

**ACTIVATION OF REDUCING AGENTS. SODIUM HYDRIDE CONTAINING COMPLEX  
REDUCING AGENTS 26.  
NEW EFFICIENT DESULFURIZING NICKEL CONTAINING REAGENTS.**

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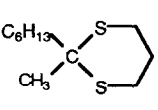
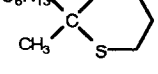
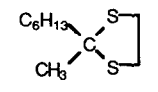
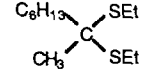
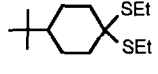
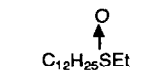
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*Abstract : It is shown that nickel containing Complex Reducing Agents NaH-RONa-NiX<sub>2</sub> as such or in the presence of ligands are very efficient in desulfurizing organic compounds such as sulfur containing heteroaromatic substrates, aryl thioethers, dithioketals, sulfoxides or sulfones.*

The desulfurization of organic compounds is a fundamental reaction for the production of non-polluting fuels<sup>1a,b</sup> as well as an important organic synthetic method.<sup>2a,b</sup> The most powerful and versatile reagents used to remove carbon-sulfur bonds are nickel-containing reagents. Among them, Raney nickels<sup>3a-g</sup> and nickel boride ("Ni<sub>2</sub>B")<sup>4a-e</sup> are heterogeneous, widespread reagents. Disadvantages of the former are their tedious preparations, hazardous handling<sup>5</sup> and the difficulty to accurately determine the weight of Ni used.<sup>3</sup> Moreover, in a number of cases, Raney nickel desulfurization fails to give the desired products.<sup>3b,d,f</sup> Ni<sub>2</sub>B is more convenient. It is not pyrophoric and the amount of Ni used is easily determined.<sup>4</sup> However its lower reactivity limits its use.<sup>4b,c</sup>

The desulfurization properties of Raney nickels and Ni<sub>2</sub>B have been attributed mainly to the large amount of hydrogen adsorbed on the surface of the finely divided catalyst.<sup>3a,d,6</sup> On the other hand it has been shown that, under homogeneous conditions, single electron transfer (SET) plays an important role during desulfurization.<sup>1,2b,7</sup> Thus, heterogeneous nickel reagents possessing a high SET ability might be good desulfurizing reagents in the absence of hydrogen.

TABLE - DESULFURIZATION OF ORGANIC COMPOUNDS

Run	Substrate	Reagent	Solvent	Ni/S eq <sup>(a)</sup> (weight)	Time (hours)	Products (%) (b)
1	dibenzothiophene	NiCRA-bpy 4/2/1/2	DME	6 (11)	5	biphenyl (98)
2	phenoxathiin	NiCRA-PPh <sub>3</sub> 4/2/1/4	DME	1.5 (2.75)	17.5	diphenyl- ether (31)    dibenzofu- furan (67)
3		NiCRA-PPh <sub>3</sub> 4/2/1/4	PhH	10 (18.34)	47	" (91)    " (8)
4	phenothiazin	NiCRA-bpy 4/2/1/2	DME	10 (18.34)	32	diphenylamine (> 99)
5	thianthrene	NiCRA-bpy 4/2/1/2	DME	5 (9.17)	18	biphenyl (> 99)
6		NiCRA-bpy 4/2/1/2	DME	1.25 (2.29)	89	benzene(83) + biphenyl(8) + dibenzothiophene (3)
7	thioanisole	NiCRA 5/2/1	THF	10 (18.34)	2	benzene (98)
8		NiCRA 10/2/1	THF	30 (55)	3	C <sub>8</sub> H <sub>18</sub> (97)
9		NiCRA-bpy 4/2/1/2	DME	10 (18.34)	3	 C <sub>6</sub> H <sub>13</sub> CH-SC <sub>3</sub> H <sub>7</sub> (> 99)
10		NiCRA 5/2/1	THF	10 (18.34)	18.5	C <sub>8</sub> H <sub>18</sub> (92)
11		NiCRA 5/2/1	THF	30 (55)	1.25	C <sub>8</sub> H <sub>18</sub> (> 99)
12	4-tertbutylcyclohexane 1,3-dithiane	NiCRA 10/2/1	THF	30 (55)	17.5	tert-butylcyclohexane (96)
13	4-tertbutylcyclohexane 1,2-dithiane	NiCRA 5/2/1	THF	30 (55)	17.5	tert-butylcyclohexane (> 99)
14		NiCRA 5/2/1	THF	30 (55)	10	tert-butylcyclohexane (96)
15	3,3-ethylene dithiocholestane	NiCRA 5/2/1	THF	30 (55)	2	cholestane (> 99)(c)
16	 C <sub>12</sub> H <sub>25</sub> SEt	NiCRA 5/2/1	THF	25 (45.86)	19	C <sub>12</sub> H <sub>26</sub> (> 99)
17	dibenzothiophene sulfone	NiCRA-bpy 4/2/1/2	DME	10 (18.34)	18	biphenyl (77)
18	C <sub>12</sub> H <sub>25</sub> SO <sub>2</sub> Et	NiCRA 5/2/1	THF	25 (45.86)	19	C <sub>12</sub> H <sub>26</sub> (66)

(a) Ni/S = Nickel/sulfur

(b) Determined by GC analysis

(c) Isolated yield.

We have previously shown that non-pyrophoric nickel-containing complex reducing agents (NiCRA\* and NiCRAL\*) are powerful reducing and coupling reagents.<sup>8</sup> We have attributed these properties to the presence of sodium alkoxides which could increase the SET ability of the Ni(0) species included in the polymeric reagent.<sup>9</sup> Thus it could be expected that NiCRAs might be new desulfurizing reagents. This hypothesis has been verified and we report the first results obtained with a number of representative substrates.

From the data gathered in the Table, a number of interesting features emerge :

- CRALs are as efficient as Raney nickel in desulfurizing heteroaromatic substrates. The excellent yield obtained with dibenzothiophene (run 1) must be emphasized since this substrate is recognized as one of the most resistant to desulfurization.<sup>1a</sup> Moreover, the reactions observed with phenoxathiin (runs 2 and 3) and thianthrene (runs 5 and 6) underline the versatility of CRALs since a simple change in the nature of the solvent (runs 2 and 3) or in the reagent/substrate ratio change the pathway taken in the reaction.
- With aryl alkyl ether (run 7), CRAs must be preferred to CRALs.
- Desulfurization of dithioketals is easily carried out with CRAs, the efficiency of which depends on the nature of the sulfur substituents. This property could be used to perform selective desulfurizations. Such a feasibility is presently under investigation. Interestingly, it must be noted that 3,3-ethylene dithiocholestane is hardly desulfurized by Ni<sub>2</sub>B<sup>4c</sup> while NiCRA is very efficient in performing this reaction (run 15). With 1,3-dithiane the replacement of NiCRA by NiCRAL led to a half desulfurization with formation of thioether (run 9). This interesting reaction is also under study.
- Finally it has been found that NiCRAs are also efficient in desulfurizing sulfoxides and sulfones (runs 16, 17 and 18).

The above results display the versatility of CRAs and CRALs in desulfurization of organic substrates. Use of these reagents in selective desulfurization is presently under active investigation.

#### General procedure

To a suspension of dry Ni(OAc)<sub>2</sub> (if necessary 2,2'-bipyridyl or triphenylphosphine) and degreased NaH in solvent (30 ml) under nitrogen at 63°C was added a solution of tertioamylalcohol in solvent (10 ml). After stirring 2 hours at 63°C, the substrate and the adequate internal standard (C<sub>10</sub>-C<sub>16</sub>) in solvent (10 ml) were then

\*In this paper we have adopted the convention of ref. 9. Thus a NiCRAL prepared from NaH, tAmONa, nickel acetate and 2,2'-bipyridyl or triphenylphosphine will be abbreviated NiCRAL (x/y/z/t) where the molar ratio NaH/tAmONa/Ni(OAc)<sub>2</sub>/bpy or PPh<sub>3</sub> (in that order) is equal to x/y/z/t.

added over a period of 2-3 minutes. The reaction was monitored by GC analysis of small aliquots by comparison with authentic samples using a Girdel 300 chromatograph (flame ionization) equipped with 1.80 m OV101 column. After classical work-up, the product was isolated by chromatography on silica gel and characterized by direct comparison (GC, <sup>1</sup>H NMR, IR) with authentic samples. Volatile products must be isolated by distillation instead chromatography.

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