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Synthesis of 6-Substituted Pyrimidines by the Wittig Reaction. III (1,2). Via 2-Amino-4-hydroxy-5-phenylbutyl-6-pyrimidylmethyl Triphenyl Phosphonium Bromide

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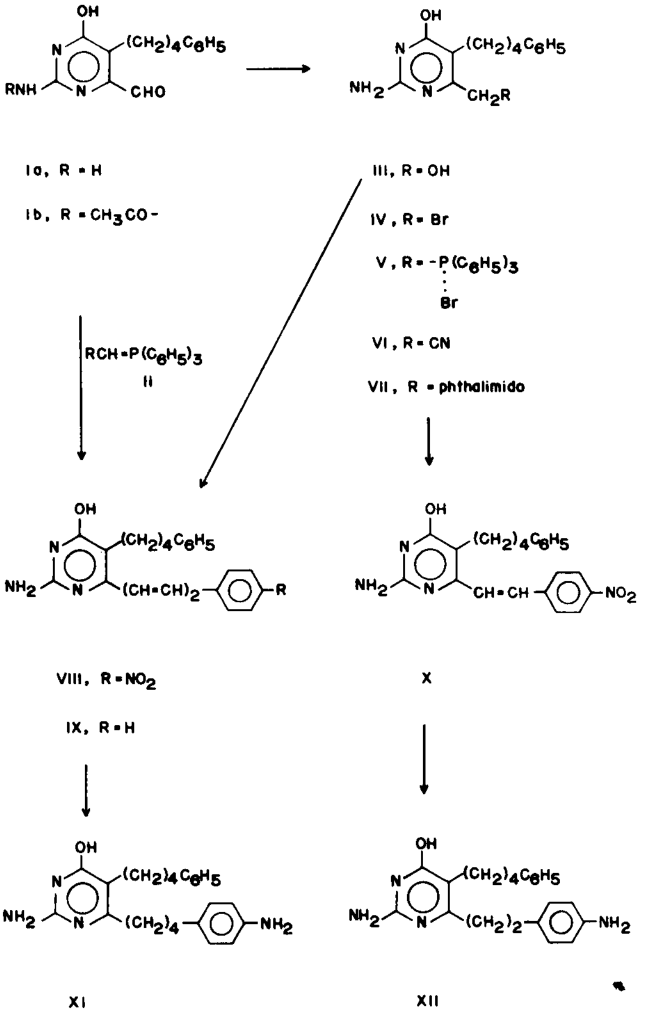
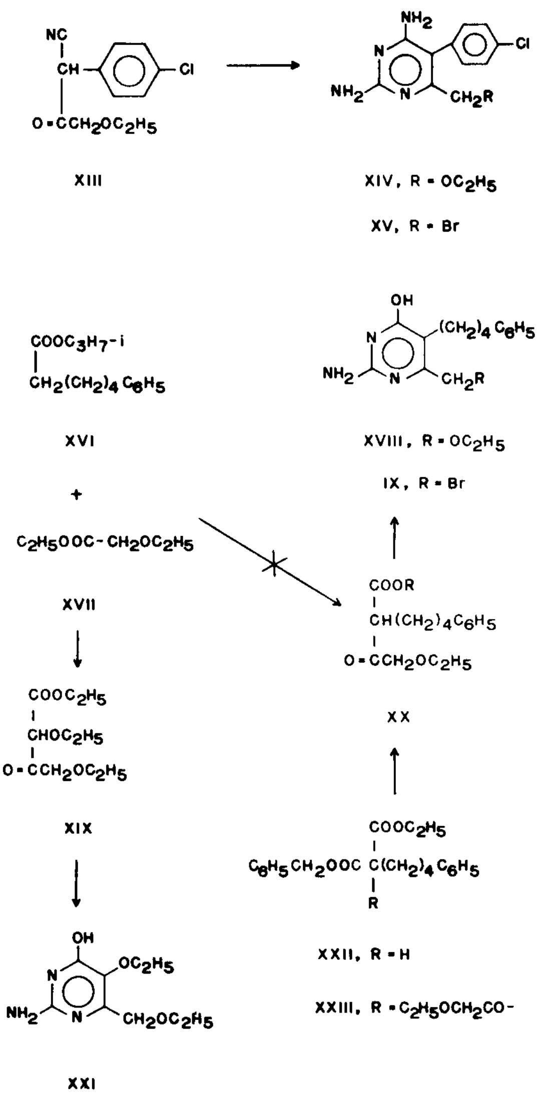
2-Amino-6-bromomethyl-5-phenylbutyl-4-pyrimidinol (IV) smoothly alkylated triphenyl phosphine, resulting in a 95% yield of the phosphonium salt (V). This Wittig reagent (V) readily condensed with *p*-nitrobenzaldehyde, *p*-nitrocinnamaldehyde, or cinnamaldehyde in *N,N*-dimethylformamide to give the 6-(*p*-nitrostyryl) (X), 6-(*p*-nitrophenyl-1,3-butadien-1-yl) (VIII), and 6-(phenyl-1,3-butadien-1-yl) (IX) pyrimidinols in 72, 67 and 44% yields, respectively. Catalytic reduction of VIII and IX afforded the corresponding 6-(*p*-aminophenylethyl) (XII) and 6-(*p*-aminophenylbutyl) (XI) 4-pyrimidinols.

In the preceding papers of this series were described the syntheses of some 2-amino-5-phenylbutyl-4-pyrimidinols with functionalized 6-substituents such as VIII and IX by condensation of 2-amino-4-hydroxy-5-phenylbutylpyrimidine-6-carboxaldehyde (Ia) (3a) or its N^2-acetyl derivative (Ib) (1b) with a variety of Wittig reagents (II) (4) bearing functionalized R groups (3). A possible alternate route to VIII, IX and X was condensation of a nitrophenyl aldehyde with a pyrimidyl Wittig reagent such as V. Since no Wittig reagent of type II, where R is a pyrimidine ring, could be found in the literature, it was of interest to see if a Wittig reagent with a functionalized pyrimidine such as V could be synthesized and - if so - would the reagent undergo normal condensation with an aldehyde. The synthesis of V and its bromomethyl precursor (IV), as well as some of the reactions of IV and V, are the subjects of this paper.

The hydrochloride of the pyrimidine-6-carboxaldehyde (Ia) (3a) was reduced catalytically to the 6-carbinol (III) in 80% yield using a palladium-charcoal catalyst. When III was refluxed in acetic acid containing 10% anhydrous hydrogen bromide, it was smoothly converted to the 6-bromomethylpyrimidine (IV) hydrobromide in 72% yield; with aqueous sodium bicarbonate, the hydrobromide of IV could be converted to the free base which was sufficiently pure for further reactions, and was stable enough to be fully purified.

The bromomethylpyrimidine (IV) reacted smoothly with triphenyl phosphine in a refluxing mixture of benzene and tetrahydrofuran to give a 95% yield of pure phosphonium salt (V). Since the infrared spectrum of V showed no $C{=}NH^+$ band near 5.9 μ





but did have a C-P$^+$ band at 9.04 μ, it was clear that the V had the structure indicated and was not a hydrobromide salt of a pyrimidyl-ylide which would show C=NH$^+$ absorption near 5.9 μ and no C-P$^+$ absorption at 9.04 μ; thus the ylide moiety is a stronger base than the pyrimidine moiety of V.

Condensation of the pyrimidyl phosphonium salt (V) with cinnamaldehyde in *N,N*-dimethylformamide in the presence of potassium *t*-butoxide gave a readily crystallizable product (IX) that was obtained pure in 44% yield and was identical with IX prepared from Ia. Similarly, *p*-nitrocinnamaldehyde and *p*-nitrobenzaldehyde condensed with V to give VIII and X in 67 and 72% yields, respectively; in the latter case sodium methoxide was used. Again, the more electrophilic was the aldehyde, the higher was the yield (1b,3a). Catalytic hydrogenation of VIII and X with a platinum oxide catalyst gave pure XI and XII in reasonalbe yields.

Of the three routes to 6-substituted pyrimidines with Wittig reagents the pyrimidylmethyl phosphonium salt (V) gave the highest yields, the 2-acetamidopyrimidinol-6-carboxaldehyde (Ib) gave the next highest yields (1b), and the 2-aminopyrimidinol-6-carboxaldehyde (Ia) gave the poorest yields (3a); this order is most probably related to the relative electronegativity of the aldehyde partner.

The bromomethylpyrimidinol (IV) could also be functionalized by more classical chemistry. Reaction of IV with sodium cyanide in *N,N*-dimethylformamide gave the 6-cyanomethyl pyrimidinol (VI) in 63% yield of analytically pure material; it is probable that the 6-side-chain of VI could be catalytically reduced to an aminoethyl group since such a reaction was successful with 2-amino-5-cyanoethyl 6-methyl-4-pyrimidinol (5). Similarly, the bromomethyl pyrimidinol (IV) reacted smoothly with potassium phthalimide in *N,N*-dimethylformamide to give the 6-phthalimidomethyl-4-pyrimidinol (VII) in 75% yield.

Prior to the successful synthesis of the 2-aminopyrimidinol-6-carboxaldehyde (Ia) (3), and its subsequent conversion to the bromomethyl pyrimidinol (IV), an alternate route to IV was investigated. Since 6-bromomethyl-5-(*p*-chlorophenyl)-2,4-diaminopyrimidine (XV) hydrobromide had been successfully synthesized via XIII and the ethoxymethyl pyrimidine, XIV (6), a similar route to IV via XVIII was investigated. In contrast to *p*-chlorophenylacetonitrile, which Claisen condensed smoothly with ethyl ethoxyacetate (XVII) to give the intermediate, XIII, a similar condensation with isopropyl 6-phenylhexanoate (XVI) (7) proceeded awry. Apparently the α-methylene group of ethyl ethoxyacetate (XVII) is far more reactive than the α-methylene group of the 6-phenylhexanoate (XVI); thus self-condensation of XVII to XIX took place and none of the desired mixed Claisen product (XX) was formed. Condensation of XIX with guanidine gave the unusual pyrimidine, XXI.

An alternate route to the β-keto ester, XX, was then investigated; this route started with ethyl benzyl malonate and proceeded through the monobenzyl ester, XXII, by acylation to XXIII with ethoxyacetyl chloride, then hydrogenolysis to the desired XX. Although the sequence appeared to be successful (8), it was fairly lengthy compared to the synthesis of IV via Ia; since the latter synthesis emerged about this time, the synthesis of XX was not pursued further.

EXPERIMENTAL

Melting points were taken in capillary tubes on a Mel temp block and those below 230° are corrected. Ultraviolet spectra were determined in 10% ethanol, unless otherwise indicated, with a Perkin-Elmer 202 recording spectrophotometer. Infrared spectra were determined in potassium bromide pellet with a Perkin-Elmer 137 B recording spectrophotometer. Thin layer chromatograms (TLC) were run on Brinkmann silica gel GF and spots were detected by visual examination under ultraviolet light.

2-Amino-6-hydroxymethyl-5-phenylbutyl-4-pyrimidinol (III) hydrochloride.

A solution of 4.0 g. (13 mmoles) of Ia hydrochloride (3a) in 100 ml. of 2-methoxyethanol and 100 ml. of ethanol was shaken with hydrogen * at 2-3 atmospheres in the presence of 0.2 g. of 5% palladium-charcoal for 6 hours when 1 mole-equivalent of hydrogen had been absorbed; during this time part of the product separated from solution. The mixture was warmed on a steam-bath to dissolve the product, 2 g. of Celite were added, and the mixture was filtered. The filtrate was spin-evaporated *in vacuo*. The crystalline residue was recrystallized from aqueous 2-methoxyethanol to give 3.2 g. (80%) of white plates, m.p. 254-255°; λ max (*p*H 1): 269 mμ (ε, 9,200); (*p*H 13): 286 mμ (ε, 8,200); λ max 2.99, 3.07, 3.15 (OH, NH); 5.94 (C=NH$^+$); 6.23, 6.48, 6.70 (NH, C=O, C=C, C=N); 9.56 (C-O-H); 13.34, 14.29 μ (C_6H_5).

Anal. Calcd. for $C_{15}H_{19}N_3O_2 \cdot HCl$: C, 58.2; H, 6.51; N, 13.6. Found: C, 57.9; H, 6.63; N, 13.6.

2-Amino-6-bromomethyl-5-phenylbutyl-4-pyrimidinol (IV).

A solution of 5.0 g. (16.3 mmoles) of III hydrochloride in 75 ml. of glacial acetic acid containing 10% anhydrous hydrogen bromide was refluxed for 12 hours, then cooled. The hydrobromide salt was collected on a filter, then washed successively with 20 ml. of acetic acid and 20 ml. of ether; yield, 4.9 g. (72%) of white crystals, m.p. 222-225°; λ max (*p*H 1): 278 mμ (ε, 8,800); (*p*H 7): 306 (ε, 8,000); (*p*H 13): 300 mμ (ε, 6,300); λ max 2.93, 3.00, 3.12, 3.21 (NH); 5.90 (C=NH$^+$); 6.27, 6.46, 6.76 (NH, C=O, C=N, C=C); 13.40, 14.32 μ (C_6H_5).

Anal. Calcd. for $C_{15}H_{18}BrN_3O \cdot HBr$: C, 43.2; H, 4.59; N, 10.1. Found: C, 43.3; H, 4.68; N, 10.3.

A solution of 3.9 g. of hydrobromide salt in 25 ml. of cold dimethyl sulfoxide was poured in a thin stream into 250 ml. of vigorously stirred saturated aqueous sodium bicarbonate. The free base of IV was collected on a filter, washed with water and dried *in vacuo*; yield, 3.0 g. (95%) of nearly white crystals, m.p. 134-136°, that were suitable for further transformations. An analytical sample was prepared by solution in tetrahydrofuran without heating, then addition of petroleum ether (b.p. 30-60°): white crystals, m.p. 134-135°; λ max 2.95, 3.00 (NH); 6.05-6.35 (broad), 6.72 (NH, C=O, C=N, C=C); 13.4-13.8 (broad), 14.41 μ (C_6H_5, C-Br).

Anal. Calcd. for $C_{15}H_{18}BrN_3O$: C, 53.6; H, 5.40; N, 12.5. Found: C, 53.2; H, 5.48; N, 12.3.

2-Amino-4-hydroxy-5-phenylbutyl-6-pyrimidylmethyl triphenyl phosphonium bromide (V).

A mixture of 2.0 g. (6 mmoles) of IV free base, 1.75 g. (6.6 mmoles) of triphenyl phosphine, 15 ml. of reagent tetrahydrofuran and 15 ml. of benzene was refluxed with magnetic stirring for 8 hours. The mixture was cooled, then the product was collected on a filter and washed successively with 20 ml. of benzene and 10 ml. of ether. Two recrystallizations by solution in 10 ml. of ethanol at 40° and addition of ether gave 3.4 g. (95%) of white crystals, m.p. 274-275°; λ max (10% MeOEtOH): 303 mμ (ε, 10,000); λ max 3.00, 3.14 (NH); 6.11, 6.18, 6.31, 6.72 (NH, C=C, C=N, C=O); 6.99, 8.87 (P-C); 9.04 (C-P$^+$); 13.42, 13.98, 14.50, 14.62 μ C_6H_5, P-C).

Anal. Calcd. for $C_{33}H_{33}BrN_3OP$: C, 66.2; H, 5.56; N, 7.02. Found: C, 66.0; H, 5.79; N, 7.25.

2-Amino-4-hydroxy-5-phenylbutylpyrimidine-6-acetonitrile (VI).

A mixture of 620 mg. (1.84 mmoles) of IV, 5 ml. of *N,N*-dimethylformamide, and 300 mg. (6 mmoles) of sodium cyanide was magnetically stirred at 100° for 2 hours. The cooled mixture was diluted with 50 ml. of cold water, then acidified to *p*H 5-6 with acetic acid. The product was collected on filter, washed with water, and dried. Recrystallization from aqueous ethanol with the aid of decolorizing carbon, followed by two more recrystallizations from aqueous ethanol gave 330 mg. (63%) of light yellow crystals, m.p. 184-185°; λ max (*p*H 1): 266 mμ (ε, 8,400); (*p*H 7): 295 mμ (ε, 9,900); (*p*H 13): 284 mμ (ε, 8,800); λ max 3.00, 3.10-3.23 (broad) (NH); 4.30, 4.43 (weak C≡N); 6.04, 6.13, 6.30, 6.73 (NH, C=O, C=N, C=C); 13.65, 14.42 μ (C_6H_5).

Anal. Calcd. for $C_{16}H_{18}N_4O$: C, 68.1; H, 6.43; N, 19.8. Found: C, 67.6; H, 6.17; N, 19.8.

2-Amino-5-phenylbutyl-6-phthalimidomethyl-4-pyrimidinol (VII).

A mixture of 336 mg. (1 mmole) of IV, 204 mg. (1.1 mmoles) of potassium phthalimide and 2.5 ml. of *N,N*-dimethylformamide was magnetically stirred at ambient temperature for 30 minutes, then heated on the steam bath for 15 minutes. Dilution with 20 ml. of cold water gave a white solid that was collected on a filter and washed with water. Recrystallization from aqueous ethanol gave 300 mg. (75%) of white crystals, which gradually decomposed over 200°; λ max (10% MeOEtOH), (*p*H 1): 271 mμ; (*p*H 7): 301 mμ; (*p*H 13): 288 mμ; λ max 2.90, 3.00, 3.10-3.30 (NH); 5.70, 5.86 (phthalyl C=O); 6.10, 6.18, 6.27, 6.60, 6.72 (NH, C=O, C=C, C=N); 13.5-14.0 (broad), 14.06, 14.40 μ (phenyl CH).

Anal. Calcd. for $C_{23}H_{22}N_4O_3$: C, 68.6; H, 5.51; N, 13.9. Found: C, 68.3; H, 5.91; N, 13.9.

2-Amino-6-(*p*-nitrophenyl-1,3-butadien-1-yl)-5-phenylbutyl-4-pyrimidinol (VIII).

To a magnetically stirred solution of 600 mg. (1 mmole) of V and 177 mg. (1 mmole) of *p*-nitrocinnamaldehyde in 10 ml. of *N,N*-dimethylformamide protected from moisture was added 224 mg. (2 mmoles) of potassium *t*-butoxide. After being stirred for 6 hours, the mixture was diluted with 40 ml. of water and acidified with 0.5 ml. of glacial acetic acid. The orange precipitate was collected on a filter and washed with water. The crude product was stirred with 25 ml. of cold 2 *N* aqueous sodium hydroxide. The insoluble gummy material remaining after decantation was dissolved in 10 ml. of 2-methoxyethanol. The warm solution was clarified with decolorizing carbon, then water was added to turbidity. The warm solution was acidified with 0.2 ml. of glacial acetic acid, then cooled. The product was again recrystallized from aqueous 2-methoxyethanol to give 280 mg. (67%) of yellow crystals that gradually decompose over 230°, but moved as a single spot on TLC in chloroform-ethanol (4:1). The compound had λ max (MeOEtOH), 377 (ε, 32,000); λ max (10% MeOEtOH, *p*H 13): 396 mμ (ε, 25,300); λ max 2.90-3.05, 3.10-3.30 (NH); 6.05, 6.13, 6.25, 6.30 (NH, C=O, C=N, C=C); 6.63, 7.51 (NO_2); 11.70 (*p*-C_6H_4); 13.44, 14.45 μ (C_6H_5).

Anal. Calcd. for $C_{24}H_{24}N_4O_3$: C, 69.2; H, 5.81; N, 13.4. Found: C, 69.0; H, 6.07; N, 13.2.

2-Amino-5-phenylbutyl-6-(*p*-nitrostyryl)-4-pyrimidinol (X).

To a magnetically stirred mixture of 2.09 g. (3.35 mmoles) of V, 20 ml. of *N,N*-dimethylformamide, and 0.505 g. (3.35 mmoles) of *p*-nitrobenzaldehyde protected from moisture was added 0.366 g. (6.70 mmoles) of sodium methoxide. After 6 hours at ambient temperature and 1 hour at 100°, the hot solution was diluted with water to turbidity, then cooled. The product was collected on a filter and washed with 10 ml. of methanol. Two recrystallizations from 2-methoxyethanol-water gave 0.950 g. (72%) of yellow crystals, m.p. 236-237°. This material was a 2-methoxyethanol solvate that moved as a single spot on TLC in chloroform-ethanol (5:1) and had λ max (*p*H 1): 351 mμ; (*p*H 7): 367 mμ; λ max 3.04, 3.25 (OH, NH); 5.93, 6.05, 6.12, 6.31 (NH, C=C, C=N, C=O); 6.65, 7.50 (NO_2); 11.93 (*p*-C_6H_4); 13.40, 14.50 μ (C_6H_5). Usual drying failed to remove completely the 2-methoxyethanol of crystallization.

Anal. Calcd. for $C_{22}H_{22}N_4O_3 \cdot {}^1/_4CH_3OCH_2CH_2OH$: C, 65.9; H, 5.85; N, 13.5. Found: C, 65.8; H, 5.99; N, 13.6.

After being dried at 100° for 2 days in high vacuum the solvent free compound was obtained.

Anal. Calcd. for $C_{22}H_{22}N_4O_3$: C, 67.7; H, 5.68; N, 14.4. Found: C, 67.5; H, 5.75; N, 14.1.

2-Amino-5-phenylbutyl-6-(4-phenyl-1,3-butadien-1-yl)-4-pyrimidinol (IX).

Reaction of 1.20 g. (2 mmoles) of V with 0.300 g. of cinnamaldehyde and 0.448 g. (4 mmoles) of potassium *t*-butoxide in 10 ml. of *N,N*-dimethylformamide for 16 hours at ambient temperature was performed as described for VIII. Acidification with 0.5 ml. of glacial acetic acid and dilution with 25 ml. of water gave a solid that was collected on a filter and washed with water. The solid was stirred with 25 ml. of 1 *N* aqueous sodium hydroxide for 1 hour at room temperature, then collected on a filter and washed with water. The solid was dissolved in hot 2-methoxyethanol. The hot solution was treated with 2 ml. of glacial acetic acid, then water was added to turbidity. After being cooled, the mixture was filtered. The product was recrystallized twice from 2-methoxyethanol-water to give 0.330 g. (44%) of light yellow crystals that slowly decomposed over 200°, but moved as a single spot on TLC in 5:1 chloroform-methanol.

This compound was identical with the product obtained by condensation of Ia with cinnamyl triphenyl phosphonium chloride (3a) as shown by infrared and ultraviolet spectra and by co-movement on TLC in 4:1 chloroform-ethanol.

2-Amino-6-(*p*-aminophenylbutyl)-5-phenylbutyl-4-pyrimidinol (XI).

A solution of 1.75 g. (4.2 mmoles) of VIII in 200 ml. of 2-methoxyethanol was shaken with hydrogen at 2-3 atmospheres in the presence of 200 mg. of platinum oxide catalyst until 5 mole-equivalents of hydrogen were absorbed. The mixture was filtered through a Celite pad, then spin-evaporated *in vacuo*. Three recrystallizations from aqueous ethanol - the first with the aid of decolorizing carbon - gave 0.80 g. (53%) of nearly white crystals, m.p. 103-105°; λ max (*p*H 1): 268 mμ (ε, 9,300); (*p*H 13): 282 mμ (ε, 9,300); λ max 2.90 (H_2O); 3.00, 3.28 (NH); 5.90, 6.08, 6.13, 6.23, 6.67, 6.72 (NH, C=O, C=C, C=N); 12.30 (p-C_6H_4); 13.50, 14.40 μ (C_6H_5). The compound moved as a single spot on TLC in 4:1 chloroform-ethanol.

Anal. Calcd. for $C_{24}H_{30}N_4O \cdot {}^1/_2H_2O$: C, 72.2; H, 7.80; N, 14.0. Found: C, 72.4, 72.5; H, 7.51, 7.85; N, 13.9, 13.6.

2-Amino-6-(p-aminophenethyl)-5-phenylbutyl-4-pyrimidinol (XII).

Hydrogenation of 613 mg. (1.57 mmoles) of X as described for the preparation of XI did not go to completion until a second amount of fresh catalyst was added. Crystallization from aqueous ethanol and two recrystallizations from ethanol gave 260 mg. (46%) of pure product as white needles, m.p. 65-66° (turbid); λ max (pH 1): 268 mμ; (pH 13): 236, 283 mμ; λ max 2.99, 3.25 (NH); 6.10 (broad), 6.66 (NH, C=C, C=N, C=O); 12.25 (p-C_6H_4); 13.60, 14.36 μ (C_6H_5).

Anal. Calcd. for $C_{22}H_{26}N_4O$: C, 72.9; H, 7.23; N, 15.5. Found: C, 73.1; H, 7.36; N, 15.1.

Claisen Condensation of Ethyl Ethoxyacetate and Isopropyl 6-Phenylhexanoate (XVI): Ethyl 2,4-Diethoxy-3-keto-butyrate (XIX).

To a stirred mixture of 5.28 g. (40 mmoles) of ethyl ethoxyacetate and 4.68 g. (20 mmoles) of isopropyl 6-phenylhexanoate (7) protected from moisture was added 1.72 g. (40 mmoles) of a 55.6% dispersion of sodium hydride in mineral oil over a period of 15 minutes. The mixture was stirred at ambient temperature for 4 hours, while excessive foaming was controlled by intermittent cooling in an ice-bath. The mixture was poured into 100 ml. ice-water, rapidly extracted with three 25-ml. portions of ether, then 50 g. of ice was added to the aqueous phase. The pH of the mixture was adjusted to 5 with 1 N ice-cold hydrochloric acid and extracted with four 25-ml. portions of ether. The combined extracts were washed with water, dried over magnesium sulfate, then evaporated *in vacuo*; yield, 2.6 g. of an oil; λ max (1% NaOEt in ethanol): 288 mμ. The crude keto-ester (XIX) was used without purification.

2-Amino-6-ethoxymethyl-5-ethoxy-4-pyrimidinol (XXI).

A mixture of 2.6 g. crude XIX (about 12 mmoles), 1.2 g. (6.7 mmoles) of guanidine carbonate and 10 ml. t-butyl alcohol was refluxed gently with magnetic stirring for 18 hours. The mixture was cooled to room temperature and the supernatant brown liquid decanted from a crystalline precipitate. The residue was suspended in 10 ml. t-butyl alcohol, collected on a filter and washed with 10 ml. cold methanol. The product was recrystallized from methanol; yield 1.23 g. (48%), m.p. 224-225°, λ max (pH 1): 271 mμ; (pH 7): 288 mμ; (pH 13): 287 mμ; λ max 2.97, 3.20 (NH), 6.04, 6.42, 6.70 (NH, C=O, C=C, C=N); 8.09, 8.68, 9.01, 9.65 μ (ether C-O-C).

Anal. Calcd. for $C_9H_{15}N_3O_3$: C, 50.7; H, 7.09; N, 19.7. Found: C, 50.7; H, 7.32; N, 19.8.

The product showed one spot on TLC in benzene-methanol (1:4). TLC of the decanted supernatant liquid showed a spot corresponding with the product as well as a major spot on the solvent front; this fraction was not investigated further.

REFERENCES

(1a) Paper number XXXVIII in the series on Analogs of Tetrahydrofolic Acid; (b) for the previous paper of this series see B. R. Baker and J. H. Jordaan, *J. Heterocyclic Chem.*, 3, 319 (1966).

(2) This work was supported in part by grants CA-05867, CA-06624, and CA-08695 from the National Cancer Institute, U. S. Public Health Service; J.H.J. is indebted to the Republic of South Africa Atomic Energy Board for a fellowship.

(3) For the use of such compounds as inhibitors of dihydrofolic reductase see (a) the references in B. R. Baker and J. H. Jordaan, *J. Heterocyclic Chem.*, 3, 315 (1966); (b) B. R. Baker, "Design of Active-Site-Directed Irreversible Enzyme Inhibitors. The Organic Chemistry of the Enzymic Active-Site," John Wiley and Sons, New York, N. Y., in press.

(4) For recent reviews on the Wittig reaction see (a) A. Maercker in "Organic Reactions", A. C. Cope, Ed., John Wiley and Sons, New York, N. Y., 1965, Vol. 14, pp. 270-490; (b) H. J. Bestman, *Angew. Chem. Intern. Ed. Engl.*, 4, 583, 646 (1965).

(5) B. R. Baker and J. K. Coward, *J. Pharm. Sci.*, 54, 714 (1965).

(6) B. R. Baker and J. H. Jordaan, *J. Heterocyclic Chem.*, 2, 21 (1965).

(7) B. R. Baker and J. H. Jordaan, *ibid.*, 2, 162 (1965).

(8) Benzyl ethyl malonate has been successfully used for preparation of α-substituted--β--keto esters (9); the use of dibenzyl malonate for preparation of ketones (9,10) is also pertinent to the projected synthesis of XX.

(9) B. R. Baker, R. E. Schaub, M. V. Querry, and J. H. Williams, *J. Org. Chem.*, 17, 77 (1952).

(10) D. E. Ames, R. E. Bowman, R. G. Mason, *J. Chem. Soc.*, 174 (1950).

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