Studies of Pyrazines. Part 8.[1] Pyrolysis of 2-Alkoxypyrazines; Substituent Effects and Stereospecificity

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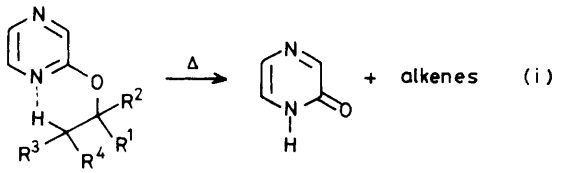
Twelve 2-alkoxypyrazines (R = Pr^i, Bu^s, 1,2-dimethylpropyl, 1,2,2-trimethylpropyl, t-butyl, t-pentyl, 1,1,2-trimethylpropyl, 1,1,2,2-tetramethylpropyl, octyl, neopentyl, ±-*erythro*- and ±-*threo*-2-deuterio-1,2-diphenylethyl) have been pyrolysed to elucidate the substituent effects on the rate and stereospecificity of the reaction. Activation parameters (log A and E_a) for the first eight compounds listed were determined. The reaction was accelerated by α-substitution; this was a combination of both polar and steric effects. The stereospecificity of the reaction was high.

It is well known that a pyrazine ring shows high thermal and oxidation stability, as a pyridine ring does.[2] Pyrazine itself was only partially decomposed in the vapour phase, even at 1 270 K, to acetylene and hydrogen cyanide.[3] Previously, we reported the thermal stability of 2- and 2,5-disubstituted pyrazine derivatives,[4] and proved that 2,5-dialkylpyrazines were more thermally stable than 2,5-dialkoxy-, 2-alkoxy-, 2-alkylthio-, and 2-alkylamino-pyrazines. Moreover, alkylpyrazine derivatives with long alkyl chains have been used as synthetic lubricants with high thermal and oxidation stability.[5] However, it is complicated to prepare thermally stable alkylpyrazines or the precursor compounds in good yield and/or in pure form.[6,7] On the other hand, it is easy to prepare 2-alkoxypyrazines (1) in good yield and in the pure form, although (1) undergoes an intramolecular thermal-hydrogen abstraction reaction on heating to give pyrazin-2-one (2) and alkenes [equation (i)],[4,8] as does *O*-ethylcaprolactim.[9] This thermal instability of (1) seems to be dependent on the structure of the alkoxy group. Behun and Kan have reported the thermal and oxidation stability of many kinds of pyrazine derivatives,[5b] but it is difficult to find kinetic investigations of the pyrolysis of pyrazine derivatives and analogous compounds, except for esters and 2-ethoxypyridine.[10]

In this paper, we wish to describe the substituent effect on the pyrolysis of eight 2-alkoxypyrazine derivatives (1a)—(1h) in which the substitution at the α- and β-positions have been varied, and to report the stereospecificity of the reaction [equation (i)]. The decrease in (1) obeyed good first-order kinetics so that activation parameters (log A and E_a) could be obtained. Polar and steric substituent effects on the rate constants were correlated to Taft's substituent constants; and the high stereospecificity was found in the reaction of (1l).



(1), R = $CR^1R^2CHR^3R^4$ (2)

Group I: a, R = Pr^i; b, R = Bu^s; c, R = 1,2-dimethylpropyl; d, R = 1,2,2-trimethylpropyl
Group II: e, R = Bu^t; f, R = t-pentyl; g, R = 1,1,2-trimethylpropyl; h, R = 1,1,2,2-tetramethylpropyl
Group III: i, R = octyl; j, R = neopentyl; k, R^1 = H, R^2 = R^3 = Ph, R^4 = D; l, R^1 = H, R^2 = R^3 = Ph, R^4 = H, and H in (1) is replaced by D

Results and Discussion

Pyrolysis of 2-Alkoxypyrazines (1).—The rate constant, k, for a unimolecular homogeneous gas-phase pyrolysis is expressed by equation (ii), where x is the conversion of (1)

$$k = \frac{1}{t_r} \cdot \ln \frac{1}{1-x} \qquad \text{(ii)}$$

and t_r is the residence time. The decreases of (1a)—(1h) obeyed good first-order kinetics. In Table 1, the activation parameters (log A and E_a; correlation coefficients for the Arrhenius plots, r, *ca.* 0.999) determined are compared with those of the corresponding alkyl acetates,[11,12] which have been considered to proceed through a concerted polar six-membered cyclic transition state.[13] The activation parameters of (1) are not too different from those of the alkyl acetates and those of 2-ethoxypyridine [log (A/s^{-1}) = 12.22, E_a/kcal mol^{-1} = 46.8].[10] The following facts, [(*a*)—(*d*)], support the conclusion that our reaction also proceeds through an analogous six-membered cyclic transition state [equation (i)].[14] (*a*) In a mass spectrum of 2-(2,2,2-trideuterioethoxy)pyrazine at 16 eV,[15,16] most of the hydrogen (98.6%) was abstracted from the β-position (Scheme 1); (*b*) 2-octyloxypyrazine (1i) yielded no isomers except for oct-1-ene; (*c*) 2-neopentyloxypyrazine (1j), which had no β-hydrogen, resisted the pyrolysis stubbornly; and (*d*) a plot of log $(k_{rel})_{acetate}$ *versus* log$(k_{rel})_{2\text{-alkoxypyrazine}}$ gave a straight line with a slope [8] of 1.0.

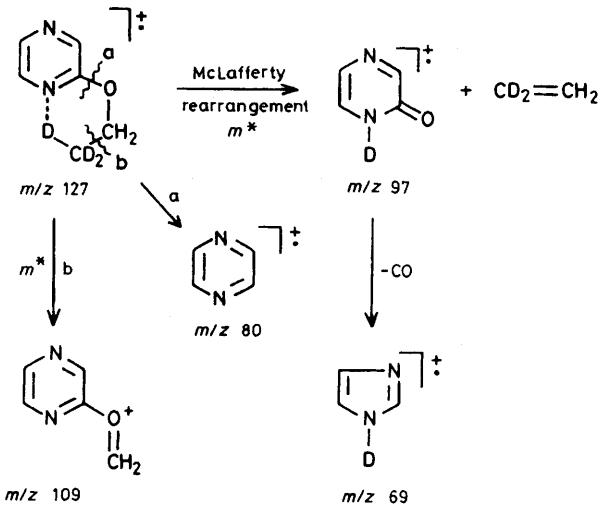
Relative rate constants, k_{rel} and k'_{rel}, (corrected with a statistical factor) at 500 °C, shown in Table 1, indicate that the tertiary compounds (1) (group II) are more reactive than the secondary (group I), as occurs for acetates.[17] Although the substitution effect on the rate in group I is not so remarkable as in group II, it is well beyond experimental error and clearly shows that substitution increases the rate, as occurs in the case of group II. Since substitution at the β-position is expected to have less effect on the rate than substitution at the α-position,[18] the change in the rate in Table 1 would result from substitution on the α-carbon. In order to clarify the rate-acceleration effect, log k_{rel} was plotted against ^{13}C n.m.r. chemical shifts of the α-carbon, but a linear relationship was not obtained. However, Taft's treatment [equation (iii)] [19]

$$\log (k_{rel}) = \rho_I \sigma_I + \delta E_s \ (\text{or} = \rho^* \sigma^* + \delta E_s) \qquad \text{(iii)}$$

Table 1. Activation parameters and relative rate constants for pyrolysis of 2-alkoxypyrazines (1a)—(1h) and those of the corresponding alkyl acetates

Group	Compound (1)	log (A/s^{-1}) [a]	E_a/kcal mol^{-1} [a]	Temperature range (°C) [a]	k_{rel} [b]	k'_{rel} [b,c]
I	(a)	13.2 (0.1)	47.1 (0.1)	465—525	1.00	1.00
		[13.4] [d]	[46.34] [d]	[313—362] [d]		
	(b) [e]	12.9 (0.2)	45.7 (0.6)	468—495	1.25	1.50
		[13.3] [d]	[46.6] [d]	[303—359] [d]		
	(c) [e]	14.1 (0.1)	49.8 (0.3)	459—487	1.37	2.06
	(d) [e]	13.2 (0.2)	47.2 (0.7)	457—484	0.94	1.88
II	(e)	12.6 (0.1)	39.2 (0.1)	357—387	42.9	28.6
		[13.15] [d]	[40.0] [d]	[241—291] [d]		
	(f) [e]	13.5 (0.1)	40.2 (0.3)	357—389	178	133
		[13.43] [d]	[40.26] [d]	[228—289] [d]		
	(g) [e]	15.2 (0.3)	45.6 (0.8)	346—387	265	227
		[14.22] [f]	[41.3] [f]	[287—337] [f]		
	(h) [e]	15.6 (0.3)	46.0 (0.8)	331—360	514	514

[a] Correlation coefficients for the Arrhenius plots r *ca.* 0.999, standard deviation in parentheses, and literature value for the corresponding acetates in brackets. [b] At 500 °C. [c] Corrected by a statistical factor. [d] Quoted from ref. 11. [e] By a relative rate method. [f] Quoted from ref. 12.



Scheme 1.

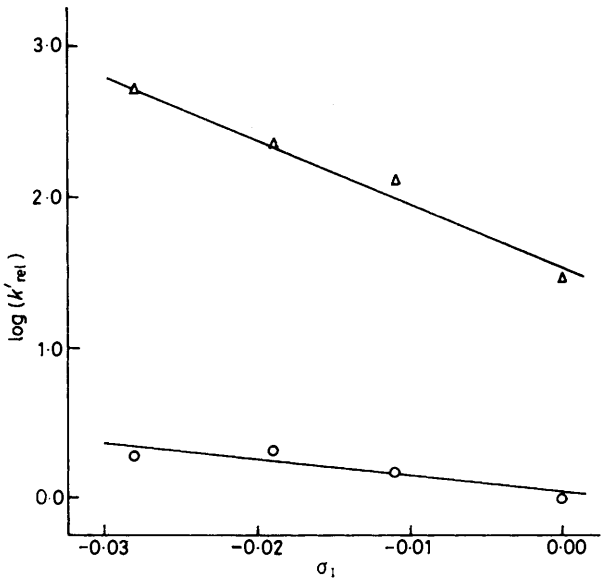
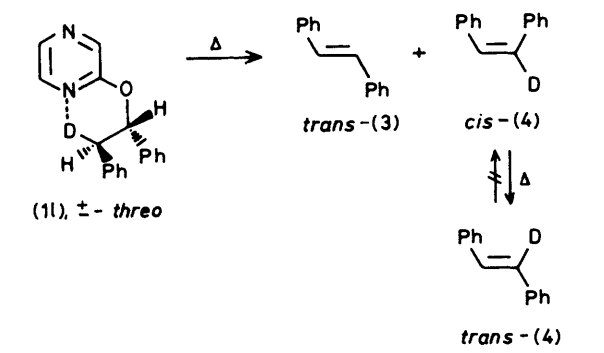


Figure 1. Taft plot for pyrolysis of secondary (group I) and tertiary (group II) 2-alkoxypyrazines (1). Group I, (1a)—(1d) (circles, from right to left); group II, (1e)—(1h) (triangles, from right to left). The slopes of the lines, ρ_I, are −11 for group I (correlation coefficient r = 0.90) and −44 for group II (r = 0.99)

seemed hopeful. Although there was no correlation with the steric substituent constants (E_s) alone, a reasonably good correlation (Figure 1) is found with the polar substituent constants σ_I[19d,19e] to give ρ_I values of −11 (correlation coefficient r = 0.90) for group I, and −44 (0.99) for group II. The Taft's σ^* values gave more scattered plots than did the σ_I values. If δ values were assumed to be −0.19 (or −0.25) for group I and −0.22 (or −0.40) for group II, improved correlations ($r_{max.}$ = 0.996 or 0.998; 0.997 or 0.996) were obtained to give ρ_I (or ρ^*) values of −21 (or −2.2) and −56 (or −6.1), respectively. Although such an approach is purely artificial until ρ_I or ρ^* can be independently determined, it is obvious that the substituent effects on the rate are a combination of both polar and steric contributions. The negative sign of ρ_I or ρ^* is indicative of polar acceleration by substituents and of the transition state with a carbocation character of the α-carbon. On the other hand, the negative sign of δ may be indicative of steric acceleration by the substituents on the α-carbon.

Stereospecificity.—The stereochemical behaviour of (1) in the reaction was investigated through the pyrolysis of ±-



Scheme 2.

Table 2. Pyrolysis of ±-*erythro*- and ±-*threo*-2-(2-deuterio-1,2-diphenylethoxy)pyrazines, (1k) and (1l) [a]

Compound (1)	$^2H_1$ purity of (1) (%) [b]	Stilbene composition [% (g.c.)] *trans*	*cis*	$^2H_1$ content in *trans* product (%)	Stereospecificity [c]
(k)	84.3			61.1	
(l)	92.4	94.9	5.1	7.6	0.877

[a] At 220 °C for 7 h. [b] From mass spectrum. [c] Not corrected by isotope effect.

Table 3. Yields and physical and spectral properties for 2-alkoxypyrazines (1)

Compd. (1)	Yield (%)	B.p. (°C/mmHg)	U.v. (EtOH) λ/nm	ε/l mol^{-1} cm^{-1}	I.r.[a] ν/cm^{-1}	M.s.[b] *m/z*	Found (%) (required) C	H	N
(b)	82	90.5/24.0	213	12 000	3 060	152	63.01	7.84	18.43
			281	4 790	1 584			$C_8H_{12}ON_2$	
			295	4 170	1 380		(63.13	7.95	18.41)
(c)	84 [c]	104/23.5	213	12 900	3 055	166	65.26	8.40	16.91
			281	5 130	1 580			$C_9H_{14}ON_2$	
			294	4 470	1 390		(65.03	8.49	16.85)
					1 380				
(d)	96 [c]	89/7.5	214	11 400	3 050	180	66.63	9.23	15.35
			280	4 800	1 583			$C_{10}H_{16}ON_2$	
			295	4 200	1 380		(66.63	8.95	15.54)
					1 370				
(e)	41 [c]	76.5/19.0	214	11 900	3 070	152	63.18	7.92	18.42
			279	5 130	1 570			$C_8H_{12}ON_2$	
			297	3 620	1 255		(63.13	7.95	18.41)
(f)	33	114/22.2	213	13 200	3 055	166	65.14	8.54	16.89
			280	5 370	1 584			$C_9H_{14}ON_2$	
			296	4 070	1 390		(65.03	8.49	16.85)
					1 370				
(g)	23 [c]	109/21.0	216	11 300	3 050	180	66.53	8.88	15.56
			282	5 000	1 580			$C_{10}H_{16}ON_2$	
			295	3 500	1 385		(66.63	8.95	15.54)
					1 375				
(h)	30 [c]	m.p. 55.0—56.5 [d]	215	11 000	3 060 [e]	194	67.75	9.40	14.26
			283	4 800	1 580 [e]			$C_{11}H_{18}ON_2$	
			296	3 600	1 365 [e]		(68.00	9.34	14.42)
					1 195 [e]				
(i)	47	154/15.0	212	9 910	3 050	208	69.19	9.75	13.12
			280	4 600	1 585			$C_{12}H_{20}ON_2$	
			295 (sh)		1 380		(69.19	9.68	13.45)
(j)	62 [c]	101/25.0	212	12 600	3 055	166	65.18	8.46	16.61
			280	5 370	1 584			$C_9H_{14}ON_2$	
			294	4 470	1 195		(65.03	8.49	16.85)
(k)	55 [c]	m.p. 89.9—90.5 [f]	281	8 510	3 035 [g]	277			
			296	6 900	1 602 [g]				
					1 585 [g]				
(l)	60	m.p. 90.2—91.5 [h]	281	8 510	3 030 [g]	277			
			296	6 900	1 600 [g]				
					1 582 [g]				

[a] Neat liquid film. [b] $M^{+\cdot}$. [c] THF was employed as a solvent. [d] Purified by sublimation, *ca.* 40 °C at 20 mmHg. [e] In acetone. [f] From ether. [g] KBr disk. [h] From ethanol.

erythro- and ±-*threo*-2-(2-deuterio-1,2-diphenylethoxy)-pyrazines (1k) and (1l) (at 220 °C for 7 h in sealed Pyrex tubes).[20,21] The reaction mixture of (1l) (conversion, *ca.* 13%) included *cis*- and *trans*-stilbenes (*cis* : *trans* = 5.1 : 94.2), (2), and the unreacted starting material. The *trans*-stilbene was isolated by means of preparative h.p.l.c. and its deuterium content was determined by m.s.; 7.6% of the deuterium in the starting material was retained in the *trans*-product (Table 2). This fact indicates that the *trans*-product is composed of *trans*-stilbene [*trans*-(3)] and α-deuterio-*trans*-stilbene [*trans*-(4)], and that the *trans*-(4) was formed from *cis*-(4) through thermal *cis*–*trans* isomerization (Scheme 2).[22] Generally, the thermal isomerization of *cis*-stilbene to the *trans*-isomer takes place easily, but its reverse reaction is difficult without light.* Therefore, the stereospecificity in the pyrolysis of (1l) is estimated to be 0.877 at 220 °C (without correction by either the isotope effect or thermal decomposition of stilbenes [20]).

The ±-*erythro*-isomer (1k) was also pyrolysed in the same manner, and 61.1% of deuterium was retained in the product. Such an unexpectedly low deuterium content should result from the low isotope purity of the starting material (1k) (see Tables 2 and 4). If the reaction was initially caused by a radi-

* Downing and Wright have reported that *trans*-stilbene does not isomerize at 330—340 °C to the *cis*-isomer,[23] while Jones and Schmelts have observed the isomerization reaction at 700 °C.[24] Therefore, the *trans*-(4) should not isomerize to the *cis*-(4) under our experimental conditions (200 °C, 7 h).

Table 4. ^{1}H N.m.r. spectra of 2-alkoxypyrazines (1) [a]

Compd. (1)	δ (*J*/Hz) [b,c]
(b)	0.98 (3 H, t, 7.0, CH_2CH_3), 1.33 (3 H, d, 5.5, $CHCH_3$), 1.52—1.92 (2 H, m, CH_2), 5.12 (1 H, se, 5.5, CH), 8.4 (2 H, m, Py), 8.15 (1 H, d, 1.4, Py)
(c)	0.98 (3 H, d, 6.6, CH_3), 0.99 (3 H, d, 6.6, CH_3), 1.27 (3 H, d, 6.6, $OCHCH_3$), 1.97 (1 H, o, 6.6, CH), 5.02 (1 H, qn, 6.6, OCH), 8.03 (2 H, m, Py), 8.13 (1 H, d, 1.4, Py)
(d)	0.98 [9 H, s, $C(CH_3)_3$], 1.24 (3 H, d, 6.6, $CHCH_3$), 4.97 (1 H, q, 6.6, CH), 8.0 (2 H, m, Py), 8.14 (1 H, d, 1.4, Py)
(e) [d]	1.56 (9 H, s, CH_3), 7.88 (2 H, m, Py), 7.95 (1 H, d, 1.5, Py)
(f)	0.92 (3 H, t, 7.5, CH_2CH_3), 1.55 (6 H, s, CH_3), 1.96 (2 H, q, 7.5, CH_2), 8.00 (2 H, m, Py), 8.06 (1 H, d, 1.3, Py)
(g)	0.95 [6 H, d, 7.0, $CH(CH_3)_2$], 1.53 [6 H, s, $C(CH_3)_2$], 2.49 (1 H, sp, 7.0, CH), 7.97 (2 H, m, Py), 8.06 (1 H, d, 1.4, Py)
(h)	1.07 [9 H, s, $C(CH_3)_3$], 1.60 [6 H, s, $C(CH_3)_2$], 7.99 (2 H, m, Py), 8.06 (1 H, d, 1.1, Py)
(i) [d]	0.89 (3 H, t, 5.9, CH_3), 1.15—1.55 (10 H, m, CH_2), 1.75 (2 H, m, 6.6, β-CH_2), 4.24 (2 H, t, 6.6, α-CH_2), 7.9 (2 H, m, Py), 8.07 (1 H, d, 1.6, Py)
(j) [d]	1.02 (9 H, s, CH_3), 3.95 (2 H, s, CH_2), 7.97 (2 H, m, Py), 8.15 (2 H, d, 1.8, Py)
(k)	3.36 (1 H, d, 8.0, CHD), [e,f] 6.23 (1 H, d, 8.0, OCH), [e,f] 7.2—7.3 (10 H, m, Ph), 7.96 (2 H, m, Py), 8.23 (1 H, d, 1.4, Py)
(l)	3.13 (1 H, d, 5.7, CHD), [f] 6.23 (1 H, d, 5.7, OCHPh), [f] 7.2—7.3 (10 H, m, Ph), 7.96 (2 H, m, Py), 8.23 (1 H, d, 1.4, Py)

[a] 100 MHz in $CDCl_3$, internal Me_4Si. [b] s, Singlet; d, doublet; t, triplet; q, quartet; qn, quintet; se, sextet; sp, septet; o, octet; m, multiplet. [c] Py, Pyrazine proton; Ph, phenyl proton. [d] Measured in CCl_4. [e] Including 11.4% of CH_2 signal of the undeuteriated isomer ($^2H_0$ isomer). [f] $\Delta\nu_{AB}$ and ν_X, 23 and 623 Hz; J_{AB}, J_{AX}, J_{BX}, $\Delta\nu_{AB}$, and ν_X in a spectrum of $^2H_0$ isomer 12.7, 5.49, 8.03, 22.0, and 617 Hz, respectively.[25]

Table 5. ^{13}C N.m.r. spectra of 2-alkoxypyrazines (1) [a]

Compd. (1)	δ [b]
(a)	21.8 (CH_3), 68.9 (OCH), 136.0 (Py–C), 136.4 (Py–C), 140.4 (Py–C), 159.9 [Py–C(2)]
(b)	9.7 (CH_2CH_3), 19.1 ($CHCH_3$), 28.9 (CH_2), 73.6 (OCH), 136.0 (Py–C), 136.4 (Py–C), 140.4 (Py–C), 160.3 [Py–C(2)]
(c)	16.2 (CH_3), 17.9 (CH_3), 18.3 ($OCHCH_3$), 32.9 [$CH(CH_3)_2$], 76.7 (OCH), 136.0 (Py–C), 136.5 (Py–C), 140.4 (Py–C), 160.4 [Py–C(2)]
(d)	14.3 (CH_3), 25.9 ($OCHCH_3$), 34.6 (quat. C), 79.0 (OCH), 135.9 (Py–C), 136.4 (Py–C), 140.3 (Py–C), 160.5 [Py–C(2)]
(e)	28.4 (CH_3), 81.0 (OC), 135.8 (Py–C), 137.7 (Py–C), 139.9 (Py–C), 160.4 [Py–C(2)]
(f)	8.3 (CH_2CH_3), 25.8 (CH_3), 33.8 (CH_2), 83.4 (OC), 135.8 (Py–C), 137.7 (Py–C), 140.0 (Py–C), 160.5 [Py–C(2)]
(g)	17.4 [$CH(CH_3)_2$], 22.9 [$C(CH_3)_2$], 36.4 (CH), 86.1 (OC), 135.8 (Py–C), 137.7 (Py–C), 140.0 (Py–C), 160.5 [Py–C(2)]
(h)	20.4 (CH_3), 25.3 [$OC(CH_3)$], 38.9 (quat. C), 87.5 (OC), 135.8 (Py–C), 138.0 (Py–C), 139.9 (Py–C), 160.8 [Py–C(2)]
(j)	26.6 (CH_3), 31.6 (quat. C), 75.8 (OCH), 136.1 (Py–C), 136.3 (Py–C), 140.4 (Py–C), 160.8 [Py–C(2)]
(l)	42.3, 43.1, and 43.9 (t, CDH), 78.0 (OCHPh), 126.4 (Ph–C), 126.6 (Ph–C), 127.7 (Ph–C), 128.2 (Ph–C), 129.5 (Ph–C), 136.0 (Py–C), 136.5 (Py–C), 137.1 (Ph–C), 140.3 (Py–C), 159.4 [Py–C(2)]

[a] FT mode with complete proton decoupling in $CDCl_3$. [b] Py–C, pyrazine ring carbon; Ph–C, benzene ring carbon.

cal α-fission of the oxygen–carbon ether linkage, the deuterium contents in the stilbenes produced from (1k) and (1l) should be equal to *ca.* 50% (without isotope-effect correction). However, they are different from each other. This high stereospecificity in the reaction gives support to the presence of a concerted six-membered cyclic transition state [equation (i) and Scheme 2], as do the kinetic data. Regiospecificity or regioselectivity of the reaction [equation (i)] was not examined in this work.

Experimental

All the m.p.s and b.p.s are uncorrected. The u.v. spectra were recorded on a Hitachi EPS-3T spectrophotometer, and the i.r. spectra on a Hitachi model 260-10 spectrophotometer. The ^{1}H n.m.r. spectra were recorded with either a JEOL SNM-FX-100 or a JNM 4H-100 spectrometer for solutions in deuteriochloroform, and the ^{13}C n.m.r. spectra were recorded with the former spectrometer in FT mode with complete proton decoupling at ambient temperature. The chemical shifts are reported in δ (internal standard Me_4Si). The mass spectra were recorded with a Hitachi RMU-7M double-focusing mass spectrometer at 70 or 16 eV. The unpublished u.v. and n.m.r. data are summarized in Tables 3,4, and 5. The analytical and kinetic g.c. determinations were carried out with a Shimadzu GC-4CPF apparatus equipped with a 2 m by 4 mm glass column of 10% silicone GE SE-30 liquid phase on Shimalite W support (60—80 mesh), except for the pyrolysis of (1a), (1e), and (1i) (10% PEG 20M on Diasolid A), and operated in a temperature-programmed mode (80 ⟶ 180 °C, 6 °C min^{-1}). The peak area was calculated on a Shimadzu ITG-2A type digital integrator. The preparative g.c. was performed on the same apparatus using a 2 m by 6 mm copper column of the former packing. The preparative and analytical h.p.l.c. were performed on a Hitachi 634 apparatus equipped with a 0.5 m by 2 mm column of Hitachi gel No. 3010 eluted with methanol–acetone (85 : 15 v/v). Elemental analyses were performed at the Institute of Physical and Chemical Research.

Materials.—All 2-alkoxypyrazines (1a)—(1j) were prepared by the method reported previously.[4] In the case of hindered alcohols, potassium was employed instead of sodium. Yields and physical properties are summarized in Table 3. Alcohols, except for 3,3-dimethylbutan-2-ol, 2,3,3-trimethylbutan-2-ol, ±-*erythro*- and ±*threo*-2-deuterio-1,2-diphenylethanol, and 2,2,2-trideuterioethanol, were commercially available.

3,3-*Dimethylbutan*-2-*ol*. To 4.9 g (0.12 mol) of lithium aluminium hydride in 250 ml of dry ether were slowly added 15.3 g of t-butyl methyl ketone in 40 ml of dry ether, and the resultant mixture was refluxed for 17.5 h. The usual treatment of the reaction mixture gave an oily product. Yield 74%, b.p. 116 °C (lit.,[26] 120—121 °C).

2,3,3-*Trimethylbutan*-2-*ol*. To 9.0 g (0.37 mol) of magnesium (activated by stirring for 8 h in a stream of nitrogen) in 200 ml of dry ether were added 42.6 g (0.3 mol) of methyl iodide in

40 ml of dry ether under an atmosphere of nitrogen at such a rate as to maintain gentle reflux, and the mixture was refluxed for four more hours. To the resultant mixture were slowly added 25 g (0.25 mol) of t-butyl methyl ketone in 40 ml of dry ether, and the mixture was refluxed for 10 h. After hydrolysis of the complex formed, the product was extracted with ether. The extract was then washed with aqueous $Na_2S_2O_3$ and evaporated to give the solid hydrate of the alcohol in good yield. The hydrated alcohol in ether was treated with 30 g of barium oxide at 100 °C for 1 h and distilled to give the water-free alcohol. Yield 89%, b.p. 134 °C (lit.,[27] 131—132 °C), m.p. 15—17 °C.

±-erythro-2-*Deuterio*-1,2-*diphenylethanol*. *trans*-Stilbene oxide was reduced by lithium aluminium deuteride in dry ether. Yield 68%, m.p. 64—64.5 °C (from light petroleum) (lit.,[20] 64.4—65.4 °C), deuterium content 90.7%-d_1; $\nu_{max.}$ (KBr) 3 325 (OH), 3 125 (Ar–H), and 2 860 cm^{-1}; *m/z* (16 eV) 200 ($M^{+\cdot}$-d_2, 0.52%), 199 ($M^{+\cdot}$-d_1, 3), 198 ($M^{+\cdot}$-d_0, 0.25), 108 (PhC^+HOH, 9), and 93 ($PhCH_2D^+$, 100).

±-threo-2-*Deuterio*-1,2-*diphenylethanol*. *cis*-Stilbene (10 g, 0.054 mol) was oxidized with *m*-chloroperbenzoic acid in CH_2Cl_2 at 25 °C.[28] Yield 80%, m.p. 36—37 °C (from hexane) (lit.,[20] 37—37.5 °C); $\nu_{max.}$ (KBr) 3 080, 3 060, 3 025, 2 970, 1 260, 928, and 840 cm^{-1}. The *cis*-stilbene oxide thus obtained was reduced by lithium aluminium deuteride in the same way as the *trans*-isomer. Yield 83%, m.p. 63.5—64.9 °C (from hexane) (lit.,[20] 64.4—65.4 °C), deuterium content 80.5%-d_1; $\nu_{max.}$ (KBr) 3 300 (OH), 3 020, and 2 860 cm^{-1}; *m/z* (16 eV) 200 ($M^{+\cdot}$-d_2, 0.54%), 199 ($M^{+\cdot}$-d_1, 2), 198 ($M^{+\cdot}$-d_0, 0.30), 107 ($PhCHO^+$, 69), 93 ($PhCH_2D^+$, 100), and 79 (49).

±-erythro- *and* ±-threo-2-(2-*Deuterio*-1,2-*diphenylethoxy*)*pyrazine*, (1k) *and* (1l). To the corresponding alcohol (3.6 g, 18 mmol) in 20 ml of THF were added potassium (0.64 g, 16.4 mg-atom) in small portions, and the resultant mixture was warmed (50 °C). After cooling to room temperature, 2-chloropyrazine (2 g, 17.5 mmol) was added with stirring. The mixture was refluxed for 24 h, and poured into saturated aqueous ammonium chloride, and then completely extracted with ether to give the product after evaporation of the solvent. Yield and physical and spectral properties of (1k) and (1l) are shown in Tables 3, 4, and 5. Deuterium contents are shown in Table 2.

2,2,2-*Trideuterioethanol*. To 4.5 g (0.12 mol) of lithium aluminum hydride in dry ether (200 ml) were slowly added 16.2 g (0.12 mol) of phenyl 2,2,2-trideuterioacetate in dry ether (50 ml), which was prepared from tetradeuterioacetic acid by a reported method.[29] The resultant mixture was refluxed for 20 h and treated with wet ether, water, and then dilute NaOH solution. The ethereal layer gave 0.3 g of pure product, yield 5.4%.

2-(2,2,2-*Trideuterioethoxy*)*pyrazine*. To the corresponding alcohol (0.3 g, 6.3 mmol) in THF (3 ml) was added potassium (0.7 g, 5.9 mg-atom), and the mixture was treated with 2-chloropyrazine (6.3 mmol) in the manner described previously. Yield 60% (g.c.). For analysis, the pure product was isolated by means of preparative g.c. [purity 99.9% (g.c.), deuterium content 82.2%-d_3]; *m/z* (16 eV) 129 (2.4%), 128 (10.4), 127 ($M^{+\cdot}$-d_3, 84.4), 126 ($M^{+\cdot}$-d_2, 18.2), 125 ($M^{+\cdot}$-d_1, 6.7), 124 ($M^{+\cdot}$-d_0, 6.1), 111 (1.3), 110 (7.9), 109 ($C_4H_3N_2OCH_2^+$, 100), 98 (5.6), 97 ($C_4H_3DN_2O^{+\cdot}$, 66.6), 96 ($C_4H_4N_2O^{+\cdot}$, 20.0), 82 (3.3), 81 (18.0), 80 ($C_4H_4N_2^{+\cdot}$, 63.7), 69 (33.7), and 68 (18.1). The data show that 96.8% of the hydrogen was abstracted from the β-position.[15]

Apparatus.—The pyrolyser used in kinetic runs was designed in our laboratory, and is similar to a model described by Cramers and Keulemans, who have reported that silver does not cause a catalytic thermal decomposition of organic compounds.[30] The reactor was coupled with a gas chromatograph, in series, in order to analyse all of the products formed in the reaction. A residence time, t_r, is calculated by equation (iv) with the assumption that a change in the number of moles induced by the reaction has very little influence on t_r in this system, where f_c is a correction factor, F is the flow rate of the

$$t_r = f_c \cdot \frac{V}{F} \quad \text{(iv)}$$

$$f_c = \frac{P_2}{P_1}\cdot\frac{T_1}{T_2}\cdot(1 + 3\alpha\cdot\Delta T) \quad \text{(v)}$$

carrier gas at temperature T_1 (K) under atmospheric pressure P_1; P_2 is the pressure in the reactor at T_2 (K), and α is the thermal expansion coefficient of silver, $10^5\alpha/K^{-1} = 2.05$ (temperature range: 273.15—1 173.15 K).[31] Pyrolysis of ethyl acetate at 520 °C allowed us to determine an effective volume of the reactor, V, from which an effective length of the reactor at room temperature was calculated (1 059 mm). It was in excellent agreement with the actual value (1 054 mm).

Kinetics.—Under the experimental conditions employed in this work, conversion of a substrate has been reported to vary with its sample size.[30] However, the sample size smaller than 0.1 μl did not affect the conversion of either ethyl acetate or (1) at 521.6 °C. Therefore, 0.06 μl was employed as the sample size in all kinetic runs.

Eight 2-alkoxypyrazines (1a)—(1h) were pyrolysed by one of the following two methods in kinetic runs, and no by-products except (2) and alkenes were observed in all cases.

Method A, absolute rate method. The mixture (0.06 μl) of (1a) or (1e) with an appropriate internal standard (*o*-xylene or mesitylene) was injected with a micro injector into the reactor heated previously to the reaction temperature. The decrease of (1) agreed well with first-order kinetics. The temperature ranges, activation parameters, and relative rate constants (k_{rel}, k'_{rel}) are shown in Table 1.

Method B, relative rate method. The pyrolysis of the other 2-alkoxypyrazines (1b)—(1d) and (1f)—(1h) was performed by a relative rate method using *o*-xylene as an internal standard, and (1a) or (1e) as a reference substance. The results are shown in Table 1.

Pyrolysis of 2-*Octyloxypyrazine* (1i).—The compound (1i) was pyrolysed at 550 °C. Only oct-1-ene was found as a product in the pyrolysate; (2) was undetectable when a PEG 20M column was used.

Pyrolysis of 2-*Neopentyloxypyrazine* (1j).—When (1j) was heated at 555.6 °C (t_r = 3.68 s), the destruction of (1j) was smaller than 8%, and small amounts of four products were formed. Most of (1j) was recovered.

Pyrolysis of ±-erythro- *and* ±-threo-2-(2-*Deuterio*-1,2-*diphenylethoxy*)*pyrazine*, (1k) *and* (1l), *in Preparative Scale*.—One gram of (1k) or (1l) was divided into ten parts, and each part was pyrolysed in an evacuated sealed Pyrex tube (d_{out} = 8 mm, l = 50 mm) at 220 ± 1 °C for 7 h at the same time, using an electrically heated metal block with ten holes (d = 9 mm). Products from one tube were analysed by means of h.p.l.c. (or g.c.) to calculate the yield of *trans*-stilbene; from the others the *trans*-stilbene was isolated by means of preparative h.p.l.c. The deuterium content was determined by m.s. (Table 2). Conversion of (1k), *ca.* 35% (h.p.l.c.); yield of *trans*-stilbene, 73.4% (h.p.l.c.) [based on the consumed (1k)]. Conversion of (1l), *ca.* 13% (g.c.), *cis*–*trans* ratio of the stilbenes in the reaction mixture, 5.1 : 94.9.

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