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N,N'-Dialkylethylenediamines by Reduction of Dialkyloxamides[1a,b]

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Lithium aluminum hydride has proved to be an efficient agent for the reduction of acid amides to amines. It seemed to be of interest to try the reduction of N,N'-dialkyloxamides in which the two carbonyls are adjacent. This has been found to go smoothly and to give a good yield of a product which does not require extensive purification. There are several more or less satisfactory ways of preparing the N,N'-dialkylethylenediamines, but our method may prove useful in special cases, particularly for symmetrical alkyl-aryl compounds.

TABLE I

N,N'-DIALKYLETHYLENEDIAMINES, R—NH—CH_2CH_2—NH—R

R	Source	B.p. °C.	B.p. Mm.	Yield, %	d^{25}_{4}[e]	$n^{25}\mathrm{D}$	Diphenylurea derivative, m.p., °C.
Ethyl[a]	Diacetate	148–150	760	50	0.804	1.4298	197–199[f]
Ethyl	Oxamide	148–150	760	53	.809	1.4296	197–199[f,g]
Butyl[b]	Dibutyrate	74–77	3	72	.811	1.4382	174–176[b,h]
Butyl	Oxamide	73–78	3	63	.811	1.4387	174–175[h]
Decyl[c]	Dicaprate	180–183	0.7	61	...	....	86–86.5[i,j]
Decyl[d]	Oxamide	184–190	1	56	...	....	85.5–86[i]

[a] W. R. Boon, *J. Chem. Soc.*, 307 (1947). [b] A. E. Frost, S. Chaberek and A. E. Martell, THIS JOURNAL, **71**, 3842 (1949). [c] F. Linsker and R. L. Evans, *ibid.*, **68**, 1432 (1946), recorded m.p. 0–2°, found, m.p. 28–30°. [d] Dihydrochloride. *Anal.* Calcd. for $C_{22}H_{48}N_2Cl_2$: C, 64.38; H, 11.70; N, 6.77; Cl. 17.15. Found: C, 63.71; H, 11.82; N, 6.79; Cl, 17.08. [e] ±0.005. [f] Mixed m.p. 196–197°. [g] *Anal.* Calcd. for $C_{20}H_{26}N_4O_2$: N, 15.81. Found: N, 16.02. [h] Mixed m.p. 174–176°. [i] Mixed m.p. 86–87°. [j] *Anal.* Calcd. for $C_{36}H_{58}N_4O_2$: N, 9.68. Found: N, 9.84.

In order to check the identity and purity of our products we also prepared them by the reduction of the isomeric diacylethylenediamines. As in the case of the substituted oxamides, the reduction proceeded evenly to give good yields of pure dialkylethylenediamines.

$$\left.\begin{array}{l}\mathrm{RCH_2NHCOCONHCH_2R}\\ \mathrm{RCONHCH_2CH_2NHCOR}\end{array}\right\rangle\!\!\rightarrow \mathrm{RCH_2NHCH_2CH_2NHCH_2R}$$

This has been done with three pairs of amides with the results shown in Table I in which the boiling points, density and refractive index all checked. The diphenylurea derivatives correspond in each set.

Experimental

The Dialkyloxamides.—These were conveniently prepared by adding ethyl oxalate to a slight excess of the amine in water or in alcohol. The melting points of the products were 176° for diethyl, 154° for dibutyl, and 123° for didecyl, which were in agreement with recorded values.[3,4] The ethylene bis-amides were materials from a previous investigation.[5]

General Procedure for Reduction.—In a two-liter, three-necked flask, fitted with a dropping funnel, sealed stirrer and a long reflux condenser closed with a drying tube, a solution of 15 g. of lithium aluminum hydride in 600 ml. of anhydrous ether was prepared. The bis-amide, 30 g. in the form of a well mixed ether slurry, was added to the hydride solution at such a rate that the ether refluxed at a moderate rate.

In some cases it was found that the use of a soxhlet extractor was more convenient, although there was no appreciable increase in yield. In either case when all of the reactants had been brought together the contents were vigorously stirred under reflux for four hours and then allowed to stand overnight. The reaction mixture was decomposed by the dropwise addition of water regulated at such a rate that the capacity of the condenser was not exceeded. After reflux had ceased, a 10-ml. excess of water was added and the mixture stirred an additional hour. The suspension was filtered and the residue was washed three times with 50-ml. portions of ether. The ethereal filtrate was dried over potassium hydroxide and the ether stripped off. Distillation in vacuum over a pellet of potassium hydroxide yielded the products as colorless liquids. The decyl compound solidified in the receiver. As these liquids are strong absorbants of CO_2, it was advisable to purge the apparatus with nitrogen.

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[2] Professor Emeritus, Johns Hopkins University, Baltimore 18, Md.

[3] L. M. Rice, C. H. Grogan and E. E. Reid, THIS JOURNAL, **75**, 242 (1953).

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Aluminum Monochlorodilaurate, a Non-thickener for Hydrocarbons[1]

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Aluminum difatty acid soaps, depending on the nature of the third substituent, show marked and as yet unexplained differences in their ability to increase the viscosity of hydrocarbon solvents. The hydroxy compounds are excellent thickeners and widely used in greases and flame warfare, while the alcoxy,[3] the cresoxy[3] and perhaps the carboxy[4]

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[1] Based upon the M.S. thesis of D.M. Chin, University of Southern California, Los Angeles 7, California, August, 1950, and presented in part before the Division of Colloid Chemistry during the 118th Meeting of the American Chemical Society at Chicago, Illinois.

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