Sodium Borohydride Reduction of Alkoxythallated Compounds of Olefins

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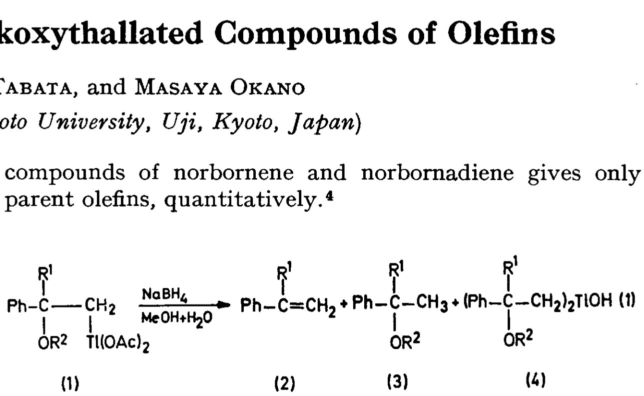
Summary Alkaline $NaBH_4$ reduction of alkoxythallated compounds of olefins gives a mixture of the parent olefins, alkyl ethers, and dialkylthallium compounds; hydrogen for replacement of thallium arises from the solvent and not from $NaBH_4$.

THE alkaline $NaBH_4$ reduction of oxymercurated compounds of olefins has been shown to proceed *via* formation of an organomercuric hydride (RHgH) which undergoes homolytic dissociation to produce R· and ·HgH radicals,[1,2] and that hydrogen for replacement of mercury arises from $NaBH_4$ and not from the solvent.[1-3] We report here the first example of alkaline $NaBH_4$ reduction of alkoxythallated compounds of olefins (**1**) and the fact that hydrogen for replacement of thallium arises from the solvent and not from $NaBH_4$. Reduction with $NaBH_4$ of acetoxythallated compounds of norbornene and norbornadiene gives only parent olefins, quantitatively.[4]



An aqueous alkaline solution of $NaBH_4$ (5 mmol) was added to a stirred solution of (**1**)† (10 mmol) in MeOH at 20 or 50 °C; after 1 h, a mixture of the parent olefin (**2**), alkyl ether (**3**), and dialkylthallium compound (**4**) was obtained [equation (1); Table 1]. When the di-isobutyrate analogue of (**1**) was used instead of the diacetate, only a

TABLE 1
Reduction of (**1**) *with* $NaBH_4$[a]

(1) R^1	(1) R^2	Temp. (t/°C)	React. Time/h	Products (% yield)[b] (2) + (3)	(2):(3)[c]	(4)[d]	(2) + (3) + (4)
H	Me	20	1	71	(92: 8)	14	85
H	Et	20	1	59	(75:25)	35	94
H	Pr^n	20	1	47	(80:20)	37	84
H	Pr^i	20	1	49	(72:28)	32	81
H	Me	50	1	79	(87:13)	6	85
H	Et	50	1	75	(75:25)	9	84
H	Pr^n	50	1	62	(77:23)	7	69
H	Pr^i	50	1	73	(65:35)	25	98
Me	Me	20	1	75	(98: 2)	0	75
Me	Et	50	1	81	(90:10)	0	81

[a] (**1**) (10 mmol), $NaBH_4$, (5 mmol), 3N-NaOH (20 ml), MeOH (40 ml). [b] Based on (**1**). [c] Determined by g.l.c. The structure of (**3**) was also determined by n.m.r. spectroscopy. [d] Isolated and determined as chloride after work-up with NaCl.

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† The synthesis of (**1**; R^1 = H, R^2 = Me) has already been reported (H. J. Kabbe, *Annalen*, **1962**, **656**, 204). The detailed synthesis, and structural determination of (**1**) by n.m.r. spectrometry will be reported elsewhere.

slight variation of the amount and the ratio of (**2**) and (**3**) was observed.

It was shown that a 1:1 ratio of (**1**) to reducing agent was sufficient for reduction to (**2**) and (**3**); use of excess of $NaBH_4$ favoured formation of (**4**). In all cases the inorganic thallium produced in the reduction was determined as TlCl and was equivalent to the sum of the amounts of (**2**) and (**3**) formed.

In order to ascertain the origin of hydrogen for replacement of the $Tl(OAc)_2$ group of (**1**), (**1**; $R^1 = H$, $R^2 = \text{Pr}^i$) was reduced with $NaBD_4$ or with $NaBH_4$ and MeOD or D_2O as solvent (see Table 2, which includes results for tetrahydrofuran, the usual solvent for oxymercuration–demercuration of olefins). These data clearly reveal that the hydrogen arises from the solvent and not from $NaBH_4$; *i.e.*, 1-isopropoxy-1-phenyl-2-deuterioethane [^{2}H]-(**3**) is formed only in deuterium-containing solvents. Reduction of the mercury analogue of (**1**; $R^1 = H$, $R^2 = \text{Pr}^i$) with $NaBD_4$ under similar conditions gave a high yield of [^{2}H]-(**3**) and no (**3**; $R^1 = H$, $R^2 = \text{Pr}^i$), which is consistent with previous results with other oxymercurials.

TABLE 2.

Reduction of (**1**; $R^1 = H$, $R^2 = \text{Pr}^i$) *with* $NaBD_4$ *or in deuteriated solvents.*[a]

Reducing agent (5 mmol)	Solvent (ml)		Products (% yield;[b] $R^1 = H$, $R^2 = \text{Pr}^i$)			
		(**2**)	(**3**)	[^{2}H]-(**3**)[c]	(**4**)	(**2**) + (**3**) + (**4**)
$NaBD_4$	MeOH + 3N-$NaOH/H_2O$ (40) (20)	51	29	0	18	98
$NaBH_4$	MeOD + 5N-$NaOD/D_2O$ (10) (15)	45	0	13	31	89
$NaBH_4$	THF + 3N-$NaOH/H_2O$ (30) (20)	48	4	0	37	89
$NaBH_4$	THF + 3N-$NaOD/D_2O$ (30) (20)	63	0	2	33	98

[a] (**1**) (10 mmol); 50°; 1 h. [b] Based on (**1**). (**2**), (**3**), and [^{2}H]-(**3**) were determined by g.l.c. [c] 1-Isopropoxy-1-phenyl-2-deuterioethane. Isolated by preparative g.l.c. and determined by n.m.r. spectroscopy.

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