[Contribution from the Shell Development Company, Emeryville, California]

Reactions of Acrolein and Related Compounds. VI. Condensations with Amines

By H. Finch, E. A. Peterson and S. A. Ballard

Nitrogen-substituted 1,3-propenediamines have been prepared by the reaction of acrolein or methacrolein with primary or secondary amines. Hydrogenation of the 1,3-propenediamines gave 1,3-propanediamines. When the propenediamines were heated with other amines, one or both of the amine components of the propenediamine were replaced by the reacting amine. Amine exchange and hydrogenation reactions have been carried out concurrently over a nickel catalyst yielding unsymmetrical 1,3-propanediamines.

The reaction of acrolein with piperidine and with dimethylamine to give N,N,N′,N′-tetraalkylated-1,3-propenediamines has been described by Mannich, Handke and Roth.[1] This reaction has now been extended to methacrolein, and to primary amines. It has also been found that amine exchange reactions may be carried out between the 1,3-propenediamines and alkylamines. Either one or both of the amine groups of the propenediamine can be replaced depending, among other factors,[2] on the extent of substitution of nitrogen of the substituting amine and of the amine groups of the propenediamine. With the alkylamines and ammonia, amine exchange occurs rapidly with one amine group of the propenediamine if the substituting amine is of the same or lower order than the amine group of the propenediamine. Substitution of the second amine group is slow with substituting amines of the same order, and rapid with amines of higher order than the substituted group. The main products of these amine exchange reactions are summarized in the reaction system.

For example the reaction of N,N′-diisopropyl-1,3-propenediamine with 1,3-dimethylbutylamine gave mainly N-(1,3-dimethylbutyl)-N′-isopropyl-1,3-propenediamine and a small amount of the disubstituted product, N,N′-di-(1,3-dimethylbutyl)-1,3-propenediamine. N,N′-Diisopropyl-1,3-propenediamine and piperidine gave 1,3-bis-(1-piperidyl)-propene, and none of the product corresponding to substitution of a single amine group. Reaction of N,N′-diisopropyl-1,3-propenediamine, ammonia and hydrogen over a nickel catalyst gave N-isopropyl-1,3-propanediamine. In this reaction only very small amounts of the disubstitution product, 1,3-propanediamine, were formed.

The position of the double bond in these propenediamines has not been established. In the propenediamines prepared from acrolein and primary amines isomers involving the $>\mathrm{C{=}C{-}N}< \longrightarrow >\mathrm{C{-}C{=}N}{-}$ system are predictable; however, comparison of the infrared spectra of representative propenediamines prepared from acrolein and secondary amines, in which this type of isomerization is not possible, with propenediamines from acrolein and primary amines failed to indicate differences which could be attributed to the olefinic bond.

Catalytic hydrogenation of the 1,3-propenediamines yields the corresponding saturated propanediamines and varying amounts of cleavage products. If the reduction is carried out in the presence of an amine, hydrogenation and amine exchange may occur simultaneously. Thus hydrogenation of N,N′-diisopropyl-1,3-propenediamine yields mainly N,N′-diisopropyl-1,3-propanediamine and somewhat smaller amounts of isopropyl-*n*-propylamine and isopropylamine. If the hydrogenation is carried out in ammonia solution the main product is N-isopropyl-1,3-propanediamine.

The reaction of diisopropylamine with acrolein failed to give a stable propenediamine. Distillation of the crude condensation product yielded diisopropylamine and a polymer. However hydrogenation of the condensation product in ammonia over a nickel catalyst gave an appreciable yield of N,N-diisopropyl-1,3-propanediamine, indicating that the propenediamine was probably present in the crude reaction product of diisopropylamine and acrolein.

Experimental

Properties of the propenediamines and propanediamines prepared from acrolein and methacrolein are listed in Table I. Typical preparations are described below.

Preparation of N,N′-Diisopropyl-1,3-propenediamine.—Forty-two grams of acrolein was added at a rate of one-half gram per minute to a stirred mixture of 40 g. of anhydrous potassium carbonate in 224 g. of isopropylamine at a temperature of 5–10°. Potassium carbonate was removed by filtration and the product was fractionated at 4 mm. pressure yielding 64 g. of N,N′-diisopropyl-1,3-propenediamine (55% conversion on acrolein) and 22 g. of higher boiling amines. Properties of the propenediamine are given in Table I.

Preparation of N,N′-Diisopropyl-1,3-propanediamine.—The crude isopropylamine–acrolein condensation product prepared from 153 g. of acrolein and 790 g. of isopropylamine was hydrogenated over Raney nickel at 105° and 1000 p.s.i.g. Hydrogen absorption required 6 hours. Fractionation of the products gave 105 g. of isopropylpropylamine (b.p. 97–98°, equiv. wt., 100), 231 g. of N,N′-diisopropyl-1,3-propanediamine (53% conversion on acrolein) and 47 g. of higher boiling amines. Properties of the diamine are given in Table I.

Reaction of N,N′-Diisopropyl-1,3-propenediamine with 1,3-Dimethylbutylamine.—A mixture of 77 g. of N,N′-diisopropyl-1,3-propenediamine and 202 g. of 1,3-dimethylbutylamine[3] was refluxed for two hours under a fractionating column. A total of 35 g. of isopropylamine was recovered at the stillhead. When no more isopropylamine was produced the kettle contents were distilled at reduced pressure yielding 54 g. of N-(1,3-dimethylbutyl)-N′-isopropyl-1,3-propenediamine (double bond position uncertain) and 17 g. of N,N′-di-(1,3-dimethylbutyl)-1,3-propenediamine. Hydrogenation of the propenediamines in 1,3-dimethylbutylamine as solvent gave the saturated propanediamines. Properties of the products were in agreement with those of N,N′-di-(1,3-dimethylbutyl)-1,3-propanediamine prepared from 1,3-dimethylbutylamine, acrolein and hydrogen, and N-(1,3-dimethylbutyl)-N′-isopropyl-1,3-propanediamine prepared by the reaction of N,N′-di-(1,3-dimethylbutyl)-1,3-propenediamine with isopropylamine and hydrogen (Table I).

Preparation of N-Isopropyl-1,3-propanediamine.—A solution of 28 g. of acrolein in 45 ml. of ether was added slowly

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(1) Mannich, Handke and Roth, *Ber.*, **69**, 2112 (1936).

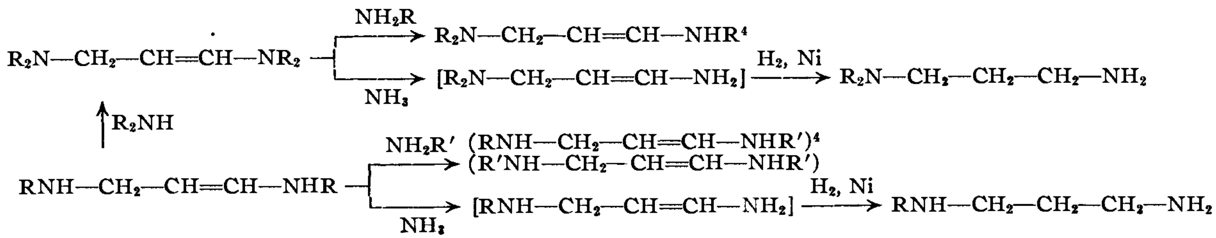
(2) Steric factors, relative basicity of the exchange amine and the propenediamine, and factors influencing equilibrium may be important in governing the rate of exchange.

(3) Prepared by the method of E. J. Schwoegler and H. Adkins, This Journal, **61**, 3501 (1939).

TABLE I

Compound	B.p. °C.	B.p. Mm.	Refractive index, n^{20}_D	Density, d^{20}_4	Analyses, % Found C	Found H	Found N	Found Basicity, eq./100 g.	Calculated Formula	Calculated C	Calculated H	Calculated N	Calculated Basicity eq./100 g.	Yield, % on acrolein or methacrolein
Products from the reaction of acrolein with secondary amines and hydrogen														
N,N,N',N'-Tetraethyl-1,3-propenediamine	82	5	1.4650	0.8308	71.60	13.08	15.2	1.085	$C_{11}H_{24}N_2$	71.68	13.12	15.2	1.086	65
N,N,N',N'-Tetraethyl-1,3-propanediamine	133	80	1.4381	.8101	70.73	13.86	14.6	1.052	$C_{11}H_{26}N_2$	70.90	14.07	15.0	1.073	26[a]
Products from acrolein and methacrolein with primary amines and hydrogen														
N,N'-Diethyl-1,3-propanediamine	174	760		.8207	64.12	13.84	20.7	1.525	$C_7H_{18}N_2$	64.56	13.93	21.5	1.536	30[a]
N,N'-Di-(2-ethylhexyl)-1,3-propanediamine	112–116	0.5	1.4575		76.52	14.01	9.3	0.656	$C_{19}H_{42}N_2$	76.44	14.18	9.4	0.670	29[a]
N,N'-Diisopropyl-1,3-propenediamine	46	4	1.4323	.8003	69.20	12.90	18.0	1.28	$C_9H_{20}N_2$	69.17	12.90	17.9	1.282	55
N,N'-Diisopropyl-1,3-propanediamine	77	15	1.4325	.8048	68.09	14.00	17.8	1.26	$C_9H_{22}N_2$	68.29	14.01	17.7	1.265	53[a]
N,N'-Di-(1,3-dimethylbutyl)-1,3-propenediamine	95	0.5		.8192	75.16	13.11	11.4	0.799	$C_{15}H_{32}N_2$	74.93	13.42	11.6	0.832	40
N,N'-Di-(1,3-dimethylbutyl)-1,3-propanediamine	124	5	1.4438	.8177	74.25	14.10	11.4	0.825	$C_{15}H_{34}N_2$	74.31	14.13	11.5	0.825	51[a]
N.N'-Diisopropyl-2-methyl-1,3-propenediamine	80	20	1.4282	.7956	70.66	13.00	13.5	1.159	$C_{10}H_{22}N_2$	70.53	13.02	16.4	1.174	76
N,N'-Diisopropyl-2-methyl-1,3-propanediamine	89	20	1.4319	.8054	69.74	13.87	15.8	1.13	$C_{10}H_{24}N_2$	69.70	14.04	16.3	1.161	58[a]
Products from the reaction of 1,3-propenediamines with amines, ammonia, and hydrogen														
3-(1-Piperidyl)propylamine	101	25	1.4757	.9024	67.17	12.79	19.5	1.392	$C_8H_{18}N_2$	67.55	12.75	19.7	1.406	68[b]
N-Isopropyl-3-(1-piperidyl)propylamine	77–80	3	1.4617	.8661	71.32	13.12	14.9	1.07	$C_{11}H_{24}N_2$	71.68	13.12	15.2	1.086	23[b]
N-Propyl-3-(1-piperidyl)-propylamine	86–88	3	1.4638	.8690	71.66	13.12	15.4	1.08	$C_{11}H_{24}N_2$	71.68	13.12	15.2	1.086	49[b]
N,N-Diethyl-1,3-propanediamine	169	760	1.4413	.8264	64.45	13.85	21.4	1.511	$C_7H_{18}N_2$	64.56	13.93	21.5	1.535	79[c,d]
N-Phenyl-N',N'-diethyl-1,3-propenediamine	85–87	1			76.47	9.80	13.6	0.477	$C_{13}H_{20}N_2$	76.42	9.87	13.7	0.489	39[d]
N-Ethyl-N'-isopropyl-1,3-propanediamine	183	760	1.4348	.8101	66.74	13.98	19.2	1.39	$C_8H_{20}N_2$	66.60	13.97	19.4	1.386	40[d]
N-Isopropyl-1,3-propanediamine	162	760	1.4417	.8303	62.04	13.76	24.4	1.72	$C_6H_{16}N_2$	62.01	13.88	24.2	1.720	64[d]
N-(1,3-Dimethylbutyl)-N'-isopropyl-1,3-propanediamine	89	5	1.4392	.8104	72.10	14.00	13.6	0.988	$C_{12}H_{23}N_2$	71.93	14.08	14.0	0.998	58[3]
N,N-Diisopropyl-1,3-propanediamine	57	3	1.4472	.8386	68.08	13.97	17.7	1.26	$C_9H_{22}N_2$	68.29	14.01	17.7	1.265	38[2]

[a] Hydrogenation of the crude aldehyde–amine condensation product. [b] Concurrent amine exchange and hydrogenation of the crude aldehyde–amine condensation product. [c] Concurrent amine exchange and hydrogenation of the 1,3-propenediamine. [d] Yield on 1,3-propenediamine.



to 150 g. of isopropylamine at 5–10°. Excess amine and ether were removed under vacuum and the crude product (90 g.) was hydrogenated in solution in 52 g. of ammonia at 100° and 2000 p.s.i.g. using Raney nickel as catalyst. Fractionation of the product gave 0.7 g. of amines boiling in the range of 1,3-propanediamine, 37 g. of N-isopropyl-1,3-propanediamine (64% conversion on acrolein), and 11 g. of higher boiling material. Properties of the diamine are listed in Table I.

Reaction of N,N'-Diisopropyl-1,3-propenediamine with Piperidine.—A mixture of 75 g. of N,N'-diisopropyl-1,3-propenediamine and 172 g. of piperidine was refluxed for two hours under a fractionating column. A total of 40 g. of iso-

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(4) The double bond position in these 1,3-propenediamines has not been established.

propylamine was withdrawn from the stillhead. The kettle contents were fractionated at reduced pressure yielding 75 g. of 1,3-bis-(1-piperidyl)-propene, b.p. 96–100° (0.5 mm.); equiv. wt. 101, calcd. $C_{13}H_{24}N_2$ 104; lit.[1] b.p. 150–152°, 12 mm.) and 11 g. of higher boiling amines. Hydrogenation of the propenediamine gave 1,3-bis-(1-piperidyl)-propane, b.p. 116–118° (4 mm.), equiv. wt., 105, calcd. $C_{13}H_{26}N_2$ 105; lit.[1] b.p. 135–137° (12 mm.).

Preparation of N-Phenyl-N',N'-diethyl-1,3-propenediamine.—A mixture of 159 g. of N,N,N',N'-tetraethyl-1,3-propene diamine (prepared from acrolein and diethylamine) and 186 g. of aniline was refluxed for 1.5 hours under a fractionating column at 15 mm. pressure and a kettle temperature of 105°. Diethylamine was collected in a Dry Ice trap and 60 g. of aniline was slowly distilled from the mixture. Fractionation of the kettle contents gave 69 g. of N-phenyl-N',N'-diethyl-1,3-propenediamine and 64 g. of higher boiling amines. Properties of the propenediamine are listed in Table I.

EMERYVILLE, CALIFORNIA RECEIVED OCTOBER 12, 1951

[CONTRIBUTION FROM SHELL DEVELOPMENT COMPANY]

Reactions of Acrolein and Related Compounds. VII. Reactions of 2-Alkoxydihydropyrans

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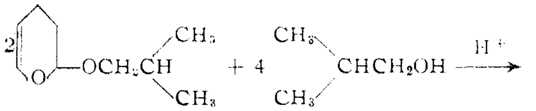
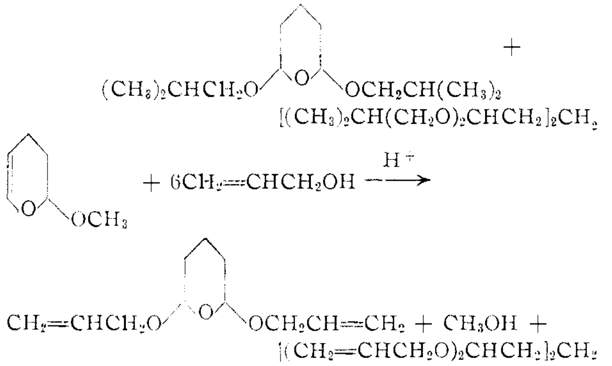
Recently a new class of compounds, the 2-alkoxy-3,4-dihydro-2H-pyrans have been made readily available by thermal addition of vinyl ethers to conjugately unsaturated carbonylic compounds. Reaction of these agents with alcohols, capric acid, phenol and hydrogen cyanide are reported. Reaction with ammonia leads to pyridine and other nitrogen bases. Thermal cleavage gives the isomeric 5-alkoxy-4-pentenals.

2-Alkoxy-3,4-dihydro-2H-pyrans, a new class of compounds, have been prepared[1-4] by heating conjugated carbonylic compounds, such as acrolein, with vinyl ethers. Reactions of the 2-alkoxy-3,4-dihydro-2H-pyrans may be related to the presence of a vinyl ether and an acetal linkage sharing a single oxygen atom. Hydrolysis leads to glutaraldehyde and substituted glutaraldehydes.[2,5] An interesting by-product isolated for the first time from hydrolysis of 2-methoxy-3,4-dihydro-2H-pyran is 2-(6-methoxytetrahydropyranyl) ether. Hydrogenation[3,4] leads to the 2-alkoxytetrahydropyrans which have been converted to 2-hydroxytetrahydropyran by hydrolysis. Hydrogenation in aqueous solution with catalytic amounts of acetic acid leads to 1,5-pentanediols.[6] Other novel reactions of the 2-alkoxydihydropyrans are presented in the following sections.

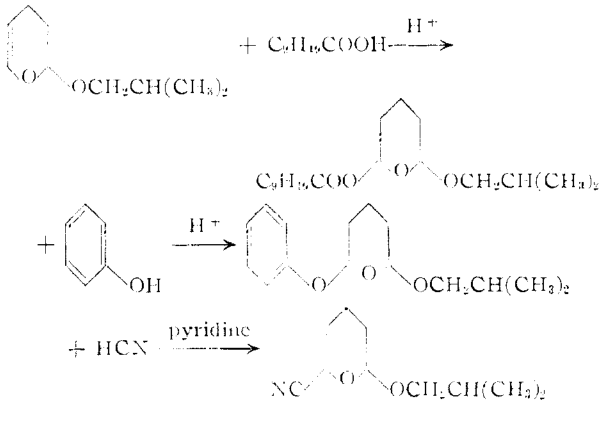
Reactions with Alcohols.—In acidic solution, with alcohols, the 2-alkoxydihydropyrans enter into a fairly complex equilibrium involving 2,6-dialkoxytetrahydropyrans (by addition to the vinyl ether) and glutaraldehyde tetraalkyl acetals (by alcoholysis of the vinyl ether and acetal). If the alkoxy group of the entering alcohol is different from that attached to the dihydropyran, then either mixed products are formed or the alkoxy group originally present may be displaced completely under controlled conditions:





Thus the acid-catalyzed reaction of isobutyl alcohol with 2-isobutoxydihydropyran has given 2,6-diisobutoxytetrahydropyran and glutaraldehyde tetraisobutyl acetal; and the reaction of 2-methoxydihydropyran with excess allyl alcohol has given 2,6-diallyloxytetrahydropyran and glutaraldehyde tetraallyl acetal.

Addition of Acidic Agents.—From the addition of capric acid to 2-isobutoxydihydropyran with a trace of hydrochloric acid as catalyst, an 87% yield of the caprate of 2-isobutoxy-6-hydroxytetrahydropyran was obtained.



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[1] C. W. Smith, D. G. Norton and S. A. Ballard, U. S. Patent 2,514,168, 1950.

[2] R. I. Longley and W. S. Emerson, THIS JOURNAL, **72**, 3079 (1951).

[3] C. W. Smith, D. G. Norton and S. A. Ballard, *ibid.*, **73**, 5267 (1951).

[4] W. E. Parham and H. E. Holmquist, *ibid.*, **73**, 913 (1951).

[5] C. W. Smith and S. A. Ballard, U. S. Patent 2,546,018 (1951).

[6] C. W. Smith, U. S. Patent 2,546,019 (1951).