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Triazines. XXII. Fluoro-*s*-triazines

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RECEIVED MARCH 24, 1958

A number of new fluoro-*s*-triazines has been prepared from the corresponding chloro compounds by means of the Swarts reagent. This exchange reaction which is not possible with aryl chlorides or other chloroheterocycles proceeds readily with the chloro-*s*-triazines. Fluoro-*s*-triazines are much more reactive than the corresponding chloro compounds.

Substitution of chlorine by fluorine in organic compounds by means of antimony tri- or pentafluoride (Swarts reagent) has been reported.[3] The use of this reagent, however, is limited so far to certain types of organic chlorine compounds. In general, only polychloro compounds bearing at least two chlorine atoms at the same carbon atom react, for instance, groups like $-CCl_3$, $-CHCl_2$ and $>CCl_2$. Structures like $-CH_2Cl$, $>CHCl$ or $\geqslant CCl$, as well as chlorine bound directly to an aromatic nucleus or to a heterocyclic compound of aromatic character, like pyridine, pyrimidine or thiophene, are known to be inert against this reagent even if the relatively reactive 2-chloro isomers were used.[4]

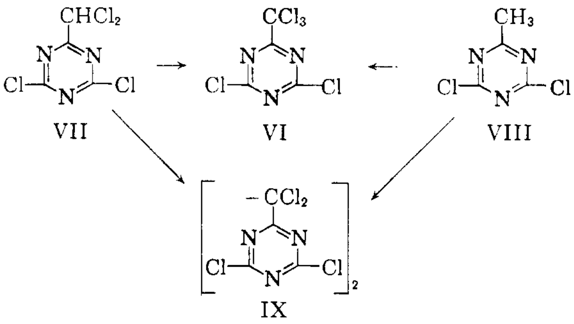
We have now found that chlorine atoms attached directly to a carbon atom of the *s*-triazine ring can be easily replaced by fluorine by means of the Swarts reagent. If other attackable halogen atoms are present in side chains, they will be simultaneously substituted by fluorine. Table I lists a number of fluoro-*s*-triazines thus prepared.

The only one of the compounds listed above which has found mention in the literature so far is the 2,4,6-trifluoro-*s*-triazine or cyanuric fluoride (I). Hueckel claims, without experimental details, to have obtained I by reaction of cyanogen iodide with mercuric fluoride at 160°.[5] It is doubtful, however, if he ever had the pure compound in his hands, since he reports a boiling point of 150°, while I boils actually about 80° lower.

The fluoro-*s*-triazines are much more volatile than the corresponding chloro compounds. While they are thermally quite stable, the reactivity of the fluorine bound directly to the nucleus seems to surpass by far that of the chloro-*s*-triazines. This is a remarkable exception of the general rule that the carbon–fluorine bond is stronger than that of carbon to other halogens. In line with the high reactivity of the fluorine is the observation that at least the more volatile members of this series are rather toxic. Inhalation of their vapors causes symptoms similar to a phosgene intoxication.

Water hydrolyzed I and II at room temperature almost instantaneously to the corresponding hydroxy compounds, namely, cyanuric acid and 2,4-dihydroxy-6-trifluoromethyl-*s*-triazine. In the case of III initial hydrolysis was followed by ring cleavage resulting in trifluoroacetylurea. The fluorine was also easily replaced by alkoxy- or amino groups. Results of these reactions will be reported later.

While the fluoro-*s*-triazines I, III, IV and V were prepared from the already known corresponding chloro compounds, the starting material for II, 2,4-dichloro-6-trichloromethyl-*s*-triazine (VI), was obtained by chlorination of either the 2,4-dichloro-6-dichloromethyl-*s*-triazine (VII)[6] or the 2,4-dichloro-6-methyl-*s*-triazine (VIII).[7] As a by-product of both reactions there was obtained a considerable amount of 1,2-bis-(2′,4′-dichloro-*s*-triazinyl-6′)-tetrachloroethane (IX).



Acknowledgment.—We are very much indebted to the Olin Mathieson Chemical Corporation for their generous support of this work. Furthermore we wish to thank the Nilok Chemical, Inc., for their gift of cyanuric chloride.

Experimental[8]

Starting Materials.—For the preparation of I commercial cyanuric chloride (Nilok Chemical, Inc.), recrystallized once from ligroin,[9] was used. The fluorotriazines III, IV, and V were prepared from 2,4-bis-trichloromethyl-6-chloro-*s*-triazine,[10] 2,4-dichloro-6-phenyl-*s*-triazine and 2-chloro-4,6-diphenyl-*s*-triazine,[11] resp.

2,4-Dichloro-6-trichloromethyl-*s*-triazine (VI).—(a) A stream of chlorine was passed into crude 2,4-dichloro-6-dichloromethyl-*s*-triazine[6] (VII, 65.5 g.) for 30 hours, while the reaction flask was kept between 170 and 190° and irradiated with ultraviolet light. After cooling, 35.6 g. of colorless crystals were separated by suction from 34 g. of unchanged oily starting material.

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[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] Preceding communication: E. Kober and Ch. Grundmann, THIS JOURNAL, **80**, 5547 (1958).

[3] A. Henne, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 49.

[4] Unpublished results of E. Kober and H. Ulrich.

[5] W. Hückel, *Nachr. Akad. Wiss. Gottingen, Math. phys. Klasse, math.-phys.-chem. Abtlg.*, 36 (1946); *Chem. Zentr.*, **117**, 1, 1827 (1946). The contents of this paper are the subject of our pending U. S. Patent Application Serial No. 609348 filed Sept. 12, 1956. Before release of this paper could be obtained from our sponsor, a publication from A. F. Maxwell, J. S. Fry and L. A. Bigelow (THIS JOURNAL, **80**, 548 (1958)) appeared which describes the preparation of I by essentially the same procedure.

[6] Ch. Grundman and E. Kober, THIS JOURNAL, **79**, 944 (1957).

[7] W. Hentrich and M. Hardtmann, U. S. Patent 1,991,689.

[8] Melting points were determined with the Fisher–Johns apparatus; microanalyses are from Schwarzkopf Microanalytical Laboratories, Woodside, N. Y., and Spang Microanalytical Laboratory, Ann Arbor, Mich.

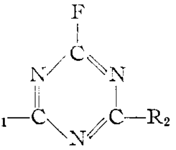
[9] Here, and in the following, a fraction boiling between 90 and 97° was used.

[10] H. Schroeder and Ch. Grundmann, THIS JOURNAL, **78**, 2447 (1956).

[11] A. Ostrogovich, *Chem. Ztg.*, **36**, 738 (1911).

TABLE I

FLUORO-*s*-TRIAZINES



No.	R_1	R_2	Empiric formula	Name, *s*-triazine	B.p., °C.	Yield, %	Calcd. C	Calcd. H	Calcd. F	Calcd. N	Found C	Found H	Found F	Found N
I	F	F	$C_3F_3N_3$	2,4,6-Trifluoro-	70–71	91	26.68	..	42.20	31.12	26.52	..	42.26	31.24
II	F	CF_3	$C_4F_5N_3$	2,4-Difluoro-6-trifluoromethyl-	76–78	73	25.96	..	51.33	22.71	26.12	..	51.43	22.61
III	CF_3	CF_3	$C_5F_7N_3$	2,4-Bis-trifluoromethyl-6-fluoro-	82–83	79	25.54	..	56.58	17.88	25.54	..	56.56	17.83
IV	F	C_6H_6	$C_9H_5F_2N_3$	2,4-Difluoro-6-phenyl-	98.5–99.5[a]	73	55.97	2.61	19.66	21.76	55.15	2.21	[b]	21.58
V	C_6H_5	C_6H_5	$C_{15}H_{10}FN_3$	2,4-Diphenyl-6-fluoro-	108–109.5[a]	80	71.70	4.01	7.56	16.72	71.77	4.04	7.42	16.68

[a] M.p. [b] Not determined.

The oil was treated once more as described above, whereupon a further crop of crystals (34 g.) was obtained. The combined crystalline fractions were recrystallized once from a small amount of ligroin and then sublimed at 110° and 1 mm. pressure, whereupon 45 g. (60%) of pure VI was obtained as colorless needles, m.p. 119–121°.

Anal. Calcd. for $C_4Cl_5N_3$: C, 17.97; Cl, 66.31; N, 15.72. Found: C, 18.20; Cl, 65.74; N, 15.50.

The residue of the sublimation consisted of **1,2-bis-(2′,4′-dichloro-*s*-triazinyl-6′)-tetrachloroethane (IX)**, which was purified by recrystallization from ligroin, yielding colorless needles (15 g., 23%), m.p. 187–189°.

Anal. Calcd. for $C_8Cl_8N_6$: C, 20.72; Cl, 61.16; N, 18.12. Found: C, 20.94; Cl, 60.36; N, 18.18.

(b) The amount of 60 g. of 2,4-dichloro-6-methyl-*s*-triazine (VIII)[7] was chlorinated as described above. After cooling, the dark pulpy reaction product was extracted several times with ligroin, leaving behind a dark insoluble residue (4.5 g.). The ligroin was removed *in vacuo* from the combined extracts and the remainder fractionated. From the main fraction (b.p. 71–83° (1 mm.), 44.5 g.) 2.9 g. of VI crystallized and was separated by filtration. A second fraction (b.p. 210–220° (1 mm.), 11.5 g.) crystallized immediately and consisted of almost pure 1,2-bis-(2′,4′-dichloro-1,3,5-triazinyl-6′)-tetrachloroethane (IX).

The oily remainder of the main fraction, consisting of a mixture of partially chlorinated products, was again chlorinated as described above, yielding 42.3 g. of a solid mixture of VI and IX, which was recrystallized once from ligroin and then separated by sublimation as described above. In this way a total yield of 29.5 g. of VI (33%) and 20.2 g. of IX (24%) was obtained.

Fluorination of Chloro-*s*-triazines.—A Swarts reagent, consisting of approximately 10 moles of antimony trifluoride, one mole of antimony trichloride and three moles of chlorine was used in all experiments. An excess of about 70% of SbF_3 above the theoretical requirement was applied. The reagent was preheated to 160–180° and the chloro-triazine added in small portions. For I, II and III the reaction was completed by refluxing at the above temperature (oil-bath) for about 24 hours, followed by fractionated distillation through an effective column. Two more fractionations yielded then the pure compounds as colorless, mobile liquids with an aggressive, pungent odor, especially in the case of II. Because of the toxic nature of these fluorotriazines, inhalation of their vapors should be carefully avoided and all operations be carried out under an effective hood.

In the case of the less volatile fluorotriazines IV and V, no refluxing occurred. After 24 hours the semi-solid reaction mixture was cooled to room temperature, and the cake decomposed with ice-water. The remaining solid was separated by filtration, washed with cold water, dried, and extracted with boiling ligroin. Upon cooling to −25° IV separated in long needles. A further crop was obtained after concentration of the mother liquor. Sublimation at 0.5 mm. pressure between 70 and 90° yielded pure IV. In the case of V a tarry by-product separated first from the ligroin extracts at 0°. The filtrate from this tar yielded the crude V after complete evaporation of the solvent. Pure V was obtained after one recrystallization from ligroin or acetone–water. Both phenyl-substituted fluorotriazines IV and V formed colorless and odorless needles without aggressive properties.

Hydrolysis of the Fluoro-*s*-triazines.—When 5.8 g. of 2,4,6-trifluoro-*s*-triazine (I) was added at 0° with stirring to 50 ml. of water, an exothermic reaction occurred and a colorless solid was formed. This material was identified as **cyanuric acid** by its known reactions. The yield was essentially quantitative.

The 2,4-difluoro-6-trifluoromethyl-*s*-triazine (II) reacted likewise exothermically with cold water. The crystalline compound, m.p. 182–186° dec., which separated from the reaction mixture was identified by analysis as **2,4-dihydroxy-6-trifluoromethyl-*s*-triazine** (in form of its dihydrate).

Anal. Calcd. for $C_4H_2F_3N_3O_2 \cdot 2H_2O$: C, 22.13; H, 2.78; F, 26.26; N, 19.36. Found: C, 22.05; H, 2.63; F, 26.25; N, 19.49.

The 2,4-bis-trifluoromethyl-6-fluoro-*s*-triazine (III) reacted more slowly with water at room temperature. Decomposition was practically complete after four hours, resulting in a crystalline deposit which could be sublimed at 1 mm. pressure between 70–80°. The colorless needles, m.p. 189°, thus obtained, proved to be **trifluoroacetylurea**, indicating the breakdown of the *s*-triazine ring.

Anal. Calcd. for $C_3H_2F_3N_2O_2$: C, 23.09; H, 1.94; F, 36.52; N, 17.95. Found: C, 23.03; H, 2.02; F, 36.62; N, 17.80.

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