non-selective reduction agent

SYNHYDRID

Lučební závody Kolín

ISO 9001:2001
ISO 14001:2005

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SYNHYDRID

Characteristics and composition:

SYNHYDRID is a 70% solution of bis-(2-methoxyethoxy)sodium aluminum-hydride in toluene.

Chemical formula of effective substance: $NaAlH_2(OCH_2\text{-}CH_2\text{-}OCH_3)_2$.

Thanks to its excellent chemical and physical properties, this agent is ideal for the hydrogenation of carboxyl and carbonyl compounds and their derivatives. It is suitable for the continual isothermal polymerization of 6-caprolactam at temperatures higher than the melting point of the polymer. Its high thermal stability allows for the completion of reduction at temperatures as high as 170°C.

Physical-chemical properties:

Solution	Appearance	Colorless to yellow liquid
	Viscosity (mPa.s/20°C)	ca 65
	Specific weight (g/cm^3/20°C)	ca 1.03
	Boiling point (°C)	ca 110
	Flash point (°C)	4*)
	Effective substance contents (% weight)	min. 70
	Active hydrogen contents - % of volume - % of weight	 ca 0.70 ca 0.72
	Electrical conductivity (S/cm)	$1.83.10^{-4}$
	Amount of solution containing 1g of the atom of hydrogen - cm^3 - g	 ca 139.7 ca 144.4
Effective substance	Hydrolyzing heat (kJ/mol)	87.09
	Decomposition temperature (°C)	Above 200
	Fire point (°C)	150
	Specific weight (g/cm^3)	1.222
	Relative molecular weight (according to MAH/1977)	202.159
	Solubility	Ethers, aromatic hydrocarbons

*) Abel-Pensky

After the evaporation of toluene, the evaporated residue can be dissolved in benzene, xylene, tetrahydrofuran, diethyl ether, etc. In most cases, the simple mixing of the original toluene solution with solvent is sufficient.
Brief contact with humid atmosphere (for instance, while measuring a required amount) causes only negligible losses of the contents of active hydrogen. Furthermore, special measures preventing a reaction mixture from the effects of humidity do not have to be taken even when the solvent boils.
It is only during prolonged reactions (2 and more hours) that the reaction mixture should be protected from coming into contact with atmospheric humidity in a standard way (for instance, by means of solid sodium hydroxide or potassium hydroxide, silica gel, etc.). **SYNHYDRID** is highly reactive. On the other hand, it displays good stability when exposed to oxidation by atmospheric oxygen. Its high thermal resistance allows for the ultimate safety of reductions run at as much as 170°C.

SYNHYDRID enters into vigorous reaction with water and alcohols to form hydrogen according to equations below:

$$NaAlH_2(OCH_2CH_2OCH_3)_2 + 2\,H_2O \rightarrow 2\,H_2 + NaAlO_2 + 2\,CH_3OCH_2CH_2OH$$

$$NaAlH_2(OCH_2CH_2OCH_3)_2 + 2ROH \rightarrow 2\,H_2 + NaAl(OR)_2(OCH_2CH_2OCH_3)_2$$

Organic compounds containing carbonyl or carboxyl groups are reduced to corresponding alcohols:

1)
$$2\,RCH{=}O + NaAlH_2(OCH_2CH_2OCH_3)_2 \rightarrow NaAl(OCH_2R)_2(OCH_2CH_2OCH_3)_2 \xrightarrow{H_2O} RCH_2OH$$

2)
$$2\,RCOR' + NaAlH_2(OCH_2CH_2OCH_3)_2 \rightarrow NaAl(OCH\begin{matrix}/R\\ \backslash R'\end{matrix})_2(OCH_2CH_2OCH_3)_2 \xrightarrow{H_2O} \begin{matrix}R\backslash\\ CHOH\\ R'/\end{matrix}$$

3)
$$2\,RCOH + 3\,NaAlH_2(OCH_2CH_2OCH_3)_2 \rightarrow NaAl(OCH_2R)_2(OCH_2CH_2OCH_3)_2 + 2\,NaAlO(OCH_2CH_2OCH_3)_2 \xrightarrow{H_2O} 2\,RCH_2OH$$

4)
$$2\,RCOOR' + NaAlH_2(OCH_2CH_2OCH_3)_2 \rightarrow NaAl(OCH_2R)_2(OCH_2CH_2OCH_3)_2 + NaAl(OR')_2(OCH_2CH_2OCH_3)_2 \xrightarrow{H_2O} 2\,RCH_2OH$$

Amides, substituted amides, nitriles, nitro-compounds, oximes, ketimines and aldimines are reduced to corresponding amine compounds.

Applications:
SYNHYDRID is a non-selective reduction agent. It is used for reductions in organic chemistry, mainly in the situations where the generation of maximum possible yields is required. As a rule, a reduced substance is dosed by parts and added to the solution of **SYNHYDRID** inserted into a reaction vessel. High stability also allows for the reverse completion of reduction; i.e. for adding **SYNHYDRID** by small parts to the solution of a reduced substance. In most cases, reduction reactions in the presence of **SYNHYDRID** are quite fast, their reaction time being approx. 1 hour. After the reduction is terminated, the reduction mixture is decomposed by adding 10% solution of hydrochloric acid, sulfuric acid or 20% solution of sodium hydroxide. It is also possible to hydrolyze a reaction mixture with water and to filter off precipitated sodium aluminate, or to dissolve it in HCl, H_2SO_4 or in the solution of NaOH.

Examples of possible applications:
As stated above, **SYNHYDRID** can be used for reduction of compounds containing carbonyl and carboxyl groups (aldehydes, ketones, oximes, carboxylic acids, esters, anhydrides, acylhalides, arylaldehydes, lactone, amides, imides, lactames, nitriles, chlorinated hydrocarbons). The table below features some typical examples of **SYNHYDRID**-aided reductions of organic substances along with obtained yields compared to the yields achieved during reductions with $LiAlH_4$.

Starting material		Yield (%)	
		$LiAlH_4$	SYNHYDRID
Benzaldehyde	benzylalcohol	85	96*)
Heptanal	1-heptanol	86	97*)
2-butanone	2-butanol	80	95*)
Cyclohexanone	cyclohexanol	-	95*)
2-cyclohexanone	2-cyklohexanol	70	80*)
Cyclohexanonoxime	Cyklohexylamine	75	89
Benzoic acid	benzylalcohol	81	97
Benzoylchloride	benzylalcohol	72	87
Dimethyladipan	1,6-hexandiol	83	92
Dimethyltereftalane	1,4-di(hydroxymethylbenzene)	58	87
Ftalanhydrid	1,2-di(hydroxymethylbenzene)	87	88
etylester kyseliny nikotinové	3-pyridylckarbinol	82	82
N-fenylacetamide	N-etylaniline	92	84
Caprolactam	Hexametylenimine	95	81
Benzolnitrile	Benzylamine	83	81
Chlorbenzene	Benzene	-	traces*)
Brombenzene	Benzene	-	53*)
Chlorheptane	Heptane	-	40*)
1-bromheptane	Heptane	-	80*)

*) Yields were determined analytically or by the method of gas chromatography.
Other yields were obtained during preparative reactions.

It is worth making a special note of the use of **SYNHYDRID** during the anion polymerization of 6-caprolactam. The initiator of the polymerization of 6-caprolactam is its alkali salt. So far alkali salts have been regularly used for this purpose: either the hydroxides of alkali metals or, more rarely, alkali metals alone. The downside of the application of the hydroxides of alkali metals is monomer losses due to which the monomer has to be regenerated (5-10% of weight). Naturally, this is connected with loss of energy and material.
When **SYNHYDRID** is applied it is not necessary to prepare the initiator separately. Therefore, the process can be completed without a great part of operational equipment. Unlike previously used initiators, a catalytic system resulting from the reaction of 6-caprolactamu with **SYNHYDRID** is not too sensitive to the presence of water or impurities. Therefore, it can also be used for the polymerization of relatively less pure caprolactam.

In the present practice, the **SYNHYDRID**-initiated process of the anion polymerization of 6-caprolactam represents the simplest method of the production of lactame-based polyamides and copolyamides. The polymerization process was successfully verified with regard to the preparation of polyamide castings, low-temperature anion polymerization in moulds (below the melting point of a polymer), as well as with regard to the continual preparation of granules at temperatures greater than the melting point of a polymer. It can also be used for the preparation of lactame-based powder polymers of the polyamide type.

Occupational safety and hygiene:
SYNHYDRID is a highly flammable and caustic substance. When in contact with water, it produces extremely flammable gases. It ignites in contact with dry cellulose cotton wool, wood wool, and cleaning wool.
SYNHYDRID is classified as a dangerous preparation. It must be handled according to the instructions provided on labels and in the safety data sheet.

Packaging and storage:
SYNHYDRID is stored in the original sealed packaging and in a dry, covered warehouse at temperature range of up to +30°C for period of 12 months.

Liquidation of packaging material and unused residues
The unused residues of Synhydrid can be deactivated by means of alcohols or organic ketones, ideally in the atmosphere of nitrogen, or they can be destroyed by burning in approved chemical waste incinerators.
Empty packaging should be filled up with nitrogen and returned to the manufacturer.