isolated to give 210 mg (38 %) of yellow crystals, m.p. 114–124 °C. Recrystallisation from ether/methanol raised the m.p. to 130–131.5 °C with shrinking at 125 °C (lit.[4] m.p. 132–134 °C). The NMR spectrum was in accord with that published.[18]

5,6-Dihydroyangonin (*2d*). Treatment of *1d* (0.492 g, 0.002 mol) in methanol/ether with excess of diazomethane gave, after removal of solvent, 0.50 g of a light orange oil containing a small amount of crystals. Recrystallisation was carried out without success. Separation by preparative TLC (silica gel, ether as eluent, $R_F = 0.45$) afforded 0.075 g (14 %) of crystals, m.p. 103–107 °C. Recrystallisation from ether/methanol raised the m.p. to 120–121 °C (lit.[20] m.p. 123 °C). NMR (DMSO-d_6): δ 2.54 (s, 1 H), 2.67 (d, 1 H, $J_{5,6} = 3$), 3.78 (s, 3 H), 4.80–5.15 (m, 1 H), 5.20 (s, 1 H), 6.19 (q, 1 H, $J_{7,8} = 16$, $J_{6,7} = 5$), 6.70 (d, 1 H, $J_{7,8} = 16$), 6.90–7.60 (aromatic H).

(R.S)-*Marindinin.* 4-Hydroxy-6-phenylethyl-5,6-dihydro-2-pyrone (0.436 g, 0.002 mol) in dry acetone (20 ml) was stirred for 15 h at room temp. with anhydrous potassium carbonate (1 g) and dimethyl sulfate (0.315 g, 0.0025 mol). On work-up as described for (*R,S*)-kawain 0.48 g of a slight yellow oil was obtained. It soon solidified and was recrystallized from ether to give the title compound (0.21 g, 45 %) m.p. 68–70 °C (lit.[19] m.p. 73–74 °C). The NMR spectrum was in accord with that published.[18]

*4-Methoxy-6-(*α-trans*-2-methoxystyryl)-5,6-dihydro-2-pyrone* (*2b*). Compound *1b* (0.49 g, 0.002 mol) was methylated by the method given for (*R,S*)-kawain to yield 0.52 g of brown syrup, which was separated by preparative TLC (silica gel, ether as eluent, $R_F = 0.5$). The title compound was isolated as partly crystalline material (0.260 g, 50 %). Crystallisation was unsuccessful. NMR (DMSO-d_6) 2.52 (m, 1 H), 2.69 (m, 1 H), 3.78 (s, 3 H), 3.85 (s, 3 H), 5.1 (m, 1 H), 5.23 (s, 1 H), 6.35 (q, 1 H, $J = 15$ and 6), 6.8–7.6 (complex, 5 H).

*4-Methoxy-6-(*α-trans*-3-methoxystyryl)-5,6-dihydro-2-pyrone* (*2c*). Compound *1c* (0.49 g, 0.002 mol) was methylated by the method given for (*R,S*)-kawain to yield 0.50 g of light brown syrup. Separation by preparative TLC (silica gel, ether as eluent, $R_F = 0.5$) afforded a nearly colourless syrup (0.220 g, 42 %) of the title compound. When left in ether/methanol for 2 weeks at 4 °C 0.059 g of crystals of *2c* was obtained, m.p. 82–84 °C. NMR (DMSO-d_6) 2.52 (m, 1 H), 2.65 (m, 1 H) 3.78 (s, 6 H), 5.06 (m, 1 H), 5.23 (s, 1 H), 6.35 (q, 1 H, $J =$ 15.5 and 5), 6.1–7.4 (complex, 5 H).

*4-Methoxy-6-(*trans*-1-propenyl-5,6-dihydro-2-pyrone* (*2h*). Compound *1h* (2.5 g, 0.015 mol) was methylated as described for (*R,S*)-kawain to give 2.07 g (82 %) of crystalline material, m.p. 77–79 °C. Recrystallized from ether *2h* melted at 79–80 °C. NMR ($CDCl_3$) 1.70 (d, 3 H, $J_{8,9} = 5$), 2.38 (s, 1 H), 2.50 (d, 2 H, $J_{5,6} =$ 2), 3.70 (s, 3 H), 4.50–5.00 (m, 1 H), 5.08 (s, 1 H), 5.50 (q, 1 H, $J_{7,8} = 16$, $J_{6,7} = 5$), *ca.* 5.85 (m, 1 H, $J_{8,7} = 16$) (Found: C 63.90; H 6.88. Calc. for $C_9H_{12}O_3$: C 64.27; H 7.19).

4-Methoxy-6-(1,2-dibromopropyl)-2-pyrone (*3a*). *N*-Bromosuccinimide (1.96 g, 0.011 mol)

was added to a solution of *2h* (1.68 g, 0.01 mol) in tetrachloromethane (60 ml). The mixture was heated under reflux for 2.5 h while being irradiated with a tungsten lamp. When cooled, the mixture was filtered, the filtrates were washed with water and dried (Na_2SO_4). Removal of solvent *in vacuo* left a brown oil, which on trituration with ether afforded 1.17 g (36 %) of crystals. When recrystallized from ether the title compound melted at 114–116 °C. NMR ($CDCl_3$) *ca.* 1.90 (complex, virtual coupling,[21] 3 H), 3.75 (s, 3 H), *ca.* 4.50 (complex, virtual coupling,[21] 2 H), 5.42 (d, 1 H, $J=2$), 5.94 (d, $J=2$) (Found: C 33.44; H 3.40; Br. 47.99. Calc. for $C_9H_{10}Br_2O_3$: C 33.16; H 3.10; Br 49.02).

When the above reaction was performed with 0.022 mol of *N*-bromosuccinimide the yield was raised to 42 %.

*4-Methoxy-6-(*trans*)1-propenyl)-2-pyrone* (*4a*). Compound *3a* (0.173 g, 0.0005 mol) dissolved in 1 ml of glacial acetic acid and 5 ml of ether was treated with 0.1 g of zinc dust for 10 min. Water (0.5 ml) was added and the solution was decanted from undissolved zinc. More ether was added and the solution was extracted twice, each time with 5 ml of water, and once with 5 ml of 2 N NaOH. After drying and evaporation of the ether 77 mg (93 %) of colourless needles, m.p. 98–99 °C, were left. After recrystallisation from ether/light petroleum the m.p. was 102–103 °C (lit.[9] m.p. 102–103 °C). The NMR and IR spectra were in accord with those published.

Acknowledgement. We thank Dr. J. P. Jacobsen for valuable discussions in connection with some of the NMR spectra.

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Received December 1, 1975.