Kinetics of Reactions in Heterocycles. Part XV.[1] Reactions of 2-, 6-, or 8-Methylthio-1-, -3-, -7-, or -9-methylpurines and Related Compounds with Methoxide Ions in Methanol

By **Rodney J. Badger** and **Gordon B. Barlin,*** Medical Chemistry Group, John Curtin School of Medical Research, Australian National University, Canberra, Australia

Kinetics have been measured and Arrhenius parameters calculated for the reactions of some 2-, 6-, or 8-methylthio-1-, -3-,-7-, or -9-methylpurines, 2-methylthio-1 (and 3)-methyl-1,3,5-triazaindene, and 2-methylsulphonyl-1-methylbenzimidazole with methoxide ions in methanol. The positional order of reactivity in the 1-methylpurines was 6 > 2 > 8 and in the 3-methylpurines 6 > 8.

KINETICS of reactions of substituted 7- and 9-methylpurines towards nucleophiles have been examined previously.[2-7] However no quantitative data are available in substituted 1- and 3-methylpurines but qualitative studies in the polysubstituted compounds [8,9] have been recorded, and some reactions of 2-, 6- and 8-monosubstituted 1- and 3-methylpurines with hydroxide ions have been described.[10] In this paper we report kinetic studies of reactions of some 2-, 6-, and 8-methylthio-1-, -3-, -7-, and -9-methylpurines, and of 2-methylthio-1-, and -3-methyl-1,3,5-triazaindene and 2-methylsulphonyl-1-methylbenzimidazole for comparison with methoxide ions in methanol. This nucleophilic system was chosen to give a measure of the reactivity in the substituted 1- and 3-methyl series because of observed ring opening reactions with hydroxide ions in water.[10] Of the purines examined, 1- and 3-methyl-8-methylthio- and 7- and 9-methyl-2-methylthio-purines were unreactive towards 0.5N-sodium methoxide at 50° for 24 h. In the kinetic reactions with methoxide ions, smooth conversions to the corresponding methoxy-compounds occurred and the products were either isolated or identified by their u.v. spectra except for 6-methoxy-1-methylpurine which could not be isolated but gave a stable u.v. spectrum and was converted in aqueous alkali to 6-hydroxy-1-methylpurine which was characterised.

Typical kinetic runs {Table 1 [given in Supplementary Publication No. SUP 21748 (3 pp.) †].} indicated that

† Details of Supplementary Publications are given in Notice to Authors No. 7 in *J.C.S. Perkin II*, 1975, Index issue. Items less than 10 pp. are supplied as full size copies.

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TABLE 2

Kinetic results for the reactions of methylthio-*N*-methylpurines and related compounds with methoxide ions in methanol

Temp. (°C) [a]	10^4[MeO$^-$]/M	10^5[Azine]/M	10^3k [b]	10^3k corr. [c]	$t_{\frac{1}{2}}$ [d]	$t_{\frac{1}{2}}/t_{\frac{1}{2}}'$ [e]	Analyt. λ [f]/nm
			2-Methylthio-1-methylpurine [g]				
29.4	522	63.1	1.724	1.744			248
40.2	548	73.1	5.28	5.41	2 403	1.99	248
40.2	274	36.55	5.30	5.42	4 793		248
49.6	548	74.6	11.76	12.07			248
			6-Methylthio-1-methylpurine [g]				
22.55	518	3.995	4 249	4 261			308
31.1	517	4.935	6 610	6 703			308
40.9	516	5.91	11 380	1 162	11.88		308
40.9	258	2.95	11 560	1 181	23.04	1.94	308
			6-Methylthio-3-methylpurine [g]				
29.4	532	185.6	0.939	0.952			312
39.4	505.5	192.8	2.621	2.68			312
47.9	505.5	188.0	5.889	6.100	2 352		312
47.9	252.75	94.4	5.848	6.058	4 738	2.01	312
			6-Methylthio-9-methylpurine [g]				
60.9	1 067.5	111.39	0.309	0.324			287
71.45	1 095	111.39	0.840	0.893			287
79.7	1 067.5	111.39	1.750	1.884	3 720		287
79.7	533.75	55.695	1.735	1.866	7 508	2.02	287
			6-Methylthio-9-β-D-ribofuranosylpurine [g]				
61.0	1 013	117.8	0.580 1	0.608 7			287
69.7	1 013	117.8	1.217	1.293			287
80.25	1 013	117.8	3.059	3.294	2 244		287
80.25	506.5	58.9	2.967	3.20	4 627	2.06	287
			8-Methylthio-7-methylpurine [g]				
19.6	478	118.6	1.851	1.851			293
29.6	548	97.4	4.74	4.80			293
38.3	478	103	10.07	10.31	1 448		293
38.3	239	51.5	9.95	10.19	2 931	2.02	293
			8-Methylthio-9-methylpurine [g]				
29.6	1 013	200.6	0.661 5	0.668 8			289
40.0	1 013	184.0	1.707	1.748			289
49.25	1 095	181.3	3.796	3.925	1 675		289
49.25	547.5	90.67	3.818	3.945	3 331	1.99	289
			2-Methylthio-1-methyl-1,3,5-triazaindene [h]				
80.3	1 045	134.3	64.84	69.81			277
90.9	1 045	134.3	143.2	156.5			277
99.6	1 045	134.3	295.4	326.3	2 256		277
99.6	522.5	67.15	286.2	317.2	4 651	2.06	277
			2-Methylthio-3-methyl-1,3,5-triazaindene [h]				
61.2	975	119.7	0.500	0.525			288.5
71.05	975	119.7	1.230	1.308	5 798		288.5
71.05	487.5	59.85	1.174	1.244	12 157	2.09	288.5
83.25	975	119.7	3.536	3.822			288.5
			2-Methylsulphonyl-1-methylbenzimidazole [g]				
50.2	536.5	156.9	5.403	5.597			270

[a] ±0.1°. [b] In l mol^{-1} s^{-1}; the standard deviation was generally <2%. [c] Corrected for solvent expansion. [d] Time for 50% reaction in s. [e] The ratio of t for two experiments at the same temperature but with the reactant concentrations in one being 0.5 times that in the other. [f] Analytical wavelength for the determination of percentage reaction. [g] pH 8 Buffer was used to stop the reactions, and for spectroscopic measurements. [h] pH 10 Buffer was used to stop the reactions, and for spectroscopic measurements.

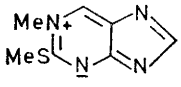
TABLE 3

Rate coefficients and Arrhenius parameters for reactions with methoxide ions

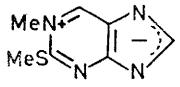
Compound	$10^3k^a_{20°}$	E_a [b]/kJ mol^{-1} (kcal mol^{-1})	log A [c]	$\Delta H^{\ddagger}$ [b]/kJ mol^{-1} (kcal mol^{-1})	$\Delta S^{\ddagger}$ [d]/J mol^{-1} K^{-1} (cal mol^{-1} K^{-1})
2-Methylthio-1-methylpurine	0.65	77.4 (18.5)	10.64	74.9 (17.9)	50.6 (12.1)
6-Methylthio-1-methylpurine	3.78×10^3	36.9 (8.82)	7.2	34.3 (8.2)	115.5 (27.6)
6-Methylthio-3-methylpurine	0.342	81.4 (19.45)	11.03	78.7 (18.8)	61.9 (14.8)
6-Methylthio-9-methylpurine	0.35×10^{-2}	89.8 (21.5)	10.6	87.0 (20.8)	51.5 (12.3)
6-Methylthio-9-β-D-ribofuranosylpurine	0.76×10^{-2}	87.0 (20.80)	10.4	84.1 (20.1)	55.2 (13.2)
8-Methylthio-7-methylpurine	1.93	70.3 (16.8)	9.38	67.8 (16.2)	73.2 (17.5)
8-Methylthio-9-methylpurine	0.242	72.8 (17.4)	10.4	70.3 (16.8)	54.4 (13.0)
2-Methylthio-1-methyl-1,3,5-triazaindene	2.48×10^{-3}	83.7 (20.0)	9.2	80.8 (19.3)	78.7 (18.8)
2-Methylthio-3-methyl-1,3,5-triazaindene	7.1×10^{-3}	86.2 (20.6)	10.2	83.3 (19.9)	59.0 (14.1)

[a] In l mol^{-1} s^{-1}, calculated from the experimental results. [b] Accurate to ±2.1 kJ mol^{-1}. [c] Accurate to ±0.3 unit. [d] Accurate to ±1.2 J mol^{-1} K^{-1}.

regular kinetics were observed generally from 10—90% reaction. Details of all kinetic runs (Table 2) revealed ($t_{\frac{1}{2}}$ values) that the reactions were bimolecular and they obeyed second-order kinetics. Rate coefficients at 20° and the Arrhenius parameters (Table 3) show that, at 20°, 6-methylthio-1-methylpurine was 5 800 and 11 000 times more reactive than its 2-methylthio-isomer and 6-methylthio-3-methylpurine respectively. This was due mainly to a much lower energy of activation (8.82 kcal mol^{-1}) for 6-methylthio-1-methylpurine although log A (7.2) was also lower. These reactivity differences can be explained in a manner similar to that used by Bergmann *et al.*[8] In the canonical structures of 2- and 6-methylthio-1-methylpurine the negative charge is spread over position 3 and the imidazole ring [*e.g.* as in (I) and (II)]. Although the



(I)



(II)

positive centre at N-1 is at an equal distance from the 2- and 6-positions, the approach of a nucleophile to position 2 is less favoured because of the repulsion by the partial negative charge at N-3. Accordingly 6-methylthio-1-methylpurine was more reactive than its 2-methylthio-isomer; and for similar reasons more reactive than 6-methylthio-3-methylpurine. As 8-methylthio-1- and -3-methylpurines were unreactive under the conditions of the kinetic studies, the order of positional reactivity in the 1-methylpurines was 6 > 2 > 8 and in the 3-methylpurines 6 > 8. 6-Methylthio-3-methylpurine, with the lower energy of activation, was 100 times more reactive than its 9-methyl isomer. These results are consistent with the likely contributions by canonical studies similar to those discussed above.

6-Methylthio-9-β-D-ribofuranosylpurine as expected showed reactivity, E, and log A values comparable with its 9-methyl analogue.

8-Methylthio-7-methylpurine was 8 times more reactive than 8-methylthio-9-methylpurine consistent with the lower E value of the former and with stabilisation of the intermediates.[7] 8-Methylthio-9-methylpurine at 20° was 69 times more reactive than 6-methylthio-9-methylpurine towards methoxide ions (due to a much lower energy of activation) compared with 50 times [3] for reactions of the corresponding chloro-*N*-methylpurines towards ethoxide ions and 0.36 times [2] for the same compounds with piperidine in ethanol at 40°. The order of reactivity for these studies of purines which gave measurable rates with methoxide ions in methanol was thus 6-SMe-1-Me > 8-SMe-7-Me > 2-SMe-1-Me > 6-SMe-3-Me > 8-SMe-9-Me > 6-SMe-9-Me. The qualitative work of Bergmann [8] is in agreement with these results. The 3-deaza-analogues of 8-methylthio-7- and -9-methylpurine, *viz.* 2-methylthio-3- and -1-methyl-1,3,5-triazaindene, were 3.7 × 10^{-3} and 1 × 10^{-2} times as reactive as the corresponding purines, and the energies of activation were 3.8 and 2.6 kcal mol^{-1} higher respectively in the triazaindenes. 2-Methylthio-3-methyl-1,3,5-triazaindene was 2.86 times more reactive at 20° than its 1-methyl isomer due to a higher frequency factor (10.2 compared with 9.2). This higher reactivity is probably due to additional stabilisation of the transition state of the 3-methyl isomer.

Comparison of the calculated rate coefficients for the reactions of 2-methylthio-1- and -3-methyl-1,3,5-triazaindene at 50.2°, 4.78 × 10^{-5} and 1.91 × 10^{-4} respectively with that determined experimentally for 2-methylsulphonyl-1-methylbenzimidazole, 5.6 × 10^{-3} l mol^{-1} s^{-1}, revealed that the normal difference in reactivity between methylsulphonyl and methylthio-compounds, 5 × 10^{3}—3.7 × 10^{5} fold [11] was more than sufficient to outweigh activation by N-5 in the methylthio-1,3,5-triazaindenes and make 2-methylsulphonyl-1-methylbenzimidazole the more reactive.

It was not possible to study the kinetics of replacement of the methylthio-group from 1-methyl-2-methylthiobenzimidazole by methoxide ions because under the conditions required to effect reaction (2.82 × 10^{-3}M-methylthio-compound, 0.265M-methoxide ion, 145.8°, $t_{\frac{1}{2}}$ 3 632 s, k_2 7.2 × 10^{-4} l mol^{-1} s^{-1}), the product of reaction was 1-methylbenzimidazol-2(3*H*)-one as shown by the u.v. spectra with maxima at pH 9 of 278 nm and pH 14 of 287 nm.

The preparations of the compounds required in this study have been reported previously [7,10] or are described below. It was not possible to methylate 8-methylsulphonylpurine with methyl iodide in dimethylformamide and acetonitrile as described for 1-methyl-8-methylthiopurine hydriodide.[12]

EXPERIMENTAL

Compounds were examined for impurities by paper chromatography on Whatman No. 1 paper with (a) 3% aqueous ammonium chloride, and (b) butan-2-ol–5N-acetic acid (7 : 3) as solvent, and also by t.l.c. and were recrystallised to constant m.p.

Analyses were performed by the Australian National University Analytical Services Unit. Solids for analysis were dried at 100° unless otherwise stated and each m.p. was taken in a Pyrex capillary.

U.v. spectra were measured with a Unicam SP 1800 spectrophotometer and ε values were checked on a Unicam SP 1700 instrument. ^{1}H N.m.r. spectra were recorded at 60 MHz and 35° with a Varian T-60A spectrometer. Ionization constants were determined spectrophotometrically.[13]

1-Methyl-2-methylthiopurine had m.p. 243—245° (lit.,[10] 243—245°), pK_a 5.1 ± 0.2, $\lambda_{max.}$ (pH 8.0) 246.5 (log ε 4.46) and 278 nm (3.77).

2-*Methoxy*-1-*methylpurine*.—1-Methyl-2-methylthiopurine (0.1 g) and sodium methoxide solution (10 ml, 0.1M) were allowed to stand at room temperature for 0.5 h. The mixture was neutralised with carbon dioxide, evaporated to dryness, and the product extracted into chloroform and recrystallised from benzene to yield 2-*methoxy*-1-*methylpurine*

[11] G. B. Barlin and W. V. Brown, *J. Chem. Soc.* (*B*), 1968, 1435.

[12] U. Reichman, F. Bergmann, D. Lichtenberg, and Z. Neiman, *J.C.S. Perkin I*, 1973, 793.

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(0.05 g, 55%), m.p. >200° (decomp.) (Found, for material dried at 100° for 2 h: C, 51.4; H, 5.12; N, 33.8. $C_7H_8N_4O$ requires C, 51.2; H, 4.9; N, 34.1%), δ($CDCl_3$) 4.00 (MeN), 4.33 (MeO), and 8.25 and 8.58 (6- and 8-H), $\lambda_{max.}$ (pH 9.0) 276 nm (log ε 3.91).

Reaction of 1-Methyl-6-methylthiopurine with Sodium Methoxide.—Sodium methoxide solution (0.01 ml, 0.5N) was added to a solution of 1-methyl-6-methylthiopurine hydriodide [14] (0.005 g) in methanol (2.0 ml). After 5 min the u.v. spectrum was found to have stabilised at $\lambda_{max.}$ 266 nm. The solution was diluted with N-sodium hydroxide solution and the product identified as 6-hydroxy-1-methylpurine [15] by chromatographic and u.v. spectral comparison with an authentic specimen.

8-Methoxy-7-methylpurine.— 7-Methyl-8-methylthiopurine [7] (0.070 g) and sodium methoxide solution (5.0 ml, 0.5M) were refluxed for 20 min. The solution was then carefully neutralised with carbon dioxide and evaporated to dryness, and the product extracted into chloroform, which was evaporated *in vacuo* to yield *8-methoxy-7-methylpurine* (0.035 g, 56%), m.p. 156—160° (from benzene) (Found: C, 51.4; H, 5.1; N, 34.2. $C_7H_8N_4O$ requires C, 51.2; H, 4.9; N, 34.1%). δ($CDCl_3$) 3.60 (MeN), 4.27 (MeO), and 8.60 and 9.02 (6- and 2-H).

9-Methyl-6-methylthiopurine was prepared by methylation [16] of 6-mercapto-9-methylpurine and the product extracted in chloroform. It had m.p. 173—175° (lit.,[16] 171—172°) (Found: C, 46.6; H, 4.4; N, 31.2. Calc. for $C_7H_8N_4S$: C, 46.7; H, 4.4; N, 31.1%).

6-Methylthio-9-β-D-ribofuranosylpurine was purchased from the Sigma Chemical Company and had m.p. 165—166° (lit.,[17] 163—164°) (Found: N, 18.8. Calc. for $C_{11}H_{14}N_4O_4S$: N, 18.8%).

6-Methoxy-9-methylpurine.—9-Methyl-6-methylthiopurine (0.100 g) and sodium methoxide (10 ml, 0.25M) were refluxed for 3 h. The solution was cooled, neutralised with carbon dioxide, and taken to dryness. The product was extracted with ether and recrystallised from light petroleum (b.p. 60—80°) to yield 6-methoxy-9-methylpurine (0.068 g, 75%), m.p. 152—154° (lit.,[16] 152—153°) (Found: C, 51.4; H, 4.8; N, 34.75. Calc. for $C_7H_8N_4O$: C, 51.2; H, 4.9; N, 34.1%), δ($CDCl_3$) 3.81 (MeN), 4.17 (MeO), 7.83 (8-H), and 8.50 (2-H).

9-Methyl-8-methylthiopurine was prepared by methylation [18] of the mercapto-compound. It had m.p. 148—150° (from water) (lit.,[18] 147°) (Found: C, 46.75; H, 4.4; N, 31.4. Calc. for $C_7H_8N_4S$: C, 46.7; H, 4.4; H, 31.1%), δ($CDCl_3$) 2.88 (MeS), 3.78 (MeN), and 8.83 and 8.90 (2- and 6-H).

8-Methoxy-9-methylpurine.—9-Methyl-6-methylthiopurine (0.100 g) and sodium methoxide solution (5.0 ml, 0.25M) were refluxed for 1 h. The solution was cooled, neutralised with carbon dioxide, evaporated to dryness, and the product extracted with ether and subjected to t.l.c. (alumina–chloroform). The material of higher R_F was collected and sublimed to give 8-methoxy-9-methylpurine (0.035 g, 38%), m.p. 149—151° (Found: C, 51.5; H, 5.1; N, 34.2. $C_7H_8N_4O$ requires C, 51.2; H, 4.9; N, 34.1%), δ($CDCl_3$) 3.60 (MeN), 4.23 (MeO), and 8.75 and 8.80 (2- and 6-H).

8-Methylsulphonylpurine.—8-Methylthiopurine [19] (0.22 g) was dissolved in acetic acid (20 ml, 12N) and a solution of potassium permanganate (0.35 g) in water (20 ml) added over 2 h with stirring. The mixture was cooled in ice and decolourised with sulphur dioxide and on standing (and scratching) gave 8-methylsulphonylpurine (0.205 g, 78%), m.p. 305—310° (decomp.) (lit.,[18] 300°), δ(DMSO) 3.50 ($MeSO_2$) and 9.07 and 9.37 (2- and 6-H).

1-Methyl-2-methylthio-1,3,5-triazaindene was prepared by literature procedures [20] and recrystallised from light petroleum (b.p. 60—80°). It had m.p. 100—102° (lit.,[20] 98—98.5°) (Found, for sample dried at 80° and 0.1 mmHg: C, 53.5; H, 5.1; N, 23.9. Calc. for $C_5H_9N_3S$: C, 53.6; H, 5.1; N, 23.4%).

3-Methyl-2-methylthio-1,3,5-triazaindene was prepared according to literature procedures [20] and recrystallised from light petroleum (b.p. 60—80°). It had m.p. 126—128° (lit.,[20] 124—125°) (Found: C, 53.7; H, 5.1; N, 23.9. Calc. for $C_5H_9N_3S$: C, 53.6; H, 5.1; N, 23.4%).

2-Methoxy-1-methyl-1,3,5-triazaindene.—1-Methyl-2-methylthio-1,3,5-triazaindene (0.100 g) and 0.5M-sodium methoxide (5 ml) were heated in a sealed tube at 100° for 3 h. The mixture was poured into cold water, adjusted to pH 11, and extracted with chloroform. The product was recrystallised from light petroleum (b.p. 60—80°) to yield *2-methoxy-1-methyl-1,3,5-triazaindene* (60%), m.p. 82—84° (Found, for material dried at 25° and 0.1 mmHg: C, 44.5; H, 7.6; N, 19.4. $C_8H_9N_3O,3H_2O$ requires C, 44.2; H, 6.9; N, 19.35%), pK_a 7.12 ± 0.08 (265 nm); $\lambda_{max.}$ (pH 4.0) 265 nm (log ε 3.71), $\lambda_{max.}$ (pH 10.0) 267 nm (log ε 3.65).

2-Methoxy-3-methyl-1,3,5-triazaindene.—3-Methyl-2-methylthio-1,3,5-triazaindene (0.100 g) and 0.5M-sodium methoxide (5.0 ml) were heated at 100° for 3 h. The mixture was poured into cold water, adjusted to pH 11, and extracted with chloroform. The product was recrystallised from light petroleum (b.p. 60—80°) to yield *2-methoxy-3-methyl-1,3,5-triazaindene* (0.065 g), m.p. 89—91° (Found, for sample dried at 25° and 0.1 mmHg: C, 44.1; H, 7.35; N, 19.3. $C_8H_9N_3O,3H_2O$ requires C, 44.2; H, 6.91; N, 19.35%); pK_a 6.75 ± 0.05 (279.5 nm), $\lambda_{max.}$ (pH 4.0) 279.5 nm (log ε 4.08), $\lambda_{max.}$ (pH 10.0) 248 (log ε 3.78), 268 (3.71), and 276 nm (3.62).

1-Methyl-2-methylthiobenzimidazole.— 1-Methyl-2-methylthiobenzimidazole hydriodide was prepared by methylation of 2-methylthiobenzimidazole [21] with methyl iodide as described by Futaki [22] except that an excess of methyl iodide was used. The hydriodide (12.0 g) in water was adjusted to pH 10, and the product extracted in chloroform and distilled to give 1-methyl-2-methylthiobenzimidazole (5.6 g), m.p. 57—59°, b.p. 98—100° at 0.15 mmHg (lit.,[23] m.p. 56°, b.p. 112—115° at 0.8 mmHg) (Found: C, 61.1; H, 5.6; N, 16.0. Calc. for $C_9H_{10}N_2S$: C, 60.7; H, 5.6; N, 15.7%), $\lambda_{max.}$ (pH 9.0) 252 (log ε 3.54), 259 (3.52), 285 (3.86), and 292 nm (3.87).

1-Methyl-2-methylsulphonylbenzimidazole.— 1-Methyl-2-methylthiobenzimidazole (2.0 g) was dissolved in 12N-acetic acid (20 ml) and stirred at 30—40° while an aqueous solution of potassium permanganate (25 ml, 7%) was added dropwise over 2 h. The mixture was decolourised with sulphur dioxide and extracted with chloroform to yield 1-methyl-2-methylsulphonylbenzimidazole (1.52 g, 65%), m.p. 133—

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135° (from water) (lit.,[24] 131—132°) (Found: C, 50.9; H, 4.8; N, 13.1. Calc. for $C_9H_{10}N_2O_2S$: C, 51.4; H, 4.8; N, 13.3%), $\lambda_{max.}$ (pH 9.0) 279 nm (log ε 4.00).

1-*Methylbenzimidazol*-2(3H)-*one*.— 1-Methyl-2-methylsulphonylbenzimidazole (0.20 g) and N-sodium hydroxide solution (10 ml) were refluxed for 1.5 h. The mixture was adjusted to pH 6 and the 1-methylbenzimidazol-2(3*H*)-one (0.122 g) collected and recrystallised from water. It had m.p. 193—195° (lit.,[25] 188—189°) (Found: C, 64.55; H, 5.6; N, 18.6. Calc. for $C_8H_8N_2O$: C, 64.9; H, 5.4; N, 18.9%), $\lambda_{max.}$ (pH 8.0) 278 nm (log ε 3.85), $\lambda_{max.}$ (pH 14.0) 242 (3.72) and 287 nm (log ε 3.91).

2-*Methoxy*-1-*methylbenzimidazole*.—1-Methyl-2-methylsulphonylbenzimidazole (0.2 g) and 0.1N-sodium hydroxide (10 ml) were refluxed for 1 h. The mixture was poured into water, adjusted to pH 10, and extracted with chloroform to yield 2-methoxy-1-methylbenzimidazole (0.085 g). It had m.p. 56—58° [from light petroleum (b.p. 60—80°)] (lit.,[26] 56—57°) (Found, for sample dried at 25° and 0.1 mmHg: C, 62.9; H, 6.6; N, 16.7. Calc. for $C_9H_{10}N_2O,0.6H_2O$: C, 63.2; H, 6.55; N, 16.4%), $\lambda_{max.}$ (pH 9.0) 238 (log ε 3.71), 274.5 (3.74), and 280.5 nm (3.71).

Kinetic Procedure.—This was similar to that described for the substituted 7- and 9-methylpurines with hydroxide ions in Part XI.[7] U.v. spectra and ionization constants (some for the ethoxy-compounds) required for this work are recorded in this paper and in refs. 3, 7, 12, 18, 20, and 27—30.

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