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 116-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).

methyl-*s*-triazine (I) exhibited interesting ovicidal activity against mites and aphids. These properties prompted us to prepare some new *s*-triazines related to 2,4-bis-trichloromethyl-6-chloro-*s*-triazine (II), the starting material for the synthesis of I, and led us to investigate in general the activity of the chlorine atom in substituted 6-chloro-*s*-triazines.

Aza-aromatic heterocycles such as pyridine, diazines or triazines are distinguished from benzene by their basicity which is due to the substitution of CH by nitrogen atoms. The electronegativity difference between nitrogen and carbon causes withdrawal of electrons to nitrogen, thereby leading to a decreased electron density at the carbon atoms. Halogen atoms attached to the carbon atoms in α-position to the nitrogen therefore are activated and undergo nucleophilic displacement reactions.

In the 1,3,5-triazines which have a regular distribution of the nitrogen atoms, the relative ease of the nucleophilic displacement of a chlorine atom in the 6-position will depend on the nature of the substituents in the 2- and 4-positions. Electron-withdrawing substituents such as the CCl_3 group which exert a strong inductive pull, will reduce the electron availability at the 6-carbon atom and consequently enhance the chlorine activity, while nucleophilic substituents such as the amino group will diminish the reactivity of the chlorine atom.

In order to extend our knowledge of the influence of different substituents, 6-chloro-2,4-diphenyl-*s*-triazine (III) and II were subjected to a number of replacement experiments. In spite of the fact that both compounds react easily with aliphatic amines at room temperature,[2,3] they should, however, have a different degree of reactivity toward nucleophilic reagents since the generally electrophilic phenyl group in contrast to the CCl_3 group is able to exert an electron release upon the electron demand of the electrophilic *s*-triazine ring.

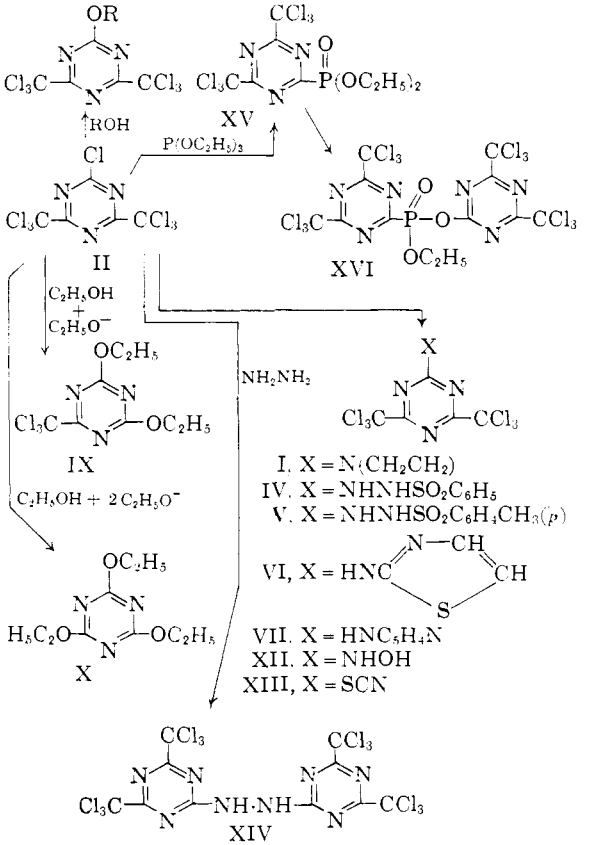
This assumption has been confirmed in their reaction with weaker bases; II reacted with benzenesulfonyl hydrazide and toluene-*p*-sulfonyl hydrazide in acetonitrile to give 2,4-bis-trichloromethyl-6-benzenesulfonylhydrazino-*s*-triazine (IV), and 2,4-bis-trichloromethyl-6-toluene-*p*-sulfonylhydrazino-*s*-triazine (V), respectively. Under the same conditions III did not react at all.

Similar results were obtained when we extended our studies to some heterocyclic amines, considerably weaker bases than aliphatic amines. 2-Aminothiazole and 2-aminopyridine did not react with III but did react with II to give the expected 6-aminothiazolyl-(2′)-2,4-bis-trichloromethyl-*s*-triazine (VI) and 6-aminopyridyl-(2′)-2,4-bis-trichloromethyl-*s*-triazine (VII). However, when an exceedingly weak base was used, 4-amino-2,6-dimethylpyrimidine, neither II nor III reacted.

In extension of the above a study of the action of alcohols with monochloro-*s*-triazines was undertaken. Alcohols are nucleophiles of moderate activity, and could react according to the literature,[4-6] only in the presence of bases with 6-chloro-*s*-triazines such as III. It is known that III and also 2,4-bis-*p*-chlorophenyl-6-chloro-*s*-triazine[3] can be recrystallized from ethanol. We have found, however, that the very reactive II is readily converted by various alcohols into the respective 2,4-bis-trichloromethyl-6-monoalkoxy-*s*-triazine in a 80–95% average yield in the absence of bases. The resistance of the new alkoxy-*s*-triazines toward the alcoholic hydrogen chloride formed as by-product in the reaction is surprising in view of the corresponding reaction of cyanuric chloride (VIII) with alcohols to give mainly alkyl chlorides and cyanuric acid and only small amounts of cyanuric esters.[7] Only under conditions which effect the rapid removal of the hydrogen chloride formed, could VIII be converted into the cyanuric esters.[8]

Secondary alcohols take part in this reaction with II as readily as primary alcohols. No definite result could be obtained with tertiary alcohols; II and *t*-butyl alcohol form a compound of an unknown structure in very poor yield. No reaction was observed with trifluoroethanol, this alcohol being too acid for the desired purpose. In this case the sodium alcoholate prepared in excess of the alcohol gave with II the monoalkoxy-compound. For the same reason, alkanethiols do not react with II. Physical and analytical data for the monoalkoxy-*s*-triazines prepared are compiled in Table I.

When the reaction of II with ethanol was carried out in the presence of one or two moles of sodium dissolved in the excess ethanol, a stepwise replacement of the trichloromethyl groups by ethoxy



(3) Ch. Grundmann and H. Schroeder, *Ber.*, **87**, 753 (1954).
(4) A. W. Hofmann, *ibid.*, **19**, 2061 (1886).
(5) J. Coutroulis and C. W. Banks, THIS JOURNAL, **67**, 1946 (1945).
(6) J. R. Dudley, J. T. Thurston, F. C. Schaefer, *et al.*, *ibid.*, **73**, 2986 (1951).
(7) P. Klason, *J. prakt. Chem.*, [2] **34**, 152 (1886).
(8) H. Huemer, German Patent 854,801 (1952).

TABLE I

MONOALKOXY-*s*-TRIAZINES

R_1	R_2	M.p., °C.	B.p., °C.	Mm.	n^t_D	t, °C.	Yield, %	Formula	Mol. wt.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Chlorine, % Calcd.	Chlorine, % Found	Fluorine, % Calcd.	Fluorine, % Found
CCl_3	CH_3	46					77	$C_6H_3N_3Cl_6O$	315.9	20.84	20.77	0.87	0.89	12.15	12.33	61.51	61.93		
CCl_3	CH_2CH_3		135	0.1	1.5332	30	90	$C_7H_5N_3Cl_6O$	359.8	23.36	23.43	1.40	1.35	11.95	11.90	59.12	59.03		
CCl_3	$(CH_2)_3CH_3$		146	.3	1.5289	27	90	$C_9H_9N_3Cl_6O$	387.9	27.86	28.08	2.34	2.18	10.83	10.90	54.84	55.21		
CCl_3	$(CH_2)_4CH_3$		151	.25	1.5260	25	91	$C_{10}H_{11}N_3Cl_6O$	402.0	29.88	29.63	2.76	2.79	10.45	10.64	52.93	53.01		
CCl_3	$CH(CH_3)_2$		157	.4	1.5321	25	80	$C_8H_7N_3Cl_6O$	373.9	25.70	25.61	1.89	1.90	11.24	11.57	56.90	57.14		
C_2F_5	CH_2CH_3		122	.15	1.3588	23	71	$C_9H_5N_3F_{10}O$	361.2	29.93	30.28	1.40	1.95	11.64	11.63				
CCl_3	CH_2CF_3		116	.65	1.5055	28	92	$C_7H_2N_3F_3Cl_6O$	413.9	20.31	20.24	0.48	0.78	10.15	10.49	51.40	52.04	13.77	13.88

groups was achieved leading to 4,6-diethoxy-2-trichloromethyl-*s*-triazine (IX) and 2,4,6-triethoxy-*s*-triazine (X).

A corresponding nucleophilic replacement of CCl_3 groups with ammonia and amines in the *s*-triazine series was first reported by Weddige[9] using tris-trichloromethyl-*s*-triazine (XI) in his studies and has been encountered in numerous *s*-triazines since.[10] The controlled exchange of CCl_3 groups by alkoxy groups has not been reported previously and could not be achieved by the action of sodium ethylate in excess ethanol on XI, the reaction giving X exclusively, even in the presence of only one mole of sodium.[11]

Agricultural screening revealed that the 6-alkoxy-2,4-bis-trichloromethyl-*s*-triazines possess outstanding activity as pre-emergence grass-specific herbicides. These findings are particularly interesting since it has been reported recently[12] that *s*-triazine derivatives of related structure, 6-alkoxy-2,4-dichloro-*s*-triazines, are highly effective as herbicides.

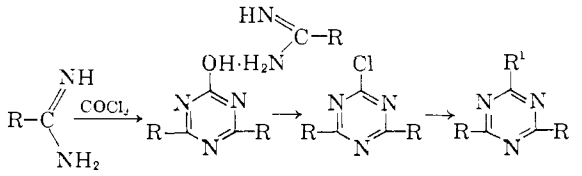
In view of these results it appeared desirable to replace the 6-chlorine atom by other functional groups. II reacted with hydroxylamine and KSCN to give the expected 2,4-bis-trichloromethyl-6-hydroxylamino-*s*-triazine (XII) and 2,4-bis-trichloromethyl-6-thiocyano-*s*-triazine (XIII); the latter compound did not display any insecticidal activity in contrast to the previously known 2,4-diamino-6-thiocyano-*s*-triazine.[13]

Two moles of II reacted with one mole of hydrazine to give di-N,N′-(2,4-bis-trichloromethyl-triazinyl (6))-hydrazine (XIV). The symmetrical structure was proved by the fact that XIV does not react with N_2O_3; II reacted with triethyl phosphite quite violently giving a black reaction mixture from which only a small amount of a distillable product could be obtained. Analysis of the latter product shows it to be O-ethyl-O′-2,4-bis-trichloromethyl-*s*-triazinyl-(6)-2,4-bis-trichloromethyl-*s*-triazinyl-(6)-phosphonate (XVI). Therefore the 6-chlorine atom had first reacted in a normal Michaelis–Arbuzow reaction to give O,O′-diethyl-2,4-bis-trichloromethyl-triazinyl-(6)-phosphonate (XV), but this intermediate reacted with an additional mole of II by splitting off ethyl chloride to XVI.

In continuation of earlier work on 6-monohydroxy-*s*-triazines[2] we attempted the synthesis of hydroxy-*s*-triazines from bromine and fluorine substituted amidines. Pentafluoropropionamidine (XVII) and heptafluorobutyramidine (XVIII)[14,15] reacted with phosgene to the expected hydroxy-*s*-triazine salts XIX and XX which were chlorinated to give 2,4-bis-pentafluoroethyl-6-chloro-*s*-triazine (XXI) and 2,4-bis-heptafluoropropyl-6-chloro-*s*-triazine (XXII).

Probably because of the strongly electronegative perfluoroalkyl groups, XXI and XXII showed the

(9) A. Weddige, *J. prakt. Chem.*, [2] **33**, 81 (1886).
(10) A. Kreutzberger, THIS JOURNAL, **79**, 2629 (1957).
(11) E. Kober, unpublished results.
(12) H. Koopman, J. H. Uhlenbrock and J. Daams, *Nature*, **180**, 146 (1957).
(13) J. J. Roemer and D. W. Kaiser, U. S. Patent 2,650,220.
(14) D. R. Husted, U. S. Patent 2,676,985 (1954).
(15) W. L. Reilly and H. C. Brown, THIS JOURNAL, **78**, 6032 (1956).



XVII, R = C_2F_5 XIX, R = C_2F_5
XVIII, R = C_3F_7 XX, R = C_3F_7
XXI, R = C_2F_5 XXIII, R = C_2F_5
XXII, R = C_3F_7 R′ = $HNHNSO_2C_6H_4CH_3$
XXIV, R = C_3F_7
R′ = $NHNHSO_2C_6H_4CH_3$
XXV, R = C_2F_5
R′ = OC_2H_5

expected reactivity toward nucleophilic agents in the replacement of the chlorine atom. Both compounds reacted with *p*-toluenesulfonylhydrazine to give XXIII and XXIV, while XXI reacted with ethanol to give XXV.

In the synthesis of the corresponding 2,4-bis-polybromoalkyl-*s*-triazine derivatives our attempts to prepare two starting compounds for the Pinner synthesis, dibromoacetamidine-HCl and tribromoacetamidine-HCl, met with failure. Ethyl dibromoacetimidate and ethyl tribromoacetimidate were obtained as hydrochlorides from the corresponding nitriles, but all attempts to convert them into the amidines were unsuccessful.

It appears to be noteworthy to describe a qualitative preliminary test for the reactivity of monochloro-*s*-triazine derivatives. Upon addition of triethylamine to a monochloro-*s*-triazine in ether or benzene solution sometimes the formation of a precipitate is observed. The compound then formed probably is a quaternary ammonium salt, insoluble in the mentioned solvents. This reaction takes place only in the case of sufficiently reactive chlorine atoms and therefore is indicative of the carbon–chlorine bond nature.

An example is the correlation of the following four chloro-*s*-triazines: 2,4-bis-trichloromethyl-6-chloro-*s*-triazine (II), 2,4-bis-dichloromethyl-6-chloro-*s*-triazine (XXVI),[2] 2,4-bis-monochloromethyl-6-chloro-*s*-triazine (XXVII)[2] and 6-chloro-2,4-dimethyl-*s*-triazine (XXVIII).[2] Whereas II and XXVI react instantaneously with triethylamine, XXVII reacts in a considerably slower rate and XXVIII does not react at all and could therefore be dechlorinated catalytically in the presence of triethylamine.[2] It might be mentioned that most of the dichlorosubstituted *s*-triazines and trichloro-*s*-triazine (cyanuric chloride) undergo a rapid reaction with triethylamine.

In a recent investigation[16] on the infrared spectra of 1,3,5-triazine derivatives, mainly substituted melamines, the sharp but medium strength band near 12.25 μ was assigned to an out-of-plane ring vibration of the *s*-triazine ring. This band was found to shift toward longer wave lengths upon introduction of strongly electrophilic groups such as chlorine onto the triazine ring.

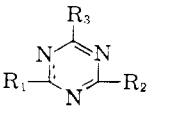
A similar band shift was indicated for the very strong absorbance around 6.5 μ which is assigned to a C=N stretching mode (in-plane vibration of the triazine ring). Padgett and Hamner reported that substituted monochloro-*s*-triazines show this band at 6.4 to 6.5 μ, but that this band is observed at 6.7 μ in cyanuric chloride.

A study in this Laboratory of the infrared spectra of *s*-triazines dealt with the shift of the wave length of the major band around 6.5 μ (1538 cm.$^{-1}$) in accordance with the character of the substituents.

Table II presents this characteristic frequency of 19 *s*-triazine compounds, all of them in the region of 1563 to 1506 cm.$^{-1}$ (6.4 to 6.64 μ). Only those *s*-triazines which gave sharp maxima are recorded and, except for the first two, none of these compounds may exist in other tautomeric structures.

TABLE II

CHARACTERISTIC INFRARED FREQUENCY OF *s*-TRIAZINES



R_1	R_2	R_3	Cm.$^{-1}$	Lit. ref.
CH_3	CH_3	OH	1563	2
CH_3	CH_3	NH_2	1562	2
CH_3	CH_3	H	1558	2
OC_2H_5	OC_2H_5	OC_2H_5	1558	(X)
OCH_3	OCH_3	CHN_2	1558	17
H	H	H	1555	18, 19
CCl_3	OC_2H_5	OC_2H_5	1540	(IX)
CH_3	CH_3	Cl	1538	2
CH_3	Cl	Cl	1529	20
CCl_3	CCl_3	CCl_3	1529	(XI)
CHN_2	Cl	Cl	1528	17
CCl_3	CCl_3	Cl	1527	(II)
CH_2Cl	CH_2Cl	Cl	1527	2
$COOC_2H_5$	$COOC_2H_5$	$COOC_2H_5$	1527	21
$CHCl_2$	$CHCl_2$	Cl	1523	2
C_6H_5CO	C_6H_5CO	C_6H_5CO	1523	22
CH_3CCl_2	CH_3CCl_2	Cl	1522	2
COCl	COCl	COCl	1520	22
Cl	Cl	Cl	1506	23

It is evident that substitution on the ring results in a considerable influence on the wave length of this band; electrophilic groups cause a shift to smaller frequencies (or longer wave lengths, respectively) and electron donor groups cause the reverse effect.

Acknowledgment.—The author is very much indebted to the Olin Matheson Chemical Corp. for their generous support of this work. He also wishes to express his appreciation to Dr. C. J. Grundmann for his interest in the work and for stimulating discussions. Furthermore he is grateful to Miss D. M. Robins for infrared spectroscopic analyses and to Dr. R. Rätz for his helpful discussions regarding the Michaelis–Arbuzow reaction.

(16) W. M. Padgett II and W. F. Hamner, THIS JOURNAL, **80**, 803 (1958).

(17) Ch. Grundmann and E. Kober, THIS JOURNAL, **79**, 944 (1957).

(18) J. Goubeau, E. L. Jahn, A. Kreutzberger and Ch. Grundmann, *J. Phys. Chem.*, **58**, 1078 (1954).

(19) J. E. Lancaster and N. B. Colthup, *J. Chem. Phys.*, **22**, 1149 (1954).

(20) W. Hentrich and M. Hardtmann, U. S. Patent 1,911,689.

(21) E. Ott, *Ber.*, **52**, 661 (1919).

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

(23) A. Roosens, *Bull. soc. chim. Belg.*, **59**, 377 (1950).

Experimental[24]

The following procedure is representative of the synthesis of substituted monoalkoxy-*s*-triazines by alcoholysis of substituted monochloro-*s*-triazines.

2,4-Bis-trichloromethyl-6-ethoxy-*s*-triazine.—A solution of 35 g. (0.1 mole) of 2,4-bis-trichloromethyl-6-chloro-*s*-triazine (II) in 100 ml. of ethanol was kept at 65° for 30 minutes. After evaporation of the excess ethanol the remaining liquid was dissolved in 100 ml. of petroleum ether with the separation of a small amount of trichloroacetylurea, m.p. 153°. It was filtered off and the filtrate was evaporated to remove the solvent. The residual bis-trichloromethyl-ethoxy-*s*-triazine was purified by vacuum distillation.

In the case of 2,4-bis-trichloromethyl-6-methoxy-*s*-triazine the product obtained was purified by recrystallization from petroleum ether. *Anal.* of trichloroacetylurea, recrystallized from ligroin. Calcd. for $C_3H_3Cl_3N_2O_2$ (205.4): N, 13.63; Cl, 51.77. Found: N, 13.40; Cl, 51.48.

4,6-Diethoxy-2-trichloromethyl-*s*-triazine (IX).—A solution of sodium (0.69 g., 0.03 mole) in 30 ml. of absolute ethanol was added to a cold solution of II (10.5 g., 0.03 mole) in 70 ml. of ethanol. The precipitated sodium chloride was filtered off and the filtrate was evaporated. The residue was distilled *in vacuo*, b.p. 124° (0.1 mm.), m.p. 21°, $n^{30}D$ 1.5112, yield 6.5 g. (76%). *Anal.* Calcd. for $C_8H_{10}Cl_6N_3O_2$ (286.6): C, 33.53; H, 3.52; Cl, 37.12; N, 14.66. Found: C, 32.54; H, 2.93; Cl, 37.42; N, 14.96.

2,4,6-Triethoxy-*s*-triazine (X).—Sodium metal (0.79 g., 0.034 mole) was dissolved in 15 ml. of absolute ethanol and was added to a solution of II (6 g., 0.017 mole) in 50 ml. of cold ethanol. After 10 minutes the ethanol was evaporated. X was isolated from the dark-brown viscous residue by distillation *in vacuo*. It crystallized after refrigeration for 24 hours and was recrystallized from petroleum ether. The yield was 1.3 g. (41%), m.p. 26°, $n^{30}D$ 1.4765. Its identity was proved by its undepressed mixed melting point with an original sample prepared from cyanuric chloride and sodium ethanolate.[25]

2,4-Bis-trichloromethyl-6-trifluoroethoxy-*s*-triazine.—A solution of Na (0.79 g., 0.034 mole) in 30 ml. of CF_3CH_2OH was added with stirring to a mixture of II (12 g., 0.034 mole) and 20 ml. of CF_3CH_2OH. Only a moderate evolution of heat was observed. The mixture was stirred for 2 hours at 65° and then reacted neutral. The separated NaCl was filtered off, the excess alcohol evaporated and 50 ml. of petroleum ether added to the residue. The solution was filtered again, the filtrate evaporated and the reaction product distilled *in vacuo*. The yield was 13 g. (92%); physical and analytical data are given in Table I.

2,4-Bis-trichloromethyl-6-toluene-*p*-sulfonylhydrazino-*s*-triazine (V).—A solution of II (2.1 g., 0.006 mole) in 10 ml. of acetonitrile was added to a solution of toluenesulfonyl hydrazide (2.2 g., 0.012 mole) in acetonitrile. The theoretical amount (1.3 g.) of toluenesulfonyl hydrazide hydrochloride separated overnight and was filtered off. The filtrate was evaporated to dryness *in vacuo* and the remaining product was recrystallized twice from benzene; yield 2.66 g. (90%), m.p. 183–184°. *Anal.* Calcd. for $C_{12}H_9Cl_6N_5SO_2$ (500.0): C, 28.82; H, 1.82; Cl, 42.52; N, 14.02; S, 6.41. Found: C, 28.71; H, 1.82; Cl, 42.61; N, 13.99; S, 6.34.

2,4-Bis-trichloromethyl-6-benzenesulfonylhydrazino-*s*-triazine (IV).—According to the above procedure II (2.1 g., 0.006 mole) in 10 ml. of CH_3CN and benzenesulfonyl hydrazide (2 g., 0.012 mole) in 25 ml. of CH_3CN reacted to form V which was recrystallized from benzene. The yield was 2.5 g. (87%), m.p. 178–180°. *Anal.* Calcd. for $C_{11}H_7Cl_6N_5SO_2$ (486.0): C, 27.18; H, 1.45; Cl, 43.77; N, 14.41; S, 6.60. Found: C, 27.16; H, 1.43; Cl, 43.51; N, 14.40; S, 6.97.

6-Aminothiazolyl-(2′)-2,4-bis-trichloromethyl-*s*-triazine (VI).—Two grams of II (0.006 mole) reacted with 1.19 g. (0.012 mole) of 2-aminothiazole in acetonitrile to form VII which separated rapidly from the solution and was suctioned off after 3 hours. It was recrystallized twice from dioxane; yield 1.98 g. (80%), m.p. 280–283°. *Anal.* Calcd. for $C_8H_3Cl_3N_5S$ (413.9): C, 23.21; H, 0.73; Cl, 51.39; N, 16.92; S, 7.75. Found: C, 23.57; H, 0.78; Cl, 51.01; N, 16.56; S, 7.72.

6-Aminopyridyl-(2′)-2,4-bis-trichloromethyl-*s*-triazine (VII).—The reaction of II (21 g., 0.06 mole) with 12.1 g. (0.12 mole) of 2-aminopyridine in acetonitrile produced VII, which was recrystallized twice from ligroin. The yield was 18.3 g. (75%), m.p. 241°. *Anal.* Calcd. for $C_{10}H_6Cl_6N_5$ (408.9): C, 29.37; H, 1.48; Cl, 52.02; N, 17.13. Found: C, 29.32; H, 1.34; Cl, 52.15; N, 17.09.

2,4-Bis-trichloromethyl-6-hydroxylamino-*s*-triazine (XII).—A methanolic solution of hydroxylamine was prepared by adding 3.3 g. of sodium to the solution of $NH_2OH \cdot HCl$ (9.8 g., 0.14 mole) in 60 ml. of methanol. The precipitated NaCl was filtered off, and the hydroxylamine solution was added to 25 g. (0.07 mole) of II in 100 ml. of anhydrous ether with shaking and ice-cooling. The reaction mixture then was evaporated *in vacuo;* the viscous residue was extracted with ether. The filtrate was evaporated again, the remaining oil was dissolved in hot ligroin; XII crystallized from it upon cooling, m.p. 109–112°. For further purification it was recrystallized twice from ligroin; yield of XII, 21.8 g. (88%), m.p. 135°. *Anal.* Calcd. for $C_5H_2Cl_6N_4O$ (346.8): C, 17.32; H, 0.58; Cl, 61.34; N, 16.15. Found: C, 17.15; H, 0.72; Cl, 61.21; N, 16.82.

2,4-Bis-trichloromethyl-6-thiocyano-*s*-triazine (XIII).—A solution of KSCN (1.4 g., 0.014 mole) in 20 ml. of acetonitrile was added to a solution of II (4.9 g., 0.014 mole) in 20 ml. of acetonitrile. The reaction mixture was kept at 50° for 20 min., then the precipitated KCl was filtered off by suction. The filtrate was evaporated at reduced pressure; the remaining product was distilled *in vacuo*. The yield was 3.3 g. (63%), b.p. 130° (0.1 mm.). Compound XIII solidified after refrigeration, m.p. 62°. *Anal.* Calcd. for $C_6Cl_6N_4S$ (372.9): C, 19.32; Cl, 57.05; N, 15.03; S, 8.60. Found: C, 19.47; Cl, 57.05; N, 15.03; S, 8.58.

Di-N,N′-(2,4-bis-trichloromethyl-triazinyl-(6))-hydrazine (XIV).—To an ice-cooled solution of II (30 g., 0.085 mole) in 120 ml. of ether was added dropwise with shaking the solution of hydrazine (3.0 g., 0.094 mole) in 20 ml. of methanol. The addition was stopped when the reaction mixture turned from yellow into red-brown. The solvents were evaporated, and the $NH_2NH_2 \cdot HCl$ formed during the reaction was removed by recrystallization of the reaction product from ligroin; yield of XIV: 21.7 g. (77%), m.p. 245°. *Anal.* Calcd. for $C_{10}H_2Cl_{12}N_8$ (659.7): C, 18.21; H, 0.31; Cl, 64.50; N, 16.99. Found: C, 18.03; H, 0.75; Cl, 64.30; N, 17.05.

O-Ethyl-O-2,4-bis-trichloromethyl-*s*-triazinyl-(6)-2,4-bis-trichloromethyl-*s*-triazinyl-(6)-phosphonate (XVI).—An amount of 7 g. (0.02 mole) of II was added in small portions with stirring and ice-cooling to triethyl phosphite (3.3 g., 0.02 mole). After keeping the reaction mixture at 145° for 2 hours, the product obtained was subjected to vacuum distillation to give a small amount of XVI besides a large charred residue. The yield was 1.5 g. (19.7%), b.p. 118° (1 mm.), $n^{29}D$ 1.5230. Repetition of the experiment gave XVI in a 14% yield, but no distillable products were obtained when the experiment was run with 20 g. of II. *Anal.* Calcd. for $C_{12}H_5Cl_{12}N_6O_3P$ (737.7): C, 19.54; H, 0.68; Cl, 57.68; N, 11.39; P, 4.20. Found: C, 20.19; H, 1.28; Cl, 57.02; N, 11.48; P, 4.07.

2,4-Bis-heptafluoropropyl-6-hydroxy-*s*-triazine heptafluorobutyramidine Salt (XX).—An amount of 21 g. (0.1 mole) of heptafluorobutyramidine was dissolved to a great extent in 450 ml. of water at 3° by rapid stirring. By alternate addition of the solutions of $COCl_2$ (8 g., 0.08 mole) in 40 ml. of toluene and of NaOH (6.4 g., 0.16 mole) in 16 ml. of H_2O, the *p*H of the mixture was maintained at 8–9. Addition was completed within 5 minutes and the viscous product precipitated during the reaction was dried *in vacuo* over P_2O_5. Purification was achieved by dissolving it in ethanol and precipitating with ice-water. The yield was 13 g. (61%) of product, m.p. 127°. *Anal.* Calcd. for $C_{13}H_4F_{21}N_5O$ (645.2): C, 24.20; H, 0.63; F, 61.84; N, 10.86. Found: C, 24.30; H, 0.73; F, 61.28; N, 10.95.

2,4-Bis-pentafluoroethyl-6-hydroxy-*s*-triazine pentafluoropropionamidine salt (XIX) was prepared according to the above procedure, treating pentafluoropropionamidine (32.4 g., 0.2 mole) in 400 ml. of H_2O with $COCl_2$ (16 g., 0.16 mole) in 80 ml. of toluene and 12.8 g. (0.32 mole) of NaOH in 32 ml. of H_2O. The yield was 22 g. (67%), m.p. 185°. *Anal.* Calcd. for $C_{10}H_4F_{15}N_5O$ (495.2): C, 24.27; H, 0.81; F, 57.55; N, 14.15. Found: C, 24.39; H, 0.92; F, 57.49; N, 14.30.

2,4-Bis-heptafluoropropyl-6-chloro-*s*-triazine (XXII).—A mixture of 34 g. of XX and 60 g. of $POCl_3$ was refluxed for 3 hours. Then the main portion of the excess $POCl_3$ was

(24) Melting points are uncorrected (Fisher–Johns); analyses are by Galbraith Microanalytical Laboratories, Knoxville, Tenn.

(25) A. W. Hofmann, *Ber.*, **19**, 2074 (1886).

removed by careful distillation at 60 mm. (b.p. 49°). The remaining product was distilled over a Widmer column at 150 mm. to give some $POCl_3$ (b.p. 60°) and the wanted product (b.p. 110°). The yield was 18 g. (76%), b.p. 153° (760 mm.), $n^{25}D$ 1.3420. *Anal.* Calcd. for $C_9ClF_{14}N_3$ (451.6): F, 58.90. Found: F, 58.28.

2,4-Bis-pentafluoroethyl-6-chloro-*s*-triazine (XXI) was obtained in analogy to the above procedure, refluxing 24 g. of XIX and 50 g. of $POCl_3$. The yield was 13 g. (77%), b.p. 125° (760 mm.), b.p. 84° (150 mm.), $n^{25}D$ 1.3538. *Anal.* Calcd. for $C_7ClF_{10}N_3$ (351.6): Cl, 10.09; F, 54.04; N, 11.95. Found: Cl, 10.50; F, 53.89; N, 11.92.

2,4-Bis-heptafluoropropyl-6-toluene-*p*-sulfonylhydrazino-*s*-triazine (XXIV).—To XXII (2.7 g., 0.006 mole) in 10 ml. of acetonitrile was added 2.2 g. of toluene-*p*-sulfonyl hydrazide (2.2 g., 0.012 mole). After 3 hours at room temperature the precipitated toluene-*p*-sulfonylhydrazide-HCl was filtered off and the filtrate was evaporated *in vacuo*. The residual XXIV was recrystallized from ligroin; yield 3.03 g. (83.5%), m.p. 109–111°. *Anal.* Calcd. for $C_{16}H_9F_{14}N_5SO_2$ (601.3): S, 5.33. Found: S, 5.33.

2,4-Bis-pentafluoroethyl-6-toluene-*p*-sulfonylhydrazino-*s*-triazine (XXIII).—An amount of 1.1 g. (0.0031 mole) of XXI in 10 ml. of acetonitrile was allowed to react by the above procedure with toluene-*p*-sulfonyl hydrazide (1.16 g., 0.0062 mole); yield of XXIII, 1.35 g. (85%), m.p. 109–113° after recrystallization from ligroin. *Anal.* Calcd. for $C_{14}H_9F_{10}N_5SO_2$ (501.3): Calcd.: S, 6.39. Found: S, 6.33.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE STAMFORD LABORATORIES, RESEARCH DIVISION, AMERICAN CYANAMID CO.]

New Knowledge of Thioammeline

BY RICHARD P. WELCHER, DONALD W. KAISER AND V. P. WYSTRACH

RECEIVED JANUARY 26, 1959

A reinvestigation of the chemistry of thioammeline has resulted in the improvement and extension of Rathke's procedure[1] for its preparation so that high yields of thioammeline and N-substituted thioammelines can be obtained. The amphoteric behavior of thioammeline has been clarified by determining the ionization constants of thioammeline hydrochloride and the sodium salt of thioammeline, and correlating their molecular spectra and structures. These results have led to the identification of the "yellow intermediate" as thioammeline hydrochloride. Several new N-substituted thioammelines and S-alkyl thioammelines were prepared. Among the latter, S-carboxymethylthioammeline is noteworthy for its anomalous infrared spectrum.

Introduction.—In his preparation of thioammeline[2] (4,6-diamino-*s*-triazine-2-thiol) from cyanoguanidine, ammonium thiocyanate and hydrochloric acid, Rathke[1a] first obtained a "yellow intermediate" which gave thioammeline on treatment with ammonium hydroxide. He reported the "yellow intermediate" as thioammeline thiocyanate, but did not actually characterize it.

While preparing thioammeline in this way, we found Rathke's surmise to be incorrect. The purpose of our investigation was to study the conditions and scope of this reaction, to examine in more detail the amphoteric nature of thioammeline, and to identify the "yellow intermediate."

Results and Conclusions.—Our study showed that Rathke's use[1] of two moles each of ammonium thiocyanate and hydrochloric acid in the preparation of thioammeline was unnecessary. We obtained a 74% yield of free thioammeline directly by using an approximately 1:1:1 molar ratio of cyanoguanidine, ammonium (or sodium) thiocyanate and hydrochloric acid. The use of excess acid gave a still higher yield of thioammeline, but it was mixed with thioammeline hydrochloride.

The scope of the reaction was extended too by using 3-substituted 1-cyanoguanidines. 1-Cyano-3-phenyl-, 1-cyano-3-dodecyl- and 1-cyano-3,3-dibutylguanidine gave high yields of the corresponding N-substituted thioammelines (4-amino-6-substituted-amino-*s*-triazine-2-thiols).[3]

Thioammeline can also be prepared in a non-aqueous system. Werner and Bell obtained thioammeline in 10% yield as a by-product in the preparation of guanidine thiocyanate by fusion of cyanoguanidine with two moles of ammonium thiocyanate.[4] Using a 1:1 molar ratio in this fusion process lowered the yield of guanidine thiocyanate[5] without raising the yield of thioammeline. We found that the use of a solvent such as methyl isobutyl ketone markedly changed the course of the reaction, giving 50–60% yields of thioammeline.[6]

To learn more about the amphoteric nature of thioammeline we prepared its hydrochloride[7] and its sodium salt. Both compounds can be readily titrated, with aqueous base and acid, respectively. As a base thioammeline has a pK_B of 10.2; as an acid thioammeline has a pK_A of 7.8. These values agree fairly well with the ionization constants determined spectrophotometrically in these laboratories[8] using a reported method.[9]

The infrared spectra of solid thioammeline, its salts and S-alkyl thioammelines (2-alkylthio-4,6-diamino-*s*-triazines) have been correlated with their structures. The S-alkyl thioammelines, which appear to have the structure Ia with three double bonds in the ring, show a characteristic sharp band of medium intensity near 810 cm.$^{-1}$. This ring structure will be referred to as the "normal"[10] triazine structure. The sodium salt of thioammeline, strongly resembling the S-alkyl thioammelines in its spectrum, is assigned the normal triazine structure Ib. Thioammeline itself, lacking

(1) (a) B. Rathke, *Chem. Ber.*, **18**, 3102 (1885); (b) **20**, 1059 (1887).

(2) J. Ponomareff, *Compt. rend.*, **80**, 1384 (1875).

(3) D. W. Kaiser and R. P. Welcher (to American Cyanamid Co.), U. S. Patent 2,820,033 (1958).

(4) E. A. Werner and J. Bell, *J. Chem. Soc.*, **117**, 1133 (1920).

(5) T. L. Davis and H. W. Underwood, THIS JOURNAL, **44**, 2595 (1922).

(6) R. P. Welcher and D. W. Kaiser (to American Cyanamid Co.), U. S. Patent 2,780,623 (1957).

(7) P. Klason, *J. prakt. Chem.*, [2] **33**, 296 (1886).

(8) H. A. Strauss, R. C. Hirt and R. G. Schmitt, to be published.

(9) F. T. King and R. C. Hirt, *Appl. Spectros.*, **7**, 164 (1953).

(10) N. Colthup, to be published.