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# Reduction of Ethylenic Insaturations by in situ Generated Hydrogen[1a)]

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Selective hydrogenation of carbon-carbon double bond can be easily performed by simultaneous addition of substrate and $Me_3SiCl$ or water to NiCRA. It is shown that it is possible to reduce dienes selectively in olefins and carbon-carbon double bond in the presence of carbonyl, ester or acid groups.

The studies performed for some years in our laboratory on what we called Complex Reducing Agents(MCRA) NaH-RONa-$MX_n$,‡ disclose the strange and versatile properties of these unexpensive, readily prepared and handled new reagents. Thus, MCRA may be usefully used to perform chemical chemo[2)] or regioselective reductions[3)] as well as coupling condensations[4)] or carbonylations.[5)]

A few years ago, we also showed that MCRA may be used for the preparation of Ni and Pd catalysts for very interesting heterogeneous hydrogenation.[6)] On the other hand, we also discovered that addition of $Me_3SiCl$ to MCRA (MCRASi) considerably increased the reactivity without loss of the selectivity. Thus ZnCRASi selectively hydrosilylated carbonyl derivatives[7)] and NiCRASi selectively reduced carbon-carbon double bond.[2)]

Moreover, we observed a hydrogen evolution during the preparation of NiCRASi. So we wondered if it would not be possible to use the catalytic properties of NiCRA together with the hydrogen formation in order to perform catalytic hydrogenation. In the present publication, we report the first results obtained in this way. First of all, we compared the reactivity of preformed NiCRASi with the reagent we called "Simultaneous NiCRASi" (abbreviated Sim.NiCRASi). In a reduction performed with Sim.NiCRASi, substrate and $Me_3SiCl$ are simultaneously added to NiCRA. From the data reported in the Table, it appears that Sim.NiCRASi was more reactive than NiCRASi and that the selectivity was conserved.

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‡ In this paper, we have adopted the convention of Ref. 1b. 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.

These encouraging results led us to think that $Me_3SiCl$ could be replaced by a much less expensive reagent such as water.

It is well known that NaH reacts violently (if not explosively) with water. Interestingly, although MCRA are much more powerful reducing agents than NaH, we observed that they react much less violently with water. Thus, as far as water addition is not performed very rapidly, there is no hazard in performing this reaction.

With this result in hand, we performed a third kind of reaction during which the substrate was simultaneously added with water to NiCRA. The reagent thus used was called Sim.NiCRA-$H_2O$.

It clearly appears from the results reported in the Table that Sim.NiCRA-$H_2O$ was still more reactive than Sim.NiCRASi. Reaction times were shorter and, when possible, the yields were higher. Interestingly Sim.NiCRA-$H_2O$ has not lost the selectivity of NiCRASi or Sim.NiCRASi.

It must be emphasized that we also found that it was possible to perform the same kind of reductions by simply adding an alcohol such as $Am^tOH$ for example to a mixture of NaH-$Ni(OAc)_2$ and the substrate. This simpler procedure, although of interest, was much less reproducible than the hydrogenation described above.

Works are continuing in order to extend the application field of these interesting reductions.

General procedure is the following : As previously described,[2)] CRA were prepared under nitrogen in DME or THF (30 ml) by dropwise addition of $Am^tOH$ in a stirred mixture of NaH and anhydrous nickel acetate at 65 °C. After 2 hours stirring at 65 °C, CRA was ready for use.

Preparation of NiCRASi : 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 30 min stirring at 45 °C NiCRASi was ready for use.

Preparation of Sim.NiCRASi : In the case of Sim.NiCRASi, the temperature is adjusted if necessary and the mixture of $Me_3SiCl$ (10 mmol) and substrate (10 mmol) in DME or THF (20 ml) was added over a period of 5-10 min.

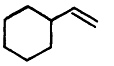
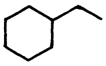
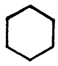
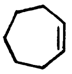
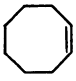
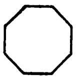
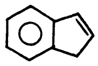
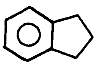
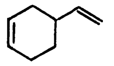
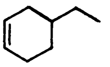
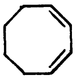
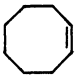
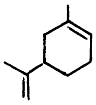
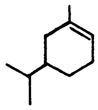
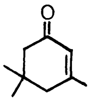
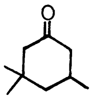
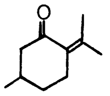
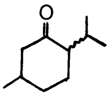
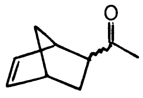
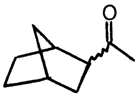
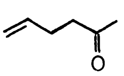
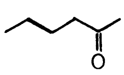
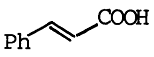
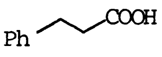
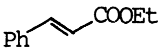
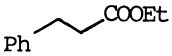
Preparation of Sim.NiCRA-$H_2O$ : In the case of Sim.NiCRA-$H_2O$, the procedure is similar to those of Sim.NiCRASi. The addition of the mixture of water (10 mmol) and substrate (10 mmol) in DME or THF (20 ml) was performed over a period of 10 min.

The reactions were 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 flash chromatography on a silica column and characterized by direct comparison (GC, $^1H$ NMR, IR) with authentic samples.

Table 1. Reduction and selective reduction of carbon-carbon double bond with Sim.NiCRASi and Sim.NiCRA-$H_2O$[a]

| Substrate | Product | Comp. x/y/z/t | T/°C | Sol-vent | NiCRASi | | Sim.NiCRASi | | Sim.NiCRA-$H_2O$ | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | t/h | Yield/%[b] | t/h | Yield/%[b] | t/h | Yield/%[b] |
| Octène-1 | Octane | 5/2/1/1 | 25 | DME | 2 | 90 | 1 | 95 | 0.5 | 98 |
|  |  | 5/2/1/1 | 25 | DME | 1 | 99 | 0.5 | 99 | 0.33 | 97 |
|  |  | 5/2/1/1 | 45 | DME | 48 | 33 | 17 | 62 | 17 | 72 |
|  |  | 5/2/1/1 | 45 | DME | 8 | 99 | 2 | 99 | 1 | 98 |
|  |  | 5/2/1/1 | 45 | DME | 18 | 8 | 17 | 35 | 16 | 65 |
|  |  | 5/2/1/1 | 45 | DME | 48 | 93 | 12 | 99 | 1 | 99 |
|  |  | 5/2/1/1 | 25 | DME | 1 | 98 | 0.5 | 95 | 0.1 | 96 |
|  |  | 5/2/1/1 | 65 | DME | 0.5 | 99 | 0.25 | 99 | 0.25 | 99 |
|  |  | 8/2/1/1 | 65 | DME | 96 | 66 | 42 | 90 | 18 | 90 |
|  |  | 5/1/1/1 | 45 | THF | 0.75 | 93(88) | 0.25 | 85(83) | 10 min | 93(89) |
|  |  | 5/1/1/1 | 45 | THF | 2.5 | 97(94) | 0.75 | 96(92) | 0.25 | 98(92) |
|  |  | 5/1/1/1 | 25 | THF | 1 | 99(95) | 1 | 95(90) | 0.25 | 95(92) |
|  |  | 5/1/1/1 | 25 | THF | 0.25 | 75 | 2 min | 90 | 8 min | 90.5 |
|  |  | 6/1/1/1 | 45 | THF | 2 | 87(81) | 0.5 | 95(87) | 0.25 | 99(94) |
|  |  | 5/1/1/1 | 45 | THF | 3 | 80(75)[c] | 1 | 85(75)[c] | 0.25 | 84(81)[c] |

a) The reactions were performed on a 10 mmol scale (1 equivalent) in DME or THF (50 ml).

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

c) The presence of small amounts of phenyl-3 propionic acid was observed.

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