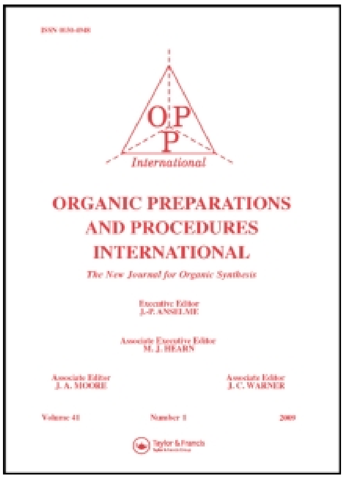

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UTILITY AND APPLICATIONS OF BORANE DIMETHYLSULFIDE IN ORGANIC SYNTHESIS. A REVIEW

Robert O. Hutchins[a]; Frank Cistone[a]
[a] Department of Chemistry, Drexel University, Philadelphia, PA

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UTILITY AND APPLICATIONS OF BORANE DIMETHYLSULFIDE IN ORGANIC SYNTHESIS.

A REVIEW

Robert O. Hutchins* and Frank Cistone

Department of Chemistry, Drexel University
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INTRODUCTION

During the past 40 years boron hydride reagents have assumed ever increasing importance in organic synthesis primarily because of their ability to provide potent hydride sources for a number of useful transformations, most notably the selective reductions of functional groups and the addition of boron and hydrogen to alkenes and alkynes (hydroboration) to give organoboranes.[1] These latter derivatives display vast utility as synthetic intermediates both for the formation of functional groups and in carbon-carbon bond generating reactions. In fact, organoboranes provide what is certainly one of the most useful classes of organometallic intermediates available to synthetic chemists. The development of and extensive contributions to this area by Professor H. C. Brown was recognized by the award of the 1979 Nobel Prize in Chemistry.[1h]

Over the years the most commonly used reagent system for hydroborations and borane reductions has been the commercially available solution of borane in tetrahydrofuran (BH_3THF) and hundreds of synthetic applications of this combination have been reported.[1c-f] However, in spite of its usefulness, BH_3THF is afflicted with several adverse characteristics, the most important ones being: (1) the low concentration of borane (1M, 1.5 wgt. % BH_3); (2) sodium borohydride (5%) must be added to inhibit cleavage of

THF. This can induce unwanted side-reactions especially in molecules containing moieties susceptible to attack by borohydride; (3) BH_3·THF is relatively sensitive to air and moisture; (4) the reaction medium is limited to dilute solutions in THF, which is relatively expensive, or to THF-solvent mixtures which are even more dilute ($<$ 1M).

In 1971 Adams and co-workers[2] introduced borane dimethylsulfide complex[3] (BMS) as an alternative source of borane for hydroborations and reductions. Subsequent investigations have demonstrated substantial advantages of this complex over BH_3·THF. First, BMS provides a commercially available, convenient, concentrated form of borane (10M) that is easily handled and is stable for months at room temperature under N_2 or Ar (indefinitely at 0°C). Furthermore, BMS is soluble in a wide variety of aprotic solvents including hexane, benzene, toluene, ethyl ether, ethyl acetate and methylene chloride, thus vastly expanding the range of media available for reactions. Finally, the reagent is uncontaminated with other offending reducing agents (i.e. $NaBH_4$). The properties and characteristics of BMS are presented in Table I.[4]

The available evidence suggests that BMS may be substituted for other sources of borane and affords equal or superior results in both hydroboration and reduction applications. Also, convenient and simple work-up procedures have been introduced recently which allow the selective oxidation of either the sulfide (with NaOCl) or organoborane (with H_2O_2/OH^-).[5] Other borane methylsulfide complexes have been reported including $BH_2Cl{\cdot}S(CH_3)_2$,[6a,e] $BHCl_2{\cdot}S(CH_2)_2$,[6a] $BHBr_2{\cdot}S(CH_3)_2$,[6b] similar iodo derivatives[6c] and BH_3·1,4-oxathiane;[6d] these show great potential promise for future synthetic developments.

Literature descriptions of the uses of BMS in hydroborations and reductions are discussed separately below.

TABLE I. Properties of Borane Dimethylsulfide

Formula	$BH_3S(CH_3)_2$
Molecular Weight	75.97
Physical State	Colorless Liquid
Density (20°)	0.801 g/mL
Borane Content	100 μL = 1 mmol; 100 mL = 1 mol
Active Hydrogen	3.95%
Stability	reacts slowly with atmospheric moist-forming a crust of boric acid which protects the reagent; best stored at 0°C
Solubility	soluble: hexane, benzene, toluene, xylenes, ethyl ether, DME, diglyme,ethyl acetate, methylene chloride insoluble: water (reacts slowly) reacts: alcohols, protic solvents, acetone and other ketones, aldehydes

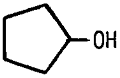
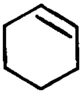
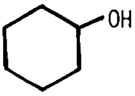
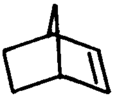
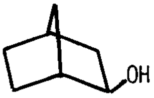
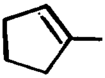
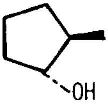
I. HYDROBORATION

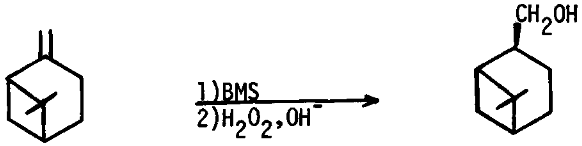
As mentioned, BMS appears comparable to other sources of BH_3 for hydroborations (Eq. 1) and the utility is greatly augmented by the handling ease, convenience and enhanced concentrations available. Evidently, BMS is

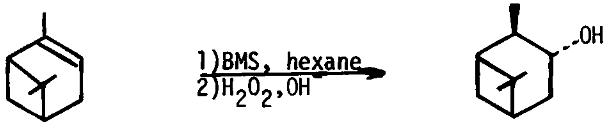
(1)

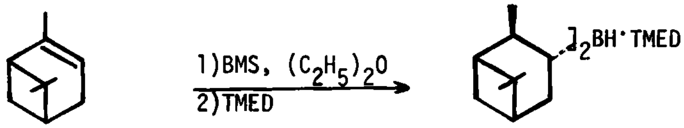
generally the reagent of choice for this extremely useful and important reaction. Table II collects literature examples of successful conversions and illustrates the versatility of the reagent.

TABLE II. Hydroborations With Borane Dimethylsulfide

Entry	Reaction		Product(s) (% Yield)		Ref.
1	$CH_3(CH_2)_2CH{=}CH_2$	$\xrightarrow{\text{BMS, }C_6H_6}$	$CH_3(CH_2)_4]_3B$		2
2	$CH_3(CH_2)_3CH{=}CH_2$	$\xrightarrow[\text{2) }H_2O_2,OH^-]{\text{1)BMS}}$	$CH_3(CH_2)_5OH$ +	$CH_3(CH_2)_3CHOHCH_3$	7
		ethyl ether	94	6 (100)	
		hexane	94	6 (100)	
		THF	94	6 (100)	
		$C_6H_5CH_3$	94	6 (98)	
		CH_2Cl_2	94	6 (99)	
		$CH_3CO_2C_2H_5$	94	6 (100)	
		CH_3CN	94	6 (81)	
3	$CH_3(CH_2)_3C(CH_3){=}CH_2$	$\xrightarrow[\text{2)}H_2O_2,OH^-]{\text{1)BMS, hexane}}$	$CH_3(CH_2)_3CH(CH_3)CH_2OH$ (100)		7
4	$CH_3CH_2CH{=}CHCH_2CH_3$	$\xrightarrow[\text{2)}H_2O_2,OH^-]{\text{1)BMS, hexane}}$	$CH_3CH_2CHOH(CH_2)_2CH_3$		7
5	$C_6H_5CH{=}CH_2$	$\xrightarrow[\text{2)}H_2O_2,OH^-]{\text{1)BMS, hexane}}$	$C_6H_5(CH_2)_2OH$ + (86)	$C_6H_5CHOHCH_3$ (14)	7
6		$\xrightarrow[\text{2)}H_2O_2,OH^-]{\text{1)BMS, hexane}}$	 (97)		7
7		$\xrightarrow[\text{2)}H_2O_2,OH]{\text{1)BMS, hexane}}$	 (100)		7
8		$\xrightarrow[\text{2)}H_2O_2,OH^-]{\text{1)BMS, hexane}}$	 (94)		7
9		$\xrightarrow[\text{2)}H_2O_2,OH^-]{\text{1)BMS, hexane}}$	 (100) $<$1% cis		7

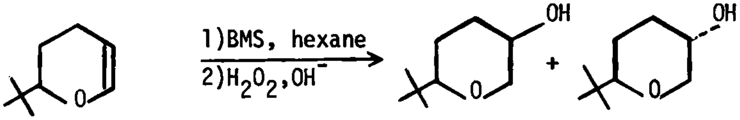
10  (85) 1a,7

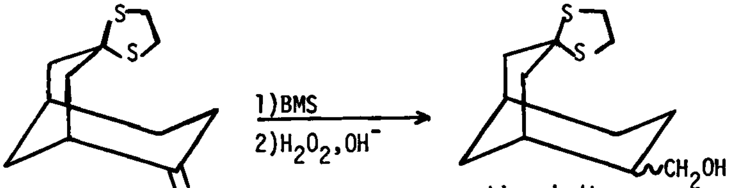
11  (92) 7

12  8,9

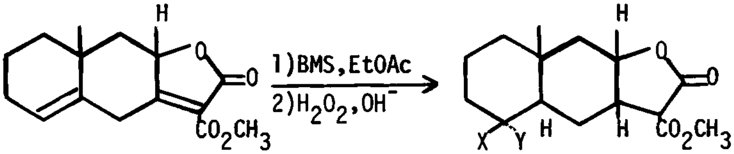
13 $(CH_3)_3CCH{=}CHD$ Z $\xrightarrow[2)H_2O_2,OH^-]{1)BD_3S(CH_3)_2,THF}$ $(CH_3)_3CCHDCHDOH$ threo (84) 10

14 $(CH_3)_3CCH{=}CHD$ E $\xrightarrow[2)H_2O_2,OH^-]{1)BD_3S(CH_3)_2,THF}$ $(CH_3)_3CCHDCHDOH$ erythro (85) 10

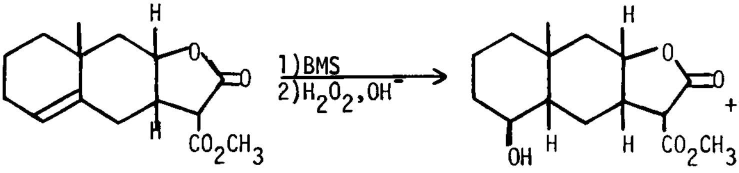
15  11

16  (78) 12

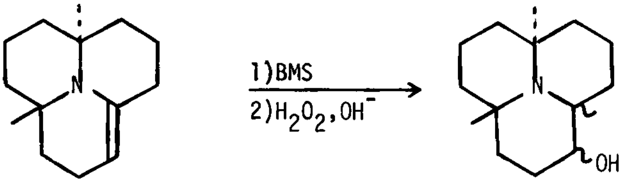
ratio *cis*/*trans* =2:3

17  13

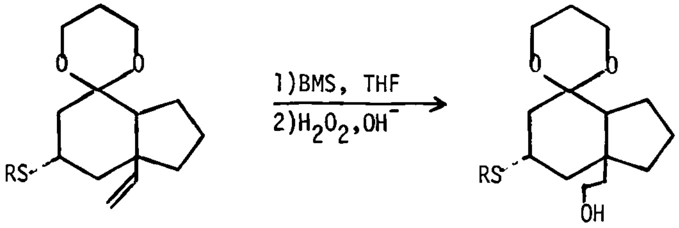
(a)X=H, Y=OH (32)
(b)X=OH, Y=H (5)
+ ca. 5% tertiary alcohol

18


(61) 13
+trace trans

19


(95) 14

20


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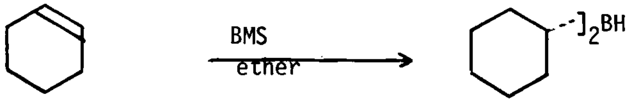
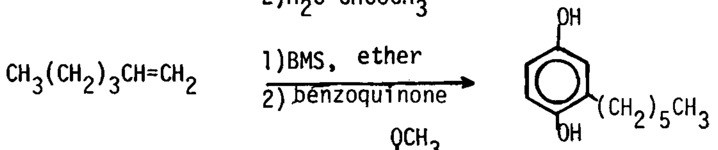
21


1a,15

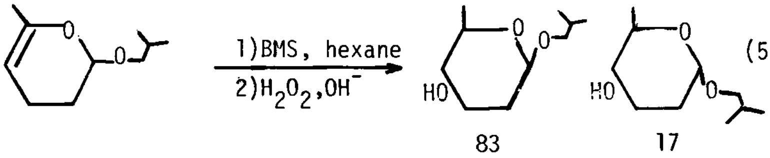
22 $CH_3(CH_2)_3CH{=}CH_2 \xrightarrow[2)\,H_2C{=}CHCOCH_3]{1)\,BMS,\ ether} CH_3(CH_2)_7COCH_3$ (81) 16

23


(96) 16

24 $R'CH{=}CH_2 \xrightarrow{BMS} R_3B \xrightarrow[2)\,C_2H_5OH, H_2O_2, OH^-]{1)\,Li\overset{OCH_3}{C}{=}CH_2} RCOCH_3$ 17

five examples(75-97)

25


(59) 47

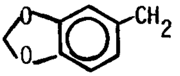
26 $$\begin{tikzcd} R'CH=CH_2 \arrow[r, "1)BMS,\ (C_2H_5)_2O", "2)LiC\equiv C(CH_2)_3CH_3"'] & R_3BC\equiv C(CH_2)_3CH_3 \arrow[d, "\substack{1)C_6H_5SeCl\\ 2)H_2O,(CH_3)_3NO\\ 3)H_2O_2}"] \\ & RCOCH=CH(CH_2)_3CH_3 \end{tikzcd}$$ 18

$R = CH_3CH_2$- (71)
$R = CH_3(CH_2)_5$- (61)
$R = CH_3(CH_2)_3$- (64)
$R = CH_3(CH_2)_4$- (60)
R = cyclopentyl (70)
R = cyclohexyl (71)

27 $R'CH=CH_2 \xrightarrow[2)pyr.HCl.CrO_3]{1)BMS,\ CH_2Cl_2} RCHO$ 19

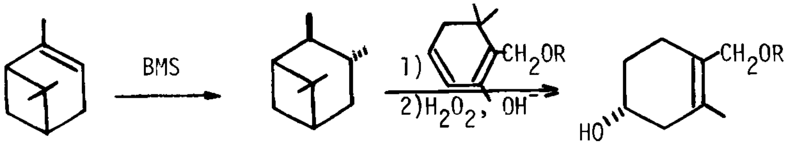
		ratio ald./ketone
$R = CH_3(CH_2)_4$-	(72)	19
$R = CH_3(CH_2)_6$-	(70)	16
$R = CH_3(CH_2)_8$-	(74)	19
$R = CH_3(CH_2)_{10}$-	(78)	17
$R = (CH_3)_3CCH_2$-	(64)	49
R = cyclohexyl-	(71)	99

28 $$\begin{tikzcd} (CH_3)_2C=CHCH_3 \arrow[r, "BMS"] & (CH_3)_2CHCH(CH_3)]_2BH \arrow[d, "RCH=CH_2"] \\ RCH_2CHO & Sia_2BCH_2CH_2R \arrow[l, "pyr.HCl.CrO_3"'] \end{tikzcd}$$ 20

$R = CH_3(CH_2)_5$- (71)
$R = CH_3(CH_2)_7$- (72)
$R = CH_3(CH_2)_9$- (69)
R = 3-cyclohexenyl (67)
$R = CH_3CO_2(CH_2)_3$- (63)
$R = CH_3O_2C(CH_2)_8$- (62)
R =  (55)

29 $(CH_3)_2C=CHCH_3 \xrightarrow{BMS} [(CH_3)_2CCH(CH_3)]_2BH$ 21,22 23,46

30 $(CH_3)_2C=CHCH_3 \xrightarrow[2)(C_2H_5)_3N]{1)BMS} (CH_3)_2CHC(CH_3)_2BH_2N(C_2H_5)_3$ 24

31				50
32	3β-hydroxyandrost-5-en-17-one $\xrightarrow{BMS}$	3β,6α-dihydroxy-5α-androstan-17-one	(76)	25
		3β,6β-dihydroxy-5β-androstan-17-one	(18)	

II. SELECTIVE REDUCTIONS

Investigations of selective reductions with BMS indicate similar capabilities as obtainable with BH_3·THF, the major difference being that the former should be utilized at room temperature or above.[1d-f] As in hydroborations, reductions may be conducted in a variety of solvents including hexane, toluene, ethyl ether, triglyme, methylene chloride and trimethylborate. This latter compound appears to be an important additive for the reduction of aromatic carboxylic acids.[27] BMS reacts with alcohol solvents to afford excellent yields of trialkylborates[28] (Eq. 2).

$$3ROH + BH_3S(CH_3)_2 \longrightarrow B(OR)_3 + S(CH_3)_2 + 3H_2 \qquad (2)$$

For reductive applications, Table III lists the expected products from treatment of several functional groups with borane, listed in approximate order of decreasing reactivity. All of these reductions have not as yet been explored using BMS, but, in analogy to BH_3·THF and other borane sources,[1e] should provide similar results.

The differences in reactivity exhibited by various substrates suggest that several useful selective reductions can be accomplished such as the reduction of carboxylic acids preferentially in the presence of nitriles, esters, nitro, etc. Several such selective converstions are grouped in Table IV along with other BMS reductions taken from the literature. Finally, BMS has been utilized to prepare poly(2-vinylpyridine)borane which, in turn, was used to reduce aldehydes and ketones.[45]

Table III. Functional Group Reductions With Borane[48]

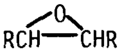
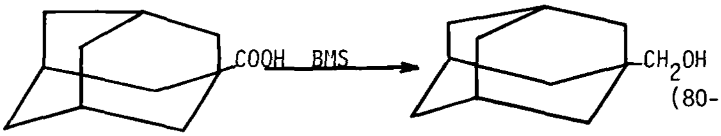
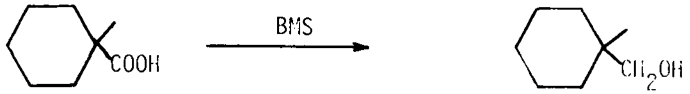
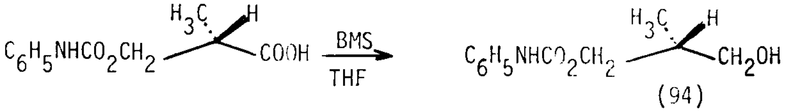
RCOOH	$\xrightarrow{\text{very fast}}$	RCH_2OH ·
RCH=CHR	$\xrightarrow{\text{very fast}}$	$RCH_2CH(B)R$
RCHO	$\xrightarrow{\text{fast}}$	RCH_2OH
R_2CO	$\xrightarrow{\text{moderate}}$	R_2CHOH
RC≡N	$\xrightarrow{\text{moderate}}$	RCH_2NH_2
$R_2C{=}NOH$	$\xrightarrow{\text{moderate}}$	R_2CHNH_2
	$\xrightarrow{\text{slow}}$	$RCHOHCH_2R$
$RCONH_2$	$\xrightarrow{\text{slow}}$	RCH_2NH_2
RCOOR'	$\xrightarrow{\text{slow}}$	RCH_2OH + R'OH
RCOCl	$\xrightarrow{\text{very slow}}$	(alcohol ?)
R-X	$\xrightarrow{\text{very slow}}$	N.R.
$R\text{-}NO_2$	$\xrightarrow{\text{very slow}}$	N.R.

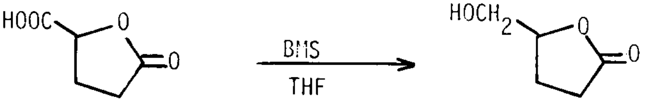
Table IV. Reductions of Various Groups With BMS

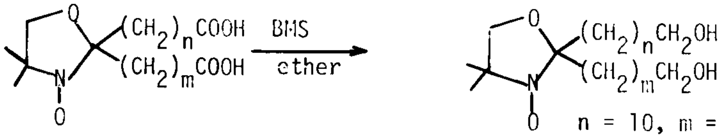
Entry	Reaction		Product(s) (% Yield)		Ref.
1	$CH_3(CH_2)_4COOH$	$\xrightarrow{\text{BMS}}$	$CH_3(CH_2)_4CH_2OH$		26
		ether	(100)		
		THF	(100)		
		toluene	(99)		
		hexane	(100)		
		triglyme	(91)		
		trimethylborate	(100)		
2	$CH_3(CH_2)_7COOH$	$\xrightarrow[\text{ether}]{\text{BMS}}$	$CH_3(CH_2)_7CH_2OH$	(65)	29
3	$Br(CH_2)_{10}COOH$	$\xrightarrow[\text{ether}]{\text{BMS}}$	$Br(CH_2)_{10}CH_2OH$	(95-98)	29
4			(80-90)		30

5  (80-90) 30

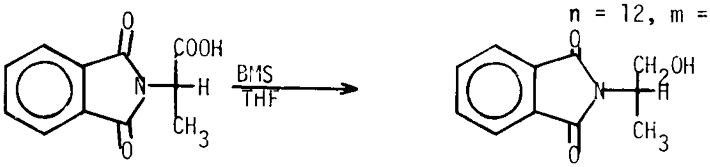
6 $(CH_3)_2C(COOH)_2 \xrightarrow{BMS} (CH_3)_2C(CH_2OH)_2$ (80-90) 30

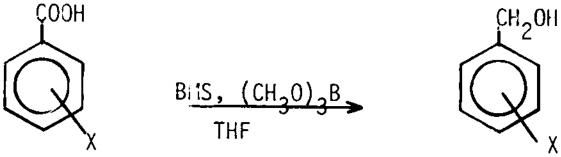
7  31-33

8  (84-ca. 97) 34,35

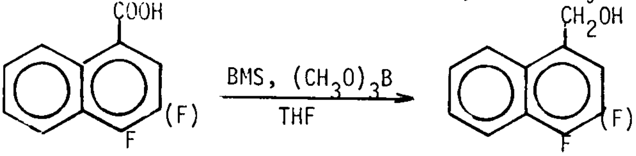
9  36

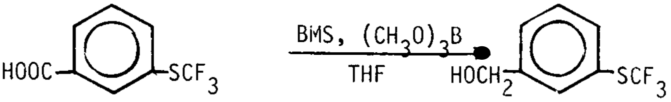
n = 10, m = 5 (96)
n = 12, m = 3 (90)

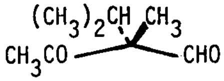
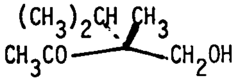
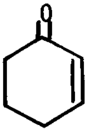
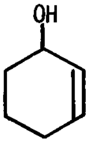
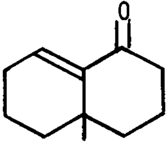
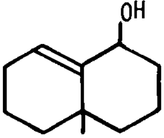
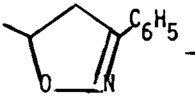
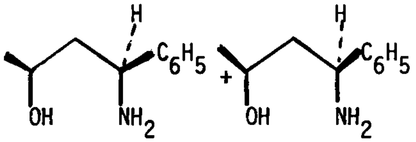
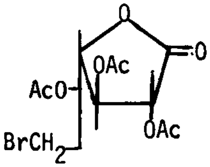
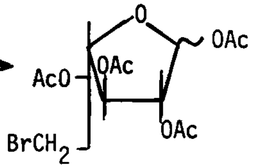
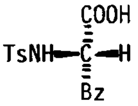
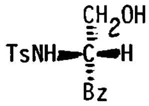
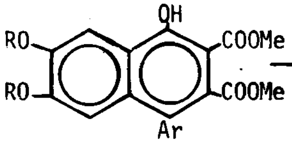
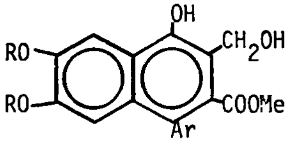
10  (60) 43

11  27

X = o-chloro (94)
X = o-bromo (88)
X = o-iodo (100)
X = m-hydroxy (99)
X = o-amino (94)
X = p-nitro (98)
X = 4,4'-sulfonyldi (99)

12  37

13  38

14		BMS / ether			39
15		BMS / THF		(94)	25
16	$C_6H_5CH{=}CHCHO$	BMS / THF	$C_6H_5CH{=}CHCH_2OH$	(82)	25
17		BMS / THF		(65)	25
18	17 -hydroxyandrost-4-en-3-one	BMS / THF	androst-4-en-3β,17β-diol	(79)	25
19	17 -hydroxyestr-4-en-3-one	BMS / THF	estr-4-en-3 ,17 -diol	(60)	25
20	$(CH_3)_3CCOCH{=}CHO^-$	BMS / THF	$(CH_3)_3CCHOHCH_2CH_2OH$	(76)	40
21		BMS / THF	 6:4 ratio		42
22		$[(CH_3)_2CH(CH_3]_2BH$ (from BMS); Ac_2O		(25)	23
23		BMS		(99)	49
24		BMS / THF			26

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