

TABLE II
 ADDUCTS OF VINYL ETHERS AND UNSATURATED ALDEHYDES

No.	Adduct	Boiling point		n_D^{20}	d_4^{20}	Theory		Analyses, %	
		$^{\circ}\text{C}$.	Mm.			C	H	Found C	Found H
I	2-Methoxy-3,4-dihydro-2H-pyran ^{a,c}	127.6	760	1.4423	1.0013	63.13	8.83	63.09	8.86
II	2-Ethoxy-3,4-dihydro-2H-pyran ^c	132-132.3	760	1.4410	0.9712	65.59	9.44	65.52	9.40
III	2-Isobutoxy-3,4-dihydro-2H-pyran ^{a,b}	109	100	1.4374	0.9225	69.19	10.32	65.39	9.40
		177	760					68.87	10.37
IV	2-(2-Ethylhexyloxy)-3,4-dihydro-2H-pyran	110.5	10	1.4504	0.9123	73.54	11.43	73.58	11.43
								73.58	11.48
V	2-Phenoxy-3,4-dihydro-2H-pyran ^a	90-96	3	1.5372	1.1364	74.97	6.88	74.75	6.91
VI	2-Phenylthio-3,4-dihydro-2H-pyran ^a	125	5	1.5844	1.1178	68.71	6.29	68.70	6.30
								68.61	6.36
VII'	2,2'-Bis-(3,4-dihydro-2H-pyranyl)-ether ^a	95-100	10	1.4846	1.1063	65.91	7.75	65.69	7.74
IX	2-Methoxy-5-methyl-3,4-dihydro-2H-pyran ^c	52-58	100	1.4462	0.9784	65.59	9.44	65.28	9.40
								65.33	9.43
X	2- <i>n</i> -Butoxy-5-methyl-3,4-dihydro-2H-pyran ^d	107	50	1.4448	0.9165	70.55	10.65	70.15	10.68
								70.22	10.73
XI	2-Methoxy-4-methyl-3,4-dihydro-2H-pyran ^{c,e}	79-80	100	1.4400	0.9629	65.59	9.44	65.24	9.46
								65.29	9.45
XII	2-Isobutoxy-4-methyl-3,4-dihydro-2H-pyran ^c	122	10	1.4370	0.9090	70.55	10.65	69.94	10.68
								69.96	10.71
XIII	2-Isobutoxy-6-methyl-3,4-dihydro-2H-pyran	117-119	100	1.4387	0.9155	70.55	10.65	69.90	10.58
								69.87	10.60

^a These adducts all gave the orange, highly-insoluble bis-2,4-dinitrophenylhydrazone of glutaraldehyde, m.p. 193.7-194.7°. *Anal.* Calcd. for $\text{C}_{17}\text{H}_{18}\text{N}_8\text{O}_8$: N, 24.34. Found: N, 24.1, 24.6. B. D. Shaw (*J. Chem. Soc.*, 300 (1937)) gives a melting point of 169-172° for this derivative. ^b 2-Isobutoxydihydropyran gave the dioxime of glutaraldehyde, m.p. 176-176.5°. Shaw reports a m.p. of 175° while J. v. Braun and W. Sobocki (*Ber.*, 44, 2526 (1911)) report a melting point of 178°. ^c This adduct gave the orange, highly-insoluble bis-2,4-dinitrophenylhydrazone of β -methylglutaraldehyde, m.p. 202.2-202.7° (from ethyl acetate). *Anal.* Calcd. for $\text{C}_{18}\text{H}_{18}\text{N}_8\text{O}_8$: C, 45.57; H, 3.83; N, 23.62. Found: C, 45.68; H, 3.85; N, 23.50. ^d 2-*n*-Butoxydihydropyran gave the orange, highly-insoluble bis-2,4-dinitrophenylhydrazone of α -methylglutaraldehyde, m.p. 198-198.5°. *Anal.* Calcd. for $\text{C}_{18}\text{H}_{18}\text{N}_8\text{O}_8$: C, 45.57; H, 3.83. Found: C, 45.51; H, 3.88. ^e The physical constants of these compounds agree closely with those previously reported by Longley and Emerson.³

(2,5-dimethyl-3,4-dihydro-2H-pyran)-carboxaldehyde) boiling at 100-105° (100 mm.), n_D^{20} 1.4521 and 21 g. of residue.

The material boiling at 85.5° (100 mm.) was 2-methoxy-5-methyl-3,4-dihydro-2H-pyran and as such corresponded to a 21% conversion to product in a 26% yield based on methacrolein and a 99% yield based on methyl vinyl ether.

Anal. Calcd. for $\text{C}_7\text{H}_{12}\text{O}_2$: C, 65.59; H, 9.44. Found: C, 65.28, 65.53; H, 9.40, 9.43.

The 306 g. of methacrolein dimer represents a 55% conversion to product.

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[CONTRIBUTION FROM THE SHELL DEVELOPMENT COMPANY]

Reactions of Acrolein and Related Compounds. II. Addition of Unsaturated Esters and of Methacrylonitrile

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Unsaturated esters (such as methyl acrylate, methyl methacrylate, vinyl acetate and methyl acrylate) and methacrylonitrile have been added to acrolein, methacrolein and crotonaldehyde to give substituted 3,4-dihydro-2H-pyrans. Similar additions of vinyl ethers and olefins are presented in papers I and III of this series. The structures of most of the adducts have been established and in every case the β -carbon of the aldehyde was attached to the unsubstituted olefinic carbon atom.

Discussion

In the preceding paper the thermal addition of vinyl ethers to unsaturated carbonylic compounds is described. This reaction has been extended to the addition of the carbon-to-carbon double bond of several unsaturated esters and of methacrylonitrile to the 1,4-positions of unsaturated aldehydes to give substituted dihydropyrans. In general the reaction conditions were similar to those used for the dimerization of acrolein or addition of vinyl ethers to acrolein, *i.e.*, heating the mixture of reagents under autogenous pressure at

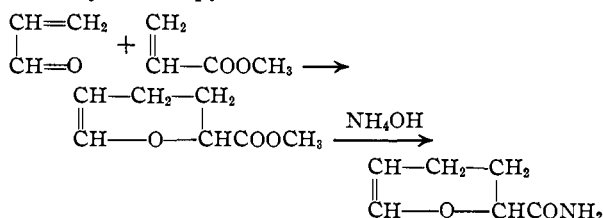
170-200° for one to two hours. The conditions have been found critical in only one case, the addition of methacrylonitrile to acrolein. At lower temperature or shorter reaction times than that shown in the table the conversion to product decreased rapidly while with higher temperatures and longer reaction times an exothermic reaction set in so that safety discs were ruptured. Subsequent to the completion of our work there appeared in this country reports¹ of the similar

(1) Schultz, Fiat Final report 1157, PB 85174, pp. 17, 18; Schultz and Wagner, *Angew. Chem.*, 63, 112 (1950).

addition of acrylonitrile and of methyl acrylate to acrolein.

Side reactions which decrease the amount of desired product are: (1) dimerization of the aldehyde, (2) polymerization of one or both of the addenda, and (3) further addition of aldehyde to the primary product.

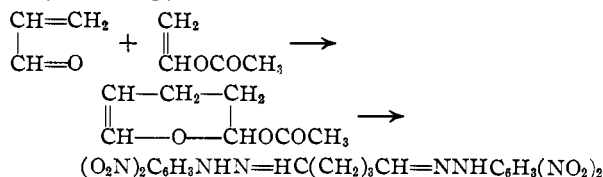
In order to determine the direction of addition the structures of most of the adducts were investigated. In all cases studied the β -carbon of the aldehyde was joined to the unsubstituted carbon of the olefinic bond of the ester or nitrile. The adduct of methyl acrylate and acrolein was established as 2-carbomethoxy-3,4-dihydro-2H-pyran by its reaction with concentrated ammonium hydroxide to give an amide which was identified as 3,4-dihydro-2H-pyran-2-carboxamide, previously obtained by R. R. Whetstone and S. A. Ballard² of these laboratories from acrolein dimer, 2-formyl-3,4-dihydro-2H-pyran.



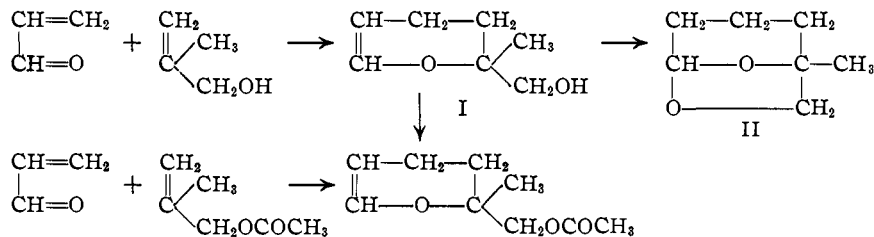
By analogy the adduct of methyl methacrylate and acrolein is assumed to be 2-carbomethoxy-2-methyl-3,4-dihydro-2H-pyran. Since the adduct of methacrylonitrile and acrolein gave the same amide as that from the adduct of methyl methacrylate and acrolein, the product is considered to be 2-cyano-2-methyl-3,4-dihydro-2H-pyran.

The structure of the methyl methacrylate-methacrolein adduct has been established as 2-carbomethoxy-2,5-dimethyl-3,4-dihydro-2H-pyran by hydrolysis to the corresponding acid previously obtained by Whetstone³ from methacrolein dimer, 2-formyl-2,5-dimethyl-2H-pyran.

Since the adduct of vinyl acetate and acrolein gave the bis-2,4-dinitrophenylhydrazone of glutaraldehyde, this product must be 2-acetoxy-3,4-dihydro-2H-pyran.



Two isomeric products from the thermal addition of methallyl alcohol to acrolein have been obtained. Apparently the usual addition occurs to give (I) 2-methyl-3,4-dihydro-2H-pyran-2-methanol, a part of which undergoes internal acetal formation to give (II) 4-methyl-2,8-dioxabicyclo-(3,2,1)octane



Acetylation of I gave an acetate whose boiling point, refractive index and infrared absorption spectrum were in agreement with corresponding properties for the adduct of methallyl acetate and acrolein. Since II was the lower boiling isomer with quite low hydroxyl value and bromine number the cyclic acetal structure seems probable. A similar compound has been obtained by Whetstone⁴ by cyclization of 3,4-dihydro-2H-pyran-2-methanol.

The accompanying table reveals the reactions which have been investigated along with properties of the products. One representative example has been given in detail.

Experimental

2-Carbomethoxy-2-methyl-3,4-dihydro-2H-pyran.—A mixture of 100 g. (1 mole) of methyl methacrylate, 56 g. (1 mole) of acrolein and 1.5 g. of hydroquinone was heated in a steel vessel at 180° for one hour. Upon distillation, there was obtained 16 g. of acrolein, 46 g. of methyl methacrylate, 3 g. of acrolein dimer, 63 g. of a material boiling at 119–120° (1 mm.), n_D^{20} 1.4549, and 23 g. residue. The material boiling at 119–120° (1 mm.) was shown to be 2-carbomethoxy-2-methyl-3,4-dihydro-2H-pyran and as such represents a 40% conversion to product and 56% yield based on acrolein or 74% yield based on methyl methacrylate.

Anal. Calcd. for $\text{C}_8\text{H}_{12}\text{O}_3$: C, 61.51; H, 7.76. Found: C, 61.45, 61.54; H, 7.74, 7.76.

Conversion of 2-Carbomethoxy-3,4-dihydro-2H-pyran to the Amide.—A mixture of 2 g. of the dihydropyran from acrolein and methyl acrylate was warmed on the steam-bath with 15 ml. of concd. ammonium hydroxide for five minutes. After the solution had stood overnight, the crystals which separated were collected on a filter, washed well with water and dried. The 3,4-dihydro-2H-pyran-2-carboxamide melted at 112.5° and gave no depression of melting point when mixed with an authentic sample of 3,4-dihydro-2H-pyran-2-carboxamide.²

Conversion of 2-Carbomethoxy-2-methyl-3,4-dihydro-2H-pyran to the Amide.—A mixture of 2 g. of 2-carbomethoxy-2-methyl-3,4-dihydro-2H-pyran and 15 ml. of concentrated ammonium hydroxide was allowed to react at room temperature overnight. The resulting solution was extracted with chloroform and the extract was evaporated to dryness. The residue was recrystallized from isoöctane yielding 1.5 g. of 2-methyl-3,4-dihydro-2H-pyran-2-carboxamide which melted at 86.4–87.4°.

Anal. Calcd. for $\text{C}_7\text{H}_{11}\text{O}_2\text{N}$: N, 9.92. Found: N, 9.78, 9.78.

Conversion of 2-Cyano-2-methyl-3,4-dihydro-2H-pyran to the Amide.—A mixture of 1 g. of the dihydropyran from acrolein and methacrylonitrile and 10 ml. of 10% aqueous sodium carbonate was refluxed until all of the oil had gone into solution. The solution was extracted with chloroform and extract was evaporated to dryness. The residue was recrystallized from isoöctane yielding 0.5 g. of 2-methyl-3,4-dihydro-2H-pyran-2-carboxamide melting at 86.2–87.2°. The melting point of a mixture of this material with the 2-methyl-3,4-dihydro-2H-pyran-2-carboxamide prepared in the preceding experiment was not depressed.

2,5-Dimethyl-3,4-dihydro-2H-pyran-2-carboxylic Acid.—A mixture of 3 g. of the dihydropyran from methacrolein and methyl methacrylate and 15 ml. of 40% sodium hydroxide was refluxed for 30 minutes. The solution was cooled

(2) R. R. Whetstone and S. A. Ballard, *THIS JOURNAL*, **73**, 5280 (1951).

(3) R. R. Whetstone, U. S. Patent 2,479,283 (1949).

(4) R. R. Whetstone, U. S. Patent 2,511,891 (1950).

TABLE I
ADDITION OF UNSATURATED ESTERS AND METHACRYLONITRILE TO UNSATURATED ALDEHYDES

A	Addenda ^f B ^e	Temp., °C.	Time, hr.	Adducts	Conv. ^d to product, %	Yield, ^e %
Acrolein	Methyl acrylate	195	1	2-Carbomethoxy-3,4-dihydro-2H-pyran	3	7A, 8B
Acrolein	Methyl methacrylate	180	1	2-Carbomethoxy-2-methyl-3,4-dihydro-2H-pyran	40	56A, 74B
Acrolein	Methacrylonitrile	190	2	2-Cyano-2-methyl-3,4-dihydro-2H-pyran ^a	5	13A, 78B
Acrolein	Vinyl acetate	180	2	2-Acetoxy-3,4-dihydro-2H-pyran ^b	9	32B
Acrolein	Methallyl acetate	200	1.5	2-Methyl-3,4-dihydro-2H-pyran-2-methanol acetate	9
Acrolein	Methallyl alcohol	200	1	4-Methyl-2,8-dioxabicyclo-(3,2,1)-octane	21
				2-Methyl-3,4-dihydro-2H-pyran-2-methanol	11
Methacrolein	Methyl methacrylate	150-170	1	2-Carbomethoxy-2,5-dimethyl-3,4-dihydro-2H-pyran	16	37A, 57B
Crotonaldehyde	Methyl methacrylate	200	4	2-Carbomethoxy-2,4-dimethyl-3,4-dihydro-2H-pyran	7

^a For proof of structure of this crude product b.p. 113° (100 mm.); n_D^{20} 1.4508; N, 10.6 (theory 11.4); see the conversion to the amide in the Experimental section. ^b The structure of this adduct was established by conversion to the known bis-2,4-dinitrophenylhydrazone of glutaraldehyde, m.p., mixed m.p. 192°. ^c The unsaturated esters and methacrylonitrile contained 1% of hydroquinone. ^d Moles of adduct / moles of addenda A charged. ^e Moles of adduct / moles of addenda consumed. ^f In these experiments the molar ratio of addenda A:B was 1 except for the first experiment which was 0.85.

TABLE II
PHYSICAL PROPERTIES AND ANALYSES

	Boiling point °C.	Mm.	n_D^{20}	d_4^{20}	Theory		Found		Infrared bands	
					C	H	C	H	Ester	Olefinic
2-Carbomethoxy-3,4-dihydro-2H-pyran	91	25	59.14	7.09	59.52	7.19	5.72 μ	6.05 μ
2-Carbomethoxy-2-methyl-3,4-dihydro-2H-pyran	119-120	100	1.4549	1.0774	61.51	7.76	61.45	7.74	5.74 μ	6.05 μ
							61.54	7.76		
2-Acetoxy-3,4-dihydro-2H-pyran ^a	77-78	20	1.4596	1.1178	5.75 μ	6.03 μ
2-Methyl-3,4-dihydro-2H-pyran-2-methanol acetate	60-63	1	1.4574	63.53	8.29	63.43	8.23	5.8 μ	6.1 μ
							63.50	8.32		
2-Methyl-3,4-dihydro-2H-pyran-2-methanol ^b	63-66	1	1.4700	65.59	9.44	65.48	9.35
							65.58	9.35		
4-Methyl-2,8-dioxabicyclo-(3,2,1)-octane	87.5-89.5	100	1.4500	1.0446	65.59	9.44	65.23	9.09
							65.16	9.12		
2-Carbomethoxy-2,5-dimethyl-3,4-dihydro-2H-pyran	114-115	50	1.4550	1.0430	63.51	8.29	63.74	8.34
							63.69	8.40		
2-Carbomethoxy-2,4-dimethyl-3,4-dihydro-2H-pyran	115	50	1.4459	63.51	8.29	63.18	8.26
							63.19	8.24		

^a Anal. Calcd. for C₇H₁₀O₃: bromine no., 112.7. Found: bromine no., 113.2. ^b Anal. Calcd. for C₇H₁₂O₂: bromine no., 124.5. Found: bromine no., 103.5.

and made acidic to methyl red. The crystals which formed were removed by filtration and recrystallized from petroleum ether. The 2,5-dimethyl-3,4-dihydro-2H-pyran-2-carboxylic acid melted at 62.7-63.5°; the melting point of a mixture with authentic 2,5-dimethyl-2H-pyran-2-carboxylic acid³ was not depressed.

Acetylation of 2-Methyl-3,4-dihydro-2H-pyran-2-methanol.—A 22-g. sample of the 2-methyl-3,4-dihydro-2H-pyran-2-methanol from the reaction of acrolein with methallyl alcohol was added to 42 g. of acetic anhydride contain-

ing 0.1 g. of sodium acetate and allowed to react at room temperature for three days. Upon distillation there was obtained besides acetic anhydride and acetic acid, 15.5 g. of the acetate of 2-methyl-3,4-dihydro-2H-pyran-2-methanol, b.p. 60-63° (1 mm.), n_D^{20} 1.4567, d_4^{20} 1.0487.

Anal. Calcd. for C₉H₁₄O₃: C, 63.51; H, 8.29; sapon. equiv., 170.2. Found: C, 63.62, 63.62; H, 8.41, 8.39; sapon. equiv., 171.5.

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