Reaction of 1,3-Diaryl-2,3-dibromo-1-propanones With Urea in Basic and Acidic Medium. Synthesis of Pyrimidine, Imidazoline and Imidazolidine Derivatives

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Reaction of 1,3-diaryl-2,3-dibromo-1-propanones **1** with urea in basic medium afforded 4,6-diaryl-5-bromo-5,6-dihydropyrimidine-2(1*H*)-ones **4**. Oxidation of these bromopyrimidines **4** in dimethylsulphoxide gave 4,6-diaryl-1,6-dihydropyrimidine-2,5-diones **6**, which were further converted to their thione analogues **7**. Reaction of 1,3-diaryl-2,3-dibromo-1-propanones **1** with urea, phenylurea and *sym*-diphenylurea in glacial acetic acid medium gave in appreciable yields 4-phenyl-5-α-(bromoarylmethyl)imidazolin-2-one **8** and 1,3-diphenyl-4-aroyl-5-arylimidazolidin-2-one **11** respectively.

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Pyrimidine derivatives play a very vital role in many biological processes. The 5-substituted pyrimidines are particularly important because of their significant utility in diverse pharmacological studies (1-6). In a programmed research directed towards the construction of physiologically active new heterocycles, we have synthesised a few 5-bromopyrimidines starting from easily available chalcone dihydrodibromide precursors.

It is reported that a pyrimidine ring could be formed by the reactions of urea, thiourea or guanidine with α,β-unsaturated carbonyl compounds such as malonic ester, acetoacetic ester, *etc.* (6,7).

Condensation of benzalacetophenones (chalcones) with thiourea and benzoylphenylacetylene with urea in presence of ethanolic sodium ethoxide afforded 4,6-diphenyl-3,4-dihydro-2(1*H*)-pyrimidinone in appreciable yields. Reaction of chalcone dihydrodibromides with 1,2-diamines in presence of triethylamine is reported to produce novel bridgehead nitrogen heterocycles (10,11). An ethanolic solution of chalcone dihydrodibromide reacts with thiourea to produce free sulphur in addition to chalcone (12). It is thought probable that the chalcone dihydrodibromides could effectively interact with thiourea in sodium ethoxide to give corresponding 5-bromopyrimidine derivatives.

Condensation of 1,3-diphenyl-2,3-dibromo-1-propanone (**1**) with thiourea in refluxing ethanolic sodium ethoxide solution gave two compounds which were separated by column chromatography. One of the compounds was identi-

CHART I

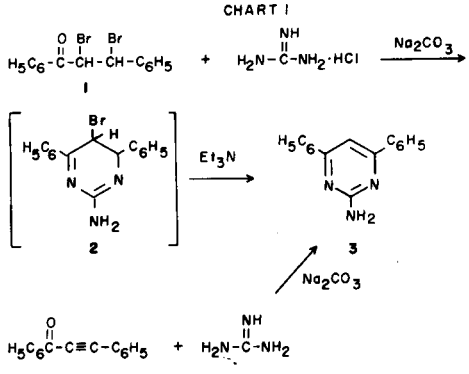


Table I

Physical Data of 4,6-Diaryl-5-bromo-5,6-dihydropyrimidin-2(1*H*)-one (**4a-f**)

Compound	Ar	Ar_1	Mp °C	Yield %	% Yield of Chalcone	Molecular Formula	Analysis Calcd. (Found) C	H	N
4a	C_6H_5	C_6H_5	143	66	5	$C_{16}H_{13}BrN_2O$	58.36 (58.23)	3.95 (3.86)	8.51 (8.37)
4b	C_6H_5	p-ClC_6H_4	162	35	3	$C_{16}H_{12}BrClN_2O$	52.89 (52.82)	3.30 (3.24)	7.71 (7.63)
4c	p-ClC_6H_4	C_6H_5	189	45	4	$C_{16}H_{12}BrClN_2O$	52.89 (52.91)	3.30 (3.21)	7.71 (7.57)
4d	p-ClC_6H_4	p-ClC_6H_4	125	55	6	$C_{16}H_{11}BrCl_2N_2O$	48.36 (48.30)	2.77 (2.68)	7.05 (6.93)
4e	C_6H_5	p-BrC_6H_4	118	62	5	$C_{16}H_{12}Br_2N_2O$	47.06 (47.00)	2.94 (2.87)	6.86 (6.82)
4f	p-$CH_3C_6H_4$	C_6H_5	166	89	7	$C_{17}H_{15}BrN_2O$	59.47 (59.38)	4.67 (4.57)	8.16 (8.07)

fied as benzalacetophenone (mp, mmp and superimposable ir). The other compound could not be identified because it readily decomposes at room temperature.

When chalcone dihydrodibromide was refluxed with ethanolic guanidine hydrochloride containing aqueous sodium carbonate, a yellow crystalline compound melting at 118° was obtained. This compound was found to be unstable at room temperature. In another experiment this material before decomposition was taken up in benzene and was stirred overnight with triethylamine to give a stable compound which melts at 138°. The physical data of this compound was found to be in close agreement with the known 2-amino-4,6-diphenylpyrimidine which was further prepared from benzoylphenylacetylene and guanidine in presence of sodium carbonate (9). We propose a tentative structure **2** for the unstable intermediate and **3** for the dehydrobrominated product (Chart 1). Thus our initial objective to get 5-bromopyrimidine derivatives by the action of thiourea or guanidine with chalcone dihydrodibromide was met with failure.

When, chalcone dihydrodibromide (1,3-diphenyl-2,3-dibromo-1-propanone) was allowed to react with urea in ethanolic sodium ethoxide solution, a crude solid was isolated, which was washed successively with petroleum ether (60-80°) and cold ethanol to remove traces of chalcone that were formed. The solid **4** after recrystallisation showed strong ir (nujol) bands at 1700 cm^{-1} for carbonyl absorption in addition to well defined peaks at 1580 and 3300 cm^{-1} corresponding to C=N and N-H groupings respectively. In the pmr spectrum for **4a** (Ar = Ar′ = C_6H_5), there are two doublets observed around δ 5.6-6.4, indicating presence of C*H*Ph and C*H*Br protons in addition

CHART 2

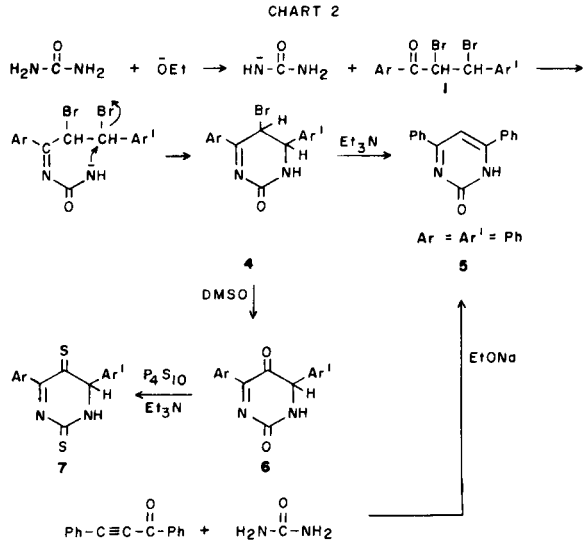


Table II

Physical Data of 4,6-Diarylpyrimidin-2,5-dione (**6a-f**) and Their Thio Analogues **7a-f**

Compound	Ar	Ar_1	X	Mp °C	Yield %	Molecular Formula	Analysis Calcd. (Found) C	H	N
6a	C_6H_5	C_6H_5	O	122	72	$C_{16}H_{12}N_2O_2$	72.72 (72.53)	4.54 (4.37)	10.60 (10.57)
6b	C_6H_5	*p*-ClC_6H_4	O	147	82	$C_{16}H_{11}ClN_2O_2$	64.43 (64.25)	3.69 (3.50)	9.39 (9.25)
6c	*p*-ClC_6H_4	C_6H_5	O	94	80	$C_{16}H_{11}ClN_2O_2$	64.43 (64.16)	3.69 (3.38)	9.39 (9.31)
6d	*p*-ClC_6H_4	*p*-ClC_6H_4	O	109	66	$C_{16}H_{10}Cl_2N_2O_2$	57.83 (57.80)	3.01 (2.92)	8.43 (8.42)
6e	C_6H_5	*p*-BrC_6H_4	O	179	50	$C_{16}H_{11}BrN_2O_2$	55.98 (55.77)	3.20 (3.05)	8.16 (8.01)
6f	*p*-$CH_3C_6H_4$	C_6H_5	O	126	80	$C_{17}H_{14}N_2O_2$	73.38 (73.19)	5.03 (4.92)	10.07 (9.93)
7a	C_6H_5	C_6H_5	S	95	46	$C_{16}H_{12}N_2S_2$	64.84 (64.73)	4.05 (3.95)	9.46 (9.37)
7b	C_6H_5	*p*-ClC_6H_4	S	134	50	$C_{16}H_{11}ClN_2S_2$	58.18 (58.02)	3.33 (3.12)	8.48 (8.42)
7c	*p*-ClC_6H_4	C_6H_5	S	108	60	$C_{16}H_{11}ClN_2S_2$	58.18 (57.97)	3.33 (3.09)	8.48 (8.35)
7d	*p*-ClC_6H_4	*p*-ClC_6H_4	S	173	33	$C_{16}H_{10}Cl_2N_2S_2$	52.75 (52.47)	2.74 (2.69)	7.69 (7.61)
7e	C_6H_5	*p*-BrC_6H_4	S	104	46	$C_{16}H_{11}BrN_2S_2$	51.20 (51.07)	2.93 (2.85)	7.47 (7.33)
7f	*p*-$CH_3C_6H_4$	C_6H_5	S	120	43	$C_{17}H_{14}N_2S_2$	65.81 (65.62)	4.51 (4.37)	9.03 (9.01)

to the complex multiplet around δ 7.2-8.25 (11 H, 10 Ar*H* and 1 N*H*). There is no indication of an enolic (OH) group in the assigned structure.

The genesis of **4** could be envisaged with the initial formation of an anil, which under the basic conditions, displaces a bromine atom intramolecularly (Chart 2). The structure of **4** is confirmed, when a typical member of the series (**4a**, Ar = Ar′ = C_6H_5) was dehydrobrominated employing triethylamine to afford 4,6-diphenyl-2(1*H*)-pyrimidone (**5**), which was confirmed by comparison (mp, mmp superimposable ir) with an authentic specimen obtained from benzoylphenylacetylene and urea (9).

Suprisingly under identical conditions, the reaction of chalcone dihydrodibromide with phenylurea or diphenylurea did not afford any new product and instead, the starting materials were fully recovered. It is presumed that due to the nonavailability of free amino groups in phenylurea (due to the formation of $PhNHCONH^-$ with NaOEt) and diphenylurea, the initial attack at the carbonyl function of chalcone dihydrodibromide is precluded.

Oxidation of these bromo compounds **4** in dimethylsulphoxide at room temperature afforded their corresponding ketones **6**. The versatile application of DMSO in the oxidation of alkyl halides in heterocyclic systems has been reported by us earlier (13). Compound (**6a**, Ar = Ar′ = Ph) showed well defined ir peaks at 3300 (NH), 1700 (C=O), 1640 (amide C=O) and 1580 (C=N) cm^{-1} and the pmr (deuteriochloroform) spectrum showed a sharp singlet at δ 5.8 corresponding to the benzylic proton besides the complex multiplet centered around δ 7.6 for the bulk aromatic and the NH protons.

Ketones and their thio analogues are likely to possess analogous chemical behaviour and the thiated heterocycles are supposed to be potential pharmacological agents. All the 4,6-diaryldihydropyrimidin-2,5-diones **6a-f** were rapidly converted to their thio analogues **7a-f** by employing a reagent of choice, triethylamine solubilised phosphorus pentasulphide in acetonitrile (14,15). The thione analogues are crystalline compounds with well defined melting points (Chart 2).

The reaction of urea with diphenyltriketone in glacial acetic acid medium was reported (15). Interestingly, when urea was made to react with 1,3-diaryl-2,3-dibromo-1-propanone **1** in acetic acid, the reaction path altered with the

CHART 3

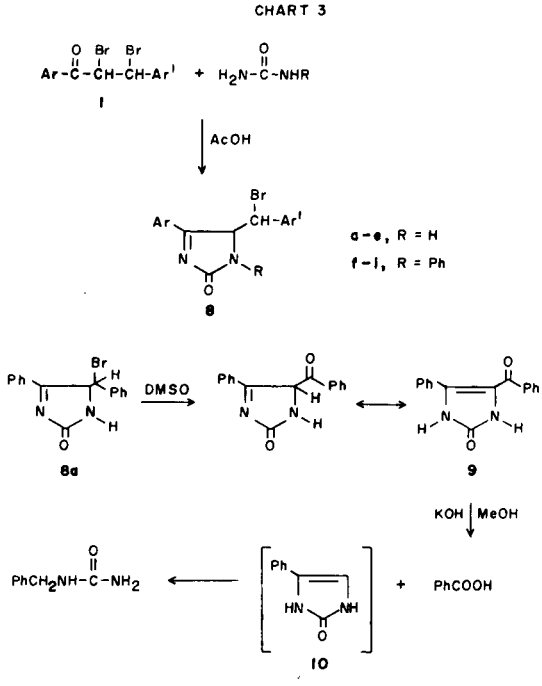


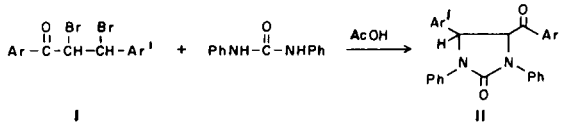
Table III

Physical Data of 4-Aryl-5-bromoarylmethylimidazolin-2-one **8a-i**

Compound	Ar	Ar_1	R	Mp °C	Yield %	Molecular Formula	Analysis Calcd. (Found) C	H	N
8a	C_6H_5	C_6H_5	H	280	61	$C_{16}H_{13}BrN_2O$	58.36 (58.19)	3.95 (3.82)	8.51 (8.49)
8b	C_6H_5	*p*-ClC_6H_4	H	274	49	$C_{16}H_{12}BrClN_2O$	52.89 (52.64)	3.30 (3.21)	7.71 (7.67)
8c	*p*-ClC_6H_4	C_6H_5	H	191	53	$C_{16}H_{12}BrClN_2O$	52.89 (52.73)	3.30 (3.17)	7.71 (7.69)
8d	*p*-ClC_6H_4	*p*-ClC_6H_4	H	265	60	$C_{16}H_{11}BrCl_2N_2O$	48.36 (48.09)	2.77 (2.68)	7.05 (6.89)
8e	*p*-$CH_3C_6H_4$	C_6H_5	H	185	63	$C_{17}H_{15}BrN_2O$	59.47 (59.29)	4.37 (4.23)	8.16 (8.11)
8f	C_6H_5	C_6H_5	C_6H_5	248	45	$C_{22}H_{17}BrN_2O$	65.19 (64.99)	4.19 (4.11)	6.91 (7.03)
8g	C_6H_5	*p*-ClC_6H_4	C_6H_5	242	54	$C_{22}H_{16}BrClN_2O$	60.14 (59.92)	3.64 (2.71)	6.37 (6.39)
8h	*p*-ClC_6H_4	C_6H_5	C_6H_5	282	47	$C_{22}H_{16}BrClN_2O$	60.14 (60.11)	3.64 (3.60)	6.37 (6.43)
8i	*p*-ClC_6H_4	*p*-ClC_6H_4	C_6H_5	125	57	$C_{22}H_{15}BrCl_2N_2O$	55.81 (55.69)	3.17 (3.05)	5.91 (5.97)

isolation of an entirely different compound **8a-f**. This is attributed to the fact that the formation of urea anion is impossible in acidic medium and in that case the possible attack of urea on the carbon bearing halogen would be different. The structure of **8** was based on chemical degradation and spectral studies (Chart 3).

The pmr spectra of **8a** (Ar = Ar′ = Ph, R = H) showed a triplet at δ 6.6 for the ring hydrogen (C*H*) and a doublet at δ 5.4 for benzylic proton with J = 5 Hz in addition to complex multiplet for bulk aromatic protons. The triplet integrating for a single proton is ascribed to the mixed coupling of the imidazoline proton with the benzylic proton in the side chain and the N*H* hydrogen. When **8a** was heated in DMSO at 150-160° for 2 hours, 4-phenyl-5-benzoylimidazolidin-2-one (**9**) was obtained. The ir spectrum of **9** revealed sharp bands at 1685 cm^{-1} (amide carbonyl) in addition to the peak at 1710 cm^{-1} for the carbonyl group. The pmr (carbon tetrachloride) spectrum of **9** produced only a complex multiplet around δ 7.2-7.9 integrating for 12 protons (10 Ar*H* and 2 N*H*). Compound **9** was further hydrolysed by methanolic potassium hydroxide to afford benzylurea and benzoic acid. The isolation of benzylurea could be rationalised in terms of the formation of an intermediate **10**, which could undergo further ring rupture.



I II

Reaction of 1,3-diaryl-2,3-dibromo-1-propanones **1** with phenyl and *sym*-diphenylurea in hot glacial acetic acid medium gave new products **8f-i** and **11** respectively. The participation of NH groups of *sym*-diphenylurea in the nucleophilic displacement of both the bromine atoms is being facilitated in acid medium to afford **11**. Compound 1,3,5-triphenyl-4-benzoylimidazolidin-2-one (**11a**) (Ar = Ar′ = Ph) in the infrared region showed two sharp bands at 1720 and 1645 cm^{-1} for the carbonyl and amide carbonyl groups. The pmr spectrum reveals a singlet for two protons at δ 5.75 besides the multiplet beyond δ 7.1 for aromatic protons, thus confirming the general structure **11**. The present investigation aimed at the synthesis and reactions of 5-halopyrimidines however led to the development of a sequence in the formation of five membered analogues starting from chalcone dihydrodibromides. All these compounds are under active screening for their pharmacological evaluation.

EXPERIMENTAL

Melting points are uncorrected. Infrared spectra were obtained on a Perkin-Elmer model 137; proton magnetic spectra were determined with a Varian A-60 D spectrometer, using tetramethylsilane as the internal standard. The chemical shifts are given in δ units. Column chromatography was performed in silicagel (Merck) using petroleum ether:benzene (1:1) as eluent.

Reaction of Chalcone Dihydrodibromide With Guanidine. Isolation of **2**.

To a refluxing solution of chalcone dihydrodibromide (0.94 g, 0.005 mole) and guanidine hydrochloride (0.53 g, 0.005 mole) in absolute ethanol (25 ml) was added a solution of sodium carbonate (0.41 g, 0.005 mole, 10 ml) dropwise over 0.5 hour. Heating was continued for an additional 5 hours and the reaction mixture was concentrated *in vacuo*, diluted with water (10 ml) and extracted from benzene. Evaporation of the benzene extract gave a crystalline yellow compound, mp 118°. This material became unstable immediately at room temperature.

Reaction of **2** With Triethylamine. Isolation of 2-Amino-4,6-diphenylpyrimidine **3**.

The unstable compound **2** (0.5 g) was immediately dissolved in benzene (5 ml) and stirred overnight with triethylamine (0.5 ml) at room temperature. The solvent was removed *in vacuo* to give a gummy material, which was washed with water and subsequently redissolved in benzene. Addition of petroleum ether (60-80°) to the benzene extract afforded a crystalline yellow solid which was characterised as 2-amino-4,6-diphenylpyrimidine (**3**), mp 138° (lit (9) mp 138-139°); ir (potassium bromide): ν max cm^{-1} 1634 (C=N), 3300 (NH_2); nmr (deuteriochloroform): δ 5.7 (broad, 2H, NH_2 protons) and 7.2-8.0 (m, 11 H, aromatic and olefinic protons).

Reaction of Benzoylphenylacetylene with Guanidine. Isolation of 2-Amino-4,6-diphenylpyrimidine (**3**).

To a refluxing solution of benzoylphenylacetylene (2.06 g, 0.01 mole) and guanidine hydrochloride (0.85 g, 0.01 mole) in ethanol (10 ml) was added a solution of sodium carbonate (0.55 g, 0.005 mole, 10 ml) portion wise over 2 hours. Refluxing was continued further for 10 hours, the reaction mixture was concentrated under reduced pressure, diluted with

Table IV

Physical Data of 1,3-Diphenyl-4-aroyl-5-arylimidazolidine-2-one **11a-d**

Compound	Ar	AR_1	Mp °C	Yield %	Molecular Formula	Analysis Calcd. (Found) C	H	N
11a	C_6H_5	C_6H_5	175	70	$C_{28}H_{22}N_2O_2$	80.38 (80.31)	5.26 (5.29)	6.69 (6.72)
11b	C_6H_5	*p*-ClC_6H_4	162	55	$C_{28}H_{21}ClN_2O_2$	74.33 (74.28)	4.64 (4.52)	6.19 (6.03)
11c	*p*-ClC_6H_4	C_6H_5	182	65	$C_{28}H_{21}ClN_2O_2$	74.33 (74.42)	4.64 (4.61)	6.19 (6.03)
11d	*p*-ClC_6H_4	*p*-ClC_6H_4	194	49	$C_{28}H_{20}ClN_2O_2$	69.13 (69.08)	4.11 (4.18)	5.76 (5.81)

water (50 ml) and extracted from benzene. The benzene extract was dried (magnesium sulfate) and removal of the solvent *in vacuo* gave a solid which was dried and recrystallised from benzene to give 2-amino-4,6-diphenylpyrimidine (**3**), (1.9 g, 76%), mp 139° (lit (9) mp 138-139°).

Reaction of 1,3-Diphenyl-2,3-dibromo-1-propanone with Urea in Sodium Ethoxide. Isolation of 4,6-Diphenyl-5-bromo-5,6-dihydropyrimidine-2(1*H*)-one (**4**).

A mixture of 1,3-diphenyl-2,3-dibromo-1-propanone (10.92 g, 0.03 mole) and urea (1.8 g, 0.03 mole) was heated under reflux for 4 hours. Alcohol was removed under reduced pressure to give a residue, the aqueous solution of which was neutralised from acetic acid to give a solid. This was separated, thoroughly washed with petroleum ether (60-80°) and cold ethanol (5 ml). The compound was recrystallised from boiling ethanol to afford 4,6-diphenyl-5-bromo-5,6-dihydropyrimidine-2(1*H*)-one (**4**), (2.05 g, 66%), mp 143°; ir (nujol): ν max cm^{-1} 1700 (C=O), 1580 (C=N), 3300 (NH); nmr (deuteriochloroform): δ 5.7 (d, J = 5 Hz, CHPh), 6.3 (d, J = 5 Hz, -CHBr), 7.2-8.25 (11*H*, 10 Ar*H* and 1N*H*). Analogous compounds were also prepared and reported in Table I.

Reaction of **4** With Triethylamine. Isolation of 4,6-Diphenylpyrimidine-2(1*H*)-one (**5**).

4,6-Diphenyl-5-bromo-5,6-dihydropyrimidine-2-one (0.2 g, 0.00035 mole) in dichloromethane (10 ml) and triethylamine (0.5 ml) was stirred overnight. The residue after evaporation of the solvent was added to water and extracted from ether. The ether extract was dried and on evaporation gave a yellow solid which was recrystallised from benzene to give 4,6-diphenylpyrimidin-2(1*H*)-one (**5**), mp 235° (lit (16) mp 237-239°); ir (nujol): ν max cm^{-1} 1635 (C=N), 3100 (NH).

Preparation of 4,6-Diphenyl-2(1*H*)-pyrimidone (**5**).

An alcoholic solution of urea (0.9 g, 0.015 mole) in ethyl alcohol (10 ml) was added to a solution of benzoyl phenylacetylene (3.12 g, 0.015 mole) and sodium ethoxide (1.02 g, 0.015 mole) in ethyl alcohol (50 ml). The mixture was refluxed for 1 hour and the solvent was removed under reduced pressure to give a residue which was dissolved in water (50 ml) and extracted from ether to remove the unreacted material. On cooling followed by acidification (acetic acid 8 ml) a crude product was isolated which was recrystallised from benzene to give 4,6-diphenyl-2(1*H*)-pyrimidone (**5**), 2.51 g, 75%), mp 235° (lit (16) mp 237-239°); ir (nujol): ν max cm^{-1} 1635 (C=N), 3100 (NH).

Oxidation of **4** With Dimethylsulphoxide (DMSO). Isolation of 4,6-Diphenylpyrimidine-2,5-dione (**6**).

4,6-Diphenyl-5-bromo-5,6-dihydropyrimidin-2-one (3.29 g, 0.001 mole) in dimethyl sulphoxide (5 ml) was stirred at ambient temperature for 60 hours and the resulting mixture was poured into cold water (20 ml). A solid separated which was filtered, washed with water, dried and recrystallised from ethanol to give 4,6-diphenylpyrimidine-2,5-dione (2 g, 72%), mp 122°; ir (nujol): ν max cm^{-1} 1700 (C=O), 1640 (amide carbonyl), 1580 (C=N) and 3300 (NH); nmr (deuteriochloroform): δ 5.8 (s, C*H*Ph), 7.6 (bm, 11H, 10 Ar*H* and 1N*H*).

Transformation of **6** to its Corresponding Thione With Triethylamine Solubilised Phosphorus Pentasulphide. Isolation of 4,6-Diphenylpyrimidine-2,5-dithione (**7**).

4,6-Diphenylpyrimidine-2,5-dione (0.25 g, 0.001 mole) in acetonitrile (8 ml) was treated with phosphorus pentasulphide (0.45 g, 0.001 mole) and to this stirred suspension was added triethylamine (0.41 g, 0.004 mole) in three portions, while cooling the mixture in ice water to moderate the exothermic reaction. The resulting solution was left at room temperature for 24 hours and poured into cold water. The product was filtered, washed with water and recrystallised from ethanol to give 4,6-diphenylpyrimidine-2,5-dithione (**7**) (0.14 g, 46%), mp 95°.

Physical data of the analogous compounds are discussed in Table II.

Typical Reaction of 1,3-Diphenyl-2,3-dibromo-1-propanone With Urea in Glacial Acetic Acid Medium. Isolation of 5-Aryl-4-α-bromobenzylimidazolin-2-one (**8a**).

1,3-Diphenyl-2,3-dibromo-1-propanone (1.82 g, 0.005 mole) and urea (0.3 g, 0.005 mole) in glacial acetic acid (20 ml) was refluxed for 3 hours. After completion of the reaction, the mixture was cooled, where white crystals were separated. The solid was filtered, washed thoroughly with petroleum ether (60-80°) and vacuum dried to give 5-phenyl-4-α-bromobenzylimidazolin-2-one (**8a**), (1 g, 61%), mp 280°; ir (nujol): ν max cm^{-1} 1680 (C=O), 3200 (NH); nmr (DMSO-d_6): δ 5.4 (d, J = 5 Hz, C*H*C_6H_5), 6.6 (t, 1H, C*H*), 7.1-8.4 (11*H*, 10 aromatic protons and 1 NH). Similarly compounds **8a-e** prepared were from urea and **8f-i** were prepared from phenylurea and are reported in Table III.

Oxidation of 5-Phenyl-4-α-bromobenzylimidazolin-2-one. Isolation of 4-Phenyl-5-benzoyl-2-imidazolinone (**9**).

5-Phenyl-4-α-bromobenzylimidazolin-2-one (**8a**, 0.5 g, 0.0015 mole) in dimethyl sulphoxide (15 ml) was refluxed for 2 hours at 150-160° in an oil bath. The reaction mixture was cooled and added to cold water (30 ml). A pale yellow precipitate was separated, filtered, dried and crystallised from carbon tetrachloride to afford 4-phenyl-5-benzoyl-2-imidazolinone (**9**), (0.25 g, 73%), mp 115°; ir (potassium bromide): ν max cm^{-1} 1685 (C=O), 1710 (C=O), 3380-3420 (NH); nmr (carbon tetrachloride): δ 7.2-7.9 (m, 12H, 10 Ar*H* and 2 N*H*).

Hydrolysis of **9** by Methanolic Potassium Hydroxide.

4-Phenyl-5-benzoyl-2-imidazolinone (**9**, 0.26 g, 0.001 mole) was stirred with saturated methanolic potassium hydroxide (5 ml) for 4 hours. Methanol was removed *in vacuo* to give a solid which was very well stirred with water. The insoluble portion was again filtered, washed with cold water to give benzylurea, (0.1 g, 70%) mp 145° (lit (18) mp 145-147°). The filtrate on acidification gave benzoic acid (0.1 g, 80%), mp 118°.

Typical Reaction of 1,3-Diphenyl-2,3-dibromo-1-propanone With *sym*-Diphenylurea. Isolation of 1,3-Diphenyl-4-benzoyl-5-phenylimidazolidin-2-one.

A mixture of 1,3-diphenyl-2,3-dibromo-1-propanone (1.82 g, 0.005 mole) and *sym*-diphenylurea (1.4 g, 0.005 mole) in glacial acetic acid (40 ml) was refluxed for 3 hours. The reaction mixture was cooled, added to cold water (100 ml) and neutralised with liquid ammonia to give a precipitate which was filtered and dried. Recrystallisation from hot ethanol gave green needles of 1,3-diphenyl-4-benzoyl-5-phenylimidazolidin-2-one (**11a**) (1.52 g, 72%) mp 175°; ir (potassium bromide): ν max cm^{-1} 1720 (C=O), 1645 (amide C=O); nmr (benzene-d_6): δ 5.75 (s, 2H), 7.1-7.8 (m, aromatic protons). Following identical procedure, four compounds **11a-d** have been prepared and reported in Table IV.

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