Secondary and Tertiary Amines Derived From Pelargonaldehyde and Methyl Azelaaldehydate[1]

E. H. PRYDE, D. E. ANDERS[2] and J. C. COWAN,
Northern Regional Research Laboratory,[3] Peoria, Illinois 61604

Abstract

Reductive alkylation of ammonia with pelargonaldehyde or with methyl azelaaldehydate over Raney nickel catalyst produced dinonylamine or bis(8-carbomethoxyoctyl)amine in good yields. Tertiary amine formation was minimized by the use of two immiscible solvents. When 10% palladium on charcoal was used in place of the nickel catalyst, trinonylamine and tris(8-carbomethoxyoctyl)amine were formed in good yield in the absence of solvents.

Introduction

Reductive alkylation of ammonia with certain aliphatic aldehydes gave primary amines in good yields (1). The aldehydes included caproaldehyde, pelargonaldehyde and azelaaldehydic esters obtained by reductive ozonolysis of soybean esters (24). Methyl and butyl 9-aminononanoate, for example, were formed in more than 90% yields when a nonpolar solvent, excess ammonia and Raney nickel catalyst were used. We then extended our studies to the preparation of symmetrical secondary and tertiary amines from pelargonaldehyde and methyl azelaaldehydate.

Experimental Procedures

Materials

Crude pelargonaldehyde and methyl azelaaldehydate were purified to 99%+ by sodium bisulfite treatment (17). Active Raney nickel catalyst (No. 28, Raney Catalyst Div., W. R. Grace & Co.) was treated with a solution of nonylamine in ethanol for 52 hr and then washed free of amine with ethanol. The 10% palladium on charcoal was obtained from Matheson, Coleman and Bell.

Analyses

Amine content was determined by titrating the amine products with 0.1 N hydrochloric acid to the bromphenol blue end point. GLC analyses were obtained with an F&M Model 500 temperature programmed chromatograph. The analyses were made with a 4 ft × ¼ in. column packed with 20% methyl silicone gum (General Electric SF-96) on Chromosorb W. The chromatograph was programmed at 15°/min from 200 to 300 C, at which temperature the column was held for 10–15 min more. Helium flow was 50 cc/min; thermal conductivity detector current, 150 ma; inlet port T, 225 C; block T, 315 C. The methyl silicone liquid phase did not resolve nonylamine from 1-nonanol. A cyanoethylmethyl silicone gum (General Electric XE-60) did resolve these two but was not suitable for the secondary and tertiary amines.

Exploratory Runs. A number of exploratory runs were carried out with pelargonaldehyde to define approximately optimum conditions of time, temperature and solvent (Table I). In a typical experiment, pelargonaldehyde (5.0 g, 0.035 mole), ammonium hydroxide (1.15 ml of a 29.9% solution, 0.018 mole), heptane (50 ml), methanol (50 ml) and Raney nickel (3 g) were placed in a 300 ml hydrogenation bomb. The bomb was sealed, placed in a rocker mechanism, charged with hydrogen and rocked for 4 hr at 75 C and 1000 psig. The bomb was cooled and its contents were filtered. The filtrate was evaporated in a rotary evaporator at room temperature and reduced pressure. The residue (5.0 g) was analyzed by GLC. The analysis showed the presence of nonylamine (4.3%), dinonylamine (81.0%), trinonylamine (3.4%) and 1-nonanol (8.4%).

Dinonylamine. The exemplary reaction described above was repeated on a larger scale with the same molar ratio of reactants but with lower ratios of catalyst and solvent. Pelargonaldehyde (25.0 g, 0.176 mole), ammonium hydroxide (5.75 ml of a 29.9% solution, 0.0905 mole), heptane (75 ml), methanol (75 ml) and Raney nickel catalyst (3 g) were placed in a Magnedash autoclave. The mixture was agitated for 4 hr at 75 C and 1000 psig of hydrogen. The product (25.2 g) had the following composition by GLC analysis: Nonylamine, 5.4%; dinonylamine, 81.0%; trinonylamine, 3.2%; and 1-nonanol, 8.7%. By distillation through a 4 in. × 1 in. Vigreux column, a main fraction (20.0 g, 80% yield) was collected which boiled at 122–124 C/0.05 mm. GLC analysis indicated 99.1% dinonylamine; titration with 0.1000 N hydrochloric acid also indicated a purity of 99.1%.

Analysis. Calculated for $C_{18}H_{39}N$: C, 80.22; H, 14.59; N, 5.19. Found: C, 80.22; H, 14.54; N, 5.30.

Dinonylamine was also prepared by reductive alkylation of nonylamine (6.0 g, 0.042 mole) with pelargonaldehyde (6.0 g, 0.042 mole) in ethanol. Yield was 81%.

Trinonylamine. Substitution of palladium for the nickel catalyst and omission of solvent resulted in a higher proportion of the tertiary amine (Table I). Pelargonaldehyde (10.0 g, 0.0703 mole), ammonium hydroxide (2.30 ml of a 29.9% solution, 0.036 mole) and 10% palladium on charcoal (1.0 g) were placed in a 50 ml rocker-type hydrogenation bomb and agitated for 4 hr at 100 C and 1000 psig of hydrogen. The product (10.0 g) had the following composition by GLC analysis: Nonylamine, 3.7%; dinonylamine, 6.8% and trinonylamine, 84.1%. By distillation, a main fraction (8.1 g, 87% yield) was collected which boiled at 205 C/0.25 mm. Elemental analysis indicated the presence of oxygen-containing impurities, probably of the aldol type. After redistillation, a fraction boiling at 183 C at 0.14 mm had the correct analysis.

Analysis. Calculated for $C_{27}H_{57}N$: C, 81.94; H, 14.52; N, 3.54. Found: C, 82.08; H, 14.65; N, 3.52.

Bis(8-carbomethoxyoctyl)amine. Methyl azelaaldehydate (5.0 g, 0.0268 mole), ammonium hydroxide (0.85 ml of a 29.9% solution, 0.0134 mole), heptane (50 ml), methanol (50 ml) and Raney nickel catalyst (3.0 g) were agitated at 75 C and 1000 psig of hydrogen for 4 hr (Table II). The product had the

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[1] Presented at the AOCS meeting, Cincinnati, 1965.

[2] Present address: Petroleum Research Laboratory, Bureau of Mines, Laramie, Wyoming.

[3] No. Utiliz. Res. Dev. Div., ARS, USDA.

TABLE I

Secondary and Tertiary Amine Formation by Reductive Alkylation of Ammonia With Pelargonaldehyde[a]

Reaction conditions				Product analysis, GLC, %					
Catalyst	Solvent	Temp., C	Pressure, psig	Nonanal	Nonyl-amine	Dinonyl-amine	Trinonyl-amine	1-Nonanol	Other
Raney Ni	None	50	200	9.7	10.3	36.8	25.0	0.0	19.2
Raney Ni	None	50	1000	15.2	7.2	25.0	22.8	0.0	29.8
Raney Ni	None	100	1000	0.0	4.4	72.1	8.0	9.8	5.7
Raney Ni	None	140	2200	0.0	8.4	62.0	5.1	7.4	17.1
Raney Ni	Water	140	2000	0.0	0.0	31.2	14.6	51.2	3.0
Raney Ni	Methanol	140	3300	0.0	1.7	68.4	13.7	11.0	5.2
Raney Ni	Hexanol	75	1000	0.0	(24.8–X)[b]	28.4	30.8	X[b]	16.0
Raney Ni	Heptane	75	1000	0.0	11.0	64.6	9.4	6.5	9.5
Raney Ni	Cyclohexane	140	2100	0.0	10.3	62.7	4.6	13.2	9.2
Raney Ni[c]	Heptane/methanol	50	1000	0.0	6.5	65.4	9.1	7.6	11.4
Raney Ni	Heptane/methanol	75	500	0.0	6.9	79.0	4.1	4.8	5.2
Raney Ni	Heptane/methanol	75	1000	0.0	4.3	81.0	3.4	8.4	2.9
Raney Ni[d]	Heptane/methanol	75	1000	0.0	12.1	81.0	1.4	4.7	0.8
Raney Ni[e]	Heptane/methanol	75	1000	0.0	5.4	81.0	3.2	8.7	1.7
Raney Ni	Heptane/methanol	85	42	0.0	21.2	48.9	15.0	2.8	12.1
Raney Ni	Heptane/methanol	100	3000	0.0	10.2	73.0	1.7	9.7	5.4
Raney Ni	Heptane/methanol	140	2700	0.0	7.9	72.2	2.7	12.9	4.3
Raney Ni	Cyclohexane/ methanol	75	1000	0.0	23.1	50.4	0.0	24.0	2.5
Raney Ni	Methyl cyclohexane/ water	140	2300	0.0	6.2	46.4	6.1	34.2	7.1
10% Pd/C[c]	None	75	1000	7.4	8.2	8.4	76.0	0.0	0.0
10% Pd/C	None	100	1000	0.0	3.7	6.8	84.1	0.0	5.4
10% Pd/C	None	100	3000	0.0	3.3	6.6	84.2	0.0	5.9
10% Pd/C[f]	None	100	3500	0.0	0.0	0.8	73.2	20.0	6.0
10% Pd/C	Heptane/methanol	75	1000	0.9	1.3	32.4	59.1	0.0	6.3

[a] Aldehyde-ammonia ratio, 2:1; reaction time, 4 hr.
[b] The nonanol and nonylamine peaks were not resolved for this particular sample.
[c] Reaction time, 5 hr.
[d] Reused catalyst from preceding run.
[e] Quantity of pelargonaldehyde used, 25 g, was five times the amount used in the other runs.
[f] Aldehyde-ammonia ratio, 3:1.

following composition according to GLC analysis: Methyl 9-aminononanoate, 6.9%; bis(8-carbomethoxyoctyl)amine, 81.0%; and methyl 9-hydroxynonanoate, 12.1%. Attempts to distill this product at 0.06 mm resulted in condensation and gelation. A small amount of white solid, mp 44–45 C, was isolated by crystallization from ether.

Analysis. Calculated for $C_{20}H_{39}O_4N$: C, 67.18; H, 11.00; N, 3.92. Found: C, 66.95; H, 10.99; N, 3.49.

Tris(8-carbomethoxyoctyl)amine. Methyl azelaaldehydate (5.0 g, 0.0268 mole), ammonium hydroxide (0.85 ml of a 29.9% solution, 0.0134 mole) and 10% palladium on charcoal were agitated in a rocker bomb for 4 hr at 100 C and 3000 psig of hydrogen. Catalyst was removed by filtration. The filtrate was diluted with methanol and dried over Drierite. After filtration and removal of solvent, there remained 5.0 g of an oily product.

Analysis. Calculated for $C_{30}H_{57}NO_6$: C, 68.27; H, 10.89; N, 2.65. Found: C, 68.33; H, 11.10; N, 3.10.

Results and Discussion

The reductive alkylation of ammonia with pelargonaldehyde or methyl azelaaldehydate should lead either to secondary or to tertiary amines, depending upon the molar ratio of reactants in accordance with the equations:

$$2\,RCHO + NH_3 + 2H_2 \longrightarrow (RCH_2)_2NH + 2H_2O$$
$$3\,RCHO + NH_3 + 3H_2 \longrightarrow (RCH_2)_3N + 3H_2O$$
$$R = CH_3(CH_2)_7 \text{ or } CH_3OOC(CH_2)_7$$

However, an aldehyde-ammonia ratio of 2:1 usually leads to mixtures of primary, secondary and tertiary amines (9). For example, butyraldehyde forms mono-, di- and tributylamines in 31%, 17% and 8% yields, respectively (26). Dibutylamine was obtained in yields of 80% when butylamine was reductively alkylated with butyraldehyde in the presence of ammonia. Preparation of symmetrical, secondary amines in good yield then becomes a two-step process involving formation of the primary amine in the first step. Our investigations show that aliphatic, symmetrical, secondary amines can be prepared in better than 80% yield in a one-step process from the aldehyde and ammonia.

Dinonylamine has been prepared by the catalytic hydrogenation of nonanenitrile (6,15) and by amination of nonyl alcohol (11); trinonylamine, by the reaction of dinonylamine with nonylbromide (6); and bis(8-carbomethoxyoctyl)amine, from 9-chlorononanoic acid (18). Homologous iminodiesters have been prepared by the reaction of an ω-haloester with an ω-aminoester (22), with ammonia (10,12,18,19) or with methyl- or ethylamine (13). Other intermediates for the synthesis of homologous iminodiesters include ω-cyanoalkanamides (2–4) and an ω-oximinoester (8). Bis(10-carboxydecyl)amine has been identified in nylon-11 (7).

In exploratory experiments with pelargonaldehyde, reaction variables tested were temperature, pressure and solvent (Table I). Preselected reaction conditions, based on earlier experiments on the preparation of primary amines (1), included a 4 hr reaction time and the nickel catalyst. An aldehyde-ammonia ratio of 2:1 was used.

With no auxiliary solvent, a maximum yield of 72% dinonylamine was obtained when the temperature was 100 C and the pressure 1000 psig of hydro-

TABLE II

Reductive Alkylation of Ammonia with Methyl Azelaaldehydate

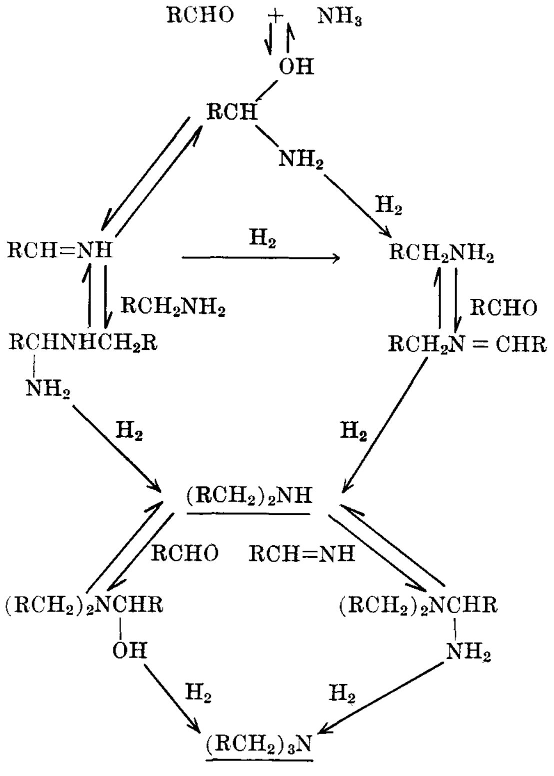
Reaction conditions					Product analysis, GLC, %				
Solvent	Catalyst	Aldehyde-ammonia ratio	Temp., C	Pressure, psig	Primary amine	Secondary amine	Tertiary amine	Methyl 9-hydroxy-nonanoate	Other
None	Pd/C	2:1	100	3000	0.0	0.0	85.0	0.0	15.0
Heptane/methanol	Ni	2:1	75	1000	6.9	81.0	Trace	12.1	0.0
Heptane/methanol	Ni	1:20	75	1000	97.2	0.0	0.0	2.8	0.0

gen. Lower temperatures and pressures resulted in incomplete reaction and high tertiary amine formation.

The homogeneous solutions from methanol, heptane or cyclohexane gave dinonylamine in yields of 63–68%. The heterogeneous mixture resulting when water was added gave 1-nonanol in 51% yield and dinonylamine in a yield of only 31%. With 1-hexanol, 31% of trinonylamine was formed. Trinonylamine formation was least with cyclohexane (less than 5%).

Use of two immiscible solvents resulted in yields of dinonylamine as high as 80%. The heptane/methanol system giving the 80% yield was preferable to the cyclohexane/methanol and methylcyclohexane/water systems. Tertiary amine formation was unusually low (1–4%) in the heptane/methanol system over the temperature range 75–140 C and pressure range 500–3000 psig. Application of the heptane/methanol system to the preparation of bis(8-carbomethoxyoctyl)amine from methyl azelaaldehydate resulted in 81% yield of the desired product and a trace of the tertiary amine (Table II). In the same solvent system but with excess ammonia, methyl 9-aminononanoate was formed in 97% yield, and methyl 9-hydroxynonanoate was the only other product detected.

Reasons for the improved yields and low tertiary amine formation are suggested from a consideration of the various reactions and equilibria involved as shown in the following scheme (9):



In a two-phase system, there may be some restriction on reactions leading to the tertiary amine as the result of varying degrees of polarities for reactants and solvents. Thus, more polar reactants ($RCHO$, $RCH = NH$, RCH_2NH_2) will have a relatively high equilibrium concentration in the more polar solvent, and the less polar reactants ($RCH_2N = CHR$, $RCH_2NHCH = CH_2R'$, $(RCH_2)_2NH$) will concentrate in the less polar solvent. Reactions leading to the tertiary amine are then less likely to occur, e.g., the reaction of $RCH_2N = CHR$ with RCH_2NH_2.

Preparation of tertiary amine as the main product was no problem when palladium on charcoal was used (Tables I and II). Although the stoichiometry of the reaction demands an aldehyde-ammonia ratio of 3:1, results were best when an aldehyde-ammonia ratio of 2:1 was used.

Several potential uses for these materials have been described. Dinonylamine has good antibacterial activity (6) and has been used to produce a thioamide said to be useful as an insecticide or an accelerator (14). Trinonylamine has been used as an extractant for inorganic anions (23,30), for hydrofluoric acid (25), for hydrofluoric acid and uranyl fluoride (27,28) and for thallium (III) salts (29). Mixtures of tri(*n*-octyl)- and tri(*n*-decyl)amines, probably equivalent to trinonylamine in effect, have been used for recovery of americium, curium and europium salts (21). The dye receptivity of stereoregular polyolefins is said to be improved by the incorporation of trinonylamine (16). Various iminodiesters homologous to bis(8-carbomethoxyoctyl)amine have been condensed to cyclic β-ketoesters (20,22), as well as to cyclic aminoacyloins (13) and used to produce polyamides having secondary amine groups in the main chain (5).

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