Reactions between 4-Pyrimidones and Sulphur Ylides; Cyclopropanation and Ring Opening Reactions

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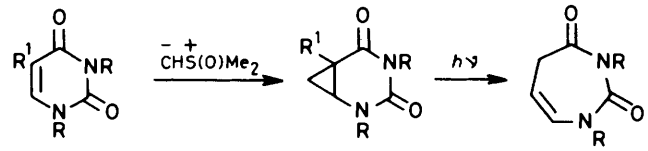
The reaction between 3-substituted 4-pyrimidones (4) and dimethylsulphoxonium methylide gives in some cases diazabicyclohept-2-enones (cyclopropapyrimidones) (13). An important side reaction is ring opening to give (*Z*)-3-aminoacrylamides (12); in the case of compound (4f) a major product is the oxopyrimidinyl ylide (16). Some attempts to open the cyclopropane ring in compound (13b) are described. A number of new bis(oxopyrimidinyl)ethanes (7)—(9) have been obtained.

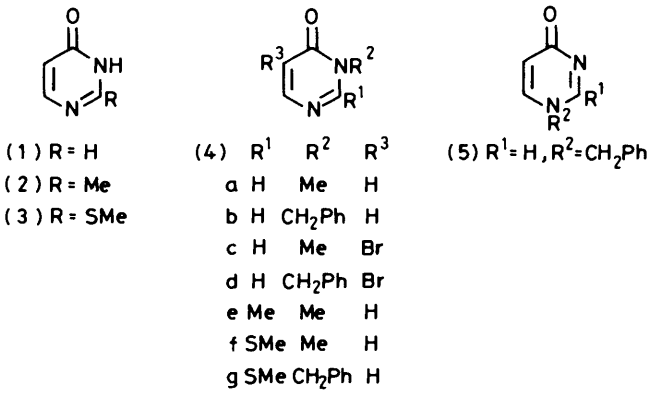
We are investigating routes to monocyclic 1,3-diazepines, which will permit the preparation of substantial quantities of these elusive species. There are three reported routes, due to Kunieda and Witkop,[1] to Moore *et al.*,[2] and to Kurita *et al.*,[3] which lead to fully unsaturated 1,3-diazepines. Of these, the last two do not seem adaptable for the production of large quantities of product, being either inefficient or providing mixtures which are difficult to separate. The route which attracted us is based on that due to Kunieda and Witkop,[1] who treated dialkyluracils with dimethylsulphoxonium methylide (DMSOM) and obtained bicyclic compounds which were subsequently expanded to give diketodiazepines; the whole approach is shown in Scheme 1. This sequence has been developed by Pandit and his co-workers,[4-7] but there are no reports of attempts to produce less substituted diazepines by modifying the precursor. We report here our attempts to use 4-pyrimidones instead of uracils in the reaction with DMSOM and other ylides.

We have prepared the 3-substituted 4-pyrimidones (4a—g), mainly by literature procedures from the pyrimidones (1)—(3), obtaining also the 1-alkyl derivative (5) and the *O*-alkyl derivative (6). The reaction between methylthiouracil (3) and 1,2-dibromoethane gave three products (7), (8), and (9), whose structures were established by n.m.r. spectroscopy. Treatment of the pyrimidones (4b) and (4g) with Lawesson's reagent[8] gave the thiones (10b) and (10g).

The products obtained from the 4-pyrimidones (4a—g) with DMSOM (11) varied with solvent. In dimethyl sulphoxide as solvent compounds (4a), (4b), and (4f) each gave two products. From compounds (4a) and (4b) the major products were the (*Z*)-3-formylaminoacrylamides (12a) and (12b). Such compounds have been postulated[9,10] in hydrolytic ring opening of 4-pyrimidones but never isolated. The minor products from compounds (4a) and (4b) were the cyclopropapyrimidones (diazabicycloheptenones) (13a) and (13b) (8% and 7% yields respectively). The structures were established by analysis and n.m.r. spectroscopy, notably the complex four-proton cyclopropane signals. When tetrahydrofuran was used as solvent no ring-opening occurred and compound (13b) could be obtained in yields up to 24%. From the pyrimidone (4f) in DMSO as solvent a small yield of cyclopropapyrimidone (13f) was formed. The major product was the sulphoxonium ylide salt (15); by using tetrahydrofuran as solvent the yield of the ylide (16) could be raised to 41%. Similar nucleophilic replacements on pyrimidones[11] and chloropyrimidines[12] are known. The ylide (16) was acetylated in quantitative yield to give compound (17). None of the other 4-pyrimidones reacted with DMSOM; nor did the 1-alkyl derivative (5), nor the thiones (10b) or (10g). No adducts were obtained from compound (4a) with carbenes, nor from compound (5) when it was heated with phenyl(tribromomethyl)mercury. The ylide (14) failed to react with the pyrimidone (4b).



Scheme 1.

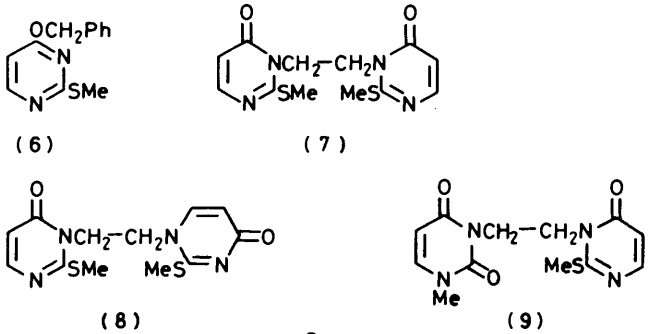


(1) R = H
(2) R = Me
(3) R = SMe

(4)

	R^1	R^2	R^3
a	H	Me	H
b	H	CH_2Ph	H
c	H	Me	Br
d	H	CH_2Ph	Br
e	Me	Me	H
f	SMe	Me	H
g	SMe	CH_2Ph	H

(5) R^1 = H, R^2 = CH_2Ph

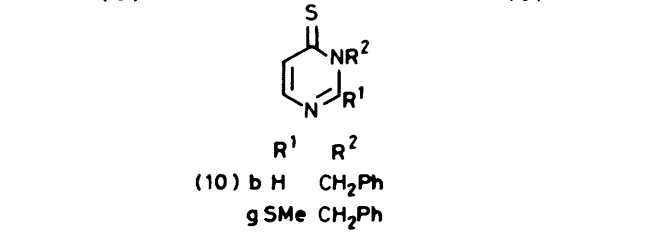


(6)

(7)

(8)

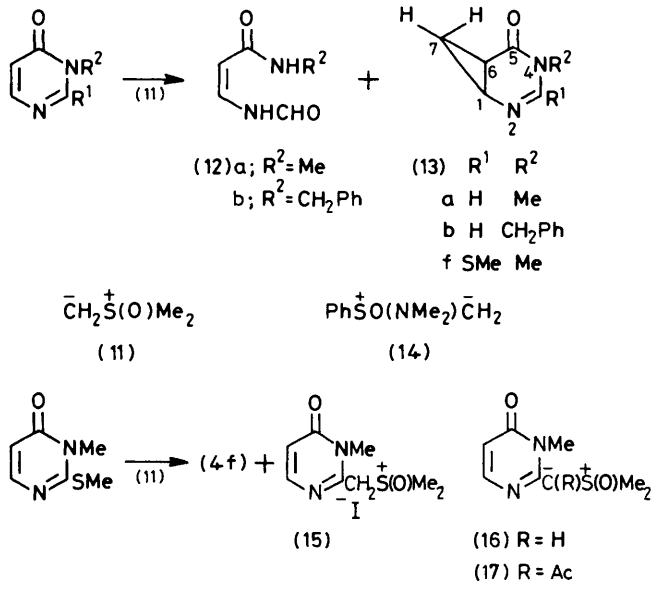
(9)



(10)

	R^1	R^2
b	H	CH_2Ph
g	SMe	CH_2Ph

Shortage of material has limited our attempts to convert the bicyclic compounds of type (13) into 1,3-diazepines. Compound (13a) was stable in boiling xylene (20 h). Compound (13 g) was decomposed when irradiated in aqueous methanol



by a medium-pressure lamp (quartz tube), but was stable to treatment with trimethyloxonium fluoroborate. Compound (13b) was stable in trifluoroacetic acid (24 h), and reacted with Lawesson's reagent to give the pyrimidine-4-thione (10b). Flash vacuum pyrolysis of compound (13b) at 500 °C gave as major product the pyrimidone (4b). In neither of the last two reactions is there any evidence for the fate of the extruded methylene group.

Experimental

M.p.s are determined on a Kofler heated stage and are uncorrected. I.r. spectra were determined in chloroform solutions and u.v. spectra in 95% ethanol, unless otherwise stated. Chromatography was on columns of Florisil, alumina, or silica.

Synthesis of 4H-*Pyrimidones and Pyrimidinethiones.*—The following compounds were prepared by literature procedures. Analytical and other data are given in Table 1 and Table 2 for new compounds.

3-*Methyl*-4-*pyrimidone* (4a) by the procedure of Jonak *et al.*[13] m.p. 122 °C (lit.,[14] m.p. 123—124 °C).

3-*Benzyl*-4-*pyrimidone* (4b) by the same procedure in 67% yield, m.p. 104—105 °C (lit.,[15] m.p. 102—105 °C). The procedure of Bauer *et al.*[15] using methanol as solvent gave compound (4b) in 35% yield (reported [15] yield 13%).

1-*Benzyl*-4-*pyrimidone* (5b) by the procedure of Bauer *et al.*[15] in 37% yield, m.p. 142—144 °C (lit.,[15] yield 12%, m.p. 142—144 °C). The isomers (4b) and (5b) were separated by chromatography on an alumina column, with petroleum containing increasing amounts of ethyl acetate as eluant.

5-*Bromo*-3-*methyl*-4-*pyrimidone* (4c). Prepared by bromination of compound (4a), m.p. 153—154 °C (lit.[16] m.p. 152—155 °C).

5-*Bromo*-3-*benzyl*-4-*pyrimidone* (4d). Prepared by the benzylation of 5-bromo-4-pyrimidone in 10% yield; see Table 1 and Table 2.

2-*Methyl*-4-*pyrimidone* (2). Prepared by the method of den Hertog *et al.*[17]. The sodium salt of ethyl formylacetate, prepared by either of two published procedures [13,18] showed large peaks in the n.m.r. spectrum assigned to sodium ethoxide. If allowance is made for this in the condensation with acetamidine hydrochloride the yield reported can be improved to 26%. Compound (2) had m.p. 210—211 °C (lit.,[17] m.p. 212.5—213 °C).

2,3-*Dimethyl*-4-*pyrimidone* (4e). Prepared by the method of Curd and Richardson [19] m.p. 65 °C (lit.,[13] m.p. 63—65 °C) in 36% yield (no yield reported).

2-*Methylthio*-4-*pyrimidone* (3). Prepared by the method of Barrett *et al.*,[20] m.p. 197—198 °C (lit.,[20] m.p. 198 °C).

3-*Methyl*-2-*methylthio*-4-*pyrimidone* (4f). Prepared by the method of Brown *et al.*, [14] m.p. 122—124 °C (lit.,[14] m.p. 122—123 °C).

3-*Benzyl*-2-*methylthio*-4-*pyrimidone* (4g). Prepared by the benzylation of compound (3) using DMF as solvent and sodium hydride as base,[21] m.p. 97—98 °C (lit.,[21] m.p. 97 °C).

1-*Benzyl*-2-*methylthio*-4-*pyrimidone* (5g). Prepared in the same alkylation reaction as the 3-substituted isomer (4g), it had m.p. 174 °C (lit.,[21] m.p. 176—177 °C). A quantity of 4-benzyloxy-2-methylthio-4-pyrimidone (6), with spectral properties identical with those reported by Gacek and Undheim [21] was also obtained.

1,2-*Bis*-(2-*methylthio*-4-*oxopyrimidin*-3-*yl*)*ethane* (7).—A solution of 1,2-dibromoethane (15 ml, 5 equiv.) in dry methanol was boiled vigorously under a nitrogen atmosphere while a solution of 2-methylthio-4-pyrimidone (3) (5 g) and potassium hydroxide (1.96 g) in methanol (25 ml) was added dropwise (3 h). The mixture was boiled (5 h), filtered, evaporated, and the residue chromatographed on alumina (activity IV). Three compounds were eluted by increasing amounts of ethyl acetate in light petroleum. The third was the bis(oxopyrimidinyl)ethane (7) (30% yield); see Tables 1 and 2.

1-(2-*Methylthio*-4-*oxopyrimidin*-1-*yl*)-2-(2-*methylthio*-4-*pyrimidin*-3-*yl*)*ethane* (8). First from the column described in the previous experiment was compound (8) (12% yield); see Tables 1 and 2.

1-(1-*Methyl*-2,4-*dioxopyrimidin*-3-*yl*)-2-(2-*methylthio*-4-*oxopyrimidin*-3-*yl*)*ethane* (9). Isolated as second compound from the above column, in 2% yield; see Tables 1 and 2.

3-*Benzylpyrimidine*-4-*thione* (10b).—The pyrimidone (4b) (4 g) and Lawesson's reagent (4.84 g) were dissolved in toluene (30 ml) and the solution boiled (4 h). Purification by chromatography on a silica column, with benzene–ethyl acetate mixtures as eluant, gave the *thione* (10b), m.p. 101—103 °C in 65% yield; see Tables 1 and 2.

3-*Benzyl*-2-*methylthiopyrimidine*-4-*thione* (10g). This was prepared by the same method in 68% yield; see Tables 1 and 2.

Reactions Between Pyrimidones and Dimethylsulphoxonium Methylide (11).—*General Procedures.* All methylide additions were performed with a nitrogen atmosphere.

(*a*) Sodium hydride (1.1 g, 0.022 mol, 50% in paraffin) was washed by decantation with light petroleum (15 ml). Dry DMSO (30 ml) was added, then trimethylsulphoxonium iodide [22] (5 g, 0.0225 mol, in one portion); the mixture was then stirred at room temperature (0.5 h). The pyrimidone (0.022 mol) was added to the methylide solution a little at a time, the mixture being stirred (0.5 h) and heated at 40—60 °C (4 h). Work-up involved *either* evaporation at 60—70 °C and 0.01 mmHg, the residue being extracted with chloroform, *or* dilution with a three-fold volume of water, and extraction with chloroform. In either case the chloroform-soluble material was purified by chromatography on Florisil (150 g). The column was made up in light petroleum (b.p. 40—60 °C) and eluted by light petroleum containing increasing percentages of ethyl acetate. First from the column was the cyclopropapyrimidone, then unchanged pyrimidone, and finally the aminoacrylamide.

(*b*) Sodium hydride, washed as in (*a*), was covered with

Table 1. New compounds derived from 4-pyrimidone and pyrimidine-4-thione

Compd.	M.p. (°C) [solvent]	Formula	Analyses (%) Found C	Found H	Found N	Required C	Required H	Required N
(4d)	140—142 [EtOH–light petroleum (b.p. 40—60 °C)]	$C_{11}H_9BrN_2O$	49.95	3.35	10.6	49.85	3.4	10.55
(7)	210 [benzene]	$C_{12}H_{14}N_4O_2S_2$	46.2	4.3	17.9	46.45	4.5	18.0
(8)	77—78 [cyclohexane]	$C_{12}H_{14}N_4O_2S_2$	46.8	4.7	18.1	46.45	4.5	18.0
(9)	98—99 [cyclohexane]	$C_{12}H_{14}N_4O_3S$	48.95	4.8	19.05	48.95	4.75	19.05
(10b)	104—106 [cyclohexane]	$C_{11}H_{10}N_2S$	65.6	4.75	13.73	65.35	5.0	13.85
(10g)	134—135 [cyclohexane]	$C_{12}H_{12}N_2S$	57.65	4.95	11.15	58.05	4.85	11.3
(15)	181 [EtOH]	$C_8H_{13}IN_2O$	36.5	4.75	10.55	36.4	4.9	10.6
(16)	190 [$CHCl_3$–benzene]	$C_8H_{12}N_2O_2S$	47.8	5.95	14.0	48.0	6.0	14.0
(17)	186 [benzene]	$C_{10}H_{14}N_2O_3S$	49.65	5.55	11.75	49.6	5.8	11.57

Table 2. Spectral data on new 4-pyrimidones and pyrimidine-4-thiones

Compd.	$\nu_{max.}$/cm^{-1}	λ/nm ($\log_{10}\varepsilon$)	^{1}H N.m.r. δ	*J* Values (Hz)	*M*/*z* (m.u.)/%
(4d)	1 660		5.15 (2 H, s), 7.4 (5 H, s), 8.2 (2 H, d)		266. 264 (M^+, 100), 160, 158 (18), 91 (87), 65 (85)
(7)	1 690	227 (3.12), 290 (5.1), 313sh	2.5 (6 H, s), 4.4 (4 H, s), 6.1 (2 H, d), 7.2 (2 H, d)	$J_{5,6}$ 6	310 (M^+, 16), 293 (16), 170 (10), 169 (100, $M - C_5H_5N_2OS$) 168 (77), 153 (74), 142 (36), 135 (26), 121 (77), 95 (23)
(8)	1 690	248 (4.17), 285 (4.06), 298sh, 310sh	2.4 (6 H, s), 4.1—4.7 (4 H, m), 6.1 (1 H, d), 6.3 (1 H, d), 7.6 (1 H, d), 8.1 (1 H, d)	$J_{5,6}$ 6	310 (M^+, 7), 169 (100, $M - C_5H_5N_2OS$)
(9)	1 700	250 (4.16), 275sh	2.4 (3 H, s), 3.8 (3 H, s), 4.2—4.7 (4 H, m), 6.0 (1 H, d), 6.3 (1 H, d), 7.7 (1 H, d), 8.1 (1 H, d)	$J_{5,6}$ 6	294 (M^+, 24), 168 (40), 154 (34), 153 (100, $M - C_5H_5N_2OS$), 127 (28), 96 (96), 84 (90), 70 (74)
(10b)	1 400	295 (4.05), 350sh	5.65 (2 H, s), 7.35 (5 H, s), 7.5 (1 H, d), 7.7 (1 H, d), 8.3 (1 H, s)	$J_{5,6}$ 6	202 (M^+, 54), 169 (28), 91 (100)
(10g)	1 220 (C=S)	238 (4.01), 295 (3.63), 360 (3.57)	2.4 (3 H, s), 6.0 (2 H, s), 7.3 (1 H, d), 7.3 (5 H, s), 7.5 (1 H, d)	$J_{5,6}$ 6	248 (M^+, 100), 233 (27), 215 (67), 201 (31, M – SMe), 128 (60), 91 (100, $PhCH_2^+$)
(15)	No C=O		3.0 (3 H, s), 3.2 (1 H, s), 3.5 (6 H, s), 4.4 (1 H, s), 5.4 (1 H, d), 7.45 (1 H, d)	$J_{5,6}$ 6	
(16)	1 670	269 (3.85), 325 (4.31)	3.2 (3 H, s), 3.5 (6 H, s), 3.9 (1 H, s), 5.7 (1 H, d), 7.5 (1 H, d)	$J_{5,6}$ 6	200 (M^+)
(17)	1 700	250 (3.83), 325sh	1.8 (3 H, s), 3.6 (6 H, s), 6.4 (1 H, d), 7.8 (1 H, d)	$J_{5,6}$ 6	242 (M^+, 42), 227 ($M - CH_3$, 55) 165 (60), 150 (36), 137 (75), 136 (100)

dry tetrahydrofuran (30 ml). Dry trimethylsulphoxonium chloride [23] was added, boiled (4 h), then the pyrimidone added, and the mixture boiled (4 h). Filtration and washing of the filtered solid with more THF was followed by evaporation of the combined filtrates, and separation of the products by chromatography, as in (*a*).

The details of yields, and physical constants of the products, are described below.

4-*Methyl*-2,4-*diazabicyclo*[4.1.0]*hept*-2-*en*-5-*one* (13a) *and* (*Z*)-3-*formylamino*-N-*methylacrylamide* (12a). Prepared from 3-methyl-4-pyrimidone (4a) the *diazabicyclohept*-2-*enone* (13a) (8% yield) had m.p. 55—58 °C [from petroleum (b.p. 40—60 °C)] (Found: C, 57.65; H, 6.45; N, 22.75. $C_6H_8N_2O$ requires C, 58.05; H, 6.45; N, 22.6%); $\nu_{max.}$ 1 680 cm^{-1}; δ 0.7 (1 H, q, 7-*exo*-H), 1.6—2.2 (2 H, m, 7-*endo*-H, 6-H), 3.2 (3 H, s, NCH_3), 3.2—3.7 (1 H, m, 1-H), 7.05 (1 H, s, 3-H); *m*/*z* 124 (M^+, 100), 110 ($M - CH_2$), 54, 95 [$M - (CH_2 + CH_3)$], 67 (82), 55 (62), and 42 (98) m.u. The *acrylamide* (32% yield) had m.p. 74—75 °C (from cyclohexane) (Found: C, 46.7; H, 6.4; N, 22.75. $C_5H_8N_2O_2$ requires C, 46.85; H, 6.25; N, 21.9%), $\nu_{max.}$ 3 300, 1 700, 1 650, and 1 625 cm^{-1}; δ 2.8 (3 H, d), 5.0 (1 H, d, *J* 8 Hz), 6.0br (1 H, NH), 7.3 (1 H, dd, *J* 8 and 8 Hz), 8.3 (1 H, s), and 11.0br (1 H, NH); *m*/*z* 128 (M^+, 44), 110 ($M - H_2O$, 11), 100 (M – CO, 94), 98 (42), 96 (16), 71 (24), 70 ($M - CH_3NHCO$, 100), 58 (11), and 42 (26) m.u.

4-*Benzyl*-2,4-*diazabicyclo*[4.1.0]*hept*-2-*en*-5-*one* (13b) *and* (*Z*)-N-*benzyl*-3-*formylaminoacrylamide* (12b). Prepared from 3-benzyl-4-pyrimidone (4b), the *diazabicycloheptenone* (13b) (27% yield by method (*b*) had m.p. 61—63 °C [from petroleum (b.p. 40—60 °C)] (Found: C, 71.8; H, 5.95; N, 14.1. $C_{12}H_{12}N_2O$ requires C, 72.0; H, 6.05; N, 14.0%), $\nu_{max.}$ 1 665 cm^{-1}; $\lambda_{max.}$ 265 nm ($\log_{10}$ ε 4.09); δ 1.7 (1 H, q, 7-*exo*-H), 2.0 (2 H, m), 3.5 (1 H, m), 4.7 (2 H. d), 7.0 (1 H, s), and 7.3 (5 H, s); *m*/*z* 200 (M^+, 71), 173 (M – HCN), 110 (21), 95 (18), 93 (28), 92 (100) m.u. The *acrylamide* (12b) [up to 24% yield, by method (*a*)] had m.p. 83—85° (from benzene) (Found: C, 64.55; H, 5.85; N, 13.8. $C_{11}H_{12}N_2O_2$ requires C, 64.7; H, 5.9; N, 13.75%), $\nu_{max.}$ 3 300, 1 720, 1 660, and 1 630 cm^{-1}; n.m.r. δ 4.5 (2 H, d) 5.0 (2 H, dd), 6.0br (1 H, exch. D_2O, NH), 7.3 (6 H, s), 8.1 (1 H, s), 11.2br (1 H, exch. D_2O, NH).

4-*Methyl*-3-*methylthio*-2,4-*diazabicyclo*[4.1.0]*hept*-2-*en*-5-*one* (13f) and *dimethylsulphoxonium*(3-*methyl*-4-*oxopyrimidin*-2-*yl*)*methylide* (16). (a) When 3-methyl-2-methylthio-4-pyrimidone (3) was treated with the methylide (11) in DMSO, and worked up by addition of water followed by extraction

with chloroform the *diazabicycloheptenone* (13f) was obtained in 7.5% yield, m.p. 79—81 °C [from benzene–light petroleum (b.p. 40—60 °C)] (Found: C, 49.55; H, 5.8; N, 16.65. $C_7H_{10}N_2OS$ requires C, 49.4; H, 5.9; N, 16.45%), $\nu_{max.}$ 1 680 cm^{-1}; $\lambda_{max.}$ 213 nm ($\log_{10}$ ε 4.05); δ 0.7 (1 H, q), 1.5—2.0 (2 H, m), 2.3 (3 H, s, SCH_3), 3.15 (3 H, s, NCH_3), 3.5 (1 H, m); *m/z* 170 (M^+, 21), 156 ($M - CH_2$, 11), 125 (100), 98 (21), and 95 (29) m.u. Concentration of the aqueous layer gave a quantity of *iodide* (15), m.p. 181 °C (from absolute ethanol). Physical data are given in Tables 1 and 2.

(b) By using method (b) it was possible to obtain the *methylide* (16) in 41% yield, m.p. 190 °C. Physical data are given in Tables 1 and 2.

Acetyl(3-*methyl*-4-*oxopyrimidin*-2-*yl*)*dimethylsulphoxonium Methylide* (17).—The ylide (16) (1 g) was boiled with a tenfold excess of acetic anhydride (5 ml) in dry chloroform (20 ml) (2 h). Removal of solvents and recrystallisation of the residue from benzene gave the ylide (17), m.p. 186 °C (1.05 g, 87%). Physical data are given in Tables 1 and 2.

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References

1 T. Kunieda and B. Witkop, *J. Am. Chem. Soc.*, 1971, **93**, 3478.
2 J. A. Moore, W. J. Freeman, R. C. Gearhart, and H. B. Yokelson, *J. Org. Chem.*, 1978, **43**, 787.
3 J. Kurita, H. Kojima, and T. Tsuchiya, *Chem. Pharm. Bull.*, 1981, **29**, 3688; J. Kurita, H. Kujima, M. Enkaku, and T. Tsuchiya, *Chem. Pharm. Bull.*, 1981, **29**, 3696.
4 H. P. M. Thiellier, G.-J. Koomen, and U. K. Pandit, *Heterocycles*, 1975, **3**, 707.
5 H. P. M. Thiellier, G.-J. Koomen, and U. K. Pandit, *Heterocycles*, 1976, **5**, 19.
6 H. P. M. Thiellier, G.-J. Koomen, and U. K. Pandit, *Tetrahedron*, 1977, **33**, 2603.
7 H. P. M. Thiellier, G.-J. Koomen, and U. K. Pandit, *Tetrahedron*, 1977, **33**, 2609.
8 H. Fritz, P. Hug, S. O. Lawesson, E. Logemann, B. S. Pedersen, H. Sauter, S. Scheibye, and T. Winkler, *Bull. Soc. Chim. Belg.*, 1978, **87**, 525.
9 O. S. Tee and M. Paventi, *J. Org. Chem.*, 1981, **46**, 4172.
10 S. David and H. Hirshfeld, *Bull. Soc. Chim. Fr.*, 1966, 527.
11 T. Kunieda and B. Witkop, *J. Am. Chem. Soc.*, 1971, **93**, 3487.
12 H. Yamanaka, S. Kondo, T. Sakamoto, S. Niitsuma, and S. Noji, *Chem. Pharm. Bull.*, 1981, **29**, 2837.
13 J. P. Jonak, G. C. Hopkins, H. J. Minnemeyer, and H. Tieckelmann, *J. Org. Chem.*, 1970, **35**, 2512.
14 D. J. Brown, E. Hoeger, and S. F. Mason, *J. Chem. Soc.*, 1955, 211.
15 L. Bauer, G. E. Wright, B. A. Mikrut, and C. L. Bell, *J. Heterocycl. Chem.*, 1965, **2**, 447.
16 O. S. Tee and S. Banerjee, *J. Org. Chem.*, 1979, **44**, 3256.
17 H. J. den Hertog, H. C. Van Der Plas, M. J. Pieterse, and J. W. Streef, *Recl. Trav. Chim. Pays-Bas*, 1965, **84**, 1569.
18 S. Gabriel, *Ber.*, 1904, **37**, 3638.
19 F. H. S. Curd and D. N. Richardson, *J. Chem. Soc.*, 1955, 1853.
20 H. W. Barrett, I. Goodman, and K. Dittmer, *J. Am. Chem. Soc.*, 1948, **70**, 1753.
21 M. Gacek and K. Undheim, *Acta Chem. Scand. Ser. B*, 1982, **36**, 2.
22 R. Kuhn and H. Trsichmann, *Liebigs Ann. Chem.*, 1958, **611**, 117.
23 E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, 1965, **87**, 1353.

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