Meso-ionic Compounds. Part 12.[1,2] Synthesis of 1-Alkyl-4-oxopyrimido-[1,2-*a*]-*s*-triaziniumolates and their 4-Thio-derivatives

By **Claude V. Greco*** and **Kanti J. Gala**, Department of Chemistry, St. John's University, Jamaica, New York 11439, U.S.A.

Treatment of 2-alkylaminopyrimidines (1) and (2) with ethoxycarbonyl isocyanate gave the acyclic urea derivatives, namely, 3-alkyl-1-ethyoxycarbonyl-3-(2-pyrimidyl)ureas (3) and (4), which cyclized to 1-alkyl-4-oxopyrimido-[1,2-*a*]-*s*-triazin-1-ium-2-olates (6) and (7) in refluxing *p*-xylene. Structural proof was obtained through spectral analyses, and an alternate synthesis in which (1) and (2) were reacted with phenoxycarbonyl isocyanate.

Reaction of (1) and (2) with ethoxycarbonyl isothiocyanate gave 2-alkylimino-1(*N*-ethoxycarbonylthiocarbamoyl)-1,2-dihydropyrimidines (8) and (9) which on treatment with trifluoroacetic acid cyclized to 1-alkyl-4-thioxopyrimido[1,2-*a*]-*s*-triazin-1-ium-2-olates (10) and (11), respectively. Similar reactions of (1) with phenoxycarbonyl isothiocyanate did not yield either the precursor (8), the carbonyl isothiocyanate (12), or the expected meso-ionic system, 1-methyl-2-thioxopyrimido[1,2-*a*]-*s*-triazin-1-ium-4-olate (13).

The insolubility and instability of (10) and (11) made purification extremely difficult, and consequently structural characterization was based on spectral analyses.

The reaction of ethylamine with (6) and (10) gave products for which the 1-alkyl-6-amino-1,2,3,4-tetrahydro-*s*-triazine structures (14) and (16), respectively, were assigned based on mass spectral analyses.

CONSIDERABLE variation of the position and nature of hetero-atoms is possible for five-membered monocyclic meso-ionic compounds of the sydnone type,[3] the meso-ionic six-membered triazine [4] and pyrimidine [5] types as well as the bicyclic systems.[6,7] When this research was initiated, little was known concerning bicyclic meso-ionic systems with two fused six-membered rings. We describe here our efforts to prepare examples of the meso-ionic pyrimido[1,2-*a*]-*s*-triazine-2,4-diones (6) and (7) and their mono-thione derivatives (10), (11), and (13).

Among the possible synthetic routes,[5,8-10] alkoxycarbonyl isocyanates [11,12] and isothiocyanates [11,13] were selected because they are easily prepared, and nucleophilic attack at the isocyanate or isothiocyanate function is enhanced by the strongly electron-attacting alkoxycarbonyl group.[14]

RESULTS AND DISCUSSION

2-Alkylaminopyrimidines (1) and (2) reacted with ethoxycarbonyl isocyanate in anhydrous ethyl acetate at room temperature to afford 3-alkyl-1-ethoxycarbonyl-3-(2-pyrimidyl)ureas (3) and (4), respectively. Their i.r. absorptions at 1 685 and 1 775 cm^{-1} for the two carbonyl groups correlate well with those observed for 1-benzyl-3-ethoxycarbonyl-1-(2-thiazolyl)urea (1 681 and 1 767 cm^{-1}) [8b] and the 4-aryl-4-(2-pyridyl)allophanate ethyl esters (1 680 and 1 765 cm^{-1}).[15] Also, 2-acetamidopyrimidine [16] exhibits a ν(CO) at 1 700 cm^{-1}. Further supports for our structural assignment were the u.v. absorptions (H_2O) at $\lambda_{max.}$ 240 (log ε 6.46) and 370 nm (5.64), which compare favourably with those of 2-acetamidopyrimidine [17] at 233 (6.33) and 365 nm (5.55). An imino-structure resulting from ring-nitrogen acylation would have produced quite different u.v. absorptions [*cf.* Experimental section, compounds (8) and (9)].

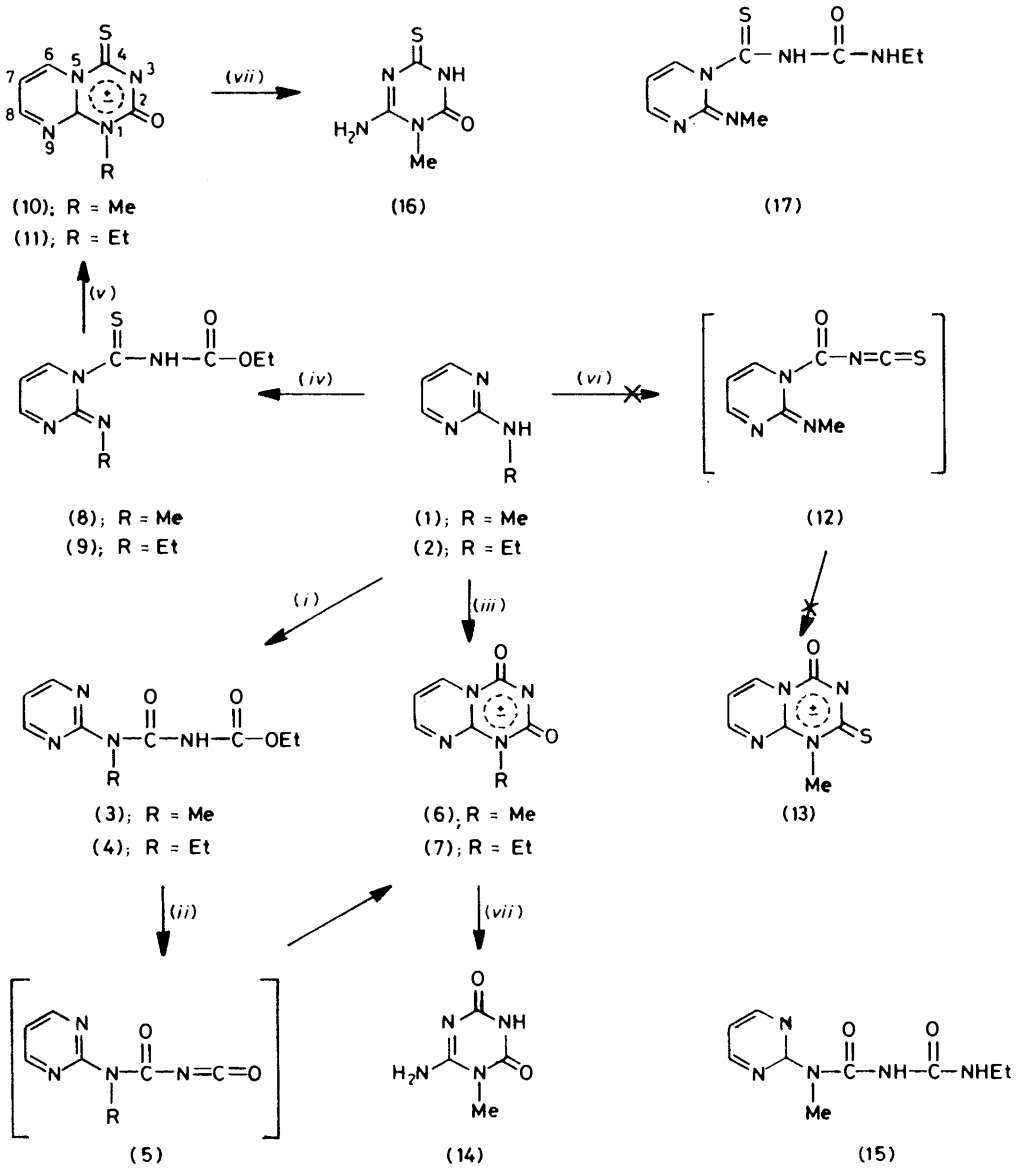
Treatment of (3) or (4) with anhydrous trifluoroacetic acid at room temperature or reflux did not result in cyclization to the respective 1-alkyl-4-oxopyrimido-[1,2-*a*]-*s*-triazin-1-ium-4-olates (6) or (7). Apparently, the nucleophilicity of the pyrimidine-ring nitrogen was impaired under these reaction conditions. As previously stated, the strongly electron-attracting alkoxycarbonyl group enhances nucleophilic attack at the adjacent isocyanate function in alkoxycarbonyl isocyanates. This fact, coupled with the reported [18] conversion of ethyl β-phenylcarbamylcrotonate to ethyl β-isocyanatocrotonate,† led us to attempt the formation of the carbonyl isocyanate (5) by removal of ethanol, by refluxing (3) or (4) at high temperatures in an inert solvent. Instead, compound (3) after 0.5 h reflux in anhydrous *p*-xylene gave the meso-ionic bicyclic compound (6), possibly by the pathway we originally planned. While our work was in progress, Kappe and Stadlbauer [15] also described this cyclization technique for the preparation of meso-ionic pyrido[1,2-*a*]-*s*-triazine-2,4-diones. Their compounds exhibited pseudocarbonyl absorptions at 1 670 and 1 725 cm^{-1}, as did our compounds (6) and (7) (1 680 and 1 750 cm^{-1}), the 4-oxo-1,6,8-trimethylpyrimido[1,2-*a*]pyrimidinium-2-olate (1 670 and 1 740 cm^{-1}),[19] and the 8-substituted-7-oxothiazolo[3,2-*a*]-*s*-triazinium-5-olates (1 669 and 1 720 cm^{-1}).[8a] The latter compounds reportedly showed a substantial downfield shift of both the thiazole ring-proton signals and the alkyl group methylene proton signals. Similar shifts were observed with the pyrimidine ring protons and the methylene protons of the 1-alkyl substituents in our compounds (6) and (7).

Phenoxycarbonyl isocyanate was employed in the synthesis of meso-ionic thiazolo- and 1,3,4-thiadiazolo-*s*-triazine-5,7-diones.[8] Application of this reagent to (1)

† By refluxing with trimethylchlorosilane and trimethylamine in toluene.

and (2) in anhydrous ethyl acetate at room temperature gave (6) and (7), as evidenced by the superimposition of their i.r. and ^{1}H n.m.r. spectra with products obtained by cyclization of ureas (3) and (4).

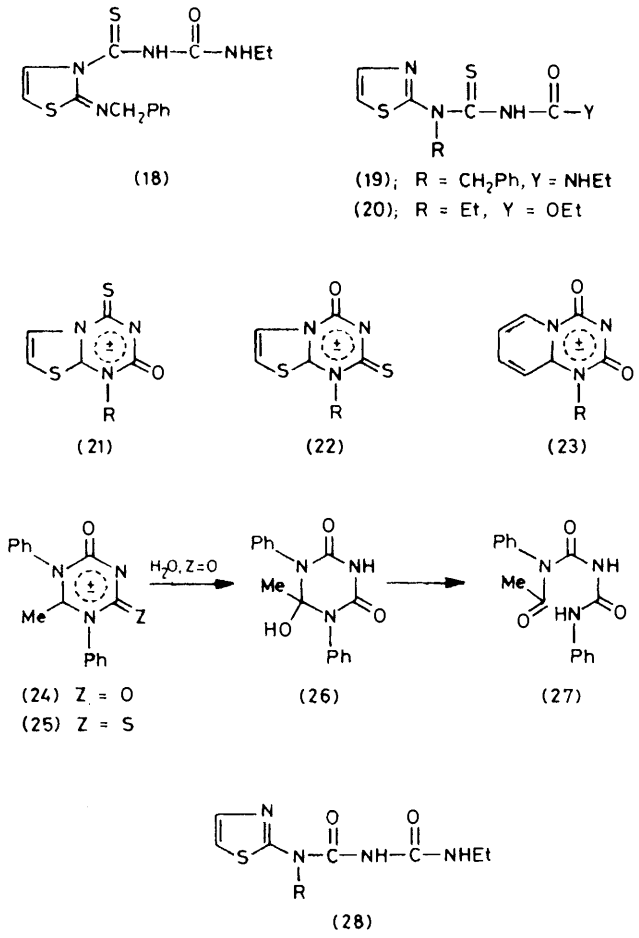
While acetic acid was found [8] to be a useful recrystallization solvent for some meso-ionic compounds prepared with phenoxycarbonyl isocyanate, any attempts to purify (6) or (7) with this solvent, anhydrous ethanol, or THF generally yielded material different from (6) or (7). Other bicyclic triazinediones [8] were reported to decompose rapidly in hot aqueous or alcoholic solutions. We achieved some purification by washing the solids with anhydrous ethyl acetate or *p*-xylene at room temperature. Hot solvent washings only resulted in further contamination. Consequently, we were unable to obtain correct elemental analyses on compounds (6) and (7). However, the alternate syntheses described, *i.e.* directly with phenoxycarbonyl isocyanate and indirectly from the urea intermediates, coupled with the correlation of the i.r. pseudocarbonyl absorptions with those of known bicyclic meso-ionic *s*-triazinediones and the substantial downfield shift of methylene hydrogens of substituents at the 1-position, is ample evidence that our structural assignments for (6) and (7) are correct.



SCHEME 1 (*i*) EtO_2CNCO in anhydrous EtOAc; (*ii*) reflux in *p*-xylene; (*iii*) PhO_2CNCO at room temperature; (*iv*) EtO_2CNCS, reflux in anhydrous EtOAc; (*v*) TFA–Et_2O; (*vi*) PhO_2CNCS; (*vii*) $EtNH_2$

A refluxing solution of ethoxycarbonyl isothiocyanate and 2-methylaminopyrimidine (1) in anhydrous ethyl acetate afforded 1-(*N*-ethoxycarbonylthiocarbamoyl)-2-methylimino-1,2-dihydropyrimidine (8) (Scheme 1). This structural assignment was supported by: (*i*) the presence of a coupled triplet (δ 1.40, *J* 2 Hz) and quartet

(δ 4.80) in the ^{1}H n.m.r. spectrum showing retention of the ethoxy-group; and (*ii*) the substantial downfield shift of the NMe protons to δ 4.40 compared to the value (δ 3.40) for the NMe protons of (1), indicating an imino- rather than an amino-structure. This argument is based on the rationale presented [8] to support the structure of 2-benzylimino-3-[(*N*-ethylaminocarbonyl)thiocarbamoyl]-Δ^2-1,3-thiazoline (18) (Scheme 2) relative to that of 1-benzyl-5-ethyl-1-(1,3-thiazol-2-yl)thiobiuret (19).



SCHEME 2

Moreover, the u.v. absorptions at 240 and 302 nm for (8) compare favourably with the 305 nm absorption of (18) *versus* the 220 and 269 nm maxima reported [8] for (19).

Although we were cognizant of the factors [8] required for synthesizing bicyclic meso-ionic compounds, employing anhydrous ethyl acetate [20] and refluxing periods of 2—10 h, we were unable to isolate any cyclized product (10).

It has been reported [21] that addition of ethoxycarbonyl isothiocyanate to a solution of 2-ethylaminothiazole yielded the acyclic structure (20), while the reverse addition was found [8] to produce the bicyclic meso-ionic compound (21; R = Et). We employed both procedures in reacting (1) and (2) with ethoxycarbonyl isothiocyanate in anhydrous ethyl acetate, and isolated only the acyclic products (8) and (9), respectively. Structural assignments were based on spectral and elemental analyses.

It has been shown [8] that reaction of phenoxycarbonyl isothiocyanate with 2-alkylaminothiazoles yields the isomeric 7-thione analogue (22). However, compound (1) with phenoxycarbonyl isothiocyanate in anhydrous ethyl acetate gave neither (13), (12), nor any other isomeric product comparable to (8) or (3).

Our initial attempts to cyclize (8) afforded poor yields of impure (10), when (8) was dissolved in a few ml of TFA and the product was precipitated with anhydrous ether. The results by this method were not consistently reproducible since excess of TFA, prolonged reaction times, or incompletely dry TFA all produced different products. Products (10) and (11) were obtained in the highest yield and purity when TFA was added to a solution of (8) or (9) in anhydrous ethyl acetate and stirred at 5 °C for 30 min. We found only a catalytic amount of TFA was required. However, we were still unable to obtain (10) or (11) of analytical purity.

Our structural assignments, therefore, were based on spectral data, including the downfield shift of all the pyrimidine ring-proton signals and the *N*-alkyl group absorptions. The pseudocarbonyl i.r. absorption (1 735 cm^{-1}) for (10) correlated well with those reported [8] for meso-ionic 8-alkyl-5-oxothiazolo[3,2-*a*]-*s*-triazine-7-thione (22) (1 669 cm^{-1}), the 5-monothione analogue (21) (1 730 cm^{-1}), and the pyridino-*s*-triazine-4-thione derivative (23) (1 730 cm^{-1}). The insolubility of (10) and (11) in most organic solvents made purification by recrystallization difficult; chromatographic purification was also unsuccessful. Solutions in dimethyl sulphoxide–water, hot acetonitrile, or TFA–ether gave an unidentified product, identical in each case to that obtained when (10) or (11) was heated in water. Sublimation was attempted (180 °C/0.2 mmHg) but this only complicated the problem by affording a different product from the hydrolysis product. This purification problem is not unusual, since similar difficulties have been encountered in the preparations of meso-ionic 1,3,4-thiadiazolo[3,2-*a*]-*s*-triazine-5,7-diones, 1,3,4-thiadiazolo[3,2-*a*]-*s*-triazin-5-one-7-thiones, and the monocyclic 1,5-disubstituted *s*-triazine-2,4-diones (24).[8,22] Many of these compounds could not be obtained analytically pure.[22] Compounds of type (24) and their monothione derivatives (25) are thermally stable, but on exposure to atmospheric moisture form covalent hydrates (26), which can exist in the ring-opened form (27). The ^{1}H n.m.r. spectrum of (24) and (27) in TFA are reported to be identical,[22] which indicates that the hydration of (24) is catalysed by traces of water in TFA. Our compound (10), after recrystallization from acetonitrile, showed a different i.r. spectrum from that of the original (10). However, the ^{1}H n.m.r. spectra of (10) and this recrystallized material were identical in TFA except for an extra singlet at δ 2.50. This indicated a partial hydration of (10) during recrystallization, but no ring-opened structure comparable to (27). The result would

be an identical ^{1}H n.m.r. spectrum plus a new *N*-methyl absorption at δ 2.50. A similar *N*-methyl absorption was present in the ^{1}H n.m.r. spectra of (10) after washing with hot ethyl acetate, or prolonged reaction in TFA–ethyl acetate solutions.

Unlike the reaction of ethylamine with other meso-ionic *s*-triazinediones, which led to open-chain biurets [*e.g.* (28)] by nucleophilic attack at the pseudocarbonyl group, compound (6) reacted with ethylamine by cleaving the pyrimidine ring. Pyrimidine ring-proton signals were absent as well as ethyl group absorptions [*i.e.* compound (15) absent] and only one signal appeared at δ 3.25, which we assigned to the methyl group of compound (14). Mass spectral analysis showed a molecular weight of 142 and a fragmentation pattern (see Experimental section) which supported assignment of the 6-amino-1-methyl-1,3-dihydro-*s*-triazine-2,4-dione structure (14).[23] With meso-ionic compounds (21) and (22), ethylamine readily cleaved the meso-ionic ring to afford (18) or (19), respectively. With compound (10) the expected compound (17) was not formed. Like compound (6), the pyrimidine ring cleaved to yield (16), as evidenced by the absence of pyrimidine ring-proton signals or ethyl group absorptions, and only the presence of an *N*-methyl signal at δ 3.65. The fragmentation pattern and molecular weight of 158 supports our assignment of structure (16) to this product.

EXPERIMENTAL

All melting points were determined on a Mel-Temp apparatus. Spectral characterizations were performed with the following instruments: i.r., Perkin-Elmer Infracord 137 (KBr pellets); u.v., Carey model 14 spectrophotometer; ^{1}H n.m.r., Varian T60 or A60A ($SiMe_4$ internal standard), all chemical shifts expressed in p.p.m. (δ). Mass spectra (70 eV) were obtained by Morgan-Schaeffer, Canada, on a Hitachi–Perkin-Elmer model RMV-6D. Combustion analyses were performed by Childers Laboratories, Milford, N.J., or Schwarzkopf Microanalytical Laboratories, Woodside, N.Y.

Reagents.—Ethyl acetate, ether, chloroform, light petroleum, and dichloroethane were dried by reported procedures.[20] 2-Aminopyrimidine, phenyl chloroformate, trifluoroacetic acid (Eastman); and oxalyl chloride, ethyl chloroformate, ethyl carbamate, and phenyl carbamate (Aldrich Chemical Co.) were used without further purification.

Ethoxycarbonyl isocyanate was prepared essentially according to Lamon's procedure.[11] Phenoxycarbonyl isocyanate was prepared as previously described.[12] Ethoxycarbonyl isothiocyanate was prepared from ethyl chloroformate and potassium thiocyanate.[11] We applied this procedure to the preparation of phenoxycarbonyl isothiocyanate [13] as described below.

The required 2-alkylaminopyrimidines (1) [24,25] and (2) [26] were prepared by rearrangement of the respective 1,2-dihydro-1-alkyl-2-iminopyrimidine hydroiodides in the presence of hot 1N sodium hydroxide, the latter formed [25,26] by the reaction of the appropriate alkyl iodide with 2-aminopyrimidine.

Phenoxycarbonyl Isothiocyanate.—Finely ground potassium isothiocyanate (10 g, 0.01 mol) suspended in anhydrous ethyl acetate (250 ml) was treated dropwise with phenyl chloroformate (15.6 g, 0.01 mol) for 0.5 h and then stirred for an additional 8 h at room temperature. Filtration of the reaction mixture and concentration of the filtrate *in vacuo* gave a residual colourless liquid (12.1 g, 68.0%), b.p. 80—85 °C at 0.1 mmHg (lit.,[13] b.p. 65—68 °C at 0.07 mmHg); $\nu_{max.}$ (neat) 2 300 (N=C=S) and 1 700 cm^{-1} (C=O). For ten preparations the yields ranged from 60 to 68%.

1-*Ethoxycarbonyl*-3-*methyl*-3-(2-*pyrimidyl*)*urea* (3).—An anhydrous ethyl acetate (40 ml) solution of 2-methylaminopyrimidine (1) (2.18 g, 0.02 mol) was added dropwise to an anhydrous ethyl acetate (40 ml) solution of ethoxycarbonyl isocyanate (2.54 g, 0.022 mol). The clear solution, obtained after 6 h of stirring, was evaporated to afford 0.92 g (20.0%) of white *crystals*, m.p. 137—138 °C [from ethyl acetate–pentane (2 : 1 v/v)] (Found: C, 48.55; H, 5.4; N, 23.9. $C_9H_{12}N_4O_3$ requires C, 48.21; H, 5.39; N, 24.99%); $\nu_{max.}$ 1 700 (C=O) and 1 800 cm^{-1} (C=O); $\lambda_{max.}$ (H_2O) (log ε) 240 (6.46) and 370 nm (5.64); δ ($CDCl_3$) 1.40 (t, 3 H, Me), 3.80 (s, 3 H, NMe) 4.60 (q, 2 H, OCH_2), 7.60 (t, 1 H, H-5), 9.60 (d, 2 H, H-4 and H-6), and 13.92 (s, 1 H, NH).

1-*Ethoxycarbonyl*-3-*ethyl*-3-(2-*pyrimidyl*)*urea* (4).—A similar procedure to that described above for (3) was employed; amine (2) (3.69 g, 0.03 mol) and ethoxycarbonyl isocyanate (3.81 g, 0.033 mol) afforded 1.8 g (25.1%) of the title *product*, m.p. 96—98 °C [from ethyl acetate–pentane (1 : 1 v/v)] (Found: C, 50.3; H, 5.9; N, 23.0. $C_{10}H_{14}N_4O_3$ requires C, 50.41; H, 5.91; N, 23.52%); $\nu_{max.}$ 1 800 (C=O) and 1 700 cm^{-1} (C=O); $\lambda_{max.}$ (H_2O) (log ε) 240 (6.50) and 370 nm (5.67); δ ($CDCl_3$) 1.30 (m, 6 H, OCMe and NCMe), 4.30 (q, 4 H, OCH_2, NCH_2), 7.10 (t, 1 H, H-5), 8.33 (d, 2 H, H-4, H-6), and 12.80 (s, 1 H, NH).

1-*Methyl*-4-*oxopyrimido*[1,2-a]-s-*triazin*-1-*ium*-2-*olate*(6).—(a) *From methylpyrimidine.* An anhydrous ethyl acetate (75 ml) solution of (1) (3.27 g, 0.03 mol) was added dropwise to an anhydrous ethyl acetate (90 ml) solution of phenoxycarbonyl isocyanate (5.13 g, 0.033 mol). After stirring for 6 h in a nitrogen atmosphere at room temperature, the white *powder* (4.67 g, 87.5%) was collected and washed (2 × 25 ml) with anhydrous ethyl acetate, m.p. 220—240 °C (decomp.) (Found: C, 45.95; H, 3.55; N, 30.9. $C_7H_6N_4O_2$ requires C, 47.19; H, 3.37; N, 31.46%); $\nu_{max.}$ 3 100 (CH), 1 750 (C=O), and 1 680 cm^{-1} (C=O); $\lambda_{max.}$ (H_2O) (log ε) 285 (6.50) and 340 nm (3.45); δ (CF_3CO_2H) 4.00 (s, 3 H, NMe), 8.00 (q, 1 H, H-7), and 9.40 (m, 2 H, H-6, H-8).

(b) *From the pyrimidylurea* (3). An anhydrous *p*-xylene solution (15 ml) of the methylpyrimidylurea (3) (0.35 g, 0.001 6 mol) was refluxed for 40 min; the precipitate was filtered from the cooled solution and washed (2 × 10 ml) with *p*-xylene to give 0.10 g (35.0%) of (6), m.p. 239—241 °C; $\lambda_{max.}$ (CH_3OH) 270 nm (log ε 5.85) (Found: C, 47.8; H, 3.35; N, 28.3%).

1-*Ethyl*-4-*oxopyrimido*[1,2-a]-s-*triazin*-1-*ium*-2-*olate* (7).—(a) *From ethylpyrimidine.* The procedure (a), identical to that described for (6) but using the amine (2), gave 3.45 g (59.8%) of *compound* (7), m.p. 200—205 °C (decomp.); $\nu_{max.}$ 3 100 (CH), 3 000 (CH), 1 750 (C=O), and 1 680 cm^{-1} (C=O); $\lambda_{max.}$ (CH_3OH) (log ε) 270 nm (5.89); δ (CF_3COOH) 1.50 (t, 3 H, CMe), 4.65 (q, 2 H, NCH_2C), 7.92 (q, 1 H, H-7), and 9.55 (m, 2 H, H-6, H-8) (Found: C, 48.85; H, 4.15; N, 25.95. $C_8H_8N_4O_2$ requires C, 50.00; H, 4.19; N, 29.15%).

(b) *From the pyrimidylurea* (4). The procedure (b) described for (6), but using the ethylpyrimidylurea (4) (0.50 g, 0.002 mol), after 20 min reflux gave white crystals (0.10 g,

26.8%), m.p. 210—214 °C (decomp.) (Found: C, 49.95; H, 4.2; N, 27.65%).

1-(N-*Ethoxycarbonylthiocarbamoyl*)-2-*methylimino*-1,2-*dihydropyrimidine* (8).—To an anhydrous ethyl acetate solution (25 ml) of (1) (1.83 g, 0.017 mol) was added neat ethoxycarbonyl isothiocyanate (2.44 g, 0.018 mol) over a 10-min period under a nitrogen atmosphere. After 4 h reflux the reaction mixture was cooled to room temperature and filtered. Evaporation of the filtrate gave an orange oil which when treated with absolute ethanol (5 ml) gave yellow crystals (0.88 g). An additional 0.61 g was collected upon evaporation of the alcohol filtrate (total yield 1.48 g, 36.2%), m.p. 108—110 °C [from ethyl acetate–pentane (1 : 1 v/v)] (Found: C, 45.15; H, 5.15; N, 23.05; S, 13.25; O, 13.4. $C_9H_{12}N_4O_2S$ requires C, 44.99; H, 5.03; N, 23.32; S, 13.34; O, 13.32%); $\nu_{max.}$ 3 200 (NH), 3 000 (CH), 1 730 cm^{-1} (C=O); $\lambda_{max.}$ (H_2O) (log ε) 240 nm (4.92); δ ($CDCl_3$) 1.40 (t, 3 H, OCMe), 4.40 (s, 3 H, NMe), 4.60 (q, 2 H, OCH_2C), 7.80 (t, 1 H, H-5), 9.60 (d, 2 H, H-4, H-6), and 14.90 (s, 1 H, NH).

1-(N-*Ethoxycarbonylthiocarbamoyl*)-2-*ethylimino*-1,2-*dihydropyrimidine* (9).—A similar procedure to that described for (8), using amine (2) (1.02 g, 0.01 mol), gave the title *compound* (9) (0.60 g, 23.5%), m.p. 136—138 °C [from ethyl acetate–pentane (1 : 1 v/v)] (Found: C, 47.3; H, 5.4; N, 21.5; O, 12.85; S, 12.95. $C_{10}H_{14}N_4O_2S$ requires C, 46.86; H, 5.51; N, 21.85; O, 12.58; S, 12.60%); $\nu_{max.}$ 3 200 (NH), 3 000 (CH), and 1 745 cm^{-1} (C=O); $\lambda_{max.}$ (CH_3OH) (log ε) 252 (5.68) and 300 nm (6.05); δ ($CDCl_3$) 2.80 (m, 6 H, NCMe and OCMe) 4.60 (q, 2 H, NCH_2), 5.40 (q, 2 H, OCH_2-C), 7.80 (t, 1 H, H-5), 9.60 (d, 2 H, H-4, H-6), and 14.80 (s, 1 H, NH).

1-*Methyl*-4-*thioxopyrimido*[1,2-a]-s-*triazin*-1-*ium*-2-*olate* (10).—Anhydrous trifluoroacetic acid (4 ml) was added to a solution of (8) (2.61 g, 0.011 mol) in anhydrous ethyl acetate (90 ml) at 5 °C. After stirring for 0.5 h at 5 °C (ice-bath), the solvent was evaporated and the residual oil treated with anhydrous ethyl ether (80 ml). The resulting precipitate (1.02 g, 47.7%) was collected, washed with ethyl acetate, and air-dried to give a yellow *powder*, m.p. 219—222 °C (decomp.) (Found: C, 44.25; H, 3.35; N, 26.45; S, 15.75. $C_7H_6N_4OS$ requires C, 43.29; H, 3.11; N, 28.84; S, 16.51%); $\nu_{max.}$ 3 100 (CH) and 1 735 cm^{-1} (C=O); $\lambda_{max.}$ (H_2O) (log ε) 240 (5.97) and 283 nm (6.37); δ (CF_3CO_2H) 4.6 (s, 3 H, NMe), 8.50 (q, 1 H, H-7), and 10.40 (m, 2 H, H-6, H-8).

1-*Ethyl*-1-*thioxopyrimido*[1,2-a]-s-*triazin*-1-*ium*-2-*olate* (11).—In a similar manner to (10), compound (9) (1.00 g, 0.004 mol) in ethyl acetate (75 ml) was treated with trifluoroacetic acid (1 ml) to give 0.16 g (20.1%) of title *product*, m.p. 170—175 °C (decomp.) (Found: C, 46.5; H, 4.1; N, 24.15; S, 15.65. $C_8H_8N_4O_6$ requires C, 44.04; H, 3.67; N, 25.69; S, 14.68%); $\nu_{max.}$ 3 110 (CH), 3 100 (CH), and 1 735 cm^{-1} (C=O); $\lambda_{max.}$ (H_2O) (log ε) 290 (6.40) and 357 nm (6.01); δ (CF_3CO_2H) 1.50 (t, 3 H, CMe), 5.00 (q, 2 H, NCH_2C), 7.90 (q, 1 H, H-7), and 9.50 (t, 2 H, H-6, H-8).

Reaction of Pyrimido[1,2-a]-s-*triaziniumolates with Ethylamine*.—(a) *Compound* (6). An absolute ethanol solution (10 ml) of compound (3) (0.5 g, 0.003 mol) was treated with ethylamine (1 ml, 70% aqueous solution) and stirred for 15 min to afford 0.31 g of white crystals, m.p. 350 °C (from water) [lit.,[22] m.p. 310—320 °C sinters, 330 °C partial sublimation (from ethanol)] (Found: C, 34.6; H, 4.5; N, 34.95. Calc. for: $C_4H_6N_4O_2$: C, 33.80; H, 4.25; N, 39.42%); $\nu_{max.}$ 3 400 (NH), 3 100, 2 950 (CH), 1 735 (C=O), and 1 650 cm^{-1} (C=O); δ (Polysol) 3.25 (s, 3 H, NMe); *m/e* 142 (M^+), 141 (M^+ — H), 114 (M^+ — CO), 113 (M^+ — CO — H), 99 (M^+ — HNCO), 98 (M^+ — HNCO — H), 87 (M^+ — CO — HCN), 86 (M^+ — 2CO), and 85 (M^+ — CO — H — CO).

(b) *Compound* (10). A suspension of (10) (0.19 g, 0.001 mol) in anhydrous chloroform (10 ml) was treated with ethylamine (0.7 ml of a 70% aqueous solution) and after stirring for 15 min the precipitate (0.07 g) was collected, m.p. 280—281 °C (from water) (Found: C,27.9; H, 4.5; N, 31.95; S, 18.1. $C_4H_8N_4O_2S$ requires C, 27.27; H, 4.54; N, 31.81; S, 18.18%); $\nu_{max.}$ 3 650 (OH or NH), 3 400 (NH), and 1 725 cm^{-1} (C=O); δ ([$^2H_6$]DMSO) 3.31 (s, 2 H, H_2O), 3.65 (s, 3 H, NMe), and 7.9 (m, 3 H, NH_2, NH); *m/e* 158 (M^+), 143 (M^+ — Me), 141 (M^+ — OH), 130 (M^+ — CO), 125 (M^+ — SH), 99 (M^+ — HNCS), and 98 (M^+ — HNCS — H).

[9/1282 *Received*, 13*th August*, 1979]

REFERENCES

[1] Part 11, C. V. Greco and J. R. Mehta, *J. Heterocyclic Chem.*, 1979, **16**, 1059
[2] K. J. Gala, Ph.D. Thesis, St. John's University, N.Y., 1977.
[3] (*a*) M. Ohta and H. Kato in ' Non-benzenoid Aromatics,' ed. J. P. Snyder, Academic Press, New York, 1969, vol. 16—1, ch. 4; (*b*) W. D. Ollis and C. A. Ramsden, *Adv.* Heterocyclic Chem., 1976, **19**.
[4] K. T. Potts and M. Sorm, *J. Org. Chem.*, 1972, **37**, 1422.
[5] T. Kappe and W. Lube, *Monatsh.*, 1971, **102**, 781.
[6] K. T. Potts and M. Sorm, *J. Org. Chem.*, 1971, **36**, 8.
[7] R. A. Coburn and R. A. Glennon, *J. Pharm. Sci.*, 1973, **62**, 1785.
[8] (*a*) R. A. Coburn and B. Bhooshan, *J. Org. Chem.*, 1973, **38**, 3868; (*b*) *cf.* also, B. Bhooshan, Ph.D. Thesis, State University of New York at Buffalo, N.Y., 1974,
[9] A. Katritzky and A. J. Waring, *J. Chem. Soc.*, 1962, 1544.
[10] H. Hageman and K. Ley, *Angew. Chem. Internat. Edn.*, 1972, **11**, 1012.
[11] R. W. Lamon, *J. Heterocyclic Chem.*, 1968, **5**, 837.
[12] A. J. Speziale, L. R. Smith, and J. E. Fedder, *J. Org. Chem.*, 1965, **30**, 4306.
[13] B. Anders, H. Malz, G. P. 215,144/1966, (*Chem. Abs.* 1966, **65**, 3908).
[14] S. Ozaki, *Chem. Rev.*, 1972, **72**, 457.
[15] T. Kappe and W. Stadlbauer, *Chem. Ber.*, 1976, **109**, 3661.
[16] D. J. Brown and L. N. Short, *J. Chem. Soc.*, 1953, 331.
[17] B. Stanovnik and M. Tisler, *Monatsh.*, 1973, **104**, 1034.
[18] H. R. Kricheldorf, *Angew. Chem. Internat. Edn.*, 1972, **11**, 128.
[19] K. T. Potts and R. K. Hsia, *J. Org. Chem.*, 1973, **38**, 3485.
[20] A. J. Gordon and R. A. Ford, ' The Chemists Companion,' John Wiley and Sons, Inc., New York, 1972, pp. 429—436.
[21] M. Nagano, T. Matsui, J. Tobitsuka, and K. Oyamada, *Chem. Pharm. Bull. Japan*, 1973, **21**, 74.
[22] H. Yamamoto and W. Pfliederer, *Chem. Ber.*, 1973, **106**, 3194.
[23] R. A. Coburn and B. Bhooshan, *J. Heterocyclic Chem.*, 1975, **12**, 187.
[24] D. J. Brown, E. Hoerger, and S. F. Mason, *J. Chem. Soc.*, 1955, 4035.
[25] C. G. Overberger and I. C. Kogan, *J. Amer. Chem. Soc.*, 1954 **76**, 1065.
[26] D. J. Brown and J. S. Harper, *J. Chem. Soc.*, 1963. 1276.