[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Preparation of Unsymmetrical Secondary Aliphatic Amines[1]

BY KENNETH N. CAMPBELL, ARMIGER H. SOMMERS AND BARBARA K. CAMPBELL

Until recently unsymmetrical secondary aliphatic amines have been difficult to prepare in quantity. One of the most promising methods of preparing these amines would appear to be by reduction of aliphatic aldimines. A survey of the literature has shown that this approach has been investigated before, with varying degrees of success. Although several workers have reported the preparation of various aliphatic aldimines,[2,3,4] there appears to be no good general description of the method of preparation. Reduction of aliphatic aldimines by sodium and alcohol has been reported to yield the secondary amines[2,4,5] but the yields are not always good; possibly considerable cleavage or polymerization of the aldimine occurs during the reduction. Skita and his co-workers[6,7] investigated the low-pressure catalytic hydrogenation of aldimines, using platinum as catalyst and acetic acid as solvent. They obtained secondary amines, but the carbon content was greater than would be expected. Winans and Adkins[8] and Henze and Humphreys[9] have shown that aldehyde-amine condensation products can be hydrogenated to secondary amines of the same carbon content at high pressures in the presence of nickel catalysts; these workers did not isolate the intermediate aldimines, and while their method gives good yields of amines, there is also need for a procedure which does not involve the use of high-pressure hydrogenation equipment.[10] We therefore undertook a study of the preparation and isolation of aliphatic aldimines, and of their catalytic hydrogenation at low pressures and temperatures.

We have found that aldimines can be obtained in a pure state and good yield from aliphatic aldehydes and amines only by observing certain precautions rather strictly. The method of Emerson, Hess and Uhle[11] could not be extended satisfactorily. The method finally adopted is a modification of the one described by Chancel[12] for propylidene propylamine; the reaction is best carried out by adding the aldehyde to the amine, without a solvent, at 0°. When the order of addition is reversed, the yields are much lower. After the addition is complete, solid potassium hydroxide is added to remove the water formed in the reaction. This step is essential; when other drying agents such as potassium carbonate or magnesium sulfate were tried, practically no aldimine was obtained on distillation, and attempts to hydrogenate the undistilled material were unsuccessful. The aldimine should be distilled from fresh potassium hydroxide. The aldimines obtained in this work were water-white when freshly distilled; they are unstable, and polymerize on standing, and should be used within a few hours after distillation.

The aldimines can be hydrogenated to secondary amines of the same carbon content at room temperature and pressures of 2–3 atmospheres with certain restrictions. The best solvent appears to be absolute ethyl alcohol. Palladium-charcoal catalyst can be used, but the hydrogenation is more rapid, and the yields of amine seem better when pre-reduced platinum oxide is used. With Raney nickel the calculated amount of hydrogen is taken up rather rapidly, but side reactions appear to predominate, and but little of the desired secondary amine is formed. The hydrogenations are best carried out in the presence of a small amount of the original primary amine in order to minimize cleavage of the aldimine.

Experimental

Preparation of Aldimines.—The aldehydes and amines were obtained from Eastman Kodak Co., and were used without further purification. Since the procedure for the condensation was the same in all cases, only a typical example is described.

A 250-ml. 3-neck conical bottom flask, fitted with reflux condenser, mercury-seal stirrer and dropping funnel, was packed in an ice-bath. It was charged with 23.6 g. (0.4 mole) of *n*-propylamine, and 28.8 g. (0.4 mole) of butyraldehyde was added gradually over a period of two hours. The reaction mixture was stirred for an additional fifteen minutes; potassium hydroxide flakes were then added, and the mixture was allowed to stand until separation into two layers appeared complete; this required about ten minutes. The organic layer was then removed, and was allowed to stand over crushed potassium hydroxide in the refrigerator overnight. The dried material was decanted into a 100-ml. conical-bottom Claisen flask, a few pellets of potassium hydroxide were added, and the material was distilled. There was a small preliminary fraction; the temperature then rose rapidly to 120°, and the bulk of the material came over at 120–124°. When the treatment with potassium hydroxide was omitted, and when another drying was substituted, the boiling point of the product rose gradually and continuously, and there was no plateau.

The data on the aldimines prepared are summarized in Table I. The indices of refraction and densities were determined on the freshly-distilled samples.

---

(1) This paper was presented before the Organic Division at the Pittsburgh meeting of the American Chemical Society, September, 1943.

(2) Henry, *Compt. rend.*, **120**, 837 (1895); *Bull. acad. roy. méd. Belg.*, (3) **29**, 489 (1895).

(3) Turcan, *Bull. soc. chim.*, (5) **3**, 283 (1936).

(4) Löffler, *Ber.*, **43**, 2041 (1910).

(5) Stoermer and von Lepel, *ibid.*, **29**, 2115 (1896).

(6) Skita and Wulff, *Ann.*, **453**, 190 (1927).

(7) Skita and Pfeil, *ibid.*, **485**, 152 (1931).

(8) Winans and Adkins, THIS JOURNAL, **54**, 306 (1932).

(9) Henze and Humphreys, *ibid.*, **64**, 2878 (1942). This paper appeared while the present work was in progress.

(10) In a private communication received recently, Dr. W. M. Lauer of the University of Minnesota reports that he has been able to adapt the procedure of Henze and Humphreys to low-pressure hydrogenation by using platinum oxide as catalyst.

(11) Emerson, Hess and Uhle, THIS JOURNAL, **63**, 872 (1941).

(12) Chancel, *Bull. soc. chim.*, (3) **11**, 933 (1894).

TABLE I

PHYSICAL CONSTANTS OF ALDIMINES

Aldimine	Yield, %	B. p., °C.[a]	n^{20}_{D}	d^{20}_{4}	*MR*D obs.	*MR*D calcd.
Ethylidenepropylamine[b]	72	74–81	1.4006	0.7342	28.2	28.0
Ethylidenebutylamine	83	98–106	1.4098	.7513	32.7	32.6
Propylidene-ethylamine[b]	70	70–76	1.4004	.7353	28.1	28.0
Propylidenebutylamine	78	118–127	1.4153	.7601	37.3	37.2
Butylidene-ethylamine	52	100–108	1.4082	.7558	32.4	32.6
Butylidenepropylamine	70	120–124	1.4149	.7611	37.2	37.2
Butylidene-iso-propylamine	64	100–111	1.4063	.7436	37.4	37.2
Butylidenecyclohexylamine[c]	60	78–88 (20 mm.)	1.4564	.8475	49.2	48.9
Isobutylidenepropylamine[b]	76	108–114	1.4087	.7456	37.5	37.2
Isoamylidenepropylamine	64	130–139	1.4170	.7615	42.0	41.8
Isoamylidenebutylamine	67	90–96 (100 mm.)	1.4217	.7687	46.7	46.4

[a] The boiling range given is that of the usable fractions; the bulk of the material in each case boiled over a much narrower range. [b] Henry[2] reported the following boiling points: ethylidenepropylamine, 75–77°, propylidene-ethylamine, 75–78°, butylidenepropylamine, 117–118°. [c] Skita and Pfeil[7] obtained a boiling point of 85–87° (16 mm.) for butylidenecyclohexylamine.

TABLE II

PHYSICAL CONSTANTS OF SECONDARY AMINES

Amine	Source	Yield,[a] %	B. p., °C.	Press., mm.	n^{20}_{D}	d^{20}_{4}	*MR*D obs.	*MR*D calcd.
Et Pr	$PrNH_2$	40	81–83	746	1.3951	0.7319	28.5	28.9
Et Pr[b]	$EtNH_2$	43	77–80	738	1.3966	.7318	28.7	28.9
Et Bu[c]	$BuNH_2$	52	109	737	1.4056	.7391	33.6	33.5
Et Bu	$EtNH_2$	33	109	734	1.4055	.7414	33.5	33.5
Pr Bu	$BuNH_2$	54	92–93	200	1.4112	.7500	38.2	38.1
Pr Bu	$PrNH_2$	45	92–93	200	1.4112	.7509	38.1	38.1
Pr *i*-Bu	$PrNH_2$	63	83–84	200	1.4065	.7416	38.2	38.1
Pr *i*-Am	$PrNH_2$	47	106–107	200	1.4159	.7564	42.9	42.8
Bu *i*-Pr	*i*-$PrNH_2$	44	121	733	1.4069	.7412	38.3	38.1
Bu *i*-Am	$BuNH_2$	58	64–65	14	1.4202	.7641	47.5	47.4
Bu cyclohexyl	Cyclohexylamine	45	87–90	12	1.4533	.8429	49.8	49.8

[a] This is the over-all yield from the primary amine. [b] From the fractionation data this appeared to be the pure material. Nitrogen analysis (Dumas) gave N; 16.3%; calculated, N, 16.1%. [c] From the fractionation data this appeared to be the purer material. Nitrogen analysis gave N, 13.6%; calculated, N, 13.8%.

Hydrogenation of Aldimines.—Preliminary runs were carried out with a microhydrogenation machine, using 0.01-mole samples of butylidenebutylamine in absolute alcohol. With 50 mg. of platinum oxide, "pre-reduced," 0.01 mole of hydrogen was absorbed in thirty minutes; with 0.1 g. of 10% palladized charcoal, the time required was seventy-five minutes, and with Raney nickel, sixty minutes. On the basis of these results "pre-reduced" platinum was chosen as catalyst, and the following procedure is typical.

A suspension of 0.20 g. of platinum oxide[13] in 50 ml. of absolute alcohol was shaken with hydrogen at 25 lb./sq. in. for ten minutes, or until no more hydrogen was absorbed. The hydrogen pressure was then released, and 31.6 g. of freshly distilled butylidenepropylamine (0.28 mole), 50 ml. of absolute alcohol and 3 ml. of propylamine were added to the catalyst mixture. The mixture was shaken with hydrogen at an initial pressure of 51 lb./sq. in. until no more hydrogen was absorbed; this required forty minutes, and 0.26 mole of hydrogen was taken up. The catalyst was removed, and the alcoholic solution was distilled through a small Whitmore–Fenske column at atmospheric pressure and a 5:1 reflux ratio until the alcohol was removed. The residue was distilled through the same column under reduced pressure. The yield of product boiling at 92–93° (200 mm.) was 20.8 g., 65% of the theoretical amount.

In the case of ethylpropylamine the amine and the alcohol boil too close together to permit of separation by distillation. In this case, therefore, the alcoholic solution of the reduction product was acidified with hydrochloric acid and evaporated to dryness. The free base was liberated from the hydrochloride by aqueous alkali, taken up in ether and the ether solution distilled through the column.

TABLE III

DERIVATIVES OF SECONDARY AMINES

Amine	M. p. of α naphthylthiourea,[a] °C.	M. p. of hydrochloride,[b] °C.	% Cl in hydrochloride Found	% Cl in hydrochloride Calculated
EtPr	122–123	223–224	28.61	28.68
EtBu	125	197	25.73	25.76
PrBu	136–137	267–268d	23.32	23.38
Pr-*i*-Bu	143–144	278–282d	23.29	23.38
Pr-*i*-Am	137–138	264–265d	21.37	21.40
Bu-*i*-Pr	91.5–92.5	195–196	23.37	23.38
Bu-*i*-Am	117.5–118.5	dec. 290	19.75	19.73
Bu-cyclohexyl-	107–108	278–283d	18.42	18.49

[a] After two recrystallizations from 95% alcohol. [b] After two recrystallizations from absolute alcohol–ether.

Two attempts were made to use Raney nickel as catalyst; in both cases the correct amount of hydrogen was taken up, but distillation of the reduction product yielded little or no secondary amine.

The unsymmetrical secondary amines prepared in this work have been reported in the literature, but in many cases the data recorded are very meager. For this reason we determined the physical constants and prepared the

---

(13) Adams, Voorhees and Shriner, "Organic Syntheses," Coll. Vol. I, 2nd ed., p. 463.

hydrochlorides and α-naphthylthioureas. The hydrochlorides were analyzed for chlorine. The data are summarized in Tables II and III. In several cases the secondary amine was prepared from both possible combinations of aldehyde and amine, and the two products shown to be identical by comparison of physical constants and derivatives.

Summary

1. A procedure has been described for the preparation of aldimines from aliphatic aldehydes and amines.

2. The catalytic hydrogenation at low temperatures and pressures of the aldimines has been studied, and several unsymmetrical, secondary aliphatic amines have been prepared, their physical constants determined and certain derivatives made.

NOTRE DAME, INDIANA RECEIVED SEPTEMBER 25, 1943

[CONTRIBUTION FROM THE NORTHERN REGIONAL RESEARCH LABORATORY[1a]]

Linear Superpolyesters from Dilinoleic Acid

BY JOHN C. COWAN AND DONALD H. WHEELER[1b]

Linear superpolymers prepared from saturated dibasic acids with other difunctional molecules have been described by Carothers.[1c] However, the preparation of linear superpolymers from dibasic acid containing non-benzoid unsaturation has not been described despite reported preparation of such α-polyesters[2] and α-polyamides.[2a]

Vorländer[3] reported the preparation of a resinous polyethylene maleate and crystalline polyethylene fumarate. Carothers[4] prepared the same polyesters, reporting that the maleate polymer was crystalline, and the fumarate resinous. In addition, Carothers reported that both polyethylene maleate and fumarate were heat-convertible to insoluble three-dimensional polymers.

Bradley[5] and Vincent[6] showed that these polyesters were oxygen-convertible and confirmed Carothers' observation on their heat-convertibility. Vincent reported that one polyester, the triethylene glycol citraconate, was very difficult to heat-convert. This observation indicated that under controlled conditions certain types of unsaturated dibasic acids might give linear superpolyesters. It was believed that the kind of unsaturation present in the acid, as well as the possible effect of steric hindrance, were important.

Dibasic acids which contain unsaturation not conjugated with the carboxyl groups, or contain unsaturation which does not easily shift to conjugation, have not been readily available until recently. By suitable polymerization,[7] and fractional distillation[8] under reduced pressures, the esters of linoleic acid of semi-drying oils can be converted to esters of dilinoleic acid.[8a] Although the structure of dilinoleic acid is not known with certainty, the following data indicate its properties[8,9]

Unsaturation	Two double bonds
Molecular weight	560
Neutral equivalent	280
Conjugation	Negligible[10]
Conjugation after alkali treatment[11]	Negligible[12]
Melting point	Non-crystalline at −60°

Bradley[8] described the preparation of the polyester of triethylene glycol dilinoleate. He obtained a viscous liquid which had an acid value of 13.1. This description indicates that the polymer was an α-polyester, having a molecular weight of approximately 4,300. No description of an attempt to prepare superpolyesters was reported. As a part of the program of the Oil and Protein Division of the Northern Regional Research Laboratory on the polymerization phenomena of semi-drying oils, an investigation of the polyesters of dilinoleic acid was undertaken.

By use of methods developed by Carothers[13] and Flory[14] superpolyesters were prepared from dilinoleic acid with ethylene, decamethylene, and hydrogenated dilinoleyl glycols.[14a] All superpolyesters were soluble in chloroform and, in

---

[1a] The Northern Regional Research Laboratory is one of four Regional Laboratories authorized by Congress in the Agricultural Research Act of 1938 for the purpose of conducting research to develop new uses and outlets for agricultural commodities. These Laboratories are operated by the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Not copyrighted.

[1b] New address: General Mills, Inc., Minneapolis, Minnesota.

[1c] Carothers and Hill, THIS JOURNAL, **54**, 1559 (1932); **54**, 1566 (1932).

[2] The terminology of Carothers to designate molecular weight ranges of a condensation polymer is used throughout this paper: α-polymers, 800–5,000; ω-polymers, 5,000–10,000; and superpolymers, above 10,000. This terminology is used merely for convenience in referring to the molecular weights of the polyesters.

[2a] Carothers, U. S. Patent 2,174,619 (1939).

[3] Vorländer, *Ann.*, **280**, 167 (1894).

[4] Carothers and Arvin, THIS JOURNAL, **51**, 2560 (1929).

[5] Bradley, Kropa and Johnston, *Ind. Eng. Chem.*, **29**, 1270 (1937).

[6] Vincent, *ibid.*, **29**, 1267 (1937).

[7] Bradley and Johnston, *ibid.*, **32**, 802 (1940).

[8] Bradley and Johnston, *ibid.*, **33**, 86 (1941).

[8a] This terminology is used since the product is apparently a dimer of linoleic acid and its structure is unknown.

[9] Jackson and Cowan, unpublished data.

[10] Bradley and Richardson, *Ind. Eng. Chem.*, **32**, 963 (1940).

[11] Kass and Burr, THIS JOURNAL, **62**, 1796 (1940).

[12] Teeter and Cowan, unpublished data.

[13] Carothers and Hill, THIS JOURNAL, **54**, 1557 (1932).

[14] Flory, *ibid.*, **62**, 1057 (1940).

[14a] Hydrogenated dilinoleyl glycol was prepared from dimethyl dilinoleate esters by high pressure hydrogenation, using Adkins catalyst. The sample used in this investigation was prepared by Organic Chemicals Manufacturers, University of Illinois.