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Dedicated to the memory of Roland K. Robins

The reaction of "magic malonates" (bis-2,4,6-trichlorophenyl malonates, **1**) with 5-aminotetrazole (**2**) in the presence of triethylamine yields the ammonium salts **3**. Upon treatment of **3** with strong acids compounds **4a-d** were obtained as a mixture of isomeric tetrazolopyrimidines (**A**) and 2-azidopyrimidines (**B**). Reaction of **4d** with bromine or suluryl chloride leads by ring opening and decarboxylation to the halogenated tetrazole derivatives **5** or **7**, respectively. The action of acetic anhydride in pyridine on **3d** yields the zwitterionic tetramic acid derivative **10**.

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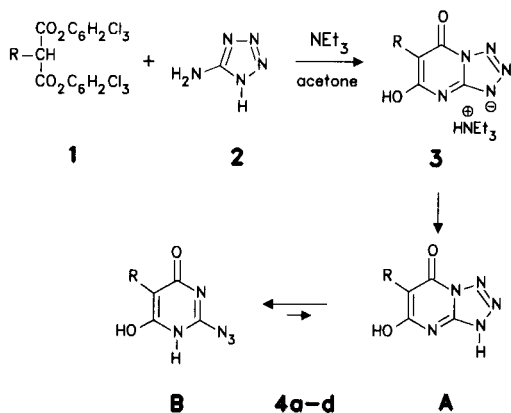
In continuation of our studies on a number of azidopyrimidines and their isomeric tetrazolopyrimidines [2-4] we have now focussed our attention to 2-azidopyrimidines and their congeners, tetrazolo[1,5-*a*]pyrimidines. This class of compounds, containing two oxygen functions in 1,3-position, should be available through a condensation of malonic acid derivatives and 5-aminotetrazole (**2**), and indeed, Reimlinger [5] had in 1970 reported the reaction of diethyl malonate with **2** at 180° leading to 2-azido-4,6-dioxo-1,2,3,4-tetrahydropyrimidine in 12% yield.

We have also tried the thermal condensation of **2** with "magic malonates" [6] *i.e.* with bis-2,4,6-trichlorophenyl malonates (**1**) [7,8] without success. However, applying the previously developed method of using **1** in the presence of triethylamine [9] afforded in boiling acetone or dioxane

the triethylammonium salts **3** in good yields (Scheme 1). The protonated ("neutral") form of these compounds could be generated with strong acids. The less water soluble compounds **4c,d** were obtained by treatment of 6 *N* hydrochloric acid; in the case of the more water soluble derivatives **4a,b** the solutions of **3a,b** in water were treated with Amberlite IR-120 (H⁺ form) and taken to dryness. The p*K*_a values for **3a/4a** in water were estimated to 3.5 (proton loss from the tetrazole moiety) and 6.3 (proton loss from the pyrimidine "OH") [10,11]. These results are in agreement with the fact, that the infrared spectra of the salts **3** show no azide absorption, while compounds **4** exhibit azide absorption bands at 2140-2130 cm⁻¹. However, the azide absorption of **4d** (in a potassium bromide disk) is very weak only, and it can be assumed that an azido-tetrazolo isomerization [12] exists in this class of compounds (These transformations can also be regarded as 1,5-dipolar cyclization/ring-opening valence isomerization [5,13]).

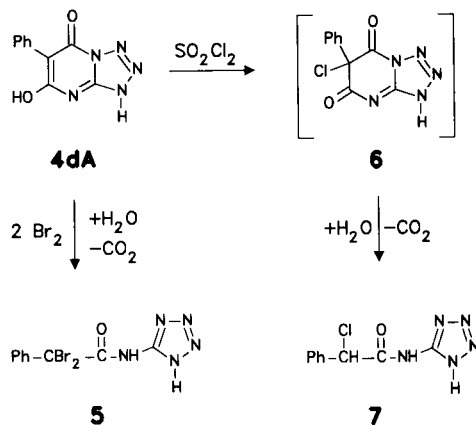
The ambivalent character of compounds **4** is also expressed in their chemical behaviour. Electrophiles attack

Scheme 1



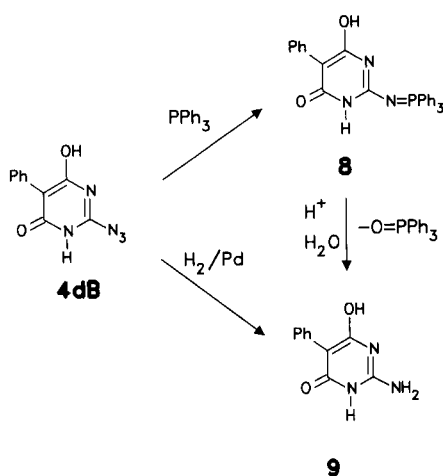
1,3,4	R
a	C ₂ H ₅
b	n-C ₄ H ₉
c	CH ₂ C ₆ H ₅
d	C ₆ H ₅

Scheme 2



at the nucleophilic C-atom of the malonyl system in the pyrimidine part of the molecule. Thus the action of an excess of bromine on **4d** in dioxane (containing some water) gives under hydrolysis and decarboxylation the dibromophenylacetaminotetrazole **5**. The action of one equivalent of sulfonyl chloride in dry dioxane and aqueous work up yields (again by hydrolytic ring-opening and decarboxylation) the monochloro tetrazole derivative **7** (Scheme 2). Quite similar reactions have been observed previously with "malonyl- α -aminopyridine" [14].

Scheme 3



On the other hand, the catalytic hydrogenation of **4d** in the presence of palladium yields smoothly the 2-amino-4-hydroxypyrimidine **9** which indicates the presence of the azido isomer [2]. Nevertheless we have prepared **9** also by the classical Staudinger reaction [2,15] via the triphenylphosphoranylideneamino derivative **8**, which may serve also as starting material for Aza-Wittig reactions (Scheme 3).

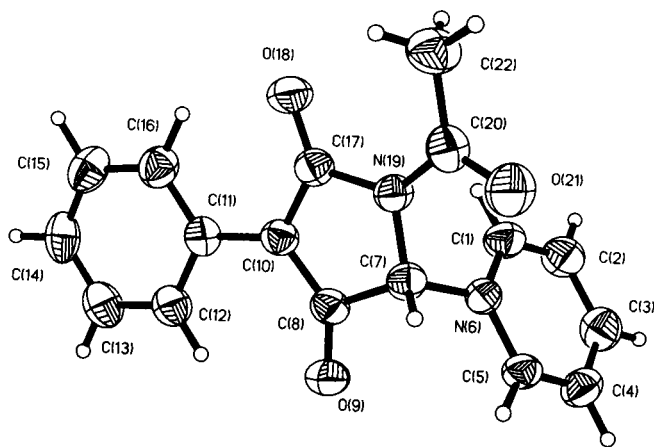


Figure 1. ORTEP drawing of **10**, thermal ellipsoids at the 50% probability level.

The acylation of proton bearing tetrazoles with carboxylic acid chlorides or anhydrides leads under the loss of nitrogen to oxadiazoles [16]. We have tried the reaction of **3d** with acetic anhydride in pyridine at 100°. However, the outcome of the reaction was quite unexpected. Elemental analyses and spectra indicated that acetylation had occurred, that two molecules of nitrogen were lost, and that the pyridine nucleus had entered into the product. An X-ray crystal structure determination revealed the consti-

Table 1
Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($\text{\AA}^2 \times 10^4$) for **10**

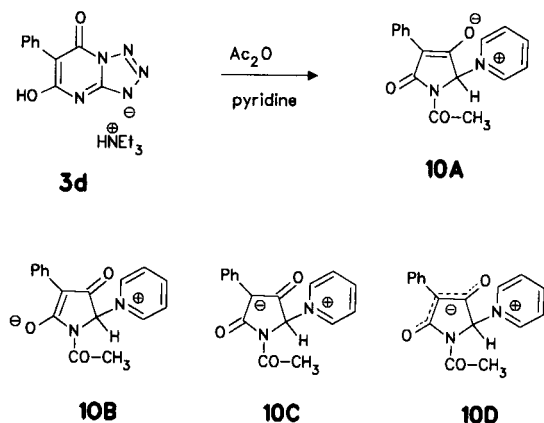
	x/a	y/b	z/c	Ueq
C(1)	3283 (4)	6687 (3)	2673 (3)	475 (21)
C(2)	4739 (4)	8006 (3)	3150 (3)	530 (23)
C(3)	5878 (4)	8469 (3)	4395 (3)	527 (22)
C(4)	5516 (4)	7606 (3)	5146 (3)	482 (21)
C(5)	4042 (4)	6301 (3)	4648 (3)	400 (19)
N(6)	2944 (3)	5853 (2)	3427 (2)	363 (14)
C(7)	1461 (3)	4321 (3)	2830 (3)	388 (18)
C(8)	2237 (3)	3124 (3)	1835 (3)	393 (18)
O(9)	3595 (3)	2978 (2)	2328 (2)	511 (14)
C(10)	1205 (3)	2448 (3)	482 (3)	385 (17)
C(11)	1408 (3)	1174 (3)	-776 (3)	396 (17)
C(12)	2658 (4)	477 (3)	-667 (3)	486 (21)
C(13)	2820 (4)	-760 (3)	-1830 (3)	562 (23)
C(14)	1739 (4)	-1333 (3)	-3123 (3)	548 (22)
C(15)	498 (4)	-667 (3)	-3258 (3)	564 (22)
C(16)	338 (4)	584 (3)	-2106 (3)	503 (21)
C(17)	-172 (3)	3118 (3)	505 (3)	395 (18)
O(18)	-1344 (3)	2866 (2)	-438 (2)	541 (14)
N(19)	1 (3)	4264 (2)	1943 (2)	382 (14)
C(20)	-1193 (4)	5018 (3)	2556 (3)	448 (19)
O(21)	-919 (3)	5745 (2)	3854 (2)	638 (16)
C(22)	-2712 (5)	4957 (5)	1634 (4)	588 (27)

Table 2
Bond Lengths ($\text{\AA}$) and Angles ($^\circ$) for **10**

C(1)-C(2)	1.361 (4)	C(10)-C(17)	1.427 (5)
C(1)-N(6)	1.348 (5)	C(11)-C(12)	1.389 (5)
C(2)-C(3)	1.374 (5)	C(11)-C(16)	1.393 (4)
C(3)-C(4)	1.369 (6)	C(12)-C(13)	1.384 (4)
C(4)-C(5)	1.360 (4)	C(13)-C(14)	1.370 (5)
C(5)-N(6)	1.342 (4)	C(14)-C(15)	1.368 (5)
N(6)-C(7)	1.498 (3)	C(15)-C(16)	1.385 (4)
C(7)-C(8)	1.533 (4)	C(17)-O(18)	1.215 (4)
C(7)-N(19)	1.420 (4)	C(17)-N(19)	1.444 (3)
C(8)-O(9)	1.239 (4)	N(19)-C(20)	1.384 (4)
C(8)-C(10)	1.390 (4)	C(20)-O(21)	1.223 (3)
C(10)-C(11)	1.468 (4)	C(20)-C(22)	1.477 (6)
C(2)-C(1)-N(6)	120.2(3)	C(10)-C(11)-C(12)	120.5(2)
C(1)-C(2)-C(3)	119.6(4)	C(10)-C(11)-C(16)	122.2(3)
C(2)-C(3)-C(4)	119.4(3)	C(12)-C(11)-C(16)	117.2(2)
C(3)-C(4)-C(5)	119.6(3)	C(11)-C(12)-C(13)	121.2(3)
C(4)-C(5)-N(6)	120.5(3)	C(12)-C(13)-C(14)	120.5(4)
C(1)-N(6)-C(5)	120.6(2)	C(13)-C(14)-C(15)	119.4(3)
C(1)-N(6)-C(7)	120.2(2)	C(14)-C(15)-C(16)	120.6(3)
C(5)-N(6)-C(7)	118.8(3)	C(11)-C(16)-C(15)	121.0(3)
N(6)-C(7)-C(8)	107.7(2)	C(10)-C(17)-O(18)	131.0(2)
N(6)-C(7)-N(19)	112.0(3)	C(10)-C(17)-N(19)	107.9(2)
C(8)-C(7)-N(19)	104.9(2)	O(18)-C(17)-N(19)	121.1(3)
C(7)-C(8)-O(9)	118.6(2)	C(7)-N(19)-C(17)	109.7(2)
C(7)-C(8)-C(10)	107.7(3)	C(7)-N(19)-C(20)	119.6(2)
O(9)-C(8)-C(10)	133.7(3)	C(17)-N(19)-C(20)	129.5(2)
C(8)-C(10)-C(11)	125.9(3)	N(19)-C(20)-O(21)	118.1(3)
C(8)-C(10)-C(17)	109.8(2)	N(19)-C(20)-C(22)	119.5(2)
C(11)-C(10)-C(17)	124.2(2)	O(21)-C(20)-C(22)	122.3(3)

tution of the product to be the zwitterionic tetramic acid derivative **10A**.

Scheme 4

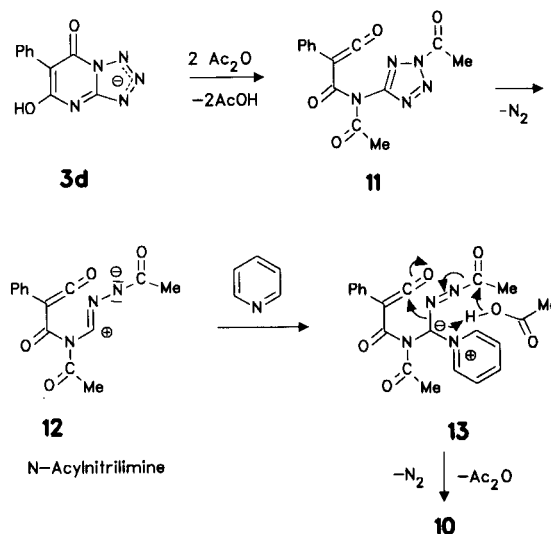


The negative charge of the molecule rests in the malonate part, and one is tempted to indicate this in writing mesomeric structures, such as **10B-D**, since many mesomeric cross-conjugated (and pseudo-cross-conjugated) mesomeric betaines containing the trimethine oxonolate (= malonate) moiety are known [8,17-19]. Inspection of bond distances in **10** reveals that formula **10A** contributes much to the real picture of **10**. Thus the bond length between C(8)-O(9) = 1.239 Å is much longer than C(17)-O(18) = 1.215 Å; The length between C(8)-C(10) = 1.390 Å is shorter than C(10)-C(17) = 1.427 Å. Not surprisingly, the malonate amide-CO is "decoupled" from the pyrrole N-atom - C(17)-N(19) = 1.444 Å - and the amide resonance of this N-atom takes place with the *N*-acetyl-CO; N(19)-C(20) = 1.384 Å. Nevertheless, all atoms of the pyrrole ring are in one plane, and the acetyl amide group [N(19), C(20), O(21) and C(22)] is in another plane. The angle between the two planes is 10.65(2.0)°. Remarkable is also the long distance between the pyridinium-N and the sp^3 carbon atom of the pyrrole nucleus: N(6)-C(7) = 1.498 Å.

The reaction mechanism leading from **3d** to the pyrrole **10** can be rationalized as follows: acetylation of the tetrazole nucleus and ring opening of the pyrimidone leads to the α -oxoketene intermediate **11**. The ring opening of such pyrimidines containing the malonyl moiety has been described frequently [9,20]. Since acetic acid is present in the reaction mixture (once acetylation has occurred), the ketene may add the acid to form a mixed anhydride between malonic acid and acetic acid [21]. However, this would not change the proposed mechanism since α -oxo-ketene and the anhydride should be in equilibrium [21]. The elimination of nitrogen from *N*-acyltetrazoles yielding *N*-acylnitrilimines, such as **12** [16], is a long known reaction which leads by 1,5-dipolar ring closure to 1,3,4-oxadi-

azoles [16]. Why this ring closure (of **12**) does not take place, and instead addition of pyridine and further fragmentation under loss of another molecule of nitrogen and the acyl group occurs is at the present time unknown to us. The formulation of the intermediate **13** is only speculative, and the sequence of the required steps not known.

Scheme 5



Summary: The condensation of malonates with 5-amino-tetrazole leads to bicyclic tetrazolopyrimidines with two acidic protons of which one can be located in the tetrazole part. It seems that the chemistry of this type of compounds has so far not been studied, and that the new reaction leading to **10** in which all nitrogen atoms of the tetrazole moiety are eliminated is due to this structure. Further studies in this series of compounds seem to be necessary [22].

EXPERIMENTAL

The melting points were determined in open capillary tubes on a Gallenkamp melting point apparatus Model MFB-595 and are uncorrected. The IR spectra were recorded on a Perkin Elmer 298 spectrophotometer using samples in potassium bromide disks. The ^1H -NMR spectra were recorded in hexadeuteriodimethyl sulfoxide and with TMS as an internal standard; the instrument used was the Varian XL 200 at 200 MHz. Elemental analyses were performed with a C,H,N-automat Carlo Erba 1106.

Triethylammonium 6-Ethyl-7-hydroxy-5-oxo-1*H*,5*H*-tetrazolo[1,5-*a*]pyrimidin-1-ide (**3a**).

To a suspension of **2** (0.43 g, 5.0 mmol) in 10.0 ml of absolute dioxane was added triethylamine (0.60 g, 6.0 mmol), and then a solution of **1a** [7] (2.45 g, 5.0 mmol) in 10.0 ml of dry dioxane was added. The reaction mixture was heated under reflux for 30 minutes, 20 ml of cyclohexane was added, and after cooling a colorless precipitate was formed which was filtered and washed with diethyl ether. The yield was 1.05 g (71%), mp 147-148°; IR: 2980 m, 2930 m, 2780 m, 2700 m, 2500 w, 1650 s, 1615 s, 1540 cm^{-1} ; ^1H NMR: δ = 1.0 (t, J = 7 Hz, 3H, 6-ethyl- CH_3), 1.25 (t, J = 7 Hz,

9H, triethylammonium-CH₃), 2.4 (q, *J* = 7 Hz, 2H, 6-ethyl-CH₂), 3.2 (q, *J* = 7 Hz, 6H, triethylammonium-CH₃). Electrolytic ionization constants (determined in water at λ_{max} = 279.9 nm), pK_{a1} = 3.5; pK_{a2} = 6.3.

Anal. Calcd. for C₁₂H₂₂N₆O₂ (282.4): C, 51.03; H, 7.87; N, 29.77. Found: C, 51.04; H, 7.88; N, 29.76.

Triethylammonium 6-(1-Butyl)-7-hydroxy-5-oxo-1*H*,5*H*-tetrazolo[1,5-*a*]pyrimidin-1-*id* (**3b**).

To a suspension of **2** (0.43 g, 5.0 mmoles) in 10 ml of dry acetone was added triethylamine (0.60 g, 6.0 mmoles), and then a solution of **1b** (2.60 g, 5.0 mmoles) in 10.0 ml of acetone. The reaction mixture was heated under reflux for 30 minutes and evaporated to dryness. The oily residue was dissolved in 50 ml of water. The aqueous solution was extracted several times with benzene (40 ml portions) and taken to dryness. The residue crystallized after several days. The yield was 0.80 g (52%), mp 106–108° dec; ir: 3500–2300 b, 1650 s, 1540 s cm⁻¹; ¹H-nmr: δ = 0.9 (t, *J* = 7 Hz, 3H, butyl-CH₃), 1.2 (t, *J* = 7 Hz, 9H, triethylammonium-CH₃), 1.1–1.6 (m, 4H, 2 butyl-CH₃), 2.35 (t, *J* = 7 Hz, 2H, butyl-CH₂), 3.2 (q, *J* = 7 Hz, 6H, 3 triethylammonium-CH₃).

Anal. Calcd. for C₁₄H₂₆N₆O₂ (310.5): C, 54.16; H, 8.46; N, 27.08. Found: C, 53.85; H, 8.18; N, 27.45.

Triethylammonium 6-Benzyl-7-hydroxy-5-oxo-1*H*,5*H*-tetrazolo[1,5-*a*]pyrimidin-1-*id* (**3c**).

As described before, **2** (5.0 mmoles) and **1c**^{xx} [7] (5.0 mmoles) were reacted in the presence of triethylamine (6.0 mmoles). To the reaction mixture 20 ml of cyclohexane were added and the mixture was kept overnight in the refrigerator. The solvents were decanted and the oily residue was heated with 30 ml of toluene. Slow crystallization occurred after cooling. The yield was 0.75 g (44%), mp 116–118°; ir: 3100–2300 b, 1650 m, 1620 m, 1540 s cm⁻¹; ¹H-nmr: δ = 1.15 (t, *J* = 7 Hz, 9H, triethylammonium-CH₃), 3.05 (q, *J* = 7 Hz, 6H, triethylammonium-CH₃), 3.6 (s, 2H, benzyl-CH₂), 6.95–7.4 (m, 5H, ArH).

Anal. Calcd. for C₁₇H₂₄N₆O₂ (344.5): C, 59.27; H, 7.04; N, 24.40. Found: C, 58.88; H, 6.82; N, 24.79.

Triethylammonium 7-Hydroxy-6-phenyl-5-oxo-1*H*,5*H*-tetrazolo[1,5-*a*]pyrimidin-1-*id* (**3d**).

To a suspension of **2** (0.43 g, 5.0 mmoles) in 10 ml of dry acetone were added triethylamine (0.6 g, 6.0 mmoles) and a solution of **1c** (2.70 g, 5.0 mmoles) in 10 ml of acetone. By heating the reaction mixture the product already precipitates. After cooling the product is filtered off and washed with diethyl ether. The yield was 1.18 g (72%), mp 213° dec; ir: 3200–2300 b, 1650 m, 1610 m, 1545 s, 1510 w cm⁻¹; ¹H-nmr: δ = 1.1 (t, *J* = 7 Hz, 9H, triethylammonium-CH₃), 3.0 (q, *J* = 7 Hz, 6H, triethylammonium-CH₃), 6.9–7.4 (m, 3H, PhH), 7.65 (dd, *J* = 8 Hz and 2 Hz, 2H, 2 *ortho*-PhH).

Anal. Calcd. for C₁₆H₂₂N₆O₂ (330.4): C, 58.15; H, 6.72; N, 25.44. Found: C, 58.11; H, 6.64; N, 25.41.

2-Azido-5-ethyl-6-hydroxy-pyrimidin-4(1*H*)-one/6-Ethyl-7-hydroxy-tetrazolo[1,5-*a*]pyrimidin-5(1*H*)-one (**4a**).

The aqueous solution of **3a** was passed through a short column of Amberlite IR-120 (H⁺ form), and the eluate was taken to dryness. The yield was quantitatively, mp 208° dec; ir: 3500–2300 b, 2130 m (N₃), 1630 s (CO), 1630 s, 1580 s cm⁻¹.

Anal. Calcd. for C₈H₇N₅O₂ (181.2): C, 39.77; H, 3.90; N, 38.66.

Found: C, 39.51; H, 3.99; N, 38.35.

2-Azido-5-(1-butyl)-6-hydroxypyrimidin-4(1*H*)-one/6-(1-Butyl)-7-hydroxytetrazolo[1,5-*a*]pyrimidin-5(1*H*)-one (**4b**).

The preparation from the salt **3b** was performed as described before using Amberlite IR-120 ion exchange resin; mp 176° dec; ir: 3400–2300 b, 2130 m (N₃), 1625 s, 1580 s cm⁻¹.

Anal. Calcd. for C₈H₁₁N₅O₂ (209.2): C, 45.91; H, 5.31; N, 33.49. Found: C, 45.53; H, 5.38; N, 33.11.

2-Azido-5-benzyl-6-hydroxypyrimidin-4(1*H*)-one/5-Benzyl-7-hydroxytetrazolo[1,5-*a*]pyrimidin-5(1*H*)-one (**4c**).

The salt **3c** was dissolved in the minimum amount of water, and the solution was acidified with concentrated hydrochloric acid. The precipitate was collected after 30 minutes of stirring, and washed with 6 *N* hydrochloric acid, mp 215° dec (ethanol); ir: 3300–2300 b, 2260 w, 2160 m, 2140 s, 1640 s, 1590 s, 1575 s cm⁻¹.

Anal. Calcd. for C₁₁H₉N₅O₂ (243.3): C, 54.31; H, 3.74; N, 28.79. Found: C, 54.19; H, 3.75; N, 28.96.

2-Azido-6-hydroxy-5-phenylpyrimidin-4(1*H*)-one/7-Hydroxy-6-phenyltetrazolo[1,5-*a*]pyrimidin-5(1*H*)-one (**4d**).

The salt **3d** was dissolved in the minimum amount of water and acidified with concentrated hydrochloric acid. After 30 minutes of stirring the precipitate was filtered off and washed with 6 *N* hydrochloric acid, mp 273° dec (dimethylformamide/water); ir: 3250–2250 b, 2140 w (N₃), 1670 s, 1605 m, 1520 m cm⁻¹.

Anal. Calcd. for C₁₀H₇N₅O₂ (229.2): C, 52.40; H, 3.08; N, 30.56. Found: C, 52.18; H, 3.31; N, 30.50.

5-(2,2-Dibromo-2-phenylacetamino)tetrazole (**5**).

The mixture of **4d** (0.50 g, 1.5 mmoles) and bromine (0.50 ml, mmoles) in 10 ml of dioxane was stirred for 15 minutes and then poured on 100 ml of ice-water. The mixture was kept for 12 hours at 4° and then filtered. The yield was 0.45 g (83%), mp 206° dec (methanol); ir: 3220 m, 1710 s, 1580 s, 1540 w cm⁻¹; ¹H-nmr: δ = 7.2–7.8 (m, 5 PhH).

Anal. Calcd. for C₉H₇Br₂N₄O (361.0): C, 29.94; H, 1.96; N, 19.40. Found: C, 30.20; H, 2.09; N, 19.77.

5-(2-Chloro-2-phenylacetamino)tetrazole (**7**).

A suspension of **4d** (1.00 g, 3.0 mmoles) in 20 ml of dry dioxane was treated with sulfuryl chloride (1.0 ml) and stirred for 30 minutes. The resulting solution is poured on 200 ml of ice-water and filtered after 12 hours at 4°. The yield was 0.53 g (75%), mp 214° dec (methanol); ir: 3260 m, 1695 m, 1605 s, 1535 m cm⁻¹; ¹H-nmr: δ = 5.85 (s, 1H, CH), 7.2–7.8 (m, 5H, PhH), 12.5 (b, 1H, NH).

Anal. Calcd. for C₉H₇ClN₄O (237.7): C, 45.44; H, 3.39; N, 29.47. Found: C, 45.18; H, 3.23; N, 29.32.

6-Hydroxy-5-phenyl-2-triphenylphosphoranylideneaminopyrimidin-4(3*H*)-one (**8**).

A mixture of **4d** (1.00 g, 3.0 mmoles) and triphenylphosphane (0.85 g, 3.2 mmoles) in 1,2-dichlorobenzene was heated under reflux for 30 minutes. The precipitate obtained after cooling was filtered and washed with toluene. The yield was 1.20 g (86%), mp 279.5–281.5° (ethanol); ir: 3200–2400 b, 1620–1510 b cm⁻¹; ¹H-nmr: δ = 7.0–8.1 (m, ArH).

Anal. Calcd. for C₂₆H₂₂N₃O₂P (463.5): C, 72.55; H, 4.79; N, 9.07. Found: C, 72.59; H, 4.74; N, 9.06.

2-Amino-6-hydroxy-5-phenylpyrimidin-4(3*H*)-one (**9**).

A) The azidopyrimidone **4d** (0.5 g, 1.5 mmol) was hydrogenated in the presence of 50 mg of 10% palladium/charcoal catalyst in 25 ml of acetic acid for 8 hours at room temperature. The mixture was then heated to bring the product into solution, the catalyst was filtered off, the filtrate was taken to dryness, and the residue digested with methanol. The precipitate was dried at 100° *in vacuo*, the yield was 0.26 g (85%).

B) A mixture of **8** (2.00 g, 2.2 mmol), acetic acid (8.0 ml), and water (2.0 ml) was heated under reflux for 30 minutes. Ethyl acetate (15 ml) was added and the suspension kept at 4° for 12 hours. The precipitate was filtered and thoroughly washed with ethyl acetate to remove triphenylphosphine oxide. The yield was 0.32 g (89%), mp 334° dec (acetic acid), lit mp 333–336° [yy]; ir: 3440 m, 3400–2300 b, 1680 m, 1600 s, 1560 m cm⁻¹.

Anal. Calcd. for C₁₀H₉N₃O₂ (203.2): C, 59.10; H, 4.47; N, 20.68. Found: C, 58.80; H, 4.50; N, 20.53.

(±)1-Acetyl-2-oxo-3-phenyl-5-(1-pyridinio)-1,5-dihydro-2H-pyrrol-4-olat (**10A**).

A mixture of **3d** (0.50 g, 1.5 mmol), acetic anhydride (1.0 ml), and dry pyridine (5.0 ml) was heated on a water bath for 4 hours. After cooling, 20 ml of ethyl acetate was added, and the crystals were collected after 12 hours, and washed with ethyl acetate. The yield was 0.35 g (80%), dark orange crystals from methanol which decompose above 200° under the loss of pyridine without melting; ir: 3110 w, 3050 w, 1700 m, 1665 s, 1600 s, 1500 m cm⁻¹; ¹H-nmr: δ = 2.5 (s, 3H, CH₃), 6.45 (s, 1H, 5-CH), 6.8–7.3 (m, 3H, PhH), 7.85–8.7 (m, 5H, 2 PhH and 3 PyH), 9.1 (dd, J = 7 Hz and 2 Hz, 2H, α-PyH).

Anal. Calcd. for C₁₇H₁₄N₂O₃ (294.3): C, 69.36; H, 4.80; N, 9.52. Found: C, 69.61; H, 4.84; N, 9.46.

X-ray structure determination of **10** (C₁₇H₁₄N₂O₃, M = 294.3): A specimen of size 0.5 mm x 0.5 mm x 0.5 mm was investigated at 293 ± 2 K on a modified STOE diffractometer (Mo-K_α radiation, λ = 0.71069 Å, graphite monochromator). Cell dimensions were determined by a least squares fit to the setting angles of 19 reflections with 9° ≤ 2θ ≤ 16°: triclinic system, space group P $\bar{1}$, a = 7.812(5) Å, b = 10.111(9) Å, c = 10.410(8) Å, α = 114.03(6)°, β = 91.51(5)°, γ = 107.19(6)°, V = 707.2(9) Å³, Z = 2, μ = 0.096 mm⁻¹, δ_c = 1.382 g cm⁻³. Intensity data were collected for a complete hemisphere of reciprocal space with 3° ≤ 2θ ≤ 50°, -9 ≤ H ≤ 9, -12 ≤ K ≤ 12, 0 ≤ L ≤ 12 (ω-scans, stationary background/peak/stationary background method, width 1.6°, variable speed, ranging from 1.88°/min to 15°/min). 2636 Reflections were measured, yielding 2486 independent reflections (R_m = 0.031) and 1617 with F/σ(F) > 3. The structure was solved by direct methods and refined by minimizing the quantity Σw(|F_o|-|F_c|)² (full matrix), all non-hydrogen atoms were refined with anisotropic a.d.p.'s, hydrogen atoms were refined with isotropic temperature factors at observed positions. Final R = Σ||F_o|-|F_c||/Σ|F_o| = 0.0486, wR = (Σw(|F_o|-|F_c|)²/Σw|F_o|²)^{1/2} = 0.0466 for 255 parameters and 1617 observations [weighting scheme 1/σ²(F)]. The final difference density map shows features up to 0.20 e Å⁻³ and down to -0.31 e Å⁻³. The Sie-

mens SHELXTL Software was used for the calculations. Atomic coordinates and equivalent isotropic displacement coefficients for non-hydrogen atoms are shown in Table 1, bond lengths and angles are reported in Table 2. Figure 1 shows a molecule and the numbering scheme, thermal ellipsoids are drawn at the 50% probability level.

REFERENCES AND NOTES

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- [10] The order of these values can be correlated with known data. Tetrazole itself (without a carbonyl group on one nitrogen): pK_a = 4.9; "malonyl-α-aminopyridine" as an example for a condensed hydroxypyrimidone system pK_a = 7.09 [11]. However, it must be emphasized that this type of hydroxypyrimidones are known to exist in their zwitterionic forms, i.e. pyrimidiniumolates [8–11].
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- [22] The unsubstituted derivative of **4** has to be studied again, since Reimlinger [5] described it as "red crystals." Our compounds **3** and **4** are colorless (λ max = 280 nm). Unfortunately, the synthesis of **4** with the unsubstituted magic malonate **1** did not work.