

總 說

油脂工業에 있어서 重要的 脂肪酸의 反應

足立 明巳

日本油化學協會副會長  
近畿大學理工學總合研究所

Important Reaction of Fatty Acids in Fatty Oil Industry

Akemi Adachi

*Vice-President of the Japan Oil Chemist's Society  
Institute for Science and Technology, Kinki University, Japan*

(Received Nov. 18, 1985)

1985年度 韓國油化學會秋季學術發表會에서 講演 脂肪酸의 化學反應]이며, 그 內容은 다음과 같으나 이 演 題는 「앞으로 工業적으로 利用價值가 있다 中에서 몇가지 項目을 選擇하여 解說할가 합니다. 고 생각되는 것을 제가 골라낸 20여 가지의 脂肪

1. Direct Esterification of Sterically Hindered Carboxylic Acids
2. Synthesis and Reactions of Isopropenyl Esters
3. Specific Synthetic Reactions by the Use of Organosilicon Compounds
4. Chemistry of Acyl Cyanides
5. Anodic Synthesis of Fatty Acids (Kolbe Reaction)
6. Selective Reduction of Carboxylic Acids to Aldehydes
7. Catalysed Hydrogenation of Unsaturated Fatty Acids to Unsaturated Alcohols
8. Recent Progress of the Halogenation Reactions of Saturated Fatty Acids
9. Reactions of Dianions of Carboxylic Acids and Ester Enolates
10. Synthesis of  $\alpha, \beta$ -Unsaturated Fatty Acids and Esters
11.  $\alpha$ -Sulfofatty Acids and Their Derivatives
12. Epoxidation and Reactions of the Oxirane Group
13. Mono- and Dihydroxylation of Unsaturated Fatty Acids
14. Permanganate Oxidation of Unsaturated Fatty Acids
15. Ozonization of Unsaturated Fatty Acids
16. Metathesis of Unsaturated Fatty Acids
17. Hydroformylation and Carboxylation of Unsaturated Fatty Acids
18. Ene-Synthesis
19. Diene-Synthesis (Diels-Alder Reaction)

- 20. Synthesis of Amines from Olefins
- 21. Addition of Aromatic Compounds to Unsaturated Fatty Acids
- 22. Addition of Sulfur Compounds to Unsaturated Fatty Acids

I. 카르복시酸과 水酸基를 가진 化合物로부터 誘導되는 에스테르

에스테르는 여러 分野에서 實用化되고 있는 重要한 化合物이다. 카르복시酸과 알코올로부터 에스테르를 合成하는 反應  $[RCOOH + R'OH \rightleftharpoons RCOOR' + H_2O]$ 은 古典적인 合成方法이기는 하나 最近에 있어서도 改良研究가 많이 實施되고 있다. 即 (1) 反應速度를 向上시키는 觸媒 (2) 生成되는 水을 除去하여 平衡을 右側으로 移行시키는 手段, (3) 立體障害이 큰 카르복시酸 또는 알코올에 對한 에스테르 生成等이다.

1. 9(10)-carboxystearic acid의 에스테르화<sup>1)</sup>

9(10)-carboxystearic acid의 alkyl 9(10)-carboalkoxystearate, alkyl 9(10)-carboalkoxystearate에의 黃酸觸媒에 依한 에스테르화의 反應速度는 末端카르복시基가 側鎖카르복시基에 比해서 約 26~27倍 以上の 反應性을 가지고 있고, 觸媒濃度에 많이 依存 된다. 2,2-dimethylpentanol의 立體障害, 2-methoxyetanol, 2-chloroethanol

의 親電子性도 反應速度를 顯著하게 느리게 한다 (Fig. 1, Table I).

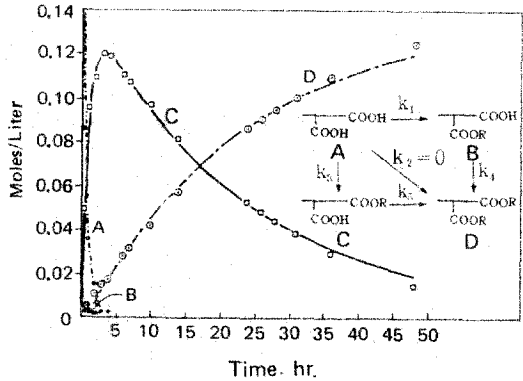


Fig. 1. Scheme and computer plot of esterification of 0.14 molar 9(10)-carboxystearic acid with 4.2 molar dimethylpentanol in benzene at 99°C using 85 mg sulfuric acid. Samples for the computer plot were methylated. (A) 9(10)-Carboxystearic acid; (B) 9(10)-carbo(dimethylpentoxy) stearic acid; (C) dimethylpentyl 9(10)-carboxystearic acid; (D) dimethylpentyl 9(10)-carbo(dimethylpentoxy) stearate.

Table I. Rates of Esterification

Experiment	Alcohol	Moles/liter	Catalyst, mg H <sub>2</sub> SO <sub>4</sub>	Pot temperature, °C	Rates, hr <sup>-1</sup>				
					k <sub>1</sub>	k <sub>3</sub>	k <sub>4</sub>	k <sub>5</sub>	k <sub>3</sub> /k <sub>5</sub>
9(10)-Carboxystearic Acid (0.1398 molar)									
1	n-Butyl	4.2	42.4	85	0.031	0.582	0.776	0.019	31
2	n-Butyl	4.2	63.1	85	0.067	1.16	1.15	0.039	30
3	n-Butyl	4.2	83.8	85		2.32		0.088	26
4	n-Butyl	2.1	85.8	83		2.60		0.104	25
5	2-Methoxyethyl	4.2	83.8	84		1.01		0.029	35
6	2-Chloroethyl	4.2	81.0	84		1.48		0.054	27
7	2,2-Dimethylpentyl	4.2	85.0	99		1.09		0.042	26
8	2,2-Dimethylpentyl	2.1	82.5	86		0.84		0.031	27
9	2-Ethylhexyl	4.2	84.5	106		2.44		0.155	16
10	2-Ethylhexyl	2.1	83.6	86		2.44		0.095	25
11	n-Octyl	2.1	80.2	87		3.83		0.155	25

Table II. Esterification of Phenols with Carboxylic Acids <sup>a</sup>

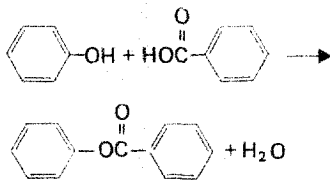
Product	Solvent	Reaction Time, Hr.	Isolated Yield, %
Phenyl benzoate	Toluene	8	94
P-Methoxyphenyl benzoate	Xylene	23	88
P-Nitrophenyl benzoate	Xylene	23	85
Phenyl butyrate	Xylene	17	86
Diphenyl isophthalate	Sulfolane/xylene	24	58
Diphenyl terephthalate	Sulfolane/xylene	23	87
Diphenyl tetramethyl-terephthalate <sup>b</sup>	Xylene	48	80
2-Naphthylisobutyrate	Xylene	5	58

<sup>a</sup> In all cases the reaction was conducted by removing water by azeotropic distillation from a solution of the phenol and carboxylic acid in a solvent containing 1 to 5 mole % of boric and sulfuric acids. Products were isolated by appropriate crystallization or distillation.

<sup>b</sup> This compound, m.p. 265-266°C., had correct analysis for carbon and hydrogen.

2. 페놀의 boric acid 촉매에 의한 에스테르화<sup>2</sup>

톨루엔中 케놀과 安息香酸을 觸媒量의 硼酸과 黃酸을 加하고 還流하여, 물을 共沸混合物로 하여 留出시키는 方法이 좋고 (8 hr 反應하면 收率 94%), 硼酸單觸 또는 黃酸單 觸媒로 使用하면 좋은 結果는 얻지 못한다. 黃酸代身 폴리磷酸을 使用해도 좋다 (Table II).



3. Acetone dimethyl ketal 를 使用하는 메틸에스테르화<sup>3</sup>

酸觸媒를 使用하는 메탄올에 의한 에스테르화는 그 메탄올은 生成수로 稀薄되기 때문에 多量必要하게 되는데, 이 欠點을 改良하고 acetone dimethyl ketal 와 같이 에스테르화하여 生成하는 물은 아세톤 및 메탄올로 되어 水反應에서도 效果의으로 에스테르화가 進行된다 (Fig. 2).

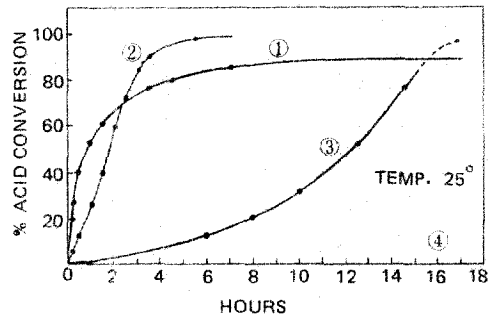
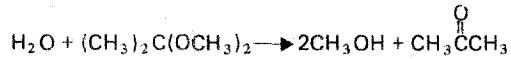
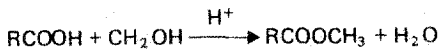


Fig. 2. Rate of Esterification of Propionic Acid

	1	2	3	4
Moles of Propionic acid	0.25	0.25	0.25	0.25
Methanol	0.75	0.25	0.075	0.00
Acetone dimethyl ketal	0.00	0.25	0.25	0.25
Hydrogen chloride	0.006	0.006	0.006	0.006

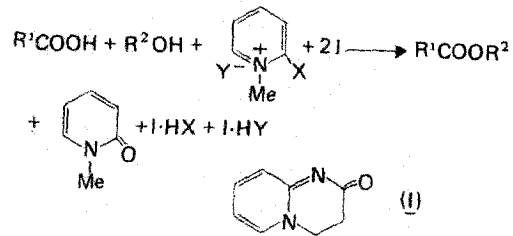
4. 에스테르화反應의 脱水觸媒<sup>4</sup>

Acid polymer로서 polystyrene copolymer의 sulfonic acid를 使用해서 capacity = 4.5 mequiv/g (Rexyn/101(H) R-231) 및 4.8 mequiv/g (Rexyn/101(H) R-204) (使用前에 100°C로 乾

燥)와  $\text{CaSO}_4$  (40 ~ 80 mesh, 180 °C로 加熱하고 無水狀態의 것을 攪친 것을 酸과 알코올의 混合物에 加하면 된다. 生기는 물이  $\text{CaSO}_4$ 에 吸收되어 에스테르生成反應의 平衡도 右側에 移動되는 效果가 同時에 나타난다(Table III).

### 5. Betaine을 使用하는 카르복시酸의 에스테르化<sup>5)</sup>

Betaine (3,4-dihydro-2H-pyrido [1,2-a] pyrimidin-2-one)의 存在下에서 1-methyl-2-fluoro 혹은 2-chloropyridinium salt를 使用하여 카르복시酸과 알코올의 같은 물反應에 依해서 좋은 收率로 해당되는 카르복시酸에스테르가 生成된다 (Table IV).



### 6. 카르복시酸의 簡便한 에스테르化<sup>6)</sup>

N, N-Dimethylphosphoramidic dichloride (A) 또는 phenyl dichlorophosphate (B)는 카르복시酸을 活性化하여 廣範한 種類의 構造를 가진 알코올과 거의 中性條件, 室溫에서 서서히 進行된다 (Table V).

Table III. Yield Data for Esterifications

Run	Alcohol	Solvent	Reaction ratio, acid:alcohol (v/v)	Time	Acid polymer: dehydrator (g/g)	Dtotal	Acid polymer	Yield, ± 5%
1	Methanol		1:10	10 min	a			67
2	Methanol		1:10	14 hr	a			82
3	Methanol	Ether, 10 ml	2:0.6	10 min	a			21
4	Methanol	Ether, 10 ml	2:0.6	17 hr	a			59
5	Methanol		1:10	10 min	10:0	16.1	R204	87
6	Methanol		1:10	10 min	3:7	6.3	R204	94
7	Methanol		1:10	10 min	3:0	4.7	R231	32
8	Methanol		1:10	20 min	3:7	6.3	R204	93
9	Methanol	Ether, 10 ml	1:2	20 min	3:7	6.3	R231	52
10	Methanol		10:0.6	120 min	3:7	7.5	R204	73
11	Methanol	Ether, 10 ml	2:0.6	20 min	3:7	7.5	R231	33
12	1-Butanol		1:10	60 min	a			58
13	1-Butanol		1:10	60 min	3:7	6.3	R231	84
14	1-Butanol		1:10	60 min	3:0	4.7	R231	26
15	1-Butanol		1:10	10 min	3:7	6.3	R204	22
16	1-Butanol		1:10	160 min	3:0	4.7	R231	58
17	1-Butanol		1:10	17 hr	3:7	6.3	R231	100
18	1-Butanol		1:10	190 min	3:0	4.7	R231	68
19	1-Butanol		1:10	14 hr	3:0	4.7	R231	100
20	1-Butanol		1:10	60 min	3:7 <sup>b</sup>		R231	52
21	1-Butanol		1:10	90 min	3:7 <sup>b</sup>		R231	65
22	1-Butanol		1:10	17 hr	3:7 <sup>b</sup>		R231	93
23	2-Propanol		1:10	17 hr	3:7	6.3	R231	91
24	2-Propanol		1:10	17 hr	3:7 <sup>b</sup>		R231	73

a. No catalytic dehydrator used in these runs. The reactions were catalyzed by p-toluenesulfonic acid.

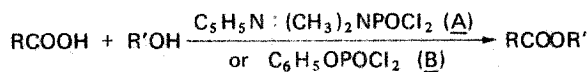
b. Anhydrous silica gel used as the drying agent.

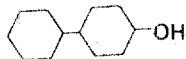
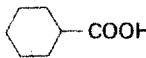
Table IV. The Synthesis of Carboxylic Esters

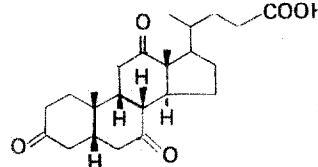
Acid <sup>a</sup>	Alcohol <sup>b</sup>	Pyridinium	Salt <sup>c</sup>	Reaction Time	Volume of Solvent	Isolated Yield
R <sup>1</sup>	R <sup>2</sup>	X	Y	(hr)	(ml)	(%)
PhCH <sub>2</sub>	PhCH <sub>2</sub>	Cl	I	3	10	96 <sup>d</sup>
PhCH <sub>2</sub>	Ph	Cl	I	3	10	78 <sup>d</sup>
PhCH <sub>2</sub>	PhCH=CHCH <sub>2</sub>	Cl	I	3	10	97 <sup>d</sup>
PhCH <sub>2</sub>	CH <sub>3</sub> CH=CHCH <sub>2</sub>	Cl	I	3	10	94 <sup>d</sup>
PhCH <sub>2</sub>	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub>	Cl	I	3	10	89 <sup>d</sup>
PhCH <sub>2</sub>	CH <sub>3</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )	Cl	I	3	10	72 <sup>d</sup>
PhCH <sub>2</sub>	(CH <sub>3</sub> ) <sub>3</sub> C	Cl	I	8	4	72 <sup>e</sup>
PhCH <sub>2</sub> CH <sub>2</sub>	PhCH <sub>2</sub>	F	TsO	6	4	74 <sup>e</sup>
CH <sub>3</sub> CH <sub>2</sub>	PhCH=CHCH <sub>2</sub>	F	TsO	7.5	4	60 <sup>e</sup>
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub>	PhCH <sub>2</sub>	F	TsO	46	4	74 <sup>e</sup>
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub>	PhCH <sub>2</sub>	F	TsO	— <sup>f</sup>	10 <sup>g</sup>	42 <sup>d</sup>

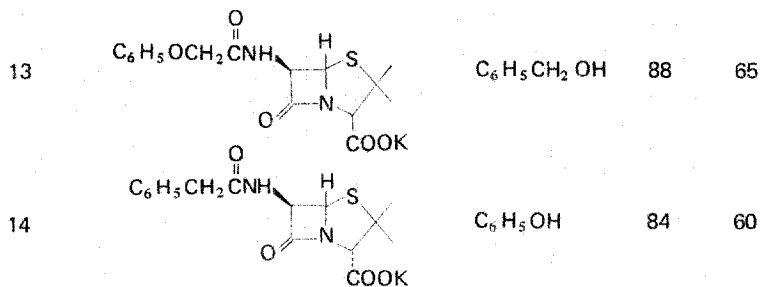
Condition ; in CH<sub>2</sub>Cl<sub>2</sub> at r.t. a. 1.0 mmol, b. 1.0 mmol, c. 1.2 mmol, d. betaine 2.4 mmol, e. betaine 4.8 mmol, f. at r.t. for 1 hr, and then reflux for 5 hr, g. in ClCH<sub>2</sub>CH<sub>2</sub>Cl.

Table V. Esterification of Carboxylic Acids



Entry	RCOOH	R'OH	Isolated Yield (%)	
			A	B
1	C <sub>6</sub> H <sub>5</sub> OCH <sub>2</sub> COOH	C <sub>6</sub> H <sub>5</sub> OCH <sub>2</sub> CH <sub>2</sub> OH	82	88
2		(CH <sub>3</sub> ) <sub>3</sub> COH	89	94
3			76	84
4		CH <sub>3</sub> CH <sub>2</sub> OH	84	97
5		C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH	70	81
6	C <sub>6</sub> H <sub>5</sub> OCH(CH <sub>3</sub> )COOH	CH <sub>3</sub> CH <sub>2</sub> OH	83	92
7		CH <sub>3</sub> OH	84	85
8		C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OH	96	95
9		(CH <sub>3</sub> ) <sub>3</sub> COH	84	90
10	CH <sub>2</sub> =CH(CH <sub>2</sub> ) <sub>8</sub> COOH	CH <sub>2</sub> =CHCH <sub>2</sub> OH	73	77
11	CH <sub>3</sub> CH <sub>2</sub> OCH <sub>2</sub> COOH	C <sub>6</sub> H <sub>5</sub> OH	96	98

12		C <sub>6</sub> H <sub>5</sub> OH	78	88
----	---	----------------------------------	----	----



7. 脂肪酸의 穩和한 에스테르化<sup>7</sup>

脂肪酸(10 meq), 알코올(1.1 meq), dicyclohexylcarbodiimide (DCC ; 1.1 meq)와 4-dimethylaminopyridine (DMAP ; 0.1 meq)을 디클로로메탄中 25°C로 24 hr 攪拌하면 에스테르가 좋은 收率로 얻어진다(Table VI).

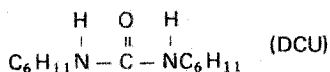
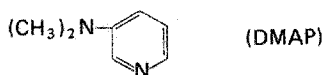
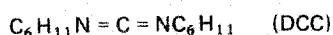
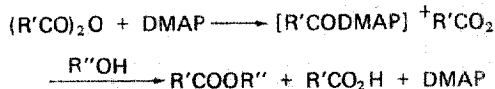
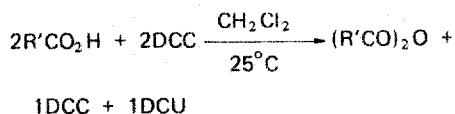


Table VI. Esterification in Quiet

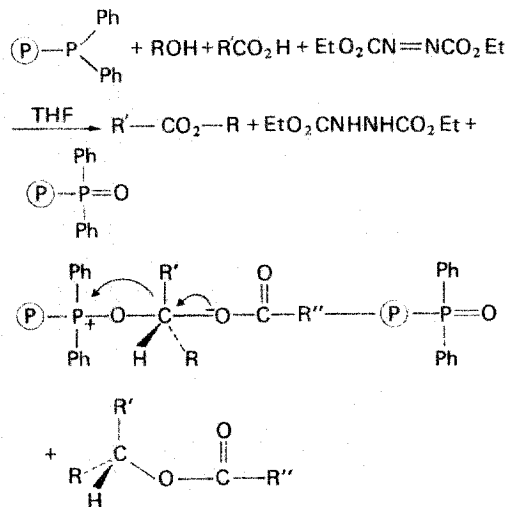
Entry	Ester	Yield(%) <sup>a</sup>
1	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> CO <sub>2</sub> CH <sub>3</sub>	74 <sup>b</sup>
2	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> CO <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	66 <sup>b</sup>
3	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> CO <sub>2</sub> CH <sub>2</sub> CCl <sub>3</sub>	84
4	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> CO <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	81 <sup>b</sup>
5	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> CO <sub>2</sub> CH <sub>2</sub>	75 <sup>b</sup>
6	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> CO <sub>2</sub> CH <sub>2</sub>	88 <sup>b</sup>
	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>14</sub> CO <sub>2</sub> -CH <sub>2</sub>	
	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>14</sub> CO <sub>2</sub> -CH	
7	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>14</sub> CO <sub>2</sub> -CH <sub>2</sub>	67 <sup>b</sup>
	Cholesteryl laurate	

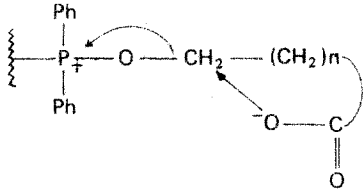
8	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> CO <sub>2</sub> CHCH <sub>3</sub> CH <sub>2</sub> ≡CH	72
9	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> CO <sub>2</sub> C(CH <sub>3</sub> ) <sub>3</sub>	68 <sup>b</sup>
10	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>16</sub> CO <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> ≡CH	85
11	H≡CCH(OTBS)(CH <sub>2</sub> ) <sub>3</sub> CO <sub>2</sub> CHCH <sub>3</sub> -CH <sub>2</sub> ≡CH	73

a. Yields are of isolated, purified material and are not optimized. All new substances gave correct combustion analysis and/or gc/mass spectra and nmr spectra. b. Known compound which provided correct physical and spectral data.

8. 重合체에 附着된 포스핀試藥을 使用한 에스테르化<sup>8</sup>

溶媒(tetrahydrofuran)에 polystyryldiphenylphosphine, 카르복시酸, 알코올 및 diethyl azodicarboxylate를 加한다. 反應은 室溫에서 短時間內에 完結된다. 長時間(3~4 hr)해도 生成物은 分解하지 않는다(Table VII).





II. 不飽和脂肪酸의 페놀化反應

不飽和脂肪酸과 페놀類와의 反應에는 黃燐, 메탄술폰酸, P-톨루엔술폰酸, 이온交換樹脂 및 活性白土 등이 觸媒로서 使用이 되고, 그 生成物은 페놀樹脂를 中心으로 한 熱硬化性樹脂用可塑劑, 페놀性 抗酸化劑 등의 用途가 있다<sup>9,10)</sup>.

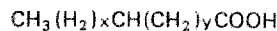
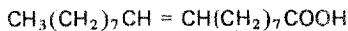
1. 메탄술폰酸觸媒에 의한 芳香族化合物의 올레酸付加<sup>11)</sup>

메탄술폰酸觸媒에 의한 페놀의 올레酸付가에 따라서 에테르型生成物(phenylether) 및 環置換生成物(hydroxyphenylstearic acid)의 2種生成物이 얻어진다. 이 2種의 生成物의 收率은 反應溫度나 觸媒量에 따라 變化했다(Table VIII).

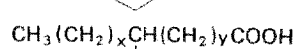
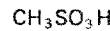
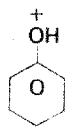
Table VII. Esterification in Phosphine Agents

Entry	Compd.	Yield, %
1	Ph CO <sub>2</sub> CH <sub>2</sub> Ph	86
2	Ph-CH=CH-CO <sub>2</sub> -CH <sub>2</sub> Ph	86
3	Ph-CH=CH-CO <sub>2</sub> -O(CH <sub>3</sub> ) <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	64
4	CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub> -CO <sub>2</sub> -C <sub>5</sub> H <sub>9</sub>	75
5	CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> -CO <sub>2</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	90
6	Cl-C <sub>6</sub> H <sub>3</sub> (Cl)-CO <sub>2</sub> (CH <sub>2</sub> ) <sub>5</sub> CH <sub>3</sub>	89
7	O <sub>2</sub> N-C <sub>6</sub> H <sub>4</sub> -CO <sub>2</sub> (H <sub>2</sub> ) <sub>6</sub> CH <sub>3</sub>	84
8	(CH <sub>3</sub> ) <sub>3</sub> CCO <sub>2</sub> CH <sub>2</sub> Ph	99
9	EtO <sub>2</sub> (CH <sub>2</sub> ) <sub>4</sub> CO <sub>2</sub> Et	79
10	CH <sub>3</sub> -CH=CH-CO <sub>2</sub> (CH <sub>2</sub> ) <sub>6</sub> CH <sub>3</sub>	92
11	(+)-PhCO <sub>2</sub> CH(CH <sub>3</sub> )(CH <sub>2</sub> ) <sub>5</sub> CH <sub>3</sub>	65
12	CH <sub>2</sub> +n C=O	10 <sup>b</sup>

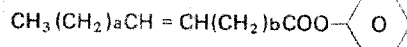
<sup>a</sup> All yields are isolated except as noted. <sup>b</sup>GC yield.



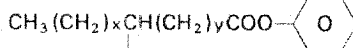
(x + y = 15) [1]



(x + y = 15) [2]



(a + b = 14) [3]



(x + y = 15) [4]



dimer [5]

trimer [6]

Table VIII. Reaction of Oleic Acid with Phenol<sup>a</sup>

Oleic acid/CH <sub>3</sub> SO <sub>3</sub> H (molar ratio)	Temperature (C)	Conversion (%)	Phenylether (%)	1-Hydroxyphenylstearate <sup>bc</sup> (%)	3 (%)	4 (%)	5+6 (%)
1/0.5	25	32	28	2	2	—	—
1/0.5	50	80	41	13	6	16	4
1/0.0	25	65	46	7	2	5	5
1/1.0	50	87	25	39	4	9	10
1/2.0	25	82	54	17	2	5	4
1/2.0	50	97	1	82	2	—	12
1/6.0	25	98	2	88	1	—	7

a Time 6 hr, oleic acid : C<sub>6</sub>H<sub>5</sub>OH = 1:5 (molar ratio).

b Ortho : para ~ 4:1.



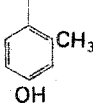

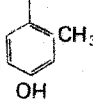
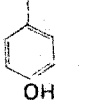

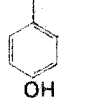
c Yields were based on oleic acid.

2. Arylstearic acid의 酸化防止와 防錆性<sup>12)</sup>

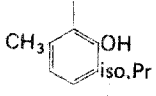
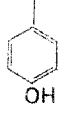
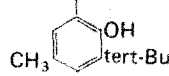

Hydroxyarylstearic acid이 潤滑油의 酸化防止 및 防錆性を 나타낸다는 것은 H. Gissers<sup>13)</sup>에 의해서 報告되어 있다. 構造가 틀리는 arylstearic acid나

2,3의 金屬鹽을 合成하여, bis(2-ethylhexyl) sebacate에 添加시켜 酸化하고 防錆性試驗을 實施했다 (Table IX).

Table IX. Effect of Molecular Structure on Antioxidant and Rust Protection

Additive	Oxidation Induction Period, Hours	Rust, Hours to Failure	Additive	Oxidation Induction Period, Hours	Rust, Hours to Failure
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH(CH <sub>2</sub> ) <sub>7</sub> COOH 	30	192	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH(CH <sub>2</sub> ) <sub>7</sub> COOH tert-Bu 	54	96
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH(CH <sub>2</sub> ) <sub>7</sub> COOH 	36	180	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH(CH <sub>2</sub> ) <sub>7</sub> COOH 	62	132
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH(CH <sub>2</sub> ) <sub>7</sub> COOH tert-Bu 	36	72	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH(CH <sub>2</sub> ) <sub>3</sub> CH(CH <sub>2</sub> ) <sub>7</sub> COOH 	240	128
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH(CH <sub>2</sub> ) <sub>7</sub> COOH tert-Bu 	37	96	[CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH(CH <sub>2</sub> ) <sub>7</sub> COO] <sub>2</sub> Ca 	70	162

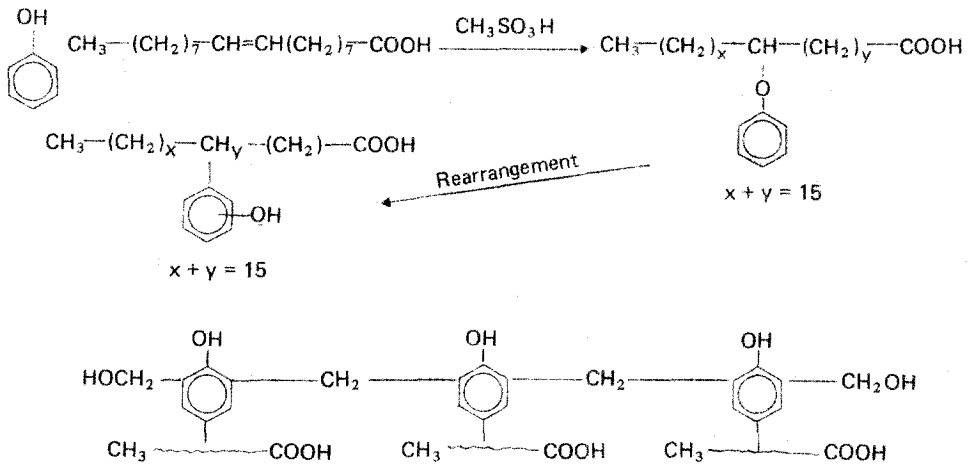


$\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{CH}_2)_7\text{COOH}$	38	96	$[\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{CH}_2)_7\text{COO}]_2\text{Ba}$	>56	186
					
$\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{CH}_2)_7\text{COOH}$	43	96	$[\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{CH}_2)_7\text{COO}]_2\text{Sr}$	81	132
					

3. Hydroxyphenylstearic acid 樹脂<sup>14</sup>

올레산에 페놀을 反應시켜 얻어지는 hydroxyphenylstearic acid를 酸 혹은 알칼리 觸媒로 과잉의 formaldehyde를 縮合하였다.

phenylstearic acid를 酸 혹은 알칼리 觸媒로 과잉의 formaldehyde를 縮合하였다.

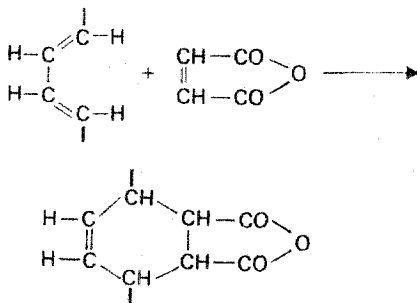


III. Diene synthesis (Diels-Alder reaction)

其 共役 디엔 결합을 가진 기름을 無水말레산과 反應시키면 Diels-Alder 反應이 進行되어 付加物을 만든다.

이 反應에 依해서 共役 디엔의 含量이 定量可能하므로 디엔價 (Diene Value)로서 오래전부터 알려져 있고 工業의으로도 利用되고 있다.

1. Diels-Alder reaction의 反應速度定數 및 活性化에너지<sup>15</sup>



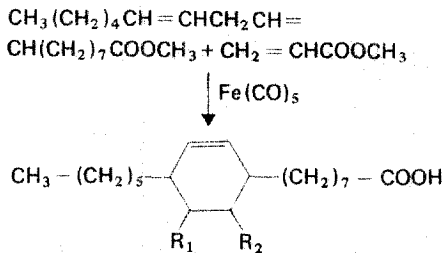
methyl cis-9,trans-11-(Cct)나 trans-9,trans-11-octadecadienoate (Ctt)에의 methyl acrylate (MA), methyl methacrylate (MMA), methyl crotonate (MC), methyl vinylacetate (MV), dimethyl acetylenedicarboxylate (DMAD), maleic (MAh) 및 dimethyl maleate (MD) 등의 付加反應의 速度定數(K)나 活性化에너지는 兩側의 構造에 따라서 差異가 있다 (Table X).

Table X. Velocity Constant of Diels - Alder Reactions

Temp. (°C)	K (mol/100g-hr) <sup>-1</sup>									
	Ctt M A	Cct M A	Ctt MMA	Ctt M C	Ctt M V	Ctt DMAD	Cct DMAD	Ctt MAh	Ctt M D	
60						0.106		36.07		
80						0.391		62.38		
100	0.092					1.141		117.68	0.108	
120	0.287		0.019			3.233	0.057		0.201	
140	0.690		0.067	0.018		6.255	0.166		0.545	
160	2.098	0.023	0.236	0.063			0.586		1.405	
180		0.055	0.642	0.173	0.026		1.503		3.345	
200		0.131	1.377	0.481	0.081		3.734			
220		0.311			0.180					
240		0.611			0.584					
260					1.065					
Activation energy (Kcal/mol)	17.2	19.2	19.6	21.3	22.2	14.9	19.3	6.5	18.2	

2. C<sub>21</sub> Dicarboxylic acid<sup>16, 17)</sup>

鐵펜 타카르보닐 [Fe(CO)<sub>5</sub>]의 存在下에서 리놀레  
 酸메틸에 아크릴酸메틸을 反應시키면 共役化反應  
 과 Diels - Alder反應이 이루어 지고 C<sub>21</sub>의 環狀  
 二鹽基酸이 얻어진다.

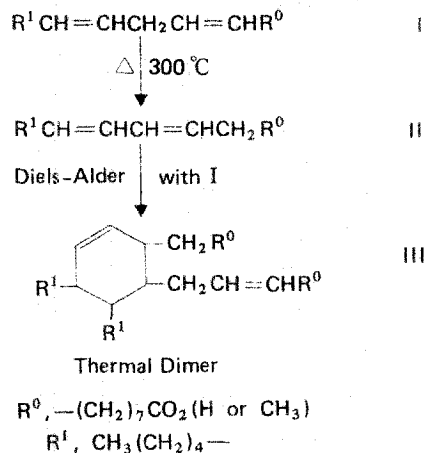


- Theoretical Molecular weight ; 352.5  
 Theoretical Acid Value ; 318.4  
 Theoretical Iodine Value ; 72.1  
 I R<sub>1</sub> = COOH R<sub>2</sub> = H  
 II R<sub>1</sub> = H R<sub>2</sub> = COOH

3. 二合體酸 (Dimer acid)<sup>18)</sup>

리놀레酸을 300°C로 熱重合하면 시클로헥센構造  
 를 가진 二合體가 生成된다. 이 反應은 리놀레酸의  
 共役異性化合物과 리놀레酸間의 Diels - Alder反應에  
 依한 것이다.

리놀레酸, 올레酸을 原料로 하는 그 二合體, 即  
 二合體酸은 分子量이 꽤 크고 二鹽基酸이므로 分子  
 內에 不飽和結合을 가지며, 適當한 反應性이 있고  
 炭化水素系溶媒에 可溶하여 그 에스테르는 蒸留精



製가 可能하다. 이것은 유사한 構造物의 混合體이기  
 때문에 結晶化나 固化가 쉽게 이루어 지지는 않고,  
 工業原料로서 安價이기 때문에 潤滑油添加劑 혹은  
 폴리에스테르, 폴리우레탄原料로 된다.

4. 모노엔酸과 共役디엔化合物과의  
 Diels-Alder反應<sup>19, 20)</sup>

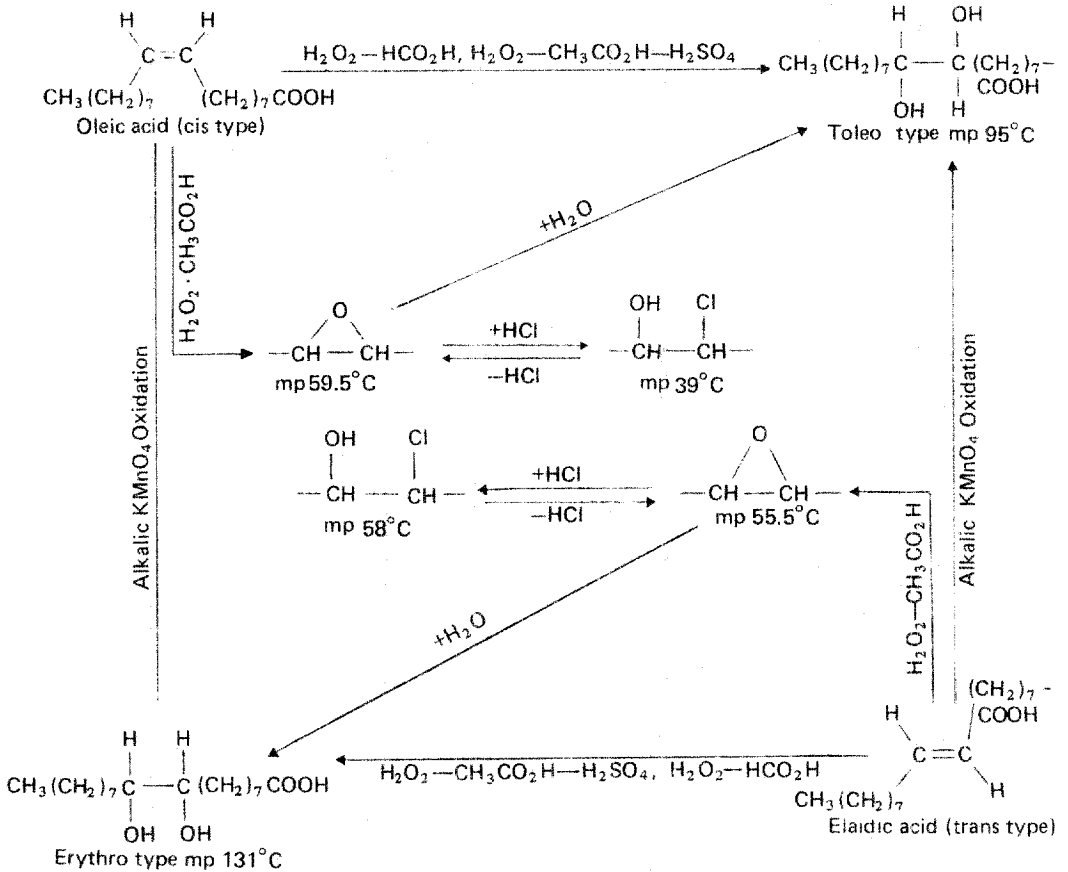
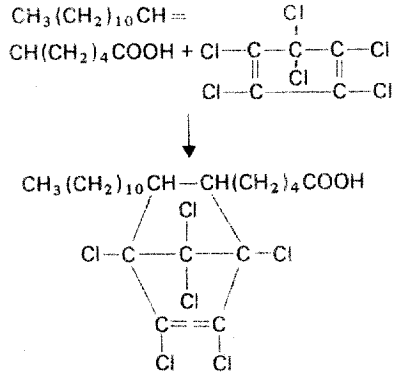
cis-6-octadecenoic (petroselinic) acid와 he-  
 xachlorocyclopentadiene과의 Diels - Alder 付加物  
 即 비닐에스테르, vinyl 5-(1,2,3,4,5,6,7-hexach-  
 lоро-3-unclelybicyclo [2,2,1]-5-hepten-2  
 yl)-pentanoate 을 課製했다. 生成物의 폴리우레  
 탄은 耐火性이다.

IV. 不飽和脂肪酸의 epoxidation 및 dihydroxylation

에폭시脂肪酸에스테르는 鹽化비닐의 安定劑겸 可塑劑로서 有效하다.

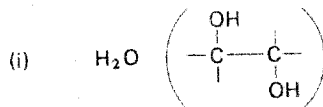
1. Epoxidation 및 dihydroxylation

不飽和脂肪酸을 H<sub>2</sub>O<sub>2</sub>-有機酸으로 酸化하면 에폭시化合物을 生成하지마는 強酸性(포름酸, 醋酸-H<sub>2</sub>SO<sub>4</sub>)이면 바로 加水分解되어 dihydroxy 化合物로 된다.



2. 에폭시化合物의 開環反應<sup>21, 23)</sup>

에폭시化合物의 開環反應은 工業的으로 重要하므로 學問的으로도 興味있는 反應이다.





3. 히드록시 脂肪酸<sup>21</sup>

토올 脂肪酸로부터 生成되는 히드록시 脂肪酸誘導體는 여러가지의 用途가 開發되어 있다(Table XI).

中心으로 되는 構造

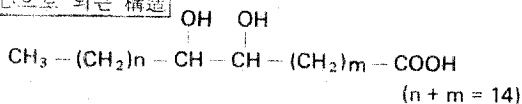


Table XI. Classifications and Structures of Hydroxy Fatty Acid Derivatives

Classification	Major structure	Use
Hydroxy fatty acid		Rust inhibitor
Condensed compound		Binder
Ester		Addition
Ester		Addition
Ester		Resin
Ethoxylate		Surface active agent
Ethoxylate		Surface active agent
Ester		Addition
Ca-salt		Addition

끝으로 韓國油化學會學術發表會의 特別講演 및 本稿 投稿에 있어서 여러가지 便利를 베풀어 주신 李容億會長, 崔國智, 金炯鳳兩副會長, 盧長淑總務 幹事, 白台鴻理事任等 많은 理事任계 깊은 感謝를 드리는 것과 同時에 貴學會의 發展을 祈願하겠습니다.

### 文 獻

1. E.J. Dufek, R.O. Butterfield, E.N. Frankel, *J. Am. Oil Chem. Soc.*, **49**, 302 (1972).
2. W.W. Lowrance, Jr., *Tetrahedron Lett.*, **1971**, 3453.
3. N.B. Lorette, J.H. Brown, Jr., *J. Org. Chem.*, **24**, 261 (1959).
4. G.F. Vesley, V.I. Stenberg, *J. Org. Chem.*, **36**, 2548 (1971).
5. T. Mukaiyama, H. Toda, S. Kobayashi, *Chem. Lett.*, **1976**, 13.
6. H.-J. Liu, W.H. Chan, S.P. Lee, *Tetrahedron Lett.*, **1978**, 4461.
7. F.E. Ziegler, G.D. Berger, *Synth. Commun.*, **9**, 539 (1979).
8. R.A. Amos, R.W. Emblidge, N. Havens, *J. Org. Chem.*, **48**, 3598 (1983).
9. Harima Technical News, **40**, 13 (1982).
10. *Chem. and Eng. News*, **1966**, Nov. 28, p. 21.
11. Y. Nakano, T.A. Foglia, *J. Am. Oil Chem. Soc.*, **61**, 569 (1984).
12. J.L. Snead, J. Messina, H. Gisser, *Ind. Eng. Chem. Prod. Res. Develop.*, **5**, 222 (1966).
13. H. Gisser, H. Messina, J. Sead, *Ind. Eng. Chem.*, **48**, 2001 (1956).
14. F. Scholnick, H.A. Monroe, A.N. Wrigley, W.C. Ault, *J. Am. Oil Chem. Soc.*, **42**, 23 (1965).
15. O. Suzuki et al., *Yukagaku*, **19**, 950, 1075, 1081 (1970), **20**, 402, 492 (1971).
16. Harima Technical News, **18**, 15 (1977).
17. M. Ishigami, S. Takeda, I. Ikeda, S. Komori, *Yukagaku*, **22**, 368 (1973).
18. A. Misono, Y. Uchida, *Yukagaku*, **15**, 363 (1966).
19. J.P. Moreau, R.L. Holmes, G. Sumrell, *J. Am. Oil Chem. Soc.*, **43**, 33 (1966).
20. C.K. Lyon, G. Fuller, *Ind. Eng. Chem. Prod. Res. Develop.*, **8**, 63 (1969).
21. T. Sasaki, *Yushi*, **18**, No. 9, 10 (1965).
22. A. Adachi, *Kagaku To Kogyo (Osaka)*, **45**, 184 (1971).
23. J.G. Smith, *Synthesis*, **1984**, 629.
24. Harima Technical News, **47**, 4 (1984).