

Solvolytic of 3,4-Dihalogeno-3,4-dihydro-2H-naphtho[1,2-b]pyrans and 1,2-Dihalogeno-2,3-dihydro-1H-naphtho[2,1-b]pyrans

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J. Chem. Research (S),
1999, 640–641
J. Chem. Research (M),
1999, 2717–2726

Rates and activation parameters are obtained for the hydrolysis of *trans*-3*ax*,4*ax*-dihalogeno-3,4-dihydro-2*H*-naphtho[1,2-*b*]pyrans and *trans*-1*ax*,2*ax*-dihalogeno-2,3-dihydro-1*H*-naphtho[2,1-*b*]pyrans¹ and the methanolysis of the latter compounds in acetone–water and acetone–methanol, respectively.

It has been shown that hydrolysis of a 3,4-dihalogeno-3,4-dihydro-2*H*-naphtho[1,2-*b*]pyran or of a 1,2-dihalogeno-2,3-dihydro-1*H*-naphtho[2,1-*b*]pyran, involved the replacement of the chlorine or bromine atom adjacent to the aromatic ring and that substitution of the second halogen atom, if bromine, required far more forcing conditions, which did not remove the analogous chlorine atom. Studies have been made of the mechanism of solvolysis of *trans*-3-*ax*,4*ax*-dihalogeno-3,4-dihydro-2*H*-naphtho[1,2-*b*]pyrans and *trans*-1*ax*,2*ax*-dihalogeno-2,3-dihydro-1*H*-naphtho[2,1-*b*]pyrans and shown that the reactions involved a carbonium ion intermediate and that the mechanism was dependent on steric and neighbouring group effects. Empirical equations were obtained for both series of compounds, expressing the experimental rate constant as a function of temperature and for the 3,4-dihalogeno-3,4-dihydro-2*H*-naphtho[1,2-*b*]pyrans as a function of the *Y* values for acetone–water.

Experimental

Materials.—Commercial acetone and Analar methanol were purified.² Water (10 cm³) or methanol (10 cm³) was added to a standard solution of the dihalogeno compound in acetone (90 cm³) at 252–309 or 251 K, respectively. 3,4-Dihalogeno-3,4-dihydro-2*H*-naphtho[1,2-*b*]pyrans **1** and 1,2-dihalogeno-2,3-dihydro-1*H*-naphtho[2,1-*b*]pyrans **3** were recrystallised from light petroleum (bp 40–60 °C).

Product Analysis.—The dihalogeno compounds 3,4-dihalogeno-3,4-dihydro-2*H*-naphtho[1,2-*b*]pyrans and 1,2-dihalogeno-2,3-dihydro-1*H*-naphtho[2,1-*b*]pyrans (0.9–1.0 g) **1** and **3** and 20% aqueous acetone (100 cm³) were boiled for 24 h. Following isolation with diethyl ether the products were chromatographed on activated alumina from diethyl ether–light petroleum (bp 40–60 °C) (1:2) to give 3-halogeno-3,4-dihydro-2*H*-naphtho[1,2-*b*]pyran-4-ols (92.7–93.8%) and 2-halogeno-2,3-dihydro-1*H*-naphtho[2,1-*b*]pyran-1-ols **2** and **4** (91.9–93.5%) respectively. Methanolysis gave the corresponding methoxy derivatives **5** and **6** as the sole products.

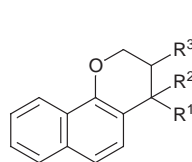
Table 2 Rate constants for the hydrolysis of *trans*-3,4-dihydro-2*H*-naphtho[1,2-*b*]pyrans and *trans*-2,3-dihalogeno-2,3-dihydro-1*H*-naphtho[2,1-*b*]pyrans

Compound	xH ₂ O ^a	10 ⁵ k ₁ /s ⁻¹ (T/K)					
3,4-Dibromo-3,4-dihydro-2 <i>H</i> -naphtho[1,2- <i>b</i>]pyran	0.175	15.7 (286.0)	38.7 (294.2)	98.5 (303.3)			
	0.311	8.11 (264.6)	25.5 (273.8)	58.1 (280.2)	—		
4-Bromo-3-chloro-3,4-dihydro-2 <i>H</i> -naphtho[1,2- <i>b</i>]pyran	0.311	8.58 (278.3)	31.7 (289.6)	45.2 (293.4)			
	0.499	12.7 (265.1)	19.2 (267.7)	37.2 (273.6)	64.5 (277.3)		
3,4-Dichloro-3,4-dihydro-2 <i>H</i> -naphtho[1,2- <i>b</i>]pyran	0.311	4.4 (299.0)	7.04 (303.9)	13.1 (309.6)			
	0.499	16.2 (287.0)	29.8 (294.0)	67.0 (298.7)	99.0 (303.3)		
3-Bromo-4-chloro-3,4-dihydro-2 <i>H</i> -naphtho[1,2- <i>b</i>]pyran	0.311	5.4 (285.9)	15.8 (296.4)	56.2 (308.0)			
	0.499	6.23 (268.0)	20.9 (277.4)	62.3 (286.1)	—		
1,2-Dibromo-2,3-dihydro-1 <i>H</i> -naphtho[2,1- <i>b</i>]pyran	0.311	6.37 (252.9)	21.5 (262.4)	39.9 (267.6)	87.5 (274.2)		
1-Bromo-2-chloro-2,3-dihydro-1 <i>H</i> -naphtho[2,1- <i>b</i>]pyran	0.311	0.98 (263.8)	3.76 (263.2)	14.4 (272.9)	46.1 (282.9)		
1,2-Dichloro-2,3-dihydro-1 <i>H</i> -naphtho[2,1- <i>b</i>]pyran	0.311	0.60 (273.2)	2.05 (282.8)	6.92 (293.0)	20.3 (303.0)		
2-Bromo-1-chloro-2,3-dihydro-1 <i>H</i> -naphtho[2,1- <i>b</i>]pyran	0.311	3.25 (273.0)	9.82 (282.5)	35.9 (292.9)	99.4 (303.0)		

^axH₂O represents molar fraction of water.

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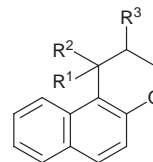
Kinetic measurements.—Rates of liberation of protons were measured at temperatures controlled to ±0.1 K. A sampling procedure was used throughout. Aliquot portions (5.0 cm³) were quenched in ice-cold acetone (150 cm³) and titrated for acid (lacmoid indicator). Blank experiments showed that the quenching was efficient, that the reaction was irreversible and that only one halogen atom was displaced in the reaction. The plot of *t* against log(*a* - *x*) was found to be linear for the solvolysis of each dihalogeno derivative, indicating that the reaction was of the first order (*a* is the initial concentration of the dihalogeno derivative and *x* the decrease after the lapse of time *t*). The rate constants were calculated at various temperatures (Table 2).



1 R¹ = R³ = halogen, R² = H

2 R¹ = OH, R² = H, R³ = halogen

5 R¹ = alkoxy, R² = H, R³ = halogen



3 R¹ = R³ = halogen, R² = H

4 R¹ = OH, R² = H, R³ = halogen

6 R¹ = alkoxy, R² = H, R³ = halogen

Initial concentrations of dihalogeno derivatives were usually ≈0.05 M, though a series of experiments showed that the rate constant did not vary significantly over the range 0.01–0.05 M. All runs were performed in duplicate and the rate constant tested for significance by the 't' test.³ Reactions were followed to 80% completion.

The values of the rate constants in Table 2 were used to obtain 'a' and 'b' (Table 4) in the equation log k₁ = a + b/T, which was used to calculate the rate constants at 293 K. The apparent activation energy of hydrolysis of each dihalogeno compound, was calculated by the method of least squares applied to the Arrhenius equation

$$E = \left(2.303 \log_{10} \frac{k_2}{k_1} \times R \times T_1 \times T_2 \right) / (T_2 - T_1)$$

and is recorded in Table 4. Also the values of k₁, can be used to calculate the free energy of activation, ΔG*, for the hydrolysis of each

Table 4 Values of a and b in $\log k_1 = a + b/T$ and of E for the hydrolysis of *trans*-3,4-dihalogeno-3,4-dihydro-2*H*-naphtho[1,2-*b*]pyran and *trans*-1,2-dihalogeno-2,3-dihydro-1*H*-naphtho[2,1-*b*]pyran in acetone–water

Compound	$x\text{H}_2\text{O}^a$	$E/\text{kJ mol}^{-1}$	a	$-b$
3,4-Dibromo-3,4-dihydro-2 <i>H</i> -naphtho[1,2- <i>b</i>]pyran	0.175	78.1 ± 1.4	10.447	4080
	0.311	76.4 ± 1.2	10.873	3990
4-Bromo-3-chloro-3,4-dihydro-2 <i>H</i> -naphtho[1,2- <i>b</i>]pyran	0.311	75.4 ± 1.6	10.085	3938
	0.499	77.0 ± 1.5	11.307	4024
3,4-Dichloro-3,4-dihydro-2 <i>H</i> -naphtho[1,2- <i>b</i>]pyran	0.311	79.4 ± 1.7	9.508	4149
	0.499	85.6 ± 1.8	11.750	4473
3-Bromo-4-chloro-3,4-dihydro-2 <i>H</i> -naphtho[1,2- <i>b</i>]pyran	0.311	77.4 ± 1.9	9.846	4039
	0.499	82.0 ± 1.1	11.763	4281
1,2-Dibromo-2,3-dihydro-1 <i>H</i> -naphtho-[2,1- <i>b</i>]pyran	0.311	70.7 ± 1.7	10.424	3698
1-Bromo-2-chloro-2,3-dihydro-1 <i>H</i> -naphtho[2,1- <i>b</i>]pyran	0.311	79.5 ± 1.2	11.332	4146
1,2-Dichloro-2,3-dihydro-1 <i>H</i> -naphtho[2,1- <i>b</i>]pyran	0.311	81.6 ± 1.1	10.380	4261
2-Bromo-1-chloro-2,3-dihydro-1 <i>H</i> -naphtho[2,1- <i>b</i>]pyran	0.311	78.9 ± 0.9	10.606	4121

^a $x\text{H}_2\text{O}$ represents molar fraction of water

Table 7 Values for m and f in $\log k_1 = mY + f$

Halide	3,4-Dibromo	4-Bromo-3-chloro	3,4-Dichloro	3-Bromo-4-chloro
m	0.81	0.76	0.98	0.95
$-f$	1.01	1.72	2.61	1.95
Eqn.	(1)	(2)	(3)	(4)

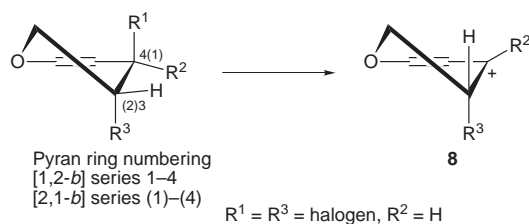
dihalogeno compound using the equation,⁴

$$\Delta G^* = 19.151 T \log \frac{kT}{h} - 19.151 T \log k_1$$

where k is the Boltzmann constant and h is Planck's constant. Values of ΔG^* for the hydrolysis at 293 K and the methanolysis at 251 K of *trans*-1,2-dihalogeno-2,3-dihydro-1*H*-naphtho[2,1-*b*]pyrans have been reported.

Discussion

Comparison of the observed vicinal coupling constants with those predicted by the Karplus $\cos^2 \phi$ equation, for the measured dihedral angles obtained from Dreiding models, show that, in all the 3,4-dihalogeno-3,4-dihydro-2*H*-naphtho[1,2-*b*]pyrans **1** and 1,2-dihalogeno-2,3-dihydro-1*H*-naphtho[2,1-*b*]pyrans **2** studied, the most probable configuration is that with the “3- and 4- and (1-) and (2-)” substituents *trans* and axial **7**.¹



The effects of the neighbouring benzophenylene group, neighbouring halogen and the oxygen atom on the mechanism of the solvolysis have been discussed. Formation of the transition state **8** relieves the eclipsing strain along the C3–C4 bond ([1,2-*b*] compounds) and the C(2)–C(1) bond ([2,1-*b*] compounds) as caused by the oxygen atom. Comparison of the rate coefficients for the hydrolysis of 1,2-dihalogeno-2,3-dihydro-1*H*-naphtho[2,1-*b*]pyrans in acetone–water shows that the ratio $k_1(\text{dibromo})/k_1(\text{dichloro})$ is approximately 3 times greater than the ratio $k_1(\text{bromo})/k_1(\text{chloro})$ for the hydrolysis of some monohalogeno-compounds.⁶

The relationship between $\log k_1$, (k_1 at 298.2 °C is estimated from Table 2) and the Y values of the acetone–water solvents⁷ for the 3,4-dihalogeno-3,4-dihydro-2*H*-naphtho[1,2-*b*]pyrans are adequately represented by plots (1)–(4) (Table 7), which is of the form $\log k_1 = mY + f$.

The slope, m , in plots (3) and (4), obtained for the two 4-chloro compounds, compare favourably with the value 0.9–1.0 observed for unimolecular ($\text{S}_{\text{N}}1$) reactions;⁸ m in plots (1) and (2) is almost within this range, suggesting that some intermediate type of mechanism may be operating ($m \approx 0.4$ is the value observed in typical $\text{S}_{\text{N}}2$ reactions⁸). The values of the thermodynamical parameters are of the usual order found for unimolecular reactions.⁹

For all the dihalogeno[2,1-*b*]pyrans the activation energy was larger in 90% acetone–water than in 90% acetone–ethanol.

Techniques used: ¹H NMR and MS

References: 9

Tables 1–7: Analytical and kinetical data

Received, 30th March 1999; Accepted, 22nd July 1999
Paper E/9/02551K

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