Fused *s*-Triazino Heterocycles. I. *s*-Triazino[2,1-*b*]quinazolinones and *s*-Triazino[1,2-*c*]quinazolinone (1)

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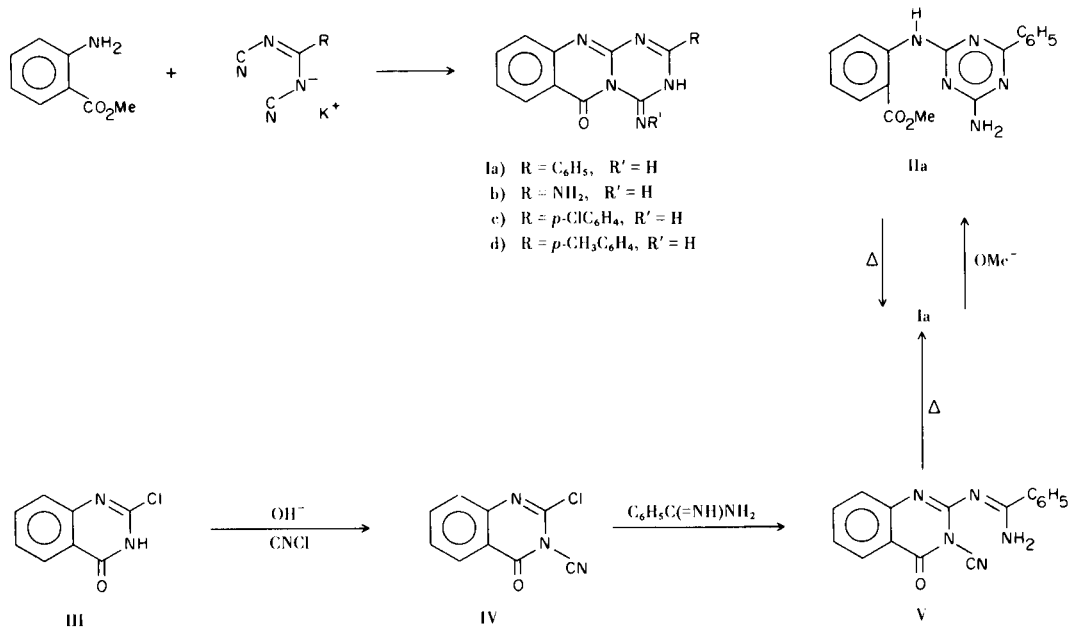
An earlier communication (2) indicated two methods whereby 2-phenyl-4-imino-3,4-dihydro-*s*-triazino[2,1-*b*]-quinazolin-6(6*H*)one (Ia) a member of a new ring system, could be prepared. The present paper confirms the structure of Ia as that originally proposed and elaborates on the use of these methods and others to prepare additional members of this new class. A preliminary result on the preparation of a new ring system *s*-triazino[1,2-c]quinazolinone is also presented.

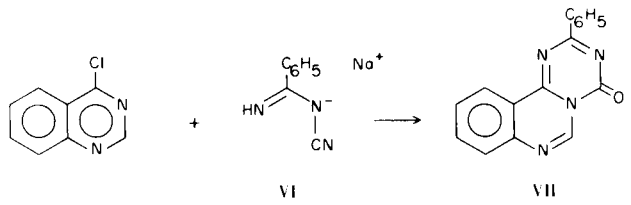
The work involved in the structure proof of Ia is outlined in Scheme I; only one of several possible tautomers of Ia is shown. The benzene sulfonic acid-catalyzed cyclization of potassium N,N^1-dicyanobenzamidine (1 mole) with methyl anthranilate (2 moles) in refluxing methanol, Method A, could have given 4-phenyl-2-imino-1,2-dihydro-*s*-triazino[2,1-*b*]quinazolin-6(6*H*)one and/or Ia. Previous work (2) had ruled out the alternate ring system, *s*-triazino[1,2-*a*]quinazolinone, also possible by this synthesis. Conversion of 2-chloro-3,4-dihydroquinazolin-4-one (III) to the sodium salt with sodium hydroxide followed by reaction with cyanogen chloride gave 2-chloro-3-cyano-3,4-dihydroquinazolin-4-one (IV) in 72% yield. Reaction of IV with benzamidine gave 2-benzamido-3-cyano-3,4-dihydroquinazolin-4-one (V) in 22% yield. Heating V for a few minutes in boiling dimethylformamide (DMF) resulted in formation of Ia. Use of IV to prepare other heterocyclic systems will be the subject of a future report.

We assume that structures Ic and Id are likewise appropriate for the products formed from the two other dicyanoarylamidine starting materials. While the mechanism whereby potassium N,N^1-dicyanobenzamidine is converted into Ia still remains unknown, it has been found that route does not involve the initial formation of IIa followed by a second ring closure to Ia. This was shown to be the case by refluxing IIa in methanol under the acidic conditions of Method A for the same period of time and recovering only unchanged IIa. Attempts to

SCHEME I



prepare another possible intermediate in the Method A synthesis, *N*-cyano-N^1-(3,4-dihydro-2-quinazolinyl-4-one)-benzamidine from *N*-cyanobenzamidine (VI) and III under acid, basic, or neutral conditions failed. However, a similar reaction using the more reactive 4-chloroquinazoline with the sodium salt of VI not only resulted in the displacement of the chloro-group but also in subsequent ring closure and loss of an imino-group to give 2-phenyl-*s*-triazino[1,2-*c*]quinazolin-4(4*H*)one (VII), a member of a new ring system.

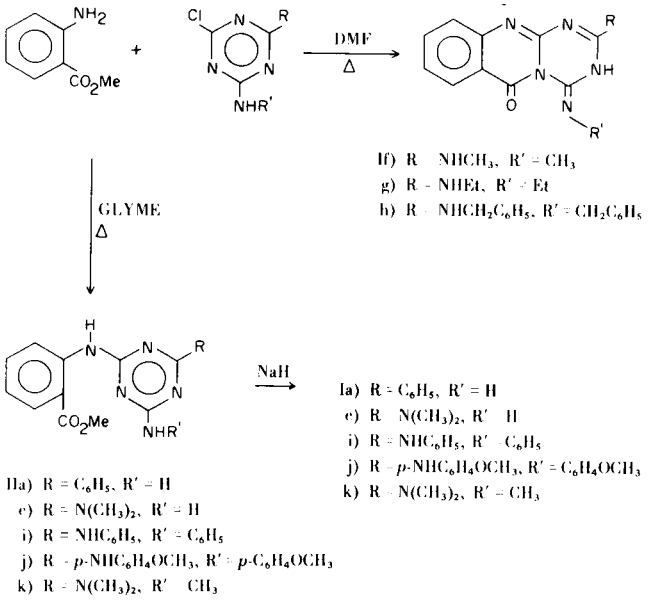


VI VII

FIGURE 1

The second method for the preparation of type I compounds suggested in the previous communication (2) was the heating of type II compounds above their melting points for a short period of time; by this means Ia had been prepared from IIa. It now appears that result was fortuitous, as none of the other II compounds (or their hydrochlorides) which were heated in the same manner gave I. Instead, the following was observed. When other members of type II were attempted under the same weakly acidic conditions used to prepare IIa, *i.e.* heating one mole of a monochloro-disubstituted *s*-triazine with 2 moles of methyl anthranilate in DMF at about 105° for 18 to 21 hours two things resulted: either I formed directly (Method B) (If, Ig, Ih in Scheme II) albeit in low yield, or II hydrochlorides formed but in a condition difficult to purify. It was found that changing the reaction solvent to 1,2-dimethoxyethane (glyme) gave the corresponding II hydrochlorides in high purity; these were easily converted to the free bases (IIa, IIe, IIi, IIj and IIk in Scheme II).

SCHEME II



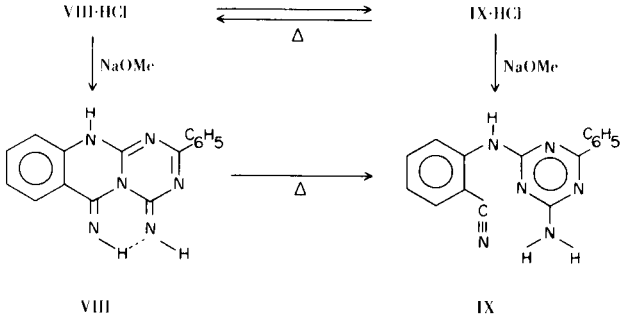
IIa) R = C_6H_5, R' = H
e) R = $N(CH_3)_2$, R' = H
i) R = NHC_6H_5, R' = C_6H_5
j) R = *p*-$NHC_6H_4OCH_3$, R' = *p*-$C_6H_4OCH_3$
k) R = $N(CH_3)_2$, R' = CH_3

If) R = $NHCH_3$, R' = CH_3
g) R = NHEt, R' = Et
h) R = $NHCH_2C_6H_5$, R' = $CH_2C_6H_5$

Ia) R = C_6H_5, R' = H
e) R = $N(CH_3)_2$, R' = H
i) R = NHC_6H_5, R' = C_6H_5
j) R = *p*-$NHC_6H_4OCH_3$, R' = *p*-$C_6H_4OCH_3$
k) R = $N(CH_3)_2$, R' = CH_3

Catalytic amounts of tri-*n*-propylamine in refluxing dimethylformamide resulted in very low yield conversion of IIj but not IIi to the corresponding I. Resorting to a more basic system (Method C) by converting the type-II compound dissolved in dry glyme to its sodium salt through the use of sodium hydride, now gave after subsequent ring closure Ii and also Ij in improved yield. Trial of Method C with IIa gave Ia in 82% yield thus being superior to any of the previous methods. With this fact in hand, the remaining type-I compounds investigated were prepared by Method C. It would appear that a steric factor may be operating as none of the following II-type compounds gave the corresponding I compounds using Method B or C; II (R = $NHCH(CH_3)_2$, R^1 = $CH(CH_3)_2$), II (R = NH-Cyclohexyl, R^1 = cyclohexyl) and 2,4-bis(dimethylamino)-6-[2-(methoxycarbonyl)phenyl]amino-*s*-triazine. The latter result may also reflect the possible need of at least one hydrogen on each of two substituted-amino groups in II.

The use of anthranilonitrile in place of methyl anthranilate with potassium dicyanobenzamidine under the conditions of Method A did not result in the formation of any type-I derivative. However, the reaction of anthranilonitrile with 2-amino-4-chloro-6-phenyl-*s*-triazine in refluxing glyme gave rise to a mixture of 2-phenyl-4,6-di-imino-4,6-dihydro-11-H-*s*-triazino[2,1-*b*]quinazoline hydrochloride (VIII HCl) (3) and 2-amino-4-(2-cyano-phenyl)amino-6-phenyl-*s*-triazine hydrochloride (IX HCl). The conversion of VIII HCl to its free base showed no

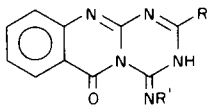


VIII IX

FIGURE 2

TABLE I

s-Triazino[2,1-*b*]quinazolin-6(6*H*)ones



Formula Number	R	R′	Method	Yield, %	M.p., °C	Molecular Formula	Analysis (%) Carbon (Found)	Hydrogen (Found)	Nitrogen (Found)
Ia	C_6H_5	H	A	51	342-343 dec.	$C_{16}H_{11}N_5O$	66.4 (66.6)	3.84 (3.90)	24.2 (24.4)
Ia			C	82					
Ib	NH_2	H	A	40	307-308 dec.	$C_{10}H_8N_6O$	52.6 (52.5)	3.53 (3.77)	36.8 (37.0)
Ic	*p*-ClC_6H_4	H	A	41	365-366 dec.	$C_{16}H_{10}ClN_5O$	59.4 (59.5)	3.12 (3.33)	21.6 (21.5)
Id	*p*-$CH_3C_6H_4$	H	A	55	337-339 dec.	$C_{17}H_{13}N_5O$	67.4 (67.3)	4.32 (4.55)	23.1 (22.8)
Ie	$N(CH_3)_2$	H	C	65	342-343 dec.	$C_{12}H_{12}N_6O$	56.3 (56.3)	4.73 (4.82)	32.8 (33.0)
If	$NHCH_3$	CH_3	B	28	318-319 dec.	$C_{12}H_{12}N_6O$	56.3 (56.3)	4.73 (4.87)	32.8 (32.5)
Ig	NHC_2H_5	C_2H_5	B	22	269-270	$C_{14}H_{16}N_6O$	59.2 (58.9)	5.68 (5.56)	29.6 (29.4)
Ih	$NHCH_2C_6H_5$	$CH_2C_6H_5$	B	23	265-267	$C_{24}H_{20}N_6O$	70.6 (70.7)	4.93 (4.85)	20.6 (20.4)
Ii	NHC_6H_5	C_6H_5	C	26	275-277	$C_{22}H_{16}N_6O$	69.5 (69.5)	4.22 (4.21)	22.1 (21.9)
Ij	*p*-$NHC_6H_4OCH_3$	*p*-$C_6H_4OCH_3$	C	23	283-285	$C_{24}H_{20}N_6O_3$	65.5 (65.5)	4.57 (4.71)	19.1 (19.3)
Ik	$N(CH_3)_2$	CH_3	C	84	216-218	$C_{13}H_{14}N_6O$	57.8 (57.8)	5.24 (5.26)	31.1 (30.9)

TABLE II

2,4-Disubstituted-6-[2-(methoxycarbonyl)phenyl]amino-*s*-triazine

Formula Number	R	R′	Cryst'n Solvent	Yield, %	M.p., °C	Molecular Formula	Analysis (%) Carbon (Found)	Hydrogen (Found)	Nitrogen (Found)
IIa	C_6H_5	H	Toluene	75	222-223	$C_{17}H_{15}N_5O_2$	63.5 (63.3)	4.72 (4.86)	21.8 (22.1)
IIe	$N(CH_3)_2$	H	Glyme	86	190-192	$C_{13}H_{16}N_6O_2$	54.2 (53.9)	5.61 (5.60)	29.2 (29.0)
IIi	NHC_6H_5	C_6H_5	Toluene	73	172-174	$C_{23}H_{20}N_6O_2$	67.0 (67.2)	4.89 (4.72)	20.4 (20.2)
IIj	p-$NHC_6H_4OCH_3$	p-$C_6H_4OCH_3$	Chloro-benzene	99	195-197	$C_{25}H_{24}N_6O_4$	63.5 (63.5)	5.13 (5.12)	17.8 (17.5)
IIk	$N(CH_3)_2$	CH_3	Methanol	87	139-141	$C_{14}H_{18}N_6O_2$	55.6 (55.9)	6.00 (6.02)	27.8 (27.6)

unexpected changes in the infrared spectrum but attempted recrystallization of VIII from nitrobenzene proved it to be heat labile and brought about gross changes in its ir, among which was the appearance of a nitrile band at 4.45 μ; this new material gave a satisfactory elemental analysis for IX. It was later found that simply heating dry VIII at 145-150° converted it completely to IX, while refluxing VIII HCl in glyme for 20 minutes resulted in its partial conversion to IX HCl.

EXPERIMENTAL

Melting points were determined in open capillaries on a Thomas-Hoover melting point bath and are uncorrected. Infrared spectra were recorded using a Perkin-Elmer Infracord Model 137. Analyses were performed by Micro-Analysis, Inc., Marshallton, Del. and by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

The chloro-*s*-triazines required for the preparation of the following I compounds listed in Table I were prepared by methods given in the literature: Ia(4a), Ie(4b), If(4b), Ig(4c), Ii(4c), Ij(4d), Ik(4b), Ih(5). Cyanogen chloride was obtained from the American Cyanamid Company. All of the type-I compounds were recrystallized from DMF.

2-Chloro-3-cyano-3,4-dihydroquinazolin-4-one (IV).

Cyanogen chloride gas was allowed to bubble into a stirred solution of 5.45 g. (0.03 mole) of III (6) in 30 ml. of 1*N* sodium hydroxide maintained at 2-5° until the *p*H decreased to 7-7.5. The precipitate which formed was stirred for an additional 5 minutes, filtered, washed with water and allowed to air dry: 4.46 g. (72%), m.p. 162-164°. An analytical sample was obtained by recrystallization from methylene chloride and cooling in a dry-ice bath: white crystals, m.p. 174-175°; ir λ (Nujol) 4.43 (C≡N), 5.75 (C=O), and 12.93 μ. No significant absorption 2.75-3.2 μ.

Anal. Calcd. for $C_9H_4ClN_3O$: C, 52.6; H, 1.97; N, 20.5. Found: C, 52.5; H, 2.12; N, 20.4.

2-Phenyl-4-imino-3,4-dihydro-*s*-triazino[2,1-*b*]quinazolin-6(6*H*)-one (Ia) and 2-Benzamidino-3-cyano-3,4-dihydroquinazolin-4-one (V) from 2-chloro-3-cyano-3,4-dihydroquinazolin-4-one (IV).

A stirred solution of 1.54 g. (0.008 mole) of benzamidine hydrochloride dihydrate in 10 ml. of methanol was treated slowly with 8 ml. of 1*N* methanolic sodium methoxide; the precipitate which formed was filtered and the filtrate was concentrated to a syrup by evaporation under reduced pressure. A stirred solution of this syrup in 20 ml. of glyme was cooled to -25° and treated in one portion with 0.80 g. (0.0039 mole) of IV. The temperature was maintained at -25 to -30° for 5 minutes and then allowed to rise to room temperature over 1 hour followed by an additional hour of stirring at room temperature. The solid material was separated by filtration and the filtrate was evaporated under reduced pressure to dryness. The yellow gummy residue was triturated with 3 ml. of methanol, filtered, washed with a little ether and then stirred with 3 ml. of water. The cream-colored solid was collected by filtration and after air drying weighed 0.25 g. (22%), m.p. 328-329° dec. An analytical sample of V was obtained by concentrating a solution of 0.05 g. of crude V in 150 ml. of methanol to about 20 ml. at reduced pressure (bath temperature < 25°), filtering the small amount of solid present and cooling the filtrate in a dry-ice bath. Collection of the white

precipitate by filtration gave, after air drying, 0.045 g., m.p. 344-345° dec. (turns yellow T >220°); ir λ (Nujol), 4.41 (C≡N), 5.88 μ (C=O).

Anal. Calcd. for $C_{16}H_{11}N_5O$: C, 66.4; H, 3.84; N, 24.2. Found: C, 66.6; H, 3.66; N, 24.5.

An attempt to recrystallize crude V from hot methanol resulted in initial solution followed by precipitation of a yellow solid, m.p. 338-339° dec; ir indicated the material to be a mixture of Ia and V. To complete the ring closure which began on heating with methanol, the yellow solid was boiled with a small amount of DMF for 3 minutes and the solution on cooling deposited bright yellow platelets, m.p. 342-343° dec.; ir λ (Nujol) 2.99 (NH), 5.91 C=O) and 13.11 μ. It was identical to that of Ia prepared by the other methods given below. Tlc of samples of Ia prepared by these various methods showed them to be the same (development solvent: ethyl acetate/methanol/conc.HCl// 75/25/0.25).

s-Triazino[2,1-*b*]quinazolin-6(6*H*)ones (I).

Method A.

A solution of 0.06 mole of a potassium N,N^1-dicyano-benzamidine, (7) 9.52 g. (0.063 mole) of methyl anthranilate, 4.37 g. (0.054 mole) of pyridine (or an additional 0.054 mole of methyl anthranilate, this latter modification giving the slightly improved yields reported in Table I) and 18.9 g. (0.12 mole) of anhydrous benzenesulfonic acid in 300 ml. of anhydrous methanol was stirred and refluxed for 18 hours. After cooling the solution to room temperature, it was treated dropwise with 60 ml. of 1*N* methanolic sodium methoxide, the final *p*H usually being around 8-9 to Hydrion-*p*H test papers. The mixture was then evaporated *in vacuo* to dryness; the solid residue was slurried with 150 ml. of ether and filtered, treated with water in the same manner, and then extracted with four 50 ml. portions of hot glyme. The crude triazino[2,1-*b*]quinazolin-6(6*H*)one remaining as insoluble residue from these hot extractions, was then recrystallized.

To investigate the effect of a higher reaction temperature with a protic solvent or the same reaction temperature with an aprotic solvent, 1-propanol and DMF were used respectively in place of methanol in the synthesis of Ia; in both cases much lower yields resulted. The negative result with the one alkyldicyanoamidine tried, sodium N,N^1-dicyanoacetamidine (7) was not too surprising as it fails to undergo the even simpler cyclization which aryldicyanoamidines do with alkyl, alkoxy and halo-substituted anilines to yield 1,4-diaryl-2,6-diimino-1,2,3,6-tetrahydro-*s*-triazines (8).

Method B.

A mixture of 0.02 mole of a 2-chloro-4,6-disubstituted-*s*-triazine, 6.05 g. (0.04 mole) of methyl anthranilate and 40 ml. of DMF was stirred and heated at 103-106° for 21 hours. The clear solution was cooled to 10° and 1*N* methanolic sodium methoxide was added dropwise until the *p*H of the solution was 8-9 (Hydrion paper). The yellow precipitate which formed was collected by filtration, washed with ether, and stirred with 25 ml. cold water for 30 minutes. The suspended solid was filtered, oven dried at 60° and recrystallized. Carrying out the same reaction in refluxing DMF lowered the yields of If, Ig, and Ih.

Method C.

An amount of 0.01 mole of 2,4-disubstituted-6-[2-(methoxycarbonyl)phenyl]amino-*s*-triazine (II) in sufficient dry glyme (dried by refluxing with and distilling from calcium hydride) to give solution at 45-55° was treated in portions with 0.48 g. (0.01 mole) of sodium hydride (50% dispersion in mineral oil). The stirred mixture was maintained at this temperature range for 2 hours and the precipitate which had formed was collected by filtration and washed with ether. The filter cake was added to 200 ml. of vigorously stirred ice and water and the *p*H was quickly adjusted to 5-6 with acetic acid. The solid was collected by filtration after being stirred for 15 minutes and then washed with water, aspirated damp-dry, oven-dried at 60° and then recrystallized.

All of the type-I compounds prepared had the following spectral characteristics in the ir: λ (Nujol) 2.95-3.17 (NH), 5.91-6.00 (C=O), and 12.95-13.11 μ (probably an aromatic peak). All were yellow solids.

2-Phenyl-4-imino-3,4-dihydro-*s*-triazino[2,1-*b*]quinazolin-6(6*H*)-one (Ia) from Fusion of 2-Amino-4-[2-(methoxycarbonyl)phenyl]-amino-6-phenyl-*s*-triazine (IIa) (9).

An amount of 2 g. of IIa in an 8 inch test tube was placed in oil bath maintained at 230-250° for 20 minutes. The white solid melted, bubbled, turned yellow and then resolidified. The crude material after Soxhlet extraction with acetone weighed 1.16 g. (65%), m.p. 335-336° dec. Recrystallization from DMF gave Ia.

2,4-Disubstituted-6-[2-(methoxycarbonyl)phenyl]amino-*s*-triazines (II).

General Procedure.

A mixture of 0.01 mole of 2-chloro-4,6-disubstituted-*s*-triazine and 3.02 g. (0.02 mole) of methyl anthranilate in 2.5 ml. of dry glyme (50 ml. was used in the preparation of IIa and IIi) was heated at reflux with stirring for 18 hours. The insoluble hydrochloride was filtered hot, washed with a small portion of glyme and then neutralized to *p*H 8-9 by adding 1*N* methanolic sodium methoxide to a stirred slurry of II HCl in DMF. The resulting mixture was poured into 150 ml. of vigorously stirred ice-water, stirred for an additional 10 minutes, and the precipitate collected by filtration; after oven-drying at 60° the compound was recrystallized using the solvent indicated in Table II.

2-Amino-4[2-(methoxycarbonyl)phenyl]amino-6-phenyl-*s*-triazine (IIa) from 2-Phenyl-4-imino-3,4-dihydro-*s*-triazino[2,1-*b*]quinazolin-6(6*H*)one (Ia) (9).

A slightly turbid solution of 1 g. (0.0035 mole) of Ia in 50 ml. of methanol was slowly treated with 9 ml. of 1*N* methanolic sodium methoxide. The heavy white precipitate which formed in a few minutes was filtered, washed with ether, and after oven-drying at 60° weighed 1 g., m.p. 221-224°. Recrystallization from toluene gave IIa identical to IIa prepared by the method used for compounds listed in Table II.

2-Phenyl-4,6-diimino-4,6-dihydro-11-H-*s*-triazino[2,1-*b*]quinazoline Hydrochloride (VIII HCl) (3) and 2-Amino-4-(2-cyanophenyl)-amino-6-phenyl-*s*-triazine (IX).

A solution of 2.36 g. (0.02 mole) of anthranilonitrile and 2.06 g. (0.01 mole) of 2-amino-4-chloro-6-phenyl-*s*-triazine in 40 ml. of dry glyme was refluxed and stirred for 18 hours. The precipitate which had formed at the reflux was filtered after cooling to room temperature and filtrate (IX F) was saved. The filter cake was washed with ether, air-dried and then oven-dried at 60°: 0.94 g., m.p. 228-230° dec.; *p*H of a dilute aqueous solution was 3-4 to Hydrion paper. After normal recrystallization methods failed, an analytical sample was obtained by extracting the crude material with three 15 ml. portions of hot glyme: VIII HCl, m.p. 233-235° dec.; ir λ (Nujol), 2.9, 3.1 μ (NH), no significant absorption 4-5 μ.

Anal. Calcd. for $C_{16}H_{12}N_6 \cdot HCl$: C, 59.2; H, 4.04; N, 25.8. Found: C, 58.9; H, 4.32; N, 25.5.

A stirred slurry of 0.85 g. of crude VIII·HCl in 10 ml. of DMF maintained at 10° was converted to the free base by dropwise addition of 1*N* methanolic sodium methoxide until a *p*H of 8-9 was reached. The mixture was poured into 75 ml. of ice water, stirred, filtered, washed with water, air-dried, then oven-dried at 60°: 0.55 g., m.p. 212-213° (a spurious m.p.; *cf.* below); ir λ (Nujol) 3.0-3.2 μ (broad NH), no significant absorption 4-5 μ. Recrystallization from nitrobenzene to obtain an analytical sample changed the melting point slightly and the infrared spectrum significantly: m.p. 213-215°; ir λ (Nujol) 2.89, 2.94, 3.06 (NH), 4.45 μ (C≡N). This material gave a satisfactory analysis for IX.

Anal. Calcd. for $C_{16}H_{12}N_6$: C, 66.7; H, 4.20; N, 29.2. Found: C, 66.9; H, 3.99; N, 29.1.

Later it was found that simply heating dry VIII at 145-150° gave IX. Thus the melting point recorded above for crude VIII is probably that of IX to which it reverts on heating.

The filtrate, IX F, was evaporated *in vacuo* and the residue was triturated with ether, filtered, and the filter cake (cyano-peak at 4.48 μ) was converted to the free base in the same manner as that used for VIII HCl. Recrystallization from nitrobenzene gave material identical to IX.

2-Phenyl-*s*-triazino[1,2-*c*]quinazolin-4(4*H*)one (VII).

A stirred solution of 2.06 g. (0.01 mole) of *N*-cyanobenzamidine (10,11) in 30 ml. of dry DMF (dried over and distilled from calcium hydride) was maintained at 2-4° while 0.48 g. (0.01 mole) of sodium hydride (50% oil dispersion) was added in portions. The mixture was stirred for an additional 30 minutes and then a solution 2.48 g. (0.015 mole) of 4-chloroquinazoline (12) in 10 ml. of dry DMF was added dropwise rapidly. The temperature rose from 2 to 6° and was held at 2 to 5° for 2 hours, then allowed to warm to room temperature. Finally after being stirred for 16 hours at 50 to 55°, the *p*H was adjusted to 4-5 with acetic acid and the mixture was evaporated *in vacuo* using a rotary evaporator. The residue was triturated with 10 ml. of methanol, filtered, and the dry filter cake was boiled with 50 ml. of toluene and filtered. The filtrate was evaporated *in vacuo* to dryness: 0.29 g. m.p. 214-218°. An analytical sample was obtained by recrystallizing from acetonitrile: m.p. 226-228°; ir λ (Nujol). No significant absorption, 2.7-3.2 or 4-5 μ; 5.93 μ (C=O).

Anal. Calcd. for $C_{16}H_{10}N_4O$: C, 70.1; H, 3.68; N, 20.4. Found: C, 70.0; H, 3.72; N, 20.3.

REFERENCES

(1) Taken in part from the Senior Honors Projects of Diane M. Taylor, 1970, Franklin J. Corbett, 1970, and John D. Ballentine, 1969.

(2) J. T. Shaw and J. Ballentine, *Chem. Commun.*, 1040, (1969).

(3) An alternate structure, 4-phenyl-2,6-diimino-2,6-dihydro-11-H-*s*-triazino[2,1-*b*]quinazoline hydrochloride, is also possible by this synthesis.

(4a) H. K. Reimschuessel and N. T. McDevitt, *J. Am. Chem. Soc.*, 82, 3760 (1960); (b) W. Pearlman and C. Banks, *ibid.*, 70, 3726 (1948); (c) J. T. Thurston, J. R. Dudley, D. W. Kaiser, I. Hechenbleikner, F. C. Schaefer and D. Holm-Hansen, *ibid.*, 73, 2983, (1951); (d) F. H. S. Curd, J. K. Landquist and F. L. Rose, *J. Chem. Soc.*, 154 (1947).

(5) 2-Chloro-4,6-bis(benzylamino)-*s*-triazine, m.p. 240-241°, was prepared using method of Thurston *et al.* (4c), *Anal.* Calcd. for $C_{17}H_{16}ClN_5$: C, 62.7; H, 4.94; N, 21.5. Found: C, 62.7; H, 4.90; N, 21.4.

(6) F. H. S. Curd, J. K. Landquist and F. L. Rose, *J. Chem. Soc.*, 755 (1947).

(7) J. T. Shaw, *J. Org. Chem.*, 27, 3890 (1962).

(8) J. T. Shaw, U. S. Patent No. 3,215,693 (1965); *Chem. Abstr.*, 64, 2110 (1966).

(9) This experiment was mentioned in a previous communication (2) but no experimental details were given.

(10) K. R. Huffman and F. C. Schaefer, *J. Org. Chem.*, 28, 1812 (1963).

(11) J. T. Shaw and R. Adams, *J. Chem. Eng. Data*, 13, 142 (1968).

(12) H. C. Scarborough, B. C. Lawes, J. L. Minielli and J. L. Compton, *J. Org. Chem.*, 27, 957 (1962).