

# 界面活性劑의 合成技術

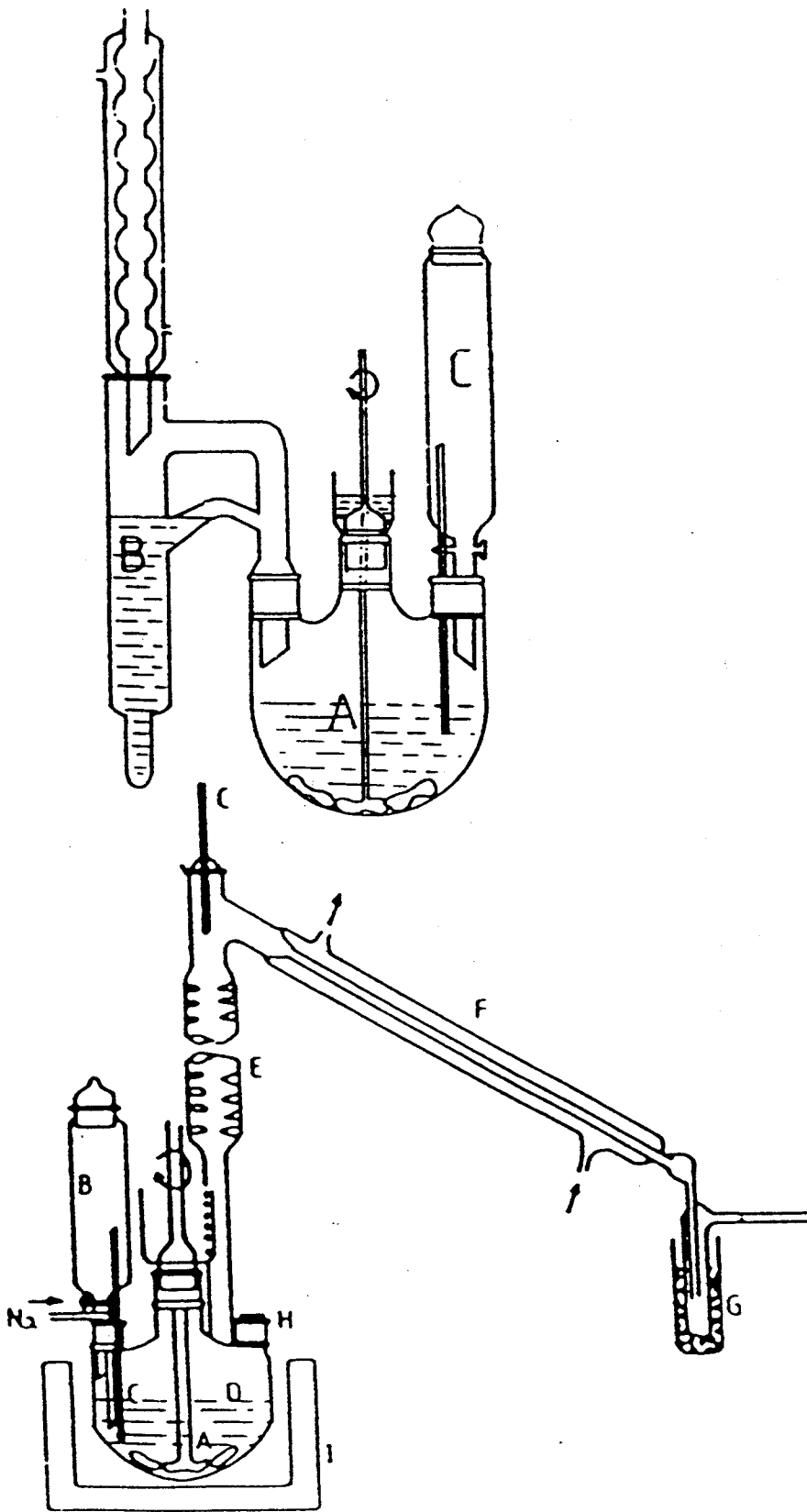
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### 3 Synthesis of Surfactants

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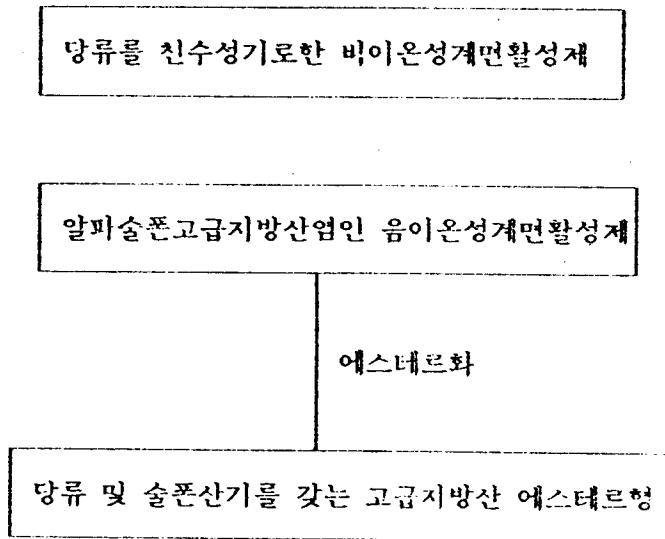
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※ 계면활성제의 새로운 문제점

- 1) 정교한 기능을 갖는 고부가가치성의 요구
- 2) 환경오염 방지책 - 천연에서 유도된 새로운 조성을 갖어 생분해가 좋은것
- 3) 새로운 조성과 기능을 갖는 화합물 개발

※ 새로운 조성을 갖는 계면활성제 창안



※ 새로이 합성된 화합물 기대성

- 1) 생물학적 특이성 갖는 세정성
- 2) 도료, 인쇄, 농약의 특이한 분산성
- 3) 섬유유의 대전방지성
- 4) 고분자 합성에 있어 새로운 유화제 개발

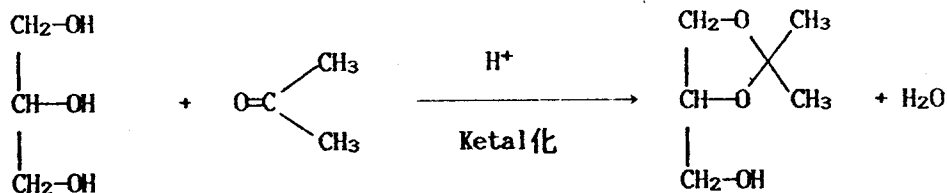
# Synthesis of Polyolic $\alpha$ -Sulfo Long Chain Alkanoates.

Materials ; 1)  $\alpha$ -sulfo fatty acid - Hydrocarbon No. 12~18

2) Sugar ; glycerol, ~~myo~~-inositol

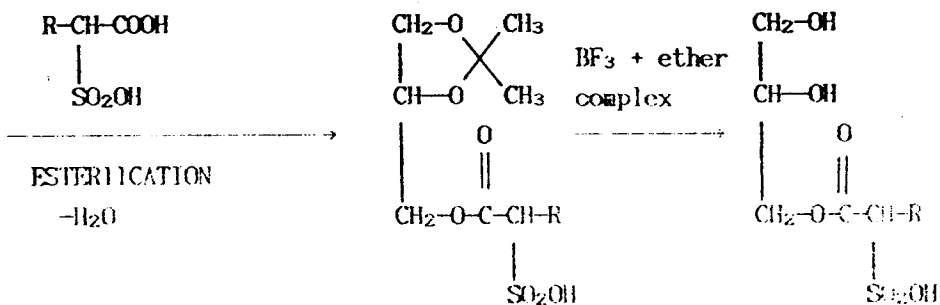
D-~~m~~annitol, sorbitol

1) 1-~~mono~~ glycerol ~~mono~~  $\alpha$ -sulfo alkanoate

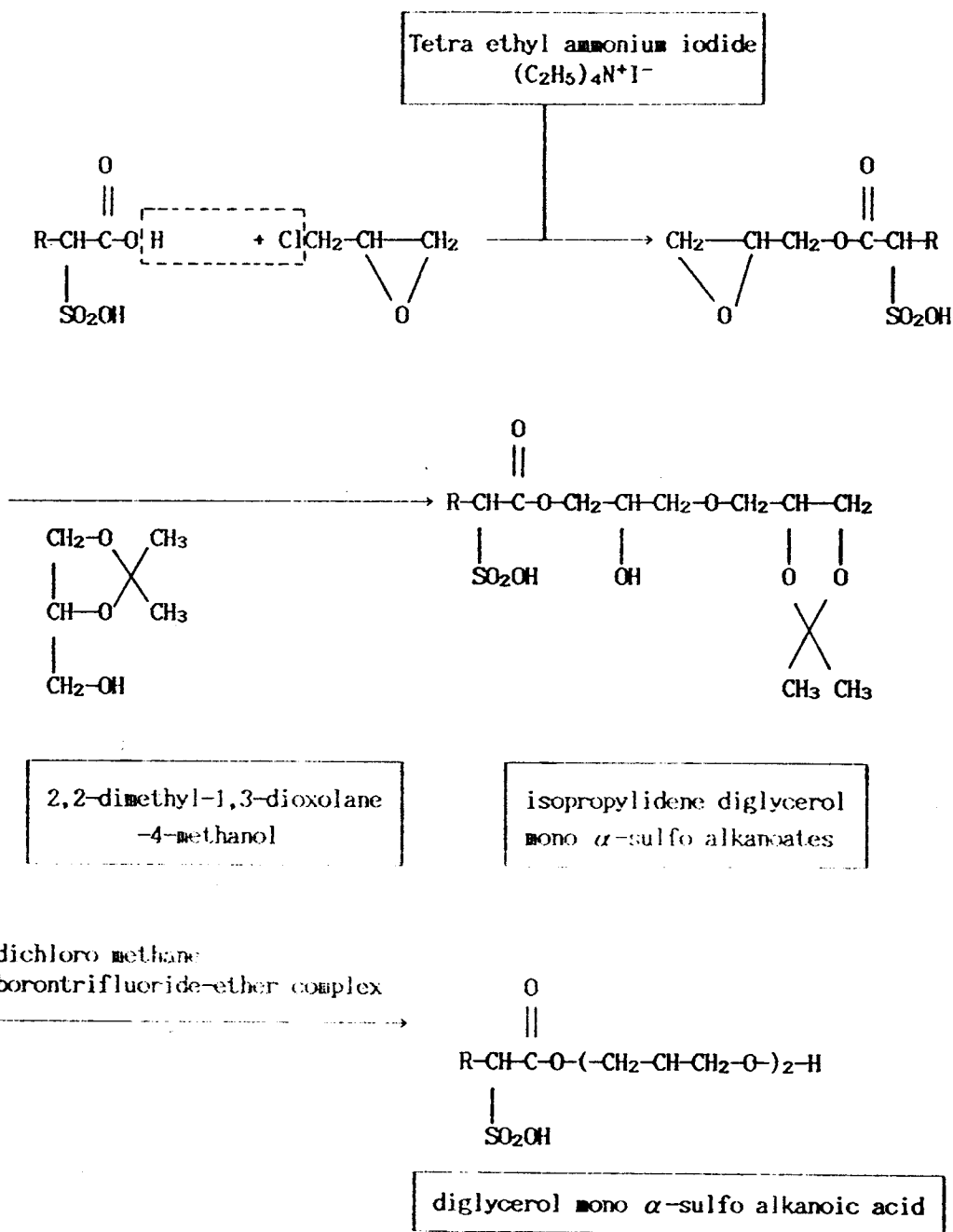


glycerol

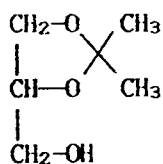
1,2-*O*-isopropylidene glycerine  
● remove H<sub>2</sub>O of azeotropic distillation with benzene



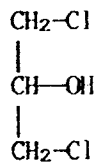
## 2) diglycerol mono $\alpha$ -sulfo alkanates



### 3) Symmetrical triglycerol-mono $\alpha$ -sulfo alkanate

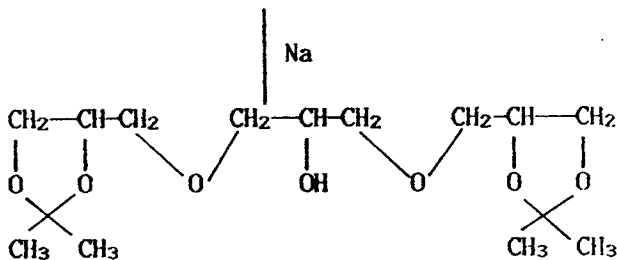


+

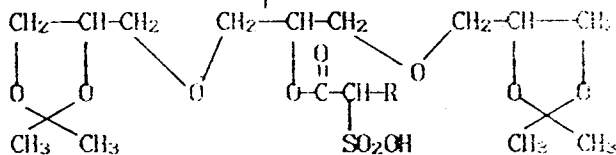
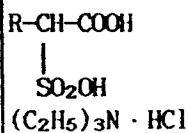


2,2-dimethyl-1,3-dioxolane  
-4-methanol

1,3-dichloro-2-propanol

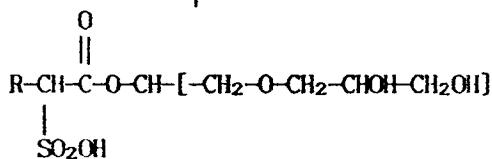


diisopropyliden triglycerol



Symmetrical diisopropyliden triglycerol mono  $\alpha$ -sulfo alkanates

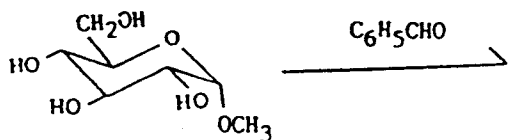
borotrifluoride-ether complex  
dichloromethane



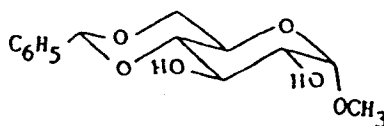
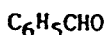
Symmetrical triglycerol mono  $\alpha$ -sulfo alkanate



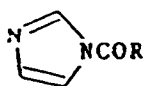
메틸  $\alpha$ -D-글루코피라노사이드 유도체



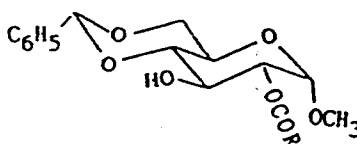
A



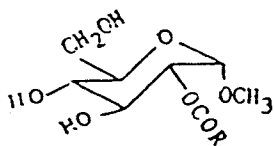
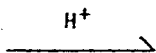
B



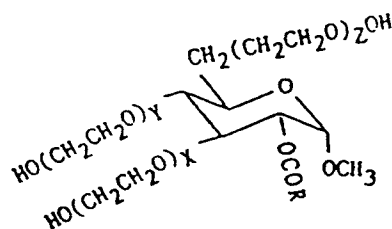
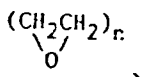
C



D



E



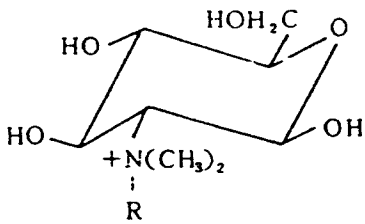
F

Scheme The starting materials, intermediates and reacted products.

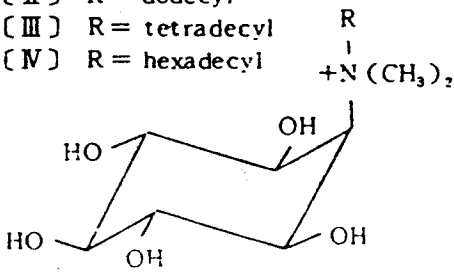
R :  $C_9H_{19}$ -,  $C_{11}H_{23}$ -,  $C_{13}H_{27}$ -,  $C_{15}H_{31}$ -,  $C_{17}H_{35}$ -

$X + Y + Z = 20$

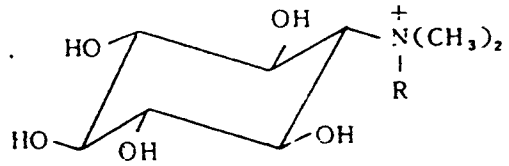
# 계면활성 아미노 당 유도체



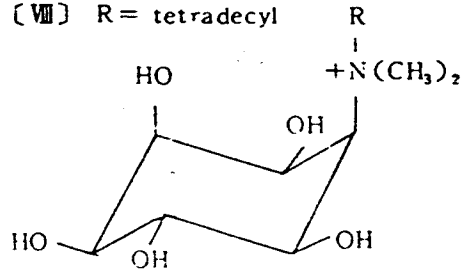
- [ I ] R = decyl
- [ II ] R = dodecyl
- [ III ] R = tetradecyl
- [ IV ] R = hexadecyl



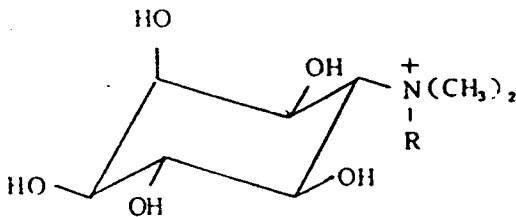
- [ IX ] R = octyl
- [ X ] R = decyl
- [ XI ] R = dodecyl
- [ XII ] R = tetradecyl



- [ V ] R = octyl
- [ VI ] R = decyl
- [ VII ] R = dodecyl
- [ VIII ] R = tetradecyl



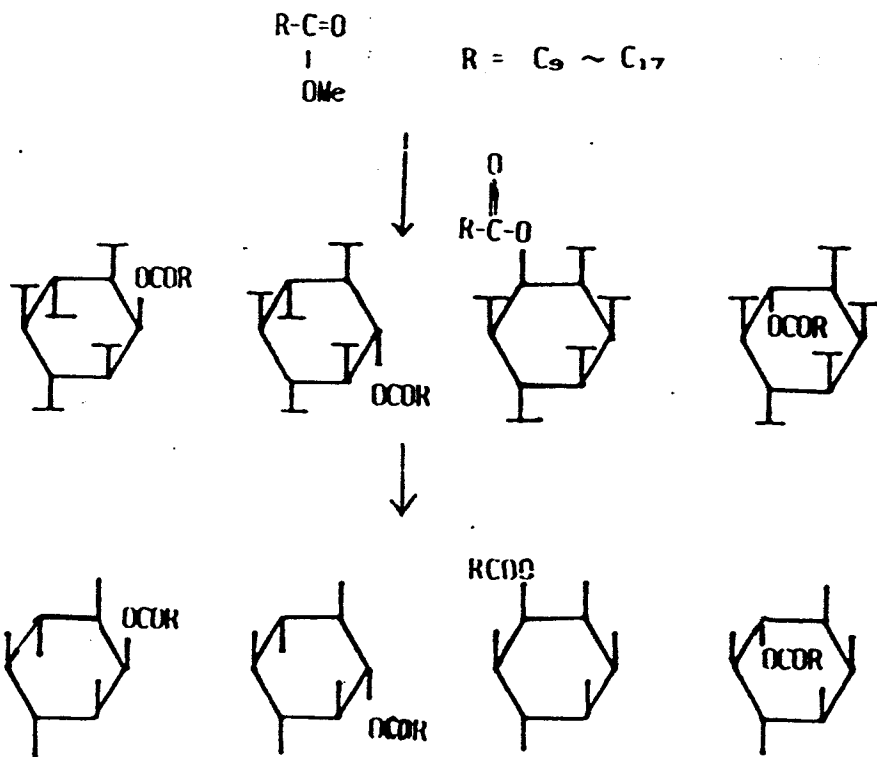
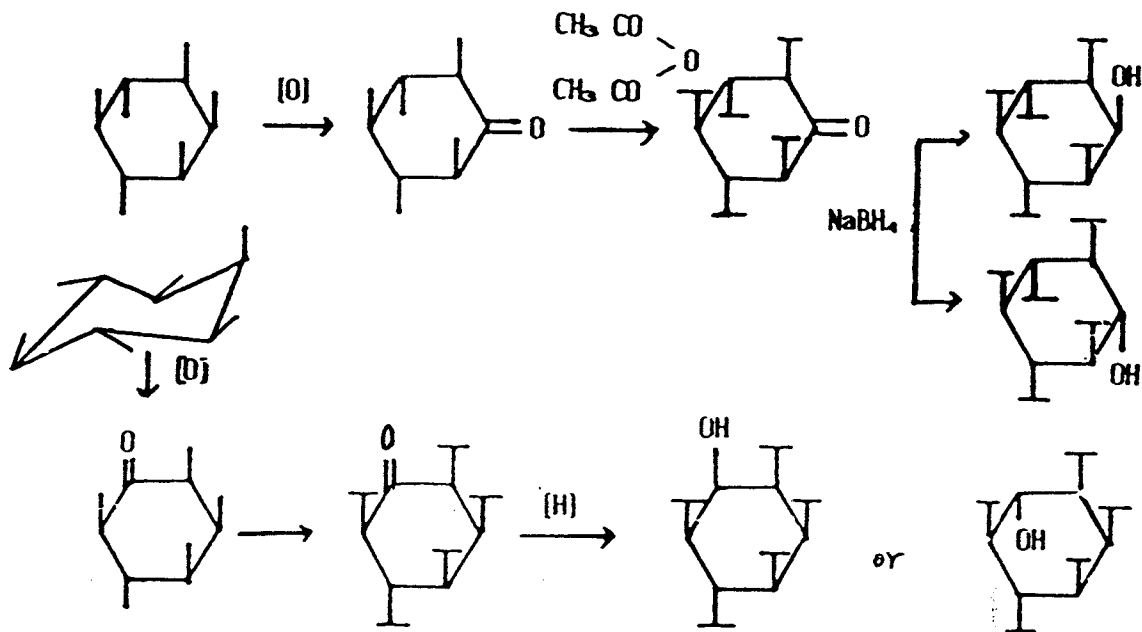
- [ XIII ] R = octyl
- [ XIV ] R = decyl
- [ XV ] R = dodecyl
- [ XVI ] R = tetradecyl



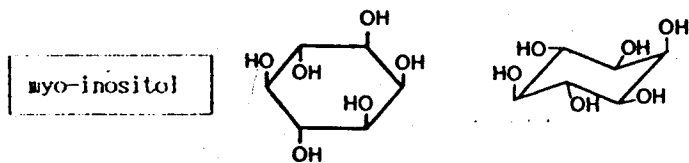
- [ XVII ] R = octyl
- [ XVIII ] R = decyl
- [ XIX ] R = dodecyl
- [ XX ] R = tetradecyl

# I. Polyolic Nonionic Surfactant

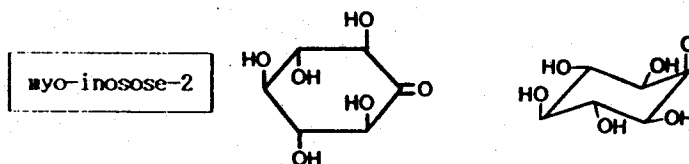
## 1) Myo-inositol Monoester



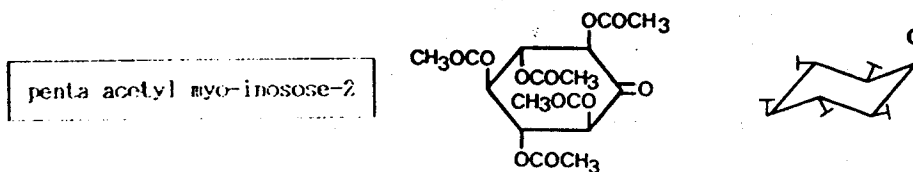
4) myo-inositol mono  $\alpha$ -sulfo alkanoate



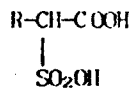
Adams oxidation catalyst  
Determination of phenyl hydrazine

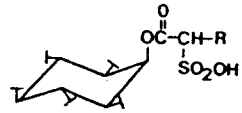
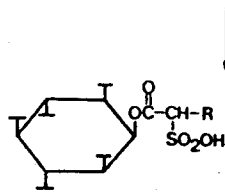


acetic anhydride  
acetylation



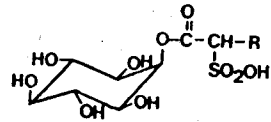
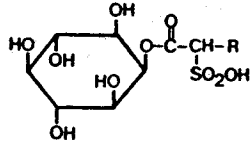
H<sup>+</sup> (Adams reduction catalyst)



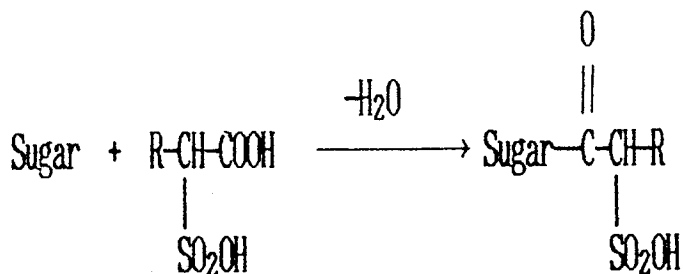


hydrolysis of saturated methanolic ammon

myo-inositol-2-mono  $\alpha$ -sulfo alkanate



5) Esterification of  $\alpha$ -sulfo alkanate of D-mannitol or Sorbitol



Synthesis method

① Direct esterification

solvent ; chloroform, benzene, toluene

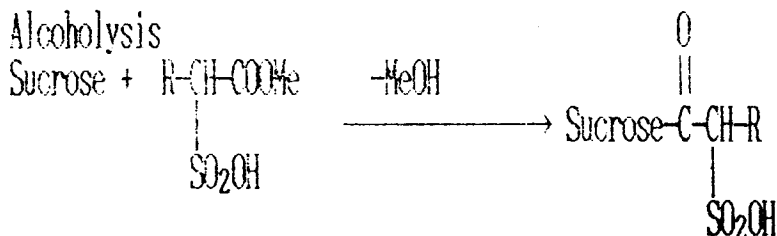
azotropic removal of water

② Acid chloride method

solvent ; dimethylformamide (DMF) + pyridine

$\alpha$ -sulfo alkanic acid dissolved with  $\text{CCl}_4$

③ Alcoholysis



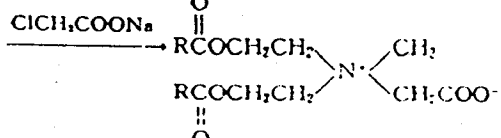
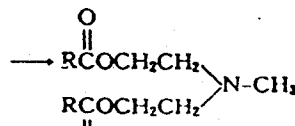
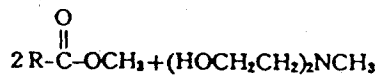
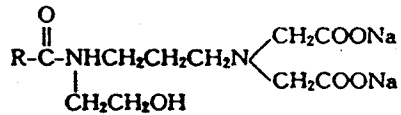
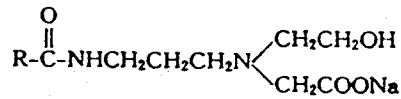
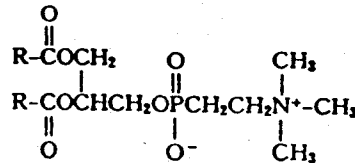
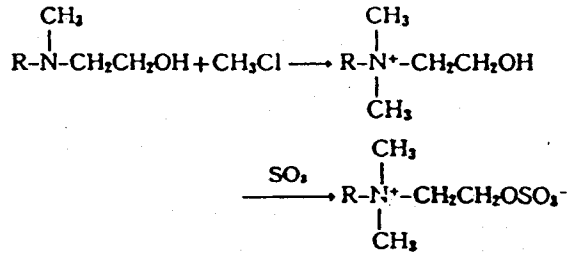
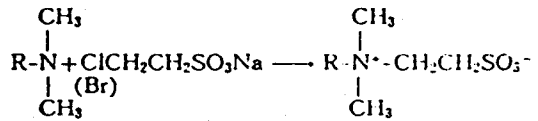
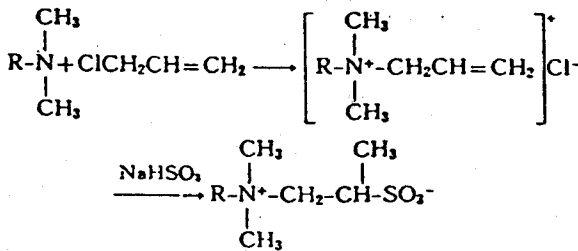
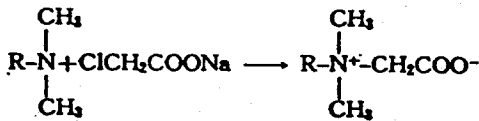
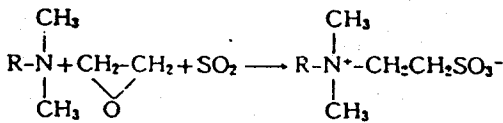
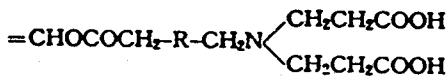
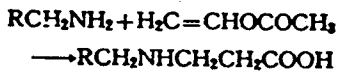
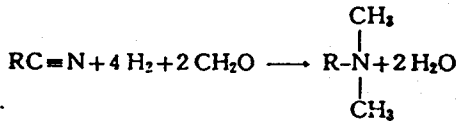
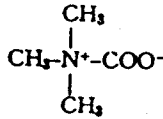
solvent ; DMF, benzene

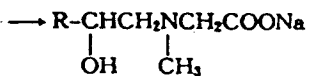
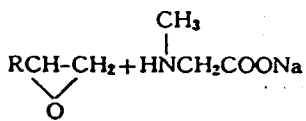
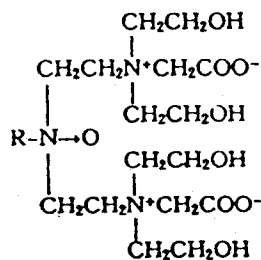
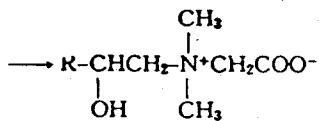
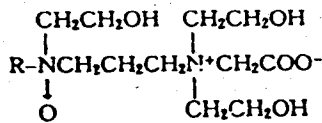
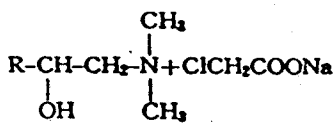
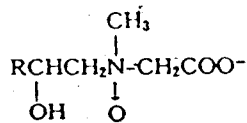
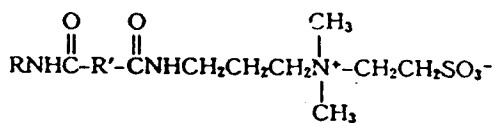
catalst ;  $\text{MeONa}$

azotropic removal of methanol

reaction appratus - Fig. 10

베타인 형 계면활성제

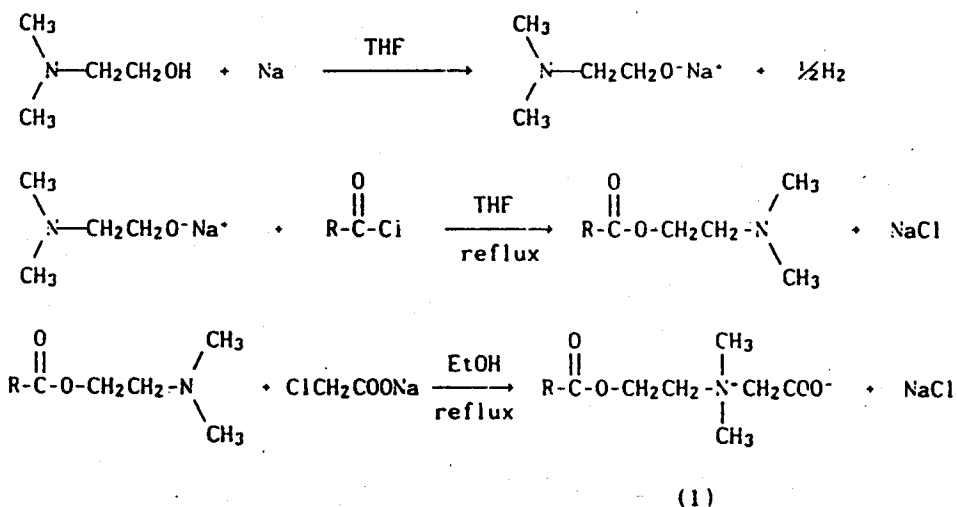






# N-알킬 카르복시 베타인 유도체

Scheme The process for the synthesis of N-alkylcarboxybetaines.

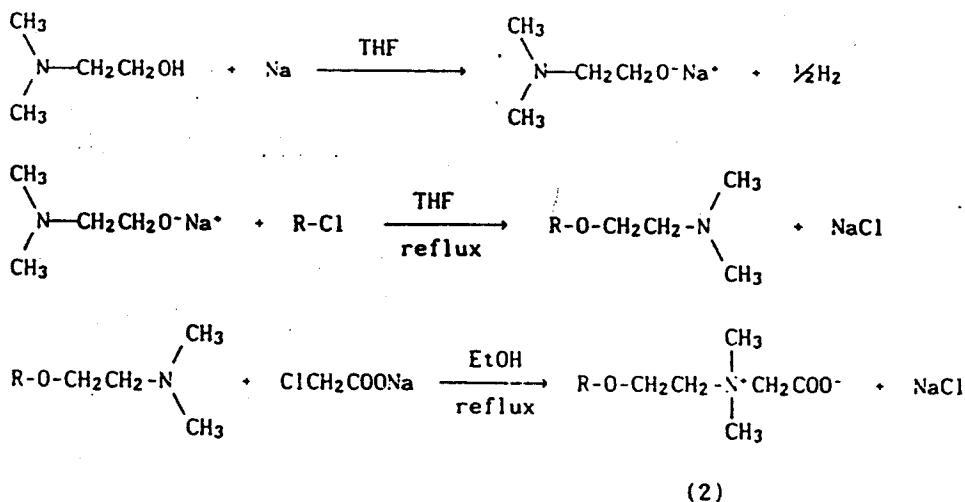


(1a) : N-(2-decanoyloxyethyl)-N,N-dimethylammonio ethanoate

(1b) : N-(2-dodecanoyloxyethyl)-N,N-dimethylammonio ethanoate

(1c) : N-(2-tetradecanoyloxyethyl)-N,N-dimethylammonio ethanoate

(1d) : N-(2-hexadecanoyloxyethyl)-N,N-dimethylammonio ethanoate

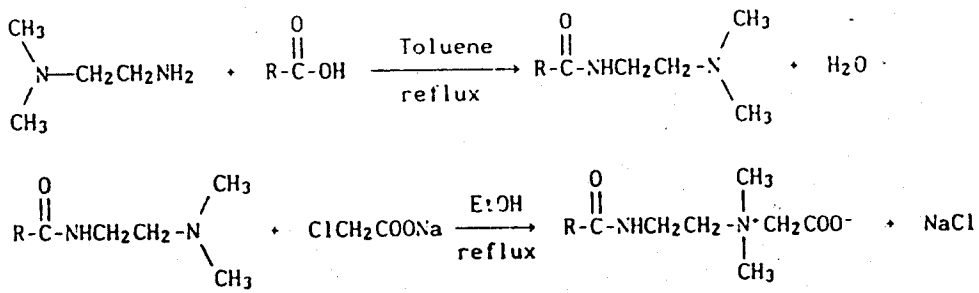


(2a) : N-(2-decanoyloxyethyl)-N,N-dimethylammonio ethanoate

(2b) : N-(2-dodecanoyloxyethyl)-N,N-dimethylammonio ethanoate

(2c) : N-(2-tetradecanoyloxyethyl)-N,N-dimethylammonio ethanoate

(2d) : N-(2-hexadecanoyloxyethyl)-N,N-dimethylammonio ethanoate



(3)

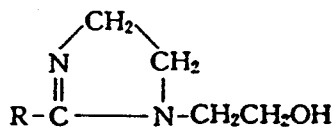
(3a) : N-(2-decanoylaminoethyl)-N,N-dimethylammonio ethanoate

(3b) : N-(2-dodecanoylaminoethyl)-N,N-dimethylammonio ethanoate

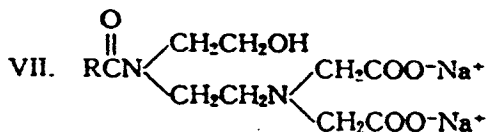
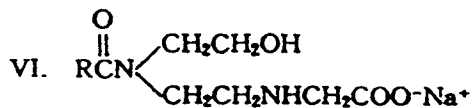
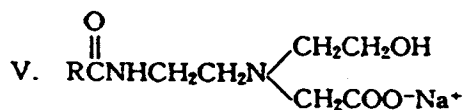
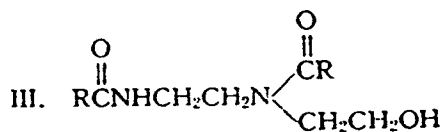
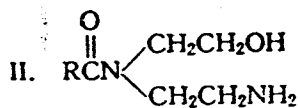
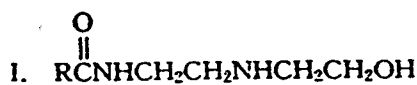
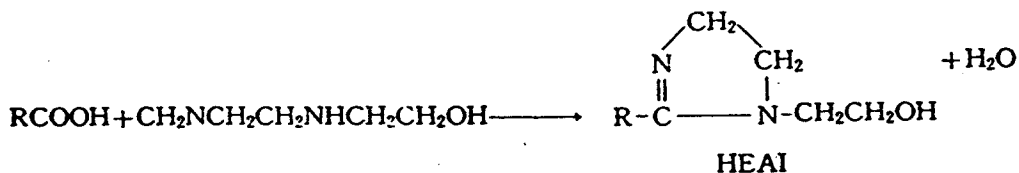
(3c) : N-(2-tetradecanoylaminoethyl)-N,N-dimethylammonio ethanoate

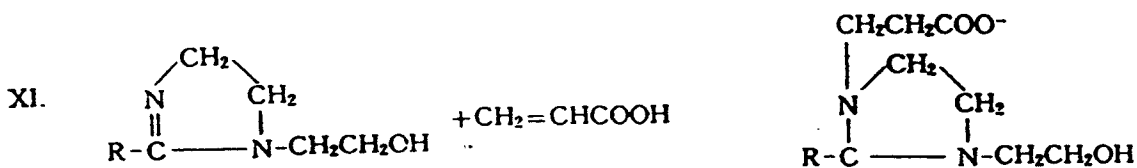
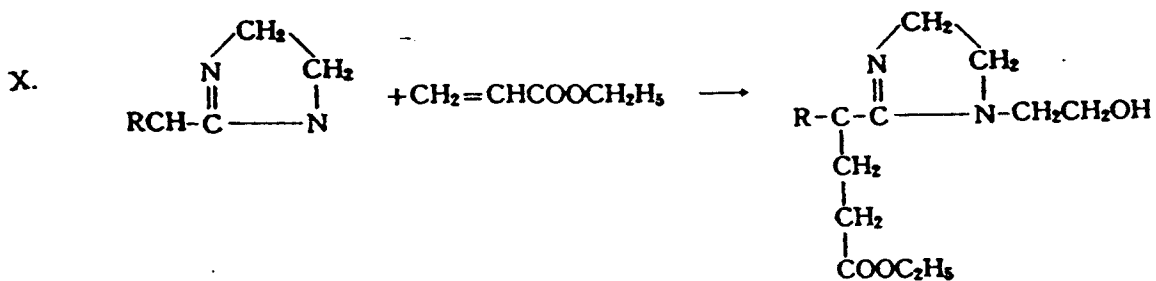
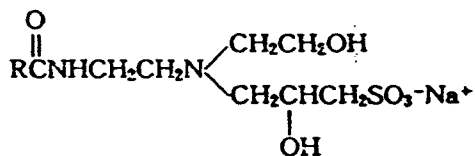
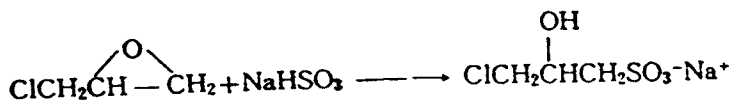
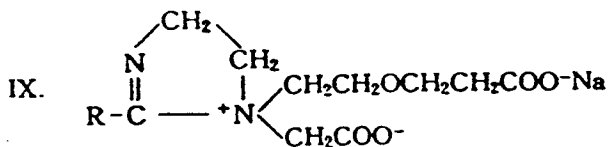
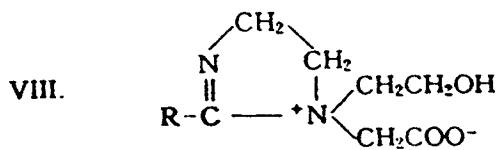
(3d) : N-(2-hexadecanoylaminoethyl)-N,N-dimethylammonio ethanoate

# 이미다졸린 형 계면활성제



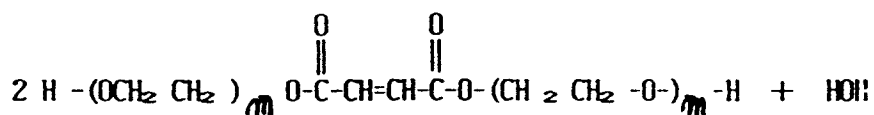
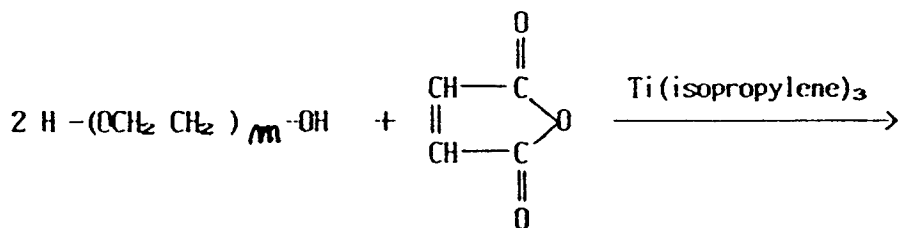
1-(2-hydroxyethyl)-2-alkyl-2-imidazoline HEAI



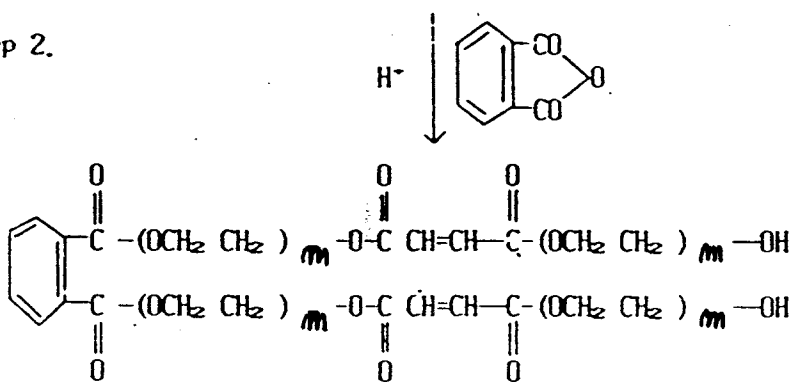


II. Maleic Anhydride - Polyethylene Glycol-Phthalic Anhydride  
Polymeric Surfactant

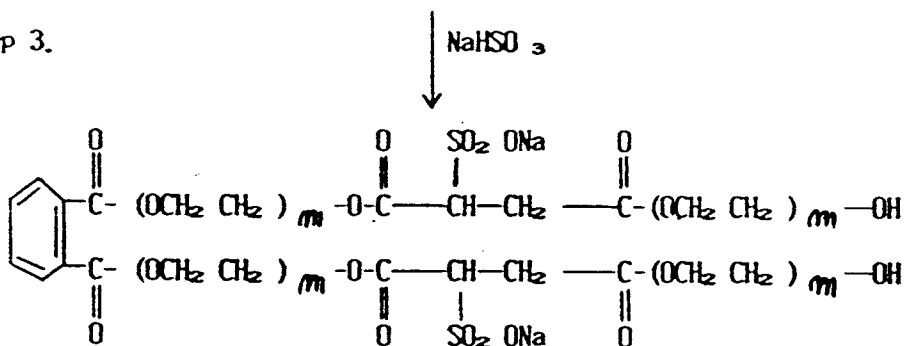
Step 1.



Step 2.

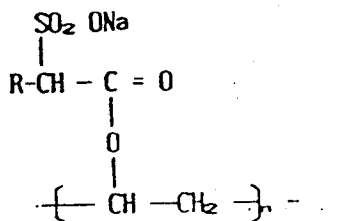
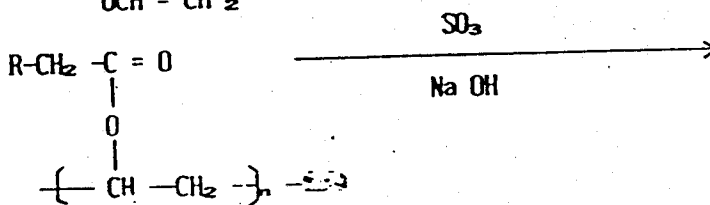
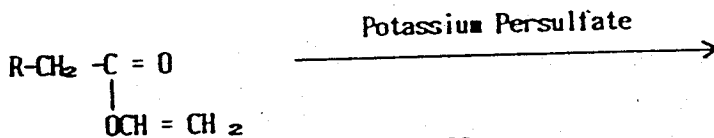
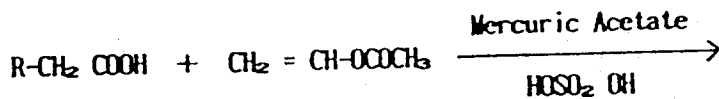


Step 3.



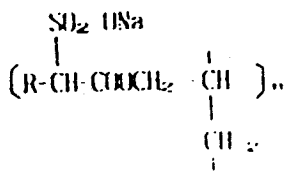
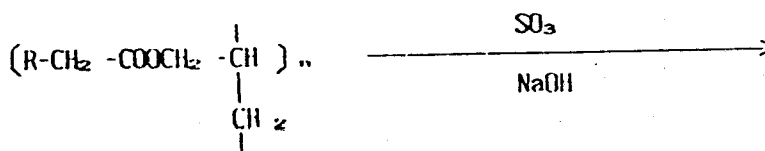
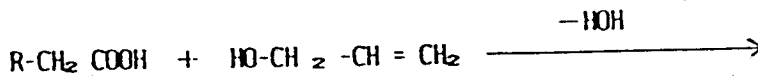
# I. Anionic Polymeric Surfactant

## 1. Vinyl $\alpha$ - Sulfo Fatty Acid Oligomer

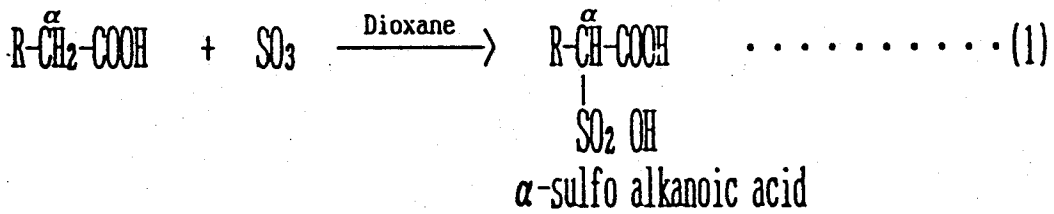


R : C<sub>10</sub> ~ C<sub>16</sub>

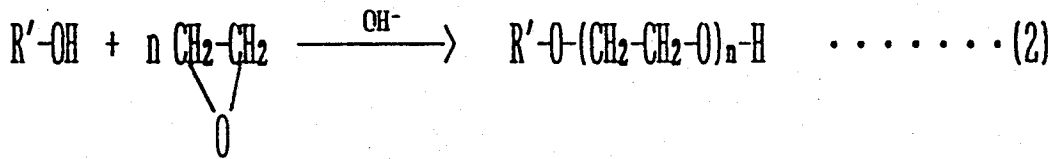
## 2. Allyl $\alpha$ -Sulfo Long Chain Aliphatic Carboxylate Polymers



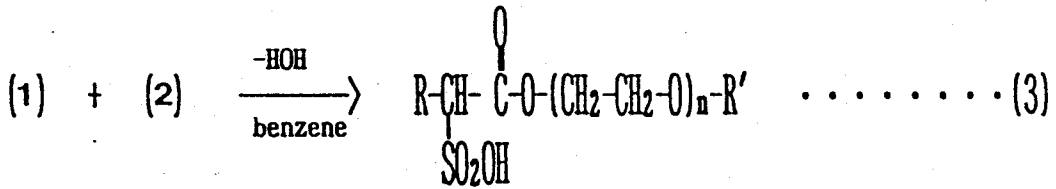
3. 알파술폰지방산 음이온성 올리고머 계면활성제



( R = C<sub>8</sub>, C<sub>10</sub>, C<sub>12</sub>, C<sub>14</sub>, C<sub>16</sub> )

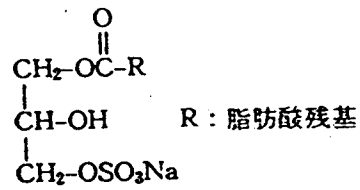


( n = 5, 10, 20 , R' = C<sub>12</sub>H<sub>25</sub> )

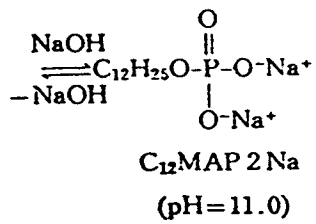
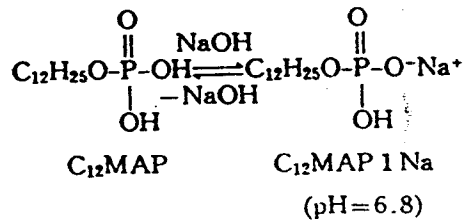


alkyl polyoxyethylene α-sulfo alkanoate

## 모노 글리세이레이트류 유도체

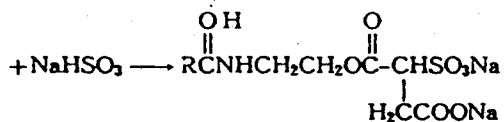
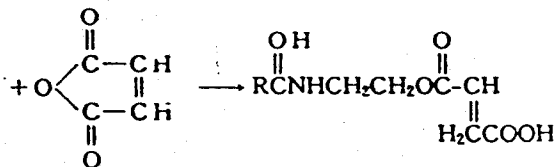
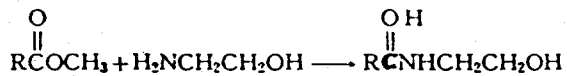
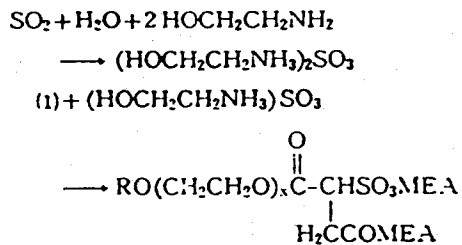
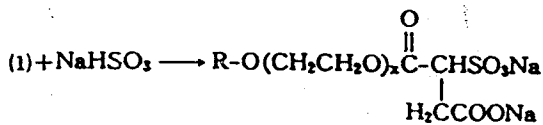
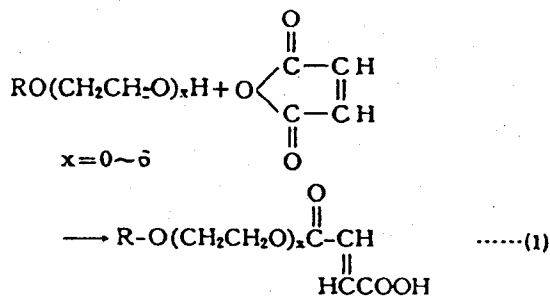


## 모노 알킬 인산염(MAP)류 유도체

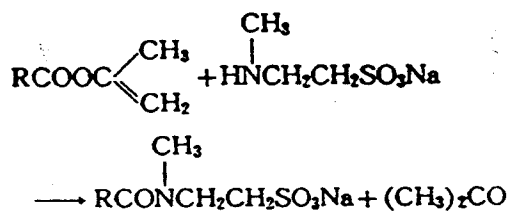
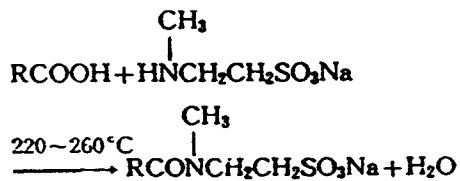
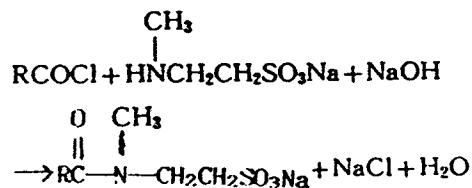




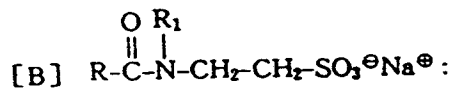
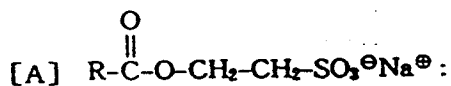
술포 숙신산 염류 유도체



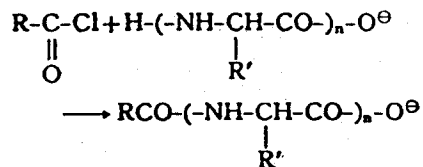
## 메틸 타우린산 염류 유도체



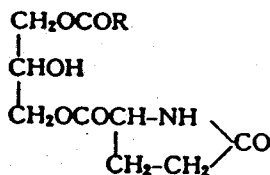
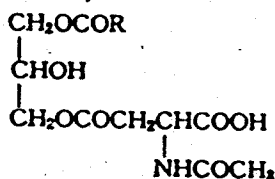
## N-아실 이세티온산 염류 유도체



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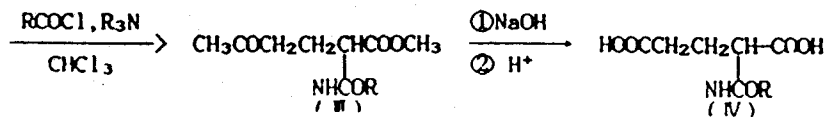
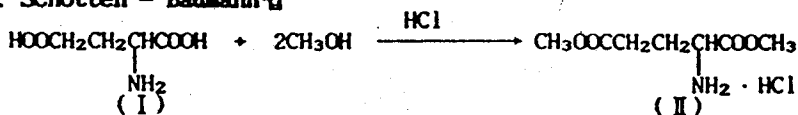


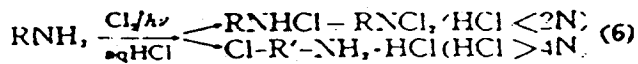
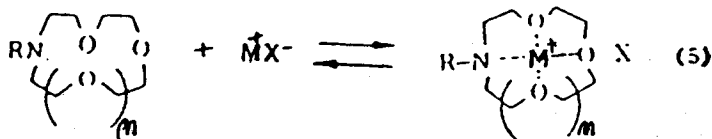
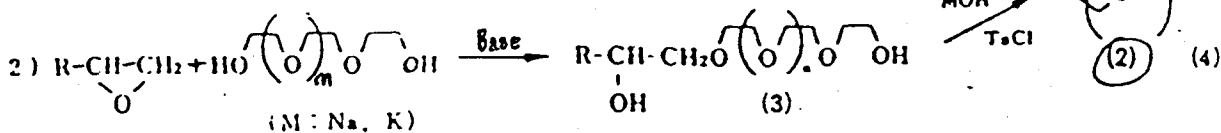
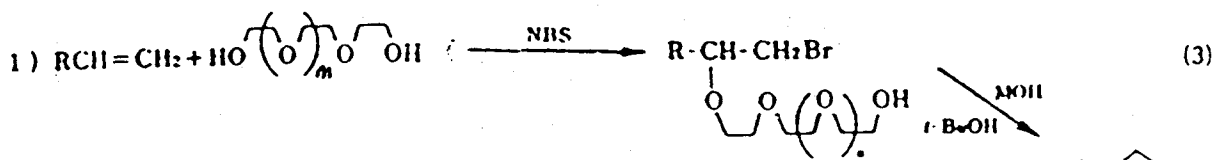
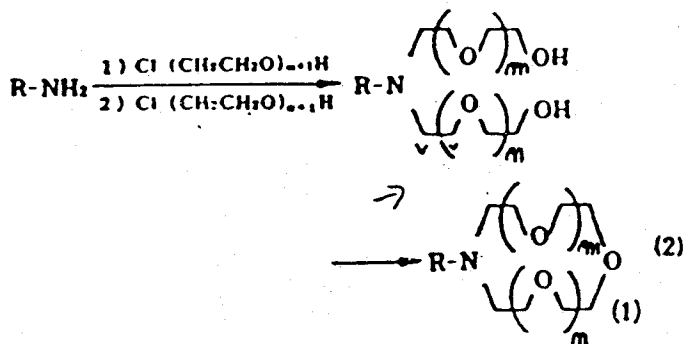
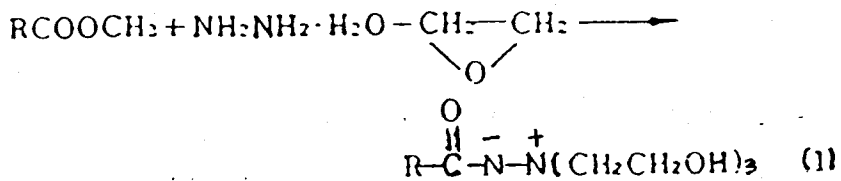
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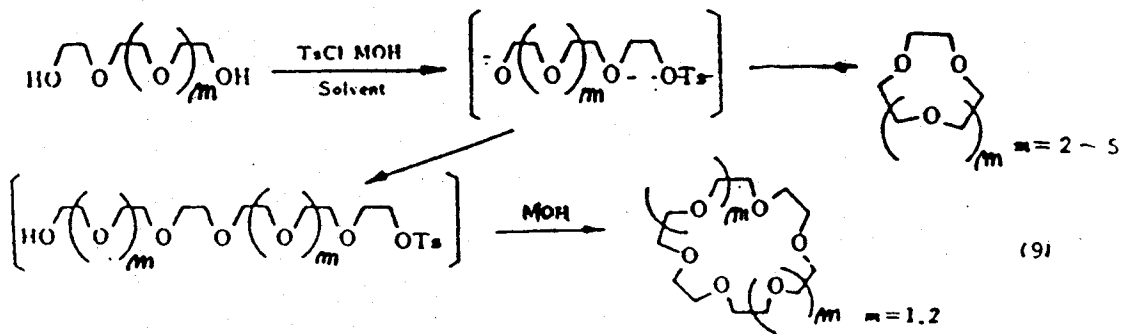
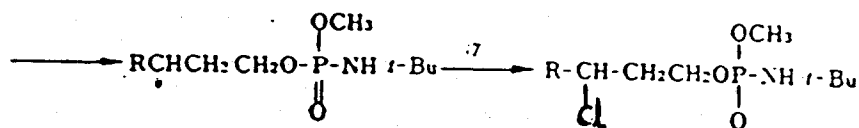
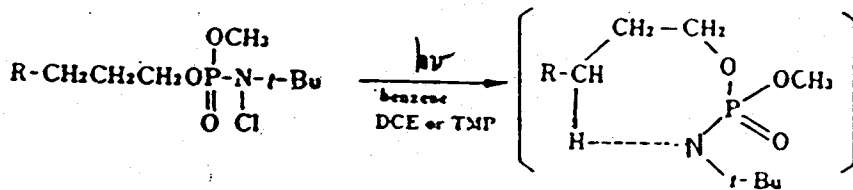
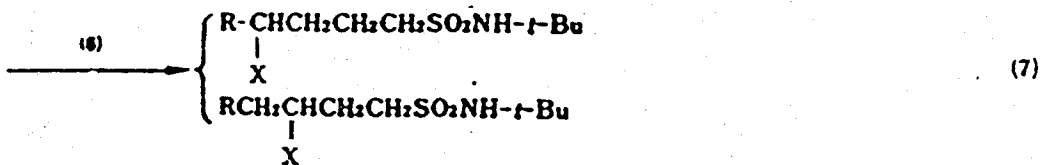
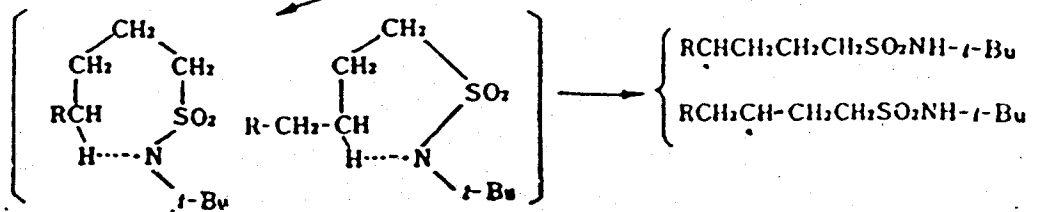
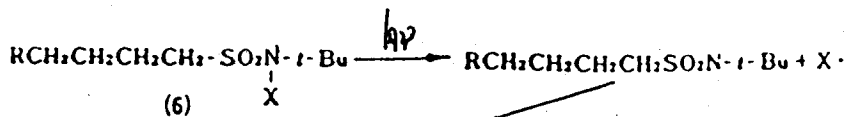


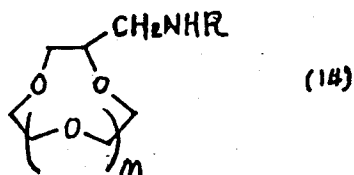
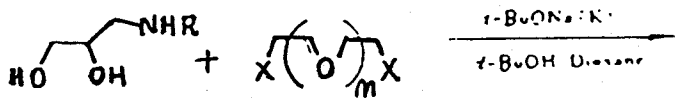
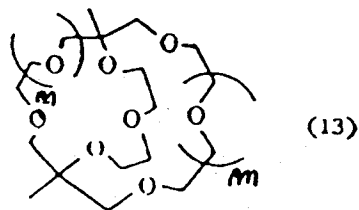
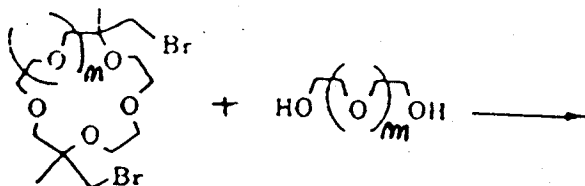
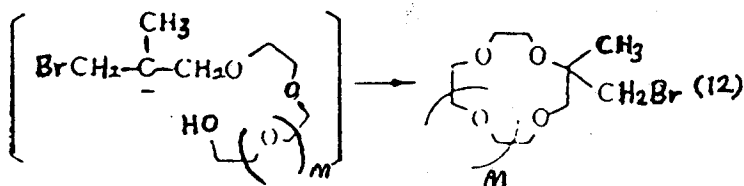
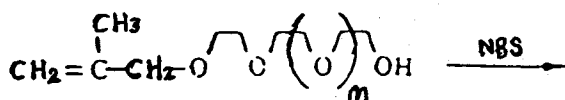
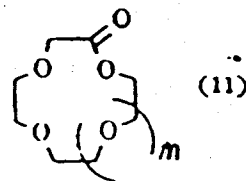
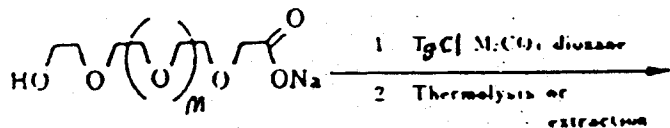
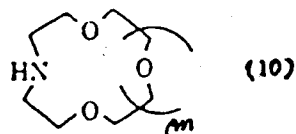
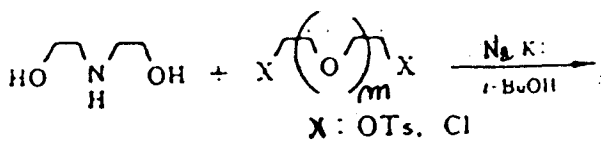
## N-알킬 글루타민산 염류 유도체

### I . Schotten - Baumann법





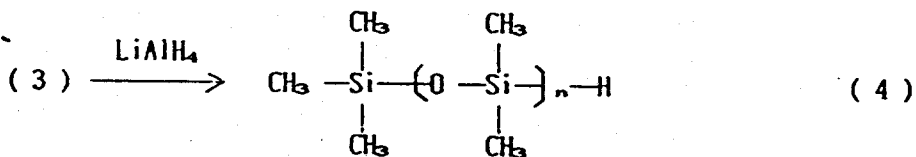
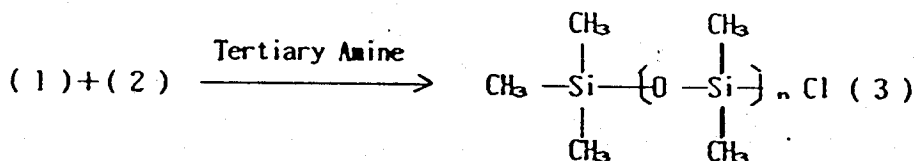
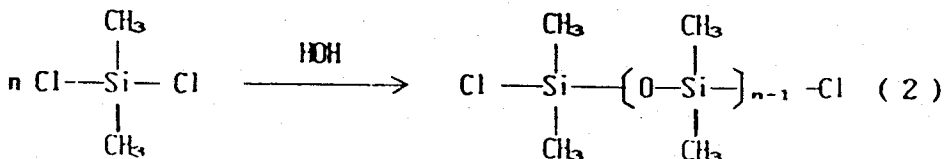
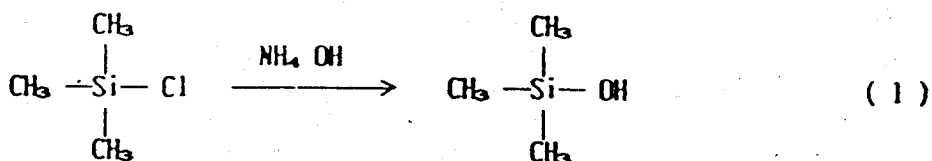




## ■. Silicon Surfactant

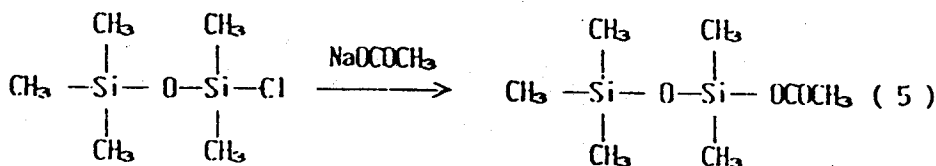
### 1. Poly Siloxane Nonionic Surfactant

a)  $\omega$ -Hydrodichloro<sup>COO<sup>-</sup></sup> polysiloxane

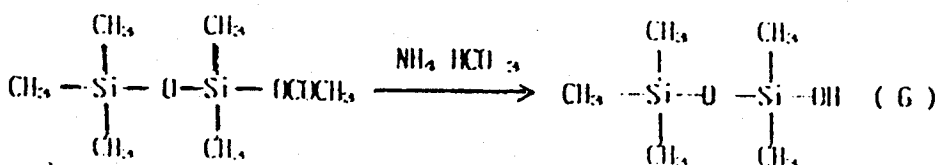


$n : 2, 3, 4$

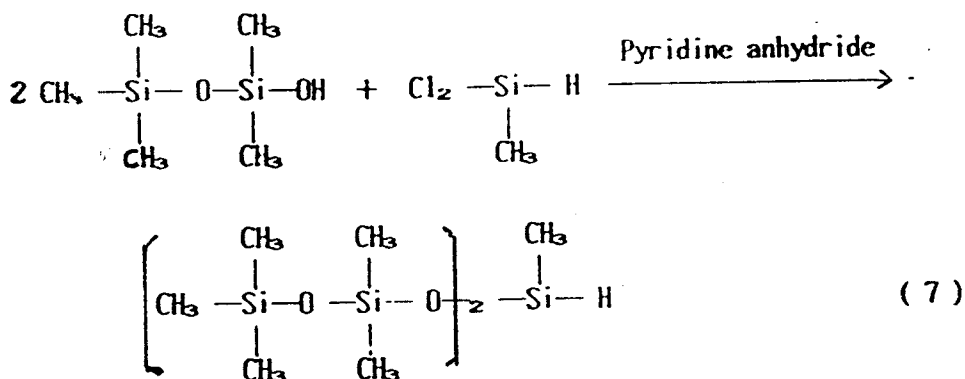
b) Acetoxy pentamethyl disiloxane



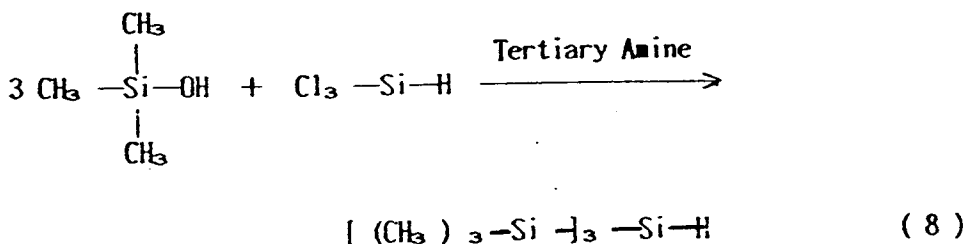
c)  $\omega$ -oxy pentamethyl disiloxane



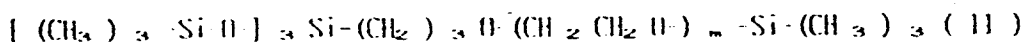
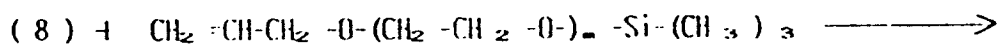
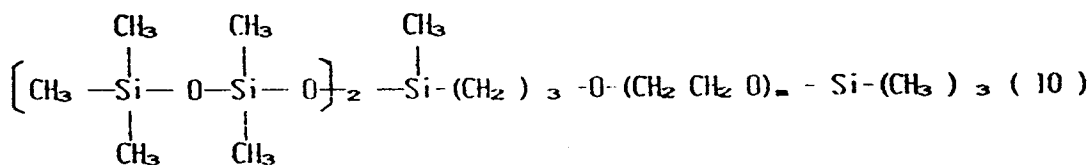
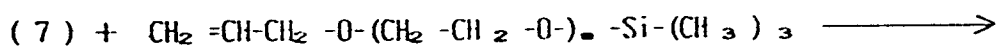
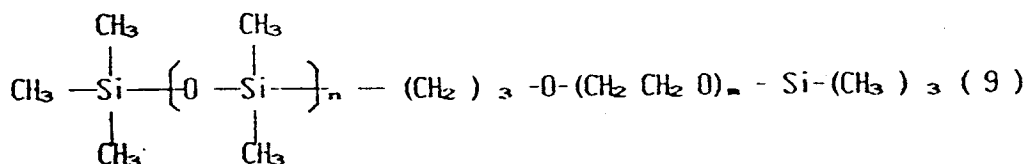
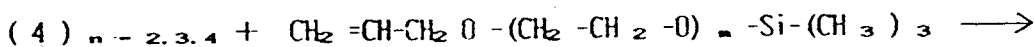
d) Bis (pentamethyl disiloxy) methyl silane



e) Tris (trimethyl siloxyl) silane



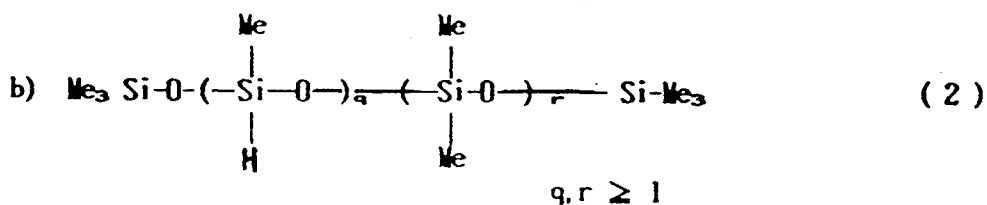
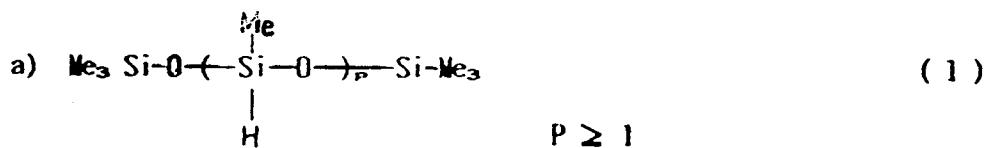
f) Silicon Nonionic Surfactant



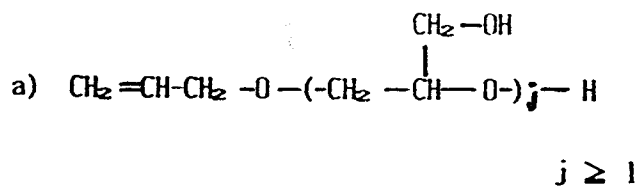


## IV. Polyolic Silicon Surfactant

### 1. Polyoxy Siloxane

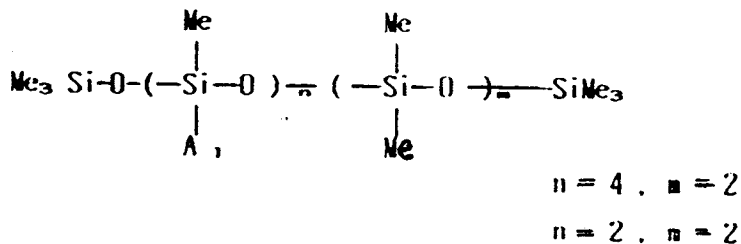
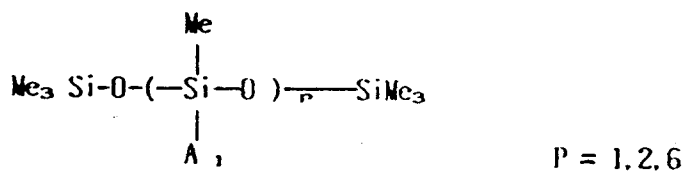


### 2. Allyl Glycidil Alcohol

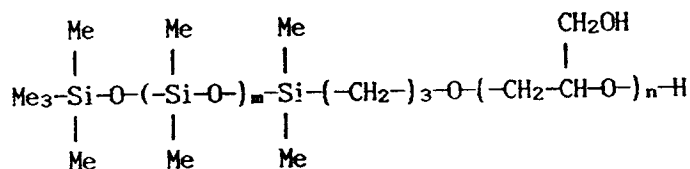


b) Sucrose, c) Glucose, d) Glycerine

### 3. Polyolic Silicon Surfactant



1) Polyolic primary polymethyl siloxane(A)



[1a] ; m=2, n=6.5 P-2-MEO-6.5

[1b] ; m=3, n=6.5 P-3-MEO-6.5

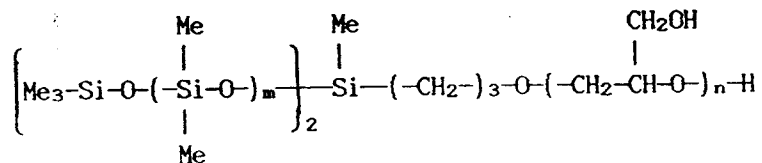
[1c] ; m=4, n=6.5 P-4-MEO-6.5

[1d] ; m=2, n=12 P-2-MEO-12

[1e] ; m=3, n=12 P-3-MEO-12

[1f] ; m=4, n=12 P-4-MEO-12

2) Polyolic secondary polymethyl siloxane(B)



[2a] ; m=2, n=6.5 S-2-MEO-6.5

[2b] ; m=3, n=6.5 S-3-MEO-6.5

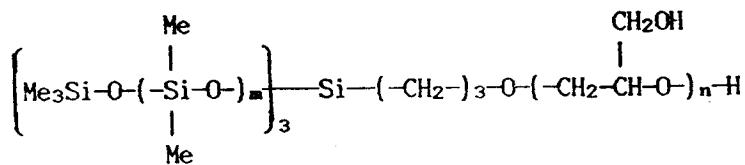
[2c] ; m=4, n=6.5 S-4-MEO-6.5

[2d] ; m=2, n=12 S-2-MEO-12

[2e] ; m=3, n=12 S-3-MEO-12

[2f] ; m=4, n=12 S-4-MEO-12

3) Polyolic tertiary polymethyl siloxane(C)



[3a] ; m=2, n=6.5 T-2-MEO-6.5

[3b] ; m=3, n=6.5 T-3-MEO-6.5

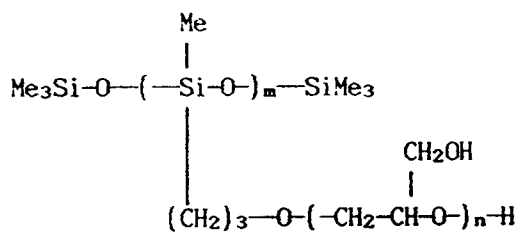
[3c] ; m=4, n=6.5 T-4-MEO-6.5

[3d] ; m=2, n=12 T-2-MEO-12

[3e] ; m=3, n=12 T-3-MEO-12

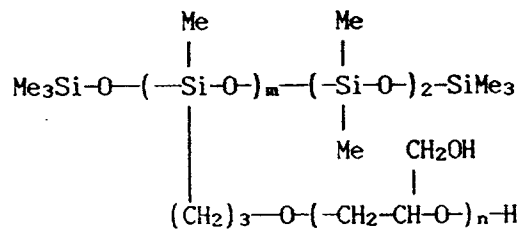
[3f] ; m=4, n=12 T-4-MEO-12

4) Polyolic side-chain modified polymethyl siloxane(D)



[4a] : m=2, n=6.5 PH-2-MEO-6.5

[4b] : m=6, n=6.5 PH-6-MEO-6.5



[5a] : m=2, n=6.5 D-2-PH-2-MEO-6.5

[5b] : m=4, n=6.5 D-2-PH-4-MEO-6.5

