Metalation of 2-Methyl-4*H*-pyran-4-one and its Reactions

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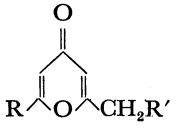
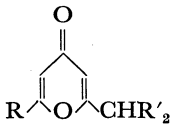
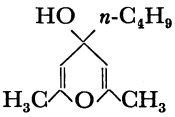
2-Methyl-4H-pyran-4-ones formed metalated products in the presence of sodium amide in liquid ammonia, and the metalated product reacted with alkyl and aralkyl halides or carbonyl compounds to give alkylated or condensed products. Self condensation reactions of 2-methyl-4*H*-pyran-4-ones also occurred in liquid ammonia to give flavone and the γ-pyrone dimer.

Boon[1] reported that 2,6-dimethyl-4*H*-pyran-4-one (**1**) reacts with benzaldehyde in an alkaline aqueous solution to give 2,6-distyryl-4*H*-pyran-4-one. 6-Methyl 1,2-diphenyl-2,3-dihydro-4-pyridone also condensed with benzaldehyde in an alkaline methanol solution to form 6-styryldihydropyridone.[2] These results indicate that the β-methyl hydrogen of an α,β-unsaturated ketone is acidic enough to react with an electrophile in an alkaline media.

This paper describes the metalation of 2-methyl-4*H*-pyran-4-one, and its reaction with some electrophiles.







1 : R=CH_3, R′=H
1′ : R=CH_3, R′=Na
3 : R=CH_3, R′=$CH_2C_6H_5$
5 : R=$CH_2CH_2C_6H_5$, R′=$CH_2C_6H_5$
6 : R=CH_3, R′=*n*-C_4H_9
8 : R=*n*-C_5H_{11}, R′=*n*-C_4H_9
9 : R=C_6H_5, R′=H
9′ : R=C_6H_5, R′=Na
10 : R=C_6H_5, R′=$CH_2C_6H_5$
12 : R=C_6H_5, R′=$CH(OH)C_6H_5$
13 : R=C_6H_5, R′=$CH(C_6H_5)CH_2COC_6H_5$
16 : R=C_6H_4-OCH_3-*p*, R′=H

4 : R=CH_3, R′=$CH_2C_6H_5$
7 : R=CH_3, R′=*n*-C_4H_9
11 : R=C_6H_5, R′=$CH_2C_6H_5$

2

Fig. 1.

Results and Discussion

Compound **1** did not give the metalated product **1′** by treating **1** with (a) sodium hydride in refluxing benzene, (b) lithium dimethylamide in ether, or (c) lithium *N*-methylanilide in ether or in tetrahydrofuran at room temperature, and **1** was recovered quantitatively in each case. Compound **1** reacted with *n*-butyl lithium in ether or in tetrahydrofuran at −78 °C under a nitrogen atmosphere to give 2,6-dimethyl-4-*n*-butyl-4*H*-pyran-4-ol (**2**), but at −20 °C or at room temperature **1** merely decomposed.

However treatment of **1** with sodium amide gave the metalated product **1′**. The formation of **1′** was proved that **1** was allowed to react with an equimolar amount of sodium amide in liquid ammonia at −78 °C under a nitrogen atmosphere, and to the resulting red solution was added an equimolar amount of benzyl bromide to give 2-methyl-6-phenethyl-4*H*-pyran-4-one (**3**) in 32% yield, accompanied by 14.5% of a mixture of dialkylated products, 2-methyl-6-(α-benzylphenethyl)-4*H*-pyran-4-one (**4**) and 2,6-diphenethyl-4*H*-pyran-4-one (**5**) (**4** : **5**=73 : 27), and 38% of the starting material **1** was recovered. When the ratio of **1** sodium amide and benzyl bromide was 1 : 2 : 2, the yields of **3** and the dialkylated products (**4**+**5**) were 31.5 and 22.5% (**4** : **5**=1 : 1), and 26% of **1** was recovered.

The reaction of **1′** with *n*-butyl bromide gave 2-methyl-6-*n*-pentyl-4*H*-pyran-4-one (**6**) (14.0% yield) and the dialkylated products (**7**+**8**) (6.5%).

2-Methyl-6-phenyl-4*H*-pyran-4-one (**8**) also formed the metalated product **9′** with an equimolar amount of sodium amide in liquid ammonia. An alkylation reaction of **9**, similar to that of **1′**, was carried out with an equimolar amount of benzyl bromide to give 2-phenethyl-6-phenyl-4*H*-pyran-4-one (**10**) in 77.0% yield. When the ratio of **9**, sodium amide and benzyl bromide was 1 : 2 : 2, the products were 2-(α-benzylphenethyl)-6-phenyl-4*H*-pyran-4-one (**11**) (75% yield) and **10** (13% yield).

Compound **9′** condensed with benzaldehyde to afford 2-(β-hydroxyphenethyl)-6-phenyl-4*H*-pyran-4-one (**12**) in 65% yield. Chalcone also reacted with **9′** to give only a Michael type addition product, 2-(4-oxo-2,4-diphenylbutyl)-6-phenyl-4*H*-pyran-4-one (**13**) in 81 % yield. The structures of all compounds were determined from their spectra and elemental analyses.

On the other hand, the formation of an aldol type condensation product by the reaction of γ-pyrone with malononitrile[3] suggested that the carbonyl group of γ-pyrone is reactive to a nucleophile. Anticipating a dimerization reaction with one part of **9** behaving as an electrophile and the other part behaving as a nucleophile, **9** was treated with sodium amide in liquid ammonia. When the molar ratio of **9** and sodium amide was 2 : 1, two new compounds **14** and **15** were obtained in 49.0 and 12.1% yields. From spectral data and elemental analyses it was deduced that **14** was 5-methyl-7-phenacylflavone and that **15** was a γ-pyrone dimer. Since the treatment of the dimer **15** with concentrated sulfuric acid or sodium amide in liquid ammonia gave **14**, the dimer **15** was considered to be an intermediate in the formation of flavone **14**. Thus this reaction is a self condensation of **9**.

However when **9** was treated with sodium methoxide

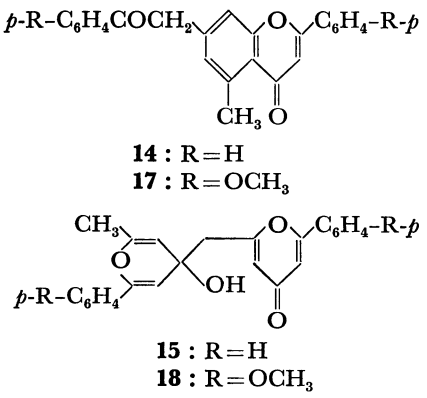


Fig. 2.

in methanol or with sodium in tetrahydrofuran, neither **14** nor **15** was detected. The formation of **14** and **15** was observed only in liquid ammonia.

A similar treatment of 2-(*p*-methoxyphenyl)-6-methyl-4*H*-pyran-4-one (**16**) gave 7-(*p*-methoxyphenacyl)-4′-methoxy-5-methylflavone (**17**)(38.5% yield) and the dimer (**18**) (7.0% yield). Treatment of the dimer **18** with concentrated sulfuric acid also gave the flavone **17**. The structures of **17** and **18** were supported by spectral data and elemental analyses.

The mechanism of the formation of the flavone **14** from γ-pyrone **9** was assumed to be an attack on the carbonyl group of **9** by the monoanion **9′** to give γ-pyrone dimer **15**, followed by elimination of water and isomerization to form the flavone **14**.

Experimental

*2,6-Dimethyl-4H-pyran-4-one (**1**).* Compound **1** was synthesized by reaction of dehydroacetic acid with concentrated hydrochloric acid,[4] mp 130—131 °C (lit,[4] 130 °C).

*2-Methyl-6-phenethyl-4H-pyran-4-one (**3**).* Procedure A: In a 200 ml three-necked flask, about 120 ml of liquid ammonia, containing 11 mmol of sodium amide, were placed. To this solution 1.24 g (10 mmol) of **1** and 20ml of dry ether were added. After stirring for 1 hr at −78 °C, 1.88 g (11 mmol) of benzyl bromide in 10 ml of dry ether was added and the mixture was stirred for an additional 3 hr at −78 °C under a nitrogen atmosphere. After quenching the reaction mixture with excess ammonium chloride, the liquid ammonia was evaporated rapidly on a water bath. Fifty ml of diluted hydrochloric acid and 50 g of crushed ice were added to the resulting residue. The resulting acidic aqueous solution was extracted with chloroform, washed with water, dried over anhydrous sodium sulfate and concentrated giving crude alkylated products. This residue was chromatographed on a silica gel (Merck 7734, 70—230 mesh) column with benzene-ethyl acetate (2 : 1 v/v). The fractions which showed R_f-values of 0.16 and 0.26 on silica gel (Merck 7721) thin layer chromatographs with benzene-ethyl acetate (2 : 1 v/v).

The fractions with R_f=0.16 were collected, concentrated and recrystallized from *n*-hexane-benzene (4 : 1 v/v) to give 694 mg (32.4%) of **3**, mp 75—77 °C (lit,[5] 76.5—77 °C).

IR(KBr): 1660 (νC=O), 1610 (C=C) and 695 cm^{-1} (phenyl).

UV λ_{max}^{EtOH} (ε): 250 (15700) and 261 nm (9060).

NMR(in $CDCl_3$): δ 2.16 (s, 3H), 2.51—3.02 (m, 4H), 5.96 (s, 2H) and 7.00—7.24 (m, 5H).

*The Dialkylated Products (**4**+**5**).* The fractions with R_f=0.26, were collected and concentrated to give 441 mg (14.5%) of the mixture (**4**+**5**), as a light brownish-yellow oil.

IR(liquid film): 1660 (νC=O), 1600 (C=C) and 750, 700 cm^{-1} (phenyl).

The ratio of **4** and **5** was determined from the NMR spectrum as follows: The NMR spectrum of the dialkylated mixture showed a singlet at δ 2.16 (intergration: 36), which corresponded to the 2-methyl protons of compound **4**. The multiplet signal at δ 7.08—7.56 (integration: 165) corresponded to the overlapping of the aromatic protons of the two isomers **4** and **5**. The integration of the ten aromatic protons of the two phenyl groups of **4** was calculated to 120. While the integration 45 was obtained for ten aromatic protons of two phenyl groups of **5**. Thus, 73% of **4** and 27% of **5** were contained in the mixture.

After **4** and **5** had been eluted, the column was again eluted with acetone, and the eluate was concentrated. The residue was crystallized from benzene to give 471 mg (38%, recovered) of the starting material, γ-pyrone (**1**), 128—130 °C.

Five mmol of **1**, 10.5 mmol of sodium amide and 10.5 mmol of benzyl bromide were treated according to procedure A. Three handred and thirtyseven mg of (31.5%) of **3**, 342 mg (22.5%) of the dialkylated products (**4**+**5**) (**4** : **5**=1 : 1) were obtained and 161 mg (26%) of **1** was recovered. Five mmol of **1**, 5.3 mmol of sodium amide and 5.3 mmol of benzyl bromide were treated according to procedure A. When the reaction was quenched after 30 min, 68 mg (11%) of **3** and 197 mg (13%) of the sole dialkylated product **4** were obtained.

NMR spectrum of **4** (in $CDCl_3$): δ 2.16 (s, 3H), 3.00 (broad s, 5H), 5.96 (d, 1H), 6.08 (broad s, 1H) and 7.10—7.56 (m, 10H).

*2-Methyl-6-pentyl-4H-pyran-4-one (**6**).* Using procedure A, from 10 mmol of **1**, 10.5 mmol of potassium amide and 10.5 mmol of *n*-butyl bromide, 252 mg (14.0%) of **6** and 153 mg (6.5%) of the dialkylated products (**7**+**8**) were obtained.

IR spectrum of **6** (liquid film): 1660 (νC=O) and 1610 cm^{-1} (C=C).

NMR spectrum of **6** (in $CDCl_3$): δ 0.90 (t, 3H), 1.12—1.72 (m, 6H), 2.20 (s, 3H), 2.45 (t, 2H) and 5.96 (s, 2H).

*Treatment of **1** with Different Bases*: Compound **1** (5 mmol) was treated with an equimolar amount of sodium hydride (50% in oil) in 50 ml of refluxing benzene, with 5 mmol of lithium dimethylamide in 50 ml of dry ether (distilled from $LiAlH_4$) at —20 °C, at room temperature or under refluxing, with an equimolar amount of lithium *N*-methylanilide in 30 ml of dry ether or in 50 ml of dry THF (distilled from $LiAlH_4$) at room temperature or under refluxing. But in each case, the metalated product **1′** which was tested for by adding benzyl bromide, was not formed, and **1** was recovered quantitatively. This was checked by thin layer chromatography and NMR.

*Treatment of **1** with n-Butyl Lithium*: Compound **1** (5 mmol) was treated with an equimolar amount of *n*-butyl lithium (15% in hexane) in 50 ml of dry THF (distilled from $LiAlH_4$) at −78 °C under a nitrogen atmosphere. After 1 hr an equimolar amount of benzyl bromide in 10 ml of dry THF was added to the resulting red solution, the mixture was then stirred for 2 hr at −78 °C. Thin layer chromatography of the reaction mixture revealed a component with R_f=0.19, which was isolated by silica gel (Merck 7734) column chromatography with benzene-ethyl acetate (2 : 1 v/v). From the spectral data it was speculated that this product was 2,6-dimethyl-4-*n*-butyl-4*H*-pyran-4-ol (**2**).

IR(liquid film): 3200—3450 (broad, νOH) and 1600 cm^{-1}

(C=C).

NMR(in $CDCl_3$): δ 0.90, 1.22—1.82, 2.12 and 6.42.

Compound **1** was also treated with *n*-butyl lithium, as described above, at −20 °C or at room temperature. However after working up as usual, a red oil was obtained. This red oil did not show a clear spot on a thin layer chromatograph, and also **1** could not be detected.

*2-Methyl-6-phenyl-4H-pyran-4-one (**9**)* was synthesized from 1-phenyl-1,3,5-hexanetrione and concentrated sulfuric acid, mp 86—88 °C (lit.[6] 87—88 °C).

*2-Phenethyl-6-phenyl-4H-pyran-4-one (**10**).* Using procedure A, from 10 mmol of **9** and 11 mmol of benzyl bromide, **10** was obtained. Eluting solvent: benzene-ethyl acetate (4 : 1 v/v), yield 2.12 g (77.0%), mp 84—85 °C (lit,[7] 85—86.5 °C).

IR(KBr): 1660 (νC=O) and 1595 cm^{-1} (C=C).

NMR (in $CDCl_3$): δ 3.01 (s, 4H, 6.00 (d, 1H), 6.62 (d, 1H), 7.15 (s, 5H) and 7.50 (m, 5H).

*2-(α-Benzylphenethyl)-6-phenyl-4H-pyran-4-one (**11**).* Following procedure A, 10 mmol of **9**, 20 mmol of sodium amide and 20 mmol of benzyl bromide were reacted. 2.75 g of the dialkylated product **11** was obtained (75%), mp 117—119 °C, accompanied by 380 mg (13%) of **10**. Eluting solvent: Benzene-ethyl acetate (4 : 1 v/v).

IR(KBr): 1640 (νC=O), 1620 (C=C) and 695 cm^{-1} (phenyl).

NMR(in $CDCl_3$): δ 2.98—3.15 (m, 5H), 5.91 (d, 1H), 6.60 (d, 1H), 7.05—7.24 (m, 10H) and 7.44—7.68 (m, 5H).

Found: C, 85.10; H, 6.19%. Calcd for $C_{26}H_{22}O_2$: C, 85.21; H, 6.05%.

*2-(β-Hydroxyphenethyl)-6-phenyl-4H-pyran-4-one (**12**).* Following procedure A, from 5 mmol of **9** and 5 mmol of benzaldehyde, 950 mg (65%) of **12** was obtained. Eluting solvent: Benzene-ethyl acetate (2 : 1 v/v). Crystallized from hot acetone, mp 163—164 °C.

IR(KBr): 3200(νOH), 1645 (C=O) and 700 cm^{-1} (phenyl).

UV λ_{max}^{EtOH} (ε): 228 (12300) and 273 nm (17800).

NMR(in $CDCl_3$): δ 3.00 (d, 2H), 3.60 (s, 1H), 5.14 (t, 1H), 6.22 (d, 1H), 6.59 (d, 1H) and 7.29—7.70 (m, 10H).

Found: C, 77.86; H, 5.40%. Calcd for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52%.

*2-(4-Oxo-2,4-diphenylbutyl)-6-phenyl-4H-pyran-4-one (**13**).* Using procedure A, **13** was synthesized from 10 mmol of **9** and 10 mmol of chalcone. Eluting solvent: Benzene-ethyl acetate (2 : 1 v/v). The fractions which contained **13** were collected, concentrated and crystallized from benzene to give 3.20 g (81%) of **13**, mp 120—122 °C, as white leaflets.

IR(KBr): 1680, 1660 (νC=O), 1625 (C=C) and 695 cm^{-1} (phenyl).

UV λ_{max}^{EtOH} (ε): 248 (19900) and 273 nm (19100).

NMR(in $CDCl_3$): δ 3.01 (m, 2H), 3.38 (d, 2H), 3.80 (m, 1H), 6.01 (d, 1H), 6.56 (d, 1H) and 7.17—7.97 (m, 15H).

Found: C, 82.15; H, 5.62%. Calcd for $C_{27}H_{22}O_3$: C, 82.21; H, 5.62%.

*5-Methyl-7-phenacylflavone (**14**).* Procedure B: In a 300 ml three-nicked flask, 10 mmol of sodium amide, 20 mmol of **9** and 200 ml of liquid ammonia were mixed. The mixture was then refluxed for 3 hr under a nitrogen atmosphere. After quenching with excess ammonium chloride, the reaction mixture was worked up as in procedure A. Thin layer chromatography of the reaction residue with benzene-ethyl acetate (1 : 1 v/v) showed two spots, R_f=0.39 and 0.20, while that of **9** was 0.26. The residue was chromatographed on a silica gel (Merck 7729, 230 mesh) column with benzene-ethyl acetate (1 : 1 v/v). The fractions with R_f=0.39 were collected, concentrated and crystallized from benzene-acetone (4 : 1 v/v) to give 1.70 g (49.0%) of **14**, mp 208—210 °C, as yellow cubic crystals.

IR(KBr): 1640 (νC=O), 1585, 1560 (C=C) and 700, 690 cm^{-1} (phenyl).

UV λ_{max}^{EtOH} (ε): 268 nm (28500).

$\lambda_{max}^{KOH/EtOH}$ (ε): 233 (38200), 268 (33200) and 354 nm (11100).

NMR(in DMSO-d_6): δ 2.31 (s, 3H), 6.12 (d, 1H, J= 2.3 Hz), 6.70 (d, 1H, J=2.3 Hz), 6.74 (s, 1H), 6.78 (s, 1H), 7.27 (m, 5H), 7.45 (m, 5H) and 10.01 (broad, disappeared in D_2O).

Mass (*m/e*): 354 (parent peak), 336 (base peak, P–18), 308, 234, 178, 102 and 77.

Found: C, 81.11; H, 5.20%. Calcd for $C_{24}H_{18}O_3$: C, 81.34; H, 5.12%.

*The γ-Pyrone Dimer (**15**).* The fractions with R_f=0.20 were collected, concentrated and crystallized from acetone-ethanol (3 : 1 v/v) to give 450 mg (12.1%) of **15**, mp 188—189 °C.

IR (KBr): 3360 (νOH), 1650 (C=O), 1620 (C=C) and 695 cm^{-1} (phenyl).

UV λ_{max}^{EtOH} (ε): 232 (21100), 273 (19400), 292 (14790) and 307 nm (6000).

NMR(in DMSO-d_6): δ 1.97 (s, 3H), 3.60 (s, 2H), 5.94 (d, 2H), 6.17 (d, 1H), 6.67 (d, 1H) and 7.10—7.47 (m, 10H).

Mass (*m/e*): 372 (parent peak), 354 (P–18), 226, 186, 105 and 77.

Found: C, 77.24; H, 5.45%. Calcd for $C_{24}H_{20}O_4$: C, 77.40; H, 5.41%.

*Conversion of **14** to **15**.* *(a) By Concentrated Sulfuric Acid*: A solution of 5 mg of **15** in 2 ml of concentrated sulfuric acid was allowed to stand at room temperature for 10 min. The reaction mixture was poured into ice-water, and the aqueous layer was extracted with ether. By treating the etheral solution as usual, compound **14** was obtained, which was compared with an authentic sample by thin layer chromatography.

(b) By Sodium Amide in Liquid Ammonia: A mixture of 50 ml of liquid ammonia, 200 mg of **15** and 60 mg of sodium amide was stirred for 3 hr. After evaporation of liquid ammonia and treatment of the residue as usual, the formation of **14** was confirmed by thin layer chromatography using an authentic sample for comparison.

*Treatment of **9** with Bases in Methanol or in Tetrahydrofuran. In Methanol*: 930 mg of **9** was added to a solution of 130 mg of sodium metal in 25 ml of absolute methanol. The mixture was stirred for 4 hr at room temperature. After concentration of the reaction mixture, the residue was added to 10 ml of chloroform and 15 ml of diluted hydrochloric acid, and extracted with chloroform. Thin layer chromatography of the chloroform layer showed neither **14** nor **15** and **9** was recovered.

In Tetrahydrofuran: A mixture of 930 mg of **9** and 130 mg of sodium metal in 80 ml of dry THF was stirred at room temperature for 2 hr. The reaction mixture was treated as described above. Neiter **14** nor **15** was detected.

*2-(p-Methoxyphenyl)-6-methyl-4H-pyran-4-one (**16**).* A solution of 50 mmol (11.7 g) of 1-(*p*-methoxyphenyl)-1,3,5-hexanetrione[6] in 40 ml of concentrated sulfuric acid was cooled to 0 °C and allowed to stand at 0 °C for 2 hr. The reaction mixture was then poured into ice-water and extracted with chloroform. The chloroform layer was washed with water and dried over anhydrous sodium sulfate. After removing chloroform, the resulting residue was crystallized from benzene to give 10.2 g (94%) of **16**, mp 144—146 °C, as colorless needles.

IR(KBr): 1670 (νC=O), 1615 (C=C) and 1510 cm^{-1} (phenyl).

UVλ_{max}^{EtOH} (ε): 224 (17600) and 304 nm (25100).

NMR(in $CDCl_3$): δ 2.33 (s, 3H), 3.84 (s, 3H), 6.11 (d, 1H), 6.57 (d, 1H), 6.95 (d, 2H) and 7.67 (d, 2H).

Found: C, 72.12; H, 5.66%. Calcd for $C_{13}H_{12}O_3$: C, 72.21; H, 5.59%.

*7-(p-Methoxyphenacyl)-4'-methoxy-5-methylflavone (**17**).* Following procedure B, from 4.32 g (20 mmol) of **16** and 10 mmol of sodium amide, **17** was prepared in 38.5% (1.6 g) yield. Compound **17** was isolated from the dimer **18** by silica gel (Merck 7729) column chromatography with benzene–ethyl acetate (2 : 1 v/v). The fractions which contained **17** were collected, concentrated and crystallized from acetone to give light yellow cubic crystals, mp 236—239 °C.

IR(KBr): 1640 (νC=O), 1610 and 1565 cm^{-1} (C=C).

UVλ_{max}^{EtOH} (ε): 225 (33100), 248 (26000), 288 (27000) and 305 nm 24500).

NMR(in DMSO-d_6): δ 2.28 (s, 3H), 3.68 (s, 3H), 3.80 (s, 3H), 6.02 (d, 1H), 6.67 (d, 1H), 6.83 (d, 2H), 6.90 (d, 2H), 6.96 (d, 2H), 7.19 (d, 2H), 7.53 (d, 2H), and 9.90 (broad, 1H).

Found: C, 75.38; H, 5.26%. Calcd for $C_{26}H_{22}O_5$: C, 75.35; H, 5.35%.

*The Dimer **18**.* The dimer eluted after the fraction **17**. Yield 300 mg (7.0%).

NMR(in $CDCl_3$): δ 1.64 (s, 3H), 2.70 (s, 2H), 3.80 (s, 3H), 3.83 (s, 3H), 6.00 (s, 1H), 6.24 (d, 1H), 6.63 (d, 2H), 6.78 (d, 2H), 6.84 (d, 2H), 7.55 (d, 2H) and 7.58 (d, 2H).

*Treatment of the Dimer **18** with Sulfuric Acid.* A mixture of 20 mg of **18** and 3 ml of concentrated sulfuric acid was allowed to stand at room temperature for 10 min. The mixture was added to 10 g of crushed ice and extracted with ether. The flavone **17** was detected by thin layer chromatography of the ether solution using an authentic sample for comparison.

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