

# EXHIBIT 14

## United States Patent Office

3,160,632

Patented Dec. 8, 1964

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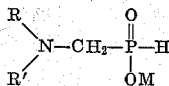
3,160,632

AMINOMETHYLENPHOSPHINIC ACIDS,  
SALTS THEREOF, AND PROCESS FOR  
THEIR PRODUCTION

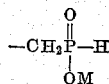
Arthur Dock Fon Toy, Park Forest, and Eugene H. Uhing, Chicago, Ill., assignors to Stauffer Chemical Company, New York, N.Y., a corporation of Delaware  
No Drawing. Filed Jan. 30, 1961, Ser. No. 85,493  
17 Claims. (Cl. 260-268)

The present invention relates to aminomethylene-phosphinic acids, salts thereof and the process of producing such compounds by reacting chloromethylphosphinic acid, or salts thereof, with ammonia, organic primary and secondary amines in the presence of a base.

The new aminomethylenephosphinic acid compounds have the general formula:



wherein R is from the group consisting of hydrogen, alkyl, aryl, alkaryl, hydroxyalkyl, and

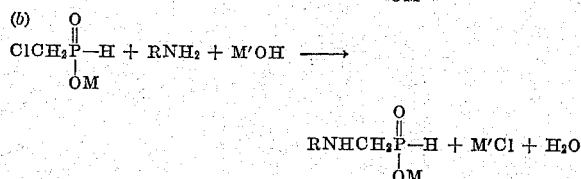
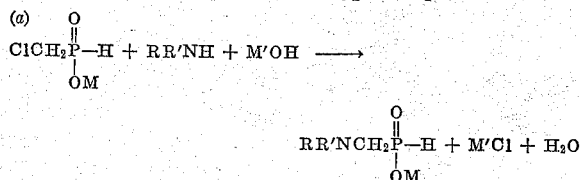


radicals, R' is from the group consisting of R, alkylene-NRR', arylene-NRR' and heterocyclic alkylene-NRR' radicals, and M represents hydrogen and salt-forming cations.

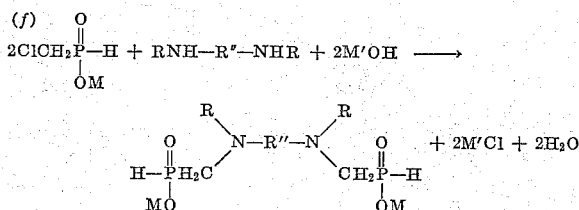
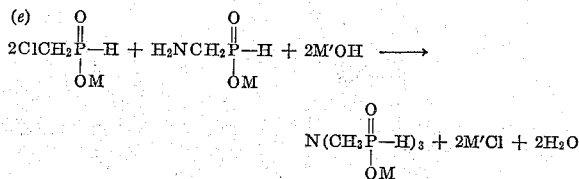
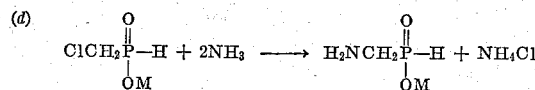
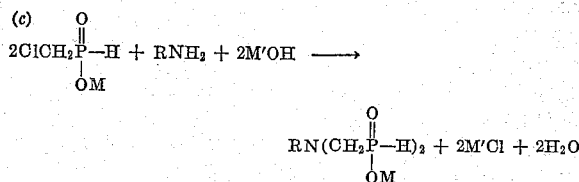
The new compounds have a wide variety of uses such as chelating agents, wetting agents, biologically active compounds and as chemical intermediates for the production of aminomethylenephosphinic acids and derivatives thereof.

In the process of producing the new compounds, the first step is to neutralize the chloromethylphosphinic acid with the appropriate amine or metal bases to form the salts and then react the salt with the appropriate amine in the presence of excess amine or other base. In general, the reaction may be carried out in one step by simply using sufficient amine or other base to form the salt and effect the reaction without initial separation of the salt. However, it is satisfactory and sometimes desirable to start with an amine or alkali base salt of chloromethylphosphinic acid and carry out the second stage reaction with the desired primary or secondary amine. With an easily volatilized amine compound, such as ammonia which is capable of forming bis and tris-methylenephosphinic type products, it is generally preferred to first prepare the amino mono-methylenephosphinic compound and then react this compound with additional amounts of the chloromethylphosphinic acid salts to form the bis and tris-methylenephosphinic derivatives.

The general reaction which takes place may be illustrated by the following selected typical equations:



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R and R' in the above typical equations are the same as shown in the above product formula, and M and M' are the same or different salt-forming cations, and R'' is an alkylene, arylene, or cycloalkylene radical.

The products of the above equations are shown in their salt forms. Where desired, the free methylenephosphinic acids may be obtained by reacting the salts with a strong acid, such as hydrochloric acid and separating the acid product from the reaction mixture.

The reaction is quite general and proceeds with a large number and variety of organic primary and secondary amines as well as ammonia and ammonium compounds. Typical organic amino compounds which we have found suitable for use in the process may be illustrated by the following general types:

45 Mono and dialkyl amines (1-18 C atoms)

Mono and diaryl amines

Alkylene di and polyamines

Phenylene diamines

45 Heterocyclic primary and secondary amines

50 Substituted alkyl primary and secondary amines

Substituted aryl primary and secondary amines

It has now been found that the above type primary and secondary amines readily react with chloromethylphosphinic acid and salts in aqueous alkaline solutions with release of hydrochloric acid and the formation of the aminomethylenephosphinic acid derivatives. In carrying out the reaction sufficient alkalinity must be present to neutralize the acidity of the chloromethylphosphinic acid and absorb the hydrochloric acid liberated by the reaction. In general, an excess of the alkaline base may be employed to drive the reaction to completion. The base may be an excess of the amine with which the desired reaction is to be carried out, but preferably the alkalinity may be obtained by the use of cheaper alkalies such as caustic soda.

The chloromethylphosphinic acid starting material may be prepared in accordance with the method described in U.S. patent application (Serial No. 65,018, filed Oct. 26, 1960) which comprises hydrolyzing chloromethylphosphonous chloride with water and removing the by-product, HCl, by vacuum.