TABLE II

ESTERIFICATION OF SUBSTITUTED AMMONIUM SALTS

Expt. no.	Reactants				Temp.,[a] °C.	Time, hr.	Conversion, %	
	Salt	Mole	Alcohol	Mole			Ester	Amine
1	Quinoline acetate	1.0	*n*-Butyl	1.0	133–149	3.6	46[b]	...
2	Diamylamine acetate	0.5	*n*-Butyl	0.55	143–168	9.5	32	44
3	Dihexylamine acetate	0.5	Furfuryl[c]	0.55	139–166	17.5	10	58
4	Triamylamine acetate	0.5	*n*-Butyl	0.55	142–165	10.0	62[d]	94
5	Trihexylamine acetate	0.5	Furfuryl[c]	0.55	140–158	24.5	30[e]	90
6	Aniline lactate	1.0	*n*-Hexyl	2.5	119–174	2.0	33	48
7	Decylamine lactate	0.34	*n*-Butyl	0.85	115–158	7.0	0[f]	0[f]
8	Dihexylamine lactate	0.5	*n*-Butyl	1.25	119–155	11.5	40	72
9	Tributylamine lactate	0.5	*n*-Butyl	1.25	110–163	5.5	68	...
10	Triamylamine lactate	0.5	*n*-Butyl	1.25	109–152	5.5	42	...
11	Trihexylamine lactate	0.5	*n*-Butyl	1.25	116–157	11.5	78	72[g]

[a] Initial and final temperatures of the reaction mixture. [b] 39% conversion to acid. [c] Toluene, 75–100 ml., was used as an entraining agent. [d] 22% conversion to free acid. [e] 50% conversion to free acid. [f] 68% conversion to *n*-decyllactamide. [g] Isolated by distillation in nitrogen.

salts of various types of organic acids are summarized in Table I.

Esterification of Amine Salts.—The procedure for esterification of amine salts with alcohols was similar to that described for esterification of ammonium salts. The temperature of the refluxing reaction mixture was generally higher than that for the ammonium salt esterifications. Water was the only component removed from the reaction mixture during esterification; the amines formed during the reaction, being high boiling, remained in the reaction mixture. The ester was isolated by distillation of the reaction mixture in vacuum.

Table II summarizes the esterification of various amine acetates and lactates with butyl and furfuryl alcohols. Excepting Experiments 3 and 7, conversion of amine salt to ester and to amine ranged from 30 to 78 and 44 to 94%, respectively.

2-Methylpentyl glycolate, a new compound, had the following properties: b.p. 66° at 1.2 mm.; n^{20}_D 1.4340; d^{20}_4 0.9864.

Anal. Calcd. for $C_8H_{16}O_3$: C, 59.97; H, 10.07; sapn. equiv., 160.2. Found: C, 60.13; H, 10.12; sapn. equiv., 160.7.

2-Ethylhexyl glycolate: The properties of this previously undescribed ester were: b.p. 94° at 2.2 mm.; n^{20}_D 1.4400.

Anal. Calcd. for $C_{10}H_{20}O_3$: C, 63.79; H, 10.71; sapn. equiv., 188.3. Found: C, 63.92; H, 10.72; sapn. equiv., 188.7.

The authors are indebted to C. O. Willits and co-workers for the analytical data.

PHILADELPHIA 18, PENNA. RECEIVED MAY 19, 1951

[CONTRIBUTION FROM THE SHELL DEVELOPMENT COMPANY]

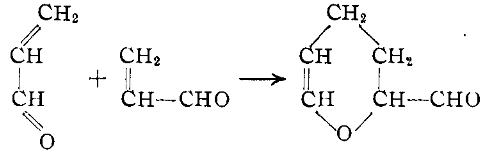
Reactions of Acrolein and Related Compounds. I. Addition of Vinyl Ethers

BY CURTIS W. SMITH, DOUGLAS G. NORTON AND SEAVER A. BALLARD

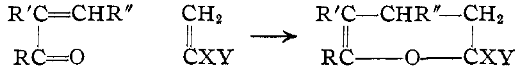
Simple thermal addition of acrolein and vinyl ethers has given the versatile 2-alkoxy-dihydropyrans in high yield. Divinyl ether, phenyl vinyl sulfide, methacrolein and crotonaldehyde also add to give 3,4-dihydro-2H-pyrans substituted in the 2- rather than the 3-position. The reaction is not reversible at 180° in the liquid phase; however, at 400° in the vapor phase 2-isobutoxy-3,4-dihydro-2H-pyran did revert in high yield to its antecedents, isobutyl vinyl ether and acrolein.

Introduction

The thermal dimerization of acrolein[1] and other conjugated carbonylic compounds involves the addition of one molecule activated at the carbon–carbon double bond to another molecule activated at the 1,4-positions of the conjugated system.



The addition has a formal similarity to the Diels–Alder reaction in that the conjugated carbonylic compound functions both as a diene (1,4-addition) and as a dienophile (1,2-addition). It was of interest to determine whether this reaction could be generalized to the extent that other 1,2-addenda could be found which would add to acrolein in the 1,4-positions. This objective has been achieved in the sense that quite a wide variety of ethylenic compounds have been added to acrolein and other conjugated carbonylic compounds in the desired manner to give a series of dihydropyrans.[2]



The presentation of these addition reactions has been divided into three parts: I, addition of vinyl ethers; II, addition of unsaturated esters, and methacrylonitrile; III, addition of olefins. A discussion of the reaction mechanism is presented in the third paper. As shown in the above equation, orientation during reaction is such that 2- rather than 3-substituted dihydropyrans are formed.

Vinyl alkyl ethers[3] react rapidly and in high

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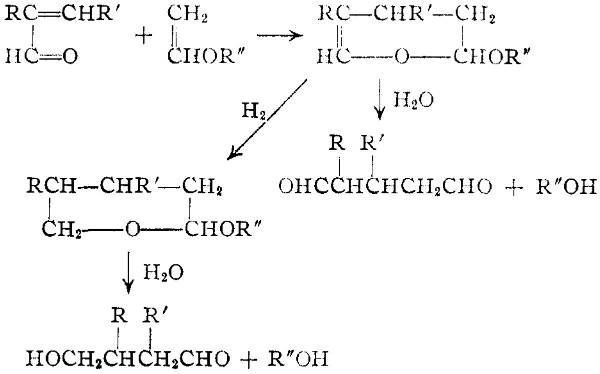
(1) K. Alder and E. Ruden, *Ber.*, **74**, ,920 (1941); K. Alder, H. Offermans and E. Ruden, *ibid.*, **74**, 905 (1941).

(2) C. W. Smith, D. G. Norton and S. A. Ballard, U. S. Patent 2,514,168 (1950).

(3) Since this paper was presented at the Philadelphia Meeting of the American Chemical Society, Division of Organic Chemistry, April 9, 1950, a paper on the addition of vinyl ethers to conjugated carbonylic compounds has been published by R. I. Longley and W. S. Emerson, THIS JOURNAL **72**, 3079 (1950). More recently Parham and Holmquist (*ibid.*, **73**, 913 (1951)) have presented the addition of vinyl *n*-butyl ether to crotonaldehyde.

yield with acrolein, crotonaldehyde and methyl vinyl ketone to give 2-alkoxy-3,4-dihydro-2H-pyrans. Divinyl ether, phenyl vinyl ether and phenyl vinyl sulfide react similarly with acrolein

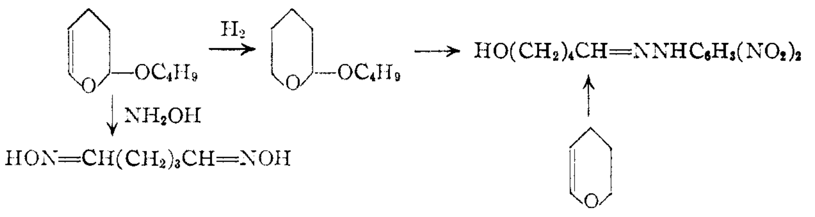


Hydrolysis of the 2-alkoxydihydropyrans provides a new and attractive method of preparing glutaraldehyde or substituted glutaraldehydes, which as a class have been previously only difficultly available. Hydrogenation of the 2-alkoxydihydropyrans followed by hydrolysis leads to δ-hydroxyvaleraldehyde or substituted δ-hydroxyvaleraldehydes.

Discussion

The conditions for carrying out the addition of vinyl ethers to unsaturated aldehydes are simple. The combined reagents are heated without solvent or catalyst for approximately one hour at 180°[4] in glass or steel pressure vessels. With methyl vinyl ether and acrolein initial autogeneous pressures of the order of 800 p.s.i.g. are developed and a high conversion (82%) to 2-methoxy-3,4-dihydro-2H-pyran was obtained after one hour reaction time.

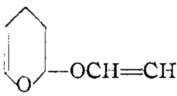
In the following section proof of structure for many of the adducts is presented. Evidence for 2-isobutoxy-3,4-dihydro-2H-pyran as the structure of the adduct of acrolein and isobutyl vinyl ether is as shown

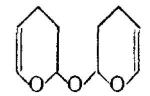


The presence of an olefinic bond and the absence of an aldehydic carbonyl in the adduct were shown by infrared absorption spectrum and by the absorption of one molar equivalent of hydrogen over Raney nickel at room temperature to give 2-isobutoxytetrahydropyran. Reaction of the 2-isobutoxytetrahydropyran with 2,4-dinitrophenylhydrazine gave a derivative which was established as the 2,4-dinitrophenylhydrazone of δ-hydroxyvaleraldehyde since a mixture with the same derivative from authentic dihydropyran caused no depression in melting point. Conversion of 2-isobutoxy-3,4-dihydro-2H-pyran to the dioxime of glutaraldehyde establishes the position of the double bond in the 5,6-position and the isobutoxy group in the 2-position since from location in these positions only does the dihydropyran ring contain two groupings, a vinyl ether and an acetal linkage, capable of hydrolysis to aldehyde linkages.

The isolation of the bis-2,4-dinitrophenylhydrazone of glutaraldehyde from adducts of acrolein with methyl vinyl ether, phenyl vinyl ether and phenyl vinyl sulfide establishes the structures of these materials as 2-methoxy-, 2-phenoxy- and 2-phenylthio-3,4-dihydro-2H-pyrans.

Two adducts were obtained from the reaction of acrolein with divinyl ether.

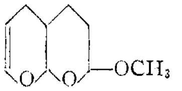




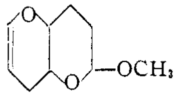
The fact that both adducts gave the bis-2,4-dinitrophenylhydrazone of glutaraldehyde corroborates the structures shown.

Similarly adducts of vinyl ethers with methacrolein and crotonaldehyde gave, respectively, the bis-2,4-dinitrophenylhydrazones of α-methylglutaraldehyde and β-methylglutaraldehyde. Apparently these derivatives are new. Longley and Emerson[3] established the structures of 2-methoxy-4-(and 5)-methyl-3,4-dihydro-1,2-pyrans by conversion to the corresponding α- and β-methylglutaric acids.

As can be seen from Table I small amounts of materials corresponding to the addition of two molecules of acrolein to one of methyl vinyl ether or isobutyl vinyl ether have been isolated. Of the two formulas, I and II, which seem feasible for these adducts, formula I is favored. There are two reasons for this choice. First, at least the major portion



I



II

of the adduct of two moles of acrolein to one of styrene (paper III, this series) has a structure similar to I. Second, without experimental evidence, the thermal trimer of acrolein has previously been assigned[5] a structure similar to I in which the methoxyl radical is replaced by a formyl grouping.

This addition reaction is not reversible at 180° in the liquid phase. Heating the adduct of methyl vinyl ether and acrolein, 2-methoxydihydropyran, at 180° for two hours under autogenous pressure caused no detectable reversion to acrolein and methyl vinyl ether. The reaction can be reversed at higher temperatures. Passing 2-isobutoxydihydropyran through a steel tube at 400° in the vapor phase caused a 47% conversion to acrolein and vinyl isobutyl ether in 94% yield. This reaction is in agreement with the known thermal cleavage of bonds beta to a double bond; and is

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(4) R. I. Longley, Jr., and W. S. Emerson[3] used much longer reaction times (12–30 hr.) and in some cases lower reaction temperatures.

(5) U. S. O. P. B. 70309 Fr. 7884–7896.

TABLE I

ADDITION OF VINYL ETHERS AND UNSATURATED ALDEHYDES

Conjugated carbonyl A	Vinyl ether B	Molar ratio B:A	Temp., °C.	Time, hr.	Adduct[b]	Conversion to product, %	Yield, %[h]
Acrolein	Methyl[a]	1.1	180	2	I I'[f]	84 0.5	88A, 98B
Acrolein	Methyl	1.1	180	1	I	82	88A, 98B
Acrolein	Methyl	1.1	180	0.5	I	67	88A, 98B
Acrolein	Ethyl	1	190	1	II	89	89A, 95B
Acrolein	Isobutyl	1	185	1	III III'[k]	86 0.5	95B
Acrolein	2-Ethylhexyl	1.1	190	2	IV	73	82A, B
Acrolein	Phenyl[i]	1	200	1	V	51	53A
Acrolein	Phenyl vinyl sulfide[j]	1	200	1	VI	77	77A, 98B
Acrolein	Divinyl ether	1	185	2	VII[e] VII'	30 45	....
Methacrolein	Methyl	1.12	190	2	IX	21	26A, 99B
Methacrolein	*n*-Butyl	1.1	195	2	X	31	......
Crotonaldehyde	Methyl	1.16	225	3	XI	64	84A, 91B
Crotonaldehyde	Isobutyl	1	185	2	XII	40	92B
Crotonaldehyde[c]	Isobutyl	1	130	6	XII	8	96B
Crotonaldehyde[d]	Isobutyl	1	130	6	XII	8	10B
Methyl vinyl ketone	Isobutyl	2	190	0.5	XIII	>20[g]	......

[a] Methyl vinyl ether. [b] See the following table for the structures of these adducts. [c] 1% Hydroquinone added. [d] 5% Di-*t*-butyl peroxide added. [e] Analysis of the product, b.p. 68–70° (50 mm.), $n^{20}D$ 1.4659 indicates it to be impure but formation of the bis-2,4-dinitrophenylhydrazone of glutaraldehyde indicates the presence of 2-vinoxy-3,4-dihydro-2H-pyran. [f] Analysis of the product, b.p. 98–100° (10 mm.), $n^{20}D$ 1.4180 indicates it to be derived from two molecules of acrolein and one of methyl vinyl ether. *Anal.* Calcd. for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.42, 63.30; H, 8.25, 8.20. A discussion of the structure is given earlier in this paper. [g] Due to accidental loss of material the conversion to product in this experiment is undoubtedly much higher than 20%. [h] A denotes yield based on conjugated carbonyl; B denotes yield based on vinyl ether. [i] Phenyl vinyl ether, b.p. 73–82° (50 mm.) was prepared by the addition of phenol to acetylene by the method of Shostakovski and Burmistrova (*C. A.*, **37**, 2336 (1943)). [j] Phenyl vinyl sulfide, b.p. 92–94° (25 mm.) was prepared by the addition of thiophenol to acetylene according to the method of Braun and Kirschbaum (*Ber.*, **53**, 1399 (1920)). [k] Analysis of the product, b.p. 74° (0.05 mm.) indicates it to be derived from two molecules of acrolein and one of vinyl isobutyl ether. *Anal.* Calcd. for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 67.45, 67.39; H, 9.57, 9.61. A discussion of the structure is given earlier in this paper.

analogous to the catalytic pyrolysis of dihydropyran over silica–alumina at 400–500° as carried out by Bremner, Jones and Beaumont[6] and by Wilson[7] to give acrolein and ethylene.

A summary of the details in these addition reactions is given in Tables I and II.

Acknowledgment.—The authors are grateful to Messrs. H. de V. Finch and K. E. Furman of these Laboratories for carrying out the pyrolysis of 2-isobutoxydihydropyran.

Experimental

Two examples of additions of vinyl ethers and unsaturated aldehydes cited in Table I are given in detail.

2-Isobutoxy-3,4-dihydro-2H-pyran.—A mixture of 436 g. (7.94 moles) of acrolein and 794 g. (7.94 moles) of isobutyl vinyl ether was heated at 185° for one hour in a nickel lined pressure vessel. After cooling, the product was distilled giving besides 44 g. of acrolein, 84 g. of isobutyl vinyl ether and 15 g. of acrolein dimer, 1063 g. of 2-isobutoxy-3,4-dihydro-2H-pyran boiling at 109° (100 mm.) and 24 g. of residue. This corresponds to an 86% conversion to 2-isobutoxy-3,4-dihydro-2H-pyran in 95% yield based on isobutyl vinyl ether. For the physical properties and analytical data on 2-isobutoxy-3,4-dihydro-2H-pyran and the 2,4-dinitrophenylhydrazone of glutaraldehyde prepared from it see Tables I and II.

The residue was distilled further and gave besides 6 g. more 2-isobutoxy-3,4-dihydro-2H-pyran, 8 g. of a high boiling oil (b.p. 74° (0.05 mm.)) derived from two molecules of acrolein and one of vinyl isobutyl ether. Analysis of this material and its derivative with 2,4-dinitrophenylhydrazine can be found in Table I. The final residue weighed 10 g.

Hydrogenation of 2-Isobutoxy-3,4-dihydro-2H-pyran.—A mixture of 52 g. of 2-isobutoxydihydropyran, 10 ml. of absolute ethanol and 5 g. of Raney nickel absorbed hydrogen slowly at room temperature and 40 p.s.i.g. and so the mixture was shaken at 1300 p.s.i.g. and 25° overnight. Distillation of the filtered product gave 47 g. (90% yield) of 2-isobutoxytetrahydropyran, b.p. 111° (100 mm.), $n^{20}D$ 1.4298, d^{20} 0.9214, which did not absorb bromine and had a minty odor.

The above product gave a yellow, alcohol-soluble 2,4-dinitrophenylhydrazone which melted at 110.3–111.3° and gave an analysis in agreement with the 2,4-dinitrophenylhydrazone of δ-hydroxyvaleraldehyde.

Anal. Calcd. for $C_{11}H_{14}N_4O_5$: C, 46.81; H, 5.00. Found: C, 46.74, 46.83; H, 5.05, 5.08.

A mixture of this material with the 2,4-dinitrophenylhydrazone of δ-hydroxyvaleraldehyde from authentic dihydropyran caused no depression in melting point.

Pyrolysis of 2-Isobutoxy-3,4-dihydro-2H-pyran.—A 118-g. sample of 2-isobutoxy-3,4-dihydro-2H-pyran was passed through a steel tube at 400° at the rate of 1 ml. per minute. Distillation of the 116 g. of product gave 20 g. of acrolein (b.p. 52–54°), 32 g. of isobutyl vinyl ether (b.p. 78–83°) (2,4-dinitrophenylhydrazone of acetaldehyde prepared, m.p. 168°) and 60 g. of unreacted 2-isobutoxy-3,4-dihydro-2H-pyran. Thus the only observed reaction was a 47% reversion to acrolein and isobutyl vinyl ether in a 96% yield.

2-Methoxy-5-methyl-3,4-dihydro-2H-pyran.—A mixture of 8 moles (560 g.) of methacrolein and 9 moles (522 g.) of methyl vinyl ether was heated rapidly in a closed steel vessel to 190° and held at that temperature for two hours. The product was cooled and distilled to give 425 g. of methyl vinyl ether, 117 g. of methacrolein boiling largely at 68–70°, 211 g. of a material boiling chiefly at 85.5° (100 mm.), $n^{20}D$ 1.4462, d^{20} 0.9785, 306 g. of methacrolein dimer[8] (2-

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(6) J. G. M. Bremner, D. G. Jones and S. Beaumont, *J. Chem. Soc.*, 1018 (1946).

(7) C. L. Wilson, *Nature*, **157**, 846 (1946).

(8) R. R. Whetstone (to Shell Development Company), U. S. Patent 2,479,283 (1949).

TABLE II

ADDUCTS OF VINYL ETHERS AND UNSATURATED ALDEHYDES

No.	Adduct	Boiling point °C.	Mm.	n^{20}D	d^{20}	Analyses, % Theory C	H	Found C	H
I	2-Methoxy-3,4-dihydro-2H-pyran[a,e]	127.6	760	1.4423	1.0013	63.13	8.83	63.09	8.86
II	2-Ethoxy-3,4-dihydro-2H-pyran[e]	132–132.3	760	1.4410	0.9712	65.59	9.44	65.52	9.40
								65.39	9.40
III	2-Isobutoxy-3,4-dihydro-2H-pyran[a,b]	109	100	1.4374	0.9225	69.19	10.32	68.87	10.37
		177	760					68.81	10.39
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
								74.74	6.87
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
								65.81	7.77
IX	2-Methoxy-5-methyl-3,4-dihydro-2H-pyran[e]	52–58	100	1.4462	0.9784	65.59	9.44	65.28	9.40
								65.33	9.43
X	2-*n*-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[e]	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 $C_{17}H_{16}N_8O_8$: 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. Sobecki (*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 $C_{18}H_{18}N_8O_8$: 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 $C_{18}H_{18}N_8O_8$: 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^{20}D 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 $C_7H_{12}O_2$: 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.

EMERYVILLE, CALIF.

RECEIVED MARCH 12, 1951

[CONTRIBUTION FROM THE SHELL DEVELOPMENT COMPANY]

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

BY CURTIS W. SMITH, DOUGLAS G. NORTON AND SEAVER A. BALLARD

Unsaturated esters (such as methyl acrylate, methyl methacrylate, vinyl acetate and methallyl acetate) 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 reports[1] of the similar

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(1) Schultz, Fiat Final report 1157, PB 85174, pp. 17, 18; Schultz and Wagner, *Angew. Chem.*, **62**, 112 (1950).