Studies of 2-Oxo- and 2-Thioxo-1,2-dihydropyrimidinium Salts

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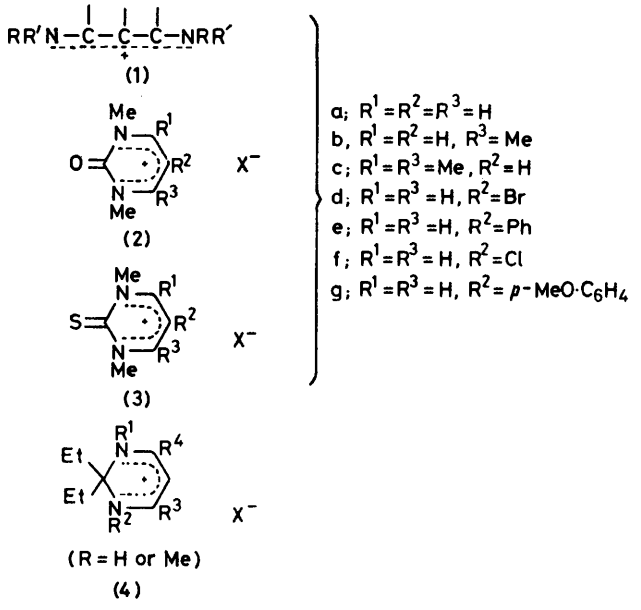
The chemistry (deuteriation, halogenation, diazo-coupling, and reaction with nucleophiles) and spectra of 2-oxo- and 2-thioxo-1,2-dihydropyrimidinium salts are compared with those of 2,2-dialkyl-1,2-dihydropyrimidinium and 2,3-dihydro-1,4-diazepinium salts, thereby demonstrating the effect of an adjacent oxo- or thioxo-group on the properties of a 1,5-diazapentadienium system.

THE 1,5-diazapentadienium system (1) has great mesomeric stability, and undergoes both electrophilic and nucleophilic substitution reactions with retention of type.[1] This meneidic character [2] has been the subject of



theoretical calculations.[3] Some study has been made of steric effects on the properties of the system by including it in rings of different sizes.[4] In the present work the effect of electronic distortion is noted by comparing the properties of 1,2-dihydro-2-oxo- (2) and 1,2-dihydro-2-thioxopyrimidinium salts (3) with those of other 1,5-diazapentadienium systems such as 2,2-dialkyl-1,2-dihydropyrimidinium salts (4) and 2,3-dihydro-1,4-diazepinium salts.

Since *N*-substituted derivatives can exist in prototropic equilibrium with hydroxy- or mercapto-pyrimidine forms it was essential to lock the compounds as oxo- or thioxo-compounds by using *NN'*-disubstituted derivatives. In the present study the previously reported 1,3-dimethyl-,[5,6] 1,3,4-trimethyl-,[7] and 1,3,4,6-tetramethyl-2-oxodihydropyrimidinium [7] salts and the hitherto unreported 5-aryl-1,3-dimethyl-2-oxodihydropyrimidinium salts were prepared by the published method,[7] and their previously unknown 2-thioxo-analogues were prepared from *NN'*-dimethylthiourea and the appropriate dicarbonyl compound or its acetal.

A much studied reaction of 1,5-diazapentadienium salts is their electrophilic substitution, which follows a path similar to that of benzene derivatives. Some previous investigations of the kinetics and mechanism of deuteriation [6,8] and bromination [9,10] of the 1,3-dimethyl-2-oxodihydropyrimidinium ion (2a) had suggested that these reactions did not proceed by simple electrophilic substitution, but rather by a stepwise process involving initial formation of a covalent hydroxy- (or deuterioxy-) adduct (5), which then, as an enamine, undergoes electrophilic attack at C-5. The adduct (5) was observed spectroscopically in basic solution.[6]

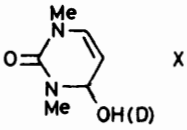
The rate of deuteriation was unexpectedly (in view of the usual deactivating effect of a ring nitrogen atom) 10^4 times greater than in the 3- or 5-position of 2-pyridone;[6,8] it is however about 10^{10} times slower than deuteriation in 5,7-dimethyldihydrodiazepinium salts. This demonstrates the salient feature of the conjugated systems present in the oxodihydropyrimidinium nucleus, namely that in this nucleus two stable delocalised systems, the 1,5-diazapentadienium system and a urea-type system, are in competition for the excess of electrons. This competition results in a greatly decreased reactivity of the normally electron-rich 1,5-diazapentadienium system towards electrophiles as compared with an unperturbed 1,5-diazapentadienium system; the 'direct' deuteriation must be even slower than the observed stepwise mechanism. In keeping with this greatly reduced reactivity, the oxodihydropyrimidinium cations, unlike other 1,5-diazapentadienium salts, do not undergo H–D exchange in deuteriotrifluoroacetic acid at room temperature.

The 1,3-dimethyl-2-thioxodihydropyrimidinium ion (3a) likewise did not undergo exchange in deuteriotrifluoroacetic acid but in stronger aqueous acid at 95—100 °C (*cf.* refs. 6 and 8) a competitive experiment showed that it slowly underwent exchange at about the same rate as its oxo-analogue. This at present remains the only unambiguous electrophilic substitution reaction observed with a 2-thioxodihydropyrimidinium nucleus.

Deuteriation also takes place at the methyl groups of

[1] D. Lloyd and H. McNab, *Angew. Chem.*, 1976, **88**, 496; *Angew. Chem. Internat. Edn.*, 1976, **15**, 459.
[2] D. Lloyd and D. R. Marshall, *Angew. Chem.*, 1972 **84** 447; *Angew. Chem. Internat. Edn.*, 1972, **11**, 404.
[3] J. Fabian and H. Hartmann, *J. Mol. Struct.*, 1975, **27**, 67; *Theor. Chim. Acta*, 1975, **36**, 351; J. Fabian, H. Hartmann, and N. Tyutyulkov, *J. Signal AM*, 1976, **4**, 101.
[4] D. Lloyd and H. McNab, *J.C.S. Perkin I*, 1976, 1784.
[5] G. C. Hopkins, J. P. Jonak, H. Tickelmann, and J. Minnemeyer, *J. Org. Chem.*, 1966, **31**, 3969.
[6] A. R. Katritzky, M. Kingsland, and O. S. Tee, *J. Chem. Soc.* (*B*), 1968, 1484.
[7] H. Baumann, G. Hansen, H. R. Müller, and M. Seefelder, *Annalen*, 1968, **717**, 124.
[8] A. R. Katritzky, M. Kingsland, and O. S. Tee, *Chem. Comm.*, 1968, 289.
[9] S. Banerjee and O. S. Tee, *J.C.S. Chem. Comm.*, 1972, 1032.
[10] S. Banerjee and O. S. Tee, *Canad. J. Chem.*, 1974, **52**, 451.

the 4-mono- and 4,6-di-methyl derivatives [(2b and c) and (3b and c)] in neutral or mildly acidic media; the



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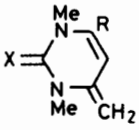
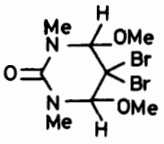


(R = H or Me, X = O or S)

(6)



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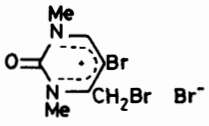

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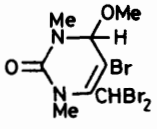

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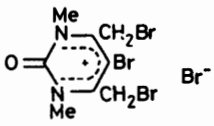


(10)

mechanism probably involves the exocyclic methylene bases (6) (*cf.* ref. 11). The reactions of the 4-methyl derivatives (2b) and (3b) with unbuffered D_2O at *ca.* 34 °C followed first-order kinetics and proceeded at similar rates (*k ca.* 10^{-5} s^{-1}).

The 5-bromo-derivative (2d) is readily prepared in high yield by bromination of (2a) in methanol. Reaction of (2a) with 2 mol. equiv. of bromine in methanol gave the dibromo-dimethoxy-compound (7), which was converted into (2d) by treatment with aqueous hydrobromic acid. A dihydroxy-analogue of (7) has been isolated from an aqueous bromination.[10] Evidence for the intermediacy of a covalent adduct akin to (5) was obtained by stopped-flow experiments, which showed that the uptake of bromine followed zero-order kinetics, consistent with a slow step not involving the electrophile.

Bromination of the trimethyl compound (2b) in methanol gave the dibromo compound (8) as the only isolable salt, even when an excess of bromine and extended reaction times were used. One mol. equiv. of bromine is taken up rapidly, and further consumption of bromine is slow. The reaction does not follow simple kinetics, but is overall about 50 times slower than for the 4-unsubstituted analogue (2a). From the chloroform extracts of the product mixture from a reaction with 3 mol. equiv. of bromine an impure yellow oil was obtained whose absorption spectra and mass spectrum (Found: M^+, 405.8343. Calc. for $C_8H_{11}{}^{81}Br^{79}Br_2N_2O_2$: M, 405.8350) were consistent with its being the tribromo-compound (9) or its 4-methoxy-isomer. Reaction of this compound with dilute aqueous hydrobromic acid readily gave the dibromo-derivative (8).

Bromination of the tetramethyl derivative (2c; X = HSO_4) is complicated by the formation of a stable complex which precipitates out of the solution. The u.v. spectrum of this complex shows a weak shoulder at 380 nm consistent with the presence of molecular bromine; there is no peak at 270 nm corresponding to the tribromide anion. Elemental analysis suggests that four atoms of bromine are associated with each dihydropyrimidinium ion. The strength of the binding forces in the complex may be judged from the fact that the sample for analysis was dried overnight at 10^{-1} Torr. Such complexing is well known in the chemistry of hydroxypyrimidines.[12] The only isolated bromination product was the tribromo-derivative (10), obtained in very low yield. The complex was decomposed by acetone to regenerate the unsubstituted salt (2c; X = Br).

Attempted bromination of the 5-phenyl compound (2e) in a number of solvents produced no reaction. Although the normal site for bromination is blocked in this case by a substituent, some 6-substituted dihydrodiazepinium salts (in which the 6-position corresponds to the 5-position in pyrimidine derivatives) nonetheless undergo attack by bromine at the 6-position;[13] some 6-phenyldihydrodiazepinium salts undergo bromination of the benzene ring.[14] Thus once again the reactivity of the 1,5-diazapentadienium system towards electrophiles is shown to be diminished by the 2-oxo-group. The 5-*p*-methoxyphenyl analogue was also unattacked by bromine.

The dimethyl compound (2a) is inert to *N*-chlorosuccinimide,[6] but reaction with a methanolic solution of chlorine provides the 5-chloro-derivative (2f).

When the 2-thioxodihydropyrimidinium salt (3a; X = Br) was treated with an excess of bromine in methanol, the brominated oxo-derivative (2d) resulted. When only 1 mol. equiv. of bromine was used, the ^1H n.m.r. spectrum of the crude product showed it to be a mixture of starting material (3a), the corresponding 2-oxo-compound (2a) and the bromo-oxo-compound (2d). This suggests that the reaction proceeds by oxodethionation followed by bromination. The ultimate fate of the sulphur atom is not known. Tests for the presence of elemental sulphur or sulphide anion gave negative results; it is probably oxidised under the reaction conditions. Similarly the trimethyl-thioxo-compound (3b) with an excess of bromine provided the dibromo-oxo-derivative (8). Like its oxo-analogue, the 5-phenyl-thioxo-compound (3e) did not react with bromine.

The oxodihydropyrimidinium ion (2a) differed from 2,2-dialkyldihydropyrimidinium salts and dihydrodiazepinium salts in being inert to *N*-chlorosuccinimide, even in boiling acetic acid for 24 h, to nitrating acids,[15] and to diazonium salts under neutral or acidic conditions.

The tri- and tetra-methyl-oxodihydropyrimidinium ions (2b and c) have been shown to couple at the methyl groups with diazonium salts.[1] A similar reaction took place with the thioxo-compound (3b), which provided, after basic work-up, the arylazomethylene derivative (11). This was identified as its hydrochloride; the site of protonation is not known.

This diazo-coupling is presumed to involve attack on the exocyclic methylene bases (6), present in equilibrium with the salts.[7] The ready formation of such bases

[11] T. J. Batterham, D. J. Brown, and M. N. Paddon-Row, *J. Chem. Soc.* (*B*), 1967, 171.

[12] O. Stark, *Annalen*, 1911, **381**, 143.

[13] C. Barnett, D. Lloyd, D. R. Marshall, and L. A. Mulligan, *J. Chem. Soc.* (*B*), 1971, 1529; C. Barnett, D. R. Marshall, and D. Lloyd, *J.C.S. Perkin II*, 1975, 325.

[14] D. Lloyd and K. S. Tucker, unpublished work.

[15] C. D. Johnson, A. R. Katritzky, M. Kingsland, and E. F. V. Scriven, *J. Chem. Soc.* (*B*), 1971, 1.

TABLE 1

Spectra of adducts (12) (for conditions see Experimental section)

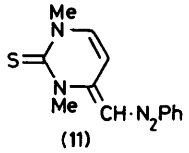
X	Y	Z *	$\lambda_{max.}$/nm	ε	τ (H-4)	τ (H-5)	τ (H-6)	τ (H-1, -3)	τ (other)	$J_{4,5}$ Hz	$J_{5,6}$ Hz	$J_{4,6}$ Hz
O	H	OH [a]	240	5 600	4.65	4.95	3.84	6.97, 7.03		4.4	7.7	0.5
S	H	OH	254sh	9 300	4.57	4.70	3.70	6.59, 6.63		4.3	7.3	0.6
			272	11 400								
O	Br	OH	252	7 700	4.69		3.62	6.99, 7.09				1.2
O	Cl	OH	250	6 300	4.72		3.66	6.98, 7.07				1.2
O	H	OMe	239	5 200	4.69	5.26	3.42	7.06, 7.13	7.00 (OMe)	4.4	7.8	*ca.* 0
S	H	OMe	250sh	5 200	4.52	4.93	3.18	6.59, 6.69	7.05 (OMe)	4.6	7.8	*ca.* 0
			276	14 400								
O	Br	OMe	252	7 200	4.58		2.93	7.01, 7.11	6.96 (OMe)			0.6
O	H	Pip	240sh	*ca.* 7 500	4.77	5.12	3.66	7.00, 7.09		4.3	7.9	*ca.* 0
S	H	Pip	254sh	*ca.* 9 500	4.63	4.84	3.45	6.61, 6.67,		4.7	7.6	*ca.* 0
			272	12 200	5.20	5.00	3.44	6.72				
O	Br	Pip	248sh	*ca.* 8 300	5.31		3.18	7.06, 7.16				*ca.* 0
O	H	MP^+			4.79	5.12	3.69					
S	H	MP^+			4.61	4.81	3.42					
O	Br	MP^+			4.80		3.23					
O	Ph	Pip			4.96		3.13	6.83, 7.01	2.4—2.7 (Ph)			
O	*p*-MeO·C_6H_4	Pip			4.98		3.28	6.94, 7.01	2.54—2.63 (Ph) 3.1—3.2 (Ph) 6.26 (OMe)			
S	Ph	Pip			4.74		2.86	6.5, 6.6	2.4—2.78 (Ph)			
S	*p*-MeO·C_6H_4	Pip			4.78		3.16	6.52, 6.6	2.47—2.58 (Ph) 2.98—3.06 (Ph) 6.24 (OMe)			

* Pip = piperidino; MP^+ = *N*-methylpiperidinio.

[a] *Cf.* ref. 16.

is in complete contrast with the behaviour of methyl-substituted dialkyldihydropyrimidinium or dihydrodiazepinium salts. The ready formation of adducts such as (5) also contrasts with the behaviour of dihydrodiazepinium salts. Both these differences again underline the diminished stability of the 1,5-diazapentadienium system in 2-oxo- and 2-thioxo-pyrimidinium ions, caused by competitive interaction of the (thio)urea group.

A variety of adducts (12), with Z = OH, OMe, or piperidino, were observed spectroscopically (see Table 1). (See ref. 16 for another recent account of the hydroxy-adducts.) Their stability is shown by the facts that



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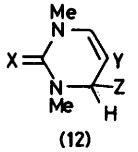

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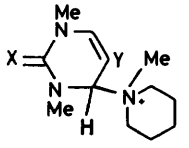

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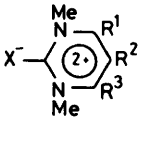


(14)

decomposition product peaks in the ^1H n.m.r. spectra of the adduct (12; X = O, Y = H, Z = OH) in aqueous M-sodium deuterioxide only became similar in intensity to those of the simple adduct after 3 days, and that the ^1H n.m.r. spectrum of the adduct (12; X = S, Y = H, Z = piperidino) remained essentially unchanged for 3 days. These adducts may be compared with the stable Meisenheimer complexes obtained from nitroarenes. None of the 5-halogeno-oxo-(or thioxo-) dihydropyrimidinium salts underwent nucleophilic substitution of the halogen atoms.

The piperidine adducts (12; Z = piperidino) might be present in unprotonated or *N*-protonated form. The *N*-methylpiperidine adducts (13) were prepared. The similarity of the chemical shifts of the protons at C-4, -5, and -6 in both the *N*-methylpiperidine and piperidine adducts of (2a) indicates that the latter are indeed *N*-protonated. Similarly it was shown that the piperidine adduct of the bromo-compound (2d) was not protonated, whereas the thioxo-compound (12; X = S, Y = H, Z = piperidino) was present in both protonated and unprotonated forms.

The methoxy-adducts were isolated as crude viscous oils and were characterised by mass spectrometry. Such adducts are assumed to be intermediates in the bromination of oxodihydropyrimidinium salts and the isolation of (12; X = O, Y = H, Z = OMe) enabled the conversion of this adduct into the bromo-compound (2d) to be observed directly. This conversion could also be carried out by treatment with *N*-bromosuccinimide, followed by work-up with dry methanolic hydrogen chloride. The formation of these methanol adducts is reversed on addition of acid.

In the i.r. spectra of the methoxy-adducts (12; X = O, Z = OMe, Y = H or Br) the carbonyl bands appeared at 1 660—1 670 cm^{-1}, intermediate between the positions for the salts (2) [*e.g.* (2a), 1 715 cm^{-2}], and *NN'*-dimethylurea (1 610 cm^{-1}), consistent with an intermediate delocalisation of electrons into the carbonyl group. The difference between the urea and (2) reflects the reduced interaction of the nitrogen lone pairs with the carbonyl function in the latter case, due to their also being part of the 1,5-diazapentadienium system.

The oxo- and thioxo-pyrimidinium salts generally show two maxima in their u.v. spectra. Those at longer

[16] O. S. Tee and M. Endo, *Canad. J. Chem.*, 1976, **54** 2681.

wavelength are characteristic of the 1,5-diazapentadienium system, and the shorter wavelength absorptions are associated with the urea chromophore. The latter are far more intense for the thioxo- than for the oxo-compounds, in keeping with the known higher absorption of thiourea itself in comparison with urea,[17] and with the greater polarity of the thioxo-group. 4(6)-Methyl groups cause hypsochromic shifts of 3 and 7 nm in the long wavelength maxima of the oxo- and thioxo-compounds, respectively, and also an increase in extinction coefficients. Similar results are found for 5(7)-methyl groups in the spectra of dihydrodiazepinium salts.[18] 5-Aryl groups cause a bathochromic shift and decreased extinction coefficients in the case of the oxo-compounds (as in dihydrodiazepinium salts [19]), but a hypsochromic shift and increased extinction coefficients in the case of the thioxo-compounds. The spectra of both oxo- and thioxo-compounds (2a) and (3a) were substantially unaltered in concentrated sulphuric acid, indicating that, unlike dihydrodiazepinium and 2,2-dialkyldihydropyrimidinium salts,[4] they are not protonated to any noticeable extent in this solvent. This reluctance to undergo 5-protonation is in accord with the kinetic and other evidence that electrophilic substitution proceeds by an alternative mechanism.

The ^{1}H n.m.r. spectra of the oxo- and thioxo-dihydropyrimidinium salts resemble those of other 1,5-diazapentadienium salts in that the signals for 4-, and 6-protons appear at much lower field than those for 5-protons, but the signals for all these protons appear at significantly lower field than in the case of 2,2-dialkyldihydropyrimidinium salts [4] or dihydrodiazepinium salts.[20] This again reflects the competition by the oxo- or thioxo-groups for the electrons of the 1,5-diazapentadienium system, and includes the effects of inductive deshielding together with mesomeric deshielding due to the canonical form (14). The signals for the protons in the thioxo-compounds (3) appear at lower field than those of the oxo-compounds (2), indicating that the major deshielding mechanism is conjugative. The presence of a 4-methyl group has little effect on the chemical shift of the 5-proton but the signal for the 6-proton is shifted upfield by more than 0.2 p.p.m. As in the case of 2,2-dialkyldihydropyrimidinium salts [4] this may reflect a relatively increased contribution from canonical form (15B), caused by the inductive effect of the 4-methyl group. The *N*-methyl signals in this compound (15) are adventitiously coincident (there are two distinct signals for these groups in the ^{13}C n.m.r. spectrum). The vicinal coupling constants have, as might be expected, a similar magnitude to those for 2,2-dialkyldihydropyrimidinium salts.[4] The signals for ring protons in the adducts (12) are also consistently at lower field for the thioxo-compounds than for their oxo-analogues.

TABLE 2

^{13}C N.m.r. spectra of salts (2) and (3) [10% solutions in $(CD_3)_2SO$; Me_4Si standard]

	R^1	R^2	R^3	δ (C-2)	δ (C-4, -6)	δ (C-5)	δ (other)
(2)	H	H	H	147.73	159.99	103.28	1,3-Me, 40.32
(3)	H	H	H	171.93	158.02	107.05	1,3-Me, 48.13
(2)	Me	H	H	148.41	156.19 172.71	105.52	1-Me, 40.10; 3-Me, 34.74; 4-Me, 21.72
(3)	Me	H	H	173.37	154.50 170.78	110.07	1-Me, 48.45; 3-Me, 42.51; 4-Me, 23.20
(2)	H	Ph	H	147.24	158.02	116.13	1,3-Me, 41.54; Ph: (1), 130.15; *o*, 125.96; *m*, 129.23; *p*, 128.87
(3)	H	Ph	H	170.58	155.6—156.3br	119.66	1,3-Me, 48.26; Ph: (1) 129.71; *o*, 126.22; *m*, 129.30; *p*, 128.92
(2)	H	*p*-MeO·C$_6$H$_4$	H	147.18	157.47	116.06	1,3-Me, 41.34; OMe, 55.31; Ph: (1), 122,34; *o*, 127.34; *m*, 114.72; *p*, 159.84
(3)	H	*p*-MeO·C$_6$H$_4$	H	~170.5br	155.66	119.66	1,3-Me, OMe, 55.31; Ph: (1), 121.76; *o*, 127.65; *m*, 114.87; *p*, 160.39

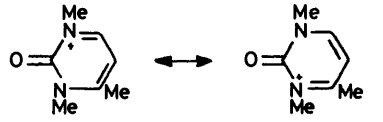
Similarly the ^{13}C n.m.r. signals for the 1,5-diazapentadienium carbon atoms uniformly appear at lower field for the compounds (2) and (3) (see Table 2) than for 2,2-dialkyldihydropyrimidinium salts [4] or dihydrodiazepinium salts.[21] A similar trend is shown by the *para*-position of the 5-phenyl substituent, which can only interact conjugatively with the 1,5-diazapentadienium system by electron withdrawal from it.[20,21] The peaks due to the 2-carbon atoms are at higher field than those in the spectra of the corresponding tetramethyl-urea or -thiourea.

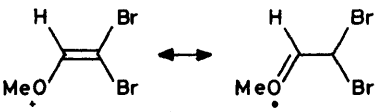
All the compounds (2) and (3) studied gave consistent mass spectra. Bromide salts show characteristic clusters at *m/e* 79—82 (Br^+ and HBr^+) and the hydrogen sulphates show intense peaks at *m/e* 48 and 64 (SO^+ and SO_2^+). The dimethyl derivatives (2a) and (3a) show the molecular ions of the cations as the base peaks, whereas the parent peaks for the tri- and tetra-methyl derivatives (2b and c) and (3b and c) are at (M_{cation} −1). In the former case vapourisation must presumably occur by some charge transfer complex mechanism.[22] Further breakdown occurs by loss of the C-2 and its substituent. Whereas the oxo-compounds lose CO [*e.g.* (2b) Found: *m** 87.7; 138 ⟶ 110 requires *m** 87.7; (2c) Found:

[17] For example, C. N. R. Rao, 'Ultraviolet and Visible Spectroscopy,' Butterworth, London, 1967, p. 28.
[18] C. Barnett, D. R. Marshall, and D. Lloyd, *J. Chem. Soc.* (*B*), 1968, 1536.
[19] K. Feldmann, E. Daltrozzo, and G. Scheibe, *Z. Naturforsch.*, 1967, **22***b*, 722.
[20] D. Lloyd, R. K. Mackie, H. McNab, and D. R. Marshall, *J.C.S. Perkin II*, 1973, 1729.
[21] D. Lloyd, R. K. Mackie, H. McNab, K. S. Tucker, and D. R. Marshall, *Tetrahedron*, 1976, **32**, 2339.
[22] See, *inter alia*, G. Hvistendahl and K. Undheim, *Tetrahedron*, 1972, **28**, 1737.

*m** 101; 152 ⟶ 124 requires *m** 101.01], the major peaks in the spectra of the 2-thioxo-compounds (3b and c) are at (*M* − 45) and *M* − 46). The loss of HCS and H_2CS in these cases presumably reflects the relative stabilities of CO and CS.

As found for 6-halogenodihydrodiazepinium salts,[23] loss of the halogeno substituent is the major breakdown mechanism for compounds (2d) and (2f), although the molecular ion of the cation is observed in both cases. The polybromo-derivatives (8) and (10) have, however,





peaks at (M_{cation} −1) and show significant loss of halogen, probably from the bromomethyl group. The 5,5-dibromo-compound (7) shows a more curious spectrum in that the major breakdown from the molecular ion (*m/e* 344/346/348) is apparently associated with the formation of the alkene (16) (*m/e* 214/216/128. Found: 213.8638. $C_3H_4{}^{79}Br_2D$ requires 213.8629), which is the base peak of the spectrum. A peak at *m/e* 130 (relative intensity 50%) is also present, which may represent the nitrogenous residue of the molecule (Found: 130.0749. $C_5H_{10}N_2O_2$ requires 130.0742).

The cation radical derived from the azomethylene derivative (11) decomposes by two routes. Simple loss of the phenylazo-group affords the base peak at *m/e* 153 (Found: *m** 90.8; 258 ⟶ 153 requires *m** 90.7), and an intense peak at *m/e* 185 (relative intensity 83%) is due to loss of MeCNS (Found: *m** 132.8; 258 ⟶ 185 requires *m** 132.6).

In the mass spectra of the methoxy-adducts (12; Z = OMe), the molecular ions are of low intensity, and the base peak is due to loss of 31 m.u. (*i.e.* OMe), a process which regenerates the stabilised 1,5-diazapentadienium system; similar regeneration of the parent system but by loss of OH has been noted with a corresponding hydroxy-adduct.[16]

EXPERIMENTAL

Electronic spectra were recorded for methanolic solutions and i.r. spectra for Nujol mulls.

1,2-*Dihydro*-1,3-*dimethyl*-2-*oxopyrimidinium Salts* (2a).—These were prepared by literature methods:[6,10,24] hydrogen sulphate, m.p. 203—205° (lit., 200—205°), $\lambda_{max.}$ 322 nm (ε 7 000), $\nu_{max.}$ 1 720, 1 600, 1 320, 1 200, 870, and 780 cm^{-1}, τ [$(CD_3)_2SO$] 0.89 (2 H, d), 2.97 (1 H, t), and 6.29 (6 H, s); *bromide*, m.p. 267.5—268° (decomp.) (from methanol) (Found: C, 35.3; H, 4.6; N, 14.0. $C_6H_9BrN_2O$ requires C, 35.1; H, 4.4; N, 13.65%); *perchlorate*, m.p. 200—200.5° (from methanol) (Found: C, 32.25; H, 4.25; N, 12.7. $C_6H_9ClN_2O_5$ requires C, 32.0; H, 4.0; N, 12.45%). The iodide, previously made by methylation,[5,6] is more conveniently made from the perchlorate by addition of 1 mol. equiv. of potassium iodide in methanol, and had m.p. 232—234°, τ (D_2O) 1.06 (2 H, d), 3.02 (1 H, t), and 6.28 (6 H, s).

1,2-*Dihydro*-1,3,4-*trimethyl*-2-*oxopyrimidinium Salts* (2b).—Prepared as described [7] (but not there analysed), the *hydrogen sulphate* (91%) had m.p. 158.5—159.5° (from methanol), $\lambda_{max.}$ 318 nm (ε 9 300), $\nu_{max.}$ 1 710, 1 620, 1 580, 1 200, 1 050, 880, and 770 cm^{-1}, τ [$(CD_3)_2SO$] 1.11 (1 H, d), 2.96 (1 H, d), 6.34 (6 H, s), and 7.28 (3 H, s) (Found: C, 33.4; H, 5.75; N, 11.0. $C_7H_{12}N_2O_5S,H_2O$ requires C, 33.05; H, 5.5; N, 11.0%). The *perchlorate* had m.p. 127—128° (Found: C, 35.15; H, 4.5; N, 11.65. $C_7H_{11}ClN_2O_5$ requires C, 35.2; H, 4.6; N, 11.75%.

1,2-*Dihydro*-1,3,4,6-*tetramethyl*-2-*oxopyrimidinium Salts* (2c).—Prepared as described [7] (but not there analysed), the *hydrogen sulphate* (50%) had m.p. 146—147° (variable, owing to hydration) (from ethanol), $\lambda_{max.}$ 316 nm (ε 11 100), $\nu_{max.}$ 1 700, 1 620, 1 570, 1 200, 1 040, 860, and 770 cm^{-1}, τ [$(CD_3)_2SO$] 2.94 (1 H, s), 6.38 (6 H, s), and 7.36 (6 H, s). Two analyses were as follows (a) (Found: C, 38.05; H, 6.0; N, 10.95. $C_8H_{14}N_2O_5S$ requires C, 38.4; H, 5.6; N, 11.2%); (b) (Found: C, 35.45; H, 6.3; N, 10.05. $C_8H_{14}N_2O_5S,H_2O$ requires C, 35.8; H, 5.95; N, 10.45%).

1,2-*Dihydro*-1,3-*dimethyl*-2-*oxo*-5-*phenylpyrimidinium Perchlorate* (2e; X = ClO_4).—Methanol (60 ml), followed by perchloric acid (60%; 4 ml), and the *NN'*-dimethylurea (1.76 g, 20 mmol), was added to the sodium salt of phenylmalonaldehyde (3.4 g, 20 mmol). After 1 h crystals of the *perchlorate* (3.6 g, 60%) were filtered off and washed with water and ether, and had m.p. 278—280°, $\lambda_{max.}$ 252 and 360 nm (ε 16 800 and 2 750), $\nu_{max.}$ 1 710, 1 570, 1 310, 1 080, 960, and 720 cm^{-1}, τ [$(CD_3)_2SO$] 0.41 (2 H, s), 2.2—2.5 (5 H, complex), and 6.14 (6 H, s) (Found: C, 47.5; H, 4.5; N, 9.2. $C_{12}H_{13}ClN_2O_5$ requires, C, 47.95; H, 4.35; N, 9.3%).

1,2-*Dihydro*-5-p-*methoxyphenyl*-1,3-*dimethyl*-2-*oxopyrimidinium Perchlorate* (2; X = ClO_4).—Prepared like its phenyl analogue, crystals of this *perchlorate* were filtered off after 10 min (70%) and washed with water, and had m.p. 232° (from propan-2-ol–dimethylformamide), $\lambda_{max.}$ 272 and 390 nm (ε 1 300 and 17 200), $\nu_{max.}$ 1 715, 1 580, 1 290, 1 180, 1 100, 835, and 760 cm^{-1}; τ [$(CD_3)_2SO$] 0.54 (2 H, s), 2.60 (4 H, AA'BB' system), 6.13 (3 H, s), and 6.17 (6 H, s) (Found: C, 47.45; H, 4.55; N, 8.65. $C_{13}H_{15}ClN_2O_6$ requires C, 47.15; H, 4.55; N, 8.45%).

1,2-*Dihydro*-1,3-*dimethyl*-2-*thioxopyrimidinium Salts* (3a).—*NN'*-Dimethylthiourea (2.6 g, 25 mmol) in ethanol (10 ml) was added to a solution of 1,1,3,3-tetraethoxypropane (5.5 g, 25 mmol) in ethanol (5 ml). The mixture was cooled in ice while concentrated sulphuric acid (1.8 ml; *ca.* 1.3-fold excess) was added, and then kept overnight at room temperature. Addition of ether (*ca.* 10 ml) caused crystallisation of the *hydrogen sulphate* (3.0 g, 50%), m.p. 153.5—154° (from methanol at −78 °C), $\lambda_{max.}$ 280 and 379 nm (ε 18 800 and 1 400), $\nu_{max.}$ 1 610, 1 580, 1 300, 1 200, 1 020, 850, and 700 cm^{-1}, τ [$(CD_3)_2SO$] 0.64 (2 H, d), 2.58 (1 H, t), and 5.99 (6 H, s) (Found: C, 29.95; H, 4.5; N, 11.5. $C_6H_{10}N_2O_4S_2$ requires C, 30.25; H, 4.2; N, 11.75%). The *bromide*, m.p. 201—201.5° (decomp.) (reprecipitated from methanol by ether) (Found: C, 32.95; H, 4.4; N, 13.05. $C_6H_9BrN_2S$ requires C, 32.6; H, 4.05; N, 12.65%), and the *perchlorate*,

[23] D. Lloyd, H. McNab, and D. R. Marshall, *Austral. J. Chem.*, 1977, **30**, 365.
[24] O. S. Tee and M. Endo, *J. Heterocyclic Chem.*, 1974, **11**, 441.

m.p. 157—158° (Found: C, 29.8; H, 3.9; N, 11.65. $C_6H_9ClN_2O_4S$ requires C, 29.95; H, 3.75; N, 11.65%), were prepared similarly.

1,2-*Dihydro*-2,3,4-*trimethyl*-2-*thioxopyrimidinium Salts* (3b).—Prepared as the dimethyl analogues, but from 3-oxobutyraldehyde dimethyl acetal (3.4 g, 25 mmol), the *hydrogen sulphate* (88%) had m.p. 156—156.5° (from methanol at −78 °C), $\lambda_{max.}$ 281 and 372 nm (ε 21 200 and 2 200), $\nu_{max.}$ 1 610, 1 570, 1 200, 1 110, 1 030, and 870 cm^{-1}, τ [$(CD_3)_2SO$] 0.86 (1 H, d), 2.56 (1 H, d), 5.95 (3 H, s), 6.02 (3 H, s), and 7.17 (3 H, s) (Found: C, 31.15; H, 5.55; N, 10.25. $C_7H_{12}N_2O_4S_2,H_2O$ requires C, 31.1; H, 5.2; N, 10.35%); the *perchlorate* had m.p. 90.5—91.5° (Found: C, 32.85; H, 4.45; N, 10.95. $C_7H_{11}ClN_2O_4S$ requires C, 33.0; H, 4.3; N, 11.0%).

1,2-*Dihydro*-2,3,4,5-*tetramethyl*-2-*thioxopyrimidinium Hydrogen Sulphate* (3c).—Prepared like the dimethyl analogue, but from acetylacetone (2.25 g, 25 mmol) this *salt* (50%) had m.p. 198—198.5° (decomp.) (from methanol at −78 °C), $\lambda_{max.}$ 283 and 366 nm (ε 21 100 and 2 900), $\nu_{max.}$ 1 610, 1 550, 1 270, 1 200, 1 100, 1 050, 1 020, and 860 cm^{-1}, τ [$(CD_3)_2SO$] 2.51 (1 H, s), 5.98 (6 H, s), and 7.24 (6 H, s) (Found: C, 35.9; H, 5.7; N, 10.25. $C_8H_{14}N_2O_4S_2$ requires C, 36.1; H, 5.25; N, 10.55%).

1,2-*Dihydro*-1,3-*dimethyl*-5-*phenyl*-2-*thioxopyrimidinium Perchlorate* (3e; X = ClO_4).—Methanol (5 ml), perchloric acid (60%; 0.6 g, 6 mmol), and *NN'*-dimethylthiourea (0.2 g, 2 mmol) were added successively to the sodium salt of phenylmalonaldehyde (0.34 g, 2 mmol), and the mixture was kept overnight at room temperature. The *perchlorate* (0.2 g, 32%) was filtered off and washed with water, and had m.p. 284—288° (from ethanol), $\lambda_{max.}$ 222sh and 307 nm (ε 19 300), $\nu_{max.}$ 1 590, 1 300, 1 100, 940, 860, and 760 cm^{-1}, τ [$(CD_3)_2SO$] 0.23 (2 H, s), 2.53 (5 H, m), and 6.53 (6 H, s) (Found: C, 45.75; H, 4.65; N, 8.65. $C_{12}H_{13}ClN_2O_4S$ requires C, 45.45; H, 4.1; N, 8.85%).

1,2-*Dihydro*-5-p-*methoxyphenyl*-1,3-*dimethyl*-2-*thioxopyrimidinium Perchlorate* (3g; X = ClO_4).—Prepared as the 5-phenyl analogue this *perchlorate* (34%) had m.p. 145—146° (from ethanol), $\lambda_{max.}$ 232 and 317 nm (ε 12 500 and 14 400), $\nu_{max.}$ 1 580, 1 300, 1 180, 1 100, 1 060, 930, 835, and 720 cm^{-1}, τ [$(CD_3)_2SO$] 0.33 (2 H, s), 2.56 (4 H, AA'BB' system), 6.15 (3 H,s), and 6.16 (6 H, s) (Found: C, 44.2; H, 5.0; N, 7.6. $C_{13}H_{15}ClN_2O_5S$ requires C, 44.95; H, 4.35; N, 8.05%).

Deuterium Exchange Experiments.—The rates of deuterium exchange at the 4-methyl groups of the trimethyl derivatives (2b) and (3b) were measured in unbuffered deuterium oxide in the n.m.r. probe (*ca.* 34 °C) over 3 h. The peak areas were measured relative to those of the 1,3-dimethyl peaks, which remained constant.

The deuterium exchange at the 5-positions of the dimethyl derivatives (2a) and (3a) was measured competitively. A mixture of the two compounds (50 mg of each) was dissolved in deuteriochloric acid (10%; 0.5 ml). After 6 days at 95—100 °C the appearance of the singlets at the centre of the 4(6)-proton doublets in the n.m.r. spectra at τ 0.90 and 1.05 confirmed the exchange of the 5-proton in the thioxo- and oxo-compounds, respectively.

5-*Bromo*-1,2-*dihydro*-1,3-*dimethyl*-2-*oxopyrimidinium Bromide* (2d; X = Br).—Bromine (0.9 g, 5.6 mmol) in methanol (10 ml) was added dropwise over 30 min to a stirred methanolic solution of the 5-unsubstituted oxopyrimidinium bromide (2a; X = Br) (1.03 g, 5 mmol). Evaporation of the solution, followed by trituration of the residue with acetone (10 ml), provided the 5-bromo-derivative (1.25 g, 88%), light yellow needles, m.p. 274–275° (decomp.) (from methanolic hydrobromic acid) (lit.,[10] 267—268°), $\lambda_{max.}$ 253 and 351 nm (ε 7 500 and 1 300), τ (D_2O) 0.82 (2 H, s) and 6.19 (6 H, s).

5,5-*Dibromo*-4,6-*dimethoxy*-1,3-*dimethyltetrahydropyrimidin*-2(1H)-*one* (7).—A solution of the 5-unsubstituted oxopyrimidinium hydrogen sulphate (2a; X = HSO_4) (1.2 g, 5 mmol) in methanol (70 ml) was added to a solution of bromine (2.0 g, 12.5 mmol) in methanol (20 ml). The mixture was kept overnight, then poured into water (50 ml), and extracted four times with chloroform. The combined extracts were washed with dilute aqueous sodium hydroxide and water, dried (Na_2SO_4), and evaporated. The oily residue crystallised on addition of ether. The *pyrimidine* (0.53 g, 31%) had m.p. 132—133° (from carbon tetrachloride), $\lambda_{max.}$ *ca.* 232 nm, $\nu_{max.}$ 1 640, 1 490, 1 400, 1 270, 1 150, 1 110, 1 060, 760, 750, and 720 cm^{-1}, τ ($CDCl_3$) 5.37 (2 H, s), 6.32 (6 H, s), and 6.98 (6 H, s) (Found: C, 27.5; H, 4.25; N, 8.2. $C_8H_{14}Br_2N_2O_3$ requires C, 27.75; H, 4.05; N, 8.1%).

Reaction of the 5,5-*Dibromo-compound* (7) *with Acid*.—When aqueous hydrobromic acid (50%; 0.1 ml) was added to a solution of the dibromo-compound (0.1 g) in acetone (3 ml), the bromo-derivative (2d; X = Br) (0.07 g, 86%), m.p. 277—278° (decomp.), immediately crystallised (spectra identical with those of an authentic sample).

5-*Bromo*-4-*bromomethyl*-1,2-*dihydro*-1,3-*dimethyl*-2-*oxopyrimidinium Bromide* (8).—Bromine (5.1 g, 32 mmol) in methanol (20 ml) was added slowly to a stirred solution of the trimethyloxopyrimidinium hydrogen sulphate (2b; X = HSO_4) (2.4 g, 10 mmol) in methanol (20 ml). The mixture was then stirred for 24 h. After removal of the solvent *in vacuo*, trituration of the residue with acetone (20 ml) provided the *dibromo-compound* (8) (1.75 g, 45%), m.p. 204.5—205° (decomp.) (varied with time of heating) (from propan-2-ol–hydrobromic acid), $\lambda_{max.}$ 261 and 356 nm (ε 6 200 and 500), $\nu_{max.}$ 1 720, 1 600, 1 540, 1 280, 1 050, and 770 cm^{-1}, τ (CF_3CO_2H) 0.91 (1 H, s), 5.22 (2 H, s), 5.95 (3 H, s), and 6.02 (3 H, s) (Found: C, 22.55; H, 2.7; N, 7.6. $C_7H_9Br_3N_2O$ requires C, 22.3; H, 2.4; N, 7.45%).

Kinetic Studies of Brominations.—The reaction of the 2-oxopyrimidinium salts (2a and b) with bromine were studied at 25 °C for aqueous solutions. The bromine solutions also contained potassium bromide. Reactions were run under first-order conditions, with the pyrimidine in 10—100-fold excess, and the progress of the reaction was followed in a stopped flow apparatus by noting the decay in the bromine absorption at 380 nm.

Reaction of 1,2-*Dihydro*-1,3,5,6-*tetramethyl*-2-*oxopyrimidinium Hydrogen Sulphate* (2c; X = HSO_4) *with Bromine*.—Bromine (1.6 g, 10 mmol) in methanol (10 ml) was added slowly to a stirred solution of the oxopyrimidinium salt (1.26 g, 5 mmol) in methanol (5 ml). The mixture was stirred for a further 30 min and a yellow precipitate (1.55 g, 66%) was then filtered off and dried overnight at 10^{-1} Torr. This *complex* had m.p. 143.5—144°, $\lambda_{max.}$ 316 nm (ε 9 400) (Found: C, 20.65; H, 3.05; N, 6.2. $C_8H_{13}Br_4N_2O$ requires C, 20.25; H, 2.75; N, 5.9%). This complex was decomposed by acetone, forming the bromide of (2c), m.p. 206—208° (decomp.) (from ethanol).

The filtrate remaining after separation of the complex was concentrated and triturated with acetone (1—2 ml). Cooling and scratching induced crystallisation of 5-*bromo*-4,6-*bis*(*bromomethyl*)-1,2-*dihydro*-1,3-*dimethyl*-2-*oxopyrimidinium bromide* (10) (0.15 g, 5%) as an orange powder. Recrystallised from methanol–hydrobromic acid, it did not melt below 330°, but decomposed extensively above 190°;

$\lambda_{max.}$ 282 nm (ε 5 300), $\nu_{max.}$ 1 700, 1 550, 1 060, 1 010, 880, and 760 cm^{-1}, τ (CF_3CO_2H) 5.12 (4 H, s) and 5.92 (6 H, s) (Found: C, 20.4; H, 2.2; N, 6.05. $C_8H_{10}Br_4N_2O$ requires C, 20.45; H, 2.15; N, 5.95%).

5-Chloro-1,2-dihydro-1,3-dimethyl-2-oxopyrimidinium Chloride (2f; X = Cl).—A freshly made solution of chlorine (*ca.* 2 mmol) in methanol [25] was added in one portion to a solution of the 5-unsubstituted oxopyrimidinium salt (2a; X = HSO_4) (0.45 g, 2 mmol) in methanol (50 ml). Methanol was removed *in vacuo*. On addition of ether to the residue the chloro-derivative (0.46 g, 90%) crystallised out; it was twice reprecipitated from dry methanolic hydrogen chloride (1M) by ether. The *chloride* had m.p. 243.5—244° (decomp.) $\lambda_{max.}$ 252 and 348 nm (ε 7 500 and 600), $\nu_{max.}$ 1 730, 1 580, 1 310, 1 080, 1 050, 960, and 760 cm^{-1}, τ ($CF_3 \cdot CO_2H$) 1.03 (2 H, s) and 6.03 (6 H, s) (Found: C, 36.8; H, 4.25; N, 14.4. $C_6H_8Cl_2N_2$ requires C, 36.9; H, 4.1; N, 14.35%).

Reaction of 1,2-Dihydro-1,3-dimethyl-2-thioxopyrimidinium Bromide (3a; X = Br) *with Bromine*.—Bromine in methanol was added slowly to a stirred solution of the thioxopyrimidinium salt (1.1 g, 5 mmol) in methanol (15 ml) until the colour persisted (*ca.* 3.6 g, 20 mmol required). A precipitate (0.2 g) was filtered off and washed with acetone. The filtrate was concentrated and triturated with acetone giving a yellow solid (0.85 g). Recrystallisation of both solids from methanolic hydrobromic acid gave identical products, whose m.p. and spectra proved that they were the 5-bromo-2-oxo-derivative (2d; X = Br) (74%). Use of only 1 mol. equiv. of bromine gave a product whose n.m.r. spectrum (in D_2O) indicated that it contained reactant and 5-bromo-2-oxo- and 5-unsubstituted 2-oxo-pyrimidinium salts [τ 1.1(d), 3.0(t), and 6.2(s)].

Reaction of 2,2-Dihydro-1,3,4-trimethyl-2-thioxopyrimidinium Hydrogen Sulphate (3b; X = HSO_4) *with Bromine*.—Bromine (2.0 g, *ca.* 12 mmol) in methanol (10 ml) was added slowly to a solution of the salt (3b; X = HSO_4) (0.51 g, 2 mmol) in methanol (5 ml), and the mixture was kept overnight. Methanol was removed *in vacuo*, and acetone (2—3 ml) was added. Addition of ether and cooling provided a product (0.18 g, 23%) whose m.p. and spectra showed it to be the 5-bromo-4-bromomethyl-2-oxo-derivative (8).

3,4-Dihydro-1,3-dimethyl-4-(phenylazomethylene)pyrimidine-2(1H)-thione (11).—A solution of benzenediazonium chloride, prepared from aniline (0.38 g, 4 mmol) in hydrochloric acid (1.4 g) and water (1 ml), and sodium nitrite (0.3 g) in water (1 ml), was added slowly to a cooled solution of the trimethylthioxopyrimidinium salt (3b; X = HSO_4) (1.16 g, 4 mmol) in water (10 ml), and the mixture was kept overnight at 0 °C. The precipitated solid was discarded, and addition of an excess of sodium acetate solution to the filtrate produced a red gelatinous precipitate (0.6 g, 58%). Recrystallisation from aqueous hydrochloric acid gave the *azomethylene compound* as its *hydrochloride*, m.p. 221.5—223.5° (decomp.) (from dimethylformamide), $\lambda_{max.}$ 278 and 453 nm (ε 19 700 and 27 000), $\nu_{max.}$ 1 650, 1 610, 1 320, 1 110, 910, and 770 cm^{-1}, τ [sat. sol. in $(CD_3)_2SO$, but too weak for integrals] 1.51 (d, 6-H), 1.82 (s, methine CH) 2.22 (d, 5-H), 2.3—2.8 (complex, Ph), and 5.89(s) and 6.10(s) (*N*- and *N'*-Me) (Found: C, 49.9; H, 5.6; N, 18.15. $C_{13}H_{15}ClN_4S,H_2O$ requires C, 49.9; H, 5.45; N, 17.9%).

Formation of 4-Hydroxy- or Deuterioxy-adducts of Oxo- and Thioxopyrimidines.—The oxo- or thioxo-pyrimidinium salt (50 mg) was dissolved in *ca.* 1M-sodium deuteroxide; the n.m.r. spectra of the solutions were characteristic of the 4-deuterioxy-adducts (12; Z = OD). The adducts were formed quantitatively only if an excess of base was present. They could not be isolated by extraction of the mixture with water, or by work-up of an attempted metathetic reaction using the hydrogen sulphate salt (2a; X = HSO_4) and barium hydroxide. Adducts were made from (2a), (2d), (2f), and (3a). The u.v. spectra of the adducts (Table 1) were recorded *in situ* for aqueous solutions *ca.* 2×10^{-2}M in sodium hydroxide.

Piperidine and N-Methylpiperidine Adducts.—The pyrimidinium salts (2a, d, e, and g) and (3a, e, and g) were severally dissolved in [$^2H_6$]dimethyl sulphoxide (0.5 ml) and piperidine (50 mg) was added; similarly adducts were made from the salts (2a and d) and (3a) and *N*-methylpiperidine. In some cases, especially when *N*-methylpiperidine was used, addition of deuterium oxide (to *ca.* 5%) improved the solubility of the product and the quality of the n.m.r. spectrum, which was characteristic of the adduct. The u.v. spectra (see Table 1) were recorded for aqueous solutions *ca.* 2×10^{-2}M in piperidine; the quoted ε values are approximate, since the maxima were merely shoulders on the long-wavelength piperidine peak.

3,4-Dihydro-4-methoxy-1,3-dimethylpyrimidin-2(1H)-one (12; X = O, Y = H, Z = OMe).—A solution of the hydrogen sulphate (2a; X = HSO_4) (2.2 g, 10 mmol) in methanol (120 ml) was mixed with a solution of sodium methoxide [from sodium (0.23 g, 10 mmol)] in methanol (20 ml). Solvent was evaporated off and the resultant semi-solid mass was washed thoroughly with ether. The inorganic residue was filtered off and the filtrate was evaporated, leaving the crude 4-methoxy-adduct (0.86 g, 56%) as an oil. Attempted distillation at 0.3 Torr resulted in decomposition of the sample. It had $\nu_{max.}$ (film) 1 650, 1 580, 1 340, 1 260, 1 040, 880, and 740 cm^{-1}. The u.v. spectra were recorded *in situ* in methanolic sodium methoxide (*ca.* 2×10^{-2}M), and the n.m.r. spectra for solutions in [$^2H_6$]dimethyl sulphoxide (see Table 1) (Found: M^+, 156.0890. Calc. for $C_7H_{12}N_2O_2$: *M*, 156.0899).

5-Bromo-3,4-dihydro-4-methoxy-1,3-dimethylpyrimidin-2(1H)-one (12; X = O, Y = Br, Z = OMe).—Prepared like its unbrominated analogue, this adduct (90%) had $\nu_{max.}$ (film) 1 670, 1 470, 1 340, 1 250, 1 040, 780, and 760 cm^{-1} (Found: M^+ 235.9992. Calc. for $C_7H_{11}{}^{81}BrN_2O_2$: *M*, 235.9983)

3,4-Dihydro-4-methoxy-1,3-dimethylpyrimidine-2-(1H)-thione (12; X = S, Y = H, Z = OMe).—Prepared like its oxo-analogue, this adduct (45%) had $\nu_{max.}$ (film) 1 670, 1 470, 1 340, 1 290, 1 230, 1 120, 1 030, and 910 cm^{-1} (Found: M^+, 172.0675. Calc. for $C_7H_{12}N_2OS$: *M*, 172.0670

Reaction of Methoxy-adducts with Acid.—(*a*) The adduct (12; X = O, Y = H, Z = OMe) (0.05 g) was dissolved in acetone (2 ml) and perchloric acid (60%; 2 drops) was added. Addition of ether precipitated the oxopyrimidinium perchlorate (2a; X = ClO_4) (0.045 g, 63%), m.p. and mixed m.p. 192—194°.

(*b*) Aqueous hydrobromic acid (50%; 2 drops) was added to a solution of the adduct (12; X = S, Y = H, Z = OMe) (0.1 g) in acetone (2 ml). Addition of ether precipitated the thioxopyrimidinium bromide (3a; X = Br) (70%), m.p. and spectra identical with those of an authentic sample.

Bromination of 3,4-Dihydro-4-methoxy-1,3-dimethylpyrimidin-2(1H)-one.—(*a*) A solution of bromine (0.16 g, 1 mmol) in chloroform (5 ml) was added in one portion to a solution of this methoxy-adduct (0.16 g, 1 mmol) in chloroform (5 ml). After 5 min the precipitated complex was filtered off and decomposed with acetone; further product was

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obtained by addition of acetone to the filtrate. The product (0.1 g, 35%) had m.p. 297—282° (decomp.) (from methanolic hydrobromic acid) and spectra identical with those of an authentic sample of the 5-bromo-oxopyrimidinium bromide (2d; X = Br).

(*b*) *N*-Bromosuccinimide (0.18 g, 1 mmol) was added to a solution of this methoxy-adduct (0.16 g, 1 mmol) in chloroform (5 ml) and the mixture was shaken until all the solid had dissolved. Solvent was evaporated off *in vacuo*. Addition of ether, followed by dry methanolic hydrogen chloride (containing 1 mmol of HCl) caused crystallisation of *5-bromo-1,2-dihydro-1,3-dimethyl-2-oxopyrimidinium chloride* (0.07 g, 25%), m.p. 255—257° (decomp.), τ (D_2O) 0.78 (2 H, s) and 6.20 (6 H, s) (Found: C, 29.85; H, 3.5; N, 12.05. $C_6H_8BrClN_2O$ requires C, 30.05; H, 3.35; N, 11.7%).

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