Tetrahedron Letters, Vol.32, No.24, pp 2759-2762, 1991
Printed in Great Britain

0040-4039/91 \$3.00 + .00
Pergamon Press plc

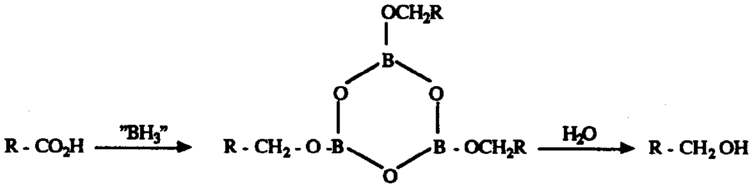
Reaction of Borane-dimethyl Sulfide Complex with Aromatic Acids : Access to Methyl Compounds or to Benzyl Dimethyl Sulphonium Salts.

H. LE DEIT, S. CRON and M. LE CORRE*

Laboratoire de Synthèse Organique, URA CNRS 415. Université de Rennes 1, Avenue du Général Leclerc, 35042 Rennes, France.

Abstract : In certain conditions, the action of borane dimethyl sulfide (BMS) with aromatic carboxylic acids leads to the corresponding methyl derivatives or, in the presence of BF_3, to the benzyl dimethyl sulphonium salts.

The reduction of carboxylic acids by boranes affords alcohols via the alkoxyboroxine intermediates[1].



Our previous work on borate esters[2] led us to re-examine the conditions for formation of the boroxine. In a paper published in 1974[3], Lane reported that borane dimethyl sulfide was less reactive towards carboxylic acids than BH_3 . THF. He recommended addition of methyl borate to increase the reaction rate.

We have carried out our experiments on the formation of boroxines at higher temperatures with an excess of BMS, avoiding the presence of borate esters by maintaining an efficient reaction rate. Under these new experimental conditions we have observed some unexpected results.

In many cases (**1a** - **1d**) the carboxylic acids give the methyl compound **4** as the principal product. (Table).

When *p*- hydroxy group is present (**1b**), a detailed investigation revealed that methyl derivative was the only product formed whatever the stoichiometry of BMS. This result indicates that the kinetic of formation of boroxine from some acids is slower than the reduction of this boroxine to the methyl compound. The aromatic derivates with electron withdrawing groups are not very reactive and in the case of **1e**, the methyl product was isolated in only 25 % yield.

The reduction of some carboxylic acids to the corresponding methyl compound has been previously reported by using B_2H_6 or BH_3 THF[4]. Our results show that the above reaction applies to a range of aromatic compounds.

Common synthetic reagent for the deoxygenation of aromatic acid is trichlorosilane[5]. The use of BMS is a less general but more simple reduction.

The activation of reduction power of Lewis borane-base complexes by boron trifluoride etherate has already been noted[6] and so we have re-examined the behaviour of some acids in the presence of one equivalent of boron trifluoride etherate.

Surprisingly, the addition of boron trifluoride etherate leads to a new reaction giving the benzyl sulphonium salt 5.

This reaction which occurs alongside the formation of the methyl product 4 can become preponderant with some acids by using a stoichiometric amount of BMS (see the table).

Synthesis of sulphonium salts by this process is, to our knowledge, the first example of a reaction in which BMS reacts as an electrophilic reagent (formation of boroxine) and then as a nucleophilic reagent : attack of boroxine. A probable mechanism which explains the above results is shown in scheme.

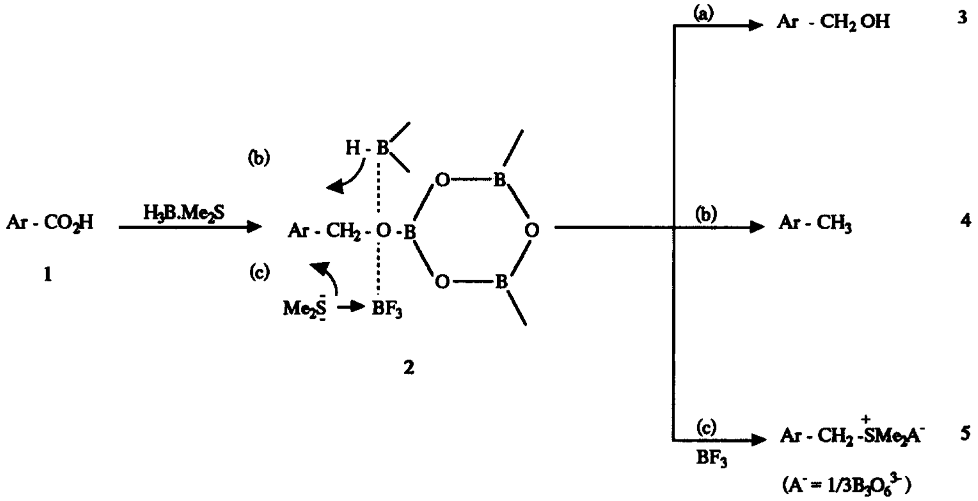


Table : Action of borane-dimethyl sulfide complex on the aromatic acids.

X - Ar - CO_2H 1		Solvent	BMS (a)	BF_3	Time (h) (b)	Yield (%) (c)
	X					Ar - CH_3
1a	4 - MeO	toluene	2	-	4	90
	"	$CHCl_2$-CH_2Cl	2	-	4	88
1b	4 - hydroxy	"	2.33	-	4	82
1c	4 - phenyl	C_6H_5Cl	2	-	4	45
1d	4 - amino	"	3	-	5	93
1e	2,4 - dichloro	"	2	-	4	25
						$Ar\,CH_2\overset{+}{S}(CH_3)_2A^-$ (d)
1c	4 - phenyl	$CHCl_2$-CH_2Cl	1	1	1	68
1e	2,4 - dichloro	"	1	1	1	65
1f	4-t - butyl	"	1	1	1	86

a) ratio : moles of BMS / mole of acid

b) after 15 min at room temperature the solution was refluxed

c) isolated products : all of the products were fully characterized by ^1H NMR spectra and physical constants (bp, mp).

d) The sulphonium compounds isolated as metaborate salts were compared with bromide analogues.

General procedure :

Borane-dimethyl sulfide was added at 0°C to a stirred suspension (or solution) of the carboxylic acid in a convenient solvent (Table). The reaction mixture was stirred for 15 min. and then refluxed. After 1-5 h the flask was cooled, 10 % aqueous sodium carbonate was added and the reaction mixture was stirred for 30 min. The organic layer was separated and the solvent was evaporated. The crude compound was distilled with a Kugelrohr apparatus. Sulphonium salts were obtained as above. Borane-dimethyl sulfide was added at 0° C. The reaction mixture was stirred at that temperature for 10 min and then boron trifluoride etherate was added. The sulphonium salts were isolated from the crude product by addition of diethyl ether.

REFERENCES

(1) Yoon N.M., Pak C.S., Brown H.C., Krishnamurthy S. and Stocky T.P., *J. Org. Chem.* 38, 2786 (1973).
Brown H.C. and Stocky T.P., *J. Am. Chem. Soc.* 99, 8218 (1977).

(2) Le Corre M. ,Gheerbrant E. and Le Deit H., *J. Chem. Soc., Chem. Commun.* 313 (1989).

(3) Lane C.F. , Myatt H.L., Daniels J. , Hopps H.B., *J. Org. Chem.* 39, 3052 (1974).

(4) Lane C.F., *Chemical Reviews*, 76, 773 (1976).

(5) Benkeser R.A. , Foley K.M., Gaul J.M. and Li G.S., *J. Am. Chem. Soc.* 92, 3232 (1970).

(6) Jones W.M. , *J. Am. Chem. Soc.* 82, 2528 (1950).

(Received in France 20 February 1991)