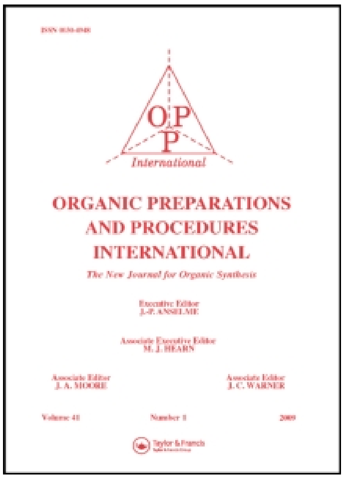

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PREPARATION OF 2-HYDROXYETHYLDIMETHYLAMINE ACYLIMIDES

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PREPARATION OF 2-HYDROXYETHYLDIMETHYLAMINE ACYLIMIDES

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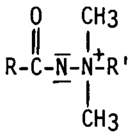
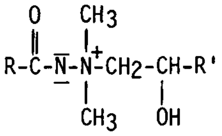
Aminimides of the general type I exist as bipolar ions which have interesting properties. Many of these aminimides have germicidal effects against microorganisms[1,2] and potential surfactant properties. When certain alkyl epoxides are substituted for R', the 2-hydroxyalkylamine acylimides (II) obtained have enhanced surfactant properties because of the possibility for interaction between the negatively charged nitrogen and the hydroxyl group[3].



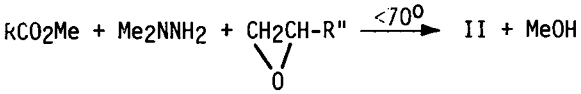
$$R{-}\overset{\overset{O}{\|}}{C}{-}\bar{N}{-}\overset{+}{N}(CH_3)_2{-}R'$$

I R,R' = alkyl



$$R{-}\overset{\overset{O}{\|}}{C}{-}\bar{N}{-}\overset{+}{N}(CH_3)_2{-}CH_2{-}\underset{OH}{CH}{-}R'$$

II R' = H, $CH_2O(CH_2)_3CH_3$



$$RCO_2Me + Me_2NNH_2 + \underset{\diagdown O \diagup}{CH_2CH}{-}R'' \xrightarrow{<70^o} II + MeOH$$

As with most aminimides, the 2-hydroxyalkylamine acylimides (II) have shown interesting catalytical properties for the polymerization of isocyanates to polyurethanes. Under certain conditions the 2-hydroxyalkylamine acylimide catalyzes the polymerization of isocyanates to polyisocyanurate foams[4], which are finding increasing uses in flame and smoke retardation[5].

Previous methods for preparing the 2-hydroxyalkylamine acylimides (II, R'=H and CH_3) involved a one-step reaction using isopropanol or *t*-butanol as solvents with the liquid reactants[6]. The alkene oxide was added as a liquid. A primary function of the solvent was to moderate the temperature of the exothermic reaction. Reaction temperatures above 70^o have a detrimental effect on the aminimide. The use of solvents limits the amount of product that can be prepared, and it was difficult to remove the final traces of solvent during purification. In addition, the use of liquid alkene oxides promotes the formation of polyglycols which cannot be removed by vacuum stripping of the product. In numerous cases the final aminimides were either viscous oils or too hydroscopic for convenient recrystallization. Several of the 2-hydroxyethylamine acylimides made by the solvent/liquid ethylene oxide method gave polyisocyanate catalysts with variable catalytic properties.

The need to obtain large quantities of 2-hydroxyethylamine acylimide rapidly with low levels of contamination from polyglycols or solvents, for the study of the kinetics of trimerization of phenylisocyanate[4], led us to develop a new method that requires no solvents. The ethylene oxide is introduced as a gas into the reaction under a nitrogen atmosphere, which not only reduces the potential flammability of ethylene oxide but also prevents possible oxidation of the 1,1-dimethylhydrazine.

Liquid ethylene oxide was allowed to distill at room temperature into the reaction solution from a standard side-arm funnel. This addition method has the added benefit of preventing any polyglycol impurities that were present in the commercial ethylene oxide from entering the reaction. It also permits visual control of the quantity of ethylene oxide added instead of relying on flow meters, etc. The rate of ethylene oxide addition can be increased by passing a stream of air around the addition funnel. This combination of ethylene oxide addition with no solvent permitted the isolation of dimethyl-2-hydroxyethylamine acetimide ($R=CH_3$, $R'=H$) in a crystalline form for the first time.

TABLE. Dimethyl-2-Hydroxyethylamine Acylimides (II, R' = H)

R	n_D^{24}	Color	Yield	mp Found	mp Lit.	IR[a] (cm^{-1}) Found	IR[a] (cm^{-1}) Lit.
$CH_3(CH_2)_{17}$[e]	-	white	75	75-78.5[b]	75-87.5[b]	1570	1570[b]
CH_3	-	white	94	92.5-94	-	1575	1575[b]
$HOCH_2$	1.5059	orange	95	-	-	1600	-
CH_3CH_2	-	yellow	101	-	-	1590	-
CH_3OCH_2	-	yellow	85	-	-	1610	-
$(CH_3)_2NCH_2$	-	yellow	80	-	-	1590	-
$CH_3(CH_2)_7$	-	white	91	-	-	1570	-
$-(CH_2)_4-$	-	white	68[c]	188	-	1570	-
$-(CH_2)_7-$	-	yellow[d]	98	43-48	-	1580	-

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[a] Carbonyl group (neat). [b] E. A. Sedor, Private Communication. [c] Hydroscopic material; some material loss during filtration. [d] Forms crystals on standing. [e] NMR($CDCl_3$): 3.44 (6H, s, CH_3), 3.79-3.95(4H, M, CH_2), 1.29. (34H, s, CH_2) from internal TMS.

EXPERIMENTAL

Infrared spectra were obtained as neat liquids on a Perkin-Elmer 297 spectrophotometer. Refractive indices were determined with a Bausch & Lomb Abbe Refractometer. Melting points were uncorrected.

Dimethyl 2-Hydroxyethylamine Acetimide. Ethyl acetate (273 g, 3.1 mol) was placed in a 1 ℓ., 3-neck round bottom flask fitted with a paddle stirrer, thermometer, Dry Ice condenser and a side-arm addition funnel under a nitrogen atmosphere. 1,1-Dimethylhydrazine (186 g, 3.1 mol) was added rapidly at room temperature with stirring. Then ethylene oxide (136 g, 3.1 mol) was allowed to pass through the reaction *via* the side-arm of the addition funnel. After 3.75 hrs, the reaction temperature was 51°. After 4.75 hrs, an IR analysis (comparison of the ester 1740 cm^{-1} peak height versus the aminimide 1575 cm^{-1} peak) of the solution indicated that the reaction was 95% complete. The pale yellow solution was stripped using a water aspirator to remove the by-product, ethanol. The resulting white solid was mixed with 50 ml of toluene to remove the last traces of ethanol as the azeotrope at 4mm/55°. A yield of 423 g (94%) of the aminimide was obtained. A sample of the aminimide recrystallized from toluene had a mp of 92.5-94°.

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