

STUDIES IN THE FORMATION OF HETEROCYCLIC RINGS CONTAINING NITROGEN

Part X. Condensation of *s*-Diphenyl and Phenyl Urea with Aromatic Aldehydes and Ammonium Acetate

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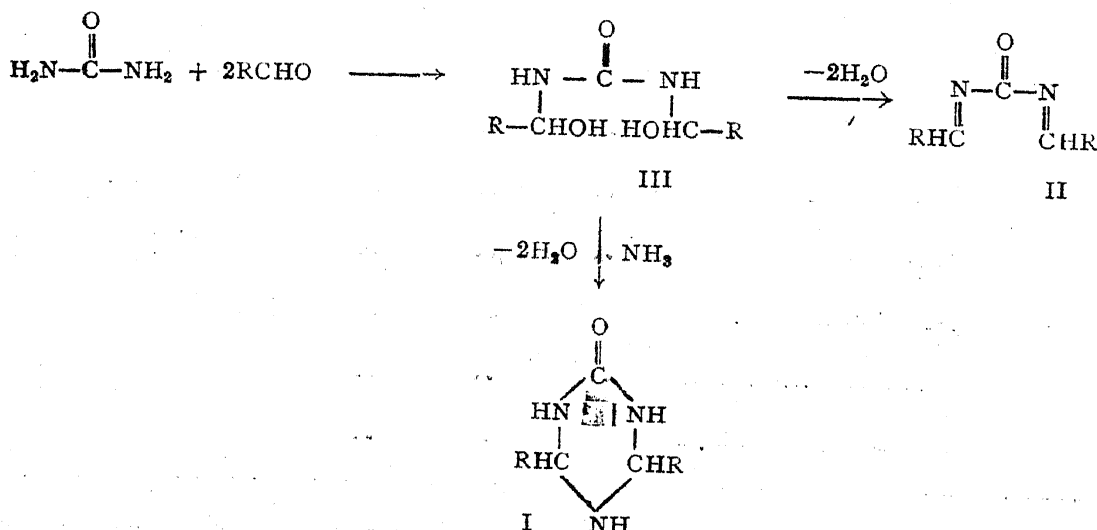
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ABSTRACT

Eight representative aromatic aldehydes with hydroxy, methoxy, nitro and chloro substituents have been condensed with *s*-diphenyl urea and ammonium acetate resulting in 2-keto-1, 3, 4, 6-tetra-aryl-hexahydro-*s*-triazines. The condensation of phenyl urea with five aldehydes and ammonium acetate, however, gave 1-phenyl-1:3-bis-(α -hydroxy aryl) ureas. The ultra-violet and infra-red spectra of these two types of compounds have been recorded.

In the condensation of urea with aromatic aldehydes and ammonium acetate reported earlier by the authors,¹ in addition to keto-hexahydro-*s*-triazines (I), 1,3-bis-arylidene ureas (II) were isolated. The formation of (II) was explained by the following step-wise mechanism:



With thiourea also analogous products, *i.e.*, thio-keto-hexa-hydro-*s*-triazines and 1:3-bis-arylidene thioureas were obtained². The only reported case of a

condensation making use of a substituted urea was by Paquin,³ who made use of dimethylol urea. It was considered worthwhile to study the condensation of some aryl-substituted ureas with a view to investigate whether or not 1:3-bis- α -hydroxybenzyl ureas (III) are the intermediate products in the formation of keto-hexahydro-*s*-triazines. It may be expected that with substituted ureas, the methylol type of compounds will be formed but not the arylidene compounds, thereby providing greater chance for the formation of keto-hexahydro-*s*-triazines.

Eight representative aldehydes containing hydroxyl, methyl, nitro and chloro-substituents have been condensed with *s*-diphenyl urea and ammonium acetate resulting in eight new 2-keto-tetra-aryl-hexahydro-*s*-triazines. The condensations have been effected in ethanol-glacial acetic acid mixture as the condensation did not proceed in ethanol. Attempts to isolate any other product or the unreacted diphenyl urea have been unsuccessful. The results of these experiments are summarised in Table I.

TABLE I
Products of condensation of s-diphenyl urea with aromatic aldehydes and ammonium acetate

Sl. No.	Name of Aldehyde	% yield of 2-keto-1:3-diphenyl-4:6-diaryl-hexa-hydro- <i>s</i> -triazines
1	Benzaldehyde	23.7
2	Salicylaldehyde	22.1
3	Anisaldehyde	10.6
4	<i>o</i> -Nitrobenzaldehyde	21.6
5	<i>m</i> -Nitrobenzaldehyde — — —	17.4
6	<i>p</i> -Nitrobenzaldehyde	45.7
7	<i>o</i> -Chlorobenzaldehyde	48.9
8	2:4-Dichlorobenzaldehyde	14.8

As was expected, the arylidene type of compounds could not be isolated in these condensations. The yield of the keto-triazines varied from 10.6% to 48.9%, the highest being in the case of *o*-chlorobenzaldehyde and the

lowest with anisaldehyde. The relatively lower yield in the case of *o*-chlorobenzaldehyde compared to that with simple urea (72.0%)¹ may be attributed to the use of acetic acid, which was found to give lower yields compared to simple alcohol.

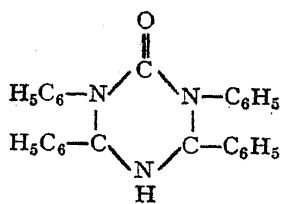
Benzaldehyde, salicylaldehyde and the three isomeric nitrobenzaldehydes on condensation with phenyl urea and ammonium acetate in 95% ethanol yielded 1-phenyl-1:3-bis-(α -hydroxy aryl) ureas alone. These hydroxy aryl ureas did not react with ammonium acetate to form keto-triazines. The results are presented in Table II.

TABLE II
Products of condensation of phenyl urea with aromatic aldehydes and ammonium acetate

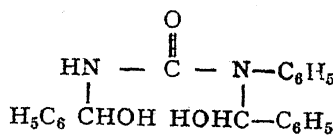
Sl. No.	Name of Aldehyde	% yield of 1-phenyl- 1:3-bis- (α -hydroxy aryl) ureas
1	Benzaldehyde	44.5
2	Salicylaldehyde	32.9
3	<i>o</i> -Nitrobenzaldehyde	28.4
4	<i>m</i> -Nitrobenzaldehyde	26.5
5	<i>p</i> -Nitrobenzaldehyde	25.0

From these studies it may be concluded that a *s*-disubstituted urea such as diphenyl urea reacts in a way similar to urea resulting in the formation of hexahydro-*s*-triazine but a mono-substituted urea such as phenyl urea reacts in a different manner, producing only α -hydroxy aryl ureas and not hexahydro-*s*-triazines. These two types of compounds may be distinguished on the basis of their ultra-violet absorption characteristics.

The absorption characteristics of 2-keto-1:3:4:6-tetraphenyl hexahydro-*s*-triazine (IV) and 1-phenyl-1:3-bis-(α -hydroxybenzyl) urea (V) have been studied.



IV



V

The ultra-violet absorption spectrum of (IV) exhibits a maximum at $255 \text{ m}\mu$ ($\log E_{\text{max.}} = 4.8798$). This is in agreement with our earlier observation.¹ The infra-red spectrum of this compound in Nujol shows a strong intensity absorption at 1650 cm.^{-1} (6.06μ) which is due to amide I band (carbonyl absorption) of the tertiary amide in the keto-*s*-triazine. The medium intensity band at 3400 cm.^{-1} (2.94μ) is assigned to secondary -NH stretching vibration and the strong band at 1550 cm.^{-1} (6.25μ) is due to HN-deformation. The ultra-violet absorption spectrum of (V) shows a maximum at $204 \text{ m}\mu$ ($\log E_{\text{max.}} = 4.0927$) and another at $241 \text{ m}\mu$ ($\log E_{\text{max.}} = 3.9867$). Thus U.V. absorption is helpful in distinguishing these two types of compounds. The amide I band in this compound appears at 1647 cm.^{-1} (6.07μ) and the amide II band (HN-deformation vibrations in secondary amide) at 1545 cm.^{-1} (6.47μ). The bands due to secondary -NH stretching appears at 3400 cm.^{-1} (2.94μ) in this compound also. A sharp weak band at 1120 cm.^{-1} (8.93μ) is assigned to -C-O- stretching vibration of the secondary alcoholic group and a very weak band at 1260 cm.^{-1} (7.93μ) may be due to -OH bending vibration of the same secondary alcoholic group.

EXPERIMENTAL

All m.p.'s are uncorrected.

A. General procedure for the condensation of *s*-diphenyl urea with aromatic aldehydes and ammonium acetate

Diphenyl urea (one mole), aromatic aldehyde (two moles), ammonium acetate (one mole) and a mixture of glacial acetic acid and ethyl alcohol in the ratio of 4:1 were slowly refluxed when a clear solution formed within a few minutes. After six hours of refluxing, the contents of the flask were cooled to room temperature and the mixture was slowly poured on crushed ice with continuous stirring. The solid that separated was dried and recrystallised from a suitable solvent. The analytical data and the properties of the new compounds are summarised in Table III.

TABLE III

No.	Aldehyde condensed	Name of compound	Crystalline shape	m.p. in °C.	Formula	Analytical values					
						Found %			Required %		
						C	H	N	C	H	N
1	Benzaldehyde	2-keto-1, 3, 4, 6-tetra-phenyl hexahydro- <i>s</i> -triazine	Colourless needles	122	$C_{27}H_{23}N_3O$	79.8	8.6	10.2	79.9	8.7	10.3
2	Salicylaldehyde	2-keto-1, 3-diphenyl-4: 6-di-(<i>o</i> -hydroxyphenyl) hexahydro- <i>s</i> -triazine	Pale yellow needles	240	$C_{27}H_{23}N_3O_3$	73.9	5.1	9.5	74.1	5.2	9.6
3	Anisaldehyde	2-keto-1, 3-diphenyl-4: 6-di-(<i>p</i> -methoxyphenyl) hexahydro- <i>s</i> -triazine	Colourless needles	234	$C_{29}H_{27}N_3O_3$	74.8	6.1	8.9	74.8	5.8	9.0
4	<i>o</i> -Nitrobenzaldehyde	2-keto-1, 3-diphenyl-4: 6-di-(<i>o</i> -nitrophenyl) hexahydro- <i>s</i> -triazine	Brownish-yellow needles	201	$C_{27}H_{21}N_5O_5$	65.3	4.1	14.1	65.5	4.2	14.1
5	<i>m</i> -Nitrobenzaldehyde	2-keto-1, 3-diphenyl-4: 6-di-(<i>m</i> -nitrophenyl) hexahydro- <i>s</i> -triazine	Pale yellow bushy needles	290	$C_{27}H_{21}N_5O_5$	65.1	4.1	14.2	65.5	4.2	14.1
6	<i>p</i> -Nitrobenzaldehyde	2-keto-1, 3-diphenyl-4: 6-di-(<i>p</i> -nitrophenyl) hexahydro- <i>s</i> -triazine	Yellow bushy needles*	210	$C_{27}H_{21}N_5O_5$	65.3	4.1	14.0	65.5	4.2	14.1
7	<i>o</i> -Chlorobenzaldehyde	2-keto-1, 3-diphenyl-4: 6-di-(<i>o</i> -chlorophenyl) hexahydro- <i>s</i> -triazine	Pale green needles	220	$C_{27}H_{21}N_3OCl_2$	68.2	4.4	8.7	68.3	4.4	8.8
8	2,4-Dichlorobenzaldehyde	2-keto-1, 3-diphenyl-4: 6-di-(2,4-dichlorophenyl) hexahydro- <i>s</i> -triazine	Colourless needles	204	$C_{27}H_{19}N_3OCl_4$	59.4	3.3	7.6	59.6	3.4	7.7

* Recrystallised from methanol. In other cases ethanol has been used as solvent.

TABLE IV

No.	Aldehyde condensed	Name of compound	Crystalline shape	m.p. in °C.	Formula	Analytical values					
						Found %			Required %		
						C	H	N	C	H	N
1	Benzaldehyde	1-phenyl-1,3-bis-(α -hydroxybenzyl) urea	Pale pink needles	189	$C_{21}H_{20}N_2O_8$	72.8	5.8	7.6	72.4	5.7	8.0
2	Salicylaldehyde	1-phenyl-1,3-bis-(α -hydroxy- <i>o</i> -hydroxybenzyl) urea	Yellow rectangular plates	140	$C_{21}H_{20}N_2O_5$	66.3	5.2	7.2	66.3	5.2	7.0
3	<i>o</i> -Nitrobenzaldehyde	1-phenyl-1,3-bis-(α -hydroxy- <i>o</i> -nitrobenzyl) urea	Yellow rectangular plates	140	$C_{21}H_{18}N_4O_7$	57.2	4.0	12.5	57.5	4.1	12.8
4	<i>m</i> -Nitrobenzaldehyde	1-phenyl-1,3-bis-(α -hydroxy- <i>m</i> -nitrobenzyl) urea	Pale yellow needles	193	$C_{21}H_{18}N_4O_7$	57.5	4.1	12.6	57.5	4.1	12.8
5	<i>p</i> -Nitrobenzaldehyde	1-phenyl-1,3-bis-(α -hydroxy- <i>p</i> -nitrobenzyl) urea	Deep orange plates	203	$C_{21}H_{18}N_4O_7$	57.4	4.1	12.7	57.5	4.1	12.8

B. General procedure for the condensation of phenyl urea with aromatic aldehydes and ammonium acetate

Phenyl urea (1 mole), aromatic aldehyde (2 moles) and ammonium acetate (1 mole) were refluxed for six hours in ethanol on a steam-bath. The reaction mixture on cooling to room temperature either solidified or the solvent was removed to get the product. The crude product was washed with hot water to remove traces of unreacted phenyl urea, and was recrystallised from a suitable solvent. The results are presented in Table IV.

Spectrophotometric determinations

(a) *Ultra-violet absorption spectra.*—The compounds were repeatedly purified from suitable solvents before the determination of the spectra. Ethanol (95%) was used as solvent. The ultra-violet spectrum was recorded on a Hilger U.V. Spectrophotometer using 1 cm. quartz cell and narrow slit width (0.12 mm.).

(i) 2-Keto-1,3,4,6-tetraphenyl-hexahydro-s-triazine
max. 255 m μ (log E_{max.} = 4.8798).

(ii) 1-Phenyl-1:3-bis-(α -hydroxybenzyl) urea
max. 204 m μ (log E_{max.} = 4.0927).
max. 241 m μ (log E_{max.} = 3.9867).

(b) *Infra-red absorption spectra.*—The absorptions were determined with the help of Infra cord Perkin Elmer 137 using sodium chloride optics. The compounds were thoroughly mixed with Nujol to get a mull. The characteristic absorptions with the corresponding intensities are recorded below:

(1) 2-Keto-1, 3, 4, 6-tetraphenyl hexahydro-s-triazine
3400 (m), 1650 (s), 1600 (s), 1550 (s), 1490 (w), 1310 (m),
1225 (s), 1145 (s), 1070 (w), 1040 (w), 1020 (w), 910 (w),
890 (w), 750 (s), 695 (s).

(2) 1-Phenyl-1,3-bis-(α -hydroxybenzyl) urea.
3400 (m), 1647 (s), 1600 (m), 1545 (m), 1490 (w), 1310 (w),
1260 (w), 1230 (w), 1120 (w), 1020 (w), 770 (w), 730 (w),
690 (m).

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