The photolysis of II in inert solvents at room temperature using 365μ also produces I,[4–6] the molar conversion of II into I for a given solvent being essentially the same as for the thermal decomposition at *ca.* 80°. Because I is effectively stable under the conditions of the photodecomposition but is destroyed readily at *ca.* 80° in solution, it was expected that the photodecomposition of II would afford a preparative route for I giving higher yields than the thermal decomposition method with a less complicated procedure. The results obtained supported expectation.

The molar conversion of II into I during the photodecomposition of II is solvent dependent.[6] Benzene was picked as the reaction solvent as a compromise between the aim to obtain the maximum conversion[5,6] of II into I and the wish to carry out the photodecomposition in a convenient, small volume of solvent with moderate volatility.

Experimental

A solution of 164 g. (1.00 mole) of Porophor N (Recrystallized) 2,2′-azobisisobutyronitrile (II) in 0.80 l. of dry reagent grade thiophene-free benzene at *ca.* 45° in 1-l. round-bottom Pyrex flask, through which dry nitrogen (Matheson, Prepurified) bubbled, was placed in a 4-l. Pyrex beaker containing running tap water at 16 ± 2°. After a preliminary purge period of 30 min., during which some II precipitated, the reaction mixture was irradiated for 48 hr. with occasional stirring, by which time all the precipitate had dissolved and the nitrogen evolution had essentially stopped. Irradiation was carried out with the flask and water-jacket inside an aluminum enclosure using two Mazda type ME/D 250 watt extra-high pressure mercury vapor projection lamps of the rectangular metal box variety set *ca.* 20 cm. apart and aimed horizontally at the center of the solution *ca.* 15 cm. away. Each lamp was run with its supplied 6-mm.-thick glass window in place.[11] Following the irradiation, the reaction mixture was concentrated under reduced pressure, filtering off precipitate at intervals, pot temperature 15 ± 5°, the pressure being taken down to 0.5 mm. The precipitate, a total of 55 g., was impure tetramethylsuccinonitrile,[12] III, repeated crystallization from ethanol yielding a pure specimen, m.p. (uncor.) 169–170°, lit.–*e.g.*, 170°,[3] 168.5–169°,[5] and 167–168°.[8] Next the brown filtered concentrate was distilled at 0.2–0.3-mm. pressure, pot temperature 30–45°, yielding 48 g. of colorless liquid I, $n^{30}\text{D}$ 1.444_6, of 96 ± 1 mole % purity estimated from the refractive index and those of mixtures of I and III with known composition (yield, 35%). Two further distillations of this material at 0.2–0.3-mm. pressure, pot temperature 28–32°, collecting the middle 80% fraction gave a product comparable to that prepared before.[3,5] N.m.r. analysis[3] showed it to contain III as the only impurity and the purity to be at least 99.0 mole %, $n^{25}\text{D}$ and $n^{30}\text{D}$, respectively, 1.447_0 and 1.444_9 (lit., $n^{20.0}\text{D}$ 1.449_1,[3] $n^{25}\text{D}$ 1.4470–1.4473,[7] $n^{30.0}\text{D}$ 1.444_9[5]).

An attempt to repeat this photopreparation with similar experimental conditions, but using 0.80-l. of dry reagent grade cyclohexane in place of the benzene and employing vigorous mechanical stirring to keep the crystals of II in suspension, was unsuccessful. After irradiating for 48 hr. and concentrating the reaction mixture as before, the residual amount of I was only a trace. This is not surprising for both II and III are essentially insoluble in cyclohexane at 16 ± 2° and, at a given temperature, II in the solid state is considerably more thermally stable than when dissolved in an inert solvent.[6]

---

(11) Examination using a Cary Model 11 spectrophotometer showed this window to be optically equivalent to *ca.* 12 mm. of Pyrex glass. Allowing for the water-jacket and reaction flask, the reaction mixture was estimated to be protected by the equivalent of *ca.* 16 mm. of Pyrex. This provides ample protection for the I formed.[8]

(12) Aside from I, this is the chief organic product of the photodecomposition of II in benzene solution at 25° using 365 μ radiation, and the photodecomposition of I under similar conditions yields II as the major product eg (P. E. Miller, N. Muller, P. Smith, and W. C. Tosch, unpublished analyses by the n.m.r. method[8]).

The Preparation of *s*-Triazine Derivatives Containing the N—O Bond. II.[1] Hydroxylamino Derivatives of *s*-Triazine

JOHN T. SHAW, ELIZABETH R. NICOTTRA, AND
RICHARD K. MADISON

*Research Department, Organic Chemicals Division,
American Cyanamid Company, Bound Brook, New Jersey*

Received May 11, 1962

A literature search revealed that hydroxylamino-*s*-triazines were only represented by two members: 2,4 - bis(*p* - chlorophenyl) - 6 - hydroxylamino-*s*-triazine[2] and 2,4-bis(trichloromethyl)-6-hydroxylamino-*s*-triazine.[3] The preparation of the latter compound involved the reaction of a chlorotriazine, 2-chloro-4,6-bis(trichloromethyl)-*s*-triazine, and hydroxylamine. This method was found to be quite useful and the compounds shown in Table I were prepared in this fashion. In those reactions where the replaceable chlorine was substituted by the hydroxylamino group, a large excess of hydroxylamine was required to obtain yields greater than 50%. The preparation of the various alkoxyamino derivatives shown in Table I followed well established procedures[4] for the preparation of aminotriazines from the corresponding halotriazines.

As a class, the unsubstituted and N-substituted hydroxylaminotriazines gave purple and sometimes dark green, blue, or black colors with ferric chloride; O-substituted derivatives did not. All of the compounds considered are white to pale lavender solids which usually melt with decomposition. The unsubstituted hydroxylaminotriazines generally showed some solubility in dilute warm acid or base; N- or O-substitution increased the alkali solubility considerably. None of the compounds tested reduced Fehling's or Tollens' reagents.

Experimental[5]

Materials and Methods.—With the exception of cyanuric chloride, which is available from the American Cyanamid

---

(1) Part I; J. T. Shaw, *J. Org. Chem.*, in press.

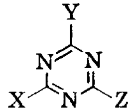
(2) C. Grundmann and H. Schroeder, *Chem. Ber.*, **87**, 747 (1954).

(3) H. Schroeder, *J. Am. Chem. Soc.*, **81**, 5658 (1959).

(4) J. T. Thurston, *et al.*, *ibid.*, **73**, 2981 (1951).

(5) All melting points are uncorrected. Microanalyses by Mr. John Kobliska and his staff.

TABLE I
HYDROXYLAMINO-s-TRIAZINE DERIVATIVES



Compound	X	Y	Z	M.p., °C.	Yield,[a] %	Method[b]	Calcd.			Found		
							C	H	N	C	H	N
1	HONH—	HONH—	HONH—	218 dec.[c]	27	D	20.7	3.44	48.2	20.4	3.39	47.9
2	HONH—	HONH—	$(C_2H_5)_2N$—	183–185 dec.	57	A	39.2	6.57	39.2	39.5	6.63	39.0
3	HONH—	HONH—	$C_6H_5N(CH_3)$—	172–175 dec.[d]	56	A	48.4	4.84	33.9	48.6	5.19	33.8
4	HONH—	HONH—	CH_3	220 dec.	43	D	30.5	4.48	44.6	30.3	4.60	44.3
5	HONH—	HONH—	o-$(MeO)C_6H_4$[e]	208–209 dec.	78	A	48.1	4.42	28.1	48.3	4.47	28.4
6	HONH—	C_2H_5NH—	C_2H_5NH—	193–196 dec.	86	A	42.4	7.07	42.4	42.1	7.01	42.2
7	HONH—	$C_5H_{10}N$—	$C_5H_{10}N$—[e]	207–209 dec.[f]	31	A	56.2	7.96	30.2	55.9	7.90	30.0
8	$HON(CH_3)$—	$HON(CH_3)$—	$(C_2H_5)_2N$—	151–152[g]	82	A-1	44.7	7.44	34.7	45.0	7.76	34.6
9	$HON(C_6H_5)$—	$HON(C_6H_5)$—	Cl—[h]	230–232 dec.	87	B	54.7	3.64	21.2	54.7	2.83	21.2
10	CH_3ONH—	CH_3ONH—	CH_3ONH—[i,j]	207–208 dec.	78	C	33.3	5.56	38.9	33.6	5.80	39.2
11	CH_3ONH—	CH_3ONH—	Cl—	167–168	55	B	29.2	3.89	34.1	29.4	3.82	34.1
12	CH_3ONH—	CH_3ONH—	$(C_2H_5)_2N$—	105–108[k]	52	C	44.7	7.44	34.7	44.5	7.39	34.6
13	CH_3ONH—	CH_3ONH—	p-Cl-C_6H_4NH—	195 dec.	90	C	44.5	4.39	28.3	44.6	4.77	28.8
14	CH_3ONH—	CH_3ONH—	C_6H_5O—	119–123	69	D	50.2	4.95	26.6	50.0	5.18	26.7
15	C_2H_5ONH—	C_2H_5ONH—	Cl—	164–165 dec.	43	B	36.1	5.19	30.0	36.2	4.28	29.8
16	n-C_4H_9ONH—	n-C_4H_9ONH—	Cl—	174–175 dec.	74	B	44.6	6.92	24.2	44.3	6.71	23.9
17	CH_3ONH—	Cl—	Cl—[l]	147–151 dec.	78	B	24.6	2.05	28.7	24.8	1.89	28.6
18	CH_3ONH—	H_2N—	H_2N—[m]	248–250 dec.	70	C	30.8	5.13	53.8	30.8	5.16	53.5
19	CH_3ONH	C_2H_5NH—	C_2H_5NH—[n]	88–91 dec.	37	C	45.3	7.55	39.6	45.2	7.24	39.3
20	CH_3ONH—	CH_3O	CH_3O—[o]	136–138	76	C	38.7	5.43	30.1	38.9	5.37	30.0
21	$CH_3ON(CH_3)$—	$CH_3ON(CH_3)$—	$CH_3ON(CH_3)$—	66–67	83	D	41.8	7.00	32.6	41.9	6.98	32.9

[a] The yield of material which was suitable for further reactions. [b] Methods A, A-1, B, and C refer to general methods which are illustrated by representative examples in the Experimental section; method D indicates a method which was sufficiently different to warrant giving the experiment in detail. [c] Recryst. from water. [d] Recryst. from methanol. [e] The product was precipitated by addition of water to reaction mixture. [f] The crude product was purified by extracting impurities away with hot isopropyl alcohol. [g] Recryst. from benzene. [h] Phenylhydroxylamine was added as a solution in dioxane. [i] The product was prepared from 2-chloro-4,6-bis(methoxyamino)-s-triazine. [j] Two moles methoxyamine/mole triazine were used; 1 eq. sodium hydroxide/mole triazine was employed to neutralize the acid released. [k] M.p. partially 93–97°, resolidifies and melts entirely 105–108°. [l] Reaction conditions: addition of methoxyamine at −1 to 10° followed by 1 eq. sodium hydroxide (per 1 eq. methoxyamine) at 2–7°, then 2 hr. at 5°; filtration and washing in the cold, and air drying on a porous plate. [m] This product was prepared from 2,4-diamino-6-chloro-s-triazine; methoxyamine/triazine = 4; 1 eq. sodium/mole triazine was used to neutralize the acid released. [n] This product was prepared from 2,4-dichloro-6-methoxyamino-s-triazine and excess ethylamine; mole ethylamine/mole triazine = 5.5; no sodium hydroxide was used. The aqueous mixture was refluxed 2 hr.; the product is an oil which solidifies on standing. [o] This product was prepared from 2-chloro-4,6-bis-(methoxy)-s-triazine; solid sodium carbonate (1 eq./mole triazine) used to neutralize the acid released. The reaction temperature was 75–80° for 0.5 hr.

Co., the various aminochlorotriazine intermediates were prepared by methods given in the literature.[4] Methoxyamine hydrochloride (E. G. Sargent Co.) and N-methylhydroxylaminehydrochloride (Aldrich Co.) were used without further purification, while O,N-dimethylhydroxylamine hydrochloride,[6] ethoxyamine hydrochloride,[7] and butoxyamine hydrochloride[7] were prepared by methods given in the literature. Wherever possible, general methods (A, B, or C) were used for the preparation of the hydroxylamino and substituted hydroxylamino-*s*-triazine derivatives shown in Table I. Experiments illustrating each of these methods are given. Experiments falling outside these general methods are reported separately (D).

Where ambiguity might arise as to what halotriazine starting material was used in a particular synthesis, the one employed is given in the footnotes to Table I. All hydroxylamino and N-substituted hydroxylamino-*s*-triazines were prepared from the corresponding chlorotriazines in one step by reaction with hydroxylamine or a substituted hydroxylamine. Many of the compounds prepared did not require recrystallization; where recrystallization was necessary, the solvent used is given in the footnotes to Table I.

2-Diethylamino-4,6-bis(hydroxylamino)-s-triazine, Method A: Hydroxylamine/Replaceable Chlorine = 4.—A solution of 469 g. (6.75 moles) of hydroxylamine hydrochloride in 560 ml. of water was neutralized at a temperature below 22° with a solution of 250 g. (6.25 moles) of 97% sodium hydroxide in 560 ml. of water. (The system was kept free of air as much as possible to avoid oxidation of the hydroxylamine.) The aqueous solution of hydroxylamine was then treated dropwise at 2–6° with 177 g. (0.80 mole) of 2,4-dichloro-6-diethylamino-*s*-triazine dissolved in 720 ml. of dioxane. After completion of the addition (70 min.), the mixture was heated for 1.5 hr. at 55–60°, refluxed at 90° for 3.5 hr., and then chilled; the product was precipitated by adding 1 l. of water. After having been filtered and dried at 65° for 24 hr., the product weighed 98.4 g.

Method A-1.—Method A is essentially followed with these exceptions: hydroxylamine/replaceable chlorine = 2; after refluxing 0.5 hr., 1 mole of aqueous sodium hydroxide per atom of replaceable chlorine is added over a 0.5-hr. period followed by 3 hr. of additional reflux; precipitation of the compound is aided by the addition of sodium chloride.

2-Chloro-4,6-bis(methoxyamino)-*s*-triazine, Method B.—An aqueous dioxane slurry of cyanuric chloride was prepared by adding in portions a solution of 27.7 g. (0.15 mole) of cyanuric chloride in 60 ml. of dioxane to 200 ml. of ice water at 0–10°. To the vigorously stirred slurry was added dropwise at 0–5° a solution of methoxyamine prepared by neutralizing a solution of 25 g. (0.3 mole) of methoxyamine hydrochloride in 73 ml. of water with 12.5 g. (0.3 mole) of 97% sodium hydroxide in 33 ml. of water at a temperature less than 25°. The addition required 43 min., the final pH being 4: the mixture was allowed to warm to 24° (a little heat finally being required); the pH was now 1. A solution of 12.5 g. (0.3 mole) of 97% sodium hydroxide in 37 ml. of water was added dropwise over a 15-min. period during which the temperature rose to 43° and the pH finally was 8. The mixture was allowed to cool to 35° over a 20-min. period, then chilled in ice for 1 hr. and filtered; the cake was washed well with water. The dry cake weighed 16.8 g. and melted partially at 167–168°.

2-Diethylamino-4,6-bis(methoxyamino)-*s*-triazine, Method C.—A slurry of 5 g. (0.025 mole) of 2-chloro-4,6-bis(methoxyamino)-*s*-triazine in 20 ml. of water was treated with 1.77 g. (0.0243 mole) of diethylamine and the mixture was slowly heated to reflux. Addition of 24.3 ml. of 1 *N* sodium hydroxide then followed at such a rate as to keep the mixture neutral or slightly alkaline. The pale yellow oil which formed became a hard plastic-like solid on cooling. The aqueous phase was decanted and the solid residue, after stirring and breaking up with fresh water, was allowed to air dry: 3.0 g., m.p. 97–104°. An amount of 2.7 g. of this material was recrystallized from 80 ml. of hexane and about 1.5 ml. benzene. The oven-dried (52°) material weighed 1.21 g. and gave a negative Beilstein test. The material was soluble in 3 *N* caustic and reprecipitated on acidification with acetic acid. (Caution—below pH 4 the material redissolves.)

2,4-Bis(hydroxylamino)-6-methyl-*s*-triazine.—An intimate mixture of 68 g. (0.976 mole) of hydroxylamine hydrochloride and 77.6 g. (0.73 mole) of sodium carbonate, when added to 400 ml. of ether, formed a slurry. To this stirred slurry was added 40 ml. of water and then the mixture was cooled to −10°, stirred for 10 min., and then treated dropwise at −10 to −5° with a solution of 40 g. (0.244 mole) of 2,4-dichloro-6-methyl-*s*-triazine in 400 ml. of ether. After completion of the addition which took 0.75 hr., the mixture was stirred at −10 to 0° for 1.5 hr. and then allowed to warm to room temperature and stirred for 4 days. The ether was decanted and the residue was stirred vigorously with 500 ml. of water, filtered, and after air drying several hours, was placed in a 60° oven and dried to constant weight; 41.3 g. of a white solid which gave a violet color with ferric chloride, m.p. 213° dec. Recrystallization of 20 g. from water acidified to pH 5 with acetic acid gave 8 g.

2,4,6-Tris(hydroxylamino)-*s*-triazine.—A solution of 167 g. (2.4 mole) of hydroxylamine hydrochloride in 200 ml. of water was cooled to −10° and neutralized by dropwise addition of a solution of 96.7 g. of 99.2% sodium hydroxide (2.4 moles), the temperature being maintained at −10 to −5°. To the resultant stirred solution at −10 to 0° was added dropwise a solution of 36.9 g. (0.2 mole) of cyanuric chloride in 100 ml. of dioxane over a period of 0.5 hr. The mixture was stirred at 0–5° for 1 hr., followed by 50–60° for 2 hr., followed by a final reflux (91°) for 1 hr. A clear violet solution formed, final pH 6. After cooling overnight and then chilling the next morning to 0°, the mixture was filtered, 15.3 g., m.p. > 300°; recrystallization of 8 g. from 120 ml. of water gave 3.5 g., m.p. 207° dec. (vigorous). Analysis of this material was 98% of theory. It was found that an analytical sample could be obtained in the following way. An amount of 6.5 g. of the crude material was stirred with 50 ml. of water at 30° for 5 hr.; after filtering and drying, there was obtained 4 g. of a pale lavender solid.

2,4-Bis(methoxyamino)-6-phenoxy-*s*-triazine.—To a solution of 2.4 g. of (0.0255 mole) of phenol and 1.02 g. (0.0255 mole) of 97% sodium hydroxide in 25 ml. of water was added 5.0 g. (0.0243 mole) of 2-chloro-4,6-bis(methoxyamino)-*s*-triazine. The mixture was refluxed for 4 hr., cooled, and the aqueous phase decanted from the taffy-like material which was placed *in vacuo* over phosphorus pentoxide. The dry material was ground up and weighed 4.4 g.

2,4,6-Tris(N-methyl-N-methoxyamino)-*s*-triazine.—A solution of 4.72 g. (0.0256 mole) of cyanuric chloride in 20 ml. of dioxane was added dropwise at 2–5° to 30 ml. of water (containing a little ice). The slurry which formed was treated dropwise at 0–5° with an aqueous solution of O,N-dimethylhydroylamine [prepared by neutralizing 10 g. (0.112) of O,N-dimethylhydroxylamine hydrochloride in 30 ml. of water with 4.22 g. (0.112) of 97% sodium hydroxide in 20 ml. of water]. The mixture was allowed to warm at 19°, a few drops of phenolphthalein added, and then an aqueous solution of 3.13 g. (0.076 mole) of 97% sodium hydroxide in 20 ml. of water was added dropwise until the solution was alkaline (4/5 of the total caustic was required). The mixture was slowly heated to reflux during which time the remaining caustic was added, and was refluxed for 15 min. after completion of the addition. The mixture was cooled, evaporated at room temperature to one third volume, and the crystals filtered and air dried, 5.5 g. This material, after recrystallization from 25 ml. of water (forms an oil which solidifies on cooling), weighed 4.1 g.

---

[6] (a) L. W. Jones, *Am. Chem. J.*, **20**, 38 (1898). (b) R. T. Major and E. E. Fleck, *J. Am. Chem. Soc.*, **50**, 1479 (1928).

[7] A. T. Fuller and H. King, *J. Chem. Soc.*, 963 (1947).