

ACTIVATION OF REDUCING AGENTS. SODIUM HYDRIDE CONTAINING COMPLEX REDUCING AGENTS 24.
BENEFICIAL EFFECT OF Me_3SiCl ON THE REDUCING PROPERTIES OF NiCRA

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Abstract : Reduction of carbon-carbon double bonds can be achieved with either NiCRA or NiCRASi (nickel containing Complex Reducing Agent activated by Me_3SiCl). Selective reduction of polyunsaturated hydrocarbons or unsaturated ketones are easily performed with both reagents.


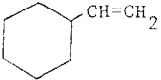
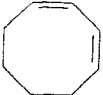

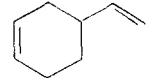
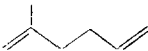
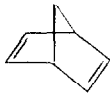
Chemical reductions are not very developed to reduce carbon-carbon double bonds : boron hydrides¹ and transition metal containing reagents² are presently the most widely used, but useful though they are, suffer from safety problem for large scale operations, cost, variable selectivity and often insufficient reactivity. Thus, new reagents with complementary properties are needed. Complex Reducing Agents (MCRA) NaH-RONa-MX_n^* constitute such reagents. We have already described a large number of applications of these easily prepared reagents, the properties of which may be modulated simply by changing the nature of the metal in MX_n^4 or of the activating alkoxide. In particular, we showed that ZnCRASi⁵ (zinc containing CRA, activated by Me_3SiCl) was an efficient and cheap reagent for quantitative selective hydrosilylation of carbonyl groups⁶. We also showed that NiCRA were able to selectively reduce carbon-carbon double bonds of polyunsaturated hydrocarbons and α,β -unsaturated ketones⁷. However the reaction times were very long with the first ones and some unsuccessful reductions were registered with the second ones.

In the present publication, we wish to report that, like ZnCRA, NiCRA are activated by Me_3SiCl leading to new reagents (NiCRASi) which easily and selectively reduce unsaturated carbon-carbon bonds.

A number of results concerning such reductions as well as the corresponding control experiments are reported in Tables I and II.

*In this paper we have adopted the convention of ref.³. Thus a MCRA (metal atom specified) prepared from NaH, RONA (alkoxide) and metallic salt will be abbreviated MCRA [x:y:z] where the molar ratio NaH/RONa/MX_n (in that order) is equal to x/y/z.

TABLE I - REDUCTION OF SOME ALKENES AND POLYUNSATURATED HYDROCARBONS

Substrate	Temperature °C	Reducing agent (a)	Reaction time (hours)	Product (%) (b)
$C_6H_{13}-CH=CH_2$	45	NiCRA	18	83 (c)
		NiCRASi	2	90-91 (d)
	45	NiCRA	17	> 98
		NiCRASi	4	> 99
$Ph-CH=CH_2$	45	NiCRA	3	> 99
		NiCRASi	1	> 99
	45	NiCRA	2.5	> 99
		NiCRASi	1	> 99
	25	NiCRA	0.75	> 98
		NiCRASi	0.25	> 99
	45	NiCRA	6-8	98.5
		NiCRASi	1	99
	45	NiCRA	2	94
		NiCRASi	1	98
	15	NiCRA	2.5	95
		NiCRASi	1	92
	45	NiCRA	1.5	72 (e)
		NiCRASi	0.5	82 (f)

(a) The reactions were performed on a 10 mmol scale (1 equivalent) in DME with NiCRA [5,2,1] or NiCRASi [5,2,1,1].

(b) Determined by GC analysis with internal standards.

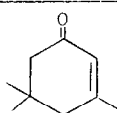
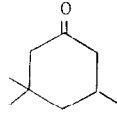
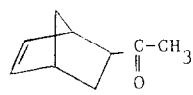
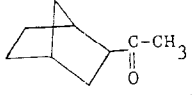
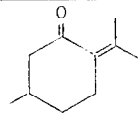
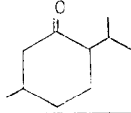
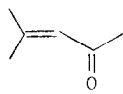
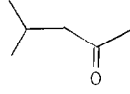
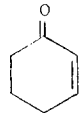
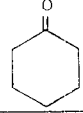
(c) 15-16 % of isomerization products were observed.

(d) 8 % of isomerization products were observed.

(e) 21 % of norbornane were formed.

(f) 12 % of norbornane were formed.

TABLE II - REDUCTION OF SOME UNSATURATED KETONES

Substrate	Temperature °C	Reducing agent (a)	Reaction time (hours)	Product (%) (b)	
	45	NiCRA	3	92 (86) (c)	
		NiCRASi	0.75	93 (88) (c)	
	0	NiCRA	3	96.5 (92)	
		NiCRASi	1	99.5 (95)	
	25	NiCRA	17	85 (82)	
		NiCRASi	2.5	97 (94)	
	25	NiCRA	0.5	96	
		NiCRASi	0.15	97	
	-78	NiCRA	0.75	16	
		NiCRASi	0.25	71 (66)	

(a) The reactions were performed on a 10 mmol scale (1 equivalent) in THF with NiCRA [5,1,1] or NiCRASi [5,1,1,1].

(b) Determined by GC analysis. Isolated yields in parentheses.

(c) The presence of small amounts of saturated alcohols was observed by GC analysis.

From Table I it appears that NiCRA and NiCRASi are able to reduce carbon-carbon double bonds. Compared to our previous results⁸, it is clear that replacement of anisole by DME strongly increases the rate of the reductions. Moreover, the activation of NiCRA by Me₃SiCl is also clearly apparent. Finally both reagents are sensitive to steric hindrance, allowing selective reductions.

Me₃SiCl also activates the reduction of α,β -unsaturated ketones. This increase in reactivity leads to better results in the regioselective reduction of these substrates (see Table II).

GENERAL PROCEDURE

As previously described⁴, CRA were prepared under nitrogen in DME or THF by dropwise addition of AmOH in a stirred mixture of NaH and anhydrous nickel acetate at 65°C. After stirring 2 hours at 65°C CRA was ready for use. In the case of NiCRASi, the temperature was allowed to cool to 45°C and chlorotrimethylsilane (10 mmol), in DME or THF (10 ml), was added dropwise. After stirring 30 minutes at 45°C, NiCRASi was ready for use.

The temperature was then adjusted and the substrate (10 mmol) and the adequate internal standard (hydrocarbon $\text{C}_7\text{-C}_{15}$) in DME or THF (10 ml) was added dropwise over a 2-3 minutes period. The reaction was monitored by GC analysis of small aliquots by comparison with authentic samples using a GIRDEL 3000 apparatus (flame ionization) equipped with 15 m SE 30 or 15 m Carbowax 20 M capillary columns.

After completion of the reaction, the excess of NaH was carefully destroyed by dropwise addition of a cold 10 % solution of HCl in water, up to the end of hydrogen evolution. The organic phase was filtered, and dried over magnesium sulfate. After removing of the solvent, the product was isolated by chromatography on a silica or alumina column and characterized by direct comparison (GC, ^1H NMR, IR) with authentic samples.

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