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Reaction of α,β-Unsaturated Ketones with Urea. Synthesis and Spectral Properties of 2(1*H*)-Pyrimidinone Derivatives

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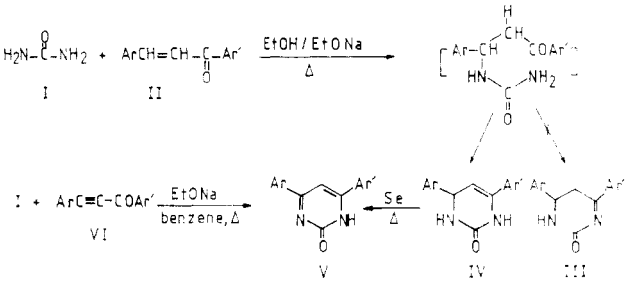
1,3-Diaryl-2-propen-1-ones react with urea to give 4,6-diaryl-3,4-dihydropyrimidinones (IVa–g) that can be further oxidized to the corresponding dehydro analogues (Va–f). The latter compounds are also obtained via interaction of aroylphenylacetylenes with urea. Spectral data, supporting the suggested structures IV and V, are presented.

The reaction of 1,3-diaryl-2-propen-1-ones (II) with urea (I) under acidic or basic conditions has been reported to give 4,6-diaryl-5,6-dihydro-2(1*H*)-pyrimidinones (III) (*1*, *2*). The procedures described therein were rather laborious. Recently we became interested in pyrimidinone syntheses, and this prompted us to reinvestigate the reaction of α,β-unsaturated ketones with urea.

When 1,3-diaryl-2-propen-1-ones (IIa–g) are refluxed with urea in the presence of sodium ethoxide in absolute ethanol for 1 h, they give the corresponding 4,6-diaryl-3,4-dihydro-2(1*H*)-pyrimidinones (IVa–g) (Scheme I), but not 4,6-diaryl-5,6-dihydro-2(1*H*)-pyrimidinones (III) as described previously by Sammour et al. (*2*). Under the same reaction conditions, the α,β-unsaturated ketones (IIh–j) afforded the corresponding 4,6-diaryl-2(1*H*)-pyrimidinone (Vd–f) (Scheme I). Prolonged refluxing (5 h) of IIe–g with urea also gave the corresponding 4,6-diaryl-2(1*H*)-pyrimidinones (Va–c). By analogy to the reaction of α,β-unsaturated ketones (II) with thiourea (*3*) and other nitrogen compounds (*4*), the formation of IV most likely involves initial 1,4-addition of urea to II and subsequent cyclization.

Scheme I



Compounds II and IV

	Ar	Ar′
a	C_6H_5	C_6H_5
b	C_6H_5	m-Cl C_6H_4
c	C_6H_5	p-$CH_3OC_6H_4$
d	C_6H_5	p-BrC_6H_4
e	C_6H_5	p-ClC_6H_4
f	C_6H_5	p-$CH_3C_6H_4$
g	p-$CH_3C_6H_4$	p-$CH_3C_6H_4$
h	p-$CH_3C_6H_4$	p-ClC_6H_4
i	p-$CH_3OC_6H_4$	p-BrC_6H_4
j	p-ClC_6H_4	p-BrC_6H_4

Compounds V

	Ar	Ar′
a	C_6H_5	p-ClC_6H_4
b	C_6H_5	p-$CH_3C_6H_4$
c	p-$CH_3C_6H_4$	p-$CH_3C_6H_4$
d	p-$CH_3C_6H_4$	p-ClC_6H_4
e	p-$CH_3OC_6H_4$	p-BrC_6H_4
f	p-ClC_6H_4	p-BrC_6H_4

Compounds VI

	Ar	Ar′
a	C_6H_5	p-ClC_6H_4
b	C_6H_5	p-$CH_3C_6H_4$
c	p-$CH_3C_6H_4$	p-$CH_3C_6H_4$

Structural Assignments

Spectroscopic data are in accord with structure IV rather than structure III. Thus, the IR spectra of the dihydropyrimidinones (IVa–g) exhibit absorptions at 3235–3215, 3090–3080, and 1685–1675 cm^{-1} which are assigned to the two –NH and the carbonyl groups, respectively (*5*). The ^1H NMR spectra of these compounds (Table I) show a multiplet in the region 5.58–4.77 ppm (2H) which corresponds to the olefinic and methine protons. The two N–H protons appear as two broad singlets in the region 8.70–8.33 and 7.60–7.30 ppm which disappear upon addition of D_2O. Furthermore, the MS data display M^+ together with characteristic peaks at *m/e* (M-

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Table I. Data for the Compounds IVa-g

compd[a]	formula[b]	mp, °C	% yield	^{1}H NMR[c] N–H	^{1}H NMR[c] C_4–H, C_5–H	^{1}H NMR[c] Ar, Ar′
IVa	$C_{16}H_{14}N_2O$	223–224	84	8.70 (br), 7.53 (br)	5.20–5.00 (2 H, m)	7.37–7.03 (10 H, m)
IVb	$C_{16}H_{13}ClN_2O$	235–236	87	8.67 (br) 7.56 (br)	5.30–5.10 (2 H, m)	7.50–7.25 (9 H, m)
IVc	$C_{17}H_{16}N_2O_2$	198–199	83	8.33 (br) 7.40 (br)	5.03–4.77 (2 H, m)	7.33–6.67 (9 H, m) 3.57 (CH_3, s)
IVd	$C_{16}H_{13}BrN_2O$	215–216	79	8.70 (br) 7.56 (br)	5.52–5.02 (2 H, m)	7.40–7.22 (9 H, m)
IVe	$C_{16}H_{13}ClN_2O$	230–231	85	8.67 (br) 7.60 (br)	5.58–5.10 (2 H, m)	7.50–7.17 (9 H, m)
IVf	$C_{17}H_{16}N_2O$	205–206	86	8.40 (br) 7.30 (br)	5.15–5.30 (2 H, m)	7.28–7.00 (9 H, m) 1.93 (CH_3, s)
IVg	$C_{18}H_{18}N_2O$	255–256	81	8.40 (br) 7.56 (br)	5.15–5.03 (2 H, m)	7.28–7.00 (8 H, m) 1.93 (2 CH_3, s)

[a] Compounds IVa–g were crystallized from methanol. [b] Elemental analyses (C, H, N, Br, Cl) were submitted for review and agree well with the theoretical values. [c] With Me_2SO-d_6, in ppm.

Table II. *m/z* Values and Relative Intensities (in Parentheses) of the Significant Ions in the Mass Spectra of Compounds IVa-g

compd	$[M]^+$	$[M - 1]^+$	$[M - 2]^+$	$[M - 3]^+$	$[M - H_2NCO]^+$	$[M - Ar]^+$	$[M - Ar']^+$
IVa	250 (44)	249 (85)	248 (20)	247 (40)	206 (2)	173 (100)	173 (100)
IVb	286/284 (40)	285/283 (60)	284/282 (4)	283/281 (6)	242/240 (8)	209/207 (70)	173 (100)
IVc	280 (59)	279 (100)	278 (18)	277 (22)	236 (18)	203 (30)	173 (22)
IVd	330/320 (11)	329/327 (15)	328/326 (1)	327/325 (1)	286/284 (3)	253/251 (12)	173 (100)
IVe	286/284 (60)	285/283 (100)	284/282 (3)	283/281 (4)	242/240 (10)	209/207 (63)	173 (52)
IVf	264 (40)	263 (70)	262 (5)	261 (10)	220 (12)	187 (100)	173 (30)
IVg	278 (36)	277 (60)	276 (4)	275 (11)	234 (10)	187 (100)	187 (100)

Table III. Data for the Compounds Va-f

compd[a]	formula[b]	mp, °C	% yield	^{1}H NMR[a] N–H	^{1}H NMR[a] Ar, C_5–H	*m/z* (rel intens)[c] $[M]^+$	*m/z* (rel intens)[c] $[M - 1]^+$
Va	$C_{16}H_{11}ClN_2O$	255–256	76	7.67 (1 H, br)	8.33–7.30 (10 H, m)	284/282 (60)	283/281 (100)
Vb	$C_{17}H_{14}N_2O$	300–301	78	7.70	8.33–7.30 (10 H, m) 2.40 (CH_3, s)	262 (75)	261 (100)
Vc	$C_{18}H_{16}N_2O$	274–275	79	7.70	8.33–7.30 (9 H, m) 2.40 (2 CH_3, s)	276 (65)	275 (100)
Vd	$C_{17}H_{13}ClN_2O$	312–313	80	7.57	8.23–7.10 (9 H, m) 2.30 (CH_3, s)	298/296 (60)	297/295 (100)
Ve	$C_{17}H_{13}BrN_2O$	275–277	78	*d*	*d*	358/356 (75)	357/355 (100)
Vf	$C_{16}H_{10}BrClN_2O$	210–211	80	*d*	*d*	364/362/360 (30)	363/361/359 (100)

[a] Compounds Va–f were crystallized from methanol. [b] Elemental analyses (C, H, N, Br, Cl) were submitted for review and agree well with the theoretical values. [c] (%) Ion abundance belongs to the light halogen isotope. [d] Insoluble.

1)$^+$, (M-2)$^+$, (M-3)$^+$, and (M–H_2NCO) (Table II). The UV spectra show absorption bands at about 350 and 280 nm attributable to π–π^* transitions of the styrene moiety (*5*).

Compounds IVe–g are oxidized upon heating with selenium at 180–200 °C for 30 min, to the corresponding 4,6-diaryl-2-(1*H*)-pyrimidinones (Va–c). The latter compounds are identical with the products obtained from the reaction of acetylenic ketones VIa–c with urea in the presence of sodium ethoxide (Scheme I). Structure V is supported by spectral data (Table III). Thus, the IR spectra of V show bands in the region 3090–3075 and 1615–1605 cm^{-1} attributed to the –NH and the carbonyl groups, respectively. The ^{1}H NMR spectra (Table III) exhibit a broad singlet in the region 7.70–7.57 ppm assigned to the –NH proton (exchangeable with D_2O). The UV spectra show absorption maxima in the ranges 350–342 and 282–258 nm ascribed to π–π^* transitions corresponding to the ^1L_b and ^1L_a bands and are characteristic of the pyrimidine nucleus (*6*).

Experimental Section

The IR spectra were recorded on a Perkin-Elmer 577 instrument using KBr pellets. The UV spectra were measured on a Pye-Unicam SP 8500 spectrophotometer. The ^{1}H NMR spectra were obtained with a Varian T 60-A spectrometer, using Me_4Si as the internal standard. The mass spectra were recorded on a Varian MAT –112 spectrometer, using the direct inlet technique. Melting points are uncorrected. Microanalyses were performed at the laboratory of the late F.Pascher/E. Pascher, Bonn, West Germany.

Reaction of 1,3-Diaryl-2-propen-1-ones with Urea. General Procedure. 1,3-Diaryl-2-propen-1-one (II) (0.03 mol) and urea (0.03 mol) were added successively to a solution of sodium ethoxide (0.03 mol) in absolute ethanol (100 mL). The reaction mixture was heated under reflux for 1 h. The solvent was evaporated and the residue was dissolved in water (150 mL). The resulting alkaline solution was acidified with acetic acid and the precipitated solid was separated by filtration. Crystallization of the crude products from methanol gave the corresponding 4,6-diaryl-3,4-dihydro-2(1*H*)-pyrimidinones (IVa–g). Under the same above reaction conditions, compounds IIh–j gave, with urea, the corresponding 4,6-diaryl-2(1*H*)-pyrimidinones (Vd–f).

Refluxing of compounds IIe–g with urea in ethanolic sodium ethoxide for 5 h also gave the corresponding –2(1*H*) pyrimidinones (Va–c). The latter compounds were obtained by oxidation of the respective dihydro-2(1*H*) pyrimidinones (IVe–g). This was accomplished by refluxing of IVe–g in absolute ethanol (in the presence of 3 mol of sodium ethoxide) for 3 h, or upon heating of IVe–g with selenium at 180–200 °C for 30 min.

Reaction of Aroylphenylacetylenes (VIa–c) with Urea. General Procedure. Aroylphenylacetylene (VI) (0.015 mol) in dry benzene (50 mL) was added to the sodium salt of urea (0.015 mol) in dry benzene (150 mL). The reaction, which gradually acquired a deep red color, was heated under reflux for 1 h. The reaction product was poured onto dilute aqueous hydrochloric acid (10%, 150 mL) and the benzene layer was separated, washed successively with water, sodium hydrogen

carbonate, and water, dried (sodium sulfate), and evaporated. Crystallization of the residual solid from methanol gave the corresponding 4,6-diaryl-2(1*H*)-pyrimidinones (Va-c) as colorless needles.

Registry No. I, 57-13-6; IIa, 94-41-7; IIb, 20426-48-6; IIc, 959-23-9; IId, 2403-27-2; IIe, 956-02-5; IIf, 4224-96-8; IIg, 21551-47-3; IIh, 19672-63-0; III, 51863-81-1; IIj, 6332-22-5; IVa, 4113-79-5; IVb, 97691-58-2; IVc, 49593-57-9; IVd, 97691-59-3; IVe, 97691-60-6; IVf, 49593-56-8; IVg, 97691-61-7; Va, 24030-13-5; Vb, 24030-10-2; Vc, 97691-65-1; Vd, 97691-62-8; Ve, 97691-63-9; Vf, 97691-64-0; VIa, 16616-42-5; VIb, 20442-65-3; VIc, 97691-66-2.

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Reactions with Heterocyclic Amidines: Synthesis of Several New Pyrazolo[1,5-*a*]pyrimidines and Pyrazolo[1,5-*c*]-*as*-triazines

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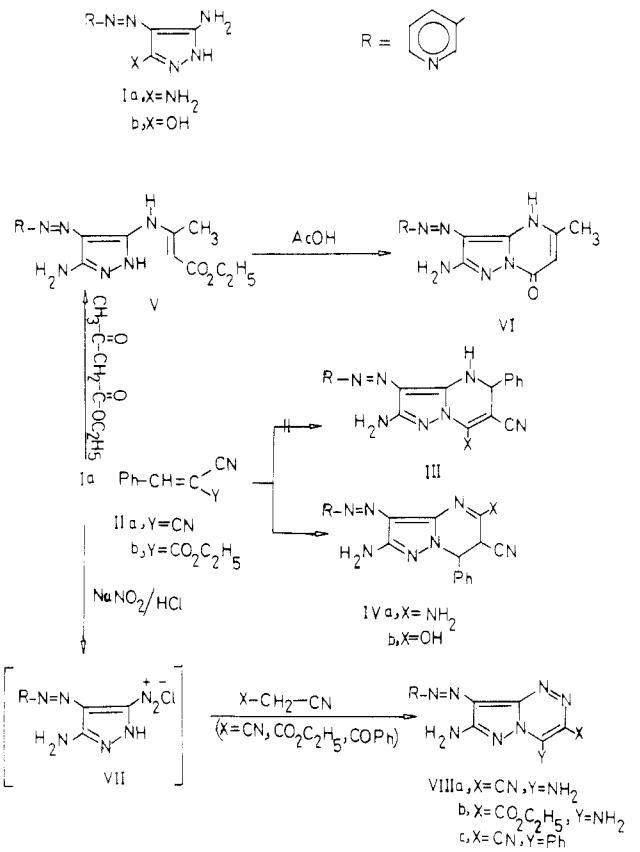
Several new pyrazolo[1,5-*a*]pyrimidines and pyrazolo[1,5-*c*]-*as*-triazines were obtained from 5-substituted-3-amino-4-(3-pyridylazo)pyrazoles (Ia,b) as starting components.

Aminopyrazoles are intermediates for the synthesis of biologically interesting pyrazole derivatives. In spite of the extensive literature reported for the chemistry of 5-aminopyrazoles (*1-3*), very little attention has been paid to the chemistry of 3,5-diaminopyrazoles (*4*) and of 3-amino-5-hydroxypyrazoles (*5*), although both compounds seem to be excellent reactants for further utility in the synthesis of fused azoles. Recently, Elnagdi et al. (*2*, *6*) have reported a new efficient synthesis of 4-arylazo-3,5-diaminopyrazoles and of 4-arylazo-3-amino-5-hydroxypyrazoles. In conjunction with this work it seemed of value to see if the reported synthesis and chemical reactivities for the above-mentioned compounds are general, and we report here the utility of 3,5-diamino-4-(3-pyridylazo)pyrazole (Ia) and 3-amino-5-hydroxy-4-(3-pyridylazo)pyrazole (Ib) (prepared following the procedure previously described by Elnagdi et al. (*2*, *6*)) for further utility in heterocyclic synthesis.

Thus, it has been found that Ia reacted with cinnamonitrile derivatives IIa,b to afford the corresponding pyrazolo[1,5-*a*]-pyrimidine derivatives IVa,b rather than the isomeric form III. Compound Ia also reacts with ethyl acetoacetate in refluxing ethanol to yield the 3-aminocrotonate derivative V. Compound V could be readily cyclized into the corresponding pyrazolo-[1,5-*a*]pyrimidine derivative VI by refluxing in acetic acid. The structure proposed for compounds IVa,b, V, and VI was established on the basis of analytical and spectral data of the resulting products. On the other hand, attempts to effect similar reactions with Ib were unsuccessful.

Compound Ia reacted with nitrous acid in presence of concentrated hydrochloric acid–acetic acid mixture to yield the corresponding diazonium salt VII which could not be isolated in pure state but its formation could be indicated via coupling with active methylene reagents. Thus, compound VII coupled with malononitrile, ethyl cyanoacetate, and benzoylacetonitrile to yield the corresponding pyrazolo[1,5-*c*]-*as*-triazines (VIIIa-c).



Experimental Section

All melting points are uncorrected. IR spectra were recorded (KBr) with a Shimadzu 408 spectrophotometer. ^1H NMR spectra obtained on an EM-390 90-MHz spectrophotometer using Me_4Si as internal indicator, and chemical shifts are expressed in ppm. Analytical data were obtained from the analytical data unit at Cairo University.

Reaction of Ia with Cinnamonitrile Derivatives IIa,b. A suspension of an equimolecular amount (0.01 mol) of Ia and

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