was about 5%. It will be referred to subsequently as mixture A.

Anal. Calcd. for phenyldibromoindole $C_{14}H_9NBr_2$: C, 47.89; H, 2.58; N, 3.99; mol. wt., 351. Calcd. for phenylbromochloroindole $C_{14}H_9NBrCl$: C, 54.84; H, 2.96; N, 4.57; mol. wt. 306. Calcd. for equimolar mixture: C, 51.22; H, 2.76; N, 4.27; mol. wt., 328. Found: C, 51.09, 51.57, 50.99, 52.73; H, 3.10, 2.90, 2.76, 2.64; N, 4.16, 4.37; Br (all halogen calcd. as Br), 46.12, 45.14; mol. wt. (Menzies-Wright), 348.

Hydrogenation of Mixture A.—A solution of 0.111 g. of mixture A and 0.2 g. of sodium hydroxide in 50 ml. of ethanol was hydrogenated at 50 p.s.i. in the presence of Raney nickel for four hours at room temperature. The mixture was filtered free of catalyst, and the latter was extracted with boiling ethanol, which was added to the original filtrate. The ethanol solution was evaporated to dryness, the residue was washed free of sodium halides with distillled water, and the organic material was dissolved in ether. The water solution gave good qualitative tests both for chloride and for bromide ions. The ether solution yielded, after removal of the solvent, a crude product from which 0.056 g. of a white crystalline product, m.p. 185–187°, was obtained by recrystallization from ethanol. No m.p. depression was observed when this sample was mixed with authentic[23] 2-phenylindole.

Reaction of Acetophenone 2,6-Dichlorophenylhydrazone with Zinc Bromide.—A slurry of 300 g. of anhydrous zinc bromide in a solution of 73 g. of acetophenone 2,6-dichlorophenylhydrazone in 500 ml. of nitrobenzene was stirred and heated at 150–175° for ten minutes. After removal of the nitrobenzene by steam distillation, the mixture was subjected to the general procedure described previously. Extraction and sublimation gave 23.6 g. of a pasty yellow material, from which 12.1 g. of faintly yellow needles, m.p. 134.5–136°, were obtained by crystallization from ethanol. Recrystallization from petroleum ether (b.p. 65–110°) yielded fine, white needles, m.p. 139–139.5°, hereafter referred to as "mixture B." The mother liquors from the first crop of crystals yielded a second crop of the same m.p. No other crystalline material could be isolated from the reaction mixture. There was no m.p. depression when mixtures B and A were mixed, and mixture B and 2-phenyl-5-bromo-7-chlorindole also showed no m.p. depression. In view of the fact that there is no appreciable m.p. depression in any of the mixtures of 2-phenyl-5,7-dihaloindoles, the failure of mixture B to show m.p. depressions with other compounds and mixtures of the series discloses nothing about its constitution.

Anal. Calcd. for phenyldichloroindole $C_{14}H_9NCl_2$: C, 64.14; H, 3.46; N, 5.34. Calcd. for phenylbromochloroindole $C_{14}H_9NBrCl$: C, 54.84; H, 2.96; N, 4.57. Calcd. for mixture 70 mole % (*ca.* 75 wt. %) in $C_{14}H_9NBrCl$: C, 57.33; H, 3.09; N, 4.78. Found: C, 57.21, 57.14; H, 3.09, 3.18; N, 4.79.

Spectra of Indoles.—Ultraviolet absorption spectra were measured with a Beckman Model DU quartz spectrophotometer. Solutions in ethanol were about 3×10^{-5} *M*.

Infrared spectra were measured with a Perkin–Elmer Model 21 double beam spectrophotometer equipped with a sodium chloride prism. The spectra were determined in carbon disulfide solutions of 20 mg. per ml. concentrations.[24]

(23) R. L. Shriner, W. C. Ashley and E. Welch, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 725.

(24) The ultraviolet and infrared spectra referred to in this paper have been deposited as Document number 5111 with the ADI Auxiliary Publication Project Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be obtained by citing the Document number and by remitting $1.25 for photoprints or $1.25 for 35 mm. microfilm, in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

PITTSBURGH 13, PENNSYLVANIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Preparation of Triazines by the Reaction of Biguanide and Esters[1]

BY C. G. OVERBERGER, FRANCIS W. MICHELOTTI[2] AND PHILIP M. CARABATEAS[2]

RECEIVED AUGUST 22, 1956

Compounds of type II and III have been synthesized by the reaction of phenyl biguanide or *p*-chlorophenyl biguanide and biguanide, respectively, with appropriate esters. Methylation experiments with 4,6-diamino-2-methyl-*s*-triazine have demonstrated that conventional techniques useful for 2-aminopyrimidine derivatives fail. Successful methylation can be achieved with methylamine hydrochloride at higher temperatures.

In previous work,[3] compounds of type II were synthesized as precursors for the synthesis of vinyltriazines. When some of these compounds were screened for biological activity,[4] it was found that they exhibited some anti-rheumatic and diuretic properties. It was therefore of interest to synthesize compounds of type II, R = CH_2Cl, X = Cl; R = CHBrCl, CF_3, $CHCl_2$, X = H and type III, R′ = CHBrCl, CH_2Cl, $CHCl_2$ to test their activity in the above mentioned areas. The general reaction is diagrammed in the reaction scheme.

Compounds of type III, R′ = CH_2Cl, CHBrCl and $CHCl_2$, were synthesized from the appropriate α-haloester and biguanide. All attempts to synthesize biguanide according to the procedure described by Rackmann[5] failed, guanylurea being isolated in every case as evidenced from the melting point, preparation of the picrate and a mixed melting point with an authentic sample of guanylurea. Biguanide was then synthesized according to the procedure described by Smolka and Friedrich[6] and the free base by that of Slotta and Tschesche.[7]

Although Thurston has reported the reaction of biguanide with haloesters to give haloalkyl guanamines,[8] compound III, R′ = CH_2Cl, was not de-

(1) This is the thirteenth in a series of articles concerned with the synthesis of monomers and their precursors; for the twelfth paper in the series, see C. G. Overberger and Alexander Lebovits, THIS JOURNAL, **78**, 4792 (1956).

(2) This paper comprises portions of theses presented by Francis W. Michelotti in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School and Philip M. Carabateas for the degree of Bachelor of Science at the Polytechnic Institute of Brooklyn.

(3) (a) C. G. Overberger and S. L. Shapiro, THIS JOURNAL, **76**, 93 (1954); (b) S. L. Shapiro and C. G. Overberger, *ibid.*, **76**, 97 (1954); (c) C. G. Overberger and S. L. Shapiro, *ibid.*, **76**, 1061 (1954).

(4) These compounds and subsequent ones reported here were suggested for biological activity by the Eli Lilly Co. and will be reported separately.

(5) K. Rackmann, *Ann.*, **376**, 169 (1910).

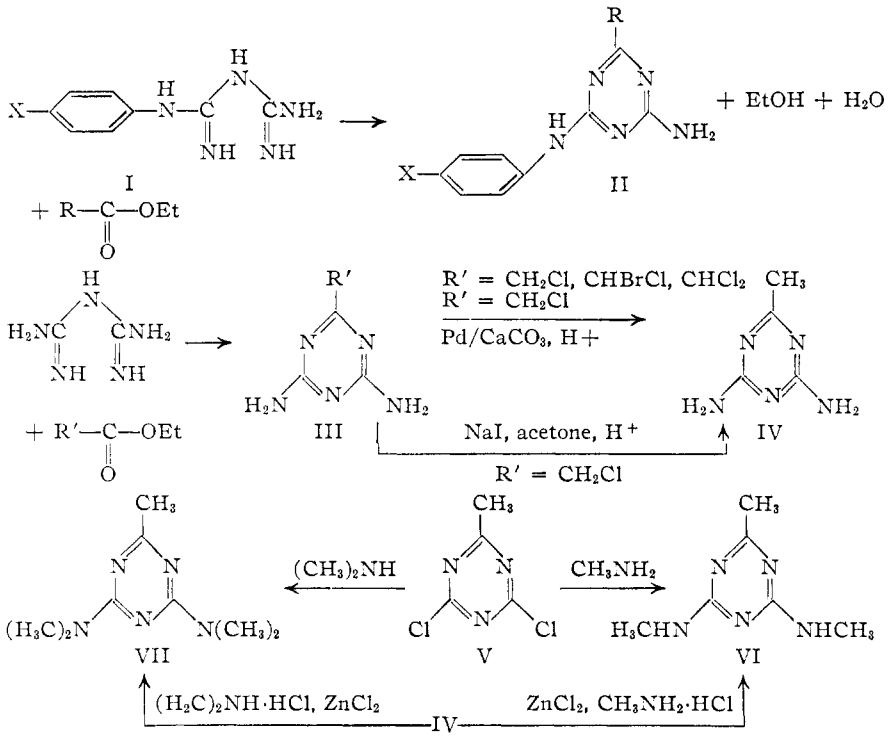
(6) A. Smolka and A. Friederich, *Monatsh.*, **10**, 86 (1889).

(7) K. H. Slotta and R. Tschesche, *Ber.*, **62B**, 1396 (1929).

(8) J. T. Thurston, U. S. Patent 2,463,471, March 1, 1949.

scribed. This compound has been prepared[9] recently by the alkoxide-catalyzed reaction of ethyl α-chloroacetate with biguanide sulfate in 45% yield. Slotta and Tschesche, who had apparently previously prepared this compound, assigned an incorrect bicyclic structure.[7] We have synthesized this compound without an alkoxide catalyst in 82% yield essentially according to the general procedure described by Thurston.[8] Catalytic hydrogenation of III, R′ = CH_2Cl, over palladium-on-calcium carbonate in acidic medium resulted in the isolation of IV, identical with the product obtained by the sodium iodide reduction in acetone of this same material. Compound IV was unequivocally synthesized from biguanide and ethyl acetate in 44% yield.

REACTION SCHEME



Similarly, III, R′ = $CHCl_2$, CHBrCl, were synthesized from biguanide with ethyl dichloroacetate and ethyl chlorobromoacetate,[10] respectively. Compound III, R′ = $CHCl_2$, was first synthesized by Nencki[11] by treating a water suspension of IV with chlorine, but no melting point was reported for this compound.

Failure of III, R′ = $CHCl_2$, to react with sodium iodide in acetone is similar to the reported inertness of II, R = $CHCl_2$, X = H, toward this same reagent.[3b]

Synthesis of II, R = CH_2Cl, X = Cl, was effected by the alkoxide-catalyzed condensation of ethyl α-chloroacetate with *p*-chlorophenylbiguanide I, X = Cl, in 33% yield. In addition to the monohydrate as described by Curd and Rose,[12] *p*-chlorophenylbiguanide exists in two anhydrous forms[13] melting at 129 and 146°.

In a recent paper, Overberger and Kogon[14] developed procedures for the methylation of 2-aminopyridine by means of methyl iodide with potassium carbonate and without base. Since Brown, Hoerger and Mason[15] have recently demonstrated that this reaction proceeds through nuclear methylation to give 1,2-dihydro-2-imino-1-methylpyrimidine hydroiodide, which in alkaline solution easily rearranges to 2-methylaminopyrimidine, it was of interest to determine whether analogous intermediates were involved in the methylation of IV with methyl iodide and base to give VI. However, this compound proved to be completely inert to methyl iodide without base and even in the presence of potassium carbonate. Attempts to methylate IV with lithium amide in refluxing benzene or xylene also failed. Methylation of IV to give VI was achieved by using a phenolic solution of methylamine hydrochloride in the presence of zinc chloride at 180° according to a general procedure for methylating alkyl guanamines as described by Thurston.[16] Compound VII was obtained in only trace amounts by a modified procedure. As proof of structure, VI and VII were independently synthesized from cyanuric chloride. The intermediate, 4,6-dichloro-2-methyl-*s*-triazine (VI), was prepared by the procedure described by Hirt, Nidecker and Bechtold.[17] Compound VI was reported by Traube and Gorniak[18] by heating acetylmethylguanidine above its melting point; the melting point 241° reported for VI, however, could not be duplicated.

In an effort to prepare 4,6-diamino-2-vinyl-*s*-triazine (not described in this paper), biguanide was treated with methyl acrylate in the absence of sodium methoxide catalyst according to the general procedure described by Thurston[19] for the preparation of α,β-unsaturated guanamines. In this case, however, we found that only the 2β-methoxyethylguanamine (III, R′ = $CH_2CH_2OCH_3$) was isolable. In the reaction of biguanide with methyl methacrylate Thurston[19] reported a 10% yield

(9) V. Ettel and J. Nosek, *Chem. Listy*, **46**, 289 (1952).
(10) H. Crompton and P. M. Triffitt, *J. Chem. Soc.*, **119**, 1874 (1921).
(11) M. Nencki, *Ber.*, **9**, 238 (1876).
(12) F. H. S. Curd and F. L. Rose, *J. Chem. Soc.*, 362 (1946).
(13) A. F. Bekhli, V. N. Ufinstev and K. S. Topchiev, *J. Appl. Chem.*, **20**, 591 (1947).
(14) C. G. Overberger and I. C. Kogon, THIS JOURNAL, **76**, 1065 (1954).
(15) D. J. Brown, E. Hoerger and S. F. Mason, *J. Chem. Soc.*, 4035 (1955).
(16) J. T. Thurston, U. S. Patent 2,385,766, September 25, 1945.
(17) R. Hirt, H. Nidecker and R. Bechtold, *Helv. Chim. Acta*, **33**, 1365 (1950).
(18) W. Traube and K. Gorniak, *Z. Angew. Chem.*, **42**, 379 (1929).
(19) J. T. Thurston, U. S. Patent 2,461,943, February 15, 1949.

of 2β-methoxyisobutyroguanamine (III, R′ = $CHCH_3CH_2OCH_3$) in addition to the main reaction product, methacryloguanamine (III, R′ = $CCH_3 = CH_2$). The diminished reactivity of the methacrylate esters in a β-addition type reaction has been observed by Pollard, Rietz and Robbins[20] and Howton.[21]

Experimental[22]

6-Amino-4-anilino-2-chlorobromomethyl-*s*-triazine (II, R = CHBrCl, X = H).—The procedure was similar to that reported in reference 3b. A sodium methoxide solution was prepared from 3.45 g. (0.15 g. atom) of sodium and 125 ml. of methanol and cooled to −40°. To this, 29.4 g. (0.15 mole) of ethyl chlorobromoacetate[10] was added with stirring, followed by 26.5 g. (0.15 mole) of phenyl biguanide with continued stirring until the mixture reached room temperature. Then a solution of 12.5 ml. of concentrated hydrochloric acid in 37.5 ml. of methanol was added and the mixture allowed to stand overnight. The mixture was then filtered, the filtrate poured into water, allowed to stand several hours and the solid removed by filtration. The first precipitate was extracted with hot acetone, the solid removed and the acetone diluted to give more crude product. The two precipitates were combined and recrystallized from a methanol–water solution with decolorizing carbon, m.p. 168–169°, 19.5 g. (41%).

Anal.[23] Calcd. for $C_{10}H_9N_5ClBr$: C, 38.18; H, 2.85; Br, 25.10. Found: C, 38.68; H, 2.99; Br, 24.99.

6-Amino-4-anilino-2-trifluoromethyl-*s*-triazine (II, R = CF_3, X = H).—Ethyl trifluoroacetate, 14.3 g. (0.1 mole), and 17.7 g. (0.1 mole) of phenyl biguanide dissolved in 150 ml. of chloroform were refluxed for 4 hr. The chloroform was removed by steam distillation. The reaction mixture was cooled and the solid removed by filtration. The precipitate was recrystallized from methanol–water, m.p. 182–183°, 14.9 g. (58%).

Anal. Calcd. for $C_{10}H_8N_5F_3$: C, 46.72; H, 3.89; N, 27.26. Found: C, 47.06; H, 3.32; N, 27.58.

4,6-Diamino-2-chloromethyl-*s*-triazine (III, R′ = CH_2Cl). —A solution of 25 g. (0.25 mole) of biguanide in 250 ml. of absolute methanol was prepared and ethyl α-chloroacetate (30.6 g., 0.25 mole) was added dropwise with stirring over a period of 0.5 hr. The mixture which warmed slightly was stirred for 2.5 hr. longer. The resulting precipitate was filtered off and dried to yield 25.3 g. of crude product. Concentration of the mother liquor to 50 ml. yielded another 10.6 g. of crude product. The two crops were combined and recrystallized from 1.3 l. of water to yield 32.2 g. of pure product (81.7% yield), browning gradually on heating and decomposing without melting at 210–214°.

Anal. Calcd. for $C_4H_6N_5Cl$: C, 30.09; H, 3.79; Cl, 22.22. Found: C, 30.32; H, 3.61; Cl, 22.25.

Hydrogenation of III, R′ = CH_2Cl.—2-Chloromethylguanamine, 2 g. (0.013 mole), was suspended in 150 ml. of water, and concentrated hydrochloric acid was added dropwise until complete solution was attained. Then 0.4 g. of palladium-on-calcium carbonate was added and the mixture hydrogenated on a Paar apparatus at three atmospheres for 24 hr.

The mixture was then filtered and the water removed under reduced pressure. The residue was recrystallized from water–methanol and dissolved again in a small volume of water. A 10% sodium hydroxide solution was added dropwise until a solid separated which on drying melted at 275°, 1.15 g. (74%) (IV).

Reaction of III, R = CH_2Cl, with Iodide Ion.—2-Chloromethylguanamine, 2.5 g. (0.016 mole), was added to a solution of 24 g. of sodium iodide in acetone followed by the addition of 2 ml. of glacial acetic acid. The reaction mixture turned dark brown almost instantly. After the reaction mixture was shaken for 4 hr., the solid was removed by filtration and the residue washed successively with 10-ml. portions of acetone and absolute ethanol. The above procedure was repeated once more and the residue was recrystallized first from a solution of 2 g. of sodium hydroxide in 40 ml. of water containing a trace of sodium bisulfite and finally from pure water, 0.5 g. of IV, m.p. 275°. A mixed melting point with an authentic sample of IV was not depressed.

4,6-Diamino-2-dichloromethyl-*s*-triazine (III, R′ = $CHCl_2$).—To a stirred solution of 8 g. (0.08 mole) of biguanide in 30 ml. of absolute methanol was added slowly 12.5 g. (0.08 mole) of ethyl dichloroacetate at such a rate as to keep the temperature below 58°. After complete addition, the mixture was stirred for 0.5 hr. longer. The precipitate which formed was filtered off and recrystallized from a large volume of water. After drying the crystals in vacuum overnight, 7.5 g. (49%) of pure product was obtained, m.p. 256–257° dec. (browning before melting).

Anal. Calcd. for $C_4H_5N_5Cl_2$: C, 24.75; H, 2.60; Cl, 36.54. Found: C, 24.48; H, 2.72; Cl, 36.78.

4,6-Diamino-2-chlorobromomethyl-*s*-triazine (III, R′ = CHBrCl).—Biguanide, 5 g. (0.05 mole), was dissolved in 25 ml. of absolute methanol to which was added 10.1 g. (0.05 mole) of ethyl chlorobromoacetate[10] slowly with stirring, the temperature being permitted to rise to 50°. Stirring was continued until the temperature began dropping, the mixture being permitted to stand until it reached room temperature. The precipitated product was filtered off, recrystallized from water and dried in vacuum for 24 hr., 6.4 g. (54.3%), m.p. 205–206° dec.

Anal. Calcd. for $C_4H_5N_5ClBr$: C, 20.14; H, 2.12. Found: C, 20.42; H, 2.31.

6-Amino-4-*p*-chloroanilino-2-chloromethyl-*s*-triazine (II, R = CH_2Cl, X = Cl).—A solution of sodium methoxide containing 1.38 g. of sodium (0.06 g. atm.) in 75 ml. of absolute methanol was prepared, to which was added 12.7 g. (0.06 mole) of *p*-chlorophenyl biguanide in small portions with stirring. To the resulting mixture was added slowly 7.5 g. (0.06 mole) of ethyl α-chloroacetate and stirring continued until considerable cloudiness developed. After 1 hr., 5 ml. of concentrated hydrochloric acid in 15 ml. of methanol was added, the mixture filtered and washed with water. The residue was recrystallized from a water–methanol solution to yield 5.3 g. (32.9%) of pure product, m.p. 180° dec. (browning before melting).

Anal. Calcd. for $C_{10}H_9N_5Cl_2$: Cl, 26.25. Found: Cl, 26.50.

4,6-Diamino-2-methyl-*s*-triazine (IV) from Biguanide.—To 2 g. of biguanide (0.02 mole) dissolved in 15 ml. of absolute methanol was added 3 g. (0.03 mole) of ethyl acetate slowly with stirring. The solution was heated and at 40° it became cloudy. The temperature was permitted to rise to 60° for 15 minutes with subsequent cooling to room temperature. The precipitated solid was filtered off and dried, 1.1 g. of product (44.4%), m.p. 275° (IV).

4,6-Dichloro-2-methyl-*s*-triazine (V).—This compound was prepared from cyanuric chloride and methylmagnesium bromide according to the procedure described by Hirt, Nidecker and Bechtold,[17] m.p. 98°.

4,6-Di-(dimethylamino)-2-methyl-*s*-triazine (VII) from 4,6-Dichloro-2-methyl-*s*-triazine (V).—A solution of 4.5 g. (0.027 mole) of 2-methyl-4,6-dichloro-*s*-triazine in 100 ml. of anhydrous ether was prepared, through which was bubbled anhydrous dimethylamine for 1.5 hr. The precipitated dimethylamine hydrochloride was filtered off and the ether filtrate was evaporated slowly at room temperature. A solid was obtained, 3.75 g. (75%), which was recrystallized twice from a very concentrated solution of low boiling petroleum ether, m.p. 45–46°.

Anal. Calcd. for $C_6H_{15}N_5$: N, 38.65. Found: N, 38.81.

4,6-Di-(monomethylamino)-2-methyl-*s*-triazine (VI) from 4,6-Dichloro-2-methyl-*s*-triazine.—After dissolving 10.5 g. (0.064 mole) of 2-methyl-4,6-dichloro-*s*-triazine in 150 ml. of absolute ether, anhydrous monomethylamine was bubbled in for 1 hr. The solid which precipitated was filtered off and recrystallized twice from water, 3.3 g. of pure product (33.7%).

Anal. Calcd. for $C_6H_{11}N_5$: N, 45.72. Found: N, 45.69.

4,6-Di-(dimethylamino)-2-methyl-*s*-triazine from 4,6-Diamino-2-methyl-*s*-triazine (IV).—In a 100-ml. round-bottom flask was placed 5 g. (0.04 mole) of 2-methyl-4,6-

(20) C. B. Pollard, E. G. Rietz and R. Robbins, THIS JOURNAL, **75**, 2989 (1953).

(21) D. R. Howton, *J. Org. Chem.*, **10**, 277 (1945).

(22) Analyses by Dr. Schwarzkopf, Woodside 77, N. Y.; Dr. K. Ritter, Basel, Switzerland.

(23) All melting points are uncorrected.

diamino-*s*-triazine (IV), 11 g. (0.135 mole) of dimethylamine hydrochloride and 1.4 g. (0.010 mole) of zinc chloride. The mixture was fused and maintained at 220–240° for 1 hr. with stirring. After cooling, 70 ml. of cold water was added and filtered. The filtrate was extracted with 100 ml. of Skellysolve A which upon evaporation yielded 0.112 g. of material, m.p. 40.5–42°. The material from two such runs was combined, dissolved in 75 ml. of Skellysolve A, insoluble material removed by filtration, and the solid was chromatographed on an alumina column. The column was eluted with pure Skellysolve A; 50-ml. fractions were taken. The materials obtained from the fourth and fifth eluates (m.p. 42–43°) were combined and recrystallized from Skellysolve A, m.p. 45–46°, and a mixed melting point with an authentic sample was not depressed, m.p. 44.5–45.5°.

4,6-Di-(monomethylamino)-*s*-triazine from 4,6-Diamino-2-methyl-*s*-triazine.—This compound was prepared by essentially the same procedure described by Thurston, m.p. 255–256°.[16]

4,6-Diamino-2-methoxyethyl-*s*-triazine (III, R′ = $CH_2CH_2OCH_3$).—A solution of 10 g. (0.1 mole) of biguanide and 9 g. (0.1 mole) of methyl acrylate in 150 ml. of absolute methanol were refluxed for 1.5 hr. On cooling, 7 g. of crude product, m.p. 205–209°, was obtained. After digesting this product with aqueous methanol at steam-bath temperature for 0.5 hr., insoluble material was removed by filtration and the solution cooled. Crystalline material, 6.5 g., was obtained, melting at 210–211°. Concentration of the original filtrate yielded another 2 g. of product; total yield, 8.5 g. (51%).

Anal. Calcd. for $C_6H_{11}N_5O$: C, 42.59; H, 6.55; N, 41.40; O, 9.46. Found: C, 42.58; H, 6.49; N, 41.32; O, 9.61.

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BROOKLYN 1, NEW YORK

[CONTRIBUTION FROM THE OHIO STATE UNIVERSITY RESEARCH FOUNDATION]

Triazines. XVIII. The Reaction of Aliphatic Diazocompounds with Chloro-s-triazines[1,2]

BY CHRISTOPH GRUNDMANN AND EHRENFRIED KOBER

RECEIVED JUNE 6, 1956

Di- and trichloro-*s*-triazines react with diazomethane and its homologs to yield α-diazoalkyl-substituted triazines. Usually only one chlorine atom is substituted. The other chlorine atoms can be replaced by alkoxy- or amino groups without affecting the diazo group. On the basis of the reactivity of the diazo group toward halogens and acids, the α-diazoalkyl-*s*-triazines resemble derivatives of diazoacetic acid.

In many of their properties the cyanuric trihalides, or 2,4,6-trihalogeno-1,3,5-triazines, resemble the halogenides of organic acids. Because the latter compounds react easily with diazomethane and its homologs to give diazoketones, a reaction of halogeno-triazines and aliphatic diazo compounds seemed possible.

Cyanuric chloride (I) reacts readily with two moles of diazomethane in ethereal solution at room temperature, liberating elementary nitrogen to form a well crystallized yellow compound, 2-diazomethyl-4,6-dichloro-1,3,5-triazine (II). The possible isomeric structures of a triazolo-triazine (IIIa and IIIb) seem to be definitely excluded by the reactions of II which are quite analogous to those of the known aliphatic diazo compounds. Furthermore the infrared spectrum of this and other diazosubstituted triazines displays the characteristic band (at 2120 cm.$^{-1}$) of the aliphatic diazo compounds.

With a large excess of diazomethane and prolonged reaction time, the second chlorine atom of the cyanuric chloride also is substituted to some extent. Because of its instability, however, we were unable to prepare the expected 2,4-bis-diazomethyl-6-chloro-triazine (IV) in a pure state. There was never any indication of the reaction of the third chlorine atom of I.

Other chloro-*s*-triazines which react as well with diazomethane as does cyanuric chloride are 4,6-dichloro-2-methyl-*s*-triazine (V) and 4,6-dichloro-2-phenyl-*s*-triazine (VI). They give the expected compounds, 6-chloro-4-diazomethyl-2-methyl-*s*-triazine (VII) and 6-chloro-4-diazomethyl-2-phenyl-*s*-triazine (VIII). 6-Chloro-2,4-diphenyl-*s*-triazine (IX) does not react. With 2,4-bis-trichloromethyl-6-chloro-*s*-triazine[3] (X), in which the chlorine attached to the nucleus is much more mobile than in IX, the reaction apparently is not only confined to the 6-position but also includes the trichloromethyl groups, thus complicating the picture.

On the other hand, diazomethane can be replaced by homologs. For instance, from I and diazoethane 2,1′-diazoethyl-4,6-dichloro-*s*-triazine (XI) is obtained; ethyl diazoacetate yields 4,6-dichloro-*s*-triazinyl-2-diazoacetic acid ethyl ester (XII). The latter reaction requires elevated temperatures and prolonged reaction time, illustrating the lower degree of reactivity of the diazoester compared to the diazoalkanes. It is not surprising, then, that the more stable diazoketones, like ω-diazoacetophenone, do not react with cyanuric chloride.

The chlorine atoms in the 4- and 6-positions of the diazomethyl substituted triazines can be replaced without alteration of the diazo group by alkoxy groups, by thioalkyl groups and by amino groups. Using this method, 2-diazomethyl-4,6-dimethoxy-*s*-triazine (XIII) and 2-diazomethyl-4,6-diethoxy-*s*-triazine (XIV) were prepared. Since the presence of the reactive chlorine atoms in the original reaction products, such as II, often involves complications, many of the reactions of the

(1) This article is based on work performed under Project 116-B of The Ohio State University Research Foundation sponsored by the Olin Mathieson Chemical Corporation, New York, N. Y.

(2) Preceding communication, Ch. Grundmann and E. Kober, *J. Org. Chem.*, **21**, 1392 (1956).

(3) H. Schroeder and Ch. Grundmann, THIS JOURNAL, **78**, 2447 (1956).