Synthesis of 1- and 3-Amino-5-*t*-butyl-1*H*- and -3*H*-*v*-triazolo[4,5-*d*]pyrimidines as Hetaryne Precursors

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Received October 27, 1986

The synthesis of the title compounds **6** and **8** has first been accomplished by reaction of *O*-mesitylsulfonylhydroxylamine with 5-*t*-butyl-3*H*-*v*-triazolo[4,5-*d*]pyrimidine (**5**) whose preparation is reported in detail. However the preferred route for the synthesis of the 3-amino derivative **8** is based upon the preparation of 3-benzylideneamino-5-*t*-butyl-3*H*-*v*-triazolo[4,5-*d*]pyrimidine (**10**), followed by the removal of the benzylidene protecting group. This critical step was effected by treatment of **10** with dilute hydrochloric acid, in the presence of 2,4-dinitrophenylhydrazine.

The diazotization of 5-amino-4-hydrazino-2-*t*-butylpyrimidine gave predominantly the tetrazolo[1,5-*c*]pyrimidine **13** along with a small amount of compound **8**.

J. Heterocyclic Chem., **24**, 705 (1987).

The method developed by Campbell and Rees [1] has been successfully applied to the generation of a number of hetaryne intermediates [2], namely 2,3-didehydropyridine and -quinoline, 3,4-didehydropyridine and -quinoline [3], and 3,6-diphenyl-4,5-didehydropyridazine [4]. Its extension to the pyrimidine series has long been delayed by the failure to obtain the required 1- or 3-amino-1*H*- or -3*H*-*v*-triazolo[4,5-*d*]pyrimidine precursors by the general route described by Fleet and Fleming [3]. Consequently, in the initial phase of our investigations [5], we focused our attention on the amination of a 3*H*-*v*-triazolo[4,5-*d*]pyrimidine with *O*-mesitylsulfonylhydroxylamine (MSH) [6]. We anticipated that a bulky substituent at position 5 would prevent any undesirable reaction onto the pyrimidine nitrogen atoms [7]. We also expected that such a substituent would enhance the solubility in the common organic solvents. 5-*t*-Butyl-3*H*-*v*-triazolo[4,5-*d*]pyrimidine (**5**) was therefore selected and its synthesis studied.

2-*t*-Butyl-4(3*H*)-pyrimidinone (**1**) was used as starting material. Nitration was achieved according to the procedure of Fox and his coworkers [8]. Next, refluxing phosphorus oxychloride converted the nitro compound **2** into 4-chloro-5-nitro-2-*t*-butylpyrimidine. The latter is so highly susceptible to hydrolysis that we found it much more convenient to treat the chloro derivative, without isolation, with concentrated ammonium hydroxide. Catalytic reduction of 4-amino-5-nitro-2-*t*-butylpyrimidine (**3**) gave the diaminopyrimidine **4** which had previously been prepared, in much lower yield, from 4,6-dihydroxy-2-*t*-butylpyrimidine [9]. Finally, diazotization of compound **4** yielded 5-*t*-butyl-3*H*-*v*-triazolo[4,5-*d*]pyrimidine (**5**).

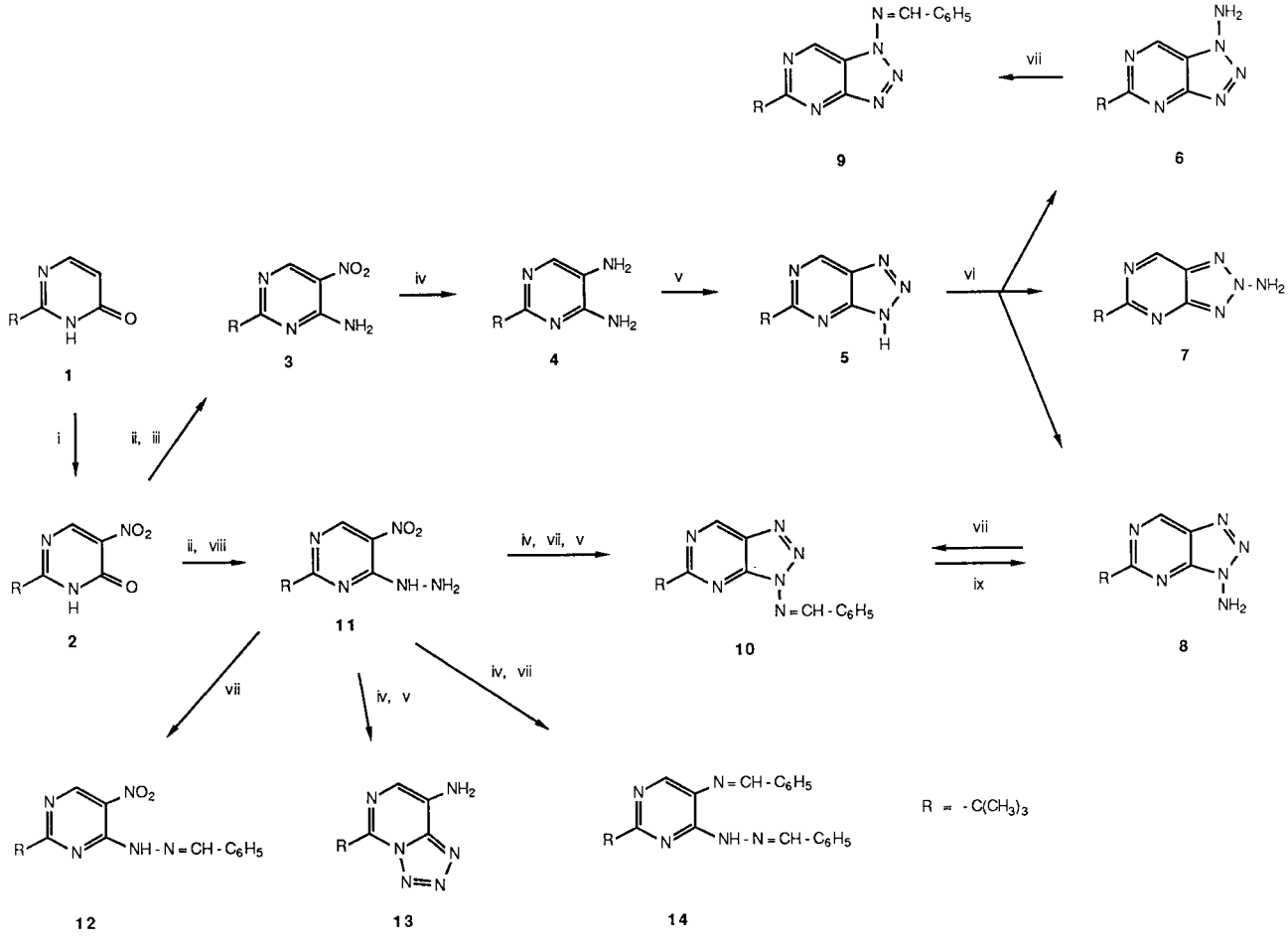
An alkali salt of the triazolopyrimidine **5** was allowed to react with *O*-mesitylsulfonylhydroxylamine (MSH). Three products were isolated from the reaction mixture, in relatively pure state, by flash chromatography. The first to be eluted was the 3-amino derivative **8**; the second, always present in lesser amounts, was the 2-amino derivative **7** and the third the 1-amino derivative **6**. The yields were variable. Compared to its isomers **6** and **7**, the 3-amino derivative **8** was found fairly stable. The location of the amino group was difficult to determine since all three compounds had very similar ^{1}H nmr spectra (see Experimental). The 1- and 3- isomers **6** and **8** could be distinguished from the minor component, tentatively formulated as the 2-isomer **7**, by their oxidation with lead tetra-acetate and the trapping of the resulting 2-*t*-butyl-4,5-didehydropyrimidine with furan [5]. They were fully identified in the form of their benzylidene derivatives **9** and **10** by an unequivocal synthesis of the latter.

This synthesis is based on the work of Fleet and Fleming [3]. 4-Chloro-5-nitro-2-*t*-butylpyrimidine was treated this time with hydrazine hydrate to afford 4-hydrazino-5-nitro-2-*t*-butylpyrimidine (**11**) which was characterized in the form of the hydrazone **12**. Compound **11** was then converted by a one-pot synthesis, *via* 5-amino-4-hydrazino-2-*t*-butylpyrimidine to 5-amino-4-benzylidenehydrazino-2-*t*-butylpyrimidine, and thence with nitrous acid to the desired product **10**. This material was shown to be identical to one of the benzylidene derivatives obtained before. The intermediate 5-amino-4-hydrazino-2-*t*-butylpyrimidine was fully characterized in the form of its derivative **14**.

The synthesis of 3-benzylideneamino-5-*t*-butyl-3*H*-*v*-triazolo[4,5-*d*]pyrimidine (**10**) prompted the study of the removal of the benzylidene protecting group, although attempts to hydrolyze analogous compounds either failed to yield the corresponding amino derivatives [3,10] or did not give clearcut results [11]. In our case, success was only achieved when the reaction was carried out with dilute hydrochloric acid in the presence of a molar equivalent of 2,4-dinitrophenylhydrazine (DNP). Indeed 3-amino-5-*t*-butyl-3*H*-*v*-triazolo[4,5-*d*]pyrimidine (**8**) was shown to be rather unstable towards acids.

Although somewhat longer than the alternative synthesis, the second route to compound **8** is much more satis-

Scheme



factory for two reasons: (a) *O*-mesitylsulfonylhydroxylamine (MSH), a moderately stable reagent, does not have to be prepared [6], (b) a mixture of isomers does not have to be separated.

Finally, we have verified that unprotected 5-amino-4-hydrazino-2-*t*-butylpyrimidine, on treatment with nitrous acid, could not afford substantial amounts of the precursor **8** [11,12]. Actually, the major product was the tetrazolo-[1,5-*c*]pyrimidine **13**, accompanied by a small amount of compound **8**. In connection with the azidoazomethine-tetrazole equilibrium [11,12,13], it is worth to mention that the large *t*-butyl group at position 2 did not preclude the tetrazole ring formation. The ir spectrum of the reaction product when taken in chloroform solution, showed the presence of strong absorptions in the tetrazole region (1000-1100 cm^{-1}) and weak aborption in the azido region (2100-2200 cm^{-1}) (see Experimental). The ^1H nmr spectrum indicated that the ratio of the 8-amino-5-*t*-butyltetrazolo[1,5-*c*]pyrimidine - 5-amino-4-azido-2-*t*-butylpyrimidine isomers amounted to 95:5.

We are currently investigating the products formed by oxidation of 3-amino-5-*t*-butyl-3*H*-*v*-triazolo[4,5-*d*]pyrimidine (**8**) in the presence of 1,3-dienes or other reagents.

EXPERIMENTAL

Melting points were obtained with a Reichert "Thermopan" microscope and are uncorrected. Spectra were recorded on the following instruments: either a Varian A-60 or a Bruker WM 250 for ^1H nmr (chemical shifts are quoted in ppm downfield from internal tetramethylsilane); Hitachi RMU 6D for ms; Perkin-Elmer 357 for ir. Microanalyses were performed by Continental Pharma, S. A., Mont-Saint-Guibert, Belgium.

2-*t*-Butyl-4(3*H*)-pyrimidinone (**1**).

Aqueous sodium hydroxide (120 ml of 5%) was added to an intimate mixture of 9.5 g (0.07 mole) of pivalamidine hydrochloride and 19.19 g (0.14 mole) of the crude sodium salt of ethyl formylacetate. The reaction mixture was stirred overnight at room temperature. The yellow solution was then acidified to *p*H 5 with concentrated hydrochloric acid. The solid that separated was filtered and washed with water. The filtrate was ex-

tracted with chloroform. The organic phase was evaporated under reduced pressure and the residue taken up in 20 ml of 10% aqueous sodium hydroxide. The insoluble material was removed by filtration and the filtrate acidified to *p*H 5. The precipitate that formed was filtered, washed with water and added to the first crop. After drying, the off-white product amounted to 9.12 g (86%), mp 150-151° (lit [14] 147-148°); ^{1}H nmr (deuteriochloroform): δ 1.42 (9H, s, -C(CH_3)$_3$), 6.32 (1H, d, J = 6.5 Hz, H_5) and 7.97 ppm (1H, d, J = 6.5 Hz, H_6); ms: M$^+$ at m/z 152.

5-Nitro-2-*t*-butyl-4(3*H*)-pyrimidinone (**2**).

One g (0.0066 mole) of 2-*t*-butyl-4(3*H*)-pyrimidinone (**1**), dissolved in a mixture of 2.16 g (0.021 mole) of potassium nitrate and 5 ml of concentrated sulfuric acid, was heated with stirring at 115° for 8 hours. The cold reaction mixture was poured into crushed ice. The aqueous solution (a precipitate was often formed) was extracted with chloroform. The organic phase was dried over magnesium sulfate. The solvent was removed to give 1.016 g to 1.192 g (78 to 92%) of the nitro derivative **2** as a yellow powder which might be recrystallized from ethanol-water 1:1 (15 ml per g), mp 209-211°; ^{1}H nmr (deuteriochloroform-hexadeuterodimethylsulfoxide): δ 1.40 (9H, s, -C(CH_3)$_3$) and 8.90 ppm (1H, s, H_6); ms: M$^+$ at m/z 197.

Anal. Calcd. for $C_8H_{11}N_3O_3$: C, 48.73; H, 5.62; N, 21.31. Found: C, 48.75; H, 5.43; N, 21.64.

4-Chloro-5-nitro-2-*t*-butylpyrimidine.

A mixture of 1 g (0.005 mole) of 5-nitro-2-*t*-butyl-4(3*H*)-pyrimidinone (**2**) and 7 ml of phosphorus oxychloride was refluxed for 3 hours, then held overnight at room temperature. The excess of phosphorus oxychloride was distilled under reduced pressure and the syrupy residue added with constant stirring to crushed ice overlayed with ether. As soon as all the ice had melted, the layers were separated. The aqueous phase was further extracted three times with ether. The combined ether layers were immediately dried over magnesium sulfate, and solid potassium carbonate was added with manual stirring to neutrality. After filtration, the chloro compound can be stored in solution over a small quantity of magnesium sulfate. Although the chloro compound was not normally isolated, evaporation of the ethereal solution gave a pale yellow oil which was not obtained crystalline after chromatography on silica gel (benzene as eluent); ^{1}H nmr (deuteriochloroform): δ 1.43 (9H, s, -C(CH_3)$_3$) and 9.15 ppm (1H, s, H_6); ms: M$^+$ at m/z 215 and 217 (3:1).

4-Amino-5-nitro-2-*t*-butylpyrimidine (**3**).

The ethereal solution of 4-chloro-5-nitro-2-*t*-butylpyrimidine (see above) was concentrated to *ca.* 10 ml and added with vigorous stirring to 23 ml of concentrated ammonia solution cooled in an ice bath. The reaction mixture was allowed to warm to room temperature and the layers were separated. The aqueous phase was further extracted with ether. The combined organic layers were dried over magnesium sulfate, filtered, and the filtrate evaporated to dryness under reduced pressure to give 0.9 g (91%) of crude **3**. The yellow solid was recrystallized from cyclohexane (25 ml per g), mp 130°; ^{1}H nmr (deuteriochloroform): δ 1.35 (9H, s, -C(CH_3)$_3$) and 9.18 ppm (1H, s, H_6); ms: M$^+$ at m/z 196.

Anal. Calcd. for $C_8H_{12}N_4O_2$: C, 48.97; H, 6.17; N, 28.56. Found: C, 49.22; H, 6.01; N, 28.21.

4,5-Diamino-2-*t*-butylpyrimidine (**4**).

A mixture of 0.5 g (0.0025 mole) of 4-amino-5-nitro-2-*t*-butylpyrimidine (**3**) in 20 ml of methanol and 0.15 g of 5% palladium on charcoal was shaken in an atmosphere of hydrogen at room temperature until 180 ml (0.0075 mole) of gas were taken up. The catalyst was removed and the reaction mixture was evaporated to dryness under reduced pressure to give 0.397 g (94%) of the crude diamino derivative **4**. The light yellow solid was recrystallized from benzene, mp 162-164° (lit [9] 163-164.5°); ^{1}H nmr (deuteriochloroform-hexadeuterodimethylsulfoxide): δ 1.30 (9H, s, -C(CH_3)$_3$), 3.97 (2H, broad signal, -NH_2), 5.65 (2H, broad signal, -NH_2) and 7.65 ppm (1H, s, H_6); ms: M$^+$ at m/z 166.

5-*t*-Butyl-3*H*-*v*-triazolo[4,5-*d*]pyrimidine (**5**).

To an ice-cooled stirred solution of 0.4 g (0.0024 mole) of 4,5-diamino-2-*t*-butylpyrimidine (**4**) in 5 ml of a 1:6 mixture of concentrated hydrochloric acid and water was added portionwise 0.207 g (0.003 mole) of sodium nitrite dissolved in 1 ml of water. After 1 hour at 0°, the solution was thoroughly extracted with ethyl acetate. The organic layer was dried over magnesium sulfate, filtered and evaporated to dryness under reduced pressure to give 0.39 g (92%) of crude **5**. The off-white solid was recrystallized from toluene (15 ml per g), mp 189-191°; ^{1}H nmr (deuteriochloroform): δ 1.63 (9H, s, -C(CH_3)$_3$) and 9.68 ppm (1H, s, H_7); ms: M$^+$ at m/z 177.

Anal. Calcd. for $C_8H_{11}N_5$: C, 54.22; H, 6.26; N, 39.52. Found: C, 54.32; H, 6.12; N, 39.22.

1-, 2- and 3-Amino-5-*t*-butyl-1*H*-, -2*H*- and -3*H*-*v*-triazolo[4,5-*d*]pyrimidines **6**, **7** and **8**.

5-*t*-Butyl-3*H*-*v*-triazolo[4,5-*d*]pyrimidine (**5**) was converted into its sodium or potassium salt either by addition of 0.265 g (0.0055 mole) of a 50% dispersion of sodium hydride to 0.885 g (0.005 mole) of **5** in 40 ml of dry ether or by addition of 10% alcoholic potassium hydroxide to the same quantity of **5** in 15 ml of ethanol containing bromothymol blue as indicator. In this case, the solvent was evaporated to dryness and the residue taken up in 20 ml of anhydrous ether. A suspension of 1.6 g (0.006 mole) of *O*-mesitylsulfonylhydroxylamine which was assumed to contain 20% of water [6] in 20 ml of dry ether was then added and the mixture was stirred overnight at room temperature. The copious solid that deposited was filtered and thoroughly washed with ether. The filtrate was dried over magnesium sulfate, treated with charcoal and evaporated under reduced pressure to yield a yellow oil. The components were separated by flash chromatography (silica gel 60). Elution with chloroform-ether 1:1 successively gave the following:

(a) 3-Amino-5-*t*-butyl-3*H*-*v*-triazolo[4,5-*d*]pyrimidine (**8**).

This compound was obtained in a yield of 26-50% (0.25-0.48 g), mp 90-97°; ^{1}H nmr: the chemical shifts were found to be almost identical to those of an authentic sample of **8** (see below); ms: M$^+$ at m/z 192.

3-Benzylideneamino-5-*t*-butyl-3*H*-*v*-triazolo[4,5-*d*]pyrimidine (**10**).

Compound **8** (0.007 g, 0.000036 mole) in 0.3 ml of methanol was treated with 0.006 ml (0.000054 mole) of freshly distilled benzaldehyde and 0.05 ml of acetic acid. The mixture was refluxed for 16 hours, then cooled to room temperature. Water was added and the off-white precipitate that deposited was collected. There was obtained 0.005 g (50%) of 3-benzylideneamino-5-*t*-butyl-3*H*-*v*-triazolo[4,5-*d*]pyrimidine (**10**), mp 114-115°, which was shown to be identical to an authentic sample of **10** (see below).

(b) 2-Amino-5-*t*-butyl-2*H*-*v*-triazolo[4,5-*d*]pyrimidine (**7**).

This compound was obtained in 5% yield (0.05 g); ^{1}H nmr (deuteriochloroform): δ 1.46 (9H, s, -C(CH_3)$_3$), 7.71 (2H, broad signal, -NH_2) and 9.36 ppm (1H, s, H_7). This compound was too unstable for elemental analysis.

(c) 1-Amino-5-*t*-butyl-1*H*-*v*-triazolo[4,5-*d*]pyrimidine (**6**).

This compound was obtained in 10 to 31% yield (0.1-0.3 g), mp 110-118°; ^{1}H nmr (deuteriochloroform): δ 1.43 (9H, s, -C(CH_3)$_3$), 6.50 (2H, broad signal, -NH_2) and 9.37 ppm (1H, s, H_7); ms: M$^+$ at m/z 192. This compound was too unstable for elemental analysis.

1-Benzylideneamino-5-*t*-butyl-1*H*-*v*-triazolo[4,5-*d*]pyrimidine (**9**).

Compound **6** (0.012 g, 0.000062 mole) in 1 ml of methanol was treated with 0.01 ml (0.000096 mole) of freshly distilled benzaldehyde and 0.15 ml of acetic acid. The mixture was refluxed for 3 days, then cooled to room temperature. The off-white crystals that appeared were collected. There was obtained 0.007 g (40%) of **9** which was recrystallized from a 8:2 methanol-water mixture, mp 180-181°; ^{1}H nmr (deuteriochloroform): δ 1.54 (9H, s, -C(CH_3)$_3$), 7.52 to 7.64 and 7.99 to 8.04 (3H and 2H, m, -C_6H_5), 9.48 (1H, s, -N=CH- or H_7) and 9.58 ppm (1H, s, H_7 or -N=CH-); ms: M$^+$ at m/z 280.

4-Hydrazino-5-nitro-2-*t*-butylpyrimidine (**11**).

The ethereal solution of 4-chloro-5-nitro-2-*t*-butylpyrimidine (see above) was concentrated to *ca.* 5 ml and added dropwise to a well-stirred mixture of 1.1 ml (0.023 mole) of hydrazine hydrate and 11 ml of anhydrous ether cooled in an ice bath. After stirring an additional 30 minutes the reaction mixture was centrifuged. The supernatant layer was separated and evaporated under reduced pressure leaving 0.924 g (86%) of an orange product which was immediately recrystallized from hexane (33 ml per g), mp 109-111°; ^{1}H nmr (deuteriochloroform): δ 1.39 (9H, s, -C(CH$_3$)$_3$), 4.43 (2H, broad signal, -NH$_2$), 9.07 (1H, broad signal, -NH-) and 9.14 ppm (1H, s, H$_6$); ms: M$^+$ at m/z 211.

Anal. Calcd. for $C_8H_{13}N_5O_2$: C, 45.49; H, 6.16; N, 33.17. Found: C, 45.35; H, 6.20; N, 33.16.

4-Benzylidenehydrazino-5-nitro-2-*t*-butylpyrimidine (**12**).

To a solution of 0.5 g (0.0023 mole) of the hydrazino compound **11** in 20 ml of methanol was added with vigorous stirring 0.24 ml (0.0023 mole) of freshly distilled benzaldehyde. A copious solid separated immediately. Evaporation of the solvent afforded 0.644 g (91%) of crude product which was recrystallized from hexane (240 ml per g) to give 4-benzylidenehydrazino-5-nitro-2-*t*-butylpyrimidine (**12**) as bright yellow fluffy needles, mp 192°; ^{1}H nmr (deuteriochloroform): δ 1.46 (9H, s, -C(CH$_3$)$_3$), 7.44 to 7.57 and 7.73 to 7.83 (3H and 2H, m, -C$_6$H$_5$), 8.20 (1H, s, -N=CH-), 9.26 (1H, s, H$_6$) and 11.09 ppm (1H, broad signal, -NH-); ms: M$^+$ at m/z 299.

Anal. Calcd. for $C_{15}H_{17}N_5O_2$: C, 59.77; H, 5.56; N, 23.44. Found: C, 60.20; H, 5.68; N, 23.41.

5-Benzylideneamino-4-benzylidenehydrazino-2-*t*-butylpyrimidine (**14**).

A mixture of 0.639 g (0.003 mole) of 4-hydrazino-5-nitro-2-*t*-butylpyrimidine (**11**) in 10 ml of methanol and 0.22 g of 5% palladium on charcoal was shaken in an atmosphere of hydrogen at room temperature until 216 ml (0.009 mole) of gas were taken up. The catalyst was removed and 0.92 ml (0.009 mole) of freshly distilled benzaldehyde was added to the filtrate which was then stirred at room temperature for 48 hours. Evaporation of the solvent under reduced pressure afforded a product which was recrystallized from a 2:8 ethanol-petroleum ether mixture. Yellow needles were obtained in low yield, mp 153-155°; ^{1}H nmr (deuteriochloroform): δ 1.46 (9H, s, -C(CH$_3$)$_3$), 7.37 to 7.95 (10H, m, two -C$_6$H$_5$), 8.14, 8.30, 8.58 (each 1H, each s, H$_6$ and two -N=CH-) and 8.97 ppm (1H, broad signal, -NH-); ms: M$^+$ at m/z 357.

Anal. Calcd. for $C_{22}H_{23}N_5$: C, 73.94; H, 6.44; N, 19.60. Found: C, 73.68; H, 6.53; N, 19.51.

3-Benzylideneamino-5-*t*-butyl-3*H*-*v*-triazolo[4,5-*d*]pyrimidine (**10**).

4-Hydrazino-5-nitro-2-*t*-butylpyrimidine (**11**) (0.617 g, 0.0029 mole) in 20 ml of methanol was hydrogenated as described above in the preparation of compound **14**. The reduction mixture was cooled to 0° and 0.3 ml (0.0029 mole) of freshly distilled benzaldehyde was added with stirring. After 2 hours, the reaction mixture was concentrated to half of its volume, diluted with 8.7 ml of 1 *M* hydrochloric acid and chilled to 0°. Sodium nitrite (0.222 g, 0.0032 mole) in a few ml of water was then added in one portion. A copious solid separated immediately. Stirring was continued for 30 minutes. The cream-colored solid was collected by filtration and dried to give 0.553 g (68%) of **10**. Recrystallization from a 8:2 methanol-water mixture (36 ml per g), with the aid of charcoal, yielded colorless needles, mp 115°; ^{1}H nmr (deuteriochloroform): δ 1.53 (9H, s, -C(CH$_3$)$_3$), 7.53 to 7.65 and 8.01 to 8.06 (3H and 2H, m, -C$_6$H$_5$), 9.52 (1H, s, -N=CH- or H$_7$) and 9.79 (1H, s, H$_7$ or -N=CH-); ms: M$^+$ at m/z 280.

Anal. Calcd. for $C_{15}H_{16}N_6$: C, 64.28; H, 5.71; N, 30.00. Found: C, 64.56; H, 5.83; N, 30.15.

3-Amino-5-*t*-butyl-3*H*-*v*-triazolo[4,5-*d*]pyrimidine (**8**).

A stirred suspension containing 0.05 g (0.00018 mole) of 3-benzylideneamino-5-*t*-butyl-3*H*-*v*-triazolo[4,5-*d*]pyrimidine (**10**) and 0.035 g (0.00018 mole) of 2,4-dinitrophenylhydrazine in a mixture of 3.6 ml of 0.1 *M* hydrochloric acid and 1 ml of ethanol was heated at 100° for 30 minutes. After cooling, the resulting solid was filtered. The filtrate was basified to *p*H 8 with concentrated ammonia solution and extracted with chloroform. The organic phase was dried over magnesium sulfate, thoroughly decolorized with charcoal and evaporated to dryness under reduced pressure to give 0.03 g (88%) of crude **8**. The off-white solid was recrystallized from petroleum ether, mp 113-115°; ^{1}H nmr (deuteriochloroform): δ 1.50 (9H, s, -C(CH$_3$)$_3$), 5.70 (2H, broad signal, -NH$_2$) and 9.46 ppm (1H, s, H$_7$); ms: M$^+$ at m/z 192.

Anal. Calcd. for $C_8H_{12}N_6$: C, 50.00; H, 6.25; N, 43.75. Found: C, 50.28; H, 6.40; N, 42.23.

8-Amino-5-*t*-butyltetrazolo[1,5-*c*]pyrimidine (**13**).

A mixture of 0.15 g (0.00071 mole) of 4-hydrazino-5-nitro-2-*t*-butylpyrimidine (**11**) in 20 ml of methanol and 0.05 g of 5% palladium on charcoal was shaken in an atmosphere of hydrogen at room temperature until 51 ml (0.00213 mole) of gas were taken up. The catalyst was then removed. The reduction mixture was concentrated to a few ml, diluted with 2.13 ml (0.00213 mole) of 1 *M* hydrochloric acid and chilled to 0°. Sodium nitrite (0.054 g, 0.00078 mole) was added in one portion. After 5 minutes, the reaction mixture was allowed to warm to room temperature, rendered alkaline with concentrated ammonia solution and extracted with chloroform. The organic phase was dried over magnesium sulfate, treated with charcoal and evaporated under reduced pressure to give a dark material. Two column chromatographies (silical gel) were needed to separate the components. Elution with chloroform-ether 1:1 successively gave (a) 0.007 g (5%) of 3-amino-5-*t*-butyl-3*H*-*v*-triazolo[4,5-*d*]pyrimidine (**8**) which was obtained as a colored oil, and (b) 0.072 g (51%) of 8-amino-5-*t*-butyltetrazolo[1,5-*c*]pyrimidine (**13**). Recrystallization of the latter from water gave white needles, mp 167-168°; ir (chloroform): 3495, 3398 (-NH$_2$), 2971 (aliphatic CH), 2135 (w, -N$_3$), 1610, 1557 (-NH$_2$, C=C, C=N), 1081, 1046, 993 (tetrazole ring) cm^{-1}; ^{1}H nmr (deuteriochloroform): tetrazole form, δ 1.62 (9H, s, -C(CH$_3$)$_3$), 4.70 (2H, broad signal, -NH$_2$) and 7.56 ppm (1H, s, H$_7$); azido form, δ 1.54 (9H, s, -C(CH$_3$)$_3$), 4.51 (2H, broad signal, -NH$_2$) and 7.95 ppm (1H, s, H$_6$); ms: M$^+$ at m/z 192.

Anal. Calcd. for $C_8H_{12}N_6$: C, 49.99; H, 6.29; N, 43.72. Found: C, 50.11; H, 6.30; N, 43.92.

Acknowledgement.

The authors wish to thank Mr. R. Polain and Mr. C. Moulard for running the spectra, and to thank the "Institut pour l'Encouragement de la Recherche Scientifique dans l'Industrie et l'Agriculture" for fellowships (to M. T. and D. C.).

REFERENCES AND NOTES

[1] C. D. Campbell and C. W. Rees, *J. Chem. Soc.* (C), 742 (1969).

[2] For recent reviews on hetaryne intermediates, see [a] M. G. Reinecke, *Tetrahedron*, **38**, 427 (1982); [b] H. C. van der Plas and F. Roeterdink, in "The Chemistry of Triple-bonded Functional Groups", Part 1, S. Patai and Z. Rappoport, eds, Wiley-Interscience, Chichester, 1983.

[3] G. W. J. Fleet and I. Fleming, *J. Chem. Soc.* (C), 1758 (1969).

[4] T. L. Gilchrist, G. E. Gymer and C. W. Rees, *J. Chem. Soc., Perkin Trans. I*, 1747 (1975).

[5] D. Christophe, R. Promel and (in part) M. Maeck, *Tetrahedron Letters*, 4435 (1978).

[6] Y. Tamura, J. Minamikawa and M. Ikeda, *Synthesis*, 1 (1977).

[7] F. Roeterdink and H. C. van der Plas, *Rec. Trav. Chim.*, **95**, 282 (1976).

[8] I. Wempen, H. U. Blank and J. J. Fox, *J. Heterocyclic Chem.*, **6**, 593 (1969).

[9] G. K. Helmkamp and N. S. Kondo, *Biochim. Biophys. Acta*, **157**, 242 (1968).

[10] E. C. Taylor, J. W. Barton and W. W. Paudler, *J. Org. Chem.*, **26**, 4961 (1961).

[11] C. Temple, Jr., R. L. McKee and J. A. Montgomery, *ibid.*, **27**, 1671 (1962).

[12] C. Temple, Jr., R. L. McKee and J. A. Montgomery, *ibid.*, **30**, 829 (1965).

[13] M. Tisler, *Synthesis*, 123 (1973).

[14] M. Calligaris, P. Linda and G. Marino, *Tetrahedron*, **23**, 813 (1967).