

Contents

1	Introduction	9
2	Synthesis, Properties and Reactivity of Sodium Dihydrido-bis(2-methoxyethoxo)-aluminate (SDMA) (B. Čásenský)	11
2.1	Synthesis of SDMA	11
2.1.1	Synthesis of SDMA from Hydrides	11
2.1.2	Direct Synthesis of SDMA	15
2.2	Properties of SDMA	21
2.2.1	State	21
2.2.2	Solubility	21
2.2.3	Thermal Stability	22
2.2.4	Stability in Solutions	22
2.2.5	Association	23
2.2.6	Solvation	24
2.2.7	Spectra	24
2.2.8	Electrical Properties	27
2.2.9	Viscosity	27
2.2.10	Specific Weight	29
2.2.11	Thermodynamic Properties	29
2.3	Reactions of SDMA with Inorganic Compounds	31
2.4	Analytical Characterization of SDMA	34
2.4.1	Sampling and Weighing of SDMA	34
2.4.2	Determination of Sodium in SDMA	34
2.4.3	Determination of Aluminium in SDMA	35
2.4.4	Determination of Hydride Anions in SDMA	35
2.4.5	Determination of 2-Methoxyethoxy Groups in SDMA	36
2.5	Handling and Safe Manipulation with SDMA	37
2.5.1	Handling SDMA	37
2.5.2	Safe Manipulation with SDMA	39
	References	40
3	Applications of Sodium Dihydrido-bis(2-methoxyethoxo)-aluminate (SDMA) in Organic Chemistry (O. Štrouf)	42
3.1	Reactions of SDMA with Organic Compounds	44
3.1.1	Reactions with Hydrocarbons	44
3.1.1.1	Reactions with Saturated Hydrocarbons	44
3.1.1.2	Reactions with Olefins	48

3.1.1.2.1	Reduction of Olefins	48
3.1.1.2.2	Alkylation of Olefins	49
3.1.1.3	Reactions with Acetylenes	50
3.1.1.4	Reactions with Aromatic Hydrocarbons	51
3.1.2	Reactions with Haloderivatives	51
3.1.2.1	Reactions with Organic Halides	51
3.1.2.2	Reactions with Other Non-Metallic Halides	66
3.1.3	Reactions with Alcohols	68
3.1.3.1	Reactions with Active Hydrogen of Alcohol	68
3.1.3.2	Hydrogenolysis of Alcohols	68
3.1.3.3	Alkylation of Alcohols	70
3.1.4	Reactions with Ethers	70
3.1.5	Reactions with Epoxides	73
3.1.6	Reactions with Disulphides	74
3.1.7	Reactions with Sulphoxides	74
3.1.8	Reactions with Sulphones	74
3.1.9	Reactions with Sulphonyl Esters	76
3.1.10	Reactions with Sulphonamides	80
3.1.11	Reactions with Quaternary Salts	81
3.1.12	Reactions with Nitro Compounds	84
3.1.13	Reactions with Nitrosamines	87
3.1.14	Reactions with Aldehydes	92
3.1.14.1	Reduction of Aldehydes	92
3.1.14.2	Hydrogenolysis of Aldehydes	93
3.1.15	Reactions with Ketones	98
3.1.15.1	Reduction of Ketones	98
3.1.15.2	Hydrogenolysis of Ketones	106
3.1.15.3	Alkylation of Ketones	114
3.1.16	Reactions with Quinones	115
3.1.16.1	Hydrogenolysis of Quinones	115
3.1.16.2	Alkylation of Quinones	115
3.1.17	Reactions with Oximes	115
3.1.18	Reactions with Carboxylic Acids	124
3.1.18.1	Reduction of Carboxylic Acids	124
3.1.18.2	Hydrogenolysis of Carboxylic Acids	128
3.1.19	Reactions with the Salts of Carboxylic Acids	129
3.1.19.1	Reduction of the Salts of Carboxylic Acids	129
3.1.19.2	Hydrogenolysis of the Salts of Carboxylic Acids	138
3.1.20	Reactions with Acyl Halides	138
3.1.21	Reactions with Acid Anhydrides	139
3.1.22	Reactions with Esters of Carboxylic Acids	139
3.1.22.1	Reduction of Esters of Carboxylic Acids	139
3.1.22.1.1	Reduction of Esters to Alcohols	139
3.1.22.1.2	Reduction of Esters to Aldehydes	144
3.1.22.2	Hydrogenolysis of Esters of Carboxylic Acids	146
3.1.23	Reactions with Lactones	147
3.1.23.1	Reduction of Lactones to Diols	147
3.1.23.2	Reduction of Lactones to Lactols	147
3.1.24	Reactions with Esters of Inorganic Acids	156
3.1.25	Reactions with Amides	159

3.1.26	Reactions with Lactams	165
3.1.26.1	Reaction with Active Hydrogen of Lactams	165
3.1.26.2	Reduction of Lactams	165
3.1.27	Reactions with Imides	171
3.1.28	Reactions with Nitriles	172
3.1.28.1	Reduction of Nitriles	172
3.1.28.1.1	Reduction of Nitriles to Amines	172
3.1.28.1.2	Reduction of Nitriles to Aldehydes	172
3.1.28.2	Rearrangement of Nitriles	173
3.1.29	Reactions with Azides	174
3.1.30	Reactions with Heterocyclic Compounds	174
3.1.30.1	Reduction of a Heterocyclic Nucleus	174
3.1.30.2	Fission of a Heterocyclic Nucleus	190
3.1.30.3	Rearrangement of a Heterocyclic Nucleus	191
3.2	Reactions of SDMA–Metal Systems with Organic Compounds	192
3.2.1	Reactions of SDMA–Copper Systems	192
3.2.2	Reactions of SDMA–Titanium Systems	193
3.2.3	Reactions of SDMA–Palladium Systems	195
3.3	Catalysis of Organic Reactions with SDMA–Metal Systems	195
3.3.1	Hydrogenation	195
3.3.1.1	Hydrogenation of Unsaturated Hydrocarbons	195
3.3.1.2	Hydrogenation of Ketones	196
3.3.2	Hydrosilylation	196
3.4	Reactions of SDMA with Organometallic Compounds	197
3.4.1	Reactions with Compounds of IVA-Group Metals	197
3.4.2	Reactions with Compounds of IIB-Group Metals	197
3.4.3	Reactions with Compounds of VB-Group Metals	198
3.4.4	Reactions with Compounds of VIB-Group Metals	198
3.4.5	Reactions with Compounds of VIIB-Group Metals	201
3.4.6	Reactions with Compounds of VIIIB-Group Metals	201
3.5	Purification of Organic Solvents	201
	References	202

4 Applications of Sodium Dihydrido-bis(2-methoxyethoxy)-aluminate (SDMA) in Polymer Chemistry (V. Kubánek) 207

4.1	SDMA-Initiated Polymerization of 6-Caprolactam	207
4.1.1	Anionic Polymerization of 6-Caprolactam	207
4.1.2	Preparation of Polymerization Charge with SDMA	208
4.1.3	SDMA-Initiated Adiabatic Anionic Polymerization of 6-Caprolactam	209
4.1.4	SDMA-Initiated Anionic Polymerization of 6-Caprolactam Above the Melting Point of the Polymer	215
4.1.5	SDMA-Initiated Precipitation Anionic Polymerization of 6-Caprolactam	217
4.1.6	SDMA-Initiated Anionic Polymerization of 6-Caprolactam in the Presence of Inorganic Fillers	217
4.2	SDMA-Initiated Anionic Polymerization of Styrene	219
4.2.1	Technological Aspects of the SDMA-Initiated Anionic Polymerization of Styrene	223
4.3	SDMA-Catalyzed Cyclotrimerization of Organic Isocyanates	224
4.4	SDMA Application in Cyclodimerization of 1,3-Butadiene	226
	References	228
	Index	