Ylides of Heterocycles. VII. [1]. I-, N-, P- and S-Ylides of Pyrimidones

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The reaction of pyrimidone derivatives **1a-d** with iodosobenzene prepared *in situ* from diacetoxyiodobenzene or dichloroiodobenzene afforded the iodonium-ylides **2a-d** in good yields. Their thermal rearrangement produced 5-iodo-4-phenoxy-pyrimidin-6(1*H*)-ones **3a-c**. Reductive deiodination of **3** gave the corresponding 4-phenoxypyrimidin-6(1*H*)-ones **4a-c**. Acid catalized treatment of the iodonium-ylides **2a-d** with nucleophiles such as pyridine, nicotinamide, isoquinoline, or triphenylphosphine produced the corresponding *N*- or *P*-ylides **7, 8, 9**, and **10**, respectively. The thiophanium-ylides **11a,c** were obtained from the iodonium-ylides **2** without the use of a catalyst. The pyridinium-ylides **7** have been also prepared from the 5-halopyrimidones **5** or **6** which in turn could be obtained from the reactive iodonium-ylides **2** with hydrochloric or hydrobromic acid, respectively.

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Malonyl heterocycles, such as 4-hydroxy-6-pyrimidones (**1**), barbituric acids, 4-hydroxy-2-pyrones, 4-hydroxy-2-pyridones, 4-hydroxy-coumarins and 4-hydroxy-2-quinolones are acidic compounds with pK_a values ranging usually between 4.0 and 6.0. The negative charge localized in the malonate anion moiety of a heterocyclic system can be compensated in two different ways yielding zwitterionic compounds: a) internally in the form of mesoionic compounds, **A**; b) externally in the form of ylides, **B**. Both types of compounds have been studied by us in the last decade and the chemistry of six-membered mesoionic compounds of type **A** has been reviewed recently [3].

A

B

Synthetic routes to pyridinium- [1,4-9], iodonium- [6,8,9], sulfonium- [8,9] and phosphonium-ylides [10] have been developed. Especially the reactive iodonium-ylides were found to be versatile synthons in the chemistry of malonyl heterocycles, and generally in the field of 1,3-dicarbonyl systems (for a literature survey see ref [6]). So far the malonyl heterocycles studied include 4-hydroxy-coumarins and 4-hydroxy-2-quinolones [4-8] as well as 4-hydroxy-2-pyrones and 2-pyridones [9] and barbituric acids [1]. In the present investigation, iodonium-, pyridinium-, isoquinolinium-, sulfonium- and phosphonium- ylides of the biologically more important pyrimidine nucleus have been prepared.

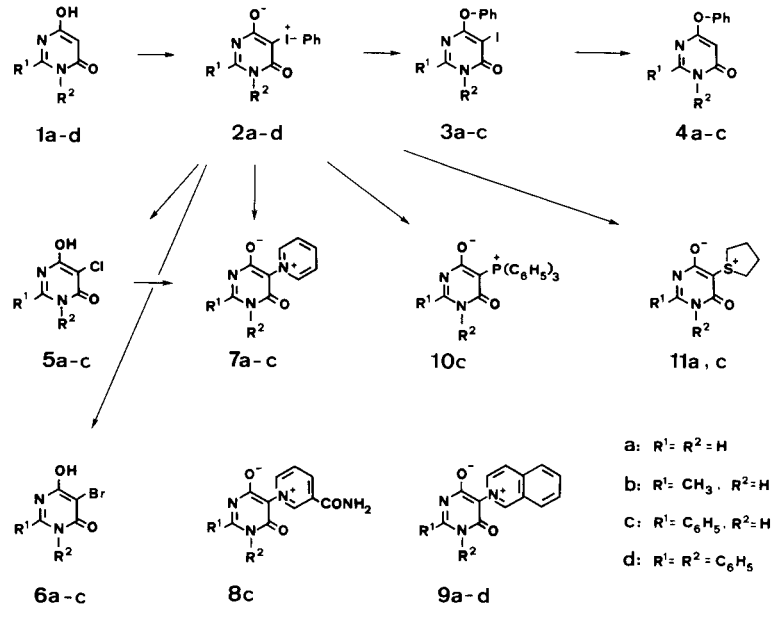
The iodonium-ylides **2a-d** were obtained by the reaction of hydroxypyrimidones **1a-d** with iodosobenzene, generated *in situ* from the reaction of diacetoxyiodobenzene or dichloroiodobenzene and sodium carbonate solution. The reaction temperature should not exceed 40°, especially in the case of the *N*-phenyl derivative **2d**. Thermal rearrangement of **2a-c** in boiling *N,N*-dimethylformamide afforded 3-iodo-4-phenoxypyrimidin-6(1*H*)-ones **3a-c**. Reductive deiodination of **3a-c** with zinc dust and glacial acetic acid produced high yields of 4-phenoxypyrimidin-6(1*H*)-ones **4a-c**.

The nitrogen ylides **7, 8, 9** and the phosphonium-ylide **10c** as well as the sulfonium-ylides **11** were obtained by nucleophilic substitution reaction on the iodonium-ylides **2a-d** using pyridine, nicotinamide, isoquinoline, triphenylphosphine, or thiophane (= tetrahydrothiophene) as nucleophiles, respectively. The pyridinium-ylide **7a** has also been prepared by the reaction of pyridine with the 5-halopyrimidones **5** or **6** which were in turn obtained by the reaction of the iodonium-ylides **2a-c** with hydrochloric or hydrobromic acid, respectively. Compound **7b** was isolated only in the form of its *p*-toluenesulfonate salt, and it is of interest to note that some ylides (**7-10**) crystallize with 0.5, 1.0 or 1.5 molecules of water (see Experimental).

The formation of nitrogen-ylides **7, 8, 9** as well as phosphorous ylides was acid catalized. In such a case protonation of the olate-oxygen is presumably the first step of the reaction [8,9,11]. In the absence of acid catalysts the rearranged compounds **3** were obtained as main products. On the other hand, high acid concentrations can result in the reaction of the iodonium-ylides **2** with the anion of the acid [11]. The reaction of the iodonium-ylides **2** with thiophane was performed in methanol without the use of acid catalysts, otherwise thiophane ring cleavage might occur as previously reported [8].

The yellow colored pyridinium- and isoquinolinium-ylides (**7-9**) show an intense greenish yellow fluorescence when irradiated with uv light of 254 or 350 nm which was also used for their identification on tlc.

The simple chloro and bromo pyridines **5** and **6** (with



the exception of **6b**) have already been described in the literature [12-16]. However, in the case of **5b** our melting point is quite different from that given previously [13] for a compound obtained from the reaction of acetamidine and diethyl chloromalonate. Also in view of the well known fact [17] that diethyl halomalonates react with *N*-nucleophiles preferentially under halogen exchange we believe that the structure presented by Gershon *et al.* [13] must be incorrect.

EXPERIMENTAL

The melting points were determined in open capillary tubes on a Büchi-Tottoli melting point apparatus, melting points above 200° were determined using a hot metal block and are uncorrected. The ir spectra were recorded on a Perkin-Elmer 421 spectrophotometer using samples in potassium bromide disks. The nmr spectra were recorded with a Varian EM-360 spectrometer at 60MHz in hexadeuteriodimethylsulfoxide (unless otherwise indicated) and with TMS as an internal standard.

6-Oxo-5-phenyliodonium-1,6-dihydropyrimidin-4-olates (**2a-d**). General Procedure.

The appropriate 4-hydroxypyrimidin-6-ones **1a-d** (10 mmoles) were dissolved in 25 ml of a solution containing 2.86 g (10 mmoles) of crystalline sodium carbonate. Diacetoxyiodobenzene (3.22 g, 10 moles) or dichloroiodobenzene (2.75 g, 10 mmoles) were suspended in 25 ml of a solution containing 2.86 g (10 mmoles) of sodium carbonate. The two solutions were mixed and stirred at 40° for 1-2 hours. The precipitate obtained was filtered, washed with water and recrystallized from the specified solvent. The following compounds were prepared by this general procedure.

6-Oxo-5-phenyliodonium-1,6-dihydropyrimidin-4-olate (**2a**).

The yield was 90%, yellowish crystals, mp 218° (water); ir: 3400-2600 m, 1615 s, 1570 m, 1560 s, 1540 m, cm^{-1}; nmr (trifluoroacetic acid): δ 7.25-7.65 (m, 3, ArH), 7.85-8.10 (m, 2, ArH), 8.95 (s, 1, C-2).

Anal. Calcd. for $C_{10}H_7IN_2O_2$: C, 38.25; H, 2.23; N, 8.92. Found: C, 38.22; H, 2.19; N, 8.91.

2-Methyl-6-oxo-5-phenyliodonium-1,6-dihydropyrimidin-4-olate (**2b**).

The yield was 87%, colorless needles, mp 205° (methanol); ir: 3500-2700 m, 1625 s, 1605 m, 1560 s, 1540 s cm^{-1}; nmr: δ 2.15 (s, 3, CH_3), 7.3-7.5 (m, 3, ArH), 7.7-7.9 (m, 2, ArH).

Anal. Calcd. for $C_{11}H_9IN_2O_2$: C, 40.28; H, 2.74; N, 8.54. Found: C, 40.16; H, 2.95; N, 8.37.

6-Oxo-2-phenyl-5-phenyliodonium-1,6-dihydropyrimidin-4-olate (**2c**).

The yield was 89%, colorless prisms, mp 225° (methanol); ir: 3100-2760 w, 1630 m, 1565 s, 1545 s cm^{-1}.

Anal. Calcd. for $C_{16}H_{11}IN_2O_2$: C, 49.27; H, 2.82; N, 7.18. Found: C, 49.20; H, 2.96; N, 7.23.

1,2-Diphenyl-6-oxo-5-phenyliodonium-1,6-dihydropyrimidin-4-olate (**2d**).

The yield was 98%, colorless needles, mp 150° (aqueous methanol); ir: 3560-3060 m, 1655 sh, 1645 m, 1585-1545 s cm^{-1}.

Anal. Calcd. for $C_{22}H_{15}IN_2O_2$: C, 56.67; H, 3.24; N, 6.01. Found: C, 56.41; H, 3.32; N, 6.03.

5-Iodo-4-phenoxypyrimidin-6(1*H*)-ones (**3a-c**). General Procedure.

6-Oxo-5-phenyliodonium-1,6-dihydropyrimidin-4-olates **2a-c** (10 mmoles) were suspended in 15 ml of dimethylformamide and heated under reflux for 15-30 minutes. The reaction mixture was then treated with charcoal, cooled and poured into 100 ml of water. The precipitate was obtained was filtered, washed with water and crystallized from the appropriate solvent.

5-Iodo-4-phenoxypyrimidin-6(1*H*)-one (**3a**).

The yield was 69%, colorless prisms, mp 260° (acetic acid); ir: 3200-2600 m, 1645 s, 1600 m, 1585 m, 1530 m cm^{-1}; nmr: δ 7.0-7.5 (m, 5, ArH), 8.05 (s, 1, C-2).

Anal. Calcd. for $C_{10}H_7IN_2O_2$: C, 38.25; H, 2.23; N, 8.92. Found: C, 38.22; H, 2.05; N, 8.81.

5-Iodo-2-methyl-4-phenoxypyrimidin-6(1*H*)-one (**3b**).

The yield was 69%, colorless needles, mp 207° (methanol); ir: 3110-2500 m, 1655 s, 1585 m, 1550 m cm^{-1}; nmr: δ 2.15 (s, 3, CH_3), 7.00-7.45 (m, 5, ArH).

Anal. Calcd. for $C_{11}H_9IN_2O_2$: C, 40.28; H, 2.74; N, 8.54. Found: C, 40.01; H, 2.83; N, 8.25.

5-Iodo-4-phenoxy-2-phenylpyrimidin-6(1*H*)-one (**3c**).

The yield was 63%, yellowish needles, mp 280° (acetic acid); ir: 3140-2800 w, 1640 s, 1590 w, 1545 m cm^{-1}.

Anal. Calcd. for $C_{16}H_{11}IN_2O_2$: C, 49.27; H, 2.82; N, 7.18. Found: C, 49.40; H, 2.88; N, 7.28.

4-Phenoxypyrimidin-6(1*H*)-ones **4a-c**. General Procedure.

5-Iodo-4-phenoxypyrimidin-6(1*H*)-ones **3a-c** (10 mmoles) were dissolved in 15 ml of acetic acid. Zinc dust was added in 3 portions while refluxed for one hour. Heating was continued for one hour and the obtained solution was filtered from remaining zinc dust. The filtrate was evaporated *in vacuo* to dryness and the residue obtained was digested with water. The precipitate was filtered and recrystallized.

4-Phenoxypyrimidin-6(1*H*)-one (**4a**).

The yield was 83%, colorless plates, mp 183° (water); ir: 3100-2500 m, 1715 s, 1590 s, 1545 w cm^{-1}; nmr: δ 5.4 (s, 1, C-5), 7.0-7.5 (m, 5, ArH), 8.1 (s, 1, C-2), 12.5 (s, 1, NH).

Anal. Calcd. for $C_{10}H_8N_2O_2$: C, 63.86; H, 4.25; N, 14.89. Found: C, 63.90; H, 4.23; N, 15.02.

2-Methyl-4-phenoxypyrimidin-6(1*H*)-one (**4b**).

The yield was 81%, colorless needles, mp 243° (methanol); ir: 3100-2550 m, 1715 s, 1590 s cm^{-1}; nmr: δ 2.3 (s, 3, CH_3), 5.2 (s, 1, C-5), 7.1-7.5 (m, 5, ArH).

Anal. Calcd. for $C_{11}H_{10}N_2O_2$: C, 65.37; H, 4.95; N, 13.86. Found: C, 65.22; H, 5.07; N, 13.80.

4-Phenoxy-2-phenylpyrimidin-6(1*H*)-one (**4c**).

The yield was 74%, creamy white crystals, mp 196° (methanol/water); ir: 3200-2800 m, 1650 s, 1600 w, 1585 m, 1560 m, 1540 m cm^{-1}; nmr: δ 5.45 (s, 1, C-5), 7.25-7.60 (m, 8, ArH), 7.9-8.2 (m, 2, ArH).

Anal. Calcd. for $C_{16}H_{12}N_2O_2$: C, 72.72; H, 4.58; N, 10.60. Found; C, 72.84; H, 4.36; N, 10.75.

5-Halo-4-hydroxypyrimidin-6(1*H*)-ones **5a-c** and **6a-c**. General Procedure.

To the suspension of 6-oxo-5-phenyliodonium-1,6-dihydropyrimidin-4-olate **2a-c** (10 mmoles) in 15 ml of ethanol 2 ml of concentrated hydrochloric or hydrobromic acid were added. The reaction mixture was heated under reflux for 15 minutes, evaporated *in vacuo* to dryness and the residue obtained was washed with petroleum ether and recrystallized.

5-Chloro-4-hydroxypyrimidin-6(1*H*)-one (**5a**).

The yield was 65%, colorless needles, mp 260° (water), lit [12] dec above 230°; ir: 3200-2500 m, 1690 s, 1660 s, 1640 s, 1585 s, 1550 s cm^{-1}.

Anal. Calcd. for $C_4H_3ClN_2O_2$: C, 32.79; H, 2.05; N, 19.11. Found: C, 33.06; H, 2.22; N, 18.93.

5-Chloro-4-hydroxy-2-methylpyrimidin-6(1*H*)-one (**5b**).

The yield was 91%, white prisms, mp 260° dec (water), lit [13] mp above 305°; ir: 3140-2600 s, 1680 sh, 1630 s, 1580 s cm^{-1}; nmr: δ 2.25 (s, 3, CH_3), 6.9 (s, broad, 2, OH, NH).

Anal. Calcd. for $C_5H_5ClN_2O_2$: C, 37.40; H, 3.11; Cl, 22.11; N, 17.44. Foundd: C, 37.55; H, 3.11; Cl, 22.18; N, 17.54.

5-Chloro-4-hydroxy-2-phenylpyrimidin-6(1*H*)-one (**5c**).

The yield was 82%, colorless crystals, mp 329° (*N,N*-dimethylformamide), lit [14] 329°.

5-Bromo-4-hydroxypyrimidin-6(1*H*)-one (**6a**).

The yield was 87%, colorless crystals, mp 20° (water), lit [15] mp 260°.

5-Bromo-4-hydroxy-2-methylpyrimidin-6(1*H*)-one (**6b**).

The yield was 60%, colorless prisms, mp 218° (water); ir: 3150-2300 m, 1670 sh, 1640 s, 1580 s cm^{-1}.

Anal. Calcd. for $C_5H_5BrN_2O_2$: C, 29.29; H, 2.46; N, 13.66. Found: C, 38.95; H, 2.50; N, 13.49.

5-Bromo-4-hydroxy-2-phenylpyrimidin-6(1*H*)-one (**6c**).

The yield was 82%, colorless crystals, mp 320° dec, lit [16] mp 320°; ir: 3100-2300 m, 1680 w, 1640 sh, 1610 s, 1585 s, 1530 s cm^{-1}.

Anal. Calcd. for $C_{10}H_7BrN_2O_2$: C, 44.98; H, 2.62; N, 10.49. Found: C, 44.90; H, 2.73; N, 10.07.

6-Oxo-5-(1-pyridinium)-1,6-dihydropyrimidin-4-olates (**7a-c**). General Procedure.

A) From the Iodonium-ylides **2** with Acetic Acid.

A solution containing 4 mmoles of 6-oxo-5-phenyliodonium-1,6-dihydropyrimidin-4-olates **2a,c** in 15 ml of methanol was treated with a mixture of 5 ml of acetic acid and 5 ml of dry pryidine, then heated under reflux on a water bath for 2-5 hours. The reaction mixture was evaporated (for **7c** the reaction mixture was concentrated to a small volume) and the residue obtained was crystallized.

B) From the Iodonium-ylides **2** with *p*-Toluenesulfonic Acid.

A solution containing 4 mmoles of the iodonium ylide **2b**, 0.95 g (5 mmoles) of *p*-toluenesulfonic acid, and 2 ml of pyridine in 25 ml of methanol was heated on a water bath under reflux for 4 hours. The reaction mixture was concentrated to a small volume and left to crystallize. A white precipitate of the *p*-toluenesulfonate salt of the pyridinium ylide was separated and recrystallized.

C) From the Halogeno Derivatives.

The halogeno derivative **5a** (10 mmoles) was dissolved in 2 ml of pyridine and heated under reflux for 12 hours, evaporated *in vacuo* to dryness, digested with petroleum ether and the residue obtained was treated with a solution of sodium bicarbonate and the whole mixture again taken to dryness. The produced pyridinium-ylide was extracted from the residue with cold methanol. After evaporation of the methanol the pyridinium-ylide was recrystallized.

6-Oxo-5-(1-pyridinium)-1,6-dihydropyrimidin-4-olate (**7a**).

Procedure A. The yield was 98%; Procedure C, yield 35%, yellow needles, mp 280° (*N,N*-dimethylformamide): ir: 3200-2700 m, 1645 s, 1625 m, 1610 s, 1590 m, 1580 s, 1550 s cm^{-1}; nmr (trifluoroacetic acid): δ 7.7-8.1 (m, 2, PyrH), 8.2-8.5 (m, 1, PyrH), 8.5-8.6 (m, 2, PyrH), 8.9 (s, 1, C-2).

Anal. Calcd. for $C_9H_7N_3O_2$: C, 57.17; H, 3.70; N, 22.21. Found: C, 57.14; H, 3.90; N, 22.23.

2-Methyl-6-oxo-5-(1-pyridinium)-1,6-dihydropyrimidin-4-olate (**7b**).

Procedure B. The yield was 63% (as the *p*-toluenesulfonate salt), colorless crystals, mp 180° (methanol); ir: 3500-2600 m, 1690 m, 1560 s, 1570 w cm^{-1}; nmr: δ **2.25** (**s**, 3, CH_3 at C-2), 2.50 (s, 3, CH_3 of *p*-toluenesulfonic acid), 7.05 and 7.45 (AA',BB', 4 H of *p*-toluenesulfonic acid, J = 8 Hz), 8.0-8.25 (m, 2, PyrH), 8.4-8.65 (m, 1, PyrH), 8.7-8.9 (m, 2, PyrH).

Anal. Calcd. for $C_{10}H_9N_3O_2 \cdot C_7H_8O_3S \cdot H_2O$: C, 51.90; H, 4.87; N, 10.68; S, 8.15; H_2O, 4.58. Found: C, 51.93; H, 4.84; N, 10.73; S, 8.38; H_2O, 4.70.

6-Oxo-2-phenyl-5-(1-pyridinium)-1,6-dihydropyrimidin-4-olate (**7c**).

Procedure A. The yield was 50%, yellow crystals, mp above 360° (*N,N*-dimethylformamide); ir: 3150-2750 m, 1635 s, 1620 s, 1595 s, 1580 s cm^{-1}; nmr (trifluoroacetic acid): δ 7.8-8.4 (m, 5, ArH + 2, PyrH), 8.6-8.8 (m, 1, PyrH), 8.8-9.0 (m, 2, PyrH).

Anal. Calcd. for $C_{15}H_{11}N_3O_2$: C, 67.92; H, 4.18; N, 15.84. Found: C, 67.75; H, 4.26; N, 15.60.

5-(3-Carbamoyl-1-pyridinium)-6-oxo-2-phenyl-1,6-dihydropyrimidin-4-olate (**8c**). 5-(2-Isoquinolinium)-6-oxo-1,6-dihydropyrimidin-4-olates (*9a-d*). 6-Oxo-2-phenyl-5-triphenylphosphonium-1,6-dihydropyrimidin-4-olate (**10c**). General Procedure.

A solution containing 4 mmoles of 6-oxo-5-phenyliodonium-1,6-dihydropyrimidin-4-olate **2-ad**, 0.95 g (5 mmoles) of *p*-toluenesulfonic acid, and the appropriate nucleophile (0.5 g, 4 mmoles of nicotinamide, or 1

ml of isoquinoline, or 1.1 g, 4.1 mmoles of triphenylphosphine) in 30 ml of methanol was heated under reflux for 4-6 hours. The reaction mixture was concentrated to a small volume and allowed to crystallize (in the case of **8c** and **9a-c**) or evaporated *in vacuo* to complete dryness (in the case of **9d** and **10c**). The residue obtained was washed with petroleum ether, digested with dilute sodium bicarbonate solution, filtered, washed with water and recrystallized. The following compounds were prepared by the above general procedure.

5-(3-Carbamoyl-1-pyridinium)-6-oxo-2-phenyl-1,6-dihydropyrimidin-4-olate (**8c**).

The yield was 25%, yellow needles, mp 355° (methanol); ir: 3500-2800 w, 1685 m, 1640 s, 1630 s, 1590 w, 1555 s cm^{-1}.

Anal. Calcd. for $C_{16}H_{12}N_4O_3 \cdot 0.5H_2O$: C, 60.57; H, 4.13; N, 17.66; H_2O, 2.84. Found: C, 60.17; H, 4.02; N, 17.35; H_2O, 3.10.

5-(2-Isoquinolinium)-6-oxo-1,6-dihydropyrimidin-4-olate (**9a**).

The yield was 54%, yellow crystals, mp 246° (*N,N*-dimethylformamide); ir: 3500-2900 w, 1640 s, 1610 m, 1570 s cm^{-1}; nmr: δ 7.8 (s, 1, C-2 of pyrimidine), 8.0-8.6 (m, 6, ArH), 9.9 (s, 1, C-1 of isoquinolinium).

Anal. Calcd. for $C_{13}H_9N_3O_2 \cdot 2H_2O$: C, 56.72; H, 4.76; N, 15.26; H_2O, 13.08. Found: C, 57.10; H, 4.43; N, 15.47; H_2O, 12.70.

5-(2-Isoquinolinium)-2-methyl-6-oxo-1,6-dihydropyrimidin-4-olate (**9b**).

The yield was 55%, yellow prisms, mp above 360° (methanol); ir: 3600-2700 w, 1670 m, 1640 s, 1610 m, 1580 m, 1535 m; nmr (trifluoroacetic acid): δ 2.65 (s, 3, CH_3), 7.8-8.2 (m, 6, ArH), 9.2 (s, 1, C-1 isoquinolinium).

Anal. Calcd. for $C_{14}H_{11}N_3O_2 \cdot 1.5H_2O$: C, 59.99; H, 5.00; N, 14.99; H_2O, 9.64. Found: C, 59.83; H, 4.84; N, 14.84; H_2O, 9.90.

5-(2-Isoquinolinium)-6-oxo-2-phenyl-1,6-dihydropyrimidin-4-olate (**9c**).

The yield was 33%, yellow needles, mp above 360° (methanol); ir: 3500-2800 w, 1645 s, 1605 m, 1595 m, 1550 s cm^{-1}; nmr (trifluoroacetic acid): δ 7.3-8.3 (m, 11, ArH), 9.2 (s, 1, C-1 isoquinolinium).

Anal. Calcd. for $C_{19}H_{13}N_3O_2 \cdot H_2O$: C, 68.46; H, 4.54; N, 12.61. Found: C, 68.50; H, 4.18; N, 12.39.

5-(2-Isoquinolinium)-6-oxo-1,2-diphenyl-1,6-dihydropyrimidin-4-olate (**9d**).

The yield was 64%, yellow prisms, mp 296° (1-propanol); ir: 3500-2900 m, 1650 m, 1630 m, 1595 s, 1540 m cm^{-1}.

Anal. Calcd. for $C_{25}H_{17}N_3O_2$: C, 76.71; H, 4.38; N, 10.74. Found: C, 76.43; H, 4.22; N, 10.62.

6-Oxo-2-phenyl-5-triphenylphosphonium-1,6-dihydropyrimidin-4-olate (**10c**).

The yield was 15%, colorless needles, mp 308° (methanol/water); ir: 3550-3000 m, 1670 w, 1590 s, 1560 s cm^{-1}.

Anal. Calcd. for $C_{28}H_{21}N_2O_2P \cdot H_2O$: C, 72.10; H, 4.97; N, 6.01; H_2O, 3.86. Found: C, 72.04; H, 4.60; N, 5.86; H_2O, 3.50.

6-Oxo-5-(1-tetrahydrothiophenium)-1,6-dihydropyrimidin-4-olate (**11a,c**). General Procedure.

A solution containing 4 mmoles of 6-oxo-5-phenyliodonium-1,6-dihydropyrimidin-4-olate (**2a,c**) in 20 ml of methanol was treated with 2 ml of thiophane and heated under reflux for 40 hours for **11a** or 16 hours for **11c**, respectively. The reaction mixture was evaporated to dryness and the residue obtained was recrystallized.

6-Oxo-5-(1-tetrahydrothiophenium)-1,6-dihydropyrimidin-4-olates (**11a**).

The yield was 51%, colorless prisms, mp 250° (*N,N*-dimethylformamide); ir: 3200-2500 m, 1645 s, 1590 s, 1540 s cm^{-1}; nmr (trifluoroacetic acid): δ 1.8-2.4 (m, 4, C-3 and C-4 of thiophane), 3.0-3.3 (m, 4, C-2 and C-5 of thiophane), 8.55 (s, 1, C-2).

Anal. Calcd. for $C_8H_{10}N_2O_2S$: C, 48.50; H, 5.05; N, 14.13; S, 16.18. Found: C, 48.25; H, 5.15; N, 14.14; S, 16.29.

6-Oxo-2-phenyl-5-(1-tetrahydrothiophenium)-1,6-dihydropyridin-4-olate (**11c**).

The yield was 85%, colorless prisms, mp 250° (methanol); ir: 3130-2760 m, 1630 s, 1585 s, 1560 s cm^{-1}; nmr (trifluoroacetic acid): δ 1.6-2.3 (m, 4, C-3 and C-4 of thiophane), 3.0-3.3 (m, 4, C-2 and C-5 of thiophane), 7.0-7.4 (m, 5, ArH).

Anal. Calcd. for $C_{14}H_{14}N_2O_2S$: C, 61.32; H, 5.11; N, 10.21; S, 11.69. Found: C, 61.25; H, 5.11; N, 10.18; S, 11.79.

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REFERENCES AND NOTES

[1] Part VI: E. Peichel and Th. Kappe, *Arch. Pharm.*, in press.

[2] On leave from the Department of Pharmaceutical Chemistry, Faculty of Pharmacy, University of Alexandria, Egypt.

[3] W. Friedrichsen, Th. Kappe and A. Böttcher, *Heterocycles*, **19**, 1083 (1982).

[4] Th. Kappe, R. Khorchid-Zadeh and H. Steininger, *Z. Naturforsch.*, **30b**, 773 (1975).

[5] G. Schindler and Th. Kappe, *Synthesis*, 243 (1977).

[6] Th. Kappe, G. Korbuly and W. Stadlbauer, *Chem. Ber.*, **111**, 3857 (1978).

[7] Th. Kappe, M. Hariri and E. Pongratz, *Monatsh. Chem.*, **112**, 1211 (1981).

[8] Th. Kappe, G. Korbuly and E. Pongratz, *ibid.*, **114**, 303 (1983).

[9] Th. Kappe, G. Korbuly and E. Pongratz, *Z. Naturforsch.*, **38b**, 398 (1983).

[10] G. Korbuly, Ph.D. Thesis, University of Graz, 1978.

[11] E. Pongratz and Th. Kappe, *Monatsh. Chem.*, in press.

[12] J. Chesterfield, L. F. W. McOmie and E. R. Sayer, *J. Chem. Soc.*, 3478 (1955).

[13] H. Gershon, K. Dittmer and R. Braun, *J. Org. Chem.*, **26**, 1875 (1961).

[14] H. Gershon, R. Braun, A. Scala and R. Rodin, *J. Med. Chem.*, **7**, 808 (1964).

[15] S. Banerjee and O. S. Tee, J. Org. Chem., **39**, 3120 (1974).

[16] E. L. Pinner, *Ber.*, **41**, 3518 (1908).

[17] R. Blank, *ibid.*, **31**, 1815 (1898); F. Kröhnke, *ibid.*, **70**, 543 (1937).