Acetylinic Ketones. Part II. (1a). Reaction of Acetylenic Ketones with Nucleophilic Nitrogen Compounds

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Aroylphenylacetylenes (I) reacted with ethyl and phenyl hydrazinecarboxylates (II) to give ω-aroylacetophenone-*N*-ethoxycarbonyl- (VIa-f) and *N*-phenoxycarbonyl- (VIg-l) hydrazones, respectively. When these were heated with acetic anhydride they were converted to 5-aryl-1-ethoxycarbonyl- and 1-phenoxycarbonyl-3-phenylpyrazoles (VII), respectively, which on hydrolysis with methanolic potassium hydroxide gave the corresponding 5(3)aryl-3(5)phenylpyrazoles (VIII).

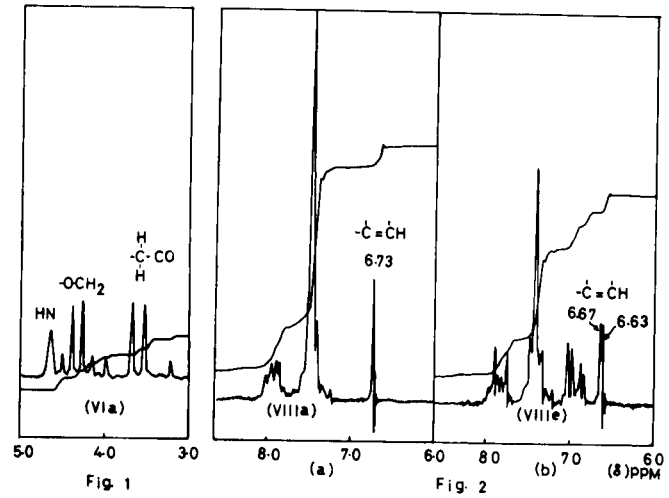
Reaction of the above acetylenic ketones with guanidine hydrochloride in the presence of sodium carbonate gave the corresponding 2-amino-6-aryl-4-phenylpyrimidines (XII). Similarly, reaction of benzoylphenylacetylene with thiourea and with urea in the presence of sodium ethoxide gave rise to 2,4-diphenylpyrimidine-2-thione (XVIII) and 2,4-diphenyl-2(1*H*)pyrimidinone (XV), respectively.

J. Heterocyclic Chem., 13, 257 (1976).

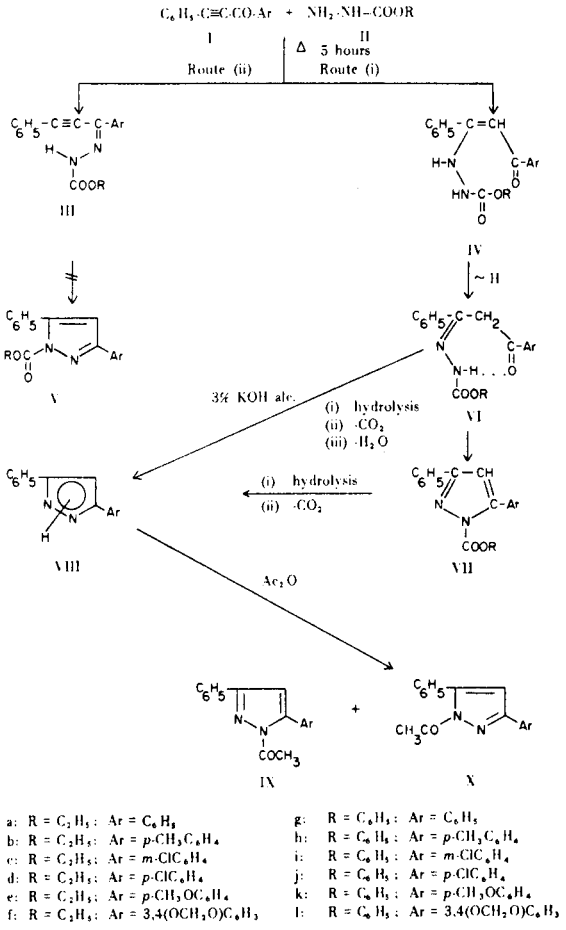
In the present investigation aroylphenylacetylenes (Ia-f) were allowed to react with esters of hydrazinecarboxylic acid (II), guanidine, thiourea and urea to study the mechanisms of the reactions and to prepare new heterocyclic compounds.

Reaction with Ethyl and Phenyl Hydrazinecarboxylates.

When benzoyl- (Ia), *p*-toluyl- (Ib), *m*-chlorobenzoyl- (Ic), *p*-chlorobenzoyl- (Id), *p*-methoxybenzoyl- (Ie), and 3,4-methylenedioxybenzoyl- (If) phenylacetylenes were refluxed with an alcoholic solution of ethyl (II; R = C_2H_5) and phenyl (II; R = C_6H_5) hydrazinecarboxylates, they gave ω-aroylacetophenone-*N*-ethoxycarbonyl- (VIa-f) and *N*-phenoxycarbonyl- (VIg-l) hydrazones, respectively (*cf.* Scheme 1). The structure of the products was established spectroscopically and chemically, Thus, the ir spectra of the products (*cf.* Table 1) were devoid of $\nu_{C\equiv C}$, which excluded structure III. The presence of a sharp band in the region 3460-3360 cm^{-1} (ν_{NH}) excluded the possibility that the compounds have structure V. The presence of a strong band in the region 1718-1705 cm^{-1}, with a shoulder at 1698-1795 cm^{-1} (these appeared as two separate bands in chloroform solution) for the ethoxycarbonyl derivatives (VIa-g), and two strong bands in the regions 1730-1700 and 1715-1685 cm^{-1} for the phenoxycarbonyl derivatives (VIg-l) indicated that these compounds contain two carbonyl groups, *i.e.*, they have either structure IV or structure VI. The nmr spectra (*cf.* Table 2), however, indicated that they have structure VI and not IV, since they show two doublets representing an AB system (J_{AB} = 9 Hz; $\Delta\nu/J < 1.0$), attributable to the CH_2-CO- protons (*cf.* Figure 1). The behaviour of the methylene group as an AB system may be attributed to the restriction of rotation of the CH_2-CO-Ar group by the weak hydrogen bonding between the NH and the carbonyl group. The spectra also show a broad signal (1H) in the region δ 4.2-4.65, which stands for one NH group. Further support for the assigned structure was gained from the mass spectrum of VIa which shows peaks at the following m/e values: (a) 310 (11.0%) $[M]^+$; (b) 292



Scheme 1



a: R = C_2H_5; Ar = C_6H_5
b: R = C_2H_5; Ar = p-$CH_3C_6H_4$
c: R = C_2H_5; Ar = m-ClC_6H_4
d: R = C_2H_5; Ar = p-ClC_6H_4
e: R = C_2H_5; Ar = p-$CH_3OC_6H_4$
f: R = C_2H_5; Ar = 3,4-$(OCH_2O)C_6H_3$
g: R = C_6H_5; Ar = C_6H_5
h: R = C_6H_5; Ar = p-$CH_3C_6H_4$
i: R = C_6H_5; Ar = m-ClC_6H_4
j: R = C_6H_5; Ar = p-ClC_6H_4
k: R = C_6H_5; Ar = p-$CH_3OC_6H_4$
l: R = C_6H_5; Ar = 3,4-$(OCH_2O)C_6H_3$

(14.3%) $[M\text{-}H_2O]^+$, which represents 1-ethoxycarbonyl-3,5-diphenylpyrazole molecular ion, formed by cyclization of VIa; (c) 220 (34.8%) fromed from the latter ion by fragmentation and rearrangement at C-N bond with loss of $CH_2{=}CH_2$ and CO_2; (d) 191 (7.9%) $[M\text{-}CH_2\text{-}CO\text{-}Ph]^+$ which is an evidence that the molecule contains a CH_2-CO-Ph group; (e) 105 (100%) $[C_6H_5\text{-}CO]^+$, which proves the presence of a benzoyl group. The electronic spectra of these compounds are identical and show an absorption maximum in the range 283-279 nm (*cf.* Table 1). This is an π-π^* transition band, since it is slightly blue shifted with decrease in solvent polarity (*cf.* VIe in Table 1).

Chemical behaviour of these compounds give further evidence for the assigned structure. Thus, compounds (VIa,d,e, and j) were easily cyclized by refluxing with acetic anhydride to the corresponding 5-aryl-1-ethoxycarbonyl- (VIIa,d and e) and 1-phenoxycarbonyl- (VIIj) pyrazoles, respectively. The structure of the latter compounds is substantiated by their ir spectra, which show a strong absorption band in the region 1774-1757 cm^{-1}

Table 1

The Electronic and Infrared Spectral Data of ω-Aroylacetophenone-*N*-ethoxycarbonyl Hydrazones (VIa-g) and ω-Aroylacetophenone-*N*-phenoxycarbonyl Hydrazones (VIg-l)

	Electronic spectra (Ethanol)		Infrared spectra (Potassium bromide)	
Compound	λ max (nm)	ε	cm^{-1}	ν
VIa	279	23,300	3400	NH
	~ 228-223	12,760	1714	C=O
			1698 (sh)	C=O
			1602	C=N
VIb	281	24,600	3395	NH
	~ 227-223	17,670	1705	C=O
			1695 (sh)	C=O
			1600	C=N
VIc	279	23,650	3378	NH
	~ 227-224	15,275	1715	C=O
			1697 (sh)	C=O
			1600	C=N
VId	281	24,630	3400	NH
	219	26,170	1705	C=O
			1697 (sh)	C=O
			1604	C=N
VIe	280	26,660	3380	NH
	~ 227-224	25,130	1705	C=O
	in cyclohexane		1695 (sh)	C=O
	278	25,500	1614	C=N
	229	20,650		
	223	21,500		
VIf	283	24,740	3380	NH
	~ 227-223	14,170	1718	C=O
			1698	C=O
			1605	C=N
VIg	279	23,110	3460	NH
	~ 227-223	14,300	1712	C=O
			1690 (sh)	C=O
			1600	C=N
VIh	279	24,100	3460	NH
	~ 226-223	18,000	1712	C=O
			1700 (sh)	C=O
			1600	C=N
VIi	279	28,400	3465	NH
	~ 227-222	20,340	1700	C=O
			1685 (sh)	C=O
			1600	C=N
VIj	277	24,500	3360	NH
	~ 227-224	23,100	1730	C=O
			1715 (sh)	C=O
			1600	C=N
VIk	280	24,280	3470	NH
	~ 226-222	23,100	1716	C=O
			1697	C=O
			1615	C=N
VII	282	26,100	3480	NH
	~ 226-222	16,770	1710	C=O
			1690	C=O
			1600	C=N

~ Shoulder

Table 2

The Nuclear Magnetic Resonance Spectral Data of ω-Aroylacetophenone-*N*-ethoxycarbonyl (VIa-f) and ω-Aroylacetophenone-*N*-phenoxycarbonyl (VIg-l) Hydrazones

Compound	δ	No. of Protons	Assignment	J (Hz)	Δ ν/J
VIa	7.3-7.97 (m)	10	Ar*H*		
	4.65 (br.)	1	N*H*		
	4.33 (q)	2	-O-C*H*$_2$-CH$_3$	3.7	
	3.83 (d)	1	-C*H*-CO (AB system)	9.0	0.45
	3.37 (d)	1	-C*H*-		
	1.28 (t)	3	-O-CH$_2$-C*H*$_3$		
VIb	7.0-7.87 (m)	9	Ar*H*		
	4.63 (br.)	1	N*H*		
	4.29 (q)	2	-O-C*H*$_2$-CH$_3$	3.3	
	3.78 (d)	1	-C*H*-CO (AB system)	9.0	0.48
	3.29 (d)	1	-C*H*-		
	2.38 (s)	3	Ar-C*H*$_3$		
	1.29 (t)	3	-O-CH$_2$-C*H*$_3$	3.3	
VIc	7.13-7.8 (m)	9	Ar*H*		
	4.62 (br.)	1	N*H*		
	4.27 (q)	2	-O-C*H*$_2$-CH$_3$	3.5	
	3.72 (d)	1	-C*H*-CO (AB system)	9.0	0.56
	3.25 (d)	1	-C*H*-		
	1.27 (t)	3	-O-CH$_2$-C*H*$_3$	3.5	
VId	7.27-7.9 (m)	9	Ar*H*		
	4.60 (br.)	1	N*H*		
	4.27 (q)	2	-OC*H*$_2$-CH$_3$	3.5	
	3.75 (d)	1	-C*H*-CO (AB system)	9.0	0.56
	3.28 (d)	1	-C*H*-		
	1.30 (t)	3	-O-CH$_2$-C*H*$_3$	3.5	
VIe	6.88-7.85 (m)	9	Ar*H*		
	4.62 (br.)	1	N*H*		
	4.33 (q)	2	-O-C*H*$_2$-CH$_3$	3.5	
	3.85 (s)	3	Ar-OC*H*$_3$		
	3.82 (d)	1	-C*H*-CO (AB system)	9.0	0.50
	3.37 (d)	1	-C*H*-		
	1.33 (t)	3	-O-CH$_2$-C*H*$_3$	3.5	
VIf	6.7-7.83 (m)	8	Ar*H*		
	5.92 (s)	2	O-C*H*$_2$-O		
	4.53 (br.)	1	N*H*		
	4.25 (q)	2	-O-C*H*$_2$-CH$_3$	3.5	
	3.7 (d)	1	-C*H*-CO (AB system)	9.0	0.50
	3.25 (d)	1	-C*H*-		
	1.28 (t)	3	-O-CH$_2$-C*H*$_3$	3.5	

Table 2 (Continued)

Compound	δ	No. of Protons	Assignment	J (Hz)	Δ ν/J
VIg	7.10-7.90 (m)	15	Ar*H*		
	4.2 (br.)	1	N*H*		
	3.82 (d)	1	H | -C-CO (AB system)	9.0	0.99
	3.38 (d)	1	| H		
VIh	7.0-7.87 (m)	14	Ar*H*		
	4.55 (br.)	1	N*H*		
	3.82 (d)	1	H | -C-CO (AB system)	9.0	0.47
	3.35 (d)	1	| H		
	2.32 (s)	3	Ar-C*H*$_3$		
VIi	7.13-7.87 (m)	14	Ar*H*		
	4.67 (br.)	1	N*H*		
	3.75 (d)	1	H | -C-CO (AB system)	9.0	0.52
	3.28 (d)	1	| H		
VIj	6.93-8.07 (m)	14	Ar*H*		
	4.67 (br.)	1	N*H*		
	3.85 (d)	1	H | -C-CO (AB system)	9.0	0.56
	3.37 (d)	1	| H		
VIk	6.83-7.93 (m)	14	Ar*H*		
	4.53 (br.)	1	N*H*		
	3.8 (s)	3	Ar-OC*H*$_3$		
	3.83 (d)	1	H | -C-CO (AB system)	9.0	0.50
	3.32 (d)		| H		
VII	6.7-7.87 (m)	13	Ar*H*		
	5.9 (s)	2	O-C*H*$_2$-O		
	4.53 (br.)	1	N*H*		
	3.80 (d)	1	H | -C-CO (AB system)	8.0	0.50
	3.33 (d)	1	| H		

(*cf.* Table 3) [*cf.* $\nu_{C=O}$ of vinyl acetate (1770 cm^{-1}) and vinyl benzoate (1754 cm^{-1})] (2). Their nmr spectra lend further support for the proposed structure, since they show a signal in the range δ 6.67-6.77 (*cf.* Table 4) attributable to the olefinic proton. Their structure was rigidly established by the fact that when refluxed with 3% methanolic potassium hydroxide they gave the corresponding 5(3)-aryl-3(5)phenylpyrazoles (VIIIa,d and e). These latter compounds were also directly obtained from the hydrazones (VI) by refluxing with 3% methanolic potassium hydroxide. Authentic samples of VIII were obtained by reacting aroylphenylacetylenes with hydrazine hydrate. The ir spectra of the pyrazoles (VIIIa-e) show a broad band at 3300-2500 cm^{-1} (ν_{NH} bonded) (3), whereas that of VIIIf shows a sharp band at 3260 cm^{-1}.

From this evidence, it was concluded that the reaction proceeds by the initial attack of the amino group at the acetylenic bond[route (i) in Scheme I].

Acetylation of the pyrazoles (VIIIa and e) by heating with acetic anhydride gave rise to the monoacetyl

Table 3

The Electronic and Infrared Spectral Data of 5-Aryl-1-ethoxycarbonyl-3-phenylpyrazoles (VIIa,d and e) and 5-Aryl-1-phenoxycarbonyl-3-phenylpyrazole (VIIj)

Compound	Electronic spectra (Ethanol) λ max (nm)	ε	Infrared spectra (Potassium bromide) cm^{-1}	ν
VIIa	263	32,520	1774	C=O
	~ 240-235	27,770		
VIId	266	28,080	1768	C=O
	~ 247-243	24,600		
VIIe	267	31,160	1772	C=O
	~ 250-240	26,050		
	229	23,530		
VIIj	269	25,580	1757	C=O
	~ 245-237	20,070		

~ Shoulder

Table 4

The Nuclear Magnetic Resonance Spectral Data of 1-Ethoxycarbonyl-(VIIa,d and e) and 1-Phenoxycarbonyl-(VIIj) 5-Aryl-3-phenylpyrazoles

Compound	δ	No. of Protons	Assignments	J (Hz)
VIIa	7.2-8.0 (m)	10	Ar*H*	
	6.67 (s)	1	=C*H*-	
	4.35 (q)	2	-O-C*H*$_2$-CH$_3$	3.5
	1.25 (t)	3	-O-CH$_2$-C*H*$_3$	3.5
VIId	7.23-8.03 (m)	9	Ar*H*	
	6.68 (s)	1	=C*H*-	
	4.40 (q)	2	-O-C*H*$_2$-CH$_3$	3.5
	1.3 (t)	3	-O-CH$_2$-C*H*$_3$	3.5
VIIe	7.9 (s)	2		
	7.2-7.57 (m)	5	Ar*H*	
	6.9 (s)	2		
	6.67 (s)	1	-C*H*=	
	4.40 (q)	2	-O-C*H*$_2$-CH$_3$	3.5
	3.83 (s)	3	Ar-OC*H*$_3$	
	1.33 (t)	3	-O-CH$_2$-C*H*$_3$	3.5
VIIj	6.93-8.07 (m)	14	Ar*H*	
	6.77 (s)	1	-C*H*=	

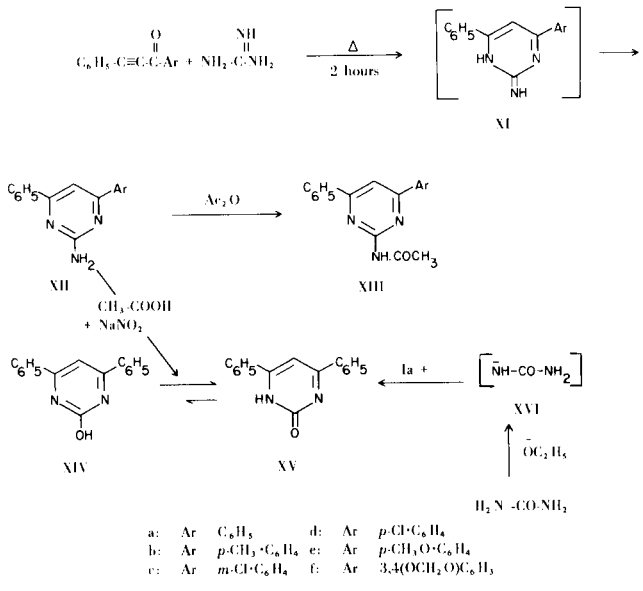
derivative (IXa or Xa), and a mixture of the acetyl derivatives (IXe and Xe), respectively. This conclusion was primarily inferred from the ir and nmr spectra of the products, and established by tlc which revealed one spot in the former product but two spots in the latter. Thus, while the ir spectrum of the acetyl derivative of VIIIa shows one strong band at 1744 cm^{-1}, that of the acetyl derivative of VIIIe shows a strong band at 1746 cm^{-1} with a shoulder at 1737 cm^{-1}. Similarly, the nmr spectrum of the former acetyl derivative shows a singlet at δ 6.73 (Figure 2a), whereas that of the latter acetyl derivative appears as two singlets at δ 6.67 and δ 6.63 (Figure 2b), indicating that it is a mixture of the two isomers IXe and Xe. The signal with the lower δ-value appears to represent the olefinic proton in isomer IXe, since it is more shielded than that in isomer Xe, being conjugated with the electron-releasing *p*-methoxyphenyl group.

Reaction of Aroylphenylacetylene with Guanidine.

When the acetylenic ketones (Ia-f) were refluxed with an alcoholic solution of guanidine hydrochloride containing aqueous sodium carbonate solution, they gave the corresponding 2-amino-6-aryl-4-phenylpyrimidines (XII) and not the imines (XI) (*cf.* Scheme 2).

The structure of the products was established spectroscopically and chemically. Thus their ir spectra (*cf.* Table 5) are devoid of $\nu_{C\equiv C}$, but show two bands in the ranges 1650-1634 and 1584-1570 cm^{-1}, characteristic of the pyrimidine system (4a). Compounds, (XIIa,c,d and f) show three sharp bands in the regions 3500-3478, 3320-3200 and 3220-3100 cm^{-1} (ν_{NH_2} + free and bonded) (5). However, the ir spectrum of a dilute chloroform solution of XIIa shows two bands only at 3552 and 3400 cm^{-1}. These correspond to *asym*- and *sym*-stretching frequencies of the free amino group, since they are related by the expression ν *sym*-(carbon tetrachloride) = 345.5 + 0.875 ν *asym*-(carbon tetrachloride) (6). The slight deviation from this expression may be attributed to solvent shift, since it is applicable in carbon tetrachloride solution. The nmr spectra of these compounds (*cf.* Table 6) lend further support for the aminopyrimidine structure XII. Thus, they show a broad signal

Scheme 2



in the range δ 5.2-5.17 (2H), which disappeared when the deuteriochloroform solution was shaken with deuterium oxide.

A strong evidence for the structure assigned to these compounds was also gained from the ms of 2-amino-4,6-diphenylpyrimidine (XIIa), which shows the molecular ion (m/e 247) as the base peak. This reflects the aromatic character of the compound and supports the amino-pyrimidine rather than the imino-dihydro-structure (XI).

Chemical reactions also indicate that these compounds have the aminopyrimidine structure (XII). Thus, when XIIa was treated with nitrous acid, it was converted to 4,6-diphenyl-2(1*H*)pyrimidinone (XV) (7), identical with the product obtained by the interaction between benzoylphenylacetylene (Ia) and urea in the presence of an alcoholic solution of sodium ethoxide. The lactam form of the latter compound XV was inferred from its nmr and ir spectra. Thus, its nmr spectrum shows no indication for the presence of enolic (OH), but only a singlet at δ 7.08 (1H; -CH=) and a multiplet centered at δ 7.74 (11H; 10 Ar*H* and 1N*H*). Its ir spectrum shows a strong band at 1635 cm^{-1} ($\nu_{C=O}$), and a broad band at 3100-2700 cm^{-1} (ν_{NH} bonded) (8) (a weak sharp band at 3400 cm^{-1} in chloroform solution). Acetylation of compounds XIIa-f with acetic anhydride gave the mono-acetyl-derivatives (XIIIa-f) (9). The ir spectra of these compounds (*cf.* Table 7) show a strong band in the range 1686-1669 cm^{-1} ($\nu_{C=O}$) (4b) and two weak bands in the range 3280-3220 and 3160-3080 cm^{-1} (ν_{NH} hydrogen bonded in the *trans-* and *cis-* forms, respectively) (4c) [chloroform solution of XIIIa shows one sharp band at

Table 5

The Electronic and Infrared Spectral Data of 2-Amino-6-aryl-4-phenylpyrimidines (XIIa-f)

	Electronic spectra (Ethanol)				Infrared spectra (Potassium bromide)	
	^1L_a band		^1L_b band			
Compound	λ max (nm)	ε	λ max (nm)	ε	cm^{-1}	ν
XIIa	251	33,150	333	13,080	1634 (s)	C=N
					1572 (s)	C=C
					3190 (m), 3300 (m), 3480 (m)	NH_2
XIIb	255	28,750	333	14,290	1635 (s)	C=N
					1570 (s), 1535 (s)	C=C
					3200 (m), 3320 (br.)	NH_2
XIIc	252	37,880	334	14,090	1637 (s)	C=N
					1575 (s)	C=C
					3200 (m), 3320 (m), 3495 (m)	NH_2
XIId	256	36,000	334	14,630	1635 (s)	C=N
					1570 (s)	C=C
					3200 (m), 3320 (m), 3500 (m)	NH_2
XIIe	252	26,000	334	19,910	1650 (s)	C=N
			~280-290	17,040	1570 (s)	C=C
					3220 (m), 3360 (br.)	NH_2
XIIf	239	30,350	341	20,630	1642 (s)	C=N
					1574 (s)	C=C
					3190 (m), 3310 (m), 3495 (m)	NH_2

~ Shoulder

Table 6

Nuclear Magnetic Resonance Spectral Data of 2-Amino-6-aryl-4-phenylpyrimidines (XIIa-f) in Deuteriochloroform

Compound	δ	No. of protons	Assignments
XIIa	7.28-8.08 (m)	10	Ar*H*
	7.32 (s)	1	C:C*H*
	5.71 (br.)	2	NH_2
XIIb	7.22-8.2 (m)	9	Ar*H*
	7.2 (s)	1	C:C*H*
	5.40 (br.)	2	NH_2
	2.42 (s)	3	Ar-CH_3
XIIc	7.22-8.13 (m)	9	Ar*H*
	7.2 (s)	1	C:C*H*
	5.45 (br.)	2	N*H*$_2$
XIId	7.33-8.27 (m)	9	Ar*H*
	7.33 (s)	1	C:C*H*
	5.3 (br.)	2	N*H*$_2$
XIIe	6.83-8.13 (m)	9	Ar*H*
	7.20 (s)	1	C:C*H*
	5.20 (br.)	2	N*H*$_2$
	3.83 (s)	3	Ar-OC*H*$_3$
XIIf	7.0-8.4 (m)	8	Ar*H*
	7.47 (s)	1	C:C*H*
	6.20 (s)	2	O-C*H*$_2$-O
	5.33 (br.)	2	N*H*$_2$

3400 cm^{-1} (ν_{NH} free)] (4c). Their nmr spectra show the signals for the ($COCH_3$) and (-CH=) protons as well as a multiplet for the aromatic and NH protons (*cf.* Table 8). The similarity of their electronic spectra (*cf.* Table 7) reflects their structural identity.

The failure to isolate an intermediate in the condensation of guanidine with acetylenic ketones made it impossible to decide the site of the initial attack. However, in the case of urea, the attack appears to occur by the anion $\bar{N}H{\cdot}CONH_2$ (XVI).

Reaction of Benzoylphenylacetylene with Thiourea.

When an alcoholic solution of thiourea (1 mole) was added to an alcoholic solution of benzoylphenylacetylene (1 mole) and sodium ethoxide (1 mole), and the mixture refluxed for 1 hour, 2,4-diphenylpyrimidine-2-thione (XVIII) was obtained in nearly quantitative yield. The structure of the product was established by chemical and spectroscopic methods. Thus, it was easily oxidized with sodium nitrite and sodium hydrogen sulphate in ethyl alcohol (10), or with sodium nitrite in acetic acid to 2,2′-bis(4,6-diphenylpyrimidinyl) disulphide (XXI). Reduction of the disulphide with tin and hydrochloric acid gave back the thione (XVIII). These reactions are characteristic of thiols and disulphides, respectively. Further support for the structure assigned to the product (XVIII) was gained from its conversion to 4,6-diphenyl-2(1*H*)-pyrimidinone (XV) by refluxing with a concentrated aqueous solution of chloroacetic acid (11) (*cf.* Scheme 3). Although these reactions exclude the imino structure (XX), they do not discriminate between the thione (XVIII) and the thiol (XIX) forms. Methylation of the thione (XVIII) with dimethyl sulfate in alkaline medium gave the corresponding S-CH_3 derivative (XXII) (12) as a colorless product.

Spectroscopic Evidence for the Structure of the Thione (XVIII), Disulfide (XXI) and Methylated Product (XXII).

The structure of the thione was rigidly established by studying its spectroscopic properties. Thus, its ir spectrum is devoid of $\nu_{S\text{-}H}$ and shows two bands at 1602 and 1550 cm^{-1} ($\nu_{C=N}$) (4d) and ($\nu_{C=C}$) (4e), respectively. This excludes the imine structure (XX) and indicates that the compound exists predominantly in the thione form (thiolactam) (13) rather than in the thiol form (XIX) (14). The thione structure was also substantiated by the electronic spectrum of the compound in ethyl alcohol. This shows two bands at 297 nm (ϵ = 24,370) and 266 nm (ϵ = 21,060) and a shoulder at 245-237 nm (ϵ = 18,170) as well as a low intensity band at 396 nm (ϵ = 1,900). This latter band, which is due to n-π^* transition in the $>C{=}\ddot{S}:$ chromophore, is a strong evidence that the compound exists in polar solvent predominatly in the thione form. The n-π^* band for $-\overset{|}{C}{=}\ddot{N}-$ in pyrimidines occurs at a much shorter wavelength (15). Besides that if the compound has the thiol structure it should show an absorption similar to that of the disulfide with nearly half the molar extinction coefficient, which is not the case. However, when the compound is dissolved in cyclohexane it gives a colorless solution, which shows absorption bands at 319 nm (ϵ = 11,920) and 257 nm (ϵ = 32,450) which is different from its absorption in ethyl alcohol but very similar to that of the disulfide (XXI) (*inter alia*) with nearly half the molar extinction coefficient. This indicated that in non-polar solvents the compound exists in the thiol form (XIX). Further evidence for the thione structure was gained from the nmr spectrum of the compound (in deuteriochloroform), which shows a signal at δ 7.9 (1H) (-CH=) and a complex pattern centered at δ 7.72 (11H; 10 ArH+ NH). No exchange with deuterium is observed when the deuteriochloroform solution is shaken with deuterium oxide.

The structure of the disulfide (XXI) was substantiated by its ir, nmr, mass and uv spectra. Thus, its ir is devoid of ν_{NH} and shows two bands at 1570 and 1515 cm^{-1}, which are characteristic of the pyrimidine ring (4a). It also shows a weak band at 460 cm^{-1} ($\nu_{S\text{-}S}$) (4f). Its nmr

Table 7

The Electronic and Infrared Spectral Data of 2-Acetamido-6-aryl-4-phenylpyrimidines (XIIIa-f)

	Electronic spectra (Ethanol)				Infrared spectra (Potassium bromide)	
	^1L_a band		^1L_b band			
Compound	λ max (nm)	ε	λ max (nm)	ε	cm^{-1}	ν
XIIIa	254	36,180	315	16,300	1670 (s)	C=O
			290	19,560	1590 (s)	C=N
					1540 (s)	C=C
					3140 (w), 3220 (w)	NH
XIIIb)	256	27,910	316	15,170	1675 (s)	C=O
			282	10,310	1594 (s)	C=N
					1535 (s)	C=C
					3140 (w), 3220 (w)	NH
XIIIc	254	36,980	318	16,210	1670 (s)	C=O
			~288-294	11,220	1600 (s)	C=N
					1540 (m)	C=C
					3080 (w), 3220 (w)	NH
XIIId	258	33,730	318	16,860	1686 (s)	C=O
			292	10,790	1595 (s)	C=N
					1543 (s)	C=C
					3160 (w), 3230 (w)	NH
XIIIe	259	21,250	325	19,270	1680 (s)	C=O
			285	13,750	1595 (s)	C=N
					1543 (m)	C=C
					3160 (w), 3230 (w)	NH
XIIIf	232	32,050	333	20,950	1669 (s)	C=O
					1590 (s)	C=N
					1540 (s)	C=C
					3140 (w), 3225 (w)	NH

~ Shoulder

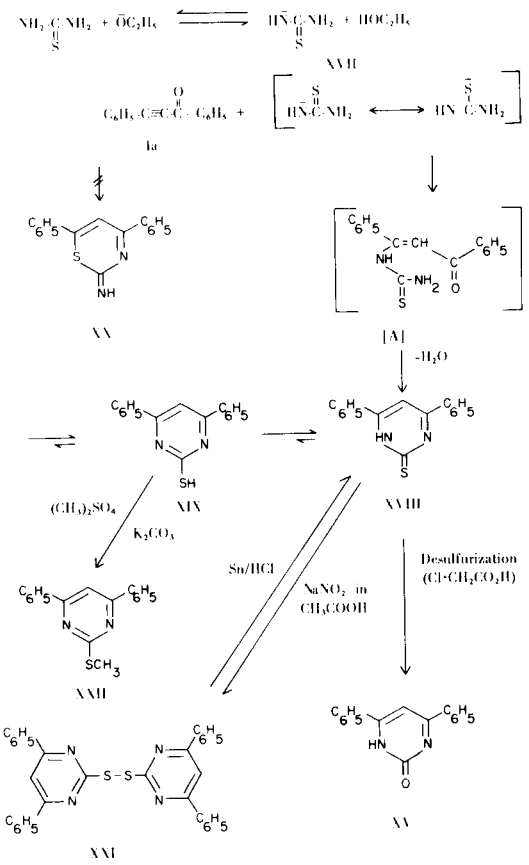
spectrum shows a signal at δ 7.83 (2H; -CH=) and a multiplet centered at δ 7.63 (20H; Ar*H*). Its mass spectrum gives additional evidence for the assigned structure, since it shows peaks at the following m/e: 526 (45%) $[M]^+$; 263 (80%) which results from the cleavage at the S-S bond; 494 (1%) $[M\text{-}S]^{+\cdot}$ and 462 (5%) $[M\text{-}2S]^+$. These latter peaks are parallel to those observed in the spectrum of diphenyl disulfide (16). Its electronic spectrum shows two bands at 320 nm (ε = 21,800) and 263 nm (ε = 53,440), which correspond to the ^1L_b and ^1L_a bands of the pyrimidine ring, respectively.

The ir spectrum of the methylated product (XXII) shows bands at 1572 cm^{-1} and 1525 cm^{-1} characteristic of the pyrimidine system [*cf.* ir of disulfide (XXI)]. The pyrimidine structure was also substantiated by its uv spectrum which shows two bands at 327 nm (ε = 8,830) and 264 nm (ε = 38,400). This reflects its similarity to the thiol form (XIX). Its nmr spectrum in deuteriochloroform, confirms the assigned structure since it shows a signal at δ 7.7 (1H) (-CH=), a multiplet centered at δ 7.7 (10H; Ar*H*) and a sharp signal at δ 2.7 (3H; SCH_3) (17).

The formation of 4,6-diphenylpyrimidine-2-thione (XVIII) can be explained by the mechanism outlined in Scheme 3. In the presence of sodium ethoxide the attack of thiourea on the acetylenic ketone appears to take place by the anion (XVII), which is a strong nucleophile, rather than by the sulfur atom. However, in the absence of a basic catalyst the thiourea attacks the acetylenic bond preferentially by the sulfur atom (18). This is probably due to the fact that the polarized C=S group is more nucleophilic than the amino group, since the latter carries a partial positive charge due to P-π conjugation

$H_2N-\overset{\overset{S}{\|}}{C}-NH_2 \longleftrightarrow H_2N=\overset{S^-}{\overset{|}{C}}-NH_2$. The initial attack by the anion XVII appears to occur at the acetylenic bond to give initially an intermediate (A) (*cf.* Scheme 3), which loses water on crystallization from glacial acetic acid to give the thione (XVIII). This is inferred from the fact that the crude product has no sharp melting point and its ir spectrum shows two sharp bands at 3490 and 3420 cm^{-1} [(ν_{NH} free) of primary amides (4g)] as well as a strong band at 1610 cm^{-1} [$\nu_{C=O}$ of α,β-unsaturated β-amino ketones (4h)]. Its nmr spectrum also lends support to the structure assigned to the intermediate (A), since it shows the following signals: (a) a broad band centered at δ 3.67 (2H), exchangeable with deuterium, and is attributed to the amino group, (b) a singlet at δ 7.38 (-CH=), and (c) a multiplet at δ 7.43-8.3 (11H; 10 Ar*H* and N*H* protons).

Scheme 3



EXPERIMENTAL

Electronic and infrared spectra were measured on Pye-Unicam SP8000, SP700, and SP1000 and Beckman IR 12 spectrophotometers, respectively. Nmr spectra were run on Varian T60A. Microananlyses were determined by Alfred Bernhardt, West Germany.

Table 8

Nuclear Magnetic Resonance Spectral Data of 2-Acetamido-6-aryl-4-phenylpyrimidines (XIIIa-f) in Deuteriochloroform

Compound	δ	No. of protons	Assignments
XIIIa	7.3-8.27 (m)	12	Ar*H* + C:C*H* + N*H*
	2.77 (s)	3	$COCH_3$
XIIIb	7.2-8.17 (m)	11	Ar*H* + C:C*H* + N*H*
	2.72 (s)	3	$COCH_3$
	2.43 (s)	3	Ar-CH_3
XIIIc	7.43-8.33 (m)	11	Ar*H* + C:C*H* + N*H*
	2.72 (m)	3	$COCH_3$
XIIId	7.27-8.27 (m)	11	Ar*H* + C:C*H* + N*H*
	2.77 (s)	3	$COCH_3$
XIIIe	6.93-8.2 (m)	11	Ar*H* + C:C*H* + N*H*
	3.87 (s)	3	Ar-OCH_3
	2.72 (s)	3	$COCH_3$
XIIIf	6.8-8.2 (m)	10	Ar*H* + C:C*H* + N*H*
	6.03 (s)	2	O-CH_2-O
	2.70 (s)	3	$COCH_3$

Reaction of Aroylphenylacetylenes with Ethyl and Phenyl Hydrazinecarboxylates.

A mixture of the aroylphenylacetylene (0.01 mole) [prepared according to the method of Parker, Raphael and Wilkinson (19)] and ethyl or phenyl hydrazinecarboxylate (0.01 mole) was refluxed in ethyl alcohol (50 ml.) for 5 hours. The reaction mixture was concentrated, and the product precipitated on cooling was crystallized from a suitable solvent to give ω-aroylacetophenone-*N*-ethoxycarbonyl- (VIa-f) and ω-aroylacetophenone-*N*-phenoxycarbonyl- (VIg-l) hydrazones, respectively (*cf.* Tables 9 and 10).

Action of Acetic Anhydride on ω-Aroylacetophenone-*N*-ethoxycarbonyl- and *N*-phenoxycarbonyl Hydrazones.

The mixture of the hydrazone derivative (VIa,d, and e) (2.0 g.) and acetic anhydride (5 ml.) was heated on a boiling water-bath for 2.5 hours. The cold reaction mixture was treated with cold 50% ethyl alcohol (20 ml.), and the precipitated solid was crystallized from cyclohexane to give the corresponding 5-aryl-1-ethoxycarbonyl-3-phenyl-pyrazoles (VIIa,d and e).

1-Ethoxycarbonyl-3,5-diphenylpyrazole (VIIa).

This compound had m.p. 105-106°, yield = 82.5%.

Anal. Calcd. for $C_{18}H_{16}N_2O_2$: C, 73.95; H, 5.52; N, 9.58. Found: C, 74.10; H, 5.57; N, 9.45.

5-(*p*-Chlorophenyl)-1-ethoxycarbonyl-3-phenylpyrazole (VIId).

This compound had m.p. 118-119°, yield = 85%.

Anal. Calcd. for $C_{18}H_{15}ClN_2O_2$: C, 66.15; H, 4.63; Cl, 10.85; N, 8.57. Found: C, 66.01; H, 4.63; Cl, 10.95; N, 8.44.

1-Ethoxycarbonyl-5-(*p*-methoxyphenyl)-3-phenylpyrazole (VIIe).

This compound had m.p. 131-132°, yield = 82%.

Anal. Calcd. for $C_{19}H_{18}N_2O_3$: C, 70.79; H, 5.63; N, 8.69; OCH_3 + OC_2H_5 as OCH_3, 19.26. Found: C, 70.94; H, 5.45; N, 8.87; OCH_3 + OC_2H_5 as OCH_3, 19.09.

Table 9

ω-Aroylacetophenone-*N*-ethoxycarbonyl Hydrazones (VIa-f)

Compound	Yield (%)	M.p. °C	Formula	Calcd. %				Found %			
				C	H	N	Cl	C	H	N	Cl
VIa	97	159-161 (a)	$C_{18}H_{18}N_2O_3$	69.66	5.85	9.04	--	69.49	5.87	9.13	--
VIb	95	161-162 (a)	$C_{19}H_{20}N_2O_3$	70.34	6.22	8.64	--	70.26	6.07	8.81	--
VIc	90	160-161 (a)	$C_{18}H_{17}ClN_2O_3$	62.66	4.96	8.16	10.28	63.07	5.05	8.02	9.93
VId	93	186-187 (a)	$C_{18}H_{17}ClN_2O_3$	62.66	4.96	8.16	10.28	62.79	4.96	8.18	10.48
VIe (c)	86	169-171 (a)	$C_{19}H_{20}N_2O_4$	67.04	5.92	8.23	--	66.90	5.88	8.4	--
VIf	82	174-175 (b)	$C_{19}H_{18}N_2O_5$	64.40	5.41	7.91	--	64.59	5.40	8.29	--

(a) Crystallized from ethyl alcohol. (b) Crystallized from 80% ethyl alcohol. (c) (OCH_3 + OC_2H_5) detected as OCH_3%; Calcd. for = 18.24; Found: 18.01.

Table 10

ω-Aroylacetophenone-*N*-phenoxycarbonyl Hydrazones (VIg-l)

Compound	Yield (%)	M.p. °C	Formula	Calcd. %				Found %			
				C	H	N	Cl	C	H	N	Cl
VIg	98	151-152 (a)	$C_{22}H_{18}N_2O_3$	73.73	5.07	7.82	--	73.49	5.04	8.28	--
VIh	80	151-152 (a)	$C_{23}H_{20}N_2O_3$	74.17	5.42	7.83	--	74.11	5.60	8.11	--
VIi	78	156-157 (b)	$C_{22}H_{17}ClN_2O_3$	67.26	4.36	7.13	9.02	67.75	4.58	7.39	9.40
VIj	89	163-164 (c)	$C_{22}H_{17}ClN_2O_3$	67.26	4.36	7.13	9.02	67.69	4.38	7.33	9.41
VIk (d)	97	156-157 (a)	$C_{23}H_{20}N_2O_4$	71.12	5.20	7.21	--	71.21	5.19	7.66	--
VIl	88	166-167 (c)	$C_{23}H_{18}N_2O_5$	68.64	4.51	6.96	--	68.49	4.72	6.94	--

(a) Crystallized from cyclohexane. (b) Crystallized from 80% ethyl alcohol. (c) Crystallized from ethyl alcohol. (d) OCH_3%: Calcd. for = 7.99; Found = 7.94.

5-(*p*-Chlorophenyl)-1-phenoxycarbonyl-3-phenylpyrazole (VIIj).

This compound was prepared as mentioned above (4 hours reflux) and had m.p. 151-152°, yield = 80%.

Anal. Calcd. for $C_{22}H_{15}ClN_2O_2$: C, 70.49; H, 4.03; Cl, 9.46; N, 7.47. Found: C, 70.61; H, 4.52; Cl, 9.15; N, 7.33.

Action of Alcoholic Potassium Hydroxide on ω-Aroylacetophenone-*N*-ethoxycarbonyl- and -*N*-phenoxycarbonyl Hydrazones (VI), and 5-Aryl-1-ethoxycarbonyl- and 1-phenoxycarbonylpyrazoles (VII).

The hydrazone derivative (VIa-l) or the pyrazole (VIIa,d,e, and j) (0.01 mole) was refluxed on a boiling water-bath with 3% methanolic potassium hydroxide (20 ml.) for 30 minutes. The solvent was removed under reduced pressure, and the remaining solid was crystallized from ethyl alcohol to give the corresponding 5(3)-aryl-3(5)phenylpyrazole (VIII) in 98-99% yield, identified by m.p. and mixed m.p. with an authentic sample, prepared by leaving a mixture of the aroylphenylacetylene (1.0 g.) and 99% hydrazine hydrate (5 ml.) at room temperature for 2-3 minutes.

3,5-Diphenylpyrazole (VIIIa).

This compound had m.p. 199-200° (20).

3(5)-*p*-Chlorophenyl-5(3)phenylpyrazole (VIIId).

This compound had m.p. 214-215° (21).

3(5)-*p*-Methoxyphenyl-5(3)phenylpyrazole (VIIIe).

This compound had m.p. 168-169° (21).

3(5)-Phenyl-5(3)-*p*-tolylpyrazole (VIIIb).

This compound had m.p. 183-184°.

Anal. Calcd. for $C_{16}H_{14}N_2$: C, 82.02; H, 6.03; N, 11.97. Found: C, 82.08; H, 6.00; N, 12.22.

3(5)-*m*-Chlorophenyl-5(3)phenylpyrazole (VIIIc).

This compound had m.p. 168-169°.

Anal. Calcd. for $C_{15}H_{11}ClN_2$: C, 71.07; H, 4.35; Cl. 13.91; N, 11.49. Found: C, 70.85; H, 4.15; Cl, 13.89; N, 11.21.

3(5)-(3',4'-Methylenedioxyphenyl)-5(3)phenylpyrazole (VIIIf).

This compound had m.p. 191-192°.

Anal. Calcd. for $C_{16}H_{12}N_2O_2$: C, 72.71; H, 4.58; N, 10.6. Found: C, 72.78; H, 4.57; N, 10.8.

Reaction of Aroylphenylacetylenes with Guanidine.

A mixture of the aroylphenylacetylene (0.05 mole) and guanidine hydrochloride (4.5 g.) in ethyl alcohol (50 ml.) was refluxed, while a solution of sodium carbonate (2.65 g.) in water (10 ml.) was added portionwise during 2 hours. Refluxing was continued for a further 10 hours, and the reaction mixture was concentrated under reduced pressure, diluted with water (50 ml.) and extracted with benzene. The products were crystallized from suitable solvents to give 2-amino-6-aryl-4-phenylpyrimidines (XIIa-f). The results are reported in Table 11.

Table 11

2-Amino-6-aryl-4-phenyl-pyrimidines (XII)

Compound	Yield	M.p. °C	Formula	Calcd. %				Found %			
				C	H	N	Cl	C	H	N	Cl
XIIa (22)	76	138-139 (a)	$C_{16}H_{13}N_3$	77.71	5.30	16.99	--	77.66	5.43	16.80	--
XIIb	83	127-128 (a)	$C_{17}H_{15}N_3$	78.13	5.79	16.08	--	78.19	5.63	15.99	--
XIIc	88	132-133 (a)	$C_{16}H_{12}ClN_3$	68.21	4.30	14.91	12.59	68.19	4.28	14.76	12.76
XIId	86	157-158 (a)	$C_{16}H_{12}ClN_3$	68.21	4.30	14.91	12.59	68.11	4.30	14.74	12.81
XIIe (c)	79	160-162 (b)	$C_{17}H_{15}N_3O$	73.62	5.45	15.15	--	74.00	5.35	15.11	--
XIIf	69	201-202 (b)	$C_{17}H_{13}N_3O_2$	70.10	4.50	14.42	--	70.25	4.69	14.29	--

(a) Crystallized from cyclohexane. (b) Crystallized from benzene. (c) OCH_3%; Calcd. for = 11.19; Found = 11.11.

Table 12

2-Acetamido-6-aryl-4-phenylpyrimidines (XIII)

Compound	Yield (%)	M.p. °C	Formula	Calcd. %				Found %			
				C	H	N	$COCH_3$	C	H	N	$COCH_3$
XIIIa	92	224-225	$C_{18}H_{15}N_3O$	74.72	5.23	14.52	14.87	74.87	5.24	14.54	14.51
XIIIb	88	150-151	$C_{19}H_{17}N_3O$	75.23	5.66	13.85	--	75.42	5.46	14.02	--
XIIIc (a)	90	174-175	$C_{18}H_{14}ClN_3O$	66.49	4.36	12.98	13.30	66.94	4.48	13.12	13.64
XIIId (b)	82	185-186	$C_{18}H_{14}ClN_3O$	66.49	4.36	12.98	13.30	66.78	4.28	13.01	12.92
XIIIe (c)	85	163-164	$C_{19}H_{17}N_3O$	71.46	5.38	13.15	--	71.63	5.17	13.39	--
XIIIf	90	145-146	$C_{19}H_{15}N_3O_3$	68.46	4.54	12.61	12.92	68.47	4.48	13.06	13.29

(a) Cl%, Calcd. for = 10.95; Found = 11.11. (b) Cl%, Calcd. for = 10.95; Found = 11.08. (c) OCH_3%, Calcd. for = 9.72; Found = 9.87.

Acetylation of 2-Amino-6-aryl-4-phenylpyrimidines.

The pyrimidine (XII) (1.0 g.) was heated with acetic anhydride (3 ml.) on a boiling water-bath for one hour. The product precipitated on addition of cold 50% ethyl alcohol (15 ml.) was crystallized from ethyl alcohol to give the corresponding 2-acetamido-6-aryl-4-phenylpyrimidines (XIIIa-f) (*cf.* Table 12).

Reaction of 2-Amino-4,6-diphenylpyrimidine with Nitrous Acid.

A soluiton of sodium nitrite (1.5 g.) in water (10 ml.) was added dropwise to a solution of 2-amino-4,6-diphenylpyrimidine (XIIa) (1.0 g.) in glacial acetic acid (15 ml.). The precipitated solid (0.8 g.) was crystallized from acetone to give 4,6-diphenyl-2(1*H*)pyrimidinone (XV), m.p. and mixed m.p. 233-234°. An authentic sample of XV was prepared by adding an alcoholic soluiton of urea (1.14 g. in 10 ml. of ethyl alcohol) to the solution of benzoylphenylacetylene (4.0 g.) and sodium ethoxide (1.3 g.) in absolute ethyl alcohol and the mixture refluxed for 1 hour, and kept at room temperature for 4 hours. The solvent was removed under reduced pressure and the residue dissolved in water (50 ml.) and crystallized from acetone to give XV in 92.5% yield, m.p. 233-234°[reported m.p. 230-234° (23a) and 237-239° (23b)].

Anal. Calcd. for $C_{16}H_{12}N_2O$: C, 77.40; H, 4.88; N, 11.30. Found: C, 77.58; H, 4.93; N, 11.28.

Reaction of Benzoylphenylacetylene with Thiourea.

An alcoholic solution of thiourea (1.11 g. in 10 ml. of ethyl alcohol) was added to a solution of benzoylphenylacetylene (3.0 g.) and sodium ethoxide (0.99 g.) in ethyl alcohol (50 ml.), and the mixture refluxed for 1 hour. The solvent was removed under reduced pressure, the residue was dissolved in water (about 50 ml.), extracted with ether to remove the unreacted material, cooled and acidified with acetic acid (8 ml.) (24). The crude precipitated product melted at about 120° (with gas evolution), solidified and remelted at about 165°. Crystallization of the crude product from acetic acid gave 4,6-diphenyl-2(1*H*)pyrimidine-2-thione (XVIII) as fine yellow crystals, m.p. 166-167°, in nearly quantitative yield [reported as colorless crystals, m.p. 160° (14)].

Anal. Calcd. for $C_{16}H_{12}N_2S$: C, 72.69; H, 4.48; N, 10.60; S, 12.15. Found: C, 73.05; H, 4.14; N, 10.48; S, 11.74.

4,6-Diphenyl-2-methylmercaptopyrimidine (XXII).

Dimethyl sulphate (8 ml.), potassaum carbonate anhydrous (16.0 g.) and the thione (XVIII) (1.0 g.) in dry acetone (50 ml.) was refluxed on a boiling water-bath for 12 hours and the reaction product worked up as usual to give the title compound (XXII) in colorless crystals (from cyclohexane), m.p. 152-153°, yield = 75%.

Anal. Calcd. for $C_{17}H_{14}N_2S$: C, 73.34; H, 5.07; N, 10.07; S, 11.52. Found: C, 73.44; H, 5.02; N, 10.07; S, 11.56.

Oxidation of 4,6-Diphenyl-(1*H*)pyrimidine-2-thione to 2,2'-*bis*-(4,6-Diphenylpyrimidinyl) Disulfide.

(a) With Sodium Nitrite in Acetic Acid.

The solution of thione (XVIII) (1.0 g.) in glacial acetic acid (10 ml.) was treated portion-wise with sodium nitrite (1.0 g.), whereby a colorless solid precipitated out. The reaction mixture was diluted with water and the precipitate filtered off. On crystal-

lization from benzene it gave 2,2'-*bis*(4,6-diphenylpyrimidinyl) disulfide (XXI), m.p. 240-241°, in quantitative yield.

Anal. Calcd. for $C_{32}H_{22}N_4S_2$: C, 72.98; H, 4.21; N, 10.64; S, 12.18; M.W. 526. Found: C, 72.87; H, 4.19; N, 10.46; S, 12.21; M.W. 526 (MS).

(b) The same compound was obtained by the method described by Ward and Day (8).

Reduction of the Disulfide (XXI) to the Thione (XVIII).

A suspension of the disulfide (0.5 g.) in concentrated hydrochloric acid (10 ml.) containing tin (0.2 g.) was refluxed for 5 minutes. The reaction mixture was diluted with water and the yellow solid was filtered off (0.35 g.). It was crystallized from acetic acid to give the thione (XVIII), m.p. and mixed m.p. 166-167°, yield = 70%.

Desulfurization of the Thione (XVIII) to the Pyrimidinone (XV).

A solution of chloroacetic acid (2 g.) in water (5 ml.) was mixed with the thione (0.5 g.) and heated on an oil-bath (150-160°) for 30 minutes. The product was filtered off and crystallized from acetone to give the pyrimidinone (XV), m.p. and mixed m.p. 233-234°, yield = quantitative.

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