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New Desulfurdimerization of Dithioketals Induced by a 2,2′-Bipyridine Ligated Nickel(0) Complex†

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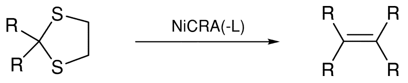
Desulfurdimerization of various aromatic dithioketals is efficiently induced by a 2,2′-bipyridine ligated nickel(0) complex under mild conditions.

The coupling reaction of carbonyl derivatives induced by $TiCl_3$, well known as the McMurry reaction, is a very useful procedure for the formation of carbon–carbon double bonds.[1] In the last decade, a new method starting from dithioketals appeared as an alternative to this reaction. Indeed, Luh *et al.* have shown that $W(CO)_6$ or $Mo(CO)_6$ promoted the desulfurdimerization of various dithioketals.[2] However, this efficient reaction needs an excess of metal carbonyl (1.5 to 4 equiv.) and must be carried out in chlorobenzene at reflux for long reaction times (24–48 h). In spite of this, the method appeared of some interest in the synthesis of bowl-like polycyclic aromatic hydrocarbons[3] or crown ethers hinged with bifluoroenylidene.[4]

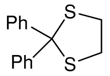
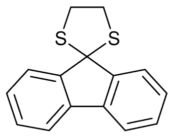
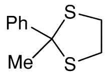
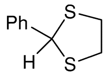
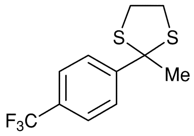
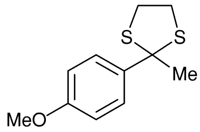
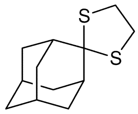
In continuing our long-term interest in the desulfurization processes[5] induced by nickel containing complex reducing agents (NiCRA),[6] we found that under mild conditions our reagents also produced desulfurdimerization of dithioketals (Scheme 1). We describe in this paper our first results in this area.



A systematic study performed with the dithioketal of benzophenone showed us that: (i) a 2,2′-bipyridine ligated nickel containing complex reducing agent (NiCRA-bpy)[7] was the best candidate to achieve desulfurdimerization of dithioketals. A non-ligated or triphenylphosphine ligated reagent did not cause the reaction. (ii) The use of a stoichiometric amount of NaH with respect to nickel salt led to the most efficient reagent for desulfurdimerization while an excess of hydride favoured the classical desulfurization process. (iii) A Ni/substrate ratio of 2, *i.e.* Ni/S = 1, led to the best yield of double bonded product. (iv) The reaction must be carried out in refluxing THF. Reactions performed in 1,2-dimethoxyethane (DME) only led to desulfurization without coupling. Under these conditions, tetraphenylethylene can be obtained in 85% isolated yield after 1 h of reaction (Run 1, Table 1).

From these results, we examined the reactivity of various dithioketals (Table 1). It appears that under mild conditions ethylenic compounds can be obtained in moderate to good yields starting from aromatic dithioketals. Under the conditions used, no reduction of ethylenic compounds was observed. It is interesting that the yields of the reaction with monoaryl derivatives were apparently lower than those with diaryl compounds. Presumably, the aryl groups stabilize the reactive intermediate which could be a radicaloid or a carbenoid species. Indeed, the mechanism of desulfurizations induced by NiCRA was previously described as proceeding by a single electron transfer in its first step.[5] On the other hand, it is worth noting that adamantan-2-one dithioketal (run 7) only led to reduction in low yield. Such behaviour was previously observed in treatment with $Mo(CO)_6$.[2a] This result may also be interpreted as a lack of stabilization of the reaction intermediate.

Table 1 Desulfurdimerization of dithioketals induced by NiCRA-bpy[a]

Run	Substrate	Ni/S	*t*/h	Isolated yield (%)[b]	Reduction (%)[c]
1		1	1	85	13
2		1	2	77	21
3		1	18	58	40
4		0.5	1	51	48
5		1	10[d]	40[e]	57
6		1	12[d]	45[f]	51
7		1	18	–	15

[a] Reaction performed on 1 mmol scale of substrate in THF at reflux. [b] Yield determined of double bonded dimeric product after isolation by flash chromatography. [c] Yield determined by GC analysis. [d] Reaction performed in THF at 45 °C. [e] $Z/E = 25/75$. [f] $Z/E = 45/55$.

In conclusion, NiCRA-bpys are effective in inducing desulfurdimerization of aromatic dithioketals in THF at reflux. The method developed appeared of interest since our reagents are easily handled and less toxic than metal carbonyl derivatives.

Experimental

Tetrahydrofuran was distilled from a benzophenone–sodium adduct and stored over sodium wire. *tert*-Butyl alcohol (Aldrich) was distilled from sodium. Nickel acetate (Fluka) was dried under vacuum (20 mmHg) at 110 °C for 16 h. 2,2′-Bipyridine (Aldrich) was recrystallized before use from hexane. Sodium hydride (65% in mineral oil, Fluka) was used after three washings with the reaction solvent under nitrogen. All reactions were performed under nitrogen.

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†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1999, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

General procedure.—A solution of Bu^{t}OH (20 mmol) in 10 ml of dry THF was added dropwise to a mixture of degreased NaH (40 mmol), Ni(OAc)$_2$ (10 mmol) and 2,2′-bipyridine (20 mmol) in 20 ml of dry THF at 63 °C. After 1 h, the black reagent formed was ready for use. The solution of dithioketal (5 mmol) in 10 ml of dry THF was then added dropwise over a period of 15 min. The reaction was monitored by GC analyses (Alltech Econo-Cap EC-5 column, 30 m × 0.32 mm ID × 0.25 μm) and GC–MS (CI, CH$_4$) analyses (HP1, 15 m × 0.32 mm ID × 0.25 m) using dodecane as internal standard. After completion, 10 ml of water was added dropwise at 25 °C. Products were then extracted by diethyl ether and separated by flash chromatography (Merck silica gel, 230–400 mesh). Their spectroscopic data are in accordance with those of authentic samples.

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