Preparation of 1,1-Bis(2-hydroxyethyl)-2-acylhydrazines by Oxyethylation of Acylhydrazines

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1,1-Bis(2-hydroxyethyl)-2-acylhydrazines were obtained in high yields by oxyethylation of acylhydrazines containing $C_{12}\sim C_{16}$ acyl group with ethylene oxide in a 2-propanol solution or in a molten state at $100\sim 140^\circ\text{C}$. The physical and spectral properties are reported.

As for the reaction examined here, the preferential formation of $\text{RCONHNH}(\text{C}_2\text{H}_4\text{O})_n\text{H}$ was reported formerly. The predominance of this kind of polyoxyethylated compound, however, could not be detected in the present investigation.

1 Introduction

Oxyethylation of compounds containing an active hydrogen such as alcohols, amies and amides with ethylene oxide has been extensively studied in the past¹⁾. Addition of ethylene oxide to an alcohol proceeds rapidly at $80\sim 90^\circ\text{C}$ when a tertiary amine is present as catalyst. On the other hand, the rate of addition of ethylene oxide to an amine can be enhanced as the reaction temperature increases^{2),3)}. In the case of an acylamide, the addition of ethylene oxide to an amide group is slower than that to a hydroxyl group produced during the reaction⁴⁾. In view of these circumstances, it seems reasonable to expect that oxyethylation of acylhydrazine would occur on the amine nitrogen, especially under higher temperature conditions where oxyethylation of amino group is favored over that of the hydroxyl group. Although oxyethylation of acylhydrazines and the utility of the products especially as textile auxiliary agents were recorded in a patent literature⁵⁾, no detailed information on their chemical structure was given. The patent noticed that it was impossible to designate the exact position of hydrogen atom which reacted with alkylene oxide.

Demchenko and his co-workers, however, recently reported the preferential formation of $\text{RCONHNH}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$ by oxyethylation of acylhydrazine with ethylene oxide at 160°C ,

and for the formation of $\text{RCONHN}(\text{CH}_2\text{CH}_2\text{O})_p\text{H}(\text{CH}_2\text{CH}_2\text{O})_q\text{H}$, a sodium metal catalyst in a 2-propanol solution was required⁶⁾.

In spite of Demchenko's report, the authors confirmed the formation of $\text{RCONHN}(\text{CH}_2\text{CH}_2\text{OH})_2$ in good yield by the reaction of acylhydrazines and ethylene oxide in a molten state or in a 2-propanol solution, as expected above. The resulting compounds may be useful as industrial raw materials⁵⁾, because of their resemblance to alkylol amides which are a good auxiliary surfactant. Furthermore, new uses of the products can be found because they possess an extra amino group.

The present procedure may be a preferable method for synthesizing 1,1-bis(2-hydroxyethyl)-2-acylhydrazines, since these compounds are hard to prepare by aminolysis of the corresponding fatty esters with 1,1-bis(2-hydroxyethyl)hydrazine⁷⁾ which can be obtained from hydrazine hydrate and ethylene oxide in a fair yield⁸⁾. This paper describes the oxyethylation conditions of acylhydrazines and spectral data of the products.

2 Experimental

Materials and method

Lauroylhydrazine, myristoylhydrazine, palmitoylhydrazine, and stearoylhydrazine were prepared by refluxing the 2-propanol solution of hydrazine hydrate and the corresponding fatty acid methyl ester. Crude acylhydrazines were

Table-1 Effect of reaction temperature and molar ratio^{a)} of reactants on yield of 1,1-bis(2-hydroxyethyl)-2-lau-roylhydrazine^{c), d)}

Molar ratio (EO:LH) ^{b)}	2 : 1	3 : 1	4 : 1	6 : 1
Temp.(°C)				
100		78 (1 : 1.05)		
120	67 (1 : 1.02)	79 (1 : 1.05)	80 (1 : 1.15)	61 (1 : 1.5)
140		71 (1 : 1.05)		

a) Reaction of lauroylhydrazine (0.26 g, 0.003 mol) and ethylene oxide in 2-propanol (4 ml) for 2 h.

b) EO=ethylene oxide, LE=lauroylhydrazine.

c) Figure shows yields of the dioxyethylated lauroylhydrazine (%), corrected by the following equation,

$$\left[1 - \frac{(\text{area due to O-CH}_2\text{-C proton})}{(\text{area due to N-CH}_2\text{-C proton})} \times \frac{1}{2} \right] \times Y,$$

Y=uncorrected yield calculated from area of N-CH₂-C proton (%).

d) Figures in parentheses show the area ratios of protons in NMR, N-CH₂-C : O-CH₂-C.

recrystallized from hexane or hexane-2-propanol to give scales. Acylhydrazines prepared were characterized by IR (KBr) (3320, 3200, 1630, and 1530 cm⁻¹), mp⁹⁾, and elemental analyses.

Reaction of acylhydrazine and ethylene oxide in a 2-propanol solution

The following procedure for lauroylhydrazine is typical. To a 2-propanol solution (4 ml) of acylhydrazine (0.003 mol), a specified amount of ethylene oxide (EO) was condensed. The solution was heated at given temperature for 2 h in a sealed glass tube. Crude reaction product was obtained by evaporation of the solvent *in vacuo* and was recrystallized from benzene to give prisms. IR (KBr) 3280, 1660, and 1530 cm⁻¹. Elemental analyses agreed with calculated values within 0.3% error. ¹H NMR (CDCl₃, δ); 0.88 (3 H, t), 1.25 (16 H, m), 1.60 (2 H, m), 2.16 (2 H, t), 2.95 (4 H, t), 3.60 (4 H, t), 4.00~4.24 (2 H, brs), and 7.12~7.67 (1 H, brs). ¹³C NMR (CDCl₃, δ); 14.0 (12-position of lauroyl group), 22.5(11), 31.8(10), 29.4(9), 29.5(8-5), 29.2(4), 25.4(3), 34.4(2), 174.6 (C=O), 59.0 and 58.7(N-C-CO, each of ethylene carbons, respectively). Mass spectrum (70 eV); *m/e* 59(ra 100), 253(91), 89(68), 271(59),

72(41), 104(18), 284(10), and 302(M⁺, trace).

Reaction of acylhydrazine in a molten state and ethylene oxide bubbled

Lauroylhydrazine was reacted with EO introduced by bubbling without solvent at 120°C. EO bubbling was continued until the absorption at 1600 cm⁻¹ due to acylhydrazine disappeared. Reaction product was recrystallized twice from benzene-hexane (1 : 1) to give pure 1,1-bis(2-hydroxyethyl)-2-lauroylhydrazine as prisms, mp 67.5~69.0°C, yield 78%. Palmitoylhydrazine gave the corresponding bis(2-hydroxyethyl) derivative as prisms in a similar procedure, mp 81.0~83.0°C, yield 73%. Myristoyl derivative as prisms, mp 74.5~76.0°C. Stearoyl derivative as prisms, mp 89.0~91.0°C.

3 Results and Discussion

The products obtained above were proved to be pure bis-oxyethylated acylhydrazines based on the sharp melting points and elemental analyses. ¹H and ¹³C NMR showed only one kind of the hydroxyethyl group. Also IR showed the characteristic absorption of secondary amide at 1530 cm⁻¹ based on -C(O)NH- group, and fragmentation of N(C₂H₄OH)₂ (*m/e* 104, *ra* 18%) was observed in mass spectra.

On the basis of the above results, despite Demchenko's report, the authors concluded that the oxyethylation product by the reaction of acylhydrazine in a 2-propanol solution or in a molten state with ethylene oxide without catalyst is 1,1-bis(2-hydroxyethyl)-2-acylhydrazine. From NMR, generation of a small amount of poly-oxyethylation product was suggested especially when an excess amount of ethylene oxide was used.

To find out the preferable reaction conditions, the reaction of acylhydrazine and ethylene oxide in a 2-propanol solution was carried out at various temperatures and in various molar ratios. The yield of 1,1-bis(2-hydroxyethyl)-2-acylhydrazine was calculated on the basis of the areas of proton signals of alkyl group. The result is shown in the Table. The calculation premises the following two assumptions; i) The rate of consecutive oxyethylation of mono-oxyethylated acylhydrazine with ethylene oxide is so favored that 1-acyl-2-(2-hydroxyethyl)hydrazine, in the reaction product, is expected to be small. ii)

The oxyethylation occurs on amino nitrogen almost exclusively.

The content of other reaction products, such as the poly-oxyethylation products, is found to be small, since the area of proton signal due to O-CH₂-C (δ =3.60 ppm), was almost equal to that due to N-CH₂-C (δ =2.95 ppm), unless a large amount of ethylene oxide was used.

As for the reaction conditions, there was no significant difference in yields between the bubbling method and the sealed tube method. Reaction in a sealed tube at 120°C, however, was preferable to the ethylene oxide bubbling method which needed a longer reaction time and resulted in a formation of a small amount of the rearranged hydrazino esters exemplified by RCOOC₂H₄N(NH₂)C₂H₄OH, with an absorption band at 1740 cm⁻¹. It was recognized that 1,1-bis(2-hydroxyethyl)-2-acylhydrazine can thus be easily produced from acylhydrazine and ethylene oxide in a high yield by the same method as in oxyethylation of an alkylamine.

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アシルヒドラジンのオキシエチル化による 1,1-ビス (-2-ヒドロキシエチル)-2-アシル ヒドラジンの合成

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炭素数 12~16 のアシルヒドラジンを 100~140°C, 2-プロパノール溶液中または熔融状態でエチレンオキシドと反応させ, 1,1-ビス (2-ヒドロキシエチル)-2-アシルヒドラジンを高収率で得, その物理的及びスペクトルの性質を明らかにした。

本反応に関しては, RCONHNH(C₂H₄O)_nH が優先的に生成するという報告があるが, 本実験ではその生成の優先性は認められなかった。