REACTION OF 3,5,6-TRICHLORO-1,2,4-TRIAZINE WITH SIMPLE NUCLEOPHILES*

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Amonolysis of trichlorotriazine *II* gives 5-amino derivative *V* selectively. After methanolysis in acid medium the latter gives aminochloromethoxytriazine *VIII*, while on reaction with sodium methanolate the isomer *X* is formed. Methanolysis of trichlorotriazine *II* with excess sodium methoxide gives trimethoxytriazine *XII* which on acid hydrolysis is converted to 6-methoxy-triazinedione *XI*. With an equimolar amount of methanolate trichlorotriazine gives 5-methoxy derivative *XIII* selectively. The reaction of trichlorotriazine *II* with two equivalents of sodium methoxide gives a mixture of isomeric chlorodimethoxytriazines *XIV* and *XV* in which isomer *XV* slightly prevails. On the basis of the results obtained the supposition is presented that the reactivity of single positions in the 1,2,4-triazine nucleus toward neutral nucleophiles decreases in the sequence 5 > 3 > 6, while with anionic nucleophiles the sequence is 5 > 6 > 3.

For the preparation of derivatives of 1,2,4-triazine-3,5-dione (*I*) or other substituted 1,2,4-triazines, 3,5,6-trichloro-1,2,4-triazine (*II*) could be a suitable intermediate. For the chemistry of 1,2,4-triazines this compound could have the same meaning as 2,4,6-trichloro-1,3,5-triazine for the chemistry of isomeric 1,3,5-triazines[2]. Trichloro derivative *II* was described only recently[1,3–5]. For the first time trichlorotriazine *II* was prepared[3,4] by reaction of phosphorus oxychloride with 6-bromo-1,2,4--triazine-3,5-dione (*III*). Distillation of the mixture gave an oily product in low yield (30%), which did not contain either hydrogen or bromine and in an exothermic reaction with methanol it gave 6-chloro-1,2,4-triazine-3,5-dione (*IV*). During the reproduction of this preparation we succeeded in obtaining pure crystalline trichlorotriazine[1] *II* after cooling of the crude product at −78°C. In our opinion the crude oily product contains a larger amount of pyrophosphoryl chloride which has a similar boiling point as trichlorotriazine and may be formed either already during the reaction or during the distillation of the mixture. Recently the preparative yield of the crystalline trichlorotriazine was increased substantially by Loving[5] and coworkers.

An extensive synthetic use of trichlorotriazine requires a detailed knowledge of the reactivity sequence of single positions of the triazine nucleus. After successful

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isolation of pure trichlorotriazine *II* we began to study this problem. In this paper we present the results concerning the reaction of trichlorotriazine with ammonia and methanol.

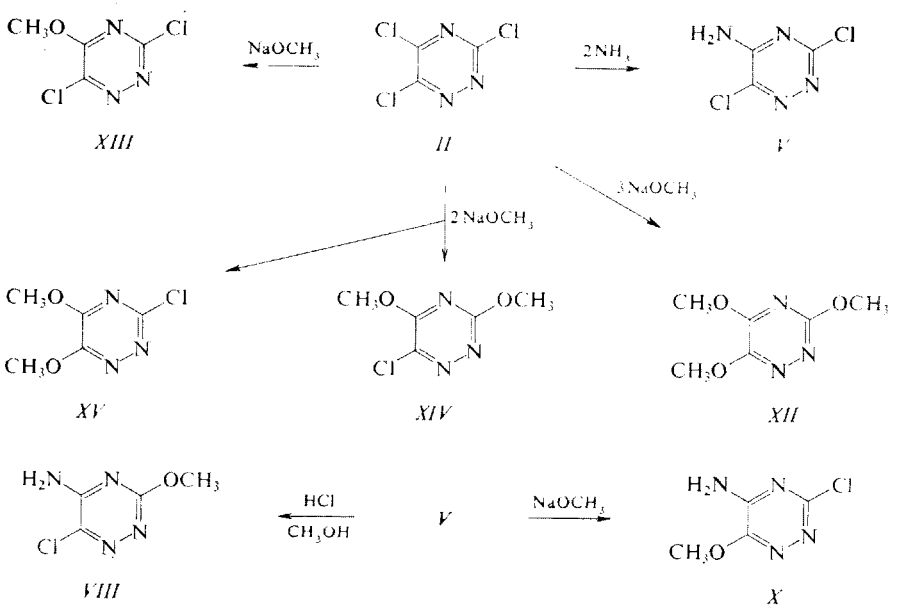
On reaction of trichlorotriazine *II* with excess dry ammonia in methanol at room temperature aminodichlorotriazine was obtained in high yield (94%), which on acid hydrolysis gave 6-chlorotriazinedione *IV* as the main product. The hydrogenolysis of aminodichloro derivative did not take place quantitatively in the presence of palladium catalyst on charcoal even when excess catalyst was used. In addition to aminochlorotriazine (yield 15%) which gave triazinedione *I* on acid hydrolysis we also obtained by preparative paper chromatography of the mother liquors an aminotriazine (yield 9%) which was not identical with the known 3-amino-1,2,4-triazine[6]. On the basis of these results we assign the aminodichloro derivative the structure of 5-amino-3,6-dichloro-1,2,4-triazine (*V*) and to its hydrogenolytic products the structure of 5-amino-1,2,4-triazine (*VI*), or 5-amino-3-chloro-1,2,4-triazine (*VII*).

When boiling aminodichlorotriazine *V* with methanolic hydrogen chloride 5-amino-6-chloro-3-methoxy-1,2,4-triazine (*VIII*) was obtained in 78% yield. Its structure followed from acid hydrolysis to 6-chlorotriazinedione *IV*. The structure of triazine *VIII* was further confirmed by its catalytic hydrogenolysis to 5-amino-3-methoxy-1,2,4-triazine (*IX*) which was identified by comparison with a product prepared by an unambiguous route[7]. This reaction simultaneously represents a further proof of the structure of aminodichlorotriazine *V*.

In contrast to acid catalysed methanolysis aminodichlorotriazine *V* afforded on reaction with methanolic sodium methoxide isomeric 5-amino-3-chloro-6-methoxy-1,2,4-triazine (*X*) in 72% yield. Its acid hydrolysis led to 6-methoxy-1,2,4-triazine-3,5-dione (*XI*). A hydrogenolytic elimination of chlorine from the position 3 of the triazine nucleus was unsuccessful.

The methanolysis of trichlorotriazine *II* with excess methanolic sodium methoxide takes place smoothly even at room temperature, under formation of 3,5,6-trimethoxy-1,2,4-triazine (*XII*). When hydrolyzed with dilute methanolic hydrogen chloride the compound gave 6-methoxytriazinedione *XI* in high yield. Methanolysis of trichlorotriazine *II* with an equimolar amount of sodium methoxide gave rise to the instable dichloromethoxy derivative (68% yield) which gives on hydrolysis 6-chlorotriazinedione *IV* and on amonolysis 5-amino-3,6-dichloro-1,2,4-triazine (*V*). From this it follows that the product obtained has the structure of 3,6-dichloro-5-methoxy-1,2,4-triazine (*XIII*). The same product was obtained in a slightly lower yield also on reaction of trichlorotriazine *II* with methanol in the presence of sodium hydrogen carbonate. Methanolysis of trichlorotriazine *II* with two equivalents of methanolic sodium methoxide gave a mixture of instable isomeric chlorodimethoxytriazines in very good yield; they could not be separated chromatographically. However, on fractional crystallization from light petroleum both 6-chloro-3,5-dimethoxy-1,2,4-triazine (*XIV*) and the isomeric 3-chloro-5,6-dimethoxy-1,2,4-triazine (*XV*)

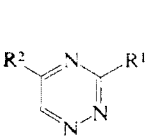
could be obtained in pure form. The structure of both isomers was demonstrated by acid hydrolysis to 6-chlorotriazinedione *IV* or 6-methoxytriazinedione *XI*. On hydrogenolysis of the mixture of isomeric triazines *XIV* and *XV* and their preparative chromatography on thin layers of alumina 3,5-dimethoxy-1,2,4-triazine (*XVI*) was obtained in a mere 25% yield, and it was identified by comparison with a sample prepared by an unambiguous synthesis[8]. 3-Chloro derivative *XV* could not be hydrogenolysed, in analogy to 3-chlorotriazine *X*, and it was regenerated in crude form from the hydrogenation mixture. In view of the result of hydrogenolysis and the chromatographic evaluation of the hydrolysate of the mixture of isomeric chlorodimethoxytriazines *XIV* and *XV*, in which 6-methoxytriazinedione *XI* prevails over 6-chlorotriazinedione *IV*, we suppose that in the mixture of isomers *XIV* and *XV* 5,6-dimethoxy derivative *XV* also prevails.

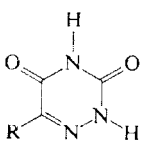


XIII *II* *V*

XV *XIV* *XII*

VIII *V* *X*





VI, $R^1 = H$; $R^2 = NH_2$
VII, $R^1 = Cl$; $R^2 = NH_2$
IX, $R^1 = OCH_3$; $R^2 = NH_2$
XVI, $R^1 = R^2 = OCH_3$

I, R = H
III, R = Br
IV, R = Cl
XI, $R = OCH_3$

The above mentioned results show that the position 5 of the triazine nucleus is most reactive both towards anionic and neutral nucleophiles. The further sequence of the positional reactivities is dependent on the character of the substituent in the position 5. In the case of strong electron donors the position 6 is preferred over the position 3 in the reaction with anionic nucleophiles, while in acid catalysed reaction substitution into position 3 prevails. If the substituent in the position 5 is a weaker electron donor this dependence remains preserved in principle for acid catalysed substitutions, while the preference of the position 6 by anionic nucleophiles is less pronounced. The sequence of substitution in the reaction with anionic nucleophiles can be explained by the fact that an indirect *ortho* and *para*-resonance deactivation of the position 3 of the triazine nucleus is stronger than the direct *ortho*-resonance deactivation of the position 6. In the reaction with neutral nucleophiles or in acid catalysed nucleophilic substitution we suppose a partial or complete cationization of the triazine nucleus caused by hydrogen bonding, or by protonation of the sp^2 hybridized triazine nitrogen atoms, which, on the contrary, has an activating effect and is manifested in the final effect by higher reactivity of the position 3 in comparison with the position 6 of the triazine nucleus. It may be stated that the reactivity of single positions of the triazine nucleus towards acid catalysed substitution and probably also towards neutral nucleophiles in neutral or basic medium decreases in the order $5 > 3 > 6$, while in the case of anionic nucleophiles the order is $5 > 6 > 3$. As the differences in reactivity of the positions 3 and 6 are relatively small, it is not excluded, that in view of numerous factors affecting the course of the nucleophilic substitution the above mentioned sequence may change in some instances.

From the present study of nucleophilic metatheses on 3,5-disubstituted 1,2,4-triazines, and from the general considerations concerning the stability of the partial negative charge in the transition state under the effect of sp^2 hybridized triazine nitrogens it follows, according to Shepherd and Fedrick[9] that the reactivity to substitution in basic medium of various positions decreases in the following order: $5 > 3 > 6$. From our results it follows that this prediction does not apply for the reactions with anionic nucleophiles. In this connection it is proper to mention that Grundman and coworkers[10] suppose, on the contrary, a higher reactivity in the position 3 of 3,5-dichloro-1,2,4-triazine when compared with the position 5 of the triazine nucleus, and that they also assign the structures to the products obtained on the basis of this supposition — without further proofs. However, our results prove convincingly the incorrectness of this supposition and justify the statement that in actual fact the structure of 5-substituted triazines is the right one for the supposed 3-substituted derivatives. The incorrectness of the results of Grundmann and coworkers[10] was already mentioned in the literature[1,9].

EXPERIMENTAL

The melting points were determined on a Kofler block and they are corrected. Unless stated otherwise the samples for analysis were dried at 22°C/0·1 Torr for 10 hours. The solutions were evaporated on a rotational evaporator at 35—40°C (bath temperature) and 15 Torr. Paper chromatography was carried out in descending arrangement on paper Whatman No 1 (preparatively on Whatman No 3MM) without previous equilibrium in systems S_1, 1-butanol–acetic acid–water (4 : 1 : 1), and S_2, ethyl acetate saturated with 3% acetic acid. Detection was carried out visually in ultraviolet light (Chromatolite). Chromatography on loose thin layers was carried out with neutral alumina (activity II—III according to Brockmann).

3,5,6-Trichloro-1,2,4-triazine (*II*)

A mixture of 6-bromotriazinedione[4] *III* (192·4 g. 1 mol) and phosphorus oxychloride (1 000 ml) was refluxed for 12 hours under stirring (bath temperature 120—125°C). The mixture was distilled (15 Torr, 60—70°C bath temperature, necessary for the elimination of $POCl_3$, and then 3 Torr; bath temperature was increased slowly up to 125°C; the condensate obtained was cooled with a mixture of dry ice and ethanol). The fraction 55—76°C/3 Torr was collected (196·5 g). This fraction was redistilled and the fraction 74—76°C/3 Torr was collected (101·6 g) from which crystals of trichlorotriazine *II* separated even during distillation. The mixture was allowed to stand in a hermetically stoppered flask at —15°C for 5 days. The crystals obtained were filtered off rapidly, washed with light petroleum (50 ml), then with cold ether (2 × 15 ml), and eventually dried *in vacuo* for 30 minutes. Yield 16·2 g. From the redistilled mother liquors another crop (5·4 g) of the product was obtained in a similar manner. The total yield was 21·5 g (12%) of trichlorotriazine *II*; m.p. 52—55°C. A sample for analysis was sublimated at 50°C/0·4 Torr (m.p. 57—58°C). For $C_3Cl_3N_3$ (184·4) calculated: 19·54% C, 22·79% N, 57·69% Cl; found: 19·49% C, 22·56% N, 57·42% Cl. When stored in a hermetically closed vessel the product does not decompose. Only a small amount of trichlorotriazine *II* could be obtained from the last mother liquors after additional redistillation. However, the fraction contained still a considerable amount of trichloro derivative *II* and it is utilizable for some reactions in which a considerable excess of a nucleophilic reagent may be used. The yields of these reactions were substantially lower than when crystalline trichlorotriazine was used.

5-Amino-3,6-dichloro-1,2,4-triazine (*V*)

A) A solution of trichlorotriazine *II* (1·84 g; 0·01 mol) in ether (50 ml) was added in several portions and under cooling with a freezing mixture and stirring to 50 ml of a 6·95M methanolic ammonia. After evaporation of the solution the residue was triturated with water (20 ml). The product was filtered off under suction, washed with icy water and dried in a vacuum over concentrated sulfuric acid and potassium hydroxide. Yield: 1·55 g (94%) of triazine *V*. When heated the product decomposes slowly above 190°C without melting (up to 300°C); on rapid heating it melts at 203—205°C (decomposition); R_F 0·79 (S_1) and 0·81 (S_2). The analytical sample was crystallized from ethyl acetate. For $C_3H_2Cl_2N_4$ (165·0) calculated: 21·84% C, 1·22% H, 33·96% N, 42·98% Cl; found: 22·02% C, 1·41% H, 34·20% N, 42·89% Cl.

B) A solution of dichloromethoxytriazine *XIII* (0·180 g; 0·001 mol) in methanolic 6·95M ammonia (10 ml) was allowed to stand at room temperature for 20 minutes. After evaporation the residue was worked up as under *A*). Yield: 0·149 g (90%) of triazine *V*; m.p. 203—205°C (decomposition) when heated rapidly, undepressed on admixture of a sample prepared as under *A*) Hydrolysis: A solution of triazine *V* (16·5 mg; 0·1 mmol) in 1M-HCl (1 ml) was heated on a

steam bath for 2 hours. After evaporation the residue was extracted with ethanol (2 ml), the insoluble part was filtered off and the filtrate evaporated. Crystallization of the residue from water gave 5·5 mg (38%) of chlorotriazine *IV*, m.p. 232–233°C, undepressed with an authentic sample[4].

5-Amino-3-chloro-6-methoxy-1,2,4-triazine (*X*)

A solution of dichloroaminotriazine *V* (0·165 g; 0·001 mol) in methanol (5 ml) and 1 ml of 1M-$NaOCH_3$ was refluxed for one hour. After evaporation of the solvent the residue was extracted with boiling ethyl acetate (50 ml) and the insoluble material filtered off and the filtrate evaporated. The residue was crystallized from a small amount of water. Yield: 0·115 g (72%) of triazine *X*; m.p. 156–157°C; R_F 0·75 (S_1) and 0·77 (S_2). For $C_4H_5ClN_4O$ (160·6) calculated: 29·92% C, 3·14% H, 34·89% N, 22·08% Cl, 19·33% OCH_3; found: 29·91% C, 3·11% H, 34·81% N, 22·38% Cl, 19·13% OCH_3.

Hydrolysis: A solution of triazine *X* (16 mg; 0·1 mmol) in 1M-HCl (1 ml) was heated on a steam bath for 2 hours. After evaporation of the solvent the residue was crystallized from water–ethanol. Yield 6·5 mg (45%) of methoxytriazine *XI*; m.p. 285–286°C (sealed capillary), undepressed with a sample described below.

5-Amino-6-chloro-3-methoxy-1,2,4-triazine (*VIII*)

A solution of aminodichlorotriazine *V* (0·33 g; 0·002 mol) in 2% methanolic hydrogen chloride (10 ml) was refluxed for 30 minutes. After cooling the solution was put on a column of Amberlite IR-45 [OH^-] (20 ml) prepared in methanol and the product was eluted with methanol (150 ml). After evaporation of the eluate the residue was extracted with boiling ethyl acetate (50 ml), the insoluble part was filtered off and the filtrate concentrated. The residue was crystallized from ethyl acetate–light petroleum mixture. Yield: 0·251 g (78%) of compound *VIII*; m.p. 169–170°C; R_F 0·75 (S_1) and 0·77 (S_2). For $C_4H_5ClN_4O$ (160·6) calculated: 29·92% C, 3·14% H, 34·89% N, 22·08% Cl, 19·33% OCH_3; found: 30·09% C, 3·13% H, 35·14% N, 22·18% Cl, 19·23% OCH_3.

Hydrolysis: A solution of triazine *VIII* (16 mg; 0·1 mmol) in 1M-HCl (1 ml) was heated on a steam bath for 2 hours. After evaporation of the solution the residue was extracted with ethanol (2 ml) and the insoluble part was filtered off and the filtrate evaporated. Crystallization of the residue from water gave 6-chlorotriazinedione *IV* (9 mg; 61%); m.p. 232–233°C, undepressed on admixture with an authentic sample[4].

Hydrogenolysis of 5-Amino-3,6-dichloro-1,2,4-triazine (*V*)

A solution of aminodichlorotriazine *V* (0·495 g; 0·003 mol) in dioxan (100 ml) was hydrogenated in the presence of N-ethylpiperidine (0·678 g; 0·006 mol) and 10% palladium on charcoal (2 g). The operation was carried out at atmospheric pressure and room temperature for 10 hours. The mixture was filtered, additional catalyst (2 g) was added and hydrogenation was continued. After filtration the solution was evaporated and the residue triturated with dioxan (10 ml). The insoluble part was filtered off under suction and crystallized from water. Yield 0·060 g (15%) of aminochlorotriazine *VII* (needles). Above 200°C the substance begins to change but it does not melt up to 250°C; R_F 0·69 (S_2). For $C_3H_3ClN_4$ (130·5) calculated: 27·61% C, 2·31% H, 42·94% N, 27·17% Cl; found: 27·71% C, 2·47% H, 42·65% N, 27·39% Cl. When hydrolysed (13 mg of substance; 0·1 mmol) with 1M-HCl (1 ml) on a steam bath for 2 hours, evaporated in a vacuum and the residue crystallized from water, the substance gave triazinedione *I* (8 mg; 70%); m.p. 280–281°C, undepressed on admixture of an authentic sample[11]. The dioxan extract

of the crude reaction mixture contains according to paper chromatography in addition to the starting compound and aminochlorotriazine *VII* also aminotriazine *VI*. The mixture was submitted to preparative paper chromatography on 4 sheets of paper in system S_2. The least moving zones were eluted with water. The eluate was evaporated, the residue dried in vacuo over concentrated sulfuric acid and KOH and sublimated at 170°C/0·1 Torr. At the end of the sublimation the temperature was raised to 200°C. The sublimate was crystallized from ethanol to give 0·025 g (9%) of 5-aminotriazine *VI* in the form of needles; m.p. 231–232°C; R_F 0·12 (S_2). For $C_3H_4N_4$ (96·1) calculated: 37·49% C, 4·20% H, 58·31% N; found: 37·65% C, 4·32% H, 58·41% N.

3,6-Dichloro-5-methoxy-1,2,4-triazine (*XIII*)

A) A solution of trichlorotriazine *II* (0·46 g; 2·5 mmol) in ether (10 ml) was added to 5 ml of methanolic 0·5M-$NaOCH_3$ under stirring and cooling with ice and the mixture was allowed to stand at room temperature for 10 minutes. After evaporation (20°C bath temperature) the residue was dried at room temperature and 0·3 Torr for 30 minutes and then extracted with ether (100 ml). The insoluble material was filtered off, the filtrate evaporated and the residual oil dried at room temperature and 0·3 Torr for 30 minutes. Crystallization from light petroleum gave 0·304 g (68%) of triazine *XIII*; m.p. 62–63°C. The substance is instable and it decomposes already after several days. For $C_4H_3Cl_2N_3O$ (180·0) calculated: 26·79% C, 1·68% H, 23·39% N, 39·40% Cl, 17·24% OCH_3; found: 26·78% C, 1·71% H, 23·29% N, 39·54% Cl, 17·54% OCH_3.

B) A solution of trichlorotriazine *II* (0·46 g; 2·5 mmol) in a mixture of methanol (3 ml), water (0·2 ml) and sodium hydrogen carbonate (0·42 g; 5 mmol) was refluxed for 30 minutes and evaporated. The residue was diluted with ice cold water (5 ml), the separated product was filtered off, washed with water and dried in a vacuum over conc. sulfuric acid and potassium hydroxide. Yield 0·240 g (53%) of triazine *XIII*; m.p. 62–63°C, undepressed with the product obtained under *A*).

Hydrolysis: A solution of triazine *XIII* (18 mg; 0·1 mmol) in 2% hydrogen chloride in methanol (1 ml) was refluxed for one hour. After evaporation the residue was extracted with ethanol (2 ml), the insoluble part filtered off and the filtrate evaporated. Crystallization of the residue from water gave chlorotriazine *IV* (10 mg; 68%); m.p. 232–233°C, undepressed on admixture with an authentic sample[4].

3,5,6-Trimethoxy-1,2,4-triazine (*XII*)

A solution of trichlorotriazine *II* (0·92 g; 0·005 mol) in ether (15 ml) was added to methanolic 1M-$NaOCH_3$ (20 ml) under stirring and cooling with ice and the solution allowed to stand at room temperature for 2 hours. Excess methoxide was neutralized with carbon dioxide, the insoluble part was filtered off and the filtrate evaporated. The residue was triturated with ether (150 ml), the insoluble fraction filtered off and the filtrate evaporated. Crystallization of the residue from cyclohexane gave 0·71 g (83%) of trimethoxytriazine *XII*, m.p. 124–125°C; R_F 0·52 (ether). For $C_6H_9N_3O_3$ (171·2) calculated: 42·09% C, 5·30% H, 24·55% N, 54·39% OCH_3; found: 42·31% C, 5·31% H, 24·32% N, 54·68% OCH_3.

6-Methoxy-1,2,4-triazine-3,5(2*H*,4*H*)-dione (*XI*)

A solution of trimethoxytriazine *XII* (0·171 g; 0·001 mol) in 2% hydrogen chloride in methanol (10 ml) was refluxed for one hour. After evaporation and crystallization of the residue from ethanol–water 0·125 g (87%) of methoxytriazine *XI* were obtained; m.p. 285–286°C (sealed

capillary); R_F 0·50 (S_1) and 0·45 (S_2). For $C_4H_5N_3O_3$ (143·1) calculated: 33·79% C, 3·52% H, 29·37% N, 21·69% OCH_3; found: 33·79% C, 3·64% H, 29·67% N, 22·00% OCH_3.

Reaction of Trichlorotriazine *II* with Two Equivalents of Methanolic Sodium Methoxide

A solution of trichlorotriazine *II* (0·92 g; 0·005 mol) in methanolic 0·2M-$NaOCH_3$ (50 ml), prepared at 0°C, was allowed to stand at room temperature for 20 minutes. The mixture was evaporated, the residue triturated with ether (30 ml), the insoluble fraction was filtered off, and the filtrate evaporated. The residue (0·80 g) does not contain any mono- or trisubstituted derivative according to thin-layer chromatography in chloroform. Crystallization from light petroleum (20 ml) gave 0·61 g (69%) of a mixture of isomeric chlorodimethoxytriazines *XIV* and *XV*; m.p. 40–55°C; R_F 0·50 (chloroform). For $C_5H_6ClN_3O_2$ (175·6) calculated: 34·20% C, 3·45% H, 23·93% N, 20·19% Cl, 35·35% OCH_3; found: 34·28% C, 3·35% H, 23·74% N, 20·10% Cl, 35·12% OCH_3. Triple crystallization of a sample (0·1 g) of the mixture from light petroleum gave pure 5,6-dimethoxy derivative *XV* (0·035 g); m.p. 92–93°C; R_F 0·50 (chloroform); on hydrolysis with hydrogen chloride in methanol this isomer (0·1 mmol) afforded dione *XI* (75%) as the main product on crystallization of the hydrolysate from ethanol–water mixture; m.p. 285–286°C (sealed capillary) undepressed with the above described product. Crystallization of the residue of the first mother liquors from light petroleum gave the second isomer (0·021 g); m.p. 60–61°C; R_F 0·50 (chloroform); hydrolysis of this isomer (0·1 mmol) with methanolic hydrogen chloride gave dione *IV* (62%) as the main product; m.p. 232–233°C (water) undepressed with an authentic sample[4]. The acid hydrolysate of the crude reaction mixture contains according to paper chromatography a larger proportion of dione *XV*, R_F 0·50 (S_1), in addition to a smaller amount of dione *IV*, R_F 0·65 (S_1).

3,5-Dimethoxy-1,2,4-triazine (*XVI*)

The crude mixture of chlorodimethoxytriazines *XIV* and *XV* (0·175 g; 0·001 mol) in ether (50 ml) was hydrogenolysed at atmospheric pressure and room temperature for one hour in the presence of 10% palladium on charcoal catalyst (1 g) and N-ethylpiperidine (0·113 g; 0·001 mol). After filtration off of the catalyst the solution was evaporated and the residue chromatographed on 15 × × 10 × 20 cm plates of alumina in chloroform as developing solvent. Working up of the more moving zones (R_F 0·58) gave 0·088 g (50%) of a syrupy mixture of the starting chloroderivatives *XIV* and *XV*. For $C_5H_6ClN_3O_2$ (175·6) calculated: 23·93% N, 20·19% Cl; found: 23·68% N, 20·21% Cl. The less moving zones (R_F 0·26) afforded 0·035 g (25%) of dimethoxytriazine *XVI*; m.p. 61–62°C (light petroleum), undepressed on admixture of an authentic sample[8]. For $C_5H_7N_3O_2$ (141·1) calculated: 42·55% C, 5·00% H, 29·78% N; found: 42·65% C, 5·15% H, 29·81% N.

5-Amino-3-methoxy-1,2,4-triazine (*IX*)

A solution of chloro derivative *VIII* (0·160 g; 0·001 mol) in dioxan (100 ml) was hydrogenated in the presence of N-ethylpiperidine (0·113 g; 0·001 mol) and 10% palladium on active charcoal (1 g) at atmospheric pressure and room temperature for 5 hours. After filtration the solution was evaporated. Crystallization of the residue from ethanol gave 0·085 g (67%) of aminomethoxytriazine *IX*; m.p. 176–178°C (resolidifies to a substance which does not melt up to 350°C), undepressed in admixture with an authentic sample[7]; R_F 0·55 (S_1) and 0·25 (S_2). For $C_4H_6N_4O$ (126·1) calculated: 38·09% C, 4·80% H, 44·43% N; found: 38·37% C, 4·97% H, 44·73% N.

Elemental analyses were carried out in the analytical department of this Institute (head Dr J. Horáček) by Mrs V. Rusová, Mrs E. Sýkorová and Mr V. Štěrba.

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