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Dramatic Acceleration of the Desulfurization, with Ni containing Complex Reducing Agents (NiCRA's)

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Abstract: Introduction of the sodium salt of 3-hydroxy-N-methylpiperidine into the aggregates of NiCRA's (NaH-RONa-NiX_2) led to unprecedented very efficient desulfurizing reagents as checked with dibenzothiophene derivatives and representative sulfurated compounds.

Desulfurization of organic compounds is an important reaction in organic synthesis as well as in the production of nonpolluting fuels.[1] In previous papers,[1c,d] we showed that nickel-containing complex reducing agents (NiCRA's and NiCRAL's)[2] are very efficient and chemoselective desulfurizing reagents. During these studies we observed that the presence of ligands such as bipyridine (bpy) improved the efficiency of the reagents.[1c,d] It was later shown that, in agreement with our hypothesis, such reagents contained $Ni^{(0)}(bpy)_2$ species[3] which could account for the observed increase of reactivity. One of the main interest of CRA's is that the nature of the matrixes surrounding $Ni^{(0)}$ may be modified not only by introduction of ligands as in NiCRAL's,[4] but also by appropriate changes in the structure of the activating alkoxides. These considerations led us to hypothesize that the presence of a nitrogen in the structure of the activating alkoxide could increase the desulfurizing properties of our reagents. In the present communication we report the first successful results obtained in this area.

The choice of the test substrate was guided by the following considerations. Dibenzothiophene (DBT) is very difficult to desulfurize and is generally used as a reference substrate in such studies.[1] However we already succeeded in its desulfurization.[1c] On the other hand the reactivity of 4,6-dimethyldibenzothiophene (DMDBT)[5] is extremely low and it was poorly desulfurized by CRA's.[1c] Thus, 4-methyldibenzothiophene (MDBT)[5] with intermediate reactivity appeared as a good candidate to check our hypothesis. Our main results are shown in Table 1.

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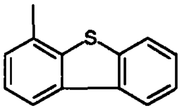
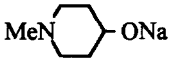
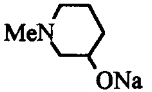
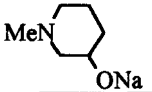
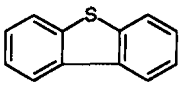
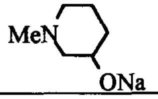
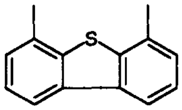
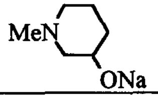
Table 1. Desulfurization of dibenzothiophenes derivatives by NiCRA.[a]

Run	Substrate	Activating Agent	Ni/S[b] (a)	t (h)	Yield[c] (%)
1	 (MDBT)	*t*AmONa	10	18	47
2			"	"	71
3			"	"	52
4			"	"	31
5			"	"	59
6			"	4.5	100 (98)
7			5	18	100 (98)
8	 (DBT)	*t*AmONa	10	10	100
9			5[d]	1.25	100 (95)
10	 (DMDBT)	*t*AmONa	10	42	15
11			"	20[e]	91 (85)

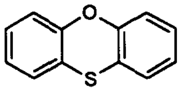
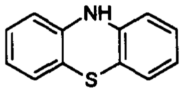
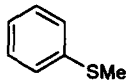
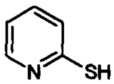
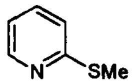
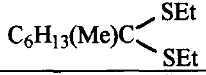
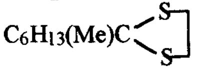
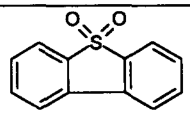
a) Reaction performed in THF (40 ml) at 65°C on 1 mmole scale of sulfurated substrate using NiCRA (5/2/1) ratio of NaH/RONa/Ni(OAc)$_2$. See Ref. 6. b) Atom Ni/atom S. c) Yield determined by GC analysis. In parenthesis, isolated yields. d) Reaction performed in THF (40 ml) at 65°C on a 2 mmoles scale using NiCRA (5/2/1) ratio of NaH/RONa/Ni(OAc)$_2$. e) Conversion was limited to 91%.

From these data it appears that, as expected, aminoalkoxides increase the desulfurizing properties of CRA's. This activation increase is very sensitive to the structure of the alkoxide. Particularly important is the distance between the nitrogen and the oxygen as illustrated in run 4 compared to run 2. We attribute the above results to bidentate interactions inside the matrix between the amino alkoxide and the metal core of the reagent. It is noteworthy that the most efficient reagent was NiCRA containing the sodium salt of N-methyl-3-hydroxy piperidine (NMHPNa), which is particularly well suited to generate rigid chelates between the lone pair of the nitrogen and the oxygen of the alkoxide.

From a practical point of view, the low Ni/S ratio used during these desulfurizations must be underlined. The same increase in reactivity was observed with DBT and DMDBT (runs 8-11).

Finally, desulfurization of representative sulfurated substrates (Table 2) confirmed the dramatic improvement achieved with NMHPNa and NiCRA.

Table 2. Desulfurization of sulfurated compounds induced by NiCRA.[a]

Run	Substrate	*t*AmONa			NMHPNa		
		Ni/S[b]	t (h)	Yield[c] (%)	Ni/S[b]	t (h)	Yield[c] (%)
1		5	90	43[d]	5	0.5	83[e]
2		"	42	42	"	4	98
3	$C_{12}H_{25}SH$	10	1	99	5	0.25	98
4	$C_{12}H_{25}SEt$	20[f]	42	34	10	42	85
5	$C_{12}H_{25}SPh$	10	2.5	67	5	2	84
6		"	18	98	"	2	98
7	Ph_2CHSEt	"	1	93	"	0.25	99
8	Ph_2CHSPh	"	4	81	10	0.25	96
9		"	1	99	5	0.25	98
10		"	1	98	"	0.25	99
11	 $C_6H_{13}(Me)C(SEt)_2$	20[d]	18	80	10	18	95
12		10	18.5	92	5	0.25	95
13		"	19	81	10	2	98

a) Reaction performed in THF (40 ml) at 65°C on 1 mmole scale of sulfurated substrate using NiCRA (5/2/1) ratio of $NaH/RONa/Ni(OAc)_2$. b) Atom Ni/atom S. c) Yield determined by GC analysis using internal standard method. d) 33 % diphenylether and 10 % dibenzofurane were isolated. e) 81 % diphenylether and 2 % dibenzofurane were isolated. f) Reaction performed in THF (40 ml) at 65°C on a 0.5 mmole scale using NiCRA (5/2/1) ratio of $NaH/RONa/Ni(OAc)_2$.

Studies are continued in order to obtain desulfurizing reagents working with Ni/S ratios close to the stoechiometry and highly chemoselectivily.

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References and notes.

1. a) Eisch, J.T.; Hallenbeck, L.E.; Han, K.I. *J. Org. Chem.* **1983**, *48*, 2963-2968; b) Eisch, J.T.; Hallenbeck, L.E.; Lucorrelli, M.A., *Fuel* **1985**, *64*, 440-442 and reference cited therein; c) Becker, S.; Fort, Y.; Vanderesse, R.; Caubère, P. *J. Org. Chem.* **1989**, *54*, 4848-4853; d) Becker, S.; Fort, Y.; Caubère, P. *J. Org. Chem.* **1990**, *55*, 6194-6198; e) Caubère, P.; Coutrot, Ph. *Comprehensive Organic Synthesis: Selectivity, Strategy & Efficiency in Modern Organic Chemistry, I.* Fleming, Ed., vol. 8 (Reduction), Pergamon Press, **1991**, 835-870.
2. a) Caubère, P. *Ang. Chem. Int. Ed. Engl.* **1983**, *22*, 599-613; b) Caubère, P. *Rev. Heteroat. Chem.* **1991**, *4*, 78-139.
3. Fox, M.A.; Merkert, J.R.; Caubère, P. *New J. Chem.* **1994**, *18*, 447-448.
4. Gallezot, P.; Leclercq, C.; Fort, Y.; Caubère, P. *J. Mol. Cat.* **1994**, *93*, 79-83.
5. A considerable improvement in the synthesis of this compound has been previously published: Kuehm-Caubère, C.; Adach-Becker, S.; Fort, Y.; Caubère, P. *Tetrahedron* **1996**, *52*, 9087-9098.
6. In a typical experiment (run 7), N-methyl-3-hydroxy piperidine (20 mmol) in 10 ml of dry THF was added dropwise to a suspension of NaH (60 mmol), $Ni(OAc)_2$ (10 mmol) in dry THF (30 ml) at 65°C. After 2 h of stirring, the reagent was ready for use and 4-methyldibenzothiophene (2 mmol) could be added in dry THF (10 ml). The reaction was monitored by GC analysis of small aliquots using internal standard method. After completion of the reaction, the excess of hydride was carefully destroyed by dropwise addition of water at 25°C until hydrogen evolution ceased. After classical workup and separation, 3-methyl-biphenyl was isolated and characterized by comparison of its spectroscopic data with those of an authentic sample.