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UNITED STATES PATENT OFFICE

2,304,830

AMIDES OF HETEROCYCLIC CARBOXYLIC ACIDS

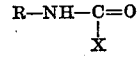
Morris Katzman, Chicago, Ill., assignor to The Emulsol Corporation, Chicago, Ill.

No Drawing. Application December 29, 1939, Serial No. 311,519

12 Claims. (Cl. 260—295)

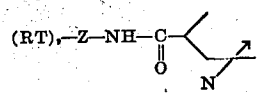
This invention relates to new chemical compounds which are, in general, amides of higher molecular weight primary aliphatic amines with carboxylic acid derivatives of heterocyclic compounds containing nitrogen in the ring.

These novel compounds are characterized by possessing interface modifying properties and other properties, as hereinafter pointed out, rendering the same highly useful for the purposes for which such agents are employed in the various arts. Many of the compounds falling within the scope of the present invention may be represented by the general formula

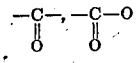


wherein R is an aliphatic organic radical containing at least eight carbon atoms, and X comprises a heterocyclic group containing nitrogen in the ring. The radical R in the above general formula is, as stated, aliphatic (including cycloaliphatic) but the best results appear to be obtained where R is an aliphatic hydrocarbon radical containing from 12 to 18 carbon atoms. It will be understood that the radical R may contain substituent groups such as halogen, amino, sulphonic, sulphate, phosphate, carboxyl, nitrile, hydroxy and similar radicals.

A more limited group of compounds which, for various purposes, are particularly useful, may be characterized by the following general formula



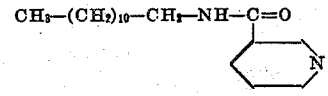
wherein R is an aliphatic radical containing at least six carbon atoms, T is —O—,

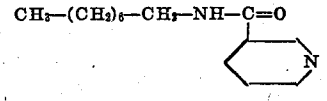


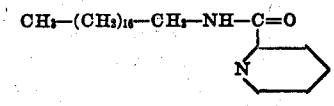
or —NH—, Z is an aliphatic radical, N is part of a heterocyclic ring, the arrow indicating that N is in the ring but the exact location of the N in the ring is not fixed, and v is one or two. Representative compounds falling within this group of compounds are those numbered 19, 20, and 24 to 35, inclusive, some of said latter compounds being quaternary ammonium derivatives.

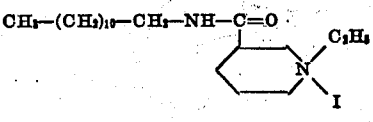
It will be seen, from the general formula, that the compounds are amides, the amido linkage resulting from condensing a higher molecular weight primary amine with a carboxylic derivative of a heterocyclic compound containing nitrogen in the ring. Among such heterocyclic compounds are nicotinic acid, iso-nicotinic acid, other pyridine carboxylic acids such as 1-pyridine-carboxylic acid, picolinic acid, quinaldine carboxylic acids, quinolinic acid, isoquinolinic acid, cinchomeronic acid, lutidinic acid, berberonic acid, alpha-carbocinchomeronic acid, homarin, and homologues and derivatives thereof such as hydroxy, methoxy and other substituted carboxylic acids of pyridine and like heterocyclic compounds as illustrated hereinafter as well as reduction products thereof.

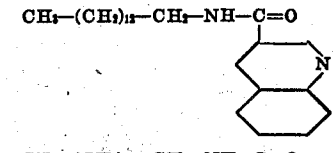
In order that the nature of the invention may become more apparent, there are listed hereinbelow representative compounds which fall within the scope of the invention:

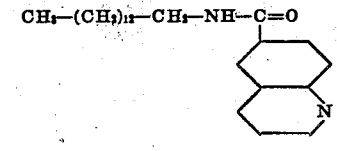
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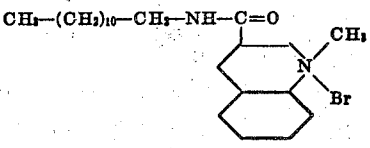
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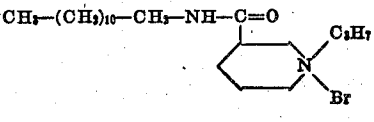
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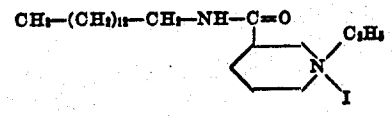
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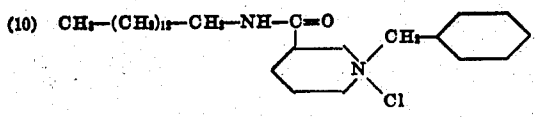
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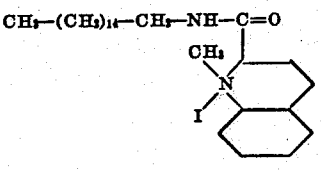
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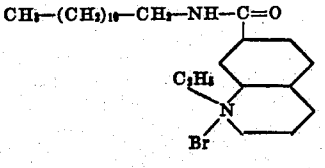
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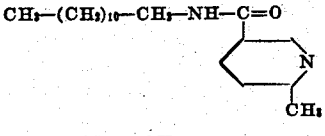
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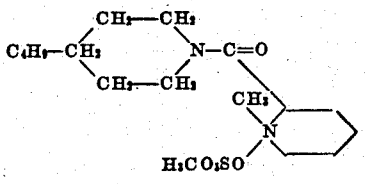
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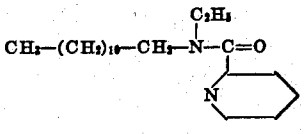
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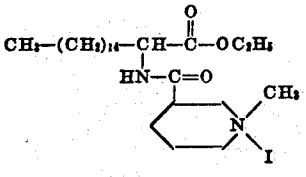
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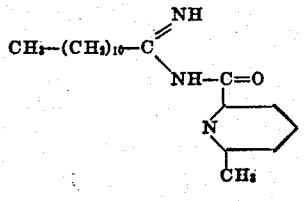
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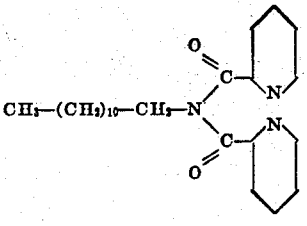
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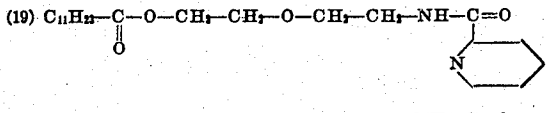
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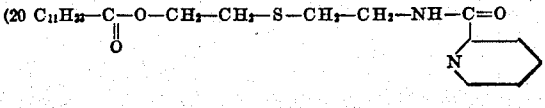
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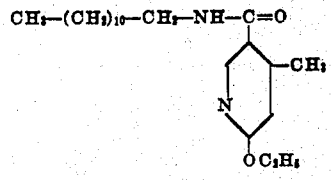
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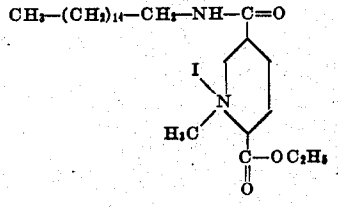
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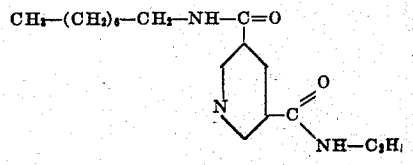
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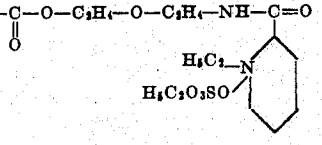
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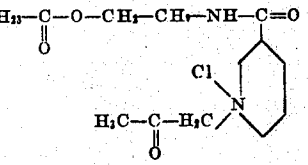
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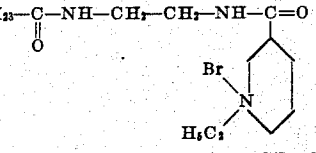
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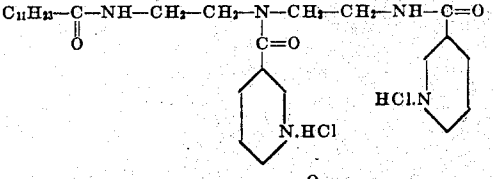
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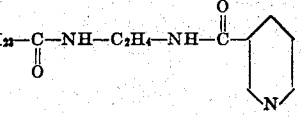
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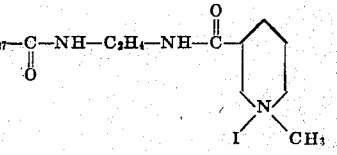
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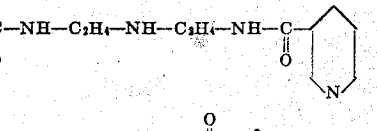
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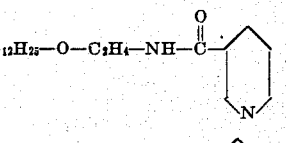
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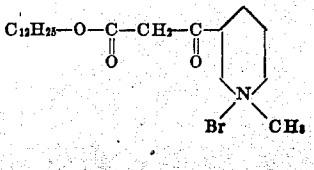
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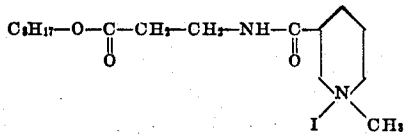
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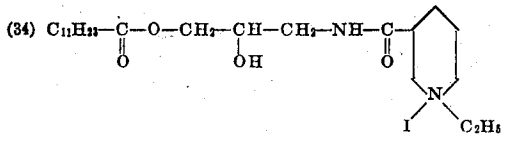
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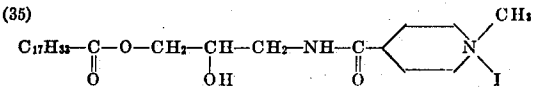
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In general, the products are produced by heating the reactants, for example, nicotinic acid, or esters or halides thereof, and lauryl amine, for one-half hour to several hours at elevated temperatures, for example, 200 to 250 degrees C., until the evolution of water ceases. The products may be purified, if desired, or may be utilized as such, or they may further be reacted to introduce other groups.

Of particular value are the quaternary ammonium compounds, illustrated by Examples 4, 7, 8, 10, 11 and 12 in the list hereinabove. These quaternary ammonium derivatives may be prepared from the reaction products of the carboxylic acid with the amine by treating said reaction products with the usual alkylating, arylating, and aralkylating agents as, for example, methyl iodide, ethyl iodide, propyl bromide, butyl bromide, cyclohexyl chloride, benzyl chloride, dimethyl sulphate, diethyl sulphate, and the like, or with organic and inorganic acids such as sulphuric, phosphoric, hydrochloric, citric, tartaric and the like.

The following examples are illustrative of methods which have been found suitable for preparing various of the compounds which are disclosed herein. It will be appreciated that other methods may be utilized, that the proportions of reacting ingredients, times of reactions, and temperatures may be varied and that supplementary processes of purification and the like may be resorted to wherever found desirable or convenient. These and other variations and modifications will be evident to those skilled in the art in the light of the guiding principles which are disclosed herein.

Example A

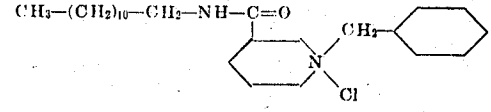
(1) 13.2 grams of nicotinic acid, having a melting point of 220 degrees C., and 16.9 grams of commercial lauryl amine were heated for 30 to 40 minutes at 220 degrees C. to 250 degrees C. until no more water was evolved. The resulting reaction product was solid at room temperature. When added to hot water, it became oily and when an excess of a strong acid such as hydrochloric acid, sulphuric acid, or phosphoric acid was added, the resulting product foamed.

(2) 15.1 grams of the reaction product of part (1) hereinabove and 15.3 grams of ethyl iodide were heated until the ethyl iodide started to reflux. The heating was then discontinued but the reaction mixture continued to reflux for several minutes and then died down. The final product was a thick syrup having exceedingly good foaming and frothing properties in both dilute acid and alkali. Apart from the surface active properties rendering the product useful for detergent, shampoo, flotation, textile treating and other purposes, as hereinafter pointed out, the product also has therapeutic, antiseptic, disinfectant, and medicinal properties.

If desired, the reaction product may be purified by washing with petroleum ether to wash out any unreacted fatty matter and excess ethyl iodide.

Example B

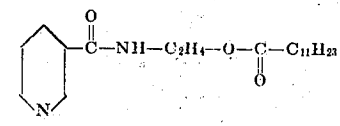
7.1 grams of the amine of lauryl amine and nicotinic acid, produced as described in part 1 of of Example A, were mixed with 7.4 grams of benzyl chloride and the resulting mixture was heated for thirty minutes on the boiling water bath. It was then extracted with petroleum ether to remove the excess benzyl chloride and the residue was then dried. It consisted substantially of a compound having the formula



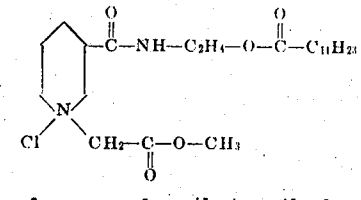
The product was water-soluble, foamed or frothed excellently and was useful for the general purposes hereinafter set forth.

Example C

(1) 12.4 grams of nicotinic acid and 6.3 grams of monoethanolamine were heated together for ½ hour at a temperature ranging from 175 degrees C. to 230 degrees C. 18.5 grams of lauric acid were then added to the reaction mixture and the entire mass was heated for one hour at a temperature of 200 degrees C.–230 degrees C., a vacuum of 140–40 mms. being utilized to draw off the water as it formed during the reaction. The reaction product was a brown plastic solid at room temperature, was relatively insoluble in water but, on the addition of hydrochloric acid, became soluble and exhibited foaming properties. It comprised essentially a compound having the following formula:



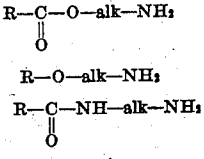
(2) 15.1 grams of the reaction product of part 1 hereof and 11 grams of methyl chloracetate were mixed together and heated for 2 hours at a temperature ranging from 60 degrees C. to 90 degrees C. The reaction product was a brown semi-viscous mass when hot. It became substantially more viscous at room temperature. It was warmed to 50 degrees C. and washed three times, each time with 100 cc. portions of petroleum ether, the petroleum ether being decanted after each washing, and the petroleum ether adhering to the residue was driven off by evacuating on the hot water bath. The product was a medium brown powder, very hygroscopic, soluble in water, and exhibited foaming properties. It comprised essentially a compound having the formula:



It is, of course, clear that methods other than those described may be employed for producing

the novel compounds of the present invention. Furthermore, the order of reacting the ingredients may be modified as will be apparent to those skilled in the art.

As previously indicated, the aliphatic radical represented by R in the general formula set forth hereinabove may be derived from various sources. Such sources include, for example, higher molecular weight mono-, di- and poly-primary aliphatic (including cycloaliphatic) amines, simple and compound, such as octyl amine, nonyl amine, decyl amine, undecyl amine, dodecyl amine, myristyl amine, cetyl amine, oleyl amine, linoleyl amine, stearyl amine, ricinoleyl amine, palmitoleyl amine, melissyl amine, ceryl amine, carnaubyl amine, myricyl amine, branched chain octyl, decyl, dodecyl, tetradecyl, hexadecyl, and octadecyl aliphatic amines as, for example, 2-ethyl hexyl amine-1, 2-n butyl octyl amine-1, 2-butyl tetradecyl amine-1, and, in general, the higher molecular weight saturated and unsaturated aliphatic straight chain and branched chain amines, those containing from 12 to 18 carbon atoms being particularly suitable. As previously pointed out, these amines may contain substituent groups of the character mentioned hereinabove and, in addition, such amines include those which are interrupted by ester, ether, sulphur, carbonyl, or amino linkages as, for example,



where R is an aliphatic alkyl group or substituted alkyl group containing at least six and preferably at least eight carbon atoms, alk is alkylene such as C_2H_4, C_3H_6, C_4H_8 and the like or (alkylene-O-alkylene)$_n$ or (alkylene-S-alkylene)$_n$ where n is an integer such as 2, 3, 4 or more. It is obvious, of course, that mixtures of any two or more of the above mentioned and similar amines may be utilized and, indeed, in commercial practice it will usually be found that commercial mixtures of such amines are more readily available and, therefore, more economical to employ.

At least many of the compounds of the present invention have utility in various arts in which interface modifying agents are employed. Many are resistant to precipitation by calcium and magnesium salts and are compatible with acid and alkali media. They may be utilized in the textile and related industries wherein they function for softening, wetting, detergent, emulsifying, penetrating, dispersing, frothing and foaming purposes. The textiles, various treatments of which in the presence of the agents of the present invention is rendered effective, comprise natural products such as cotton, wool, linen and the like as well as the artifically produced fibres (and fabrics), such as rayon, cellulose acetates, cellulose ethers and similar artificial products. It will be understood, of course, that the agents may be used in aqueous and other media either alone or in combination with other suitable salts of organic or inorganic character or with other interface modifying agents. In the dyeing of textiles they may be employed as assistants in order to bring about even level shades. They may be used in the leather industry as wetting agents in soaking, dyeing, tanning and the softening and other treating baths for hides and skins. They may be used to facilitate the preparation or enhance the stability of emulsions or dispersions of aqueous and water-repelling substances such as resins of various kinds, oils, fats, higher fatty acids, and waxes of vegetable, animal and mineral origin, and such emulsions or dispersions may be neutral, acid or alkaline in character. Their utility as emulsifying agents enables them to be employed for the preparation of emulsions which may be used for insecticidal, fungicidal and for similar agriculture purposes. They may be employed in dentifrices and for bactericidal and bacteriostatic purposes by themselves or in combination with other surface modifying agents and with other bactericidal agents. They have utility in the preparation of cosmetic creams such as cold creams, vanishing creams, tissue creams, shaving creams of the brushless and lathering type and similar cosmetic preparations. Another use to which the agents of my invention may be placed is for the treatment of paper where they may be employed, for example, as penetrating agents in the cooking of the paper pulp or the like. Their capillary or interfacial tension reducing properties enables them to be employed in the fruit and vegetable industry in order to effect the removal from fruits and the like of arsenical and similar sprays. They possess marked utility in the ore dressing industry wherein they function effectively in froth flotation processes, particularly for the sepration of silica from ores containing the same. Their interface modifying properties also permit their use in lubricating oils and the like enabling the production of effective boring oils, cutting oils, drilling oils, wire drawing oils, extreme pressure lubricants and the like. They may also be used with effect in the preparation of metal and furniture polishes, as pickling inhibitors in metal cleaning baths, shoe polishes, in rubber compositions, for breaking or demulsifying petroleum emulsions such as those of the water-in-oil type which are encountered in oil-field operations, and for various other purposes which will readily occur to those versed in the art in the light of my disclosure herein.

They may be employed for the preparation of shampoos, dentifrices and the like. In general, they may be dissolved in water or aqueous media and utilized in that form or, in the case of solid products, they may be packaged and sold in such form preferably mixed with diluents. They may also be utilized for cleansing, laundering and washing operations with advantage.

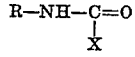
The products of the present invention may be employed alone or together with lesser or greater quantities of inorganic or organic compounds. Thus, for example, they may be employed together with salts such as sodium chloride, alkali metal phosphates including pyrophosphates and tetraphosphates, sodium sulphate, alums, perborates such as sodium perborate, and the like. They may be utilized in alkaline or acid media in the presence of sodium carbonate, sodium bicarbonate, dilute acids such as hydrochloric, sulphurous, acetic and similar inorganic and organic acids. They may also be employed in the presence of such diverse substances as hydrophillic gums including pectin, tragacanth, karaya, locust bean, gelatin, arabic and the like, glue, vegetable, animal, fish and mineral oils, solvents such as carbon tetrachloride, monoethyl ether of ethylene glycol, monobutyl ether of ethylene glycol, monoethyl nd monobutyl ethers of diethylene glycol, cyclohexanol, and the like. They may be used together with wetting, emulsifying, frothing, foaming, penetrating and de-

tergent agents such as the higher molecular weight alkyl sulphates, phosphates, pyrophosphates and tetraphosphates as, for example, lauryl sodium sulphate, myristyl sodium pyrophosphate, cetyl sodium tetraphosphate, octyl sodium sulphate, oleyl sodium sulphate, and the like; higher molecular weight sulphonic acid derivatives such as cetyl sodium sulphonate and lauryl sodium sulphonate; sulphocarboxylic acid esters of higher molecular weight alcohols such as lauryl sodium sulphoacetate, dioctyl sodium sulphosuccinate, dilauryl potassium sulpho-glutarate, lauryl monoethanolamine sulphoacetate, and the like; sulphuric and sulphonic derivatives of condensation products of alkylolamines and higher fatty acids; Turkey-red oils; compounds of the type of isopropyl naphthalene sodium sulphonate, and other classes of wetting agents.

It will be understood that the products may be employed in the form of impure reaction mixtures containing substantial proportions of the effective interface modifying agent or agents or, if desired, for any particular purposes, purification procedures may be employed to produce pure or substantially pure products. Those versed in the art are familiar with the types of purification methods which may be employed with advantage herein, particularly in the light of the disclosures made hereinabove.

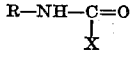
What I claim as new and desire to protect by Letters Patent of the United States is:

1. Chemical compounds of the formula



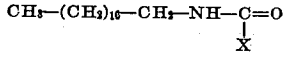
wherein R is a non-nitrogenous aliphatic radical containing from twelve to eighteen carbon atoms, and X comprises a heterocyclic group containing nitrogen in the ring, the —C=O group being linked directly to a carbon atom of X.

2. Chemical compounds of the formula



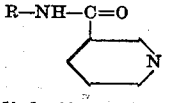
wherein R is an aliphatic hydrocarbon radical containing from eight to eighteen carbon atoms, and X comprises a heterocyclic group containing nitrogen in the ring, the —C=O group being linked directly to a carbon atom of X.

3. Chemical compounds of the formula



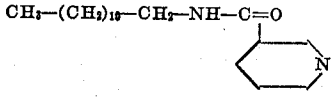
wherein X comprises a heterocyclic radical containing nitrogen in the ring, the —C=O group being linked directly to a carbon atom of X.

4. Chemical compounds of the formula

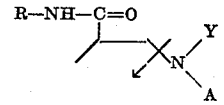


wherein R is an aliphatic radical containing from eight to eighteen carbon atoms.

5. A chemical compound having the formula

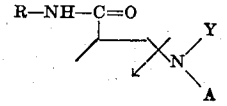


6. Chemical compounds of the formula



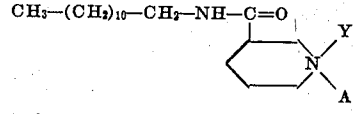
wherein R is an aliphatic radical containing at least eight carbon atoms, N is part of a heterocyclic ring, A is an anion, and Y is a member selected from the group consisting of alkyl, aralkyl, aryl, and substitution products thereof.

7. Chemical compounds of the formula



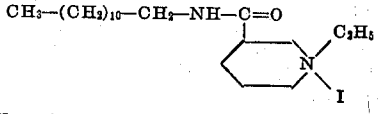
wherein R is an aliphatic hydrocarbon radical containing from eight to eighteen carbon atoms, N is part of a heterocyclic ring, A is an anion, and Y is a member selected from the group consisting of alkyl, aralkyl, aryl, and substitution products thereof.

8. Chemical compounds of the formula

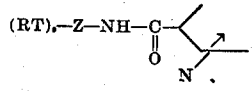


where A is halogen and Y is alkyl.

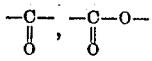
9. A chemical compound having the formula



10. Chemical compounds of the formula.

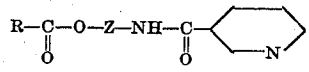


wherein R is an aliphatic radical containing at least eight carbon atoms, T is a member selected from the group consisting of —O—,



and —NH—, Z is an aliphatic radical, N is part of a heterocyclic ring, and v is one or two.

11. Chemical compounds of the formula

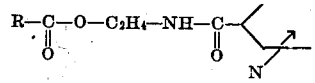


wherein



is an aliphatic acyl radical containing at least six carbon atoms, and Z is an aliphatic radical.

12. Chemical compounds of the formula



wherein



is an aliphatic non-nitrogenous acyl radical containing at least six carbon atoms, and N is part of a heterocyclic ring.

MORRIS KATZMAN.