284 (45), 169 (25), 168 (100), 167 (52), 77 (40), 46 (26).

Anal. Calcd. for $C_{19}H_{15}N_5$: C, 72.82; H, 4.83; N, 22.33. Found: C, 72.72; H, 4.87; N, 22.09.

Reaction of the Trisubstituted Chloroiminium Chloride 2f with Tetrabutylammonium Azide. The salt **2f** was prepared on a 0.022-mol scale. After the addition of the azide solution (0.055 mol) at 50–60 °C, stirring was continued at this temperature for 15 h. The solvent was distilled at atmospheric pressure, and the distillate was collected in a receiver cooled with a dry ice–acetone bath. The final pot temperature was 160 °C. The distillate was reacted with excess bromine at 0 °C, the solvent and excess bromine were removed in vacuo at room temperature (20 mm), and the residue was examined by GLC. There was no detectable 1,2-dibromocyclohexane present in this mixture.

The pot residue from above was diluted with water and extracted with dichloromethane. The extract was washed successively with dilute hydrochloric acid, sodium bicarbonate solution, and saturated salt solution. The organic phase was dried over magnesium sulfate and evaporated in vacuo. The residue was chromatographed on silica gel. The cyanamide was eluted with hexane–benzene–ethyl acetate (5:4:1) and several more polar products were removed from the column with ethyl acetate. The crude *N*-methyl-*N*-phenylcyanamide (1.15 g) was distilled in vacuo as before to give a pure specimen (0.94 g, 32%) identical with the material prepared from **2a.**

Basification of the acidic fraction from above gave, after ether extraction and the usual manipulation, nearly pure *N*-methylaniline (1.43 g, 61%).

Reaction of the Chloroiminium Chloride 2g with Azide Ion. To a solution of the iminium salt **2g** (0.0055 mol), prepared from **1g** and phosgene as described above, was added a dimethoxyethane solution of tetrabutylammonium azide (0.014 mol) and the resultant was heated at reflux temperature for 18 h. The solution was poured into water and extracted with dichloromethane. The dried (sodium sulfate) extract was evaporated in vacuo, and the residue was chromatographed on a column of silica gel using hexane–benzene (4:1) as the eluting solvent. The first fractions contained diphenylamine, the cyanamide **5b** (0.350 g, 35%), identical with the material prepared from **2b,** was eluted next, and this substance was followed by the starting material (0.50 g, 43%).

Reaction of 21b with Azide Ion. Synthesis of 22b. To a suspension of the iminium salt **21b** (0.0055 M) in dimethoxyethane (10 mL) was added a dimethoxyethane solution of tetrabutylammonium azide (0.015 mol) at 50–60 °C in the usual manner. A red-orange solid precipitated immediately. This substance was collected by filtration and dried in vacuo. It could not be recrystallized, and therefore a sample was dried in vacuo for analysis. The substance thus obtained had mp 210 °C dec, gave positive Beilstein and silver nitrate tests, and decomposed, with gas evolution and the formation of *N,N*-dicyclohexylbenzamide, on treatment with aqueous ethanolic potassium hydroxide. A mass spectrum of the red salt could not be obtained: UV (CH_3OH) 382 nm (ϵ 40 800); IR ($CHCl_3$) 1560 cm^{-1}; NMR ($CDCl_3$) δ 0.83–2.17 (m, 36 H), 2.40–3.10 (m, 4 H), 3.24–3.96 (m, 4 H), 6.53–6.77 (m, 4 H), 6.87–7.33 (m, 6 H).

Anal. Calcd. for $C_{38}H_{30}ClN_5$: C, 74.05, H, 8.83; N, 11.37. Found: C, 73.00; H, 8.80; N, 11.40.

The above data are not inconsistent with structure **22b.**

Acknowledgment. We are greatful to a referree for suggesting the mechanism of formation of the urea **18** from **11c.**

Registry No.—**1a,** 93-61-8; **1b,** 607-00-1; **1c,** 3700-30-3; **1d,** 2269-63-4; **1e,** 2591-86-8; **1f,** 23824-50-2; **1g,** 519-87-9; **2f,** 63641-02-1; **2g,** 63641-03-2; **13a,** 63641-04-3; **13b,** 63641-05-4; **13c,** 63641-06-5; **13d,** 63641-07-6; **13e,** 63641-08-7; **18,** 59849-55-7; **22b,** 63641-09-8; oxalylchloride, 79-37-8; 5-diphenylamino-2,2-dichloro-3(2*H*)-furanone, 636-41-10-1; phosgene, 75-44-5; *N*-methyaniline, 100-61-8; 1-phenyl-5-chlorotetrazole, 14210-25-4.

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Reaction of Di- and Tribromotetrahydro-4*H*-pyran-4-ones with Bases

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The reaction of 3,5-dibromotetrahydro-4*H*-pyran-4-ones (**1a,b**) with morpholine in HMPA gave enamino ketones **2a,b** and **3a,b** as the major products. The reaction of 3,3,5-tribromotetrahydro-4*H*-pyran-4-ones (**5a,b**) with silver acetate in acetic acid gave a mixture of bromo α-diketones **8a,b** and their enol acetates **9a,b** exclusively. Furthermore, dehydrobromination of **8a,b** with DBU or Dabco gave corresponding 3-hydroxy-4*H*-pyran-4-ones **10a,b.** However the reaction of diethyl 3,3,5-tribromotetrahydro-4*H*-pyran-4-one-2,6-dicarboxylate (**5c**) with silver acetate in acetic acid afforded bromo α-diketones **8c,** diethyl 3-hydroxy-4*H*-pyran-4-one-2,6-dicarboxylate (**10c**), and diethyl 3,5-dibromo-4*H*-pyran-4-one-2,6-dicarboxylate (**11**).

Of the simple tetrahydro-4*H*-pyran-4-ones, only a few have received attention in the literature with respect to their oxidation product.

In this paper, we wish to report the formation of tetrahydro-4*H*-pyran-3,4-diones and their derivatives from 3,5-dibromo- or 3,3,5-tribromotetrahydro-4*H*-pyran-4-ones.

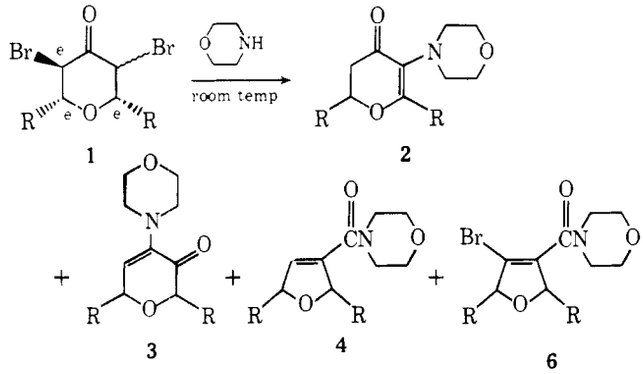
Table I. The Reaction of 1 with Morpholine in Several Solvents[a]

Dibromide	Solvent	Total yield, %[b]	Product ratio[c] 2	3	4	6
1a	HMPA	46	25	75		Tr
1b	HMPA	80	26	50	6	18
1b[d]	HMPA	80		76	6	18
1a	DMF	34	45	33	11	11
1b	DMF	72	20	20	40	20
1b[e]	DMF	55	24	24	48	4
1a	Ether	32	15	8	77	
1b	Ether	77	8	9	55	28
1b[e]	Ether	50	10	15	71	4

[a] The reaction was carried out at room temperature (15–18 °C). [b] Isolated yield. [c] The ratio was determined by GLC. [d] Large (10 equiv) excess of morpholine was used. [e] Cis isomer was used.

3,5-Dibromotetrahydro-4*H*-pyran-4-ones (**1a,b**) and 3,3,5-tribromotetrahydro-4*H*-pyran-4-ones (**5a-c**) were prepared from corresponding tetrahydro-4*H*-pyran-4-ones[1a-c] with dioxane–dibromide in ether in good yield. The reaction of *cis*-3,5-dibromotetrahydro-4*H*-pyran-4-one (**1a**) with 5 equiv of morpholine in HMPA gave 5-morpholino-2,3-dihydro-4*H*-pyran-4-one (**2a**) and 4-morpholino-3,6-dihydro-2*H*-pyran-3-one (**3a**) without any formation of Favorskii rearrangement product.

However a similar treatment of *trans*-3,5-dibromo-*cis*-2,6-dimethyltetrahydro-4*H*-pyran-4-one (**1b**) with morpholine afforded enamino ketones **2b** and **3b** as the major products together with a minor amount of 2,5-dihydro-2,5-dimethylfuran-3-carboxymorpholide (**4b**) and 4-bromo-2,5-dihydro-2,5-dimethylfuran-3-carboxymorpholide (**6b**). The

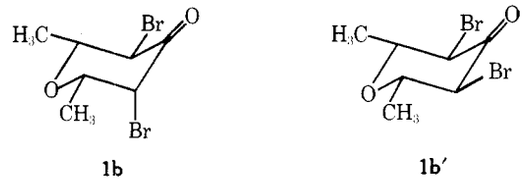


1 2 3 4 6

a, R = H
b, R = CH_3

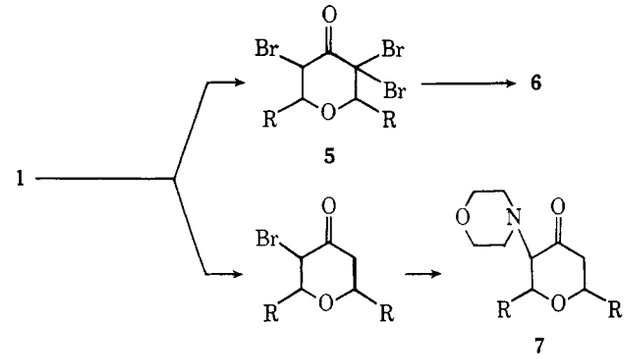
structures of these products were assigned on the basis of their IR, NMR, and mass spectra, and by elemental analysis.

The reaction of dibromide **1a,b** with morpholine in several solvents was examined and the experimental data, summarized in Table I, suggest that enamino ketones are the main products in polar aprotic solvents such as HMPA, whereas in ether, Favorskii rearrangement products predominate. Isomerization of **2** and **3** was not observed under the reaction conditions, and a large excess of morpholine increased the formation of **3** rather than that of **2.** These solvent effects are parallel to those observed in the reaction of 2,6-dibromocyclohexanone with secondary amines.[2] In the 2,6-dimethyl case, trans form **1b** was more reactive than cis form **1b.** This is due



1b **1b′**

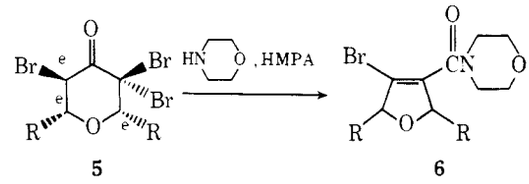
Scheme I



to the trans isomer and axial bromine undergoing a more facile back-side nucleophilic attack at C-5 by morpholine.

A possible route[3] for the formation of **6** is outlined in Scheme I. Dibromide **1** undergoes disproportionation of bromine to produce tribromide **5,** which then suffers a Favorskii rearrangement to give **6.** Although **7** has not been isolated, its presence in the reaction mixture from **1a** was suggested by GLC–mass spectroscopy.

The reaction of **5a,b** with 6 equiv of morpholine in HMPA at room temperature gave the corresponding Favorskii rearrangement products **6a,b** in quantitative yield. These results

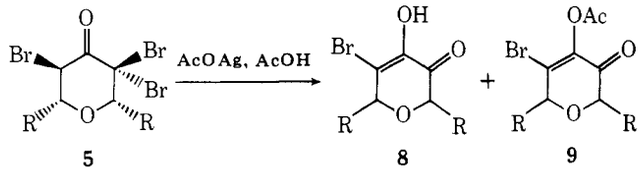


5 6

a, R = H
b, R = CH_3

suggest that the proton at C-5 was easily abstracted by morpholine, followed by ejection of the C-3 bromine atom to produce a cyclopropanone intermediate, which is then cleavaged to compound **6a,b.**

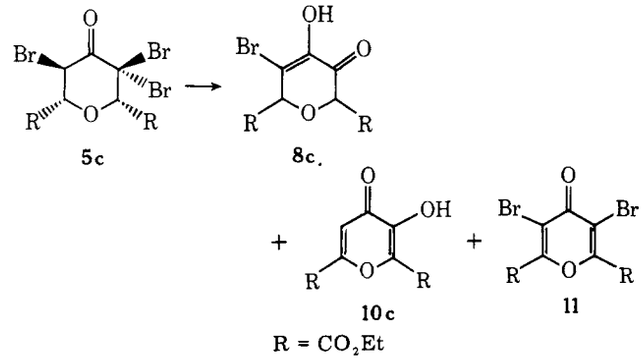
We next examined the reaction of **5a,b** with silver acetate in acetic acid, which gave hydroxypyrones **8a,b** and their enol



5 8 9

a, R = H (90%)
b, R = CH_3 (93%)

acetates **9a,b** in good yield. The proportion of these products (**8a,b**) and (**9a,b**) was determined by NMR and GLC analysis. In this case, no Favorskii rearrangement product was observed in any solvents. The reaction of **5** with silver acetate in acetonitrile afforded **9** (**a,** 90%; **b,** 88%) as a single product. Ace-



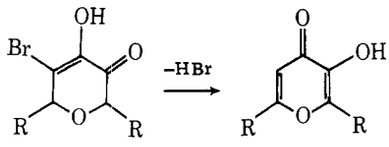
5c **8c** **10c** **11**

R = CO_2Et

tate **9** was also obtained from **8** by treatment with acetic anhydride in the presence of sodium acetate.

Similar treatment of **5c** (R = CO_2Et) with silver acetate gave hydroxypyrone **8c** (20%), diethyl meconate (**10c**, 20%), and diethyl 3,5-dibromochelidonate (**11**, 40%). It is suggested that in the case of R = CO_2Et, the proton at C-2 in the compound of **8c** initially produced is easily abstracted by weak base, permitting dehydrobromination to diethyl meconate (**10c**).

Finally, we investigated the dehydrobromination of **8a,b** with such strong bases as DBU and Dabco. The reaction of **8a** with 1,8-diazabicyclo[5.4.0]undecene (DBU) in benzene at room temperature afforded pyromeconic acid (**10a**). Similarly, 6-methyl maltol (**10b**) was obtained by the treatment of **8b**



8 **10**

a, R = H
b, R = CH_3

with diazabicyclo[2.2.2]octane (Dabco) in pyridine. The structures of 3-hydroxy-4*H*-pyran-4-ones **10a–c** were confirmed by agreement with IR, NMR, and mass spectra and mixed melting point determination with that of those authentic samples.

Experimental Section

General. All the points are uncorrected. Infrared spectra were run on a Hitachi Model 215 spectrophotometer. Proton nuclear magnetic resonance spectra were recorded on a JEOL C-60 spectrometer with tetramethylsilane as an internal reference. The mass spectra were determined on a Hitachi RMU-6E spectrometer. For column chromatography Wakogel C-200 (Wako Pure Chemical Industries) was used. *cis*-2,6-Dimethyltetrahydro-4*H*-pyran-4-one[1b] [bp 61 °C (14 mm Hg)] and *cis*-2,6-diethoxycarbonyltetrahydro-4*H*-pyran-4-one[1c] (mp 82–83 °C) were prepared by the reported method.

***cis*-3,5-Dibromotetrahydro-4*H*-pyran-4-one (1a).** Bromine (16.2 g, 0.1 mol) was added into dioxane (64 g) with stirring over a period of 30 min. Tetrahydro-4*H*-pyran-4-one[1a] (5.0 g, 0.05 mol) in 20 mL of ether was added to the mixture at 0 °C, and the mixture was then stirred for 2 h. The resulting slightly yellow tinged solution was poured into 20 mL of water. The organic layer was separated and the aqueous layer was extracted with ether. The combined ethereal solution was well washed with water and the solution was dried ($MgSO_4$). After evaporation of the ether, the residue was recrystallized from dichloromethane to give 10.5 g (82%) of **1a**: mp 156–157 °C (lit.[4] mp 156–157 °C); IR (KBr) 1745 cm^{-1}.

***trans*- and *cis*-3,5-Dibromo-*cis*-2,6-dimethyltetrahydro-4*H*-pyran-4-one (1b and 1b').** Bromination of *cis*-2,6-dimethyltetrahydro-4*H*-pyran-4-one[1b] at −15 °C by a method similar to that described for **1a** afforded only trans dibromide **1b** (87%): mp 42–43 °C; IR (KBr) 1735 cm^{-1}; NMR ($CDCl_3$) δ 1.38 (d, 3 H, *J* = 6.0 Hz), 1.57 (d, 3 H, *J* = 6.0 Hz), 3.79 (m, 2 H, 2- and 6-axial protons), 4.33 (d, 1 H, *J* = 2.0 Hz, 3-equatorial proton), 5.02 (d, 1 H, *J* = 11 Hz, 5-axial proton).

Anal. Calcd for $C_7H_{10}Br_2O_2$: C, 29.40; H, 3.52; Br, 55.88. Found: C, 29.40; H, 3.51; Br, 55.69.

When this reaction was carried out at 0 °C, a mixture of **1b** and *cis*-dibromide **1b'** was obtained and the mixture was then chromatographed on a silica gel column using benzene–hexane (1:2) as eluent to give **1b** (66.5%) and **1b'** (13.5%): mp 149–150 °C; IR (KBr) 1745 cm^{-1}; NMR ($CDCl_3$) δ 1.55 (d, 6 H, *J* = 6.0 Hz), 3.75 (d q, 2 H, *J* = 12 and 6.0 Hz, 2- and 6-axial protons), 4.40 (d, 2 H, *J* = 12 Hz, 3- and 5-axial protons).

Anal. Calcd for $C_7H_{10}Br_2O_2$: C, 29.40; H, 3.52; Br, 55.88. Found: C, 29.47; H, 3.60; Br, 55.88.

The Reaction of 1a with Morpholine. Morpholine (13.3 g, 0.15 mol) was added to a solution of **1a** (7.89 g, 0.03 mol) in 50 mL of HMPA with stirring at 0 °C. After the mixture was stirred for 24 h at room temperature, dry ether was added, and the precipitated morpholine hydrobromide was filtered off. Ether, excess morpholine, and HMPA were removed from the filtrate under vacuum and the residue [small amounts of **6a** and **7a** could be detected by GLC: **7a**, *m/e* 185 (M^+)] was chromatographed on a silica gel column using benzene–ethyl acetate (9:1). The earlier fraction gave 1.9 g (34.5%) of **3a** (mp 77.5–79 °C) and the latter fraction gave 0.63 g (11.5%) of **2a** (mp 83.5–85.0 °C). **2a:** IR (KBr) 1670, 1600 cm^{-1}; NMR ($CDCl_3$) δ 2.55 (t, 2 H, *J* = 7.5 Hz), 2.85 (m, 4 H), 3.81 (m, 4 H), 4.42 (t, 2 H, *J* = 7.5 Hz), 7.13 (s, 1 H); mass (*m/e*) 183 (M^+), 98 (base).

Anal. Calcd for $C_9H_{13}NO_3$: C, 59.00; H, 7.15; N, 7.65. Found: C, 58.59; H, 7.09; N, 7.20.

3a: IR (KBr) 1675, 1615 cm^{-1}; NMR ($CDCl_3$) δ 2.93 (m, 4 H), 3.84 (m, 4 H), 4.21 (s, 2 H), 4.52 (d, 1 H, *J* = 3.0 Hz), 6.05 (t, 1 H, *J* = 3.0 Hz); mass (*m/e*) 183 (M^+), 67 (base).

Anal. Calcd for $C_9H_{13}NO_3$: C, 59.00; H, 7.15; N, 7.65. Found: C, 58.79; H, 7.17; N, 7.39.

This reaction was carried out in ether; from **1a** (7.89 g, 0.03 mole) and 13.3 g (0.15 mole) of morpholine, **2a** (0.14 g, 2.5%), **3a** (0.27 g, 5.0%), and **4a** (1.35 g, 24.5%) were obtained. **4a:** $n^{20}D$ 1.5123; IR (neat) 1650, 1613 cm^{-1}; NMR (CCl_4) δ 3.57 (s, 8 H), 4.65 (s, 4 H), 5.87 (s, 1 H); mass (*m/e*) 183 (M^+).

The Reaction of 1b with Morpholine. Similar reaction was carried out according to the procedure for **1a** described above. In place of **1a**, **1b** (8.7 g, 0.03 mole) in HMPA was used, and the resulting oil was chromatographed on a silica gel column using benzene as eluent to afford **2b** (1.26 g, 25%), **3b** (2.52 g, 40%), **4b** (0.42 g, 5.0%), and **6b** (0.87 g, 10%). **2b:** mp 85–86 °C; IR (KBr) 1690, 1615 cm^{-1}; NMR (CCl_4) δ 1.33 (d, 3 H, *J* = 6.0 Hz), 2.08 (s, 3 H), 2.28 (d, 1 H, *J* = 7.0 Hz), 2.30 (d, 1 H, *J* = 9.0 Hz), 2.90 (m, 4 H), 3.60 (m, 5 H); mass (*m/e*) 211 (M^+), 43 (base).

Anal. Calcd for $C_{11}H_{17}NO_3$: C, 62.54; H, 8.11; N, 6.63. Found: C, 63.08; H, 8.54; N, 6.58.

3b: $n^{20}D$ 1.5068; IR (neat) 1690, 1615 cm^{-1}; NMR (CCl_4) δ 1.30 (d, 6 H, *J* = 7.0 Hz), 2.79 (m, 4 H), 3.77 (m, 5 H), 4.46 (q, 1 H, *J* = 7.0 Hz), 5.57 (d, 1 H, *J* = 2.0 Hz); mass (*m/e*) 211 (M^+), 43 (base). **4b:** $n^{20}D$ 1.5023; IR (neat) 1655, 1615 cm^{-1}; NMR (CCl_4) δ 1.24 (d, 3 H, *J* = 3.0 Hz), 1.31 (d, 3 H, *J* = 3.0 Hz), 3.55 (s, 8 H), 4.90 (br s, 2 H), 5.70 (s, 1 H); mass (*m/e*) 211 (M^+), 43 (base).

Anal. Calcd for $C_{11}H_{17}NO_3$: C, 62.54; H, 8.11; N, 6.63. Found: C, 62.23; H, 8.32; N, 6.58.

6b: mp 71–73 °C; IR (KBr) 1655, 1610 cm^{-1}; NMR (CCl_4) δ 1.26 (d, 3 H, *J* = 5.0 Hz), 1.36 (d, 3 H, *J* = 5.0 Hz), 3.60 (s, 8 H), 4.55 (m, 2 H); mass (*m/e*) 276/274 ($M^+ - CH_3$), 43 (base).

Anal. Calcd for $C_{11}H_{16}BrNO_3$: C, 45.53; H, 5.56; Br, 27.54; N, 4.83. Found: C, 45.61; H, 5.52; Br, 27.79; N, 4.69.

3,3,5-Tribromotetrahydro-4*H*-pyran-4-one (5a). Tetrahydro-4*H*-pyran-4-one (3.5 g, 0.035 mol) in 20 mL of ether was added to a stirred mixture of 30 mL of dioxane and 16.8 g (0.105 mol) of bromine at room temperature. After the mixture was stirred for 6 h at 28–30 °C, the resulting reaction mixture was then poured into water. The organic layer was separated and the aqueous layer was extracted with ether. The combined ethereal solution was washed with water, dried, and evaporated under reduced pressure. Recrystallization of the residue (13.7 g) from benzene gave 10.3 g of **5a**, mp 131.5–132.5 °C, in 86.5% yield: IR (KBr) 1740 cm^{-1}; NMR ($CDCl_3$) δ 3.60 (d, 1 H, *J* = 12 Hz), 4.04 (d, 1 H, *J* = 12 Hz), 4.40 (m, 1 H), 4.53 (d, 1 H, *J* = 12 Hz), 5.63 (d d, 1 H, *J* = 7.0 and 12 Hz, 5-axial proton).

Anal. Calcd for $C_5H_5Br_3O_2$: C, 17.83; H, 1.49; Br, 71.17. Found: C, 17.83; H, 1.50; Br, 71.44.

The following compounds were also prepared from *cis*-2,6-disubstituted tetrahydro-4*H*-pyran-4-ones:[1b,c] **3,3,5-Tribromo-*cis*-2,6-dimethyl tetrahydro-4*H*-pyran-4-one (5b),** mp 87–88 °C, in 89% yield: IR (KBr) 1745 cm^{-1}; NMR ($CDCl_3$) δ 1.54 (d, 3 H, *J* = 6.0 Hz), 1.60 (d, 3 H, *J* = 6.0 Hz), 3.65 (q, 1 H, *J* = 6.0 Hz), 3.80 (d q, 1 H, *J* = 6.0 and 11 Hz), 5.15 (d, 1 H, *J* = 11 Hz, 5-axial proton).

Anal. Calcd for $C_7H_9Br_3O_2$: C, 23.04; H, 2.49; Br, 65.70. Found: C, 23.14; H, 2.53; Br, 65.68.

Diethyl 3,3,5-tribromotetrahydro-4*H*-pyran-4-one-*cis*-2,6-dicarboxylate (5c), mp 56–58 °C, in 85% yield: IR (KBr) 1750 cm^{-1}; NMR (CCl_4) δ 1.38 (t, 6 H, *J* = 7.0 Hz), 4.35 (m, 6 H), 5.18 (d, 1 H, *J* = 11 Hz, 5-axial proton).

Anal. Calcd for $C_{11}H_{13}Br_3O_6$: C, 27.47; H, 2.73; Br, 49.84. Found: C, 27.63; H, 2.65; Br, 49.84.

The Reaction of 5a with Morpholine. Morpholine (5.2 g, 0.06 mol) was added gradually to a stirred solution of 3.37 g (0.01 mol) of **5a** in 5 mL of HMPA at 0 °C, and the mixture was then stirred for 24 h at room temperature. Dry ether was added to the reaction mixture and the precipitated morpholine hydrobromide was filtered off. Ether, morpholine, and HMPA were removed in vacuo from the filtrate and the residue was chromatographed on a silica gel column. Elution with benzene gave 2.6 g of **6a** as crystals, mp 71–73 °C, in quantitative yield:

IR (KBr) 1660 (C=O), 1620 (C=C) cm^{-1}; NMR ($CDCl_3$) δ 3.70 (br s, 8 H), 4.77 (br s, 4 H).

Anal. Calcd for $C_9H_{12}BrNO_3$: C, 41.24; H, 5.72; Br, 30.49; N, 5.34. Found: C, 41.63; H, 4.66; Br, 30.42; N, 5.21.

Similarly, **4-bromo-2,5-dihydro-2,5-dimethylfuran-3-carboxymorpholide (6b)** was obtained as crystals, mp 71–72 °C, in quantitative yield: IR (KBr) 1655 (C=O), 1610 (C=C) cm^{-1}; NMR (CCl_4) δ 1.26 (d, 3 H, J = 5.0 Hz), 1.36 (d, 3 H, J = 5.0 Hz), 3.60 (br s, 8 H), 4.55 (m, 2 H).

Anal. Calcd for $C_{11}H_{16}BrNO_3$: C, 45.53; H, 5.56; Br, 27.54; N, 4.83. Found: C, 45.61; H, 5.52; Br, 27.79; N, 4.69.

The Reaction of 5a with Silver Acetate. A mixture of 3.79 g (11.2 mmol) of **5a** and 6.0 g (40 mmol) of silver acetate in 30 mL of acetic acid was warmed at 28–30 °C with stirring. After the mixture was stirred for 3 h, the precipitated silver bromide was filtered off, and acetic acid was removed in vacuo. The residue was chromatographed on a silica gel column using benzene as eluent to give a mixture of 2.1 g of **8a** and **9a** in 90% yield (**8a/9a** = 2:1; by GLC and NMR spectroscopic assay). **8a:** mp 77–78 °C; IR (KBr) 3350 (OH), 1675 (C=O), 1650 (C=C) cm^{-1}; NMR ($CDCl_3$) δ 4.30 (m, 2 H), 4.57 (m, 2 H), 5.96 (br s, 1 H).

Anal. Calcd for $C_5H_5BrO_3$: C, 31.12; H, 2.61; Br, 41.40. Found: C, 31.17; H, 2.23; Br, 41.82.

9a: bp 91–93 °C (0.15 mm Hg); mp 50–51 °C; IR (KBr) 1780, 1710 (C=O), 1640 (C=C) cm^{-1}; NMR ($CDCl_3$) δ 2.38 (s, 3 H), 4.30 (s, 2 H), 4.65 (s, 2 H); mass (m/e) 236/234 (M^+), 43 (base).

The Reaction of 5b with Silver Acetate. By the method similar to that described above, reaction temperature was 40–45 °C for 3 h; 7.33 g of **5b** afforded a mixture of 4.75 g of **8b** (mp 62–63 °C) and **9b** [bp 108–110 °C (0.25 mm Hg), mp 125.5–126.5 °C] in 93% yield. (**8b/9b** = 1:1). Pure **8b** and **9b** were obtained by preparative GLC (20% Silicon DC-200 column 120 °C). **8b:** IR (KBr) 3340 (OH), 1680 (C=O), 1640 (C=C) cm^{-1}; NMR ($CDCl_3$) δ 1.43 (d, 3 H, J = 6.0 Hz), 1.55 (d, 3 H, J = 6.0 Hz), 4.20 (d q, 1 H, J = 2.0 and 6.0 Hz), 4.65 (d q, 1 H, J = 2.0 and 6.0 Hz), 6.33 (s, 1 H).

Anal. Calcd for $C_7H_9BrO_3$: C, 38.04; H, 4.10; Br, 36.15. Found: C, 38.10; H, 4.19; Br, 36.54.

9b: IR (KBr) 1780, 1710 (C=O), 1630 (C=C) cm^{-1}; NMR ($CDCl_3$) δ 1.40 (d, 3 H, J = 6.0 Hz), 1.62 (d, 3 H, J = 6.0 Hz), 2.27 (s, 3 H), 4.25 (d q, 1 H, J = 2.0 and 6.0 Hz), 4.77 (d q, 1 H, J = 2.0 and 6.0 Hz).

Anal. Calcd for $C_9H_{11}BrO_4$: C, 41.09; H, 4.21; Br, 30.37. Found: C, 41.02; H, 4.22; Br, 30.03.

The Reaction of 5c with Silver Acetate. A mixture of 3.30 g of **5c** and 4.0 g of silver acetate in 14 mL of acetic acid was warmed at 50–55 °C for 6 h. After workup similar to that of **5a** described above, the residue was chromatographed on silica gel and eluted with benzene–isopropyl ether (4:1) to give 1.2 g of **11** and a mixture of **8c** and **10c**. The latter fraction was rechromatographed on silica gel using benzene–isopropyl ether (6:1) to afford pure 0.6 g of **8c** and 0.4 g of **10c**. **11:** mp 121–122 °C (lit.[5] mp 126 °C); IR (KBr) 1745 and 1660 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 1.42 (t, 6 H, J = 7.0 Hz), 4.40 (q, 4 H, J = 7.0 Hz). **8c:** mp 85–87 °C; IR (KBr) 3420 (OH), 1740, 1725, 1690 (C=O), 1645 (C=C) cm^{-1}; NMR ($CDCl_3$) δ 1.30 (t, 6 H, J = 7.0 Hz), 4.27 (q, 4 H, J = 7.0 Hz), 5.27 (d, 1 H, J = 2.0 Hz), 5.43 (d, 1 H, J = 2.0 Hz), 9.57 (br s, 1 H).

Anal. Calcd for $C_{11}H_{13}BrO_7$: C, 39.19; H, 3.89; Br, 23.70. Found: C, 39.53; H, 4.13; Br, 23.21.

10c: mp 111–112 °C (lit.[6] 111.5 °C); IR (KBr) 3300 (OH), 1745, 1660 (C=O), 1610, 1595 (C=C) cm^{-1}; NMR ($CDCl_3$) δ 1.36 (t, 3 H, J = 7.0 Hz), 1.40 (t, 3 H, J = 7.0 Hz), 4.43 (q, 2 H, J = 7.0 Hz), 4.50 (q, 2 H, J = 7.0 Hz), 7.20 (s, 1 H), 7.80 (br s, 1 H).

3-Hydroxy-4*H*-pyran-4-one (10a). To a mixture of 181 mg of **8a** in 3 mL of benzene was added 220 mg of 1,8-diazabicyclo[5.4.0]undecene at 0 °C. After the mixture was stirred for 48 h at 16–18 °C, 0.2 mL of concentrated hydrochloric acid was added, and the precipitated mass was filtered off and extracted with chloroform. The organic layer was washed with water and evaporated to leave an oil of 39 mg. The oil was distilled under 50 mm Hg reduced pressure and then sublimation gave 19 mg of pure **10a:** mp 115–117 °C (lit.[7] mp 117 °C). A mixed melting point determination with an authentic sample from comenic acid[7] indicated no depression.

3-Hydroxy-2,6-dimethyl-4*H*-pyran-4-one (10b). To a mixture of 2.0 g of **8b** and **9b** (**8b/9b** = 1:1) in 6 mL of pyridine was added 0.80 g of diazabicyclo[2.2.2]octane at room temperature. After the mixture was stirred for 2 h at 70–75 °C, the precipitate was filtered off and pyridine was removed under reduced pressure. The residue was then chromatographed on silica gel using benzene as eluent to give crude **10b** (0.9 g). Sublimation of the crude crystals afforded a pure sample of **10b** (0.6 g), mp 162–163 °C (lit.[8] mp 162.5 °C), in 53% yield. The infrared spectrum and the other chemical properties were identical with those of authentic sample.[9]

Registry No.—**1a,** 63641-11-2; **1b,** 63599-80-4; **1b',** 63599-81-5; **2a,** 63599-82-6; **2b,** 63599-83-7; **3a,** 63599-84-8; **3b,** 63599-85-9; **4a,** 63599-86-0; **4b,** 63599-87-1; **5a,** 63599-88-2; **5b,** 63599-89-3; **5c,** 63599-90-6; **6a,** 63599-91-7; **6b,** 63599-92-8; **8a,** 63599-93-9; **8b,** 63599-94-0; **8c,** 63599-95-1; **9a,** 63599-96-2; **9b,** 63599-97-3; **10c,** 729-63-5; **11,** 843-08-3; tetrahydro-4*H*-pyran-4-one, 29943-42-8; *cis*-2,6-dimethyltetrahydro-4*H*-pyran-4-one, 14505-80-7; morpholine, 110-91-8.

Reference and Notes

(1) (a) Terahydro-4*H*-pyran-4-one [bp 58–59 °C (15 mm Hg)] was obtained by means of ozonolysis of 4-methylenetetrahydro-4*H*-pyran in 80% yield: ref bp 59–60 °C (13 mm Hg), G. R. Owen and C. B. Reese, *J. Chem. Soc. C*, 2401 (1970). (b) C. Eskenazi, H. Sliwa, and P. Maitte, *Bull. Soc. Chim. Fr.*, 2951 (1971). (c) J. Attenburrow, *J. Chem. Soc.*, 571 (1945).
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