

UNIROYAL

UNIROYAL CHEMICAL
Division of UNIROYAL, Inc.
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August 23, 1979

Ms. Mary Donae- *DANNEZ*
PPG Industries
P. O. Box 1000
Lake Charles, LA 70602

Dear Mary:

In response to your recent inquiry, I have enclosed our product bulletin and safety data sheet for Cyclohexene Oxide. With regard to the storage stability of this product, we are continuing testing on material that is undergoing ambient aging. Based upon results we have observed to date, Naugard CHO should be stable (i.e. meet your purchase specifications) under ambient aging for at least six months. I believe that similar studies are being conducted at Barberton under the supervision of Dr. Don. Reich and suggest that you contact him for further information.

If there is anything further that I can do to help you, please don't hesitate to call me.

Very truly yours,

UNIROYAL CHEMICAL

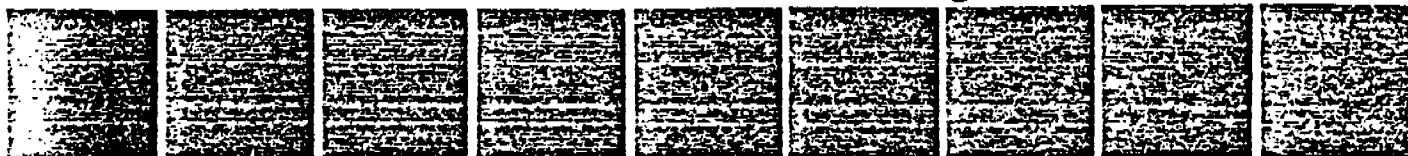
Gerald J. Hollmann

Gerald J. Hollmann
Group Leader
Specialty Chemicals

GJH:ml1

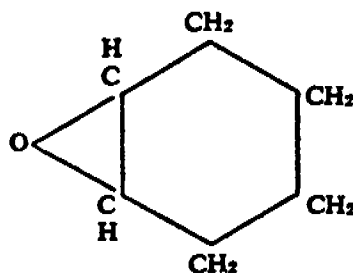
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CYCLOHEXENE OXIDE

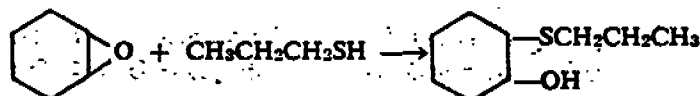
$C_6H_{10}O$



TYPICAL PROPERTIES

Appearance:	colorless liquid
Purity:	98%
Boiling Point:	266° F. (130° C.)
Specific Gravity @ 25°/25° C.	0.967
Density @ 60° F.	8.1 lbs./gal. (970.4 Kgs/m ³)
Flash Point (TOC):	80.6° F. (27° C.)
Refractive Index @ 30° C.	1.450

Alkyl and aryl mercaptans react with cyclohexene oxide in an analogous manner (11).



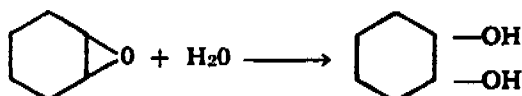
SHIPPING AND CONTAINERS

Steel Drum 425 pounds net

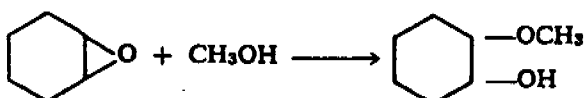
CYCLOHEXENE OXIDE, CHEMICAL REACTIONS

Cyclohexene oxide, also known as 1,2-epoxycyclohexane and 7-oxabicyclo (4.1.0) heptane, is a highly reactive compound, which resembles ethylene oxide in most of its reactions. In general, its reactions involve cleavage of the oxide ring (5, 7).

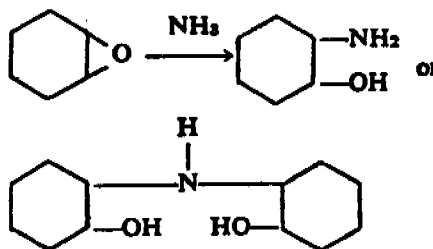
Water readily opens the oxide ring of cyclohexene oxide with the formation of cis-1,2-cyclohexanediol (2, 5, 6, 7).



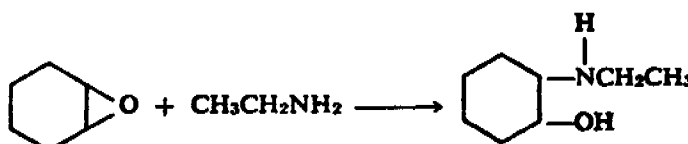
Alcohols, phenols, and naphthols also bring about cleavage of the oxide ring of cyclohexene oxide. For example, cyclohexene oxide reacts with methanol at 150° C. to give 2-methoxycyclohexanol (3, 7, 9).



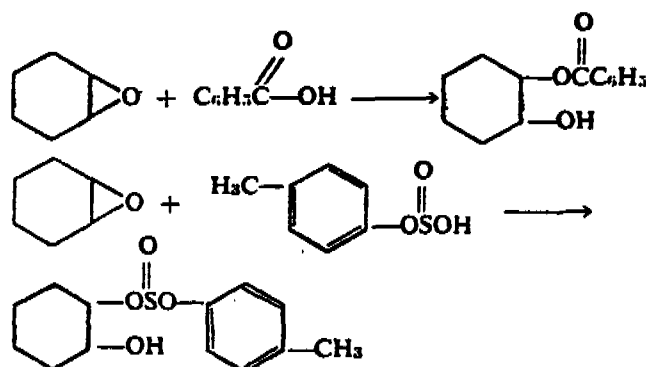
Ammonia and amines open the oxide ring with the formation of α -amino alcohols. Thus, aqueous or alcoholic ammonia reacts with cyclohexene oxide to give 2-aminocyclohexanol when the ammonia is in excess or bis (2-hydroxycyclohexyl) amine when the oxide is in excess (2, 5, 6, 7).



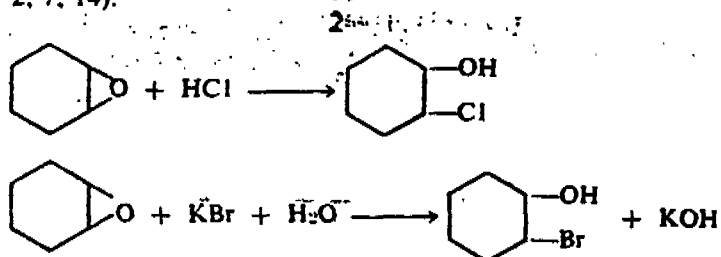
Similarly, treatment of cyclohexene oxide with alcoholic ethylamine gives 2-ethylaminocyclohexanol (6).



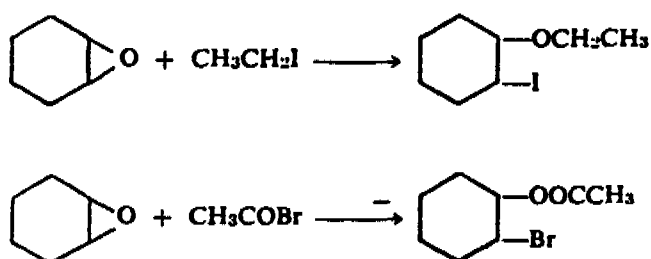
Organic acids and acid anhydrides also bring about cleavage of the oxide ring. For example, treatment of cyclohexene oxide with benzoic acid yields 1,2-cyclohexanediol monobenzoate (3), while treatment with p-toluenesulfonic acid yields 1,2-cyclohexanediol mono-p-toluenesulfonate (7).



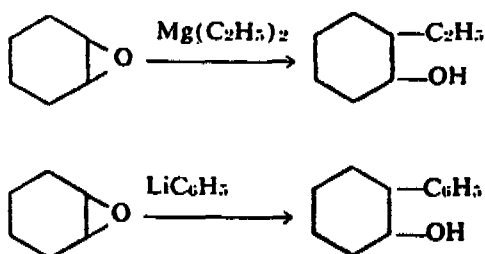
Hydrogen halides and other inorganic halides (e.g. potassium bromide, ammonium chloride, zinc chloride) combine with cyclohexene oxide to form halohydrins (1, 2, 7, 14).



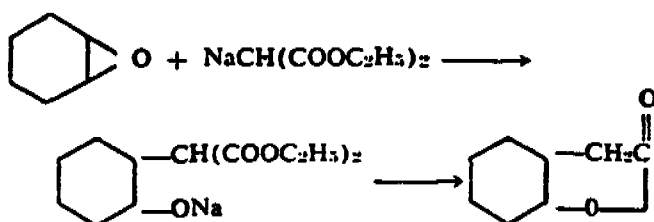
Alkyl and acyl halides also open the oxide ring (2).



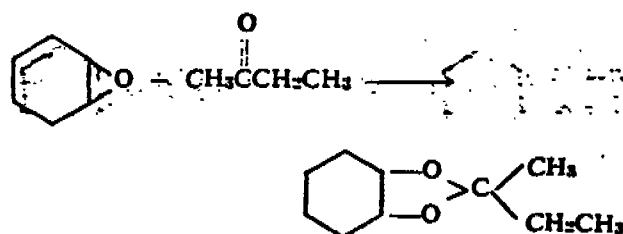
Dialkylmagnesium and aryllithium in ether solution react with cyclohexene oxide to produce 2-alkyl- or 2-arylcyclohexanol, respectively (7).



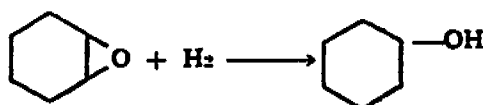
Sodiummalonic ester and similar substances, such as acetoacetic ester and cyanoacetic ester, open the oxide ring. Thus, treatment of cyclohexene oxide with sodiummalonic ester followed by hydrolysis and decarboxylation results in formation of the γ -lactone of 2-hydroxycyclohexanecarboxylic acid (7, 13).



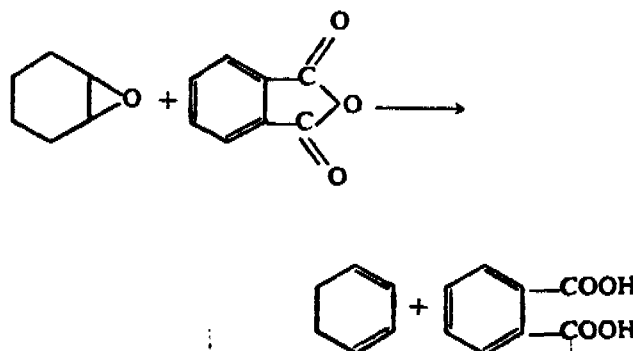
Treatment of cyclohexene oxide with aldehydes or ketones in the presence of an acidic catalyst such as stannic chloride or boron trifluoride produces cyclic acetals or ketals. For example, reaction with 2-butanone yields the ketal, 2-methyl-2-ethylhexahydro-1,3-benzodioxole (7).



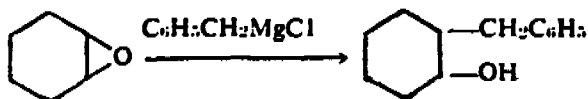
Reduction of cyclohexene oxide to cyclohexanol can be effected by reducing agents (e.g. lithium aluminum hydride in ethyl ether) or by catalytic hydrogenation over reduced nickel (5, 6, 7, 15).



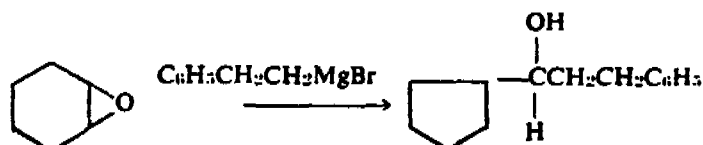
Dehydration of cyclohexene oxide to 1,3-cyclohexadiene can be accomplished by the action of thoria or phthalic anhydride (4).



An important reaction of cyclohexene oxide is the reaction with Grignard reagents, which, in some cases, results simply in the formation of the expected 2-alkyl- or 2-arylcyclohexanol. For example, 2-benzylcyclohexanol is obtained by treatment of cyclohexene oxide with benzylmagnesium chloride (7, 8).

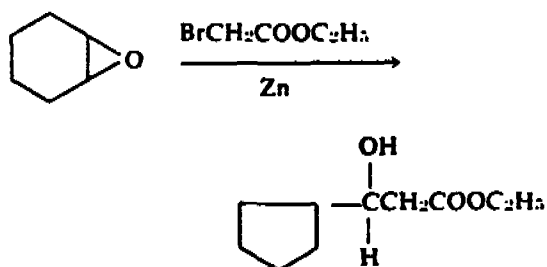


However, the reaction of a Grignard reagent with cyclohexene oxide more often leads to ring contraction. Thus, cyclopentyl β -phenylethylcarbinol is obtained by reaction of cyclohexene oxide with β -phenylethylmagnesium bromide (7, 8).

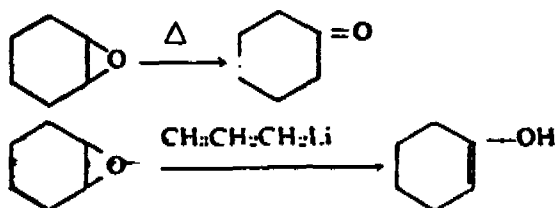


Apparently, this rearrangement is brought about by reaction of cyclohexene oxide with MgX_2 (from $2\text{RMgX} \rightleftharpoons \text{R}_2\text{Mg} + \text{MgX}_2$) to form the halohydrin which is converted to the smaller ring when heated strongly. Similarly, cyclopentylformaldehyde is formed when cyclohexene oxide is heated with magnesium bromide in dry ether (7, 8).

Rearrangement to cyclopentylformaldehyde also occurs when cyclohexene oxide undergoes the Reformatsky reaction (7).



Heating cyclohexene oxide at 630-780°C. results in its rearrangement to cyclohexanone (12), while treatment of cyclohexene oxide with propyllithium results in its rearrangement to 2-cyclohexenol (10).



APPLICATIONS

Many possible uses are envisioned for cyclohexene oxide in the drug and specialty fields because of its broad range of reactions and unique structure. Its epoxide structure is especially useful in applications where an HCl scavenger is required.

STORAGE AND HANDLING

Cyclohexene oxide is supplied in non-returnable steel drums. It is a flammable, highly reactive compound. Inhalation of vapors or contact with skin or mucous membrane should be avoided.

TOXICOLOGY BACKGROUND

Cyclohexene oxide has an acute oral LD_{50} for rats of 1.09 mls/Kg. Acute dermal LD_{50} for rabbits is 0.63 mls/Kg. Inhalation exposure of rats has an estimated LC_{50} 2650 ppm. Eye exposure of rabbits to undiluted cyclohexene is moderately severe.

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5. Brunel, Compt. rend. 137, 62, 198 (1903).

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(203) 723-3000

PRODUCT SAFETY DATA SHEET

Trade Name: CHO
Uses: Chemical Intermediate
Chemical Name: Cyclohexene oxide

Chemical and Physical Properties

Appearance: Colorless liquid - pungent odor
Boiling Point: 130°C.
Solubility: Soluble in alcohol, insoluble in water
Specific Gravity: 0.967 at 25°C.
Corrosivity: Not corrosive
Volatility: Highly volatile

Fire and Explosion Hazard

Flash Point: -81°F. (27°C.) - TOC
Autoignition Temperature: 705°F
Flammable Limits (Vol. %)
Upper: 12.36
Lower: 1.15
Special Decomposition/Reactivity Precautions: Highly reactive compound. Reactions usually involve cleavage of oxide ring.
Fire Fighting Media and Procedures: CO₂, dry chemical, foam

PRODUCT SAFETY DATA SHEET (cont.) CHO

Health Related Data

Specific Hazard: Inhalation of vapor.

Handling Precautions: Use only in well ventilated areas.
Avoid skin and eye contact.

First Aid Procedures: If eye contact occurs, flush with water and get medical attention. If skin contact occurs, wash immediately with soap and water.

Toxicology Background:

Acute Oral LD₅₀(rats): 1.09 mls/Kg

Acute Dermal LD₅₀(rabbits): 0.63 mls/Kg

Inhalation Exposure (rats):

A) Inhalation at 13,000 ppm

1 hour: 6/6 killed

1/2 hour: 0/6 killed

B) Exposure over 4 hours (rats):

4,000 ppm: 6/6 killed

2,000 ppm: 1/6 killed

C) Estimated LC₅₀ = 2650 ppm

Eye Exposure (rabbits):

A) Undiluted: Moderately severe

B) 15% solution in propylene glycol caused corneal necrosis.

C) 5% solution in propylene glycol caused traces of corneal necrosis.

Storage and Waste Disposal

Storage: Store in a cool place. Product is flammable. Avoid exposure to heat and ignition source.

Clean-up: Spills may be absorbed on inert carrier.

Disposal: Incineration is best method of disposal if allowed by environmental rules.

Data Supplied By: R. J. Dowling
Product Safety
Specialist