serum showed pronounced bluing due to the antigen-antibody reaction in the site.

Extract of castor meal which had been cooked for 32 min. at 100°C. with $Ca(OH)_2$ solution at pH 12.4 elicited no passive cutaneous anaphylaxis. The absence of the P.C.A. test in the sensitized sites indicated that all of the antigenic proteins of the seed had been so changed by the treatment that they had lost their original or native antigenicity. This result is consistent with previous knowledge that proteins are relatively quickly hydrolyzed by heating with strong alkali. It is also well known that alkaline hydrolysis of protein yields racemic aminoacid mixtures.

The samples of castor-seed meal which had been cooked for only 20 min. under the same conditions of pH and temperature were found to contain antigenic material which gave a positive P.C.A. test with anti-castor serum. This result may indicate that certain antigens had not yet been attacked during 20 min. or, more probably, that certain partially degraded castor-seed proteins retain some of their original specific antigenicity.

The results obtained in the passive cutaneous anaphylaxis tests are presented in Table I.

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Low Temperature Aminolysis of Methyl Stearate Catalyzed by Sodium Methoxide[1]

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Aminolysis of methyl stearate by both primary and secondary amine catalyzed by sodium methoxide was found to be rapid at 30°C. under anhydrous conditions. With primary amines under optimum conditions (mole ratio to ester: amine, 10; catalyst, 0.12), the minimum reaction times necessary to obtain yields of amide over 90% were: *n*-butylamine, 30 min.; *iso*-butyl-, 1 hour; allyl-, 1.8 hr.; benzyl-, 3.2 hr.; *sec*-butyl-, 16 hr.; ammonia (a heterogenous reaction requiring an optimum triethylamine to ester ratio of 2 ml./g. and a catalyst mole ratio of 0.20) 2 days. Secondary amines reacted rapidly at 30°C. (15 min. to 24 hr. for a 90% yield of amide) when the nitrogen atom was joined into a saturated ring or held at least one methyl group, but very slowly even at 100°C. when the substituent was dialkyl larger than methyl. Uncatalyzed, all reactions were extremely slow.

PART I. PRIMARY AMINE AMINOLYSIS

BASIC CATALYSTS have been used both in preparative and in kinetic studies of the aminolysis of esters. A number of preparative studies of the reaction of amines and esters, using sodium methoxide as the catalyst, showed rapid conversion to amide at high reaction temperatures but, in general, slow conversion at room temperature (1,2,3,4,5,6,7,8). None of these reports presented a study of optimum reaction conditions. In investigations of the kinetics of the aminolysis of esters at low temperatures (9,10,11, 12), a marked increase in the rate of reaction by alkoxide ion has been shown, but practical preparative conditions were not given. In the absence of any catalyst, high reaction temperatures (150°–250°C.) were often necessary to convert esters to amides rapidly and the use of pressure equipment with volatile amines was required (13,14,15,16,17,18,19,20). Studies relating the effect of structure and reactivity of both amines and esters have also been made (14) principally by Day and co-workers (21). Arnett, Miller, and Day (22) studied the effect of structure of various primary amines in reaction with methyl acetate at 25°C. This report revealed that the reactivity of the isomeric butylamines bracketed the reactivity range of most of the amines studied.

From the published results, it appeared that a general process could be developed for the preparation of amides through alkoxide catalyzed aminolysis of esters at a low temperature by a careful investigation of reaction conditions and by observance of rigorously anhydrous conditions to avoid catalyst destruction. Part I describes the results of a study of the sodium methoxide catalyzed aminolysis of methyl stearate by selected, structurally varied primary amines at 30°C. Part II reports the results with secondary amines.

The purposes of Part I are: (1) to report the optimum conditions found for the sodium methoxide catalyzed aminolysis of methyl stearate by primary alkylamines and to describe how these conditions were obtained; (2) to demonstrate that these conditions are applicable to a wide variety of primary amines and esters, and (3) to treat with three special cases. By

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optimum conditions is meant the minimum molar ratios of amine and of catalyst to ester which will provide a yield of approximately 90% at 30°C. The minimum time required to achieve such yields is, therefore, the dependent variable. The initial study was confined to the primary isomeric butylamines in view of Day's (22) report that they had a wide range of reactivity, and thus, the results would reflect on the utility of the method. Methyl stearate was used because stearamides are easily isolated by crystallization and because methyl esters are more reactive in aminolysis than other alkyl esters (23,24,25).

Experimental

Reagents:

Amines: The amines (Eastman, White Label) were stored over calcium hydride until reaction ceased and then were distilled twice from fresh calcium hydride through a helix column.

Ammonia: Anhydrous grade, rated by the supplier as 99.9% pure, was used without further treatment.

Methanol: Anhydrous grade, A.C.S. grade, was treated as were the amines.

Skellysolve B: Dried over calcium hydride and distilled from fresh calcium hydride through a Widmer column.

Methyl stearate: Prepared (26) and purified by two crystallizations, m.p. 38.0–38.5°C., saponification no. 187.8, acid no. 0.

Sodium methoxide solution: Two-molar solution was made by dissolving sodium, freshly cut and weighed under xylene, in the anhydrous methanol prepared as above. For set 2 (Table VI) of the ammonolysis reactions, a 4-molar solution was prepared.

Aminolysis reactions: The solution of the ester (0.01 mole) and amine in a stoppered flask was heated at 30 ± 0.1°C. and after 5 min. was treated with the requisite volume of methanolic sodium methoxide solution and mixed for 1 min. The crude amide, which co-precipitated with soap during the remainder of the reaction period, was isolated by filtration after the mixture had been triturated with Skellysolve B (33 ml./g. ester) at 0°C. Only the ester and amine were completely soluble at this temperature. To obtain a pure product the crude amide was refluxed with benzene (10 ml./g.) and then filtered to remove insoluble sodium stearate. The bulk of the amide (85–90% at high conversions) was recovered pure by crystallization from the filtrate at + 12°C. A secondary yield of amide was obtained from the soap by two extractions with 200 ml. benzene/g. soap. Evaporation of the benzene filtrates to dryness and cooling the original Skellysolve solution afforded small further amounts of amide. The yields of amide reported in this section of the paper are the sum of all amide fractions and the purity of all fractions was determined by melting point. Actual amide yield at high conversions was about 3–5% lower than the crude amide yield before soap removal.

Sodium stearate was acidified, crystallized, and the identity of the product formed was confirmed by mixed melting point with pure stearic acid.

The following new *N*-butylstearamides were prepared: *n*-butyl, m.p. 80.1–80.6°C.; found: C, 77.87; H, 13.48; N, 4.18. *Sec*-butyl, m.p. 81.3–81.8°C.; found: C, 78.07; H, 13.22; N, 4.18. Calcd. for $C_{22}H_{45}ON$: C, 77.78; H, 13.38; N, 4.13. Melting points were capillary melting points and were corrected.

Ammonolysis at the autogenous pressure: The requisite amount of sodium methoxide solution (see Table VI) was pipetted into a solution of the ester (0.03 mole) in triethylamine in a 7-oz. heavy-walled soft drink bottle. The methanol thus introduced was the amount required to make the solution of the desired solvent proportions in sets 1 and 2. In sets 3 and 4, additional methanol was added in the amounts needed. Excess liquid ammonia was weighed in without external cooling, the excess was allowed to escape and the bottle was sealed with a neoprene-lined one-hole crown cap and was placed in a thermostatted bath held at 30 ± 0.1°C. (The use of this cap facilitated venting by puncture of the neoprene lining when the reaction was over.) The stearamide, which precipitated during the course of the reaction, was isolated and purified by the same procedure described for the aminolysis reactions. The actual yield of stearamide was about 8% lower than the amide yield before soap removal at high conversions. In the absence of catalyst, the yield was 1.5% in 48 hr. This reaction was homogeneous initially; the catalyzed ammonolysis reactions were heterogeneous initially.

Ammonolysis at atmospheric pressure. An ammoniacal triethylamine-methanol solution was made by saturating a mixture of 22.30 g. of triethylamine and 77.68 g. of methanol by adding an excess of ammonia (as a liquid) and heating the mixture for 18 hr. at 30 ± 0.1°C. On the assumption of no loss of triethylamine, the ammonia concentration was determined by a simple acid titration and correcting for the triethylamine originally added. A sufficient volume of this mixture (about 10.7 ml./g. of ester) to give a mole ratio of ester/ammonia of 10 was added to 0.01 mole of ester containing the catalyst in 0.2 ratio and the solution was thermostatted. At the end of the reaction period, the stearamide, which precipitated during the course of the reaction (initially the reaction mixture was homogeneous) was isolated and purified by the procedure described above. The actual yield of stearamide was about 3% lower than the crude yield before soap removal at high conversions.

Results and Discussion

Throughout Part I reaction temperature is 30°C. and the molar ratios of amine and of catalyst are based on ester.

TABLE I

Optimum Reaction Conditions for Preparing the Isomeric N-Butylstearamides

Amine ratio[a] 10
Sodium methoxide ratio[a] 0.12

Amine	Reaction time, hr.	Amide yield	
		%[b]	%[c]
n-Butyl	0.5	92	96
iso Butyl	1.0	90	95
sec-Butyl	16.0	90	85

[a] Molar ratio to ester.
[b] Initial moles of ester, 0.01.
[c] Initial moles of ester, 0.25.

Optimum conditions for the preparation of the primary isomeric butylstearamides: Table I shows the optimum conditions for the preparation of the isomeric butylstearamides and the time required to attain the yields shown. A small effect on the yield

TABLE II

Rate of Aminolysis of Methyl Stearate by Primary Amines[a]

n-Butyl		*iso*-Butyl		*sec*-Butyl		*tert*-Butyl	
Time, hr.	Amide yield, %	Time, hr.	Amide yield, %	Time, hr.	Amide yield, %	Time, hr.	Amide yield, %
0.25	81.7	0.5	79.2	3	47.2	142	2.7
0.5	92.4	1.0	89.7	9	79.9	......	......
1.0	91.2	......	......	16	90.2	......	......
......	......	......	......	24	89.0	......	......
Allyl		Benzyl		Ammonia (Autogenous)[b]		Ammonia (Atmospheric)[c]	
Time, hr.	Amide yield, %	Time, hr.	Amide yield, %	Time, hr.	Amide yield, %	Time, days	Amide yield, %
0.25	66.2	0.5	55.6	4.0	22.4	2	48.5
0.5	84.4	1.0	76.2	15.5	71.4	4	74.4
1.8	95.1	2.0	88.4	30.0	87.8	7	89.8
2.5	95.9	3.2	94.6	48.0	93.0	9	90.6

[a] Molar amine to ester ratio, 10; molar sodium methoxide to ester ratio, 0.20 except for allyl and benzylamine, 0.12; initial moles of ester, 0.01 except in experiments at autogenous ammonia pressure, 0.03 mole.
[b] Solvent, 2 ml. triethylamine and 0.34 ml. methanol/g. of ester.
[c] Solvent, 10.7 ml./g. ester of solution of 0.29 g. triethylamine/g. methanol.

was observed by the experimental scale selected. Anhydrous conditions were found mandatory for optimum results. When *tert*-butylamine was used under the conditions of Table I, the yield was only 2.7% after 142 hr. and no attempt was made to determine the time required to attain an approximately 90% yield.

TABLE III

Effect of Catalyst Ratio on the Aminolysis of Methyl Stearate[a]

Amine[b]	Reaction time, hr.	Sodium methoxide ratio		Amide yield, %
		Added	Actively present[c]	
n-Butyl	0.5	0.02	0.001	2.0
		0.04	0.017	65.9
		0.08	0.052	88.0
		0.12	0.091	89.7
		0.20	0.171	92.4
iso Butyl	1.0	0.02	0	16.9
		0.04	0.014	74.5
		0.08	0.029	87.9
		0.12	0.088	90.1
		0.20	0.172	89.7
sec-Butyl	16.0	0.02	0.003	1.64
		0.04	0.011	63.2
		0.08	0.044	83.0
		0.12	0.081	88.5
		0.20	0.151	90.2
Ammonia (autogenous pressure)[d]	24.0	0.05	0.008	2.7
		0.10	0.052	39.3
		0.15	0.097	72.1
		0.20	0.130	85.8
	7.5	0.30	....	39.4
	7.5	0.40	....	44.8

[a] Initial moles of ester: aminolysis experiments, 0.01; ammonolysis experiments, 0.03.
[b] Molar amine to ester ratio, 10.
[c] Calculated to be actively present after correction for moles of soap formed.
[d] Solvent, 2 ml. triethylamine and 0.34 ml. methanol/g. ester.

TABLE IV

Effect of Amine Ratio on Yield of Isomeric N-Butylstearamides[a]

Ratio	Yield, %		
	n-Butyl	*iso*-Butyl	*sec*-Butyl
1.1	28.5	34.4	28.0
3	72.2	71.8	68.8
5	83.5	82.4	80.5
7	88.4	88.8	85.6
10	89.7	90.1	88.5
15	......	93.8	85.3

[a] Initial moles of methyl stearate, 0.01; molar sodium methoxide to ester ratio, 0.12; reaction time, *n*-butyl, 30 min.; *iso*-butyl 1 hr.; *sec*-butyl, 16 hr.

These optimum conditions were determined from investigations of the effect of varying catalyst and amine ratios on the reaction rates. In initial experiments in which the catalyst ratio was 0.20 and the amine ratio was 10, the minimum times (see Table II) required to attain an approximately 90% yield of amide were ½, 1, and 16 hr., respectively, for *n*-, *iso*-, and *sec*-butylamine. These minimum reaction times were the respective reaction periods used in a study (Table III, column 3) of the effect on amide yield of altering the catalyst ratio at a constant amine ratio of 10. The results showed that 0.12 was the minimum ratio of sodium methoxide necessary for approximately 90% yields. With reaction times held constant at ½, 1, and 16 hr. (for respectively *n*-, *iso*-, and *sec*-butylamines) and the catalyst ratio fixed at 0.12 the effect of changing the amine ration was studied next. The data in Table IV show that the minimum amine ratio was 10.

The effectiveness of sodium methoxide as a catalyst is indicated by the fact that in its absence the yield of *n*-butylstearamide was only 3.8% after 75 hr.

General applicability of the optimum conditions: The rate data in Table II for the aminolysis of methyl stearate by allyl- and benzylamine was obtained by using the optimum reaction conditions in Table I.

The order of reactivity, as determined from minimum reaction times, for the various amines studied was *n*-butyl > *iso*-butyl > allyl > benzyl > *sec*-butyl > *tert*-butyl. This agrees with the order found in kinetic studies by Day (22) for the reaction of these amines with methyl acetate catalyzed by ethylene glycol. If the minimum reaction time found in the present work for the aminolysis of methyl stearate by *n*-butylamine (30 min.) is divided by the minimum reaction time for the other amines, values for the reaction rates relative to *n*-butylamine are obtained. When these relative rates are compared with values calculated from the kinetic data of Day (22) using *n*-butylamine as the 100% basis, good agreement is found.

TABLE V

Relative Reaction Velocities for Preparing Primary Amine Acetamides and Primary Amine Stearamides

Amine	Relative k, % for methyl acetate[a]	Relative minimum reaction % for methyl stearate[b]
n-Butyl	100.0	100.0
iso-Butyl	41.1	50.0
Allyl	19.5	28.6
Benzyl	15.6	15.6
sec-Butyl	2.2	3.1

[a] At 25°C.; calculated from data in reference 22.
[b] At 30°C.

It is possible that this agreement is not purely accidental. It has been stated (10,11,12,25,27) that both modes of catalysis (alkoxide and glycol) increase the rate of nucleophilic attack on the carbonyl carbon by increasing the concentration of amine anion. It is conceivable that the relative order of amine reactivity (in both catalysis procedures) will be the same. If this is true, it should be possible to approximate the minimum reaction times (for alkoxide catalyzed aminolysis) using the rate data for the other primary amines listed by Day (22). This was actually done for the aminolysis by allyl- and benzylamine (Table II), where the calculated minimum reaction times were 2.5 and 3.2 hr., respectively. Found reaction times were 1.8 and 3.2, respectively, showing useful correlation.

Special Cases:

1. *Aminolysis at an amine ratio of 1.1.* Sometimes, it is desirable to conduct aminolysis with nearly equimolar proportions of ester and amine. Therefore, a study was made of the rate of aminolysis of methyl stearate at an amine ratio of 1.1 and a catalyst ratio of 0.12 by both *n*-butyl- and *iso*-butylamine. The minimum reaction times were found to be about 20 and 40 hr., respectively.

2. *Ammonolysis at the autogenous pressure:* Rates much slower than expected when ammonia acted as both reactant and solvent suggested that the solubility of the ester in ammonia was poor. A suitable solvent was therefore desired to increase the effective concentration of both reagents. A single suitable solvent was not found for this system but a mixture of triethylamine (a solvent for methyl stearate) and methanol (a solvent for ammonia) gave improved results. The data in Table VI show that the highest yield was obtained when 1 to 2 ml. of triethylamine and 0.34 ml. of methanol per gram of ester (representing methanol added with the catalyst) were used. From the data on the rate of ammonolysis shown in Table II it may be concluded that the minimum reaction time lies between 30 and 48 hr. Table III shows that a catalyst ratio of 0.20 was about optimum.

TABLE VI

Effect of Triethylamine/Methanol Ratio on Yield Stearamide [a]

Set 1		Set 2		Set 3	
Et_3N/ Ester,[b] ml./g.	Yield, %	Et_3N/ Ester,[c] ml./g.	Yield, %	Et_3N/ Ester,[d] ml./g.	Yield, %
0.12	45.9	0.12	32.5	0.50	53.0
0.22	53.8	0.22	40.3	0.67	53.7
0.45	61.8	0.45	45.8		
0.67	77.0	0.67	53.3	Set 4	
1.00	87.2	1.00	57.4		
1.34	86.0	......	......	MeOH/ Ester,[e] ml./g.	Yield, %
2.00	85.8	......	......		
3.00	73.5	......	......		
5.00	36.3	......	......		
7.00	14.7	......	......	0.67	35.9
......	......	......	......	1.00	34.6

[a] In 24 hr. with the use of 0.20 mole sodium methoxide per mole of ester and 10 moles ammonia per mole of ester.
[b] Also contains 0.34 ml. methanol/g. ester.
[c] Also contains 0.17 ml. methanol/g. ester.
[d] Also contains equal volume of methanol.
[e] Also contains 0.34 ml. triethylamine.

3. *Ammonolysis at atmospheric pressure:* The high rate of reaction under basic catalysis made possible ammonolysis in the absence of positive pressure but, of course, the lower solubility of ammonia in the mixed solvent at atmospheric pressure was a limiting factor in controlling the concentration of reactants. The data in Table II show that about 7 days are required to obtain a 90% yield (6). In the absence of catalyst, the yield was 17% in 9 days.

Effective catalyst concentration: The catalyst ratios given previously refer to the amount added experimentally, but there is reason to doubt whether these constitute the concentration effectively present. In all catalyzed experiments, small amounts of soap were always observed. If the number of moles of soap found be subtracted from the moles of sodium methoxide added, a correction can be made to determine the actual catalyst concentration present (Column 4, Table III). A plot of the amide yield as a function of the corrected sodium methoxide concentration is a smooth curve (as shown in Fig. 1 for *n*-butylamine, a typical example). That little or no amide was formed at low added sodium methoxide leads to the conclusion that the side reaction of soap formation was preferential and hence more rapid than amide formation. The most probable explanation for this rapid preferential reaction to form soap is the presence of water in small amounts which escaped even the stringent drying conditions used. The alternate explanation of ether formation or of β-elimination (11), which are not likely at 30°C., would be evidenced by gradually increasing amounts of soap with increasing amounts of catalyst (see Part II). This was not found in any set of experiments using primary amines. The actively present minimum catalyst ratio was then about 0.08 instead of 0.12 as was given previously.

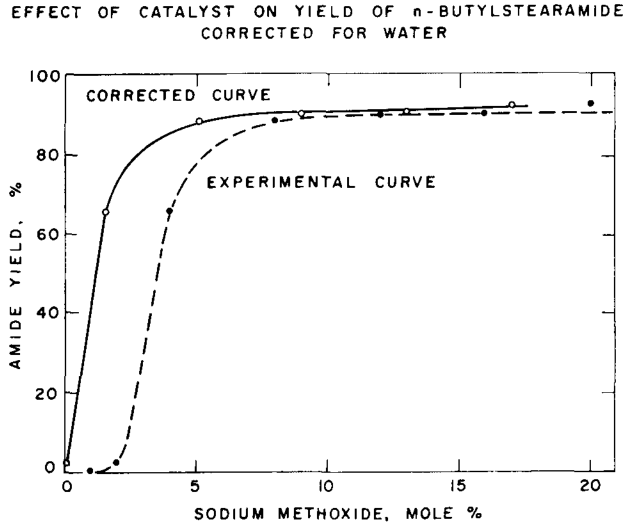

FIG. 1. Effect of catalyst ratio on yield of *n*-butylstearamide.

PART II. SECONDARY AMINE AMINOLYSIS

Secondary amines were reported to react much more slowly than primary amines with simple aliphatic esters at room temperature (28,29,30,31,32). Dimethylamine, piperidine and morpholine reacted slowly with the reactive ester methyl lactate (25) but amines with the nitrogen substituent larger than methyl did not react at all (28,32) even when sodium methoxide was used as the catalyst (32). Sodium methoxide was found to accelerate the rate of the reaction of methyl acetate with both piperidine and morpholine, however (9). With no catalyst and at high temperatures fatty morpholides formed (33) and even hindered dialkylamines were found to react with aliphatic esters at 250°C. (20).

This section reports the effect of the use of sodium methoxide on the reaction velocity at 30° and at 100°C. in the aminolysis of methyl stearate by selected, structurally varied secondary amines. Comparisons are made with the uncatalyzed reactions. Emphasis is on the difference in amine reactivity with structure under reaction conditions which gave fast reaction velocities with the primary amines. For this reason the catalyst and amine to ester ratios were held constant at 0.20 and 10, respectively, for all experiments.

Experimental

All reagents, including the sodium methoxide solution were prepared as in Part I.

General procedure: The solution of ester (0.03 mole) in the amine in a 7-oz. heavy walled soft-drink bottle was heated at 30° ± 0.1°C. for five minutes (or at 100° ± 0.1°C. for 15 minutes), the sodium methoxide was pipetted in and the bottle capped and mixed for one minute. Soap precipitated out immediately in all experiments but only methylamylstearamide co-precipitated in this series. The crude reaction mixture was poured into benzene at room temperature (20 ml./g. of ester) and filtered twice without suction to remove the insoluble sodium stearate and catalyst. Evaporation of the filtrate at 100°C. in a current of air gave the crude amide, neutral to methyl red and hence free of amine, soap, and catalyst. The crude yield of amide was obtained either from the nitrogen content or, if conversions were high, gravimetrically (see Table VIII).

In the gravimetric procedure, the crude amide was crystallized from Skellysollve B (10 ml./g.) at −25°C. and the filtrate evaporated. The soap fraction, which contained a considerable amount of occluded amine and amide, was extracted on the filter paper with 100 ml. hot benzene, dried to constant weight, and extracted twice with 250 ml. benzene. This treatment gave additional small amounts of amide as well as soap free of impurities, which permitted the estimation of the active sodium methoxide content of each experiment (see Part I). Total yield of all the amide fractions (identified by melting point) was the yield of amide reported in Table VII. Agreement with the yield reported from the nitrogen content was good where a comparison could be made.

Aminolysis by diethanolamine: Poor solubility of methyl stearate in this amine as well as its low volatility necessitated another preparative procedure. The reagents, together with extra methanol (1 ml./g. ester), were treated as in the above section. After 10 min. heating at 100°C., with occasional mixing, the reaction mixture became homogeneous. Heating was continued for 50 min. and the reaction mixture was poured into methanol (22.3 ml./g. of ester) and cooled to 0°C. This quantity of amide, plus an additional amount which crystallized at −25°C., was the crude yield reported in Table VII and was 94.2% free of amine by HCl titration (methyl red). Recrystallization from methanol (10 ml./g.) gave amide in 85% yield free of soap and amine by titration and pure by % carbon, hydrogen, and nitrogen. Sodium stearate was identified as in Part I.

The following new stearamides were prepared: dimethyl [mentioned by (34) but not characterized] m.p. 48.3–48.5°C.; found: C, 77.43; H, 13.44; N, 4.36; calcd. for $C_{20}H_{41}ON$: C, 77.18; H, 13.30; N, 4.50; methyl-*n*-amyl, m.p. 77.0–77.5°C.; found: C, 78.40; H, 13.57; N, 3.70; calcd. for $C_{24}H_{49}ON$: C, 78.43; H, 13.45; N, 3.81; piperidine, m.p. 44.0–44.3°C.; found: C, 79.23; H, 13.43; N, 3.86; calcd. for $C_{23}H_{45}ON$: C, 78.60; H, 12.93; N, 3.98. Melting points were determined by the capillary method and were corrected.

Results and Discussion

In Table VII the amines are arranged in order of decreasing reactivity. The order of diethanolamine could not be determined because it was a heterophase reaction at both 30° and 100°C. However, reaction was very rapid at 100°C. Classification of individual amines into two groups, one relatively reactive and the other unreactive, can be made. In the reactive group can be placed the first four amines which reacted to give high yields, even at 30°C. and diethanolamine, which gave a high yield in 1 hr. at 100°C. Amines in this group are characterized by having a nitrogen atom relatively unhindered by substituents. The balance of the amines listed fall in the unreactive group which have low rates of reactivity even at 100°C. Here, steric effects are much more pronounced. Thus, when the substituents on the amine nitrogen were dimethyl, methyl and alkyl, or formed a saturated ring, reaction was rapid. Hydrogen bonding is thought (28) to bend the carbon chains away from the nitrogen atom in diethanolamine, preventing the shielding of the reactive center and thus enhancing reactivity. On the other hand when the substituents were dialkyl larger than methyl little or no reaction occurred even at high temperatures. Although kinetic measurements (28) have revealed this same order of reactivity, rates with all secondary amines were reported to be slow (31). In this study the rates for the unhindered amines approached those for the alkoxide-catalyzed aminolysis by primary amines thus emphasizing the practical advantage of this catalyst.

TABLE VII

Aminolysis of Methyl Stearate by Secondary Amines

Amine ratio[a] 10
Sodium methoxide ratio[a] 0.20

Amine	Temperature, °C.	Reaction time, hr.	Active sodium methoxide[a]	Amide yield, %[b]
Dimethyl	30	<0.25	0.137	96.4[c]
Piperidine	30	<0.25	0.109	71.6
	....	2[d]	0.132	97.5
Morpholine	30	0.25	0.099	56.1
	....	2[d]	0.116	93.2[c]
Methyl-*n*-Amyl	30	1	0.091	20.0
	....	24[d]	0.119	93.0[c]
Diethanol	100	1	......	90.5[c]
Diallyl	100	1	0.091	27.6
	....	24[d]	0.069	90.4
Diethyl	100	1	0.082	23.3
	....	24	0.049	82.0
Di-*n*-Butyl	100	1	0.092	5.7
	....	24	0.025	61.0
Di-*iso*-Butyl	100	0	0.100	0[c]
	....	24	0.008	0[c]
Di-*sec*-Butyl	100	1	0.072	0[c]
	....	24	0.042	0[c]
Dimethyl	30	24	......[e]	0[c]
Piperidine	100	24	......[e]	10.4
Morpholine	100	24	......[e]	0[c]

[a] Molar ratio to ester.
[b] Calculated from % nitrogen on the crude reaction product.
[c] Determined gravimetrically.
[d] Approximate minimum reaction time.
[e] None added.

No drift in the concentration of active sodium methoxide (see Part I) with change in reaction time was found in reactions run at 30°C., although fluctuations caused by precision errors were apparent (Table VII). In a rate study at 100°C. using di-isobutylamine, however, a gradual downward drift in alkoxide concentration was observed with increase in time. All of the other hindered amines at 100°C. also showed a decrease in active sodium methoxide with increase in time in reactions run at 1 hr. and at 24 hr. It is possible that the catalyst reacts at 100°C. with ester to form soap and dimethyl ether, as has been found for methyl benzoate (35,36,37), thus imposing a limitation on the use of this catalyst in the aminolysis of esters.

A comparison of the catalyzed reactions with corresponding uncatalyzed reactions reveals the marked effect of alkoxide catalysis. Catalyzed, dimethylamine reacted in less than 15 min. at 30°C. to give a 95% yield of amide; uncatalyzed, no measurable reaction occurred in 24 hr. at this temperature. Catalyzed, piperidine and morpholine reacted within 2 hr. at 30°C. to produce yields of amide over 90%; uncatalyzed, little or no reaction occurred in 24 hr. even at 100°C.

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Correlation Between Critical Micelle Concentration, Fatty Soil Removal, and Solubilization

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Using two model soil-detergent systems (hard substrate/triglyceride; cotton/fat, mineral oil, graphite) it was shown that soil removal begins at, or near, critical micelle concentration (cmc), confirming the work of other investigators with different systems. Maximum detergency occurs at concentrations considerably in excess of cmc, varying some 6 to 10 times cmc for different surfactants. An equation for soil removal showed excellent fit of experimental values for both detergency systems.

Direct correlation between cmc, solubilization (of several materials), and soil removal was demonstrated. Marked differences between surfactant type and solubilization of triglycerides were found. The nonionic surfactants were excellent solubilizers for triolein correlating with their effective soil removal. Neither sodium oleate nor sodium tripolyphosphate effectively solubilized the triglyceride but both are effective soil removers, suggesting that their soil removal mechanism differs from the nonionics, possibly as an emulsification or displacement mechanism. Solubilization of triglyceride occurs most effectively considerably in excess of cmc.

EARLY INVESTIGATORS noted the dependence of optimum detergency upon detergent concentration, but Preston's (10) work is the most frequently quoted to show that detergency and critical micelle concentration are related. However, he stated that washing power had attained its maximum at critical micelle concentration (cmc), and that solubilization appeared to begin at cmc. Goette (5), in reviewing cmc and detergent power, noted that the peak break in the detergency curve did not necessarily coincide with cmc, and believed that further data were necessary to clarify this correlation. Removal of radioactive soils was found by Chandler and Shelberg (2) to begin with micelle formation and to increase rapidly when micelle concentration was 2- or 3-fold that of cmc. Demchenko (3) verified the practical significance of cmc, but claimed that soil removal started only when detergent concentration was in excess of cmc. The importance of cmc to soil removal therefore is well recognized and recent work suggests that the optimum in removal occurs at concentrations in excess of cmc, but systematic investigation on a sufficiently broad scale to fortify these opinions has not been available.

To help clarify the cmc-detergency correlation, it is proposed to use the data obtained for model systems using radiotagged triglycerides as soil, and substrates such as glass and metals. Detergent-concentration curves had been obtained (7, 8) for these systems, but no effort had heretofore been made to relate these curves to cmc. Additionally, data obtained for removal of graphite (by reflectance measurement) and fatty and mineral oil from cotton are included. Correlation of cmc and soil removal with solubilization data, from another paper (4), using essentially the same radiotagged fats in such systems was reserved for the present discussion.