

Desulphurization of Benzothiophene Derivatives with Nickel Boride

Thomas G. Back* and Kexin Yang

Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4

Nickel boride, conveniently generated *in situ* from nickel chloride hexahydrate and sodium borohydride, has been used to desulphurize a variety of benzothiophene derivatives to the corresponding hydrocarbons under exceptionally mild conditions.

The desulphurization of organic compounds is of increasing importance because of the growing demand for fuels with a low sulphur content, and in a variety of synthetic methods. Polycyclic aromatic sulphur compounds related to benzothiophene are of special relevance as they occur widely in fossil fuels and are particularly difficult to desulphurize by conventional methods.¹ We report that nickel boride is an effective and exceptionally convenient reagent for this purpose.

Nickel boride is a fine black solid that is easily prepared by the reduction of Ni^{II} salts with sodium borohydride in protic solvents. It is a well-known catalyst for the hydrogenation of alkenes² and a useful reagent for the reduction of many other types of functional groups.³ While a few reports of its use in desulphurizations have appeared,⁴ to the best of our knowledge, these include no examples of benzothiophene derivatives. Furthermore, many of the earlier desulphurization procedures afforded low yields and required elevated temperatures and long reaction times.

During a recent investigation of related nickel boride-mediated deselenizations,⁵ we observed that the reactivity of the nickel boride decreased rapidly with time. Similarly, drastic reductions in the yields of desulphurized products occur when the organosulphur compound is added to previously formed nickel boride. This may account for the forcing conditions required in some of the earlier desulphurization work reported in the literature. In our typical procedure, the sodium borohydride was therefore added in portions to a solution of the organosulphur compound and nickel chloride hexahydrate in methanol-tetrahydrofuran (THF). A vigorous reaction occurred, characterized by the immediate formation of nickel boride and the evolution of hydrogen. The mixture was then stirred at 0 °C for 15–60 min, the precipitate was filtered, and the product was either isolated from the filtrate or analysed by GC. The results for the desulphurization of various benzothiophenes and related compounds are listed in Table 1, along with sulphide (1) and thiol (3) for comparison. High yields of desulphurized products were obtained in this manner, except in the case of the relatively hindered

methyl dibenzothiophene (12), provided that an excess of nickel boride was employed.

Unlike Raney nickel,⁶ or certain nickel complexes⁷ that have previously been used for desulphurization, nickel boride has the advantage that it is neither pyrophoric nor air-sensitive, and can be employed at or below room temperature

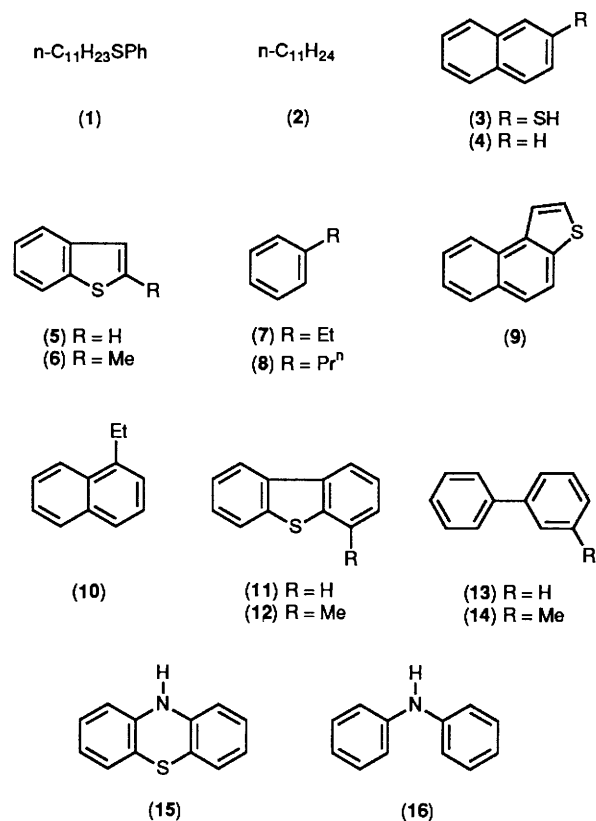


Table 1. Desulphurization with nickel boride.

Starting material	Reactant ratio ^a	Solvent (v : v) ^b	Time /min	Product	% Yield ^c
(1)	1 : 10 : 30	MeOH	15	(2)	96
(3)	1 : 7 : 21	MeOH-THF (3 : 1)	15	(4)	92
(5)	1 : 7 : 21	MeOH-THF (3 : 1)	15	(7)	73
(6)	1 : 14 : 42	MeOH-THF (3 : 1)	15	(8)	62
(9)	1 : 7 : 21	MeOH-THF (3 : 1)	15	(10)	60
(11)	1 : 7 : 21	MeOH-THF-H ₂ O (1 : 2 : 1)	60	(13)	69
(12)	1 : 14 : 42	MeOH-THF (3 : 1)	60	(14)	35
(15)	1 : 14 : 42	MeOH-THF-H ₂ O (1 : 2 : 1)	60	(16)	68 ^d

^a Molar ratio of starting material: NiCl₂·6H₂O : NaBH₄. ^b All reactions were performed at 0 °C. ^c GC yields determined with an internal standard are reported unless otherwise noted; the identity of products was confirmed by comparison of their GC-mass spectra with authentic samples. ^d Isolated yield.

in a simple Erlenmeyer flask, without protection from the atmosphere. Nickel boride is therefore an inexpensive, easily handled, and effective reagent for the desulphurization of polycyclic aromatic sulphur compounds under remarkably mild conditions.

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