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Reactions of Cyclic-enaminoketones with Diacylethylenes. Regioselective Synthesis of 4-Oxotetrahydroindole, 5-Oxotetrahydroquinoline, Pyrrolo- and Pyrido[2,3-*d*]pyrimidines

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A study has been made of the reaction of 3-aminocyclohex-2-enones and 6-amino-1,3-dimethyluracil with diacylethylene. By the selection of reaction conditions either 4-oxotetrahydroindole or 5-oxotetrahydroquinoline derivatives from 3-aminocyclohex-2-enones and either pyrrolo- or pyrido [2,3-*d*] pyrimidine derivatives from 6-amino-1,3-dimethyluracil were obtained in fairly high yields, respectively.

The Nenitzescu synthesis using *p*-benzoquinone and enaminoketone is commonly known as a useful preparation of a variety of 5-hydroxyindole derivatives.[2] Recently we have reported[3,4] the reaction of 3-aminocyclohex-2-enones (Ia—c) or 6-amino-1,3-dimethyluracil (VII) with dibenzoylethylene (DBE) in which the choice of experimental conditions can exert an important influence on the course of the reaction. Enaminoketones (Ia—c) or VII react with DBE under acidic condition to furnish 4-oxotetrahydroindoles (IIIa—c) or pyrrolo[2,3-*d*]-pyrimidine-2,4-diones (VIII), but under dehydrogenation condition 5-oxotetrahydroquinolines (IVa—c) or pyrido[2,3-*d*]pyrimidine-2,4-diones (IX). Similarly the reaction of VII with diacetylethylene gives X under acidic condition, but XI under dehydrogenation condition. The present paper describes the reactions of cyclic enaminoketones with diacylethylenes, involving a full account of the previous brief communications.[3,4]

Treatment of 3-aminocyclohex-2-enone (Ia) with DBE in ethanol under reflux for 4 hr gave a 65% yield of 5-oxohexahydroquinoline (IIa),[5] whose structure was supported by its analytical and spectral data [IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3450, 1680, and 1610; NMR ($CDCl_3$) δ: 6.48 (1H, bs, exchanged with D_2O, NH), 5.31 (1H, d, J=5 Hz, CHCOPh), 5.09 (1H, dd, J=5 and 1.5 Hz, –CH=C), 7.70 (2H, s, CH_2), 7.84 (2H, s, CH_2), 8.82 (3H, s, CH_3), and 8.91 (3H, s, CH_3); UV λ_{max}^{EtOH} nm (log ε): 251 (4.37) and 330 (3.80); Mass Spectrum m/e: 357 (M^+), 355 ($M-H_2$), and 252 (base peak, M–COPh)].

Compound (IIa) was converted to 4-oxotetrahydroindole (IIIa) by refluxing in acetic acid for 2 hr while by refluxing in xylene in the presence of palladium-carbon to 5-oxotetrahydroquinoline (IVa). These reactions are well interpreted as follows; DBE initially attacks on C_2-carbon of I to give the Michael adduct (V),[6–9] which cyclizes into IIa in ethanol or xylene

1) Location: *133-1, Yamada-kami, Suita, Osaka.*
2) G.R. Aleen, Jr, *Org. Reactions*, **20**, 337 (1973) and references therein.
3) Y. Tamura, T. Sakaguchi, T. Kawasaki and Y. Kita, *Heterocycles*, **2**, 645 (1974).
4) Y. Tamura, T. Sakaguchi, T. Kawasaki and Y. Kita, *Heterocycles*, **3**, 183 (1975).
5) Compound (IIa) is considerably unstable in chloroform solution and gives many products even in being kept at room temperature for several hours.
6) F. Bohlmann and R.M. Mader, *Tetrahedron Letters*, **1965**, 171; F. Zymalkowsky and J. Rimek, *Naturwisenschaft*, **47**, 83 (1960); F. Zymalkowsky and M. Kothari, *Arch. Pharm.*, **1970**, 1423.
7) Y. Junek and Y. Aigner, *Z. Naturforsch*, **B**, 1970, 1423.
8) N.A.T. Sluyter, U.K. Pandit, W.N. Speckamp and H.O. Huisman, *Tetrahedron Letters*, **1966**, 87; G.K. Petitt, L.E. Haenghton and K.D. Paull, *J. Org. Chem.*, **33**, 1089 (1968); M.A.T. Sluyter, W.N. Speckamp and H.O. Huisman, *Rec. Trav. Chim. Pays-Bas*, **91**, 157 (1972).
9) C. Ruangeiyanand, *Ber.*, **103**, 2403 (1970).

solution. In acetic acid, IIa is interconvertible with V and is readily converted to IIIa through intermediates (V) and (VI).

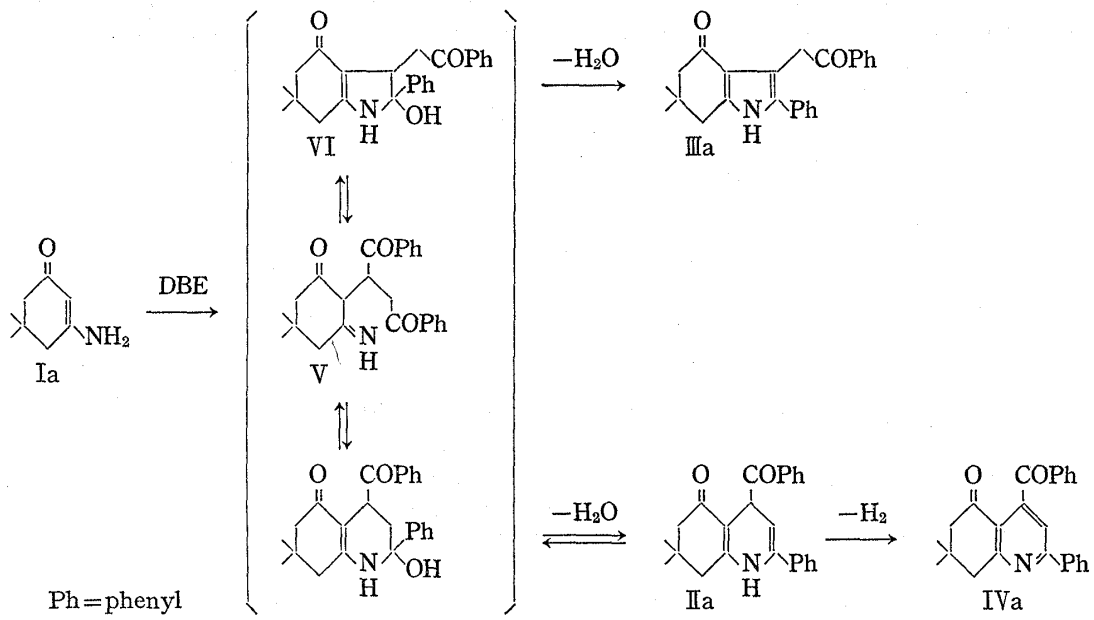
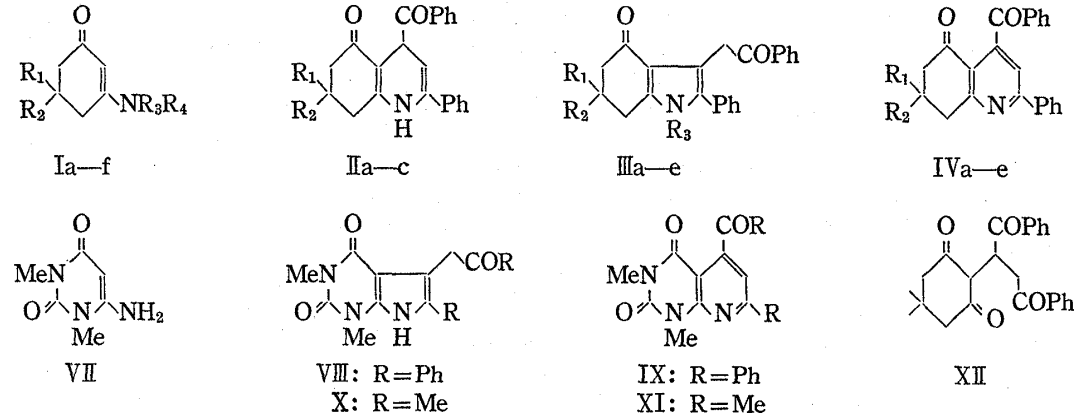


Fig. 1

For preparative purpose, following conditions were found to give better yields of IIIa and IVa. Treatment of Ia with DBE in boiling acetic acid gave a 47% yield of IIIa, and in boiling pyridine solution under oxygen bubbling a 41% yield of IVa. In the latter reaction, various dehydrogenation conditions using 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ), iodine, oxygen and palladium-carbon in polar and nonpolar solvents were cheked and the above condition was proved to give the best result. On treatment with DBE, compounds (Ib, c) similarly gave the corresponding 4-oxotetrahydroindoles (IIIb, c) and 5-oxotetrahydroquinoline derivatives (IVb, c), while 3-(monosubstituted)-aminocyclohex-2-enones (Id, e) led onesidedly to the N-substitutedtetrahydroindoles (IIId, e) and 3-(disubstituted)amino compound (If) afforded the cyclohexane-1,3-dione (XII).



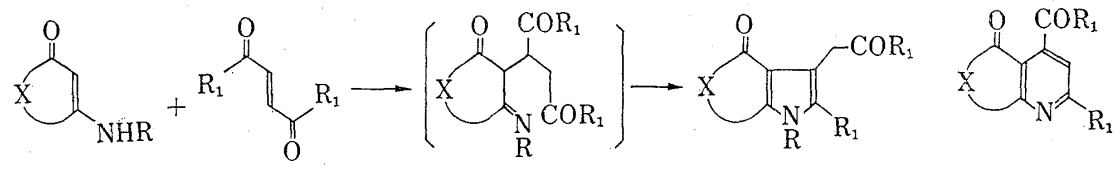
a : $R_1=R_2=Me$, $R_3=R_4=H$
b : $R_1=Me$, $R_2=R_3=R_4=H$
c : $R_1=R_2=R_3=R_4=H$
d : $R_1=R_2=R_3=Me$, $R_4=H$
e : $R_1=R_2=Me$, $R_3=CH_2Ph$, $R_4=H$
f : $R_1=R_2=R_3=R_4=Me$

Fig. 2

This regioselective and preparative synthesis for IIIa and IVa could be applied to the preparation of pyrrolo- and pyrido[2,3-*d*]pyrimidines, (VIII) and (IX). Treatment of 6-amino-1,3-dimethyluracil (VII) with DBE in acetic acid under reflux for 5 hr gave a 45% yield of

VIII, and in pyridine under oxygen bubbling gave a 48% yield of IX. Compound (VII) was also reacted with diacetylethylene to give an appreciated yield of the expected X and XI, respectively. But the reaction of VII with diformylethylene failed to give a detectable amount of the pyrimidines because of its extreme air and thermal sensitivity.

TABLE I.



Ia—e
VII

IIIa—e
VIII
X

IVa—c
IX
XI

Compd.	R	X	R_1	Reaction conditions	Compd.	Yield (%)	Compd.	Yield (%)
Ia	H	$-CH_2C(Me)_2CH_2-$	C_6H_5	$MeCO_2H$, reflux 3h	IIIa	47		
				C_5H_5N, O_2, reflux 4h			IVa	41
Ib	H	$-CH_2CH(Me)CH_2-$	C_6H_5	$MeCO_2H$, reflux 5h	IIIb	77		
				C_5H_5N, O_2, reflux 4h			IVb	39
Ic	H	$-(CH_2)_3-$	C_6H_5	$MeCO_2H$, reflux 4h	IIIc	24		
				C_5H_5N, O_2, reflux 4h			IVc	39
Id	CH_3	$-CH_2C(Me)_2CH_2-$	C_6H_5	$MeCO_2H$, reflux 4h	IIId	86		
Ie	CH_2Ph	$-CH_2(Me)_2CH_2-$	C_6H_5	$MeCO_2H$, reflux 4h	IIIe	93		
VII	H	-N(Me)CON(Me)-	C_6H_5	$MeCO_2H$, reflux 6h	VIII	45		
				C_5H_5N, O_2, reflux 5h			IX	48
	H	-N(Me)CON(Me)-	CH_3	$MeCO_2H$, reflux 5h	X	48		
				C_5H_5N, O_2, reflux 3h			XI	37

Experimental[10]

Starting Materials——3-Amino and 3-(substituted)aminocyclohex-2-enones (Ia—f) were prepared from cyclohexane-1,3-diones by the reported method.[11]

4-Benzoyl-1,4,5,6,7,8-hexahydro-7,7-dimethyl-5-oxo-2-phenylquinoline (IIa)——A suspension of the enaminoketone (Ia) (139 mg) and DBE (280 mg) in ethanol (6 ml) was refluxed for 4 hr. Evaporation *in vacuo* followed by preparative thin-layer chromatography(TLC) (alumina-chloroform) gave the hexahydroquinoline (IIa) (232 mg; 65%). Recrystallization from iso-propanol gave pale yellow crystals, mp 178—182°. *Anal.* Calcd. for $C_{24}H_{23}O_2N$: C, 80.64; H, 6.49; N, 3.92. Found: C, 80.31; H, 6.55; N, 3.84.

4-Benzoyl-1,4,5,6,7,8-hexahydro-5-oxo-2-phenylquinoline (IIc)——A suspension of the enaminoketone (Ic) (125 mg) and DBE (236 mg) in ethanol (4 ml) was refluxed for 4 hr. Work-up as described for (IIa) gave the hexahydroquinoline (IIc) (237 mg; 78%). Recrystallization from iso-propanol gave colorless crystals, mp 193.5—195°. *Anal.* Calcd. for $C_{22}H_{19}O_2N$: C, 80.22; H, 5.81; N, 4.25. Found: C, 80.07; H, 5.80; N, 4.25. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3430, 1680 and 1640; NMR ($CDCl_3$) δ:8.2—7.9 (2H, m, ArH), 7.6—7.2 (8H, m, ArH), 6.5 (1H, bs, NH, disappeared on addition of D_2O), 5.35 (1H, d, J=5 Hz, -CH-CO), 5.08 (1H dd, J=5 and 1.5 Hz, CH=), and 2.7—1.7 (6H, m, $CH_2\times3$); UV λ_{max}^{EtOH} (log ε) nm: 244 (4.32) and 309 (4.17); Mass Spectrum *m/e*: 329 (M^+), 327 ($M-H_2$), and 224 (base peak, M-COPh).

3-Benzoylmethyl-4,5,6,7-tetrahydro-6,6-dimethyl-4-oxo-2-phenylindole (IIIa)——(a) A suspension of the enaminoketone (Ia) (139 mg) and DBE (260 mg) in acetic acid (5 ml) was refluxed for 3 hr. Evaporation *in vacuo* followed by preparative TLC [alumina-chloroform] gave the indole (IIIa) (168 mg; 47%) as pale yellow crystals. Recrystallization from ethanol-water gave colorless crystals, mp 200—203° (decomp). *Anal.* Calcd. for $C_{24}H_{23}O_2N$: C, 80.64; H, 6.49; N, 3.92. Found: C, 80.52; H, 6.53; N, 3.86. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1680 and 1640

10) Infrared(IR) spectra were recorded with a Hitachi-G2 spectrometer, ultraviolet(UV) spectra with a Hitachi-124 spectrophotometer, and nuclear magnetic resonance(NMR) spectra with a Hitachi-R 20 A spectrometer (internal standard tetramethylsilane, solvent $CDCl_3$). Mass spectra were obtained with a Hitachi-RMU-6D instrument at 70 eV.

11) Y. Tamura, J. Uraoka, S. Fukumori and Y. Kita, *Chem. Pharm. Bull.* (Tokyo), **21**, 1372 (1973) and references therein.

(characteristic 4-oxo-5,6,7,8-tetrahydroindole band);[12] NMR ($CDCl_3$) δ: 9.05 (1H, bs, exch. with D_2O, NH), 8.2—7.2 (10 H, m, ArH), 4.53 (2H, s, C-CH_2CO), 2.52 (2H, s, CH_2), 2.17 (2H, s, CH_2), and 1.06 (6H, s, $CH_3\times2$); UV λ_{max}^{EtOH} nm (log ε): 273 (4.18); Mass Spectrum *m/e*: 357 (M^+) and 252 (base peak, M−COPh).

(*b*) A suspension of (Ia) (139 mg) and DBE (260 mg) in ethanol (5 ml) was refluxed for 2 days. Work-up as described in (a) gave the indole (IIIa) (143 mg; 40%).

(*c*) A solution of the 5-oxohexahydroquinoline (IIa) (20 mg) in acetic acid was refluxed for 2 hr. Evaporation *in vacuo* followed by preparative TLC [alumina-chloroform] gave the indole (IIIa) (12 mg; 63%).

3-Benzoylmethyl-4,5,6,7-tetrahydro-6-methyl-4-oxo-2-phenylindole (IIIb)——A suspension of the enaminoketone (Ib) (125 mg) and DBE (260 mg) in acetic acid (5 ml) was refluxed for 5 hr. Work-up as described for (IIIa) gave the indole (IIIb) (264 mg; 77%). Recrystallization from benzene gave colorless crystals, mp 189—191°. *Anal.* Calcd. for $C_{23}H_{21}O_2N$: C, 80.44; H, 6.16; N, 4.08. Found: C, 80.37; H, 6.04; N, 4.14. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3440, 1680 and 1640; NMR ($CDCl_3$) δ: 9.20 (1 H, bs, NH), 8.2—7.9 (2 H, m, ArH), 7.7—6.9 (8H, m, ArH), 4.54 (2H, s, =C-CH_2CO), 2.7—2.0 (5H, m, $CH_2\times2$ and -CH), and 1.2—0.8 (3H, m, CH_3); UV λ_{max}^{EtOH} nm (log ε): 243 (4.36) and 273 (4.05); Mass Spectrum *m/e*: 343 (M^+), and 238 (base peak, M−COPh).

3-Benzoylmethyl-4,5,6,7-tetrahydro-4-oxo-2-phenylindole (IIIc)——A suspension of the enaminoketone (Ic) (168 mg) and DBE (390 mg) in acetic acid (5 ml) was refluxed for 4 hr. Work-up as described for (IIIa) gave the indole (IIIc) (120 mg; 24%). Recrystallization from acetone–cyclohexane gave pale brown crystals, mp 188—190°. *Anal.* Calcd. for $C_{22}H_{19}O_2N$: C, 80.22; H, 5.81; N, 4.25. Found: C, 79.75; H, 5.75; N, 4.15. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3430, 1690 and 1650; NMR ($CDCl_3$) δ: 8.75 (1H, bs, NH), 8.2—7.9 (2H, m, ArH), 7.7—7.1 (8H, m, ArH), 4.53 (2H, s, =C-CH_2CO), and 2.8—1.6 (6H, m, $CH_2\times3$); UV λ_{max}^{EtOH} nm (log ε): 243 (4.30) and 273 (3.99); Mass Spectrum *m/e*=329 (M^+), and 224 (base peak, M−COPh).

3-Benzoylmethyl-4,5,6,7-tetrahydro-1,6,6-trimethyl-4-oxo-2-phenylindole (IIId)——A suspension of the enaminoketone (Id) (153 mg) and DBE (260 mg) in acetic acid (4 ml) was refluxed for 4 hr. Work-up as described for (IIIa) gave the indole (IIId) (319 mg; 86%). Recrystallization from iso-propanol gave colorless crystals, mp 158.5—159.5°. *Anal.* Calcd. for $C_{25}H_{25}O_2N$: C, 80.83; H, 6.78; N, 3.77. Found: C, 80.36; H, 7.01; N, 3.61. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1685 and 1640; NMR ($CDCl_3$) δ: 8.1—7.85 (2H, m, ArH), 7.6—7.1 (8H, m, ArH), 4.32 (2H, s, =C-CH_2CO), 3.38 (3H, s, NCH_3), 2.67 (2H, s, CH_2), 2.33 (2H, s, CH_2), and 1.20 (6H, s, $CH_3\times2$); UV λ_{max}^{EtOH} nm (log ε): 244 (4.32) and 275 (3.95); Mass Spectrum *m/e*: 371(M^+), and 266 (base peak, M−COPh).

3-Benzoylmethyl-1-benzyl-4,5,6,7-tetrahydro-6,6-dimethyl-4-oxo-2-phenylindole (IIIe)——A suspension of the enaminoketone (Ie) (115 mg) and DBE (130 mg) in acetic acid (4 ml) was refluxed for 4 hr. Work-up as described for (IIIa) gave the indole (IIIe) (208 mg; 93%). Recrystallization from iso-propanol gave colorless crystals, mp 179—180.5°. *Anal.* Calcd. for $C_{31}H_{29}O_2N$: C, 83.19; H, 6.53; N, 3.13. Found: C, 82.92; H, 6.65; N, 3.07. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1685 and 1640; NMR ($CDCl_3$) δ: 8.2—7.9 (2H, m, ArH), 7.6—7.2 (13H, m, ArH), 4.95 (2H, s, CH_2Ph), 4.34 (2H, s, =C-CH_2CO), 2.48 (2H, s, CH_2), 2.30 (2H, s, CH_2), and 1.06 (6H, s, $CH_3\times2$); UV λ_{max}^{EtOH} nm (log ε): 243 (4.46) and 273 (4.06); Mass Spectrum *m/e*: 447 (M^+), 342 (M−COPh), and 91 ($C_6H_5CH_2^+$).

4-Benzoyl-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-2-phenylquinoline (IVa)——(a) A suspension of the enaminoketone (Ia) (46 mg), DBE (86 mg) in pyridine (5 ml) was refluxed for 4 hr under oxygen bubbling. Evaporation *in vacuo* followed by preparative TLC (alumina–benzene:pet-ether=1:1) gave the quinoline (IVa) (48 mg; 41%). Recrystallization from iso-propanol gave colorless crystals, mp 199—200°. *Anal.* Calcd. for $C_{24}H_{21}O_2N$: C, 81.10; H, 5.96; N, 3.94. Found: C, 81.02; H, 6.19; N, 4.15. Mass Spectrum *m/e*: 355 (M^+).

(b) A suspension of the hexahydroquinoline (IIa) (100 mg) and 5% Pd-C (60 mg) in xylene (5 ml) was refluxed for 5 hr. After removal of Pd-C by filtration, the solution was worked-up as described above to give the quinoline (IVa) (83 mg; 84%).

4-Benzoyl-5,6,7,8-tetrahydro-7-methyl-5-oxo-2-phenylquinoline (IVb)——A suspension of the enaminoketone (Ib) (42 mg), DBE (87 mg) in pyridine (5 ml) was refluxed for 4 hr under oxygen bubbling. Work-up as described for (IVa) gave the quinoline (IVb) (45 mg; 39%). Recrystallization from iso-propanol gave pale yellow crystals, mp 224—226°. *Anal.* Calcd. for $C_{23}H_{19}O_2N$: C, 80.91; H, 5.61; N, 4.10. Found: C, 80.47; H, 5.87; N, 4.22. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1680; NMR ($CDCl_3$) δ: 8.2—7.3 (11H, m, ArH), 2.8—2.1 (5H, m, $CH_2\times2$ and -CH), and 2.3—2.1 (3H, m, CH_3); UV λ_{max}^{EtOH} nm (log ε): 232 (4.16), 251 (4.21), 270 (4.10) and 313 (4.32); Mass Spectrum *m/e*: 341 (M^+).

4-Benzoyl-5,6,7,8-tetrahydro-5-oxo-2-phenylquinoline (IVc)——A suspension of the enaminoketone (Ic) (37 mg), DBE (87 mg) in pyridine (5 ml) was refluxed for 4 hr under oxygen bubbling. Work-up as described for IVa gave the quinoline (IVc) (42 mg; 39%). Recrystallization from iso-propanol gave pale yellow crystals, mp 175—177°. *Anal.* Calcd. for $C_{22}H_{17}O_2N$: C, 80.71; H, 5.23; N, 4.28. Found: C, 80.35; H, 5.47; N, 4.47. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1680; UV λ_{max}^{EtOH} nm (log ε): 233 (4.26), 252 (4.30), 272 (4.20), and 313 (4.41); Mass Spectrum *m/e*: 327 (M^+).

12) H. Stetter and R. Lanterbach, *Ann.*, **655**, 20 (1962); Y. Tamura, Y. Yoshimura, T. Nishimura, S. Kato and Y. Kita, *Tetrahedron Letters*, **1973**, 351.

5-Benzoylmethyl-1,3-dimethyl-2,4-dioxo-6-phenylpyrrolo[2,3-*d*]pyrimidine (VIII)——A suspension of the uracil (VII) (155 mg) and DBE (260 mg) in acetic acid (10 ml) was refluxed for 6 hr. Evaporation *in vacuo* followed by preparative TLC (alumina-chloroform) gave the pyrrolo [2,3-d]pyrimidine (VIII) (170 mg; 45%). Recrystallization from ethyl acetate gave colorless crystals, mp 222—223.5°. *Anal.* Calcd. for $C_{22}H_{19}O_3N_3$: C, 70.76; H, 5.13; N, 11.25. Found: C, 71.02; H, 5.25; N, 11.15. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3250, 1690, 1650, and 1600; NMR ($CDCl_3$) δ: 10.33 (1H, bs, NH, disappeared on addition of D_2O), 8.3—6.8 (10H, m, ArH), 4.58 (2H, s, $=C\text{-}CH_2CO$), 3.33 (3H, s, $N\text{-}CH_3$), and 3.28 (3H, s, $N\text{-}CH_3$); Mass Spectrum *m/e*: 373 (M^+), and 268 (base peak, M—COPh).

5-Benzoyl-1,3-dimethyl-2,4-dioxo-7-phenylpyrido [2,3-*d*]pyrimidine (IX)——A suspension of the uracil (VII) (78 mg) and DBE (130 mg) in pyridine (5 ml) was refluxed for 5 hr under oxygen bubbling. Evaporation *in vacuo* followed by preparative TLC (alumina-chloroform:carbon tetrachloride=1:1) gave the pyrido [2,3-*d*]pyrimidine (IX) (88 mg; 48%). Recrystallization from dichloromethane-pet benzine gave colorless crystals, mp 288—290°. *Anal.* Calcd. for $C_{22}H_{17}O_3N_3$: C, 71.15; H, 4.61; N, 11.32. Found: C, 71.12; H, 4.15; N, 11.36. IR $\nu_{max}^{CHCl_3}$ cm^{-1} 1700 and 1650; NMR ($CDCl_3$) δ: 8.3—7.4 (11H, m, ArH), 3.90 (3H, s, $N\text{-}CH_3$), and 3.39 (3H, s, $N\text{-}CH_3$); Mass Spectrum *m/e*: 371 (M^+).

5-Acetylmethyl-2,4-dioxo-1,3,6-trimethylpyrrolo[2,3-*d*]pyrimidine (X)——A suspension of the uracil (VII) (52 mg) and diacetylethylene (41 mg) in acetic acid (5 ml) was refluxed for 5 hr. Work-up as described for (VIII) gave the pyrrolo[2,3-*d*]pyrimidine (X) (40 mg; 48%). Recrystallization from acetone gave colorless crystals, mp 182—184°. *Anal.* Calcd. for $C_{12}H_{15}O_3N_3$: C, 57.82; H, 6.07; N, 16.86. Found: C, 57.80; H, 6.31; N, 17.01. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3450, 1690, and 1640; NMR ($CDCl_3$) δ; 9.55 (1H, bs, NH), 3.84 (2H, s, $C\text{-}CH_2\text{-}CO$), 3.32 (3H, s, $N\text{-}CH_3$), 3.20 (3H, s, $N\text{-}CH_3$), 2.36 (3H, s, CH_3), and 2.04 (3H, s, CH_3); Mass Spectrum *m/e*: 249 (M^+), 206 ($M-COCH_3$), and 149 (base peak).

5-Acetyl-2,4-dioxo-1,3,7-trimethylpyrido[2,3-*d*]pyrimidine (XI)——A suspension of the uracil (VII) (52 mg) and diacetylethylene (41 mg) in pyridine (5 ml) was refluxed for 3 hr under oxygen bubbling. Evaporation *in vacuo* followed by preparative TLC (alumina-chloroform) gave the pyrido[2,3-*d*]pyrimidine (XI) (30 mg; 37%). Recrystallization from acetone gave colorless crystals, mp 203—204°. *Anal.* Calcd. for $C_{12}H_{13}O_3N_3$: C, 58.29; H, 5.30; N, 17.00. Found: C, 58.25; H, 5.38; N, 16.84. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1710, 1660, and 1570; NMR ($CDCl_3$) δ: 6.74 (1H, s, $C=C\text{-}CH$), 3.70 (3H, s, $N\text{-}CH_3$), 3.39 (3H, s, $N\text{-}CH_3$), 2.62 (3H, s, CH_3), and 2.53 (3H, s, CH_3); Mass Spectrum *m/e*: 247 (M^+), and 232 (base peak, $M-CH_3$).

2-(1,2-Dibenzoyl)ethyl-5,5-dimethyl-cyclohexane-1,3-dione (XII)——A suspension of the enaminoketone (If) (169 mg) and DBE (260 mg) in methanol (5 ml) was refluxed for 12 hr. Evaporation *in vacuo* followed by preparative TLC (alumina-chloroform) gave the dione (XII) (58 mg; 15%). Recrystallization from isopropanol-pet. ether gave colorless crystals, mp 186.5—187.5. *Anal.* Calcd. for $C_{24}H_{24}O_4$: C, 76.25; H, 6.47. Found: C, 76.57; H, 6.43. NMR ($CDCl_3$) δ: 8.2—7.7 (4H, m, ArH), 7.7—7.1 (6H, m, ArH), 5.44 (1H, dd, J=6 and 8 Hz, $\text{-}CH_2\text{-}COPh$), 4.14 (1H, dd, J=8 and 18 Hz, CH_2COPh), 3.28 (1H, dd, J=6 and 18 Hz, CH_2COPh), 2.25 (4H, s, $CH_2\times 2$), and 1.92 (6H, s, $CH_2\times 2$); Mass Spectrum *m/e*: 376 (M^+). The structure was unequivocally established by direct comparison with the sample prepared by the procedure of Michailow,[13] which involved reaction of 5,5-dimethylcyclohexane-1,3-dione and DBE in the presence of piperidine.

13) R.M. Michailow and A.J. Ally, *Chem. Chmitshesk. Shural Ser*, 1937, 2950.