297 mμ (ε 18,300), 362 mμ (ε 8,300); 0.1 *N* HCl, λ_{max} 244 mμ (ε 9,800), 303 mμ (ε 17,300), 361 mμ (ε 7,700).

Attempts to dry this compound for analysis caused some ring closure to V. When a sample was recrystallized from a dilute acid solution it also was converted again to the pyrimidopteridine (V), as shown by ultraviolet absorption spectra.

2-Acetamido-3,6,7-trimethyl-4(3H)-pteridone.—One gram (4.9 mmoles) of 2-amino-3,6,7-trimethyl-4(3H)-pteridone[4] was refluxed for 4 hours in 20 ml. of acetic anhydride protected with a tube of Drierite. The hot solution was filtered from a small amount of insoluble material. On cooling, the filtrate deposited crystals; yield 0.25 g. (20.5%), m.p. 196.5–199°. An additional 0.30 g. (45% total), m.p. 195–198°, was obtained by concentrating the mother liquor. For analytical purposes a portion of the product was recrystallized from 95% ethanol: R_f 0.87 (yellow-green) in 0.5% Na_2CO_3; ultraviolet spectra in 0.1 *N* NaOH, λ_{max} 246 mμ (ε 15,920), 287 mμ (ε 12,450), 340 mμ (ε 7,160); 0.1 *N* HCl, λ_{max} 239 mμ (ε 15,680), 281 mμ (ε 9,130), 316 mμ (ε 7,750); methanol, λ_{max} 242 mμ (ε 12,600), 275 mμ (ε 10,600), 323 mμ (ε 7,300).

Anal. Calcd. for $C_{11}H_{13}N_5O_2$ (247): C, 53.4; H, 5.3; N, 28.3. Found: C, 53.8; H, 5.6; N, 28.7.

PEARL RIVER, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

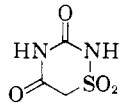
The 1,2,4-Thiadiazine Ring System. I. The Synthesis of 1,2,4,2H-Thiadiazine-3,5(4H,6H)-dione-1,1-dioxide[1]

BY R. L. HINMAN[2] AND LOUIS LOCATELL, JR.[3]

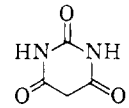
RECEIVED MARCH 26, 1959

1,2,4,2H-Thiadiazine-3,5(4H,6H)-dione-1,1-dioxide (I) has been synthesized *via* the sequence: sulfoacetic acid (III), chlorosulfonylacetic acid (V), ethyl sulfamylacetate (VII), carbethoxymethanesulfonylurea (VIb) and base-catalyzed ring closure of the last compound to I. The product I, which was characterized by analysis, neutralization equivalent and infrared spectrum, is a stable, crystalline solid, resembling barbituric acid (II) in its properties, particularly its marked acidity (pK_a' 2.7). Other attempted syntheses of I are discussed.

Analogs of naturally-occurring pyrimidines and purines have provoked considerable interest because of their potential activity as antimetabolites of the naturally-occurring heterocycles. We have been interested in preparing pyrimidine and purine analogs in which one or more ring carbons have been replaced by sulfur atoms. As our first approach, we chose the synthesis of 1,2,4,2H-thiadiazine-3,5(4H,6H)-dione-1,1-dioxide (I), which is formally related to barbituric acid (II).

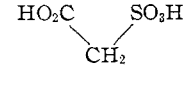


I

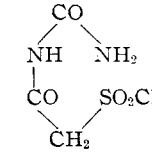


II

Although little has been reported on the 1,2,4-thiadiazine ring system, the synthesis of I has been the subject of three previous investigations.[4–6] Since these reports conflict on several points, they will be summarized briefly before the present work is discussed. Bodendorf and Senger[4] investigated several approaches to the synthesis of I, modeled after the classical synthesis of barbituric acid. They found that in the condensation of urea with either the diethyl ester or diacid chloride of sulfoacetic acid (III), the urea was acylated only by the carboxyl end of the sulfoacetic acid derivative.[7]

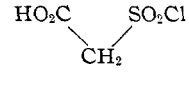


III

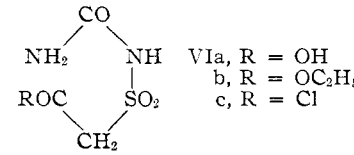


IV

Thus, the reaction of urea with sulfoacetic diacid chloride yielded IV. Attempts to effect thermally the cyclization of IV to I resulted only in decomposition of IV. Seeking to take advantage of the greater reactivity of the carboxylic function, the authors assumed that partial hydrolysis of the diacid chloride of sulfoacetic acid would yield chlorosulfonylacetic acid (V), which might react with urea to give VIa, the isomer of IV. Ring closure to I



V



VIa, R = OH
b, R = OC_2H_5
c, R = Cl

might then be effected through the more reactive carboxylic acid ester VIb or acid chloride VIc. Partial hydrolysis of the diacid chloride of sulfoacetic acid yielded a compound which analyzed for V. However, treatment of this product with urea or aniline yielded products in which the nitrogen had been acylated by the carboxylic acid end. Bodendorf and Senger concluded that the sulfonyl chloride group of the diacid chloride of sulfoacetic acid is hydrolyzed more easily than the carboxylic acid chloride end.[8] They abandoned the project at this point.

(1) Taken from the Ph.D. thesis of Louis Locatell, Jr., State University of Iowa, June, 1957. Presented before the Organic Division of the American Chemical Society at the Chicago Meeting, September, 1958.

(2) Union Carbide Research Institute, 32 Depot Plaza, White Plains, N. Y.

(3) Bakelite Co. Fellow, 1956–1957.

(4) K. Bodendorf and N. Senger, *Ber.*, **72B**, 571 (1939).

(5) J. B. Dickey, U. S. Patent 2,466,396, April 5, 1949 (to Eastman Kodak Co.); *C. A.*, **43**, 4868d (1949).

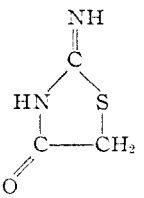
(6) P. N. Rylander and E. Campaigne, *J. Org. Chem.*, **15**, 249 (1950).

(7) Since alkyl esters of sulfonic acids are generally alkylating rather than acylating agents, acylation by the sulfonic end would not be expected in any case.

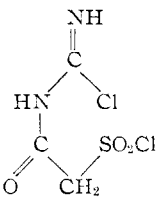
(8) Subsequent work has shown that this conclusion is erroneous, and that the sulfonyl chloride end is, as would be expected, the more stable under hydrolytic conditions. See R. Vieillefosse, *Compt. rend.*, **208**, 1406 (1939), and the remainder of the present paper.

Subsequently, in the patent literature[5] the synthesis of I was reported by a route similar to that envisaged by Bodendorf and Senger. The preparation of V was claimed by the reaction of chlorine and thioglycolic acid in aqueous solution. Treatment of V with urea in pyridine gave VIa, and esterification of the latter followed by ring closure in ethanolic sodium ethoxide produced I. It is difficult to understand why the reaction of V with urea gave VI in Dickey's hands[5] but acylation by the carboxyl end in the previous authors' experiments,[4] as well as those of others.[9] Since no descriptions of the products are given in the patent, the two conflicting reports cannot be compared. It can be inferred from the patent that compound I was a stable, crystalline substance.

During the following year an entirely different synthesis of a compound presumed to be I was described.[6] This approach involved the reaction of chlorine with 2-amino-1,3-thiazolidone-4 (VII). The reaction was assumed to proceed by way of the intermediates VIII and IV.



VII



VIII

In contrast to the stable crystalline product obtained in the previous synthesis,[5] Campaigne's product decomposed with loss of sulfur dioxide even on standing in a desiccator, a property which would not be anticipated for a compound with structure I.

The synthetic route we followed in the preparation of I is shown in equation 1.

$$V \xrightarrow[2,\ C_2H_5OH,\ HCl]{1,\ liq.\ NH_3} \underset{IX}{C_2H_5O_2CCH_2SO_2NH_2} \xrightarrow{KCNO} VIb \xrightarrow{NaOC_2H_5} I \quad (1)$$

The principal difference between this route and those proposed by Bodendorf and Senger[4] and reported in the patent literature[5] is the unambiguous synthesis we used for the preparation of the sulfonylurea VIb *via* ethyl sulfamylacetate (IX). Chlorosulfonylacetic acid (V) was prepared by hydrolysis of the diacid chloride with the calculated quantity of water. Despite great care to assure the dryness of the starting material and the solvent, the principal product was always sulfoacetic acid (III), which could be separated from V by crystallization of the latter from carbon tetrachloride. Apparently the adjacent electron-withdrawing group renders the sulfonyl chloride especially reactive, though it is still less rapidly hydrolyzed than the carboxyl chloride. No better method of synthesis of V could be found.[10] Structure V can be assigned with certainty to the product on the basis of its reaction with sodium phenoxide to give phenyl carboxymethanesulfonate, and its conversion to ethyl sulfamylacetate (IX).

The last compound, the key intermediate in the synthesis of I, was prepared by the reaction of V with liquid ammonia, followed by treatment of the reaction mixture with ethanolic hydrogen chloride. Since sulfonic acids cannot be esterified directly, the structure of the product is established by its mode of synthesis. Attempts to prepare IX by reaction of ethyl chlorosulfonylacetate ($C_2H_5O_2CCH_2SO_2Cl$) with ammonia and ammonium carbonate under a variety of conditions were unsuccessful.

Treatment of IX with potassium cyanate gave the desired sulfonylurea VIb as the potassium salt, which was used as such in the sodium ethoxide-catalyzed ring closure. The latter reaction yielded compound I in salt form, which was converted to the free acid by means of Dowex-50 ion exchange resin.

The white crystalline product was very stable. It was purified for analysis by vacuum sublimation at 190°. Analyses for carbon, hydrogen, nitrogen and sulfur agreed closely with the values calculated for formula I. The pure product was soluble in water and ethanol, and insoluble in ether and tetrahydrofuran. These properties differ markedly from those reported for I by Campaigne,[6] and are similar to those of barbituric acid itself. The final product was a much stronger acid than its sulfonylureide precursor VIb. The pK_a' value for compound I, as determined from the pH of a 0.01 M solution, was 2.7 ± 0.10, showing that the product is a stronger acid that barbituric acid (pK_a' 3.9[11]). Potentiometric titration revealed that up to pH 12 the product of cyclization behaved as a monobasic acid, whose equivalent weight as determined by titration agreed closely with the molecular weight calculated for I. That no skeletal changes took place was shown by back-titration with hydrochloric acid, whereby the original curve was retraced.

The infrared spectrum of the product also supports the assignment of formula I, since two bands were present in the carbonyl region (1725 and 1698 cm.$^{-1}$). Moreover, the existence of a sulfonamide linkage is established by the presence of two strong bands at 1368 and 1162 cm.$^{-1}$ in the regions where the symmetric and antisymmetric stretching frequencies of the sulfonyl group of a sulfonamide function are usually observed.[12] The spectrum of barbituric acid, determined under similar conditions, also

(9) *Cf.* the experiments described below, and F. Kurzer, *Chem. Revs.*, **50**, 1 (1952), especially p. 44. From this reference it is clear that the reported[4] conversion of V to VIa is a rare exception to the general observation that sulfonyl chlorides and ureas do not yield sulfonylureas.

(10) Attempts to synthesize V by the reaction of chlorine and thioglycolic acid in aqueous solution were completely unsuccessful, either under the conditions described in the patent literature,[5] or by several variations thereof. Since our results show that the sulfonyl chloride group is easily hydrolyzed, its synthesis in aqueous solution would be difficult to achieve. This was borne out by further experiments in these laboratories by Mr. B. E. Hoogenboom, who investigated the chlorination of such compounds as ethyl thioglycolate, bis-(carboxymethyl) disulfide and ethyl (sodium thiosulfato) acetate. Although oxidation to the disulfide occurred in some experiments, in no case was a sulfonyl chloride isolated. The ability of an electron-withdrawing group to activate an adjacent sulfonyl chloride toward hydrolysis has been suggested as an explanation for the failure of certain thioureas to yield sulfonyl chlorides on chlorination in aqueous solution (J. M. Sprague and T. B. Johnson, THIS JOURNAL, **59**, 2439 (1937); K. Folkers, A. Russell and R. W. Bost, *ibid.*, **63**, 3530 (1941)).

(11) J. J. Fox and D. Shugar, *Bull. soc. chim. Belg.*, **61**, 44 (1952).

(12) J. N. Baxter, J. Cymerman-Craig and J. B. Willis, *J. Chem. Soc.*, 669 (1955).

shows two bands in the carbonyl region (1748 and 1715 cm.$^{-1}$). On the other hand, whereas barbituric acid absorbs strongly in the ultraviolet,[11] aqueous solutions of I at *p*H 2, 7 or 11 showed only end absorption extending up to about 225 mμ.[13]

From these observations we conclude that the product prepared in the sequence of reactions reported in this paper is correctly formulated as 1,2,4,2H-thiadiazine-3,5(4H,6H)-dione-1,1-dioxide (I), and is a stable, acidic substance resembling barbituric acid in its properties. The product to which Dickey[5] assigned formula I may have been the same as our product, but no data are available for comparison. We were unable to repeat two steps of his synthesis, however. Neither the chlorination of thioglycolic acid[10] nor the reaction of urea with chlorosulfonylacetic acid[9] yielded the reported products.

The properties reported by Campaigne[6] for the product to which he assigned structure I differ markedly from those of the compound which we believe to be I. Campaigne's product melted at 110–120°, was insoluble in water and ethanol, was neutral in aqueous suspension, was unstable to base, and underwent spontaneous decomposition. The assignment of structure I to this unstable product rests upon three principal pieces of evidence: the analysis for sulfur (no other analytical values were reported), the formation of acetylurea by desulfuration with Raney nickel, and the hydrolysis to sulfoacetic acid by boiling aqueous sodium bicarbonate.

A number of objections can be raised to this assignment of structure. It is difficult to reconcile the reported properties with formula I. There is no reason to expect marked instability in such a compound,[14,15] and the neutral character of the product is not in keeping with the well-known acidity of compounds with structures related to I, such as the sulfonylureas[9] and saccharin. Moreover, the desulfuration and hydrolysis do not prove that a sulfur–nitrogen link exists in the product. This is the crucial point, and a considerable body of data can be found in the literature to suggest that formation of such a bond is not likely to take place under the conditions used. Thus, the proposed intermediate IV had been prepared previously by Bodendorf and Senger,[4] who, as mentioned above, were unable to convert it to I. Furthermore, a number of 2-amino-1,3-thiazolidines have been subjected to the conditions used in Campaigne's experiments, but in no case has a sulfonyl chloride or its ring closure derivative been isolated. Rather, the free sulfonic acid has been obtained.[16] Finally, it has been observed[10] that sulfonic acids rather than sulfonyl chlorides are obtained on chlorination of those thioureas which have electron-withdrawing groups on the (non-urea) carbon which bears the sulfur (*e.g.*, $RO_2CCH_2SC(=NH)NH_2 \rightarrow HO_2CCH_2SO_3H$). Since compound VII has both the thiazolidine-type ring system and an electron-withdrawing group on the sulfur-bearing carbon, it is highly unlikely that a sulfonyl chloride or a sulfonylurea formed by ring closure would be the product of the reaction.

These objections are sufficient to show that the assignment of formula I to Campaigne's product is untenable. The present report is therefore the first in which 1,2,4,2H-thiadiazine-3,5(4H,6H)-dione-1,1-dioxide (I) has been adequately characterized and described.

Experimental[17]

Chlorosulfonylacetyl Chloride.—In the initial experiments this material was prepared by the reaction of sulfoacetic acid and thionyl chloride in a sealed tube, according to the method of Vieillefosse.[18] Subsequently it was discovered by Mr. B. E. Hoogenboom in these laboratories that the diacid chloride could be prepared in high yield without the aid of pressure, by using phosphorus oxychloride. The following is a typical procedure.

A mixture of 16.0 g. (0.1 mole) of sulfoacetic acid[19] and 38.4 g. (0.25 mole) of phosphorus oxychloride was heated in an oil-bath at 125°. Intermittent heating periods of one hour each separated by short cooling periods until a total heating time of 5 hr. had been attained gave the best results. At the end of the heating period, the fluid portion of the mixture was decanted from the resinous layer of phosphoric acid, and then distilled. Phosphorus oxychloride was removed at aspirator pressure, and the residual oil distilled at 71–72° (1 mm.) (lit.[18] b.p. 90° (8 mm.)). The yield was 14.3 g. (81%). A portion of the product was redistilled at 66° (0.5 mm.). It was further identified by C, H analysis. Similar yields were obtained when the scale was increased tenfold.

Chlorosulfonylacetic Acid.—Two methods of hydrolysis of chlorosulfonylacetyl chloride were used. One was that of Vieillefosse[8]; the second was as follows: A solution of 51.5 g. (0.29 mole) of chlorosulfonylacetyl chloride in 200 ml. of benzene was placed in a flask protected from moisture and cooled in an ice-bath. Over a 3-hour period 5.25 g. (0.29 mole) of water was added with stirring. The resulting solution was allowed to stir for 9 hours more, after which the precipitated solid was collected. Two more crops of crystals were obtained by concentrating the filtrate in the cold under reduced pressure. The combined yield was 31 g. (67%) of sticky white crystals, m.p. 73–76°. The crude product was only partially soluble in carbon tetrachloride. The insoluble portion was a brown oil which was identified as sulfoacetic acid by conversion to the anilinium salt which did not depress the m.p. of an authentic sample.[20] The soluble portion was recrystallized from carbon tetrachloride, yielding a white crystalline product which melted at 77–78° (lit.[4] m.p. of chlorosulfonylacetic acid 77–78°). The yield of pure product was 11 g. (23%). Chlorosulfonylacetic acid prepared in this way remained unchanged for at least a

(13) We ascribe this difference to the fact that resonance in the thiadiazine ring system is restricted because the sulfonyl group does not readily participate in resonance. Extensive p-π conjugation is possible in barbituric acid (F. Arndt, L. Loewe and L. Ergener, *Rev. fac. sci. univ. Istanbul*, **13a**, 103 (1948); *C. A.*, **43**, 579 (1949)).

(14) The instability of the product may have been due to the presence of nitrogen trichloride. The authors[6] mention the presence of impurities with nitrogen–chlorine bonds, and the fact that some of their samples exploded unexpectedly also supports this suggestion. Because of the explosive nature of the reaction, we have made no attempt to repeat the earlier work (see also the last reference in footnote 10 for a comment on the hazardous nature of this type of reaction).

(15) Whereas Rylander and Campaigne report that the product is decomposed by nitrous acid, we have found that 1 yields a crystalline oxime in a fashion similar to barbituric acid (unpublished work with R. Abbott and S. Wawzonek).

(16) See for example: (a) S. Gabriel, *Ber.*, **22**, 1139 (1889); (b) C. Avenarius, *ibid.*, **24**, 260 (1891); (c) T. B. Johnson and J. M. Sprague, THIS JOURNAL, **58**, 1348 (1936).

(17) Melting points and boiling points are uncorrected.

(18) R. Vieillefosse, *Bull. soc. chim., France*, [5] **7**, 933 (1940).

(19) Prepared by a modification of Stillich's method (O. Stillich, *J. prakt. Chem.*, [2] **73**, 538 (1906)). Excess sodium sulfite was oxidized with hydrogen peroxide to sodium sulfate, and barium chloride was added. After the barium sulfate had been removed by centrifuging, the barium salt of sulfoacetic acid was precipitated with ammonium hydroxide. The free acid was obtained by reaction of an aqueous suspension of the barium salt with the calculated quantity of dilute sulfuric acid.

(20) O. Stillich, *ibid.*, [2] **74**, 51 (1906).

month exposed to atmospheric moisture, as shown by the constancy of the m.p. and C, H analysis during this period.

β-Phenylethyl sulfoacetate was prepared for purposes of identification. A mixture of sulfoacetic acid monohydrate (10.5 g., 0.067 mole) and 10.3 g. (0.084 mole) of β-phenylethyl alcohol was refluxed in 25 ml. of 98% formic acid for two hours. After this time 20 ml. of dry toluene was added and the mixture was distilled until approximately 28 ml. of distillate had been collected. The residual brown oil was separated and placed in a desiccator over phosphorus pentoxide. This oil failed to crystallize during two weeks. A portion was converted into the aniline salt of β-phenylethyl thioacetate which melted at 142–146° after three recrystallizations from chloroform and one from tetrahydrofuran.

Anal. Calcd. for $C_{16}H_{21}O_5NS$: C, 57.02; H, 5.68. Found: C, 56.98; H, 5.72.

Phenyl Carboxymethanesulfonate.—To 20 g. (0.22 mole) of molten phenol was cautiously added 0.26 g. (0.011 mole) of sodium in small pieces. While this mixture was still liquid 2 g. (0.011 mole) of solid chlorosulfonylacetic acid was added. After 10 minutes the entire solution was poured into ether and the ether solution was extracted with three 15-ml. portions of 5% sodium carbonate solution. Acidification of the basic extracts gave a tan oil which solidified on cooling. By recrystallization from benzene 0.65 g. (27%) of white solid, m.p. 86–87°, was obtained.

Anal. Calcd. for $C_8H_{10}O_5S$: C, 44.41; H, 3.78. Found: C, 44.55; H, 3.57.

The product was assigned the indicated structure, rather than that of phenyl sulfoacetate, on the basis of its solubility in ether and insolubility in water.

Ethyl Sulfamylacetate.—Water (2.7 g., 0.15 mole) in 100 ml. of dry ether at −10° was added slowly with swirling to 26.6 g. (0.15 mole) of chlorosulfonylacetyl chloride in 100 ml. of dry ether at −10°. The resulting solution was allowed to stand for 0.5 hours, after which it was evaporated to dryness under reduced pressure in the cold. A solution of the resulting solid in 100 ml. of dry ether was added slowly with stirring to 30 ml. of liquid ammonia in a 500-ml. three-necked flask equipped with a reflux condenser. This mixture was allowed to stir for one hour after which the flask was heated gently on a steam-bath to remove as much excess ammonia as possible. About 250 ml. of absolute ethanol was then added, and dry hydrogen chloride was passed through the refluxing, stirred mixture for one hour. After the mixture was refluxed for an additional 3 hours, it was filtered and the filtrate was evaporated under reduced pressure to a brown sirup. This sirup was extracted with three 50-ml. portions of refluxing benzene. The product precipitated from the cooled solution in shiny, yellow platelets. Recrystallization from benzene gave 3.6 g. (15%) of white crystals, m.p. 66–67°; after two more recrystallizations the melting point was 67–68°.

Anal. Calcd. for $C_4H_9NO_4S$: C, 28.78; H, 6.38; N, 8.39. Found: C, 29.37; H, 6.11; N, 8.08.

The residue from the benzene extraction was a brown oil, which made up the greater part of the product. This material crystallized when acetone was added, and after two recrystallizations from 1-propanol melted at 135–140°. It liberated ammonia when mixed with cold sodium hydroxide. A mixed melting point with an authentic sample of ammonium carbethoxymethanesulfonate was not depressed.

In an attempt to devise an alternate synthesis of ethyl sulfamylacetate with higher yields, the conversion of ethyl chlorosulfonylacetate[21] to ethyl sulfamylacetate was investigated. Neither the reaction of the sulfonyl chloride with liquid ammonia nor with solutions of dry ammonia in ether, benzene, tetrahydrofuran, pyridine or chloroform at room temperature yielded the desired product. The use of ammonium carbonate at 100° in pyridine or in the absence of solvent was also unsuccessful. In each case the procedure involved the removal of the volatile solvent and extraction of the residue with hot benzene. In all cases, evaporation of the benzene left unidentifiable oils.

Ammonium Carbethoxymethanesulfonate.—Sulfoacetic acid monohydrate, (20 g., 0.13 mole), was refluxed for four hours with 50 ml. of absolute ethanol. The ethanol was removed by distillation, a small portion of the residual oil was placed in ether and dry ammonia was passed into the mixture until no more white precipitate formed. The precipitate was collected and recrystallized twice from 1-propanol. It melted at 135–140°.

Anal. Calcd. for $C_4H_{11}NO_5S$: C, 25.95; H, 5.94. Found: C, 25.82; H, 5.90.

Potassium Carbethoxymethanesulfonylurea.—The method of Henke was followed.[22] A solution of 25 ml. of 95% ethanol, 2 g. (0.012 mole) of ethyl sulfamylacetate and 0.97 g. (0.012 mole) of potassium cyanate was refluxed for 3 hours on a steam-bath. The solution was cooled and the resulting white powder collected by filtration. The yield was 2.25 g. (79%). A small portion was recrystallized for analysis from an ethanol–water mixture.

Anal. Calcd. for $C_5H_9N_2O_6SK$: C, 24.20; H, 3.63; N, 11.28. Found: C, 23.89; H, 3.69; N, 10.91.

1,2,4,2H-Thiadiazine-3,5(4H,6H)-dione-1,1-dioxide.—Sodium (0.48 g., 0.021 mole) was dissolved in 140 ml. of dry ethanol and 5.1 g. (0.021 mole) of solid potassium carbethoxymethanesulfonylurea was added. The resulting heterogeneous mixture was refluxed with stirring for 12 hours on a steam-bath. After cooling, 4.6 g. (100%) of crude salt was collected. This was dissolved in two 50-ml. portions of water and passed down a Dowex 50 cationic exchange column in the acid form. Elution of the product was followed with *p*H paper. The fractions between *p*H 2 and 4 were collected, combined, and evaporated under a jet of dry air on a steam-bath until crystals began to form. Cooling gave 2.5 g. (74%) of white product, m.p. 226–227° (dec.) For analysis the compound was sublimed at 190° at 1 mm. pressure.

Anal. Calcd. for $C_3H_4N_2O_4S$: C, 21.95; H, 2.46; N, 17.07; S, 19.53; neut. equiv., 164. Found: C, 21.92, 21.87; H, 2.44, 2.50; N, 17.15; S, 19.24, 19.10; neut. equiv. (by potentiometric titration), 165, 164.

IOWA CITY, IOWA

(21) R. Vieillefosse, *Bull. soc. chim. France*, 351 (1947).

(22) O. Henke, U. S. Patent 2,390,253; *C. A.*, **40**, 1876 (1946).

[CONTRIBUTION FROM THE OHIO STATE UNIVERSITY RESEARCH FOUNDATION]

Some Reactions of Monochloro-*s*-triazines[1]

BY HANSJUERGEN SCHROEDER

RECEIVED MAY 4, 1959

The interaction of certain monochloro-*s*-triazines with nucleophilic reagents has been studied. With strongly electronegative substituents in the 2- and 4-position, 6-chloro-*s*-triazines react easily with very weak bases such as heterocyclic amines, and even with alcohols in the absence of bases. The infrared maxima near 6.5 μ (in-plane ring bands) of a number of *s*-triazines are presented.

Recently in a study of the Pinner synthesis of monohydroxy-*s*-triazines we described the synthesis of a series of 6-amino-*s*-triazines derived from 2,4-bis-polychloroalkyl-6-chloro-*s*-triazines.[2] Of the compounds prepared, 6-aziridino-2,4-bis-trichloro-

(1) This article is based on work performed under Project 110-B of The Ohio State University Research Foundation sponsored by the Olin Mathieson Chemical Corp., New York, N. Y.

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