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Kinetics and mechanism of oxidation of tri-n-butylstannyl alkoxides of benzhydrol and substituted benzhydrols by bromine in carbon tetrachloride

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Abstract

The tri-n-butylstannyl alkoxides (TBSA) of benzhydrols were prepared by treating the alcohols with tri-n-butyltin oxide (TBTO) and azeotropically removing the water. They were oxidised by bromine in carbon tetrachloride to the corresponding ketones. The oxidation was found to be a second order process. The effect of substituents on the rate was studied and the Hammett ρ was found to be -2.55 at 308 K. A mechanism is proposed.

Introduction

Several methods are available for the oxidation of secondary alcohols to ketones [1–3]. Tri-n-butyltin oxide (TBTO), a commercially available fungicide, has been utilised in the conversion of secondary alcohols and aromatic primary alcohols into the corresponding carbonyl compounds [4,5]. In this paper we report the results of a kinetic and mechanistic investigation of the oxidation of tri-n-butylstannyl alkoxides of benzhydrol and substituted benzhydrols by bromine in carbon tetrachloride.

Experimental

i. General. The solvents were of analytical grade and were distilled before use. Amber-coloured reaction vessels were used in order to avoid photochemical reactions, and reactions were carried out under dry nitrogen even though no differences in the rate constants were observed under aerobic conditions.

ii. Preparation of tri-n-butylstannyl alkoxides (TBSA). As a typical example the preparation of TBSA of benzhydrol (TBSAB) is described. A solution of benzhydrol (2.62 g, 20 mmol) and TBTO (5.58 g, 10 mmol) in dry benzene (70 ml) was refluxed and water removed azeotropically with a Dean–Stark apparatus [6]. Removal of the

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Table 1

Boiling point and mass spectral data for the TBSAs

TBSA [a] of	Boiling point (° C/mmHg)	Mass spectral data [b] (m/e) (Relative abundance (%))
Benzhydrol	140/0.3	57(90), 77(100), 183(90)
α-D-benzhydrol	142/0.4	57(100), 77(90), 184(70)
p-chlorobenzhydrol	136/0.3	57(100), 77(100), 217(90)
p-nitrobenzhydrol	133/04	57(100), 77(100), 183(60)
p-methylbenzhydrol	147/0.4	57(90), 77(90), 121(50), 91(50)
p-methoxybenzhydrol	151/0.8	57(100), 77(95), 134(60), 180(50)

[a] TBSA = tri-n-butylstannyl alkoxide. [b] Finnigan 4000 GE-MS spectrometer.

benzene in a rotary evaporator left the TBSAB, which was distilled (b.p. 140 ° C/0.3 mmHg, yield 3.4 g, 93%) then characterised by IR and NMR spectroscopy and mass spectrometry. The mass spectral data and boiling points are listed in Table 1.

iii. Kinetic method. The solutions of the substrate (TBSA) and bromine in carbon tetrachloride were kept in the thermostat at the planned reaction temperature for 2 h before being mixed. At appropriate times after mixing, 2 ml aliquots of the reaction mixture were removed and added to 10 ml of 5% potassium iodide in water and the residual bromine was estimated iodometrically. The pseudo first order rate constants were evaluated from the slopes of the plots of log [Br] vs. time. Second order rate constants were obtained from the k_1 values and the initial concentrations of TBSA. Reactions were also carried out under second order conditions and the corresponding rate constants evaluated from the plots of log $b(a-x)/a(b-x)$ against time. All experiments were carried out in duplicate, and rate constants were reproducible within $\pm 3\%$.

iv. Product analysis. The analysis of the product of oxidation of TBSAB is described here. The solution of TBSAB (3.72 g, 10 mmol) and bromine (AR, 1.6 g, 10 mmol) in dry carbon tetrachloride was stirred under dry nitrogen at room temperature for 2 h. The progress of the reaction was monitored by TLC (ether/n-hexane 1/2 silica gel), and when it was complete the CCl_4 was distilled off. The residual benzophenone was recrystallised from n-hexane and characterised as its 2/4 DNP derivative (m.p. 232° C; yield 3.2 g, 86%).

Results and discussion

1. The disappearance of bromine was found to be of first order in TBSA and in bromine. The total overall order was two.

2. There was no significant change in the rate in the presence of oxygen. (see Table 2).

3. Electron-releasing substituents enhance the rate of oxidation and electron-withdrawing groups lower it (Table 3). A satisfactory correlation with the σ-constants was observed, with a ρ value of -2.55 (correlation coefficient 0.99) at 308 K (Fig. 1). The large negative ρ value indicates that positive charge is developed in the transition state of the oxidation process.

4. The stoichiometry of the reaction system is 1/1.

Table 2

Oxidation rates of tri-n-butylstannyl alkoxides of benzhydrol and α-D-benzhydrol by bromine under aerobic and anaerobic conditions ([TBSAB] [a] 2.4×10^{-3} *M*, [TBSABD] [b] 2.4×10^{-3} *M*, [Br] 1.8×10^{-3} *M*, Solvent CCl_4)

Substrate	10^3 k_2 dm^3 mol^{-1} s^{-1}			
	303 K		308 K	
	in the presence of		in the presence of	
	oxygen	nitrogen	oxygen	nitrogen
TBSAB	3.43	3.43	5.04	5.04
TBSABD	1.27	1.27	2.63	2.63

[a] TBSAB = tri-n-butylstannyl alkoxide of benzhydrol, [b] TBSABD = tri-n-butylstannyl alkoxide of α-D-benzhydrol.

Table 3

Effect of substituents on the rate of oxidation ([TBSA] 2.4×10^{-3} *M*, [Br] 1.8×10^{-3} *M*, Solvent CCl_4)

TBSA [a] of	10^4 k_2 dm^3 mol^{-1} s^{-1}					
	293 K	298 K	303 K	308 K	313 K	318 K
Benzhydrol	14.0	22.0	34.3	50.4	74.0	124.0
p-chlorobenzhydrol	3.5	5.8	14.1	21.0	32.0	60.0
p-nitrobenzhydrol	0.16	0.28	0.56	0.92	1.45	2.74
p-methylbenzhydrol	33.0	49.6	89.0	132.0	205.0	308.0
p-methoxybenzhydrol	105.0	158.0	260.0	352.0	–	–

[a] TBSA = tri-n-butylstannyl alkoxide.

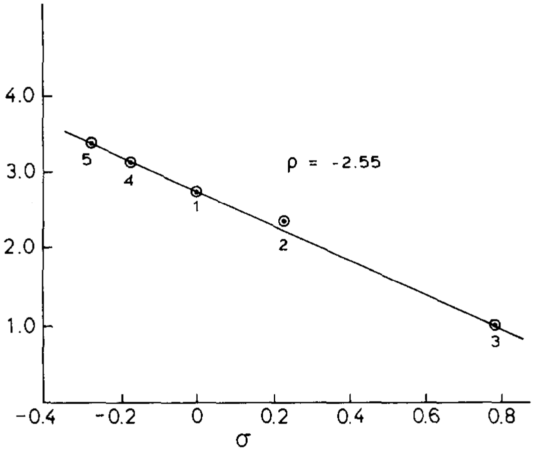

Fig. 1. Plot of k_2 against σ for reaction of $(XC_5H_4)(Ph)(CHOSnBu_3$ with Br_2 in CCl_4; the numbering of the points is: 1, X = H; 2, X = *p*-Cl; 3, X = *p*-NO_2; 4, X = *p*-Me; 5, X = *p*-OMe.

5. A considerable kinetic isotope effect was observed for the TBSAB system, the presence of an α-D substituent lowering the rate (Table 4). It thus seems that no hypobromite intermediate is involved.

6. Activation parameters were determined for each of the alkoxides studied

Table 4

Kinetic isotope effect at different temperatures ([TBSAB] [a] 2.4×10^{-3} *M*, [TBSABD] [b] 2.4×10^{-3} *M*, [Br] 1.8×10^{-3} *M*, Solvent CCl_4

Temperature	293 K	298 K	303 K	308 K	313 K	318 K
k_H/k_D	3.5	3.3	2.1	1.9	1.5	1.3

[a] TBSAB = tri-n-butylstannyl alkoxide of benzhydrol. [b] TBSABD = tri-n-butylstannyl alkoxide of α-D-benzhydrol.

Table 5

Activation parameters in the oxidation of TBSAs [a] of benzhydrols by bromine

TBSA of	ΔH (kcal mol^{-1})	ΔG (kcal mol^{-1})	ΔS (cal deg^{-1} mol^{-1})
Benzhydrol	13.7	17.6	−12.8
p-chlorobenzhydrol	15.7	17.6	−6.2
p-nitrobenzhydrol	16.5	17.7	−3.5
p-methylbenzhydrol	11.6	17.6	−19.4
p-methoxybenzhydrol	9.7	17.5	−25.8

[a] TBSA = tri-n-butylstannyl alkoxide.

(Table 5). The rate constants at various temperatures show a good isokinetic relationship.

7. An ESR study did not reveal the presence of any radical species during the reactions.

8. The observation of a significant positive isotope effect, a large negative Hammett ρ value, a negative entropy of activation, and the absence of any evidence of radical intermediates is consistent with a six-membered cyclic transition state involving a C–H cleavage, as shown in Scheme 1. This mechanism is made possible by the ability of tin to raise its coordination number to five; this enables the forming bromide ligand to coordinate to the tributyltin moiety in the transition state.

Scheme 1

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