

Preparation of Esters, Hydrazides and Amides of Carboxymethylmethyl Long-Chain Aliphatic Ammonium Chlorides

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Abstract

A series of hydrazides and amides of carboxymethylmethyl C_{12} - C_{18} aliphatic ammonium chlorides were prepared by reaction of the corresponding ethyl esters with hydrazine and alcoholic ammonia, respectively. The intermediate carbethoxymethylmethyl derivatives were readily synthesized from commercial dimethyl tertiary amines and ethyl chloroacetate. The crude products were obtained in high yields and, after recrystallization, chemical analysis verified the expected structures.

Introduction

THE REACTION of low-molecular-weight tertiary amines with ethyl chloroacetate has been used to prepare carbethoxyquaternary ammonium chlorides as intermediates in the synthesis of cationic hydrazides (3). The well-known Girard's Reagent "T" is the hydrazide of carboxymethyltrimethyl ammonium chloride (4). This N-substituted glycine hydrazide is readily reacted with dialdehyde starch (8) to yield a highly cationic product that produces wet strength in paper (5).

We wished to react the hydrazides of carboxymethylmethyl long-chain aliphatic ammonium chloride with dialdehyde starch to obtain cationic additives capable of imparting not only wet strength to paper but also a soft feel. The water-soluble hydrazides and amides of these quaternary ammonium chlorides and their methylol derivatives were also interesting because of their potential as reagents for modification of the physical properties of cellulosic fibers. Although the preparation of carboxymethylmethyl long-chain aliphatic ammonium halides is adequately described (2,7,9,10), references to the synthesis of the corresponding hydrazides and amides (6,9) are scant.

The purpose of this investigation was to prepare relatively lowcost hydrazides and amides of carboxymethylmethyl C_{12} - C_{18} aliphatic ammonium chlorides for possible industrial applications. Reaction of commercial dimethyl tertiary amines containing long-chain aliphatic radicals with ethyl chloroacetate provided the intermediate carbethoxymethylmethyl aliphatic ammonium chlorides that were converted to the corresponding hydrazides and carbamoylmethyl derivatives by reaction with hydrazine and alcoholic ammonia, respectively.

Experimental

Materials

The tertiary amines were distilled grade commercial products from Armour Industrial Chemical Company, Chicago, Ill. The series of long-chain aliphatic dimethyl amines included the Armeens DM12D, DM14D, DM16D, DM18D, DMSD, DMCD and DMHTD. These products contain a minimum of 95%

of tertiary amine in which the long-chain radicals are dodecyl, tetradecyl, hexadecyl, octadecyl, soya, coco and hydrogenated tallow, respectively. Ethyl chloroacetate was the practical grade of Distillation Products Industries, Rochester, N. Y. Hydrazine of over 95% purity was purchased from the Fairmount Chemical Company, Newark, N. J.

Carbethoxymethylmethyl Aliphatic Ammonium Chlorides

A solution of 0.2 mole of dimethyl aliphatic amine in 50 ml of absolute ethanol was refluxed with 24.5 g (0.2 mole) of ethyl chloroacetate for 4 hr. After standing 20 hr at room temperature, the ethyl ester reaction mixture was divided into three measured portions for isolation of the ester and for conversion to the hydrazide and amide. A portion equivalent to 0.075 mole of the ester in each preparation was concentrated to a crude waxy product in a rotary evaporator at bath temperature about 55°C. The ester was recrystallized from acetone at 0°C.

Hydrazides of Carboxymethylmethyl Aliphatic Ammonium Chlorides

To a portion of the ester reaction mixture equivalent to 0.075 mole of ester in a 250-ml round-bottomed flask was added 2.4 g (0.075 mole) of hydrazine, and the solution allowed to stand at room temperature for 20 hr. The reaction mixture was then concentrated in a rotary evaporator at bath temperature about 55°C to obtain the crude crystalline hydrazide, which was recrystallized from absolute ethanol.

Carbamoylmethylmethyl Aliphatic Ammonium Chlorides

To a portion of the ester reaction mixture equivalent to 0.05 mole of ester in a 250-ml round-bottomed flask was added 15 ml of ethanol containing 1.3 g of NH_3 . After standing at room temperature for 20 hr, the solution was concentrated to a crude waxy product in a rotary evaporator at bath temperature about 55°C. The amide was recrystallized from acetone.

Analyses and yields of the various products are given in Tables I, II and III. In the tables, designations of R given in quotation marks indicate the mean

TABLE I
Carbethoxymethylmethyl Aliphatic Ammonium Chlorides

R	Yield, % ^a	Mean mol wt ^b	Analysis			
			Calcd., %		Found, %	
			N	Cl	N	Cl
"Dodecyl"	45	338	4.2	10.5	4.1	10.3
"Tetradecyl"	74	369	3.8	9.6	3.9	9.7
"Hexadecyl"	73 ^c	392	3.6	9.1	3.6	9.3
"Octadecyl"	67	420	3.3	8.5	...	8.4
Soya	47	415	3.4	8.6	3.6	8.7
Coco ^d	351	4.0	10.1	3.9	9.5
Hydrogenated tallow	48	416	3.4	8.5	3.6	8.5

^a Recrystallized product.

^b Calculated from the mean molecular weight of the tertiary amine.

^c Product mp about 50°C; mp of pure compound 72-74°C (9).

^d Unctuous product.

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TABLE II

Hydrazides of Carbomethyldimethyl Aliphatic Ammonium Chlorides

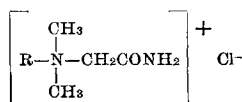


R	Yield, % ^a	Mean mol wt ^b	Analysis			
			Calcd., %		Found, %	
			N	Cl	N	Cl
"Dodecyl"	48	324	13.0	11.0	13.0	11.6
"Tetradecyl"	79	355	11.9	10.0	12.2	10.6
"Hexadecyl"	90	378	11.1	9.4	10.8	9.6
"Octadecyl"	70	406	10.4	8.8	9.9	8.4
Soya	48	401	10.5	8.9	10.6	9.4
Coco	85	337	12.5	10.5	12.4	10.6
Hydrogenated tallow	71	402	10.4	8.9	10.4	8.8

^a Recrystallized product.^b Calculated from the mean molecular weight of the tertiary amine.

TABLE III

Carbamoyldimethyl Aliphatic Ammonium Chlorides



R	Yield, % ^a	Mean mol wt ^b	Analysis			
			Calcd., %		Found, %	
			N	Cl	N	Cl
"Dodecyl"	45 ^c	309	9.1	11.5	8.7	11.5
"Tetradecyl"	59	340	8.3	10.5	7.9	10.1
"Hexadecyl"	90 ^d	363	7.7	9.8	7.5	9.4
"Octadecyl"	76	391	7.2	9.1	6.9	8.8
Soya	43	386	7.3	9.2	7.5	9.1
Coco ^e	322	8.7	11.0	8.1	10.5
Hydrogenated tallow	72	387	7.2	9.2	7.1	8.8

^a Recrystallized product.^b Calculated from the mean molecular weight of the tertiary amine.^c Product mp 53-55°C; mp of pure compound 56°C (6).^d Product mp 70-75°C; mp of pure compound 107-110°C (9).^e Unctuous product.

chain length of the aliphatic radicals in the commercial tertiary amines.

Results and Discussion

The hydrazides and amides described were prepared by the standard reactions of an ester with hydrazine (3,4) and ammonia, respectively. The yields reported are for once-recrystallized products. Since yields of recrystallized hydrazides were generally high, the initial quaternization reactions were nearly quantitative.

Melting points of the derivatives are not reported because the products were prepared from commercial tertiary amines and would not be representative of pure compounds. For example, recrystallized carbomethoxydimethyl hexadecyl ammonium chloride synthesized from Armeen DM16D melted at about 50°C in contrast to the melting point of 72-74°C for the pure substance (9).

Analysis of the products for nitrogen and chlorine, however, corresponds well with the theoretical values based on the mean molecular weights of the products, which were calculated from the mean molecular weights of the commercial tertiary amines (1).

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