

at 17 mm. This was shown to be mostly 6-methoxy-tetralin by the oxidation to 6-methoxy- α -tetralone which is described below.

6-Methoxy- α -tetralone.—The product of the reduction above was oxidized by the method of Burnop, Elliott and Linstead.¹⁵ After completion of the oxidation the product was isolated by the method of Schwenk and Papa.¹⁵ The crude 6-methoxy- α -tetralone thus obtained was recrystallized from dilute methanol. In this way, 6-methoxy- α -tetralone was obtained in 60–65% yield and had m. p. 78–79° (reported m. p. 77.5°,¹⁶ 80°,^{16a} 82°^{16b}). The semicarbazone prepared in methanol in the presence of pyridine had m. p. 236–237° (reported m. p. 235°).^{16b}

Hydrogenation of β -Naphthoic Acid in the Presence of Base.—The hydrogenation was carried out in the usual manner, using a solution of 43 g. of β -naphthoic acid in warm dioxane (total volume of 250 ml.). In the presence of several cc. of Raney nickel and 3 ml. of a 40% sodium hydroxide solution. The initial pressure was 3400 psi. After about two hours at 150° the hydrogenation was completed. The only product isolated was 5,6,7,8-tetrahydro- β -naphthoic acid, m. p. 153–154° from benzene-ligroin (reported m. p. 154–155°).¹⁶ The isomeric 1,2,3,4-tetrahydro- β -naphthoic acid has m. p. 96°.¹⁷

This reduction was repeated using enough alkali so the acid would be entirely in the form of its salt: 1.72 g. of β -naphthoic acid was placed in a small hydrogenation bomb with 20 ml. of water and 0.4 g. of sodium hydroxide. One gram of Raney nickel was added to the suspension and

hydrogenation was conducted under the same conditions of temperature and pressure as above. The reduction was complete in less than an hour. Acidification of the filtered solution gave 1.3 g. of the tetrahydro acid, m. p. 145–150°, raised by recrystallization from benzene-ligroin to 153–155°.

Acknowledgment.—The author wishes to express his appreciation to Dr. E. Leon Foreman for his interest in this work.

Summary

The catalytic hydrogenation of β -naphthol over Raney nickel is described. It is shown that in neutral or acidic medium the product is mainly *ar*-tetrahydro- β -naphthol, while *ac*-tetrahydro- β -naphthol becomes the principal product in the presence of added base.

The catalytic hydrogenation of β -naphthyl methyl ether over Raney nickel in an acidic medium is shown to result in the reduction of the unsubstituted ring with the formation of 6-methoxytetralin.

A simple preparation of 6-methoxy- α -tetralone is outlined.

The theoretical implications of these findings are discussed.

MILWAUKEE, WISCONSIN

RECEIVED AUGUST 9, 1946

(15) Schwenk and Papa, *THIS JOURNAL*, **67**, 1432 (1945).

(16) Newman and Zahm, *THIS JOURNAL*, **65**, 1097 (1943).

(17) v. Sowsinski, *Ber.*, **24**, 2354 (1891).

[CONTRIBUTION FROM THE PIONEERING RESEARCH SECTION, RAYON TECHNICAL DIVISION, E. I. DU PONT DE NEMOURS AND COMPANY, INC.]

The Preparation of N-Substituted Diamines¹

BY EMERSON L. WITTBECKER, RAY C. HOUTZ AND W. W. WATKINS

A number of disecundary and secondary-primary diamines were required for an investigation of N-substituted polyamides. The reduction of aldimines was chosen for the syntheses of these intermediates since this method has been one of the most successful for the preparation of secondary aliphatic amines.²

Dialdimines were readily prepared by adding two moles of an aldehyde to an aqueous solution of one mole of diamine. With compounds such as *i*-butyraldehyde or benzaldehyde, it was necessary only to keep the reaction temperature below the boiling point of the aldehyde. With butyraldehyde, propionaldehyde and acetaldehyde, the temperature was kept at 0–5°, since the dialdimines derived from lower or less complex aldehydes were less stable. N,N'-Di-*i*-butylidenehexamethylenediamine, for example, could be distilled in good yields, while N,N'-diethylidenehexamethylenediamine became resinous and only a 29% yield could be obtained on distillation. It was desirable, therefore, to purify the aldehydes and diamines used and then to hydrogenate the

dialdimines without drying or distilling. If the water separated as a layer, it was removed, otherwise it remained during the hydrogenation. This is in contrast to recent work² where it was reported that secondary aliphatic amines were obtained only when the aldimines were dried and distilled before hydrogenation.

Monoalldimines were prepared by adding one mole of an aldehyde to two moles of an aqueous diamine solution. While dialdimine formation was not precluded, it was reduced to such an extent that good yields of N-monosubstituted diamines were obtained after hydrogenation of the reaction mixture.

Three methods of carrying out the reduction of aldimines have been tried. A sodium-ethanol reduction was used successfully in two cases, but the most convenient laboratory method was found to be a low-pressure catalytic hydrogenation with platinum oxide catalyst. In most cases, no solvent was used except a small amount of ethanol to assure homogeneity of the undried dialdimine layer. A high pressure catalytic hydrogenation with Raney nickel catalyst was used in the preparation of N,N'-dibenzylhexamethylenediamine and N-benzylhexamethylenediamine and the

(1) This paper was presented before the Organic Division at the Atlantic City meeting of the American Chemical Society, April, 1946.

(2) Campbell, Sommers and Campbell, *THIS JOURNAL*, **66**, 82 (1944).

TABLE I
 N-SUBSTITUTED DIAMINES RHN(CH₂)_n NHR'

R and R' =	n	Preparation Method ^a	Yield, %	B. p., ° C. (mm.)	Neut. equiv.		n _D ²⁰	d ₄ ²⁰	Dihydrochloride % Cl	
					Found	Calcd.			Found	Calcd.
<i>i</i> -Butyl	6	A	81 ^b	116-117 (3)	114.6	114.2	1.4425	0.8160	23.13	23.55
<i>n</i> -Butyl	6	A	65	141 (6)	114.9	114.2	1.4472	^c	23.18	23.55
<i>n</i> -Propyl	6	A	25	106-108 (4)	101.5	100.2	1.4460	^c	29.95	25.94
<i>i</i> -Butyl	10	A	68	134-135 (3)	142.2	142.3	1.4486	.8240	19.62	19.83
Benzyl	6	B	78 ^d	190 (2)	147.6	148.2	1.5440	.9876	18.76	19.20
Hexahydrobenzyl	6	A ^e	85	195 (3)	153.7	154.2
Anisyl	6	A	86	^f	178.6	178.2
<i>p</i> -Dimethylaminobenzyl	6	A	32	^g	189.0 ^h	191.3
Ethyl	6	D	76	105 (6)	86.6	86.1	1.4434	.8226	28.63	28.93
Allyl	6	D	30	103-104 (3)	101.1	98.1	1.4664	.8581	25.99	26.35
R = H, R' =										
<i>i</i> -Butyl	6	A	46	88 (2)	86.3	86.1	1.4471	.8308	28.70	28.93
<i>n</i> -Butyl	6	A	54	96 (2)	86.6	86.1	1.4500	.8360	28.75	28.93
<i>n</i> -Propyl	6	A	48	136 (30)	79.4	79.2	1.4491	.8351	30.67	30.65
Ethyl	6	A	26	112-113 (26)	73.2	72.1	1.4500	.8449	32.57	32.66
Benzyl	6	A	56	128-129 (3)	103.6	103.2	1.5162	.9492	25.07	25.39

^a Methods A, B and C are reduction of aldimines by PtO₂-H₂, Raney nickel-H₂ and sodium-ethanol, respectively. D is a monoamine plus a dibromide. ^b The yield was 65% using Method C. ^c Solidified during this determination. ^d Yields were 50 and 64% for Methods A and C. ^e The dialdime was prepared using tetrahydrobenzaldehyde, C=C and C=N were reduced simultaneously. ^f Crystallized from ethanol, m. p., 70-71° (uncor.). ^g Crystallized from ethanol, m. p., 64° (uncor.). Nitrogen anal.: Calcd. for C₂₄H₃₅N₄: N, 14.64. Found: 14.36. ^h End-point was not sharp.

yields, in this particular case, were better than those from low-pressure reduction. The hydrogenation conditions were more critical however, because of the higher temperature necessary.

Of the fifteen N-substituted diamines synthesized only two were not easily obtainable from the corresponding aldimines. N,N'-Diethylhexamethylenediamine was obtained only in low yields by this method, perhaps because of the instability of the N,N'-diethylidenehexamethylenediamine³ while preparation of N,N'-diallylhexamethylenediamine required a method which did not involve hydrogenation. The reaction⁴ of monoamines with dihalides was satisfactory for the preparation of these two compounds. In order to inhibit the formation of tertiary amines and to obtain good yields of secondary amines, the dihalide was added dropwise to an excess of monoamine. With a mole ratio of allylamine to hexamethylene dibromide of five to one, a 30% yield of N,N'-diallylhexamethylenediamine was obtained. With a ratio of ethylamine to dibromide of forty-nine to one, a 76% yield of N,N'-diethylhexamethylenediamine resulted.

The data on the N-substituted diamines prepared are summarized in Table I.

Experimental

Aldimines.—A typical preparation is described: To 386 g. (2 moles) of a 60% aqueous hexamethylenediamine solution was added with stirring 288 g. (4 moles) of distilled *i*-butyraldehyde. The temperature was kept at 50-55° with an ice-bath. The organic dialdime layer was separated from the water layer and hydrogenated without further purification. Monaldimines were pre-

pared in a similar manner except that only 1 mole of aldehyde was used for every 2 moles of diamine, and no water layer separated.

Aldimines were formed from *i*-butyraldehyde, benzaldehyde, anisaldehyde and *p*-dimethylaminobenzaldehyde at a reaction temperature of 50-55°. For acetaldehyde, propionaldehyde, *n*-butyraldehyde and tetrahydrobenzaldehyde, 0-5° was used.

Hydrogenation.—A low pressure catalytic hydrogenation was used for the reduction of the majority of aldimines (Method A, Table I). By using a Parr Catalytic Apparatus equipped with a one-liter Pyrex bottle, relatively large quantities of N-substituted diamines were readily prepared. A typical hydrogenation is described.

Platinum oxide⁵ (0.7 g.) was reduced in the absence of the hydrogen acceptor by shaking a suspension of the catalyst in 50 ml. of absolute ethanol with hydrogen for ten minutes. To this mixture was then added the N,N'-diisobutylidenehexamethylenediamine layer from 4 moles of isobutyraldehyde and 2 moles of hexamethylenediamine. The 50 ml. of ethanol used during the activation of the catalyst was ordinarily sufficient to assure homogeneity of the undried dialdime layer. (In the cases of the dialdimines from anisaldehyde and *p*-dimethylaminobenzaldehyde, which were crystalline, it was necessary to use enough ethanol to dissolve them.) The hydrogenation was started at 55 lb./sq. in. pressure and room temperature. When hydrogen was no longer absorbed, the catalyst was removed by filtration and the N,N'-di-*i*-butylhexamethylenediamine was distilled.

N,N'-Dibenzylhexamethylenediamine was also prepared using a high-pressure hydrogenation with Raney nickel catalyst. The wet dialdime layer from 4 moles of distilled benzaldehyde and 2 moles of hexamethylenediamine was dissolved in 500 g. of cyclohexane and 1800 ml. of ethanol. This solution was hydrogenated in a 2.5-liter bomb using 40 g. of Raney nickel catalyst, 100-110° and an initial pressure of 4000 lb./sq. in. When hydrogen was no longer absorbed, the catalyst was removed by filtration, the solvents were removed by distillation, and the N,N'-dibenzylhexamethylenediamine was distilled. Good yields depended upon a rapid complete hydrogenation.

The sodium-ethanol reductions (Method C) were car-

(3) Cf. N-ethylhexamethylenediamine was prepared in 26% yield by hydrogenation of the N-ethylidenehexamethylenediamine.

(4) Martin, U. S. Patent 2,334,782.

(5) From American Platinum Works.

ried out essentially as described for N,N'-dibenzylethylenediamine.⁶

Reaction of Monoamines with Dihalides.—N,N'-Diethylhexamethylenediamine was prepared from ethylamine and hexamethylene dibromide: In a 3-liter, three-necked, round-bottomed flask equipped with a dropping funnel, mechanical stirrer and Dry Ice condenser was placed 1102 g. (24.5 moles) of ethylamine. Hexamethylene dibromide (122 g., 0.5 mole) was added dropwise over a period of one hour to the refluxing ethylamine. It was occasionally necessary to cool the flask with ice. After the reaction mixture had been stirred for an additional one and one-half hours, the excess ethylamine was distilled and recovered for use in a second run (830 g. of ethylamine and 92 g. of hexamethylene dibromide). To the combined product was added a concentrated aqueous solution of 125 g. of sodium hydroxide. The oil

(6) Mason, *Ber.*, **20**, 270 (1887).

layer was dissolved in ether and dried with anhydrous sodium sulfate. The ether was evaporated and the N,N'-diethylhexamethylenediamine was distilled.

N,N'-Diallylhexamethylenediamine was prepared in the same manner except that the mole ratio of allylamine to dibromide was only five to one and the temperature of the reaction was 25–35°.

Summary

Fifteen N-substituted diamines (disubstituted and secondary-primary) have been synthesized through (1) the catalytic hydrogenation of dialdimines or amine-aldimines or (2) the reaction of monoamines with dihalides. The first method was used in all but two cases.

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RECEIVED OCTOBER 30, 1946

[CONTRIBUTION FROM THE CENTRAL RESEARCH DEPARTMENT, MONSANTO CHEMICAL COMPANY]

Copolymerization. I. The Mechanism of Emulsion Copolymerization of Styrene and Acrylonitrile

BY REID G. FORDYCE AND EARL C. CHAPIN

The general theory of chain propagation processes in vinyl copolymerizations has been discussed by several investigators,¹⁻⁸ who have shown that the composition of copolymer molecules forming in a given system at any time is dependent primarily upon the monomer concentrations at that instant. Moreover, general equations describing the monomer-polymer composition relationship have been derived.^{1,2,5} Experimental data determined for mass polymerizations have been reported^{2,4,6,7} showing good agreement with the general equations and the numerical values of several propagation rate constant ratios have been elucidated. It appeared possible therefore that a comparison of the monomer-polymer composition curve obtained by emulsion polymerization with the curve obtained by mass polymerization might throw some light on the mechanism of emulsion polymerization.

For this work, styrene and acrylonitrile were selected as co-monomers, since Mayo, Lewis and Hulse⁴ had already determined their propagation rate constant ratios for bulk polymerization. Copolymerizations were carried out in mass using an oil soluble catalyst and in emulsion using an oil soluble and a water soluble catalyst. The polymerizations were allowed to proceed to low conversions (mainly <4%) and the initial polymer was isolated and purified. The amount of combined acrylonitrile in the initial copolymer was determined by duplicate Kjeldahl analyses.

(1) Alfrey and Goldfinger, *J. Chem. Phys.*, **12**, 205, 322 (1944).

(2) Mayo and Lewis, *THIS JOURNAL*, **66**, 1594 (1944).

(3) Wall *ibid.*, **66**, 2050 (1944).

(4) Lewis, Mayo and Hulse, *ibid.*, **67**, 1701 (1945).

(5) Walling and Briggs, *ibid.*, **67**, 1774 (1945).

(6) Alfrey and Lavin, *ibid.*, **67**, 2044 (1945).

(7) Alfrey, Merz and Mark, *J. Polymer Research*, **1**, 37 (1946).

(8) Alfrey and Goldfinger, *J. Chem. Phys.*, **14**, 115 (1946).

Results and Discussion

The results of the investigation are summarized in Table I from which the monomer-copolymer composition curves, Fig. 1, for the three series of experiments were drawn. In determining the monomer reactivity ratios for styrene and acrylonitrile, the differential form of the Mayo and

TABLE I

Monomer, mole % acrylonitrile	Time at polymerization temp., min.	Wt. % conversion	Nitrogen analyses, %		Copolymer, mole % acrylonitrile
			I	II	
(Mass polymerization at 75°, 0.05% Bz ₂ O ₂)					
6.46	120	2	2.20	2.16	15.0
12.25 ^a	120	2	3.46	3.44	22.8 ^a
22.47	120	2	4.63	4.19	28.2
32.92	120	2	5.69	5.50	34.6
48.60 ^a	120	2	6.94	6.86	41.0 ^a
62.63	120	2	7.90	7.87	45.5
80.28 ^a	...	2	9.85	9.83	53.8 ^a
(Emulsion polymerization at 60°, 0.1% Bz ₂ O ₂)					
9.36	124	0.7	2.20	2.20	15.1
17.90	...	0.7	3.54	3.41	22.9
32.92	130	4.9	5.51	5.50	34.0
45.68	66	2.6	6.34	6.10	37.7
66.25	338	3.4	7.54	7.44	43.7
(Emulsion polymerization at 75°, 0.2% K ₂ S ₂ O ₈)					
8.24	195	3.1	1.99	1.86	13.4
14.86	28	8.5	3.27	3.15	21.4
18.83	25	3.2	3.69	3.69	24.2
24.93	20	1.9	4.37	4.34	28.0
36.32	10	6.6	5.60	5.58	34.5
45.69	20	3.0	6.39	6.38	38.5
66.25	...	3.6	7.72	7.48	44.2
94.64	...	1.7	12.77	12.65	64.6

^a Data used for elucidating σ and μ .