principal components. The principal spectral basis for the assignment of A was a "secondary NH deformation" at 6.36 μ. In neither case could a conclusive identification be made from the infrared data, although the absence of other characteristic bands is in keeping with the "amino ether" postulate.

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EMERYVILLE, CALIF.

[CONTRIBUTION FROM THE RESEARCH AND ENGINEERING DIVISION, MONSANTO CHEMICAL CO.]

The Guerbet Reaction. I. The Reaction of Amines Under Guerbet Conditions

ROBERT E. MILLER

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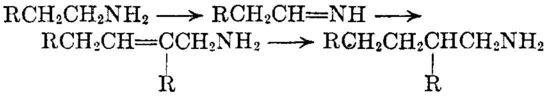
The reaction of primary amines with the structure $RCH_2CH_2NH_2$ has been studied in a Guerbet-type condensation. The principal products were the simple imines, $RCH_2CH{=}NCH_2CH_2R$, alcohols, and carbonyl compounds. With *n*-hexylamine and *n*-octylamine branched-chain trimolecular imines were also obtained. Under similar conditions nitriles were converted to amides.

Aldimines have been postulated as the initial products in the catalytic hydrogenation of nitriles.[1] Condensation of the aldimine followed by hydrogenation results in a mixture of the simple primary amine as well as the secondary and tertiary amines derived from it.

$$\begin{tikzcd} RC{\equiv}N + H_2 \arrow[r, "Ni"] & RCH{=}NH \arrow[r, "H_2"] \arrow[d, "RCH_2NH_2"] & RCH_2NH_2 \quad (1) \\ & RCH(NH_2)NHCH_2R \arrow[r, "H_2"] & (RCH_2)_2NH + NH_3 \end{tikzcd}$$

It was of interest to study the behavior of amines of the structure $RCH_2CH_2NH_2$ in a Guerbet condensation. By analogy with the Guerbet reaction of alcohols,[2] the proposed reaction assumed the formation of an aldimine or ketimine intermediate, which might then attack the β-methylene group of a second molecule of the amine. This sequence would provide a synthesis for dimeric, branched-chain, primary amines.



$$\begin{aligned} &RCH_2CH_2NH_2 \longrightarrow RCH_2CH{=}NH \longrightarrow \\ &\quad RCH_2CH{=}\underset{\displaystyle R}{\underset{|}{C}}CH_2NH_2 \longrightarrow RCH_2CH_2\underset{\displaystyle R}{\underset{|}{C}}HCH_2NH_2 \end{aligned} \quad (2)$$

Such products, however, were not isolated from this condensation. The principal reaction involved the formation of the simple imines, $RCH_2CH{=}N(CH_2)_2R$, derived from an aldol reaction of the aldimine or ketimine intermediate with the amine reactant. Subsequent condensation of a second molecule of the aldimine or ketimine with the Schiff base, or dimerization of the Schiff base followed by the loss of a molecule of primary amine,[3] resulted in the formation of branched-chain trimolecular imines. *N*-(2-*n*-Butyloctylidine)-*n*-hexylamine and *N*-(2-*n*-hexyl-2-decenylidene)-octylamine were isolated from the self-condensation of *n*-hexylamine and *n*-octylamine, respectively. The substitution reaction appears to take place solely at the β-methylene group of the alkylidene substituent rather than at a carbon atom of the imino moiety.

The formation of secondary amines, $(RCH_2CH_2)_2NH$, was only a minor reaction. Tertiary amines were not isolated. These results may be ascribed to the insufficiency of hydrogen present during the condensation. The amount of hydrogen liberated during the reaction is primarily limited to the dehydrogenation of the amine reactant. Of possible significance to the mechanism of the Guerbet condensation is the fact that hydrogen liberated during this dehydrogenation reaction was consumed in the saturation of the carbon-nitrogen double bond.

Identification of the imines was established by spectral analysis and subsequent conversion to a mixture of an amine and a carbonyl compound by acid hydrolysis.

Alcohols and/or carbonyl compounds derived from the starting material were also isolated. Since no attempt was made to provide anhydrous tripotassium phosphate, or to exclude air from the system, these products result from hydrolysis and/or oxidation of the aldimine or ketimine by the hot alkaline solution. This reaction is similar to the oxidation of the carbonyl intermediate in Guer-

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[1] (1a) H. Adkins and H. I. Cramer, *J. Am. Chem. Soc.*, **52**, 4349 (1930). (b) C. F. Winans and H. Adkins, *J. Am. Chem. Soc.*, **54**, 306 (1932). (c) W. Carothers and R. Adams, *J. Am. Chem. Soc.*, **47**, 3051 (1925). (d) B. S. Biggs and W. S. Bishop, *Ind. Eng. Chem.*, **38**, 1084 (1946). (e) J. v. Braun, G. Blessing, and F. Zobel, *Ber.*, **56**, 1988 (1932).

[2] E. F. Pratt and D. G. Kubler, *J. Am. Chem. Soc.*, **76**, 52 (1954).

[3] W. S. Emerson, S. M. Hess, and F. C. Uhle, *J. Am. Chem. Soc.*, **63**, 872 (1941).

bet reactions (Dumas-Stas reaction),[4] which gives rise to carboxylic acids.

TABLE I

The Condensation[a] of Primary Amines

RNH$_2$ R	RNH$_2$ moles	Time hr.	Temp.	% Conv. Products: Carbonyl Compound		Alcohol		Imine		Other	
n-C_6H_{13}	2.7	24	130–132	—		—		n-$C_5H_{11}CH{=}N(n\text{-}C_6H_{13})$[b,c]	12.7	$C_{18}H_{37}N$[c,d]	4.0
n-C_8H_{17}	1.9	20	150–162	—		1-Octanol[e]	3.0	$C_{24}H_{47}N$[c,f]	16.2	$(C_8H_{17})_2NH$[g]	6.4
n-C_8H_{17}	1.9	10	230[h]	n-Octanal[i]	4.0	1-Octanol	6.5	$C_{24}H_{47}N$	5.7	$(C_8H_{17})_2NH$	12.0
C_6H_{11}	7.1	12	180	Cyclohexanone[j]	1.1	Cyclohexanol[k]	8.4	$C_6H_{10}{=}NC_6H_{11}$[c,l]	2.8	Cyclohexene	1.6
C_6H_{11}	6.8	12	230[h]	—		Cyclohexanol	4.5	$C_6H_{10}{=}NC_6H_{11}$	1.8	Cyclohexene	2.6

[a] The reactions were carried out in the presence of 0.1 mole tripotassium phosphate and 1.5–5.0 wt. % of copper chromite–nickel dehydrogenation catalyst. [b] N-n-Hexylidene-n-hexylamine. [c] See Experimental section for derivatives. [d] N-(2-n-Butyloctylidene)-n-hexylamine. [e] 3,5-Dinitrobenzoate melted at 61–62°. G. B. Malone and E. E. Reid, *J. Am. Chem. Soc.*, **51**, 3426 (1929), give m.p. 60.8°. [f] N-(2-n-Hexyl-2-decenylidene)-n-octylamine. [g] Di-n-octylamine, m.p. 34–36°. O. Westphal and P. Jerchel, *Ber.*, **73B**, 1002 (1940), give m.p. 35°. [h] Reaction conducted in autoclave. [i] 2,4-Dinitrophenylhydrazone melted at 106°. [j] 2,4-Dinitrophenylhydrazone melted at 158–160°. [k] 3,5-Dinitrobenzoate melted at 112–114°. T. Reichstein, *Helv. Chim. Acta*, **9**, 802 (1926), gives 112–113°. [l] N-Cyclohexylidenecyclohexylamine.

The isolation of cyclohexanol as a by-product during the synthesis of N,N-dicyclohexylamine from cyclohexylamine over nickel catalysts at 180–210°, has been reported by Wenderlein.[5]

The possible reactions involved in the Guerbet-type condensation of amines are outlined as shown.

The reaction of nitriles was also investigated under the conditions utilized for the condensation of amines. It was desired to ascertain whether this reaction would yield the secondary and tertiary amines described by previous investigators.[1] n-Heptanenitrile was allowed to react at 210–250° for ten to twenty hours under limited hydrogen pressure. Tripotassium phosphate and a dehydrogenation catalyst were used to effect condensation. The sole product was n-heptamide (4–9%). Benzamide (7.7%) was obtained from benzonitrile under similar conditions. Amine formation was completely suppressed.

n-Octyl mercaptan was recovered quantitatively from a Guerbet-type reaction at 158–164° and twenty hours.

EXPERIMENTAL

The reactions carried out at atmospheric pressure were conducted in a three-necked flask which was fitted with a stirrer, condenser, and thermometer. In a typical experiment, n-hexylamine (277 g., 2.7 moles), tripotassium phosphate (21.2 g., 0.1 mole), and 8.0 g., of a 1:1 mixture of a copper chromite–nickel dehydrogenation catalyst were stirred and refluxed (130–132°) for 24 hr. The mixture was cooled and filtered. n-Hexylamine (212.0 g., 2.1 moles) was recovered by distillation. The major product was a crude fraction (32.0 g.) which distilled at 210–225°.

This fraction was redistilled at 88–91° (4 mm.), $n_{\rm D}^{25}$ 1.4346. Infrared analysis indicated the absence of amine groups and the presence of the imine linkage.

Anal. Calcd. for $C_{12}H_{25}N$: C, 78.55; H, 13.66. Found: C, 77.95; H, 13.79.

The imine (5.5 g.) was dissolved in ethanol and refluxed (3 hr.) with acidified p-nitrophenylhydrazine. On cooling, n-hexanal p-nitrophenylhydrazone precipitated, m.p. 85.5–86.5° (lit.[6] m.p., 83–85°).

Anal. Calcd. for $C_{12}H_{17}N_3O_2$: C, 61.25; H, 7.88. Found: C, 62.12; H, 8.05.

The imine is N-n-hexylidene-n-hexylamine.

A second fraction (10.0 g.) distilled at 151–156° (4 mm.). This material was hydrolyzed to yield n-hexylamine hydrochloride (melting point, 219°) and an aldehyde. The latter was converted to 2-butyloctanoic acid (amide m.p. 106–107°).[2] The compound is therefore N-(2-n-butyloctylidene)-n-hexylamine.

The condensation of n-octylamine represents a typical autoclave experiment. A 1-l. bottom-stirred Aminco autoclave was charged with 250.0 g. (1.93 moles) of n-octylamine, 27.0 g. (0.12 mole) of tripotassium phosphate, and 10.0 g. of a copper chromite–nickel catalyst. The mixture was stirred and heated for 10 hr. at 230°. The reaction developed 500 p.s.i.g. After the autoclave cooled, the pres-

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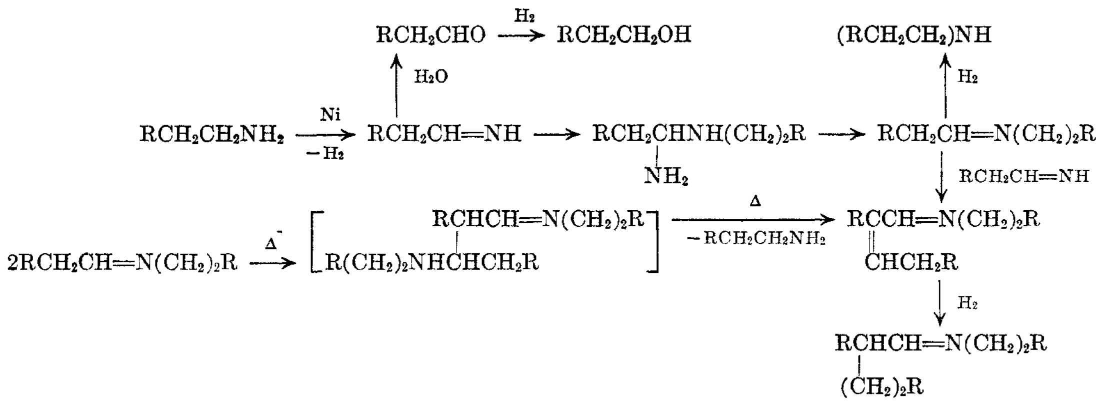
(4) J. Dumas and J. S. Stas, *Ann.*, **35**, 129 (1840). See also E. E. Reid, H. Worthington, and A. W. Larchar, *J. Am. Chem. Soc.*, 61, 99 (1939).

(5) H. Wenderlein, Ger. Patent 851,188, Oct. 21, 1952.

(6) L. Ruzicka and H. Schinz, *Helv. Chim. Acta*, **18**, 39 (1935).



(3)

sure (100 p.s.i.g.) was slowly released, the contents were filtered and distilled. *n*-Octanal (10.1 g.), *n*-octylamine (136 g.), 1-octanol (16.5 g.), and di-*n*-octylamine (28.5 g.), which distilled at 145–155° (3 mm.), were obtained in the initial distillates. A fraction (13.0 g.) distilling at 195–197° (2 mm.), n_D^{25} 1.4652, was also obtained. A very strong infrared band at 6.1–6.18 μ was attributed to superposition of the substituted imine and olefinic absorptions.

Anal. Calcd. for $C_{24}H_{47}N$: C, 82.49; H, 13.50; N, 4.01. Found: C, 82.44, 83.24; H, 12.75, 13.59; N, 3.90, 3.94.

The ultraviolet absorption spectrum of the compound exhibited a characteristic imine maximum at 231 mμ.

The imine (12.0 g.) was hydrolyzed in refluxing 20% hydrochloric acid (100 ml.). The mixture was cooled and extracted with ether. The ether extracts were dried over magnesium sulfate, the ether evaporated, and the residue refluxed with ethanolic 2,4-dinitrophenylhydrazine reagent. 2-*n*-Hexyl-2-decenal 2,4-dinitrophenylhydrazone, melting at 103.5–104.5°, precipitated on cooling.

Anal. Calcd. for $C_{22}H_{34}N_4O_4$: C, 63.28; H, 8.14. Found: C, 63.11; H, 8.83.

An attempted preparation of an oxime from this aldehyde failed.

The aqueous solution from the acid hydrolysis yielded a white, waxy solid, m.p. 192–196°. This was identified as *n*-octylamine hydrochloride (lit.[12] m.p. 198°).

The imine can now be formulated as *N*-(2-*n*-hexyl-2-decenylidene)-*n*-octylamine.

A trace (1.3 g.) of a primary amine (infrared analysis) which sublimed during the distillation was recrystallized from methanol, m.p. 108–109°.

Anal. Calcd. for $C_{24}H_{51}N$: N, 3.97. Found: N, 3.97.

This amine was diazotized and coupled with β-naphthol to give a red solid, melting point 174–176°. The identity of the amino compound is not known.

The Guerbet condensation of cyclohexylamine yielded cyclohexene, cyclohexanone, cyclohexanol, and *N*-cyclohexylidenecylohexylamine, boiling point 93–95° (2 mm.), n_D^{25} 1.4904. Migonac[7] gives a boiling point of 117–118° (9 mm.), n_D^{21} 1.4972, for this compound. The imine was refluxed with an ethanolic solution of 2,4-dinitrophenylhydrazine reagent. Cyclohexanone 2,4-dinitrophenylhydrazone, m.p. 158–160°, was isolated.

A higher boiling fraction from the cyclohexylamine reactions distilled at 180–195° (4 mm.) with decomposition. Infrared analysis showed the presence of a primary amine, but the product was not otherwise identified.

Nitrile reactions. A 300-ml. rocking autoclave was charged with 160.0 g. (1.44 moles) of *n*-heptanenitrile, 21.0 g. (0.1 mole) of tripotassium phosphate, and 8.0 g. of a 1:1 mixture of copper chromite–nickel catalyst. The reaction was pressured with 600 p.s.i.g. of hydrogen and heated to 210° for 20 hr. The hydrogen pressure fell to 200 p.s.i.g. The mixture was cooled and filtered. The filtrate was distilled at 179–181° to yield 124.0 g. of *n*-heptanenitrile. The residue contained *n*-heptamide (20.0 g.), which was recrystallized from methanol, m.p. 95.5–97°.

Anal. Calcd. for $C_7H_{15}NO$: C, 65.21; H, 11.63. Found: C, 65.24; H, 12.15.

Benzamide (m.p. 124–126° was obtained from similar treatment of benzonitrile.

DAYTON 7, OHIO

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[7] G. Migonac, *Ann. chim.*, [11], 2, 225 (1934).

[CONTRIBUTION FROM THE SHELL DEVELOPMENT COMPANY]

The Reaction of Glycidaldehyde and Mesityl Oxide Epoxide with Hydrogen Sulfide

WILLIAM J. SULLIVAN AND PAUL H. WILLIAMS

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Glycidaldehyde and the epoxide of mesityl oxide react with hydrogen sulfide to form, respectively, 3-hydroxy-2-mercaptopropionaldehyde, isolated as a dimer, and 4-hydroxy-3-mercapto-4-methyl-2-pentanone. A mechanism involving the initial addition of hydrogen sulfide to the carbonyl group is postulated to account for the formation of these products.

The direction of addition of reagents to an unsymmetrical epoxide can usually be predicted from the nature of the groups attached to the oxirane ring.[1] As one generalization it may be said that if one of the substituents on the oxirane ring is an electron-withdrawing group the effect, almost invariably, is to inhibit reaction at the attached oxirane carbon in favor of the oxirane carbon further

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[1] See R. E. Parker and N. S. Isaacs, *Chem. Rev.*, 59, 737–799 (1959) for a recent review of this subject.