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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 dibenzoyl ethylene (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 diacetyl ethylene 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 $\nu_{\text{max}}^{\text{CHCl}_3}$ cm⁻¹: 3450, 1680, and 1610; NMR (CDCl₃) δ : 6.48 (1H, bs, exchanged with D₂O, 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, CH₂), 7.84 (2H, s, CH₂), 8.82 (3H, s, CH₃), and 8.91 (3H, s, CH₃); UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 251 (4.37) and 330 (3.80); Mass Spectrum *m/e*: 357 (M⁺), 355 (M-H₂), 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 C₂-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, *Naturwissenschaften*, **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).

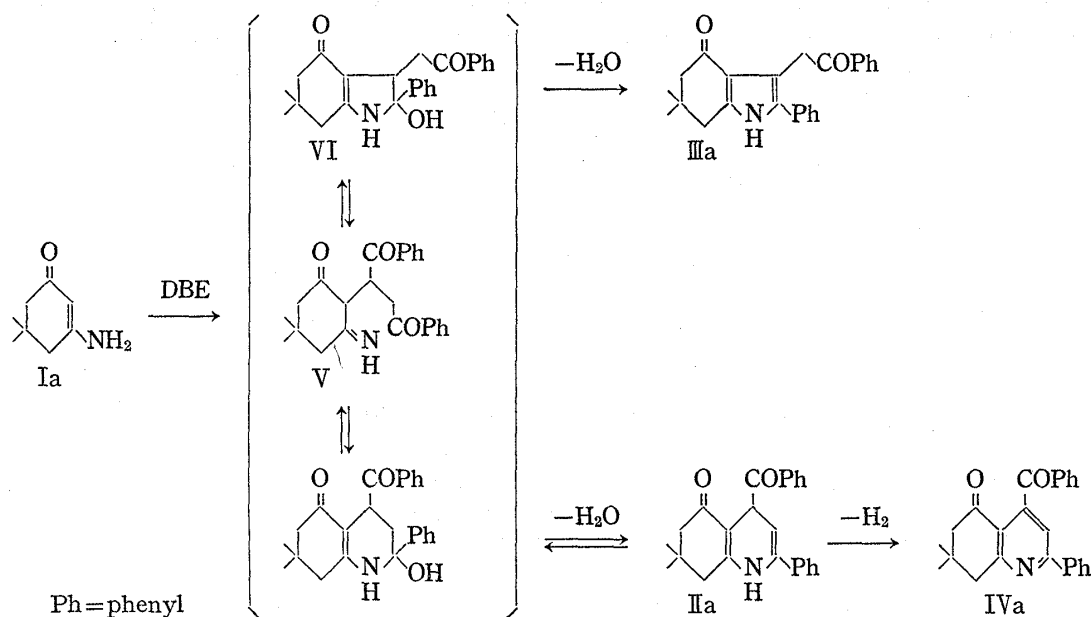


Fig. 1

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 checked 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 (IIIId, e) and 3-(disubstituted)amino compound (If) afforded the cyclohexane-1,3-dione (XII).

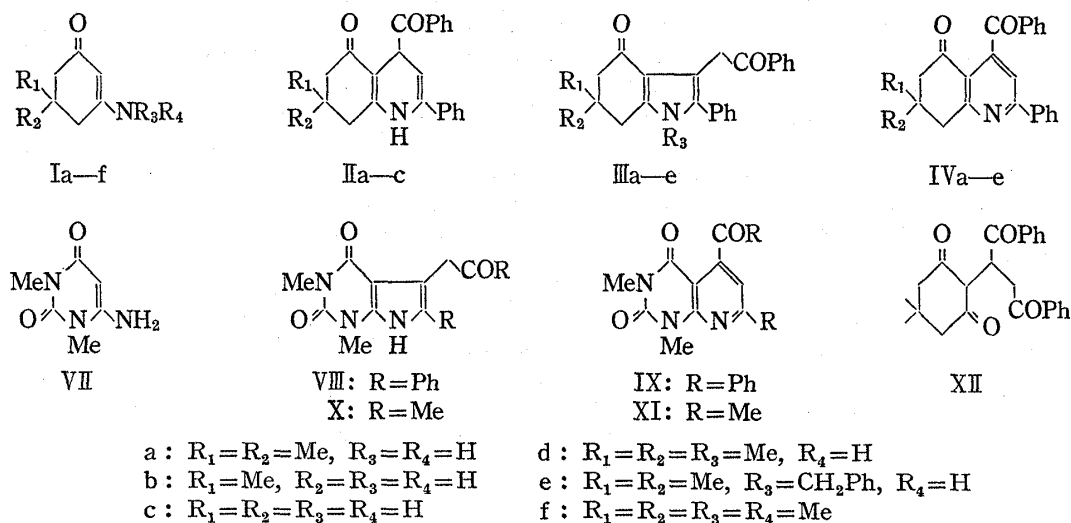


Fig. 2

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 diacetylene 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.

Compd.	R	X	R ₁	Reaction conditions	Compd.	Yield (%)	Compd.	Yield (%)
Ia	H	-CH ₂ C(Me) ₂ CH ₂ -	C ₆ H ₅	MeCO ₂ H, reflux 3h	IIIa	47		
Ib	H	-CH ₂ CH(Me)CH ₂ -	C ₆ H ₅	C ₅ H ₅ N, O ₂ , reflux 4h			IVa	41
Ic	H	-(CH ₂) ₃ -	C ₆ H ₅	MeCO ₂ H, reflux 5h	IIIb	77		
Id	CH ₃	-CH ₂ C(Me) ₂ CH ₂ -	C ₆ H ₅	C ₅ H ₅ N, O ₂ , reflux 4h			IVb	39
Ie	CH ₂ Ph	-CH ₂ (Me) ₂ CH ₂ -	C ₆ H ₅	MeCO ₂ H, reflux 4h	IIIc	24		
VII	H	-N(Me)CON(Me)-	C ₆ H ₅	MeCO ₂ H, reflux 4h			IVc	39
				C ₅ H ₅ N, O ₂ , reflux 4h	IIId	86		
				MeCO ₂ H, reflux 4h	IIIe	93		
				MeCO ₂ H, reflux 6h	VIII	45		
				C ₅ H ₅ N, O ₂ , reflux 5h			IX	48
	H	-N(Me)CON(Me)-	CH ₃	MeCO ₂ H, reflux 5h	X	48		
				C ₅ H ₅ N, O ₂ , reflux 3h			XI	37

Experimental¹⁰⁾

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 C₂₄H₂₃O₂N: 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 C₂₂H₁₉O₂N: C, 80.22; H, 5.81; N, 4.25. Found: C, 80.07; H, 5.80; N, 4.25. IR $\nu_{\text{max}}^{\text{CHCl}_3}$ cm⁻¹: 3430, 1680 and 1640; NMR (CDCl₃) δ : 8.2–7.9 (2H, m, ArH), 7.6–7.2 (8H, m, ArH), 6.5 (1H, bs, NH, disappeared on addition of D₂O), 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, CH₂ × 3); UV $\lambda_{\text{max}}^{\text{EtOH}}$ (log ϵ) nm: 244 (4.32) and 309 (4.17); Mass Spectrum *m/e*: 329 (M⁺), 327 (M-H₂), 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 C₂₄H₂₃O₂N: C, 80.64; H, 6.49; N, 3.92. Found: C, 80.52; H, 6.53; N, 3.86. IR $\nu_{\text{max}}^{\text{CHCl}_3}$ 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 CDCl₃). 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 (CDCl₃) δ : 9.05 (1H, bs, exch. with D₂O, NH), 8.2—7.2 (10H, m, ArH), 4.53 (2H, s, C-CH₂CO), 2.52 (2H, s, CH₂), 2.17 (2H, s, CH₂), and 1.06 (6H, s, CH₃ × 2); UV $\lambda_{\text{max}}^{\text{EtOH}}$ 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 C₂₃H₂₁O₂N: C, 80.44; H, 6.16; N, 4.08. Found: C, 80.37; H, 6.04; N, 4.14. IR $\nu_{\text{max}}^{\text{CHCl}_3}$ cm⁻¹: 3440, 1680 and 1640; NMR (CDCl₃) δ : 9.20 (1H, bs, NH), 8.2—7.9 (2H, m, ArH), 7.7—6.9 (8H, m, ArH), 4.54 (2H, s, =C-CH₂CO), 2.7—2.0 (5H, m, CH₂ × 2 and -CH), and 1.2—0.8 (3H, m, CH₃); UV $\lambda_{\text{max}}^{\text{EtOH}}$ 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 C₂₂H₁₉O₂N: C, 80.22; H, 5.81; N, 4.25. Found: C, 79.75; H, 5.75; N, 4.15. IR $\nu_{\text{max}}^{\text{CHCl}_3}$ cm⁻¹: 3430, 1690 and 1650; NMR (CDCl₃) 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-CH₂CO), and 2.8—1.6 (6H, m, CH₂ × 3); UV $\lambda_{\text{max}}^{\text{EtOH}}$ 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 C₂₅H₂₅O₂N: C, 80.83; H, 6.78; N, 3.77. Found: C, 80.36; H, 7.01; N, 3.61. IR $\nu_{\text{max}}^{\text{CHCl}_3}$ cm⁻¹: 1685 and 1640; NMR (CDCl₃) δ : 8.1—7.85 (2H, m, ArH), 7.6—7.1 (8H, m, ArH), 4.32 (2H, s, =C-CH₂CO), 3.38 (3H, s, NCH₃), 2.67 (2H, s, CH₂), 2.33 (2H, s, CH₂), and 1.20 (6H, s, CH₃ × 2); UV $\lambda_{\text{max}}^{\text{EtOH}}$ 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 C₃₁H₂₉O₂N: C, 83.19; H, 6.53; N, 3.13. Found: C, 82.92; H, 6.65; N, 3.07. IR $\nu_{\text{max}}^{\text{CHCl}_3}$ cm⁻¹: 1685 and 1640; NMR (CDCl₃) δ : 8.2—7.9 (2H, m, ArH), 7.6—7.2 (13H, m, ArH), 4.95 (2H, s, CH₂Ph), 4.34 (2H, s, =C-CH₂CO), 2.48 (2H, s, CH₂), 2.30 (2H, s, CH₂), and 1.06 (6H, s, CH₃ × 2); UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 243 (4.46) and 273 (4.06); Mass Spectrum m/e : 447 (M⁺), 342 (M-COPh), and 91 (C₆H₅CH₂⁺).

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 C₂₄H₂₁O₂N: 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 C₂₃H₁₉O₂N: C, 80.91; H, 5.61; N, 4.10. Found: C, 80.47; H, 5.87; N, 4.22. IR $\nu_{\text{max}}^{\text{CHCl}_3}$ cm⁻¹: 1680; NMR (CDCl₃) δ : 8.2—7.3 (11H, m, ArH), 2.8—2.1 (5H, m, CH₂ × 2 and -CH), and 2.3—2.1 (3H, m, CH₃); UV $\lambda_{\text{max}}^{\text{EtOH}}$ 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 C₂₂H₁₇O₂N: C, 80.71; H, 5.23; N, 4.28. Found: C, 80.35; H, 5.47; N, 4.47. IR $\nu_{\text{max}}^{\text{CHCl}_3}$ cm⁻¹: 1680; UV $\lambda_{\text{max}}^{\text{EtOH}}$ 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 $C_{22}H_{13}O_3N_3$: 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-CH₂CO), 3.33 (3H, s, N-CH₃), and 3.28 (3H, s, N-CH₃); 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 benzene 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-CH₃), and 3.39 (3H, s, N-CH₃); 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 diacetylene (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-CH₂-CO), 3.32 (3H, s, N-CH₃), 3.20 (3H, s, N-CH₃), 2.36 (3H, s, CH₃), and 2.04 (3H, s, CH₃); Mass Spectrum m/e : 249 (M^+), 206 (M-COCH₃), 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 diacetylene (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-CH), 3.70 (3H, s, N-CH₃), 3.39 (3H, s, N-CH₃), 2.62 (3H, s, CH₃), and 2.53 (3H, s, CH₃); Mass Spectrum m/e : 247 (M^+), and 232 (base peak, M-CH₃).

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, -CH₂-COPh), 4.14 (1H, dd, $J=8$ and 18 Hz, CH₂COPh), 3.28 (1H, dd, $J=6$ and 18 Hz, CH₂COPh), 2.25 (4H, s, CH₂ × 2), and 1.92 (6H, s, CH₂ × 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.