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✠A Rapid Synthesis of Fatty Acyl Urea Derivatives

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ABSTRACT

Fat-based aliphatic amides react with aromatic isocyanates in refluxing xylene generally within 1 hr to form crystalline acyl-aryl urea compounds in 50-80% yields. The reaction appears to be general with either component being aliphatic or aromatic. Although the reaction occurs in various solvents, xylene is the preferred solvent in which the reactions were completed within 4 hr for the chosen amides and isocyanates. The progress of the reaction was conveniently monitored by infrared through the disappearance of the intense isocyanate band at 2258 cm^{-1}.

INTRODUCTION

In the course of a screening program to develop potential bacteriostats for use in soap or nonionic surfactants, it was found necessary to prepare some acyl urea derivatives. Disubstituted acyl ureas of the type RCONHCONHR', where R and R' may be aliphatic or aromatic, are generally prepared by reacting an acyl urea with an amine at 160-170 C for 2-4 hr or with an acid chloride (1-3). The high temperatures used with the amine tend to decrease yields and complicate the reaction by dissociation of the product into an amide and an isocyanate. The reaction of isocyanates with amines or alcohols is well known as a standard approach to the formation of solid derivatives. The reaction between isocyanates and amides to form acyl urea derivatives according to the following equation is not so familiar:

$$RCONH_2 + R'NCO \xrightleftharpoons[<150]{\geq160\,C} RCONHCONHR' \qquad [1]$$

Reaction temperatures below 160 C lead to formation of the product whereas temperatures of 160-200 C lead to dissociation (1,2,4). The initial work on this synthesis was done by B. Kühn (1884) who studied the action of phenyl isocyanate with benzamide, acetamide and propionamide to yield the corresponding acyl ureas (4). He also investigated the reaction of phenyl isocyanate with anilides derived from aniline and naphthylamine. He found that acetanilide was the only secondary amide to react according to the Equation I giving N-acetyl N-phenyl N'-phenyl urea (4,5). Subsequent investigators utilized this reaction on occasion, principally to prepare aroylaryl ureas (6-9) with no details of experimental conditions. Other investigators described syntheses of various acylaryl ureas using sealed tube techniques or prolonged heating at 110 C for 18-24 hr (10-12).

An approach was developed in which an isocyanate and a fatty amide are heated in xylene with the reaction frequently being complete in 1 hr or less.

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EXPERIMENTAL

Materials

Benzamide, 1,2-dichloroethane and ethyl acetate were white label from Eastman Organic Chemicals, Rochester, NY, whereas the isocyanates were obtained from Aldrich Chemical Co., Milwaukee, WI, or Pfaltz-Bauer, Stamford, CT. The compounds were used as received. (Caution is required when handling some of the solvents, such as 1,2-dichloroethane, as this substance has carcinogenic properties.) All other solvents used were reagent grade. The amides were prepared by the low-temperature addition of an acid chloride to concentrated ammonia (13).

Synthesis of N-Stearoyl N'-3-nitrophenyl Urea

A solution of 3-nitrophenyl isocyanate was prepared by heating 1.64 g (0.01 mol) of the isocyanate with 30 mL of dry xylene and filtering off the small amount of yellow amorphous solid under a blanket of dry nitrogen. The filtrate was added to a dry, 100-mL R.B. flask equipped with a stirrer, reflux condenser and drying tube. The system was flushed with nitrogen, 2.84 g (0.01 mol) of stearamide was added and the mixture was heated to reflux. Infrared (IR) spectra of the reaction mixture taken after 30 min and 1 hr showed the complete absence of the intense NCO absorption band at 2258 cm^{-1} after 1 hr. The turbid, pale yellow reaction mixture was filtered. The filtrate was evaporated in the rotovac at 0.5 mm/50 C to constant weight. The crude product was crystallized 2 times from absolute ethanol to give 3.8 g (85% yield) of crystalline N-stearoyl N'-3-nitrophenyl urea, mp 105-106 C.

Where the isocyanate was completely soluble in the solvent, indicating the absence of contaminating diaryl urea, the amide was added to an excess of xylene and the entire system dried by azeotropic distillation of a portion of the solvent. The isocyanate was added and the synthesis was performed as indicated above. Diaryl ureas are normal contaminants of isocyanates which have been exposed to moisture in the air. In this study, the low solubility of the diaryl ureas permitted their separation from the desired products.

Infrared Spectra

IR spectra of the acyl urea derivatives were obtained as Nujol Mulls with a P.E. 257 spectrophotometer. The spectra were quite consistent for all the samples in Table I. NH-stretching bands appeared at 3220 and 3120 cm^{-1} with deviations from these values of 5-10 cm^{-1} for only a few samples. Carbonyl bands frequently were partially resolved

TABLE I

Acylaryl and Acylalkyl Urea Derivatives

		RNHCONHR'				
Compound	R	R'	mp (C)	% Yield	Reaction time (hr)	Crystallization solvent
1	Myristoyl	Phenyl	86- 87	86	0.5	Hexane
2	Decanoyl	3,4-Dichlorophenyl	109-110	70	0.5	Methanol
3	Stearoyl	3-Nitrophenyl	105-106	85	1.0	Ethanol
4	Lauroyl	4-Chlorophenyl	118-119	83	0.5	Ethanol
5	Palmitoyl	2-Nitro-4-chlorophenyl	108-109	50	1.0	Hexane/ ethanol
6	Stearoyl	Butyl	87- 88	63	2.0	Ethanol
7	Palmitoyl	3-Chlorophenyl	97- 98	83	1.3	Ethanol
8	Benzoyl	Butyl	83- 84	72	4.0	Hexane
9	Lauroyl	4-Nitrophenyl	101-102	69	0.5	Methanol
10[a]	Benzoyl	Phenyl	204-205	84	1.5	Xylene

[a]Literature mp 203-204 (12).

TABLE II

Solvent Effects in Formation of Acyl Urea Compounds

		RNHCONHR'			
Compound	R	R	Solvent	Reaction time (hr)	bp (C)
1	Decanoyl	3,4-Dichlorophenyl	Xylene	0.5	140
2	Decanoyl	3,4-Dichlorophenyl	Toluene	4.0	110
3	Decanoyl	3,4-Dichlorophenyl	Benzene	11.0	80
4	Decanoyl	3,4-Dichlorophenyl	1,2-Dichloroethane	9.0	81
5	Palmitoyl	4-Chlorophenyl	Xylene	1.3	140
6	Pelargonyl	4-Chlorophenyl	1,2-Dichloroethane	24	81

into doublets at 1720-1680 cm^{-1} with some samples showing only a single band at 1690 cm^{-1}. The strong NCO band in reaction mixtures appeared at 2258 cm^{-1}.

RESULTS AND DISCUSSION

Table I summarizes results obtained in the syntheses of various fatty acylaryl and acylalkyl urea derivatives. These compounds were prepared by heating an amide with an isocyanate in anhydrous xylene for 0.5-4 hr. Aliphatic amides generally react with aromatic isocyanates in 1 hr or less. Reaction between 2 aliphatic components (compound 6) or 2 aromatic components (compound 10) leads to essentially a doubling of the reaction time to 2 hr. However, an aromatic amide reacts with an aliphatic isocyanate (compound 8) in 4 hr. This, therefore, suggests that aromatic isocyanates are somewhat more reactive than aliphatic isocyanates. In each case, the progress of the reaction was followed by the disappearance of the intense isocyanate (NCO) band at 2258 cm^{-1}. The reaction times shown indicate the complete disappearance of this band. The yields for the reactions were quite good, ranging from 50 to 85% of theory.

Because all the reactions were done at the 0.01 molar level, the exclusion of moisture was crucial. When special care was taken to exclude moisture, the yield of product in sample 7 was increased to 93%, thus suggesting that the application of rigorously dry conditions could raise the yields shown in Table I. The exclusion of moisture is quite important because 1 mol of water eliminates 2 mol of isocyanate according to Equation II, giving a dialkyl or diaryl urea.

$$RNCO \xrightarrow{H_2O} RNHCO_2H \xrightarrow{-CO_2} RNH_2 + RNCO \longrightarrow RNHCONHR \quad [II]$$
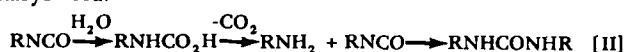
The use of xylene as a solvent serves several purposes: the reaction system can be dried by azeotropic distillation of solvent. A homogeneous system is maintained by dissolution of the reactants including amides of as low molecular weight as acetamide. Temperature control is maintained at the boiling point of xylene. This solvent permits a sufficiently high reaction temperature for rapid reaction without dissociation of the product.

Solvent effects in this reaction were studied to a limited degree and are summarized in Table II. When N-decanoyl-N'-3,4-dichlorophenyl urea was prepared in aromatic solvents, the reaction time increased with decreasing bp of the solvent. The ratio of reaction time for this compound in xylene and 1,2-dichloroethane is about 18. The ratio is essentially the same for samples 5 and 6 where a large change in reaction time would not be expected by changing the number of methylene groups in the aliphatic amide, therefore indicating that the reaction is quite temperature-dependent. However, the difference in reaction times between samples 3 and 4 where the solvents have essentially the same boiling point indicates the presence of solvent interaction.

As noted earlier, Kühn (4) found that acetanilide was the only secondary amide to react, according to Equation I, with phenyl isocyanate. In this study, N-methyl lauramide and N-ethyl lauramide were refluxed in xylene with phenyl isocyanate and 3,4-dichlorophenyl isocyanate, respectively, for 10-12 hr. No evidence for the formation of an acyl urea derivative was found and 85-90% of the amides was recovered.

Table III summarizes the elemental analyses for the various compounds in Table I, indicating that all analyses for carbon, hydrogen, nitrogen and chlorine are within experimental error.

TABLE III

Elemental Analysis of Acylurea Derivatives

			RNHCONHR'							
			% Carbon		% Hydrogen		% Nitrogen		% Chlorine	
Compound	R	R'	Theory	Found	Theory	Found	Theory	Found	Theory	Found
1	Myristoyl	Phenyl	72.79	73.05	9.89	9.75	8.08	8.12		
2	Decanoyl	3,4-Dichlorophenyl	56.83	56.65	6.73	6.92	7.80	7.81	19.73	19.54
3	Stearoyl	3-Nitrophenyl	67.08	67.09	9.23	9.11	9.39	9.43		
4	Lauroyl	4-Chlorophenyl	64.66	64.88	8.28	8.44	10.05	10.01	7.94	8.05
5	Palmitoyl	2-Nitro-4-chlorophenyl	60.85	60.80	7.99	8.22	7.81	7.65	9.25	9.45
6	Stearoyl	Butyl	72.20	72.41	12.12	12.02	7.32	7.32		
7	Palmitoyl	3-Chlorophenyl	67.54	67.73	9.12	9.38	6.85	5.97	8.67	8.52
8	Benzoyl	Butyl	65.43	65.23	7.32	7.57	12.72	12.81		
9	Lauroyl	4-Nitrophenyl	62.79	63.04	8.04	8.34	11.56	11.32		

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✠Mafura Nut Oil and Meal: Processing and Purification

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ABSTRACT

The seeds of the tropical tree known as mafura (Trichilia emetica) contain significant amounts of oil and protein. So far, commercial use of the mafura seeds has been prevented by the presence of a strong bitter and emetic taste, as well as a brownish color in both oil and meal. A refining procedure which gives edible oil with acceptable organoleptic properties has been developed. The raw meal has been extracted with aqueous alcohol to give a debittered meal with a protein content of about 36%. The amino acid composition of the meal was found to be comparable to that of other vegetable food proteins, except for a relatively low content of sulfur-containing amino acids. The brown color has been shown to result from browning reactions taking place during storage and processing. Most of the color may be removed by repeated treatments with dilute sodium hydroxide, followed by bleaching with earth and activated carbon.

INTRODUCTION

Mafura oil is obtained from the seeds of the mafura tree (Trichilia emetica) which is found in Tanzania and several other parts of East Africa as well as in some West African countries. The seeds are in the size range of 0.35-1.0 g and consist of roughly 23% of an oily shell-like husk and 77% kernel. The kernels contain 55-65% of a brownish fat (mp 41 C) and 13% protein (N x 6.25). The mafura nuts represent a potential source of nutrients which would be welcome in many areas. Unfortunately, the use of mafura oil and meal for edible purposes is prohibited by their bitter taste and by emetic properties.

An exception is the oil obtained by a method devised by certain natives in Tanzania. By boiling ripe, whole nuts for 10-15 min, drying in the sun and then agitating in water, a clear yellow oil of satisfactory quality is obtained. This oil has been shown to originate from the husk, which is known to contain 35-45% of a light-yellow oil.

In Tanzania, commercial use of mafura nuts has so far been restricted to a limited production of low-grade, inferior quality soaps. Accordingly, the price obtained by local farmers for their mafura nut crops has been low. Thus, growth and harvesting of mafura trees is discouraged. If proper refining procedures existed, the mafura oil could be a substitute for part of the sizable tallow and edible oil import while at the same time providing local employment.

The meal obtained by extraction of mafura kernels contains about 36% protein and its composition is comparable to that of other vegetable meals (1). The mafura meal can neither be used for human consumption nor for animal feed because of its bitter, emetic taste. Successful refining of the meal not only would furnish a valuable protein supply, but might also improve the economics of mafura nut processing.

The papers published on mafura nut processing during the last 80 years are relatively few (1-9). Most of the reports are analytical in nature. The only comprehensive investigation of various aspects of mafura nut oil and meal processing and purification is that of Fupi (1). Engelter