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MILD HOMOGENEOUS DEBLOCKING EMPLOYING 2-BROMO-1,3,2-BENZODIOXABOROLE[1]

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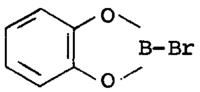
Abstract: We describe a technique using 2-bromo-1,3,2,-benzodioxaborole in methylene chloride at ambient temperature to cleave ethers and esters.

New methods for ether and ester deblocking continue to be needed. Our needs forced us to look beyond the existing techniques which are outlined in excellent reviews.[2] Exemplary of our situation is the fact that many of the high molecular weight dyes in Table I could not be cleanly or completely deblocked at -78° with boron tribromide. In these cases the borate complex intermediate would precipitate from solution before the reaction was complete. Raising the temperature to obtain a solution did not always help, because boron tribromide is a strong Lewis acid and significant amounts of side products arose, particularly with the azo dyes.[3] Using 2-bromo-1,3,2-benzodioxaborole[4] 1 in methylene chloride with or without boron trifluoride etherate as coreagent at room temperature overcame all of the above problems for the compounds we were interested in.



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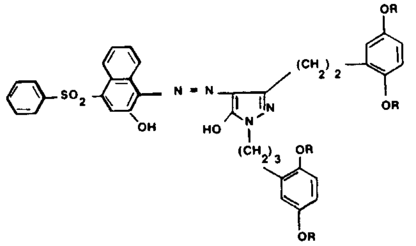
The reaction mechanism is outlined in Scheme I. The reaction provides soluble



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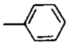
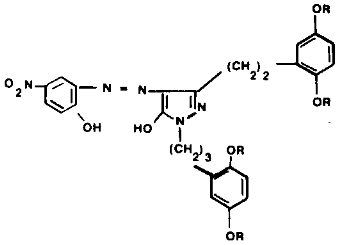


b. R=H



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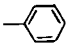
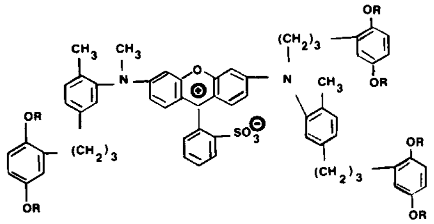
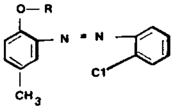


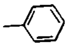
b. R=H



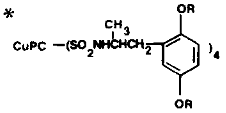
3a. R=CH$_3$

b. R=H



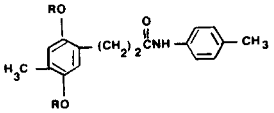
4a. R=CH$_2$—


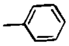
b. R=H



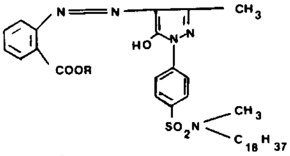
5a. R=CH$_3$

b. R=H



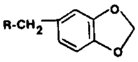
6a. R=CH$_2$—


b. R=H



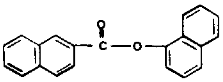
7a. R=CH$_3$

b. R=H

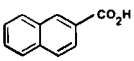


8a. $R=CH_3\overset{O}{\overset{\|}{C}}O-$

b. R=Br



9a.



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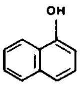
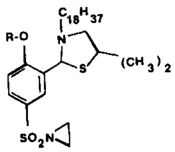
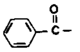
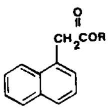


9c.



10a.


b R=H



11a. R=CH$_3$

b. R=H

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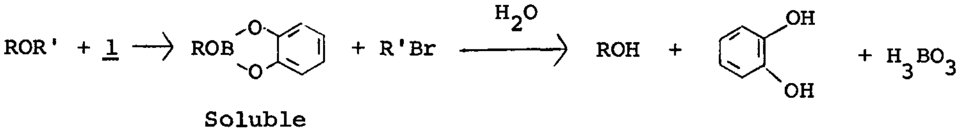
* CuPC denotes copper phthalocyanine.

intermediates which yield deblocked products on hydrolysis. Remarkable testimony to this is that the copper phthalocyanine dye 5a reaction was always homogeneous.

Scheme I



The compounds outlined in Table I were reacted by one of two procedures--either with excess 1 alone or 1 with boron trifluoride etherate as coreagent. The workup involved a quench into hexane-water to assure that all catechol was extracted into the aqueous phase.[5] Solids were collected by filtration. Organic soluble (hexane-methylene chloride) products were washed with water, saline, dried and freed of solvent. All products were fully characterized as well as compared with samples prepared by other means.[6]

Table I. Deblocking Reactions

Starting Material	Product(s)	Reactant Ratio[a]	Time(H)	Yield(%)[b]
1a	1b	1:10:1	1	82
2a	2b	1:10:1	12	85
3a	3b	1:10:1	0.5	95
4a	4b	1: 1:0	2	95
5a	5b	1:20:4	36	98
6a	6b	1:2.5:1	2	55
7a	7b	1:5:0	12	92
8a	8b	1:1:0	2mins	84
9a	9b,9c	1:3:0	24	52(9b),67(9c)
10a	10b	1:2.5:1	0.25	71
11a	11b	1:3:0	24	64

a) Reactant ratio is defined as moles of starting material:moles of 2-bromo-1,3,2-benzodioxaborole:moles of $BF_3.Et_2O$. b) Yield of isolated material. Yields were not optimized.

REFERENCES

1. This deblocking method is the subject of a U.S. patent application having an effective filing date of April 29, 1983.
2. a) M.V. Bhatt and S.U. Kulkarni, Synthesis (1983) 249.
   b) V.G. Mairanovsky, Angew. Chem. Int. Ed. Engl., 15, 281 (1976).
   c) V.N.R. Pilla, Synthesis (1980) 1.
3. The triangle of reactivity, solubility and temperature was common to most literature deblocking themes in our current needs.
4. a) W. Gerrard, M.F. Lappert and B. A. Mountfield, J. Chem. Soc. (1959) 1529.
   b) 1 was prepared in up to one kilogram amounts by reacting catechol with boron tribromide. The colorless solid fumes in the air, is pourable and was stored and used successfully for up to a year. Otherwise the reagent was stored as a methylene chloride solution.
   c) Coined name for this reagent is BOB-bromide (benzodioxaborole).
5. Since most of the products in Table I are either base soluble or oxidize when ionized, the catechol was rarely removed by washing with base. Water washing was deemed generally adequate where hexane was used as a workup solvent partner. Additionally the hexane layer adequately removed halide materials from solid products.
6. a) The theme of homogeneous deblocking of high molecular weight compounds by virtue of the solubility of monomeric borate intermediates is amply demonstrated. Extension to polymer chemistry is implied.
   b) In rebuttal to a referee's comment, the hydrolysis portion of Scheme I is outlined in Steinberg, H. "Organoboron Chemistry", Vol 1; Wiley Interscience: NY, NY, 1984; p. 563.

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