until it cooled to room temperature. Scratching and cooling induced precipitation of the product, which was collected by filtration and recrystallized from a mixture of methanol and water. Yield: 249 mg; 83%; m.p. (dec.) 202°.

Anal. Calcd. for $C_9H_9N_5O_5S$: N, 10.71. Found: N, 10.45.

Kinetic measurements of the reaction of I with vinyl acetate, in dry acetic acid, at 35°. The determination of the second order constant, k_2, was made in the manner described by Orr and Kharasch, in dry acetic acid at 35 ± .02°, and gave a value for k_2 ($l. \times mol^{-1} \times min^{-1}$) of $2.94 \times 10^{-4} \pm 4\%$.

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Alkyl 6-Alkoxytetrahydropyran-2-carboxylates[1]

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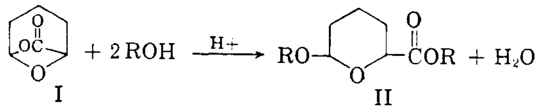
The preparation of ethyl 3,4-dihydro-2*H*-pyran-2-carboxylate[3] and the subsequent reaction with phenols to prepare ethyl 6-aryloxytetrahydropyran-2-carboxylates[4] have been reported. We wish to report the synthesis of several alkyl 6-alkoxytetrahydropyran-2-carboxylates (II) and the 2,5-dimethyl derivatives. These materials are prepared readily by the reaction of 7-oxo-6,8-dioxabicyclo [3.2.1.] octane (I) or its 1,4-dimethyl derivative with the appropriate alcohol in the presence of sulfuric acid as a catalyst and isopropyl ether as an entrainer to remove the coproduct water.

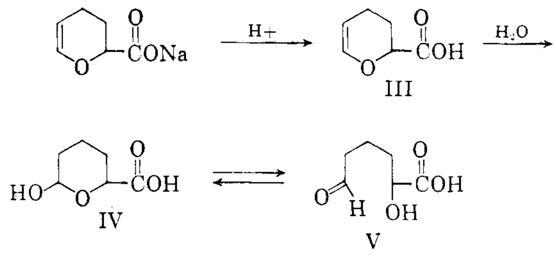


The starting lactones may be prepared from acrolein dimer or methacrolein dimer by oxidation with silver oxide[3] or oxygen,[5] by the Tishchenko reaction,[6] or by the Cannizzaro reaction.[7]

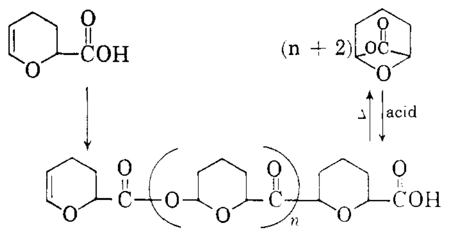
The reactant combinations that were used and the results that were obtained are shown in Table I. Good to excellent yields were obtained in all cases and the products from a single distillation were of high purity.

As a means of obtaining esters for which the alkyl groups of the ester and of the acetal functions were different, two of the acetal-esters were subjected to base-catalyzed transesterification. The reactions were conducted in a standard manner and the equilibrium was shifted by removing the exchanged alcohol by distillation. The reactant combinations used and the results obtained are summarized in Table II.

Whetstone and Ballard[3] reported that, in their attempts to isolate the free 3,4-dihydro-2*H*-pyran-2-carboxylic acid (III) by acidification of the sodium salt and extraction with ether, a viscous, water-soluble product was obtained. The acid was unstable and resinified on standing but immediate distillation provided the lactone, 7-oxo-6,8-dioxabicyclo[3.2.1]octane (I). In addition to the extracted acid, these workers isolated also a viscous solid by evaporation of the aqueous solution. On the basis of the analytical results, this material was considered to be a mixture of the hydroxy acid (IV) and 5-formyl-2-hydroxypentanoic acid (V). These materials were presumed to have formed by the acid-catalyzed hydration of the unsaturated acid (III).



We have encountered this same problem in our work even when the unsaturated acid (III) was isolated from its sodium salt under conditions designed to minimize hydration of the acid (80% acidification at 0° with mineral acid and in the presence of solvent to immediately extract the unsaturated acid.) The isolated acid resinified rapidly to form a clear, tacky solid and appeared to be in major part a homopolymer of the unsaturated acid (III), based upon analyses (elemental, functional group, and infrared) and the fact that strong heating converted the polymer to the monomeric lactone.



The lactone (I) polymerized in a few hours in the presence of ferric chloride or aluminum bromide to yield a water-insoluble polymer which appeared very similar to that obtained from the unsaturated acid (III).

The 6-hydroxytetrahydropyran-2-carboxylic acid (IV) was isolated in low yield from the aqueous solution remaining after the sodium salt had been acidi-

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(3) R. R. Whetstone and S. A. Ballard, *J. Am. Chem. Soc.*, **73**, 5280 (1951).

(4) R. R. Whetstone, U. S. Patent **2,574,444** (1951).

(5) A. E. Montagna and L. V. McQuillen, British Patent **782,430,** (1957).

(6) C. W. Smith, U. S. Patent **2,537,921** (1957).

(7) G. G. Stoner and J. S. McNulty, *J. Am. Chem. Soc.*, **72**, 1531 (1950).

TABLE I

PREPARATION OF "SYMMETRICAL" ALKYL 6-ALKOXYTETRAHYDROPYRAN-2-CARBOXYLATES

Lactone, mol.	Alcohol, mol.	Reflux time, hrs.	Product Tetrahydropyran-2-carboxylate	Yield, %	B.P. °C./mm. Hg	n_D^{20}	Sp. Gr. 20/15.6°	Carbon, %		Hydrogen, %		Sap. Equiv.	
								Calcd.	Found	Calcd.	Found	Calcd.	Found
5.6[a]	Ethyl, 20.0	25	Ethyl 6-Ethoxy-	88.7	86/2.0	1.4405	1.046	59.4	59.4	9.0	9.1	202	201
1.4[b]	Ethyl, 3.7	...	Ethyl 6-Ethoxy-	85.0	...	...	...	...	...	...	...	...	...
3.0[a]	2-Ethylhexyl, 10.0	7.0	2-Ethylhexyl 6-(2-Ethylhexoxy)-	88.7	165/0.4	1.4528	0.9405	71.2	71.3	11.4	11.2	370	368
3.0[a]	OXO-decyl, 10.0	7.5	OXO-decyl 6-OXO-decyloxy-	91.1	205–220/0.7	1.4589	0.933	73.2	73.1	11.8	12.0	426	422
1.0[a]	Allyl, 8.0	30	Allyl 6-Allyloxy-	82.0	91/0.5	1.4618	1.0261	63.7	63.4	8.0	8.2	226	227
1.0[a]	Propargyl, 6.0	1.5	Propargyl 6-Propargyloxy-	81.5	128/1.0	1.4825	1.136	64.9	64.6	6.4	6.5	222	211
2.6[c]	Ethyl, 8.4	27	Ethyl 2,5-Dimethyl-6-ethoxy-	93.5	75/0.6	1.4366	1.001	62.6	62.5	9.6	9.8	230	230

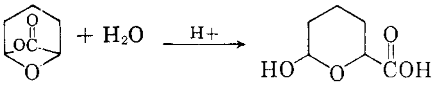
[a] 7-Oxo-6,8-dioxabicyclo [3.2.1] octane. [b] Crude 3,4-dihydro-2H-pyran-2-carboxylic acid. [c] 1,4-Dimethyl-7-oxo-6,8-dioxabicyclo [3.2.1] octane.

TABLE II

PREPARATION OF "UNSYMMETRICAL" ALKYL 6-ALKOXYTETRAHYDROPYRAN-2-CARBOXYLATES

Starting tetrahydropyran-2-carboxylate, moles	Alcohol, mol.	Product Tetrahydropyran-2-carboxylate	Yield, %	B.p. °C./mm. Hg	n_D^{20}	Sp. Gr. 20/15.6°	Carbon, %		Hydrogen, %		Sap. Equiv.	
							Calcd.	Found	Calcd.	Found	Calcd.	Found
Ethyl 6-Ethoxy-, 0.5	2-Ethylhexyl, 3.0	2-Ethylhexyl 6-Ethoxy-	76.8	144/2.0	1.4482	0.974	67.1	67.5	10.6	10.7	286	282
Ethyl 6-Ethoxy-, 0.5	Allyl, 2.0	Allyl 6-Ethoxy-	68.5	85/1.0	1.4522	1.054	61.6	61.4	8.5	8.7	214	215
Allyl 6-Allyloxy-, 0.63	2-Ethylhexyl, 3.1	2-Ethylhexyl 6-Allyloxy-	58.8	141/1.0	1.4565	0.983	68.4	68.4	10.1	9.9	298	298
Allyl 6-Allyloxy-, 1.5	OXO-decyl, 4.5	OXO-decyl 6-Allyloxy	89.5	154/0.7	1.4599	0.973	69.9	69.5	10.5	10.7	326	321

fied (with excess mineral acid) and the unsaturated acid (III) had been removed by extraction. This same hydroxy acid was prepared in essentially quantitative yield by the acid-catalyzed hydration of 7-oxo-6,8-dioxabicyclo[3.2.1]octane.



EXPERIMENTAL[8]

7-Oxo-6,8-dioxabicyclo[3.2.1]octane and 1,4-dimethyl-7-oxo-6,8-dioxabicyclo[3.2.1]octane. These materials were prepared *via* the silver-catalyzed oxidation with molecular oxygen of acrolein dimer and methacrolein dimer, respectively. The oxidation has been reported elsewhere,[6] and involves the oxidation of the aldehydes with molecular oxygen with a silver catalyst in an aqueous solution of sodium hydroxide. The products of the oxidation are the salts of the acids from which the lactones are recovered by acidification, extraction, and distillation.

Esterification procedure. For the preparation of the "symmetrical" acetal-esters, the lactone and alcohol were used in the quantities shown in Table I. These materials along with the sulfuric acid catalyst (0.5 to 0.75 weight %) were charged to the kettle of a distillation assembly which carried a liquid-liquid separating head. Sufficient isopropyl ether was added (200–400 ml.) to insure ready separation of the water of reaction during the reflux period. At the completion of the water removal, the mixtures were allowed to stand at room temperature for several hours, usually overnight. The sulfuric acid was neutralized with sodium ethoxide or sodium acetate and the mixtures distilled to recover the alkyl 6-alkoxytetrahydropyran-2-carboxylates.

Transesterification procedure. The transesterifications shown in Table II were conducted in a standard manner using sodium methoxide or sodium ethoxide as a catalyst. The acetal-ester and alcohol were mixed in the proportions shown in Table II and 0.5% catalyst (sodium methoxide or sodium ethoxide) by weight of the reactants was added. The mixtures were distilled to remove most of the lower boiling, exchanged alcohol at atmospheric pressure. The last traces of the exchanged alcohols were removed under reduced pressure followed by removal of the excess reactant alcohol and the product ester. For the last reactant combination shown in Table II, the mixture containing the catalyst was permitted to stand 16 hr. at room temperature. The coproduct allyl alcohol was then removed by distillation at essentially room temperature under reduced pressure. Inasmuch as distinctly superior results were obtained for this experiment as compared to the other reactant combinations, this may be the preferred method of performing this transesterification.

Poly(3,4-dihydro-2H-pyran-2-carboxylic acid). Four hundred g. of aqueous solution containing 100 g. of sodium 3,4-dihydro-2H-pyran-2-carboxylate which was neutral to phenolphthalein, was acidified with 26.2 g. of concentrated sulfuric acid (80% of theory) in 130 ml. of water. The acidification was conducted at 0° and in the presence of 300 ml. of ethyl ether. The aqueous layer was removed and extracted twice with 200 ml. of ether. The combined extracts were distilled (steam bath) under reduced pressure to remove the ether. The residue amounted to 59 g. and was a colorless, viscous liquid which was water-soluble and evolved carbon dioxide upon treatment with aqueous sodium bicarbonate. Immediate titration with standard base to a phenolphthalein end point gave a purity of approximately 50.5% as the monomeric acid. The value was somewhat uncertain due to the fading end point. Determination of the purity by bromination (0°) gave an approximate value of 45% purity. The infrared spectrum contained discrete absorption bands at 3.7, 5.7, 7.7, and 10.6μ characteristic of the carboxyl group and at 6.04μ characteristic of the unsaturation. In a few hours the material had resinified to a nonpourable state and was tacky.

Anal. Calcd. for $C_6H_8O_3$: C, 56.20; H, 6.29; Sap. Equiv., 128.1. Found: C, 56.70; H, 6.17; Sap. Equiv. 135.

After the polymer had stood for approximately 2 months, 31.8 g. was heated (oil bath at 160 to 200°) under 3 mm. of pressure. The vapors were passed through a gooseneck and condensed to provide 24 g. of a water-insoluble liquid. This material was identified as the lactone, 7-oxo-6,8-dioxabicyclo[3.2.1]octane, on the basis of its boiling point (65°/3 mm.; lit.[3] value is 63/3 mm.) and refractive index (n_D^{20} 1.4582; lit.[3] value is n_D^{20} 1.4587).

6-Hydroxytetrahydropyran-2-carboxylic acid. An aqueous solution of 430 ml. remaining from the acidification with excess sulfuric acid of the sodium 3,4-dihydro-2H-pyran-2-carboxylate and extraction with isopropyl ether was evaporated to dryness at room temperature. On the basis of the acid balance, the aqueous solution could have contained a maximum of 30 g. of the 6-hydroxytetrahydropyran-2-carboxylic acid. The light colored, tacky solid was extracted several times with ethyl ether and the extracts evaporated. The white solid was recrystallized from ethyl acetate to provide 2.5 g. of white prisms or needles believed to be 6-hydroxytetrahydropyran-2-carboxylic acid and which melted at 89.5–90.5°.

This same acid was prepared as follows: a suspension of 25.6 g. (0.2 mol.) of 7-oxo-6,8-dioxabicyclo[3.2.1]octane, 20 ml. of water, and 7.3 ml. of $0.5N$ sulfuric acid was shaken at room temperature. After several minutes the solution temperature increased to about 40° accompanied by a complete solution of the organic phase. The solution was neutralized with 7.3 ml. of $0.5N$ sodium hydroxide and the water evaporated below 30° using a vacuum desiccator to provide 29.2 g. of 6-hydroxytetrahydropyran-2-carboxylic acid of m.p. 89.0–90.5°. A melting point of 89.0–90.5° was observed for a mixture of the acids isolated from the two sources. The infrared spectrum contained no absorption for ethylenic unsaturation but did contain strong bands characteristic of the —OH and —COOH groups.

Anal. Calcd. for $C_6H_{10}O_4$: C, 49.3; H, 7.0; Neut. Equiv. 146. Found: C, 49.0; H, 7.0; Neut. Equiv., 147.

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The Preparation of Certain Amino-Substituted Perfluoroalkyl-s-Triazines

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As part of a study of cellulose-reactive materials, the preparation of a number of amino-substituted perfluoroalkyl-*s*-triazines was undertaken. It is known that the *N*-methylol derivatives of 2-alkyl-4,6-diamino-*s*-triazines can be used as crosslinking

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[8] All melting points are corrected, boiling points are uncorrected.