Neo Acids: Synthetic Highly Branched Organic Acids[1]

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ABSTRACT

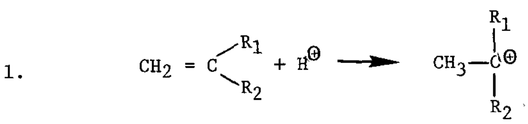
Neo acids are highly branched synthetic trialkyl acetic acids manufactured by reacting an olefin with high purity carbon monoxide under high pressure in the presence of an acidic-type catalyst. The starting olefins for neopentanoic (C_5, single isomer) and neodecanoic (C_{10}, mixed isomers) acids are isobutylene and nonene, respectively. Commercial quantities of both products have been available since 1964. Neopentanoic acid is used in the preparation of t-butyl peroxy neopentanote (pivilate), a peroxyester initiator used in polyethylene manufacture. The C_5 neo acid also finds use in a variety of other industrial end uses, e.g., pharmaceutical, agricultural chemicals, and reaction to form hindered, very stable esters. Metal salts of neodecanoic acid are used in paint driers, PVC stabilizers, and peroxyester initiators. Other reactions such as esterification, amide formation, and reaction with ethylene oxide will be discussed.

DISCUSSION

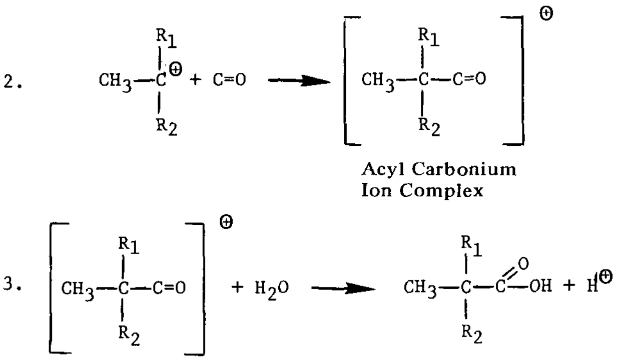
In 1964 Exxon Chemical Co., U.S.A., commercialized the manufacture of a series of highly branched synthetic acids – neo acids. This was carried out at the petrochemical center in Baton Rouge, Louisiana. Prior to this, drum quantities of similar type acids (Versatic Acids®) were marketed by Shell Chemical, imported in drums from their plant located in Holland. Availability in tank truck and tank car quantities plus domestic production rapidly increased their volume use and opened new end use areas. Initially Exxon Chemical Co., U.S.A., made available four neo acids, a C_5, C_7, C_{10}, and C_{13}. The greatest interest and demand were for the C_5 and C_{10} neo acids and that is still true. The C_7 and C_{13} neo acids are not commercial products. Another synthetic acid produced in the United States which finds use in several related areas is 2-ethylhexoic acid manufactured by Eastman Chemical and Union Carbide. This is a C_8 synthetic acid with one ethyl branch on the alpha carbon. Neo acids are completely substituted on the alpha carbon leading to sterically hindered derivatives, some more difficult to make but much more stable once synthesized.

MANUFACTURE

Neo acids are synthesized by reacting under high pressure and elevated temperature a branched olefin and high-purity carbon monoxide in the presence of an acidic catalyst and water. The highly pure and high partial pressure carbon monoxide is delivered to the reaction section after separation from a carbon monoxide-hydrogen mixture (synthesis gas) and then pressurized. The general mechanism for the preparation of neo acids involves generation of a carbonium ion (tertiary) followed by complexing with carbon monoxide and a catalyst and then hydrolysis to the free acid regenerating the catalyst for recycle. This can be summarized in the following three reactions:

1. 

$$CH_2=C\begin{matrix}R_1\\R_2\end{matrix} + H^{\oplus} \longrightarrow CH_3-\overset{R_1}{\underset{R_2}{C^{\oplus}}}$$

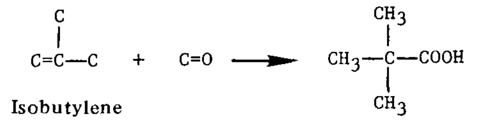
2., 3. 

$$CH_3-\overset{R_1}{\underset{R_2}{C^{\oplus}}} + C{=}O \longrightarrow \left[CH_3-\overset{R_1}{\underset{R_2}{C}}-C{=}O\right]^{\oplus}$$

Acyl Carbonium Ion Complex

$$\left[CH_3-\overset{R_1}{\underset{R_2}{C}}-C{=}O\right]^{\oplus} + H_2O \longrightarrow CH_3-\overset{R_1}{\underset{R_2}{C}}-C\begin{matrix}{=}O\\-OH\end{matrix} + H^{\oplus}$$

Preparation of neopentanoic acid (C_5):

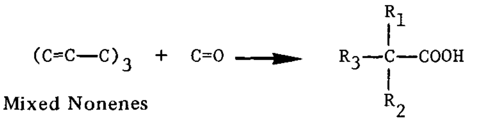


$$C{=}\overset{C}{C}-C + C{=}O \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}-COOH$$

Isobutylene

Neopentanoic Acid (C_5)
Trimethylacetic Acid
Pivalic Acid

Preparation of neodecanoic acid (C_{10}):



$$(C{=}C-C)_3 + C{=}O \longrightarrow R_3-\overset{R_1}{\underset{R_2}{C}}-COOH$$

Mixed Nonenes

Neodecanoic Acid
$R_1 + R_2 + R_3 = 8$ Carbons

For both of these neo acids the olefin feed and catalyst are pumped to the spherical reactor while the gas rich in carbon monoxide is fed to the reaction media subsurface. The complex once formed is pumped to a hydrolysis section where water is added generating the free neo acid. The crude acid is purified by distillation to remove both light and heavy ends. In order to prepare a neo acid via this method, a branched olefin with one less carbon atom is required.

Chemical reactions which do not involve the sterically hindered carbonyl group have reaction rates similar to the normal or straight chain acids, e.g., metal salt formation. Esterification, on the other hand, will be slower than the straight chain acid.

PHYSICAL PROPERTIES

Neopentanoic acid has a purity greater than 99.5% and is isomerically pure. Because of this and the high degree of symmetry, the C_5 neo acid is a solid at room temperature. The corresponding natural occurring acid, n-valeric, has a melting point of -34.5 C. This acid has associated with it a strong pungent odor typical of many lower molecular weight carboxylic acids.

Neodecanoic acid, on the other hand, is synthesized starting with an olefin of mixed nonenes (at equilibrium) yielding a C_{10} neo acid containing many isomers. This very highly branched and multi-isomer acid combination yields a liquid C_{10} neo acid with a typical hydrocarbon-type odor. The melting point is <-40 C. Two grades of neodecanoic

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[1] Presented at the AOCS Meeting, New York, May 1977.

TABLE I

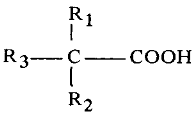
Physical Properties of Neo Acids

	Neopentanoic	Neodecanoic (Tech.)	Neodecanoic (Prime)
Color (Pt./Co.)[a]	25	2(Gardner)	75
Acid value, mg KOH/g	550	295-320	320
M.P., °C	34.4	<-40	<-40
Distillation range, °C	163-165		147-150/20 mm
Ionization const., $K_a \times 10^{-6}$	9.3	4.2	4.2
Flash pt., °F (COC)[b]	165	190 (Tag Open Cup)	195 (Tag Open Cup)

[a] Platinum-cobalt color rating.
[b] Cleveland Open Cup.

TABLE II

Typical Isomer Distribution for Neodecanoic Acid



$$R_3\text{—}\overset{R_1}{\underset{R_2}{C}}\text{—COOH}$$

Alkyl group	%
R_1 and R_2 = methyl	31
R_1 = methyl; R_2 > methyl	67
R_1 and R_2 > methyl	2
R_3 always > methyl	

acid are manufactured: (a) a prime grade with very low color and high acid value characteristics and (b) a technical grade having a higher color and lower acid value. The neo acids are synthetic, weak organic acids possessing ionization constants ranging from one-half to one-fifth that of acetic acid (K_a = 1.75 X 10^{-5}).

Typical analysis of physical properties of both neopentanoic and neodecanoic acid are summarized in Table I. Table II gives a typical isomer distribution for neodecanoic acid.

CHEMICAL REACTIONS AND END USES

Esterification

Acid-catalyzed esterification of neo acids with primary alcohols (others will tend to dehydrate) can be carried out with these sterically hindered acids provided more vigorous reaction conditions are used, e.g., higher temperature and higher catalyst concentrations. The rate of esterification is closely related to these conditions and the water entrainer used (See Table III).

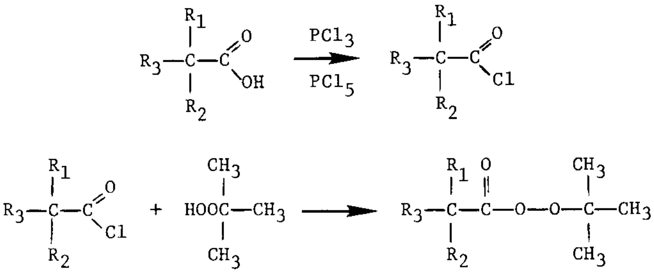
A laboratory procedure has been developed for the preparation of polyol esters of neopentanoic acid. Esters of trimethylolpropane and pentaerythritol are prepared in 95% yields using sulfuric acid as a catalyst (1 wt %) and an entrainer.

Figures 1 and 2 clearly show that once formed, simple esters of neo acids are at least 900 times more resistant to basic hydrolysis and 20 times more resistant to acidic hydrolysis than straight chain carboxylic esters in the same carbon range.

The neo acid esters, because of their hydrolytic stability over a wide pH range, should be of interest as solvents in a variety of continuous extraction processes. The lower molecular weight esters of neopentanoic acid have interesting odors for use as odorants, perfumes, or masking agents. Table IV describes some of these.

Peroxyesters

Peroxyesters can be prepared by the reaction of the acid chloride of a neo acid and the hydroperoxide or sodium salt of the hydroperoxide of t-butyl alcohol (1).



t-Butylperoxy Neo Ester

If R_1, R_2, and R_3 = CH_3 t-Butylperoxypivalate

The C_5 neo acid peroxyester is a highly efficient source of free radicals even at very low temperatures (-50 C). It is used (2) commercially because it has: (a) more controlled rate of decomposition, (b) shorter induction period, (c) improved efficiency, and (d) faster cycle times. The C_{10} neo acid also is used as a peroxyester possessing different physical characteristics and properties vs. the C_5 peroxyester, e.g., half-life.

Herbicides, Biocides

Neopentanoic acid has found use in the preparation of a series of herbicides. One of particular interest in "Sencor," the chemical name 4-amino-6-(1,1 dimethyl ethyl)-3-(methyl thio)-1,2,4-Triazin-5(4H)-one.

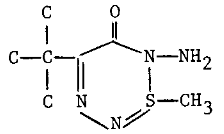
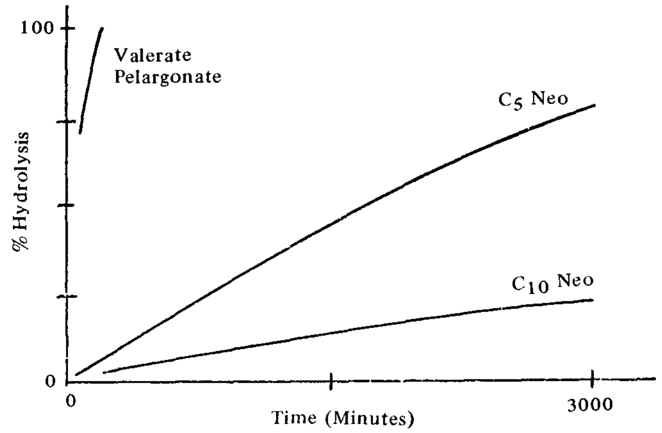


TABLE III

Typical Esterification[a] Conditions of Neo Acids

Neo acid	Entrainer	Catalyst (wt %)	Max. temp., °C	Reaction time, hr	Yield, %
C_5	Toluene	.33 PTSA[b]	140	4.0 hr	99
C_{10}	Xylene	2.0 H_2SO_4	169	3.5 hr	99.7

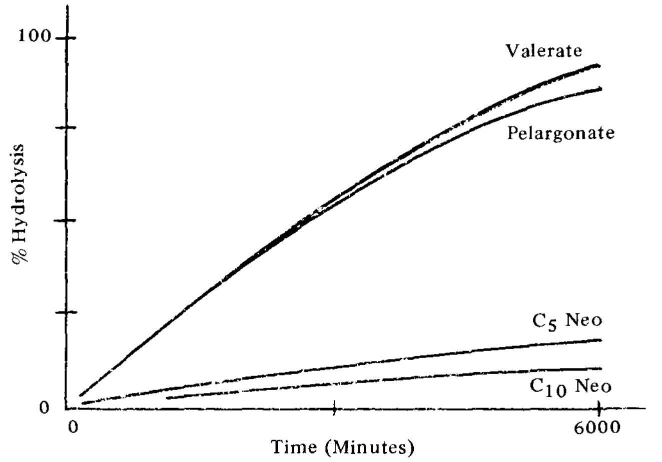
[a] One mole of neo acid and 1.2 moles of oxohexyl alcohol.
[b] p-Toluenesulfonic acid.



RELATIVE RATES AT 50 C
.1 N NaOH

Ester	Realtive Rate vs C_{10}
C_5	17.4
C_{10}	1.0
Valerate	2840
Pelargonate	900

FIG. 1. Basic hydrolysis of hexyl esters.



RELATIVE RATES AT 50 C
.1 N HCl

Ester	Relative Rate vs C_{10}
C_5	1.4
C_{10}	1.0
Valerate	27.6
Pelargonate	20.0

FIG. 2. Acidic hydrolysis of hexyl esters.

The preparation of this compound is disclosed in a U.S. Patent (3) and is discussed in more detail in a German Patent Application (4) which uses the acid chloride of neopentanoic as an intermediate.

Tributyl tin neodecanoate is reported to show biocidal activity (5) – potential applications are general inhibition of fungal growth, wood preservation, etc.

In addition, both the neopentanoic and neodecanoic acids have found interest as blocking or stabilizing groups in complex organic molecules. The steric hindrance offered can convert, e.g., a hydroxyl group to a very stable ester group.

TABLE IV

Odor Characteristics – Neo C_5 Esters

Ester of C_5 neo acid	Odor
Methyl	Citrous
n-Propyl	Fruity
n-Amyl	Orchid
Oxo-hexyl	Fruity
Benzyl	Orchid

Salts

Metal salts can be prepared using conventional techniques such as:

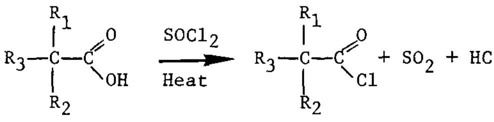
1. Reaction of neutral alkali salts of neo acids with metal halides.
2. Reaction of metal oxides and free neo acids in a refluxing hydrocarbon solvent.
3. Direct thermal fusion of the metal oxide and the acid.

The neodecanoic acid salts of Pb, Co, Mn, Zn, and Ca are used as driers in paint formulations. (Complete series of salts available from Mooney Chemical Co., Cleveland, OH.) In certain alkyds, neo acid based driers have been shown to have shorter dry times than the corresponding naphthenic acid salt (6). Also, the basic lead salt of neodecanoic is easily prepared using a ratio of 1.7 moles of acid to metal and has excellent three-year shelf stability (7).

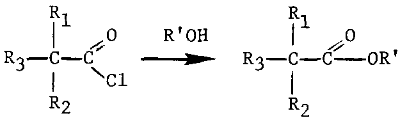
Neodecanoic acid is also very effective as a metal carrier for vinyl stabilizers (8). Some of the major differences in viscosity, air release are summarized in Tables V and VI.

Other Reactions and Applications

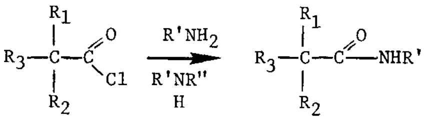
Acid chlorides are readily prepared from neo acids using an excess of thionyl chloride at reflux temperature (lab prep.) or phosphorous oxychloride, phosphorous trichloride, phosphorous pentachloride (on a commercial basis). Because of the hindered structure, neo acids require heat to maintain the reaction. Once formed, however, neo acid-based acid chlorides react similarly to their straight chain counterparts. Reaction with alcohols yields a convenient route to a variety of neo acid esters.



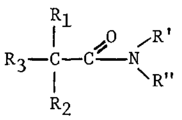
$$R_3-\overset{R_1}{\underset{R_2}{C}}-C\overset{\displaystyle O}{\underset{\displaystyle OH}{\lessgtr}} \xrightarrow[\text{Heat}]{SOCl_2} R_3-\overset{R_1}{\underset{R_2}{C}}-C\overset{\displaystyle O}{\underset{\displaystyle Cl}{\lessgtr}} + SO_2 + HCl$$



$$R_3-\overset{R_1}{\underset{R_2}{C}}-C\overset{\displaystyle O}{\underset{\displaystyle Cl}{\lessgtr}} \xrightarrow{R'OH} R_3-\overset{R_1}{\underset{R_2}{C}}-\overset{O}{\overset{\|}{C}}-OR' \qquad (I)$$



$$R_3-\overset{R_1}{\underset{R_2}{C}}-C\overset{\displaystyle O}{\underset{\displaystyle Cl}{\lessgtr}} \xrightarrow[\substack{R'NR''\\H}]{R'NH_2} R_3-\overset{R_1}{\underset{R_2}{C}}-\overset{O}{\overset{\|}{C}}-NHR' \qquad (II)$$



$$R_3-\overset{R_1}{\underset{R_2}{C}}-\overset{O}{\overset{\|}{C}}-N\overset{\displaystyle R'}{\underset{\displaystyle R''}{\lessgtr}}$$

Equations (I) and (II) show the typical formation of esters and amides via an acid chloride.

Neo alcohols can be prepared in the laboratory by reducing the corresponding acid with lithium aluminum hydride at 125 C. These hindered alcohols are interesting intermediate for the preparation of products requiring out-

TABLE V

Viscosity and Air Release in Vinyl Plastisols

Brookfield vis. (cps) 77 F Model RVF No. 3 spin.		Cd-neodecanoate blend	Cd-2-ethylhexoic blend
1 Day	2 rpm	3150	8350
	20 rpm	2500	
7 Days	2 rpm	3350	8250
	20 rpm	2610	
14 Days	2 rpm	3400	8050
	20 rpm	2775	
Air release		36 sec	44 sec

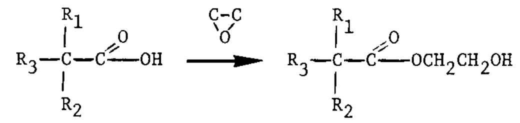
TABLE VI

Viscosities of Salts

Salt	% Metal	Vis., 77 F cp
Cd neodecanoate	13.5	85
Cd 2-ethylhexanoate	13.5	2,345
Zn neodecanoate	8	14
Zn 2-ethylhexanoate	8	12,500

standing stability, e.g., functional fluids, lubricants.

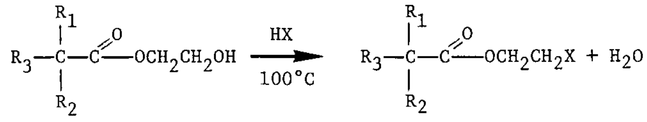
Ethoxylation of neodecanoic acid with one mole of ethylene oxide yields 2-hydroxyethylneodecanoate. The chemistry is largely that of a primary alcohol.



$$R_3-\underset{R_2}{\overset{R_1}{C}}-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{\underset{O}{C-C}} R_3-\underset{R_2}{\overset{R_1}{C}}-\overset{O}{\overset{\|}{C}}-OCH_2CH_2OH$$

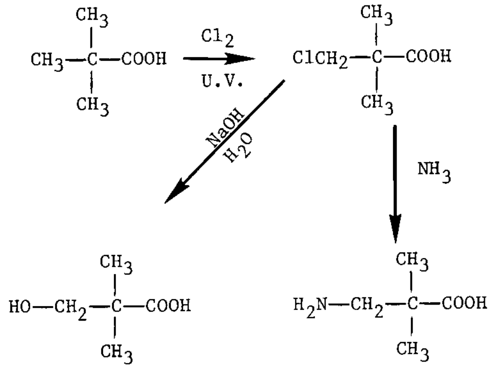
It undergoes a variety of chemical reactions such as esterification and halogenation without significant hydrolysis or ester interchange.

Contrary to what is normally observed for primary alcohols, 2-hydroxyethyl neodecanoate is directly halogenated to the alkyl halide in the presence of concentrated aqueous hydrogen halide.



$$R_3-\underset{R_2}{\overset{R_1}{C}}-\overset{O}{\overset{\|}{C}}-OCH_2CH_2OH \xrightarrow[100°C]{HX} R_3-\underset{R_2}{\overset{R_1}{C}}-\overset{O}{\overset{\|}{C}}-OCH_2CH_2X + H_2O$$

Hydroxy neopentanoic acid is prepared by monochlorination followed by alkaline hydrolysis. Amination of the mono-chloro derivative yields the amino neopentanoic acid. Fibers prepared from polyhydroxy and polyamino neopentanoic acid have been disclosed by Alderson (9) and Lincoln (10).



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