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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.

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.

$$\begin{array}{l} RCH_2NHCOCONHCH_2R \searrow \\ \qquad\qquad\qquad\qquad\qquad\qquad RCH_2NHCH_2CH_2NHCH_2R \\ RCONHCH_2CH_2NHCOR \nearrow \end{array}$$

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.

TABLE I

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

R	Source	B.p. °C.	Mm.	Yield, %	d^{25}_{4}[e]	$n^{25}\text{D}$	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.

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

[4] O. C. Dermer and J. W. Hutcheson, *Proc. Okla. Acad. Sci.*, **23**, 60 (1943).

[5] H. C. Chitwood and E. E. Reid, THIS JOURNAL, **57**, 2424 (1935).

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

BY KAROL J. MYSELS AND DORIS MAY CHIN[2]

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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.

[2] Colgate–Palmolive–Peet Fellow 1949–1950.

[3] V. R. Gray and A. E. Alexander, *J. Phys. Colloid Chem.*, **53**, 23 (1949).

[4] J. Glazer, T. S. McRoberts and J. R. Shulman, *J. Chem. Soc.*, 2082 (1950).

form solutions of very low viscosity. We have now found that the chloro compound can be prepared and is a non-thickener.

These results strongly suggest[1] that the thickening action is due to hydrogen bonding, but infrared absorption spectra[5] seem to show that no hydrogen bonds are present in these systems, which eliminates this explanation.

Experimental

The Reaction of Aluminum Chloride with Lauric Acid.—Weighed amounts of distilled anhydrous aluminum chloride and lauric acid were placed in a three-neck flask. Upon addition of cyclohexane and stirring, the reaction proceeded smoothly at room temperature. Its progress was followed by titrating the hydrogen chloride evolved. The product was frozen and the solvent removed by sublimation *in vacuo.* With two or more equivalents of lauric acid present, two equivalents of hydrogen chloride were evolved, showing that the reaction proceeded only to the formation of $AlClL_2$. Aluminum chloride gives a red color with tetralin. The products gave this same color with tetralin only when less than one equivalent of lauric acid was present. This suggests that an aluminum dichloromonolaurate as well as a monochlorodilaurate is formed. Because of the large solubility of reagents and products in hydrocarbons and their reactivity with polar solvents and traces of moisture, we have not been able to separate the components of the reaction mixture.

Aluminum Monochlorodilaurate.—Reaction of stoichiometric amounts yielded after lyophilization an extremely viscous liquid which froze at 2°. Due to this viscosity it stayed white for several days after being obtained by lyophilization. Upon standing for several weeks, or rapidly upon centrifugal compaction, it became transparent. Analysis indicated the presence of hydrolytic products and agreed with that expected if the product contained a small amount of the hydroxy dilaurate as shown by Table I.[6] It reacted rapidly with atmospheric moisture evolving hydrogen chloride and forming a white brittle coating, but the reaction did not go to completion due to protective action of the coating.

TABLE I

	Found	Theoretical	
		$AlClL_2$	89% $AlClL_2$ + 11% $AlOHL_2$
C	62.3	62.51	62.70
H	10.02	10.06	10.10
Al_2O_3	11.02	11.06	11.07
Cl	6.84	7.69	6.88

Solutions of Aluminum Chlorodilaurate.—Our product was very soluble in hydrocarbons and also soluble in acetone. Part of it reacted with any residual moisture present in dried acetone[9] forming an insoluble product and the remainder dissolved. The acetone solution gradually darkened due to the formation of condensation products by the solvent.

All solutions were fluid. A few relative viscosities were estimated either in an Ostwald viscometer or by the rate of rise of air bubbles, with the following results: in cyclohexane 1.3%, 1.05; 4.8%, 1.19; 27%, 4.5; in cetane 22%, 8. These increases in viscosity are negligible compared to those produced by the hydroxylaurate.[10]

The passage of moist air through hydrocarbon solutions caused the hydrolysis of only about one-half the chlorine present. Most of the remainder was removed during lyophilization of the hydrolyzed solution. During the hydrolysis of solutions, even of those containing 27% of the compound, we never observed any bulk gelation. Occasional small fragments of gel appeared but always redispersed. The viscosity of the solutions (as measured by the rate of rise of air bubbles) increased to about double the original value in early stages of hydrolysis and then decreased. This behavior is contrary to that observed by Condit[11] who studied a chlorine-containing product[12] of reaction of naphthenic acid with aluminum chloride and that reported for alcoxy and cresoxy soaps.[8,13]

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[5] W. W. Harple, S. E. Wiberly and W. H. Bauer, *Anal. Chem.*, **24**, 635 (1952).

[6] The difficulty of obtaining really pure compounds of this class may be judged by the following per cent. deviations from theoretical values for some recent preparations: triacetate,[7] Al_2O_3: +5%; tripropionate,[7] Al_2O_3: +10%; trilaurate,[4] Al_2O_3: +20%; *s*-butoxy dilaurate,[8] L: −24 to −36%; *s*-butoxy stearate,[8] St: 0 to −14%; cresoxy dilaurate,[8] L: −15 to −30%; dihydroxymonolaurate,[8] Al_2O_3: −20 to +6%.

[7] G. C. Hood and A. J. Ihde, THIS JOURNAL, **72**, 2094 (1950).

[8] C. G. McGee, *ibid.*, **71**, 278 (1949).

[9] J. Timmermans and L. Gillo, *Roczniki Chem.*, **18**, 812 (1938); K. J. Mysels, *J. Phys. Colloid Chem.*, **51**, 708 (1947).

[10] K. J. Mysels, *J. Colloid Sci.*, **2**, 375 (1947); H. Sheffer, *Can. J. Research*, **B26**, 481 (1948); V. R. Gray and A. E. Alexander, *J. Phys. Colloid Chem.*, **53**, 9 (1949).

[11] D. H. Condit, U. S. Patent 2,321,463 (1943).

[12] D. H. Condit, private communication.

[13] T. S. McRoberts and J. H. Shulman, *Proc. Royal Soc.* (*London*), **A200**, 136 (1949).

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The Magnetic Susceptibility of Adsorbed Paramagnetic Salts[1]

BY MAX T. ROGERS AND ROBERT VANDER VENNEN

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The only systematic study of the magnetic susceptibilities of adsorbed salts is that of Bhatnagar, Mathur and Kapur[2] who reported that salts of iron, cobalt, nickel and manganese lost their paramagnetism when adsorbed on charcoal, but not when adsorbed on silica gel. This behavior might be explained by postulating the formation of a covalent complex between the ion and the surface of the charcoal; the magnetic moments would then correspond to the diamagnetic, or weakly paramagnetic covalent complexes, rather than the strongly paramagnetic ionic complexes, in each case. However, the charcoal they used was itself paramagnetic so there is some question concerning the interpretation of their observations. Since data of this type should provide fundamental knowledge concerning the nature of the adsorption of ions we have reinvestigated this problem using adsorbents free of paramagnetic impurities.

Experimental

Apparatus.—Magnetic susceptibilities were measured by the Gouy method using a semi-micro balance. The electromagnet was constructed in the shop of the Chemistry Department; the rectangular yoke is built up from 2″ × 8″ mild steel bars with 4.5″ diam. pole pieces located centrally. The coils are each wound with 1440 turns of No. 8 d.c.c. magnet wire and double turns of wire are separated by spacers to allow the circulation of cooling oil through the windings. Current is supplied by a 7.5-kw. motor generator set and is controlled both by resistances in series with the windings and by varying the field resistance of the generator. Interchangeable pole pieces of various types are provided and the pole gap can be continuously varied. The field was calibrated after each change of pole gap using both 29.20% nickel chloride solution and distilled water as standards.[3] The iron was demagnetized between runs by rapidly reversing a continuously diminishing direct current through the windings. The glass susceptibility tubes were each divided by a septum and showed no change in weight with field strength. Measurements were always made at

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[1] This work was performed under contract NR057232, Nonr-02300 with the Office of Naval Research.

[2] S. S. Bhatnagar, K. N. Mathur and P. L. Kapur, *Ind. J. Phys.*, **3**, 53 (1928).

[3] P. W. Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1943.