of sodium hydroxide in 20 ml of water. To the hypobromite solution was added immediately a cold solution of 1.0 g (3.2 mmol) of **7a** in 20 ml of tetrahydrofuran, and the mixture was stirred at −5 to −3° for 2 hr. The insoluble material was filtered and washed with water to give 0.23 g of **6a**, mp 222.5–224°. The filtrates were separated and the aqueous layer was washed with ether. The combined organic layers were dried and evaporated. Trituration of the residue with ether gave an additional 0.40 g of **6a**, mp 220–224°, for a combined yield of 0.63 g (73.7%).

Similar procedures were used for the preparation of **6b** and **6c** (runs 5 and 6). Compound **7f** was unreactive to the reagent even under reflux, as indicated by thin layer chromatography (run 8).

In another experiment (run 3) 5 ml of 1.8 *N* sodium hypochlorite solution[1] was used in rearrangement of 0.50 g of **7a** in 8 ml of tetrahydrofuran. A similar work-up as above gave 0.15 g (35.1%) of crude **6a**. The results are summarized in Table II.

C. In Methanol (Run 4). Compound **7a** (1.0 g, 3.2 mmol) was added to a solution of 0.23 g (10 mmol) of sodium in 20 ml of methanol cooled to −7. To the solution was added 0.8 g (10 mmol) of bromine. The mixture was stirred at room temperature for 1 hr and then heated under reflux for 2 hr. The solid that separated on cooling was collected by filtration to yield 0.45 g of **6a**, mp 221.5–222.5°. The filtrates were concentrated to about one-third volume and diluted with water. Filtration of the resulting precipitate and washing with ether afforded an additional 0.12 g of **6a**, mp 219–222°, for a combined yield of 0.57 g (66.7%).

Compound **6c**, prepared from similar rearrangement of **7c**, was recrystallized from tetrahydrofuran to give a 49.7% yield of pure product, mp 267–267.5° (run 7).

Compound **6f**[16] was obtained in 6.8% yield by first treating 1.0 g of **7f** and 0.3 g of sodium in 20 ml of methanol with 0.8 g of bromine at −8° for 30 min and at room temperature for 1 hr, and then refluxing the mixture for 2 hr. The insoluble material was removed by filtration, and the filtrate was concentrated to about one-third of the original volume and diluted with water. The red oil that separated, on standing, gradually crystallized. The yellow crystals were collected by filtration, heated in refluxing toluene, cooled, and filtered to yield 55 mg of product, mp >300° (run 9).

Cyclization of Methyl 4-(4-Chloro-2-benzoylphenyl)-4-methylallophanate (11a) to 6a. A solution of 100 mg of crude **11a**[1] in 2 ml of methanol was refluxed for 2 hr, during which time no reaction occurred as indicated by thin layer chromatography. To the solution was added a small piece of sodium, and refluxing was continued for 30 min. After cooling, the precipitate was collected by filtration and washed with water to give 13 mg of **6a**, mp 222–224°. From the filtrates, an additional 10 mg of product was obtained for a combined yield of 23 mg (29.5%).

Acknowledgment. We are grateful to Mr. M. Yamamoto for his valuable comments and to Mr. Y. Kameno and Miss R. Kido for skillful technical assistance.

Registry No.—**1c**, 51806-03-2; **1d**, 51806-04-3; **1e**, 784-38-3; **2a**, 51806-05-4; **2b**, 51806-06-5; **2c**, 51806-07-6; **2d**, 51806-08-7; **2e**, 51806-09-8; **3e**, 51806-10-1; **5a**, 51806-11-2; **6a**, 20927-53-1; **6b**, 33453-19-9; **6c**, 26953-46-8; **6d**, 49830-84-4; **6e**, 40069-75-8; **6f**, 4797-43-7; **7a**, 51806-12-3; **7b**, 51806-13-4; **7c**, 51806-14-5; **7f**, 19144-18-4; **8**, 51806-15-6; **9**, 51806-16-7; **10**, 30008-50-5; **11a**, 51806-17-8; **12e**, 51806-18-9; 2-(2-hydroxyethyl)amino-5-nitrobenzophenone, 37554-73-7; sodium azide, 12136-89-9.

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(3) Compound **2d** yielded soluble quinazolinone **6d**, which could be isolated by extraction procedures.

(4) Commercial sodium azide was used without activation.[2a]

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(7) Compound **6d** was previously prepared, accompanied by the corresponding O-alkylated product, by alkylation of 1-unsubstituted quinazolinone with chloroethyl acetate and sodium hydride: unpublished studies of Mr. M. Yamamoto.

(8) This synthetic method was first used by Mr. M. Yamamoto in the conversion of 2′-benzoyl-4′-chloro-*N*-cyclopropylmethylformanilide to the corresponding 2-hydroxyquinazolinone.

(9) S. Inaba, K. Ishizumi, K. Mori, and H. Yamamoto, *Chem. Pharm. Bull.*, **19**, 722 (1971).

(10) When the same reaction was carried out at −5°, followed by evaporation of solvent and subsequent addition of water, a red, oily product (**4a**?) was obtained which was gradually converted to yellow, crystalline quinazolinone **6a**.

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(13) Mr. M. Yamamoto kindly supplied us with the sample.

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Substituent Constants for the 4,6-Dimethyl-*s*-triazinyl Group from Ionization and Fluorine Nuclear Magnetic Resonance Data[1]

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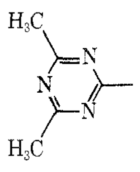
The *m*- and *p*-(4,6-dimethyl-*s*-triazin-2-yl)benzoic acids (**6a** and **6b**) have been synthesized and their pK_a's in 50% aqueous ethanol (v/v) have been determined as 5.15 and 4.94, respectively. The substituent constants calculated from the pK_a data for the 4,6-dimethyl-s-triazinyl substituent (**1**) are σ_m +0.25, σ_p +0.39, and σ_I +0.15. The corresponding dimethyl-*s*-triazinyl substituted fluorobenzenes (**3c** and **3d**) have also been synthesized and their ^{19}F chemical shifts have been determined relative to fluorobenzene in carbon tetrachloride, methanol, and dimethyl sulfoxide. The substituent constants for **1** based upon the chemical shifts in methanol are σ_I +0.18 and $\bar{\sigma}_R{}^p$ +0.19. The substituent constants are discussed.

In view of the rather limited number of heterocyclic substituents for which substituent constants have been evaluated,[2] and also the potential insights which such constants might afford, the determination of the substituent constants for the 4,6-dimethyl-*s*-triazin-2-yl substituent (**1**) was undertaken. This substituent was chosen be-



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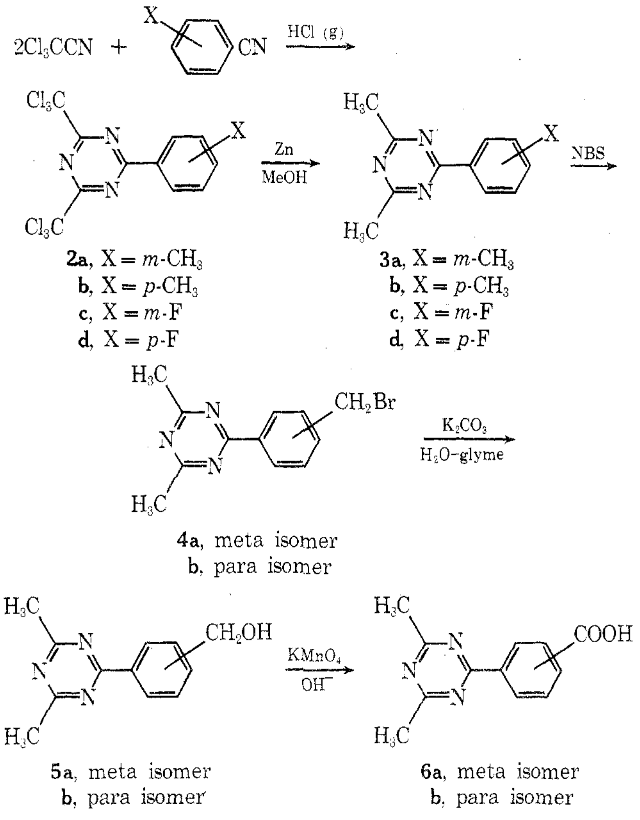
cause of the synthetic feasibility of incorporating it into molecules from which the necessary data could be obtained and also because the substituent possesses the electronegative nitrogen atoms as well as a high resonance energy of 41.2 kcal/mol.[3] Presumably, the latter would have to be lost in part when the substituent participated in direct conjugation or through resonance with the reaction centers. With respect to desirability, the unsubstituted *s*-triazine ring or parent substituent would have been preferred over **1**, but the available evidence indicated that compounds containing the former may be more difficult to synthesize[4] and also that the unsubstituted triazinyl substituent may be more susceptible to hydrolysis[5] than **1**.[6] Consequently, substituent 1 was chosen for the studies.

Scheme I



2a, X = *m*-CH$_3$
b, X = *p*-CH$_3$
c, X = *m*-F
d, X = *p*-F

3a, X = *m*-CH$_3$
b, X = *p*-CH$_3$
c, X = *m*-F
d, X = *p*-F

4a, meta isomer
b, para isomer

5a, meta isomer
b, para isomer

6a, meta isomer
b, para isomer

To determine the Hammett substituent constants for **1**, the *m*- and *p*-(4,6-dimethyl-*s*-triazin-2-yl)benzoic acids (**6a** and **6b**) were synthesized according to Scheme I. Among the unsuccessful attempts to synthesize significant amounts of **6a** and **6b**, or their precursors, were the cocyclization of (1) cyanoacetophenone with trichloroacetonitrile in the presence of hydrogen chloride,[7] (2) cyanobenzoic acid with trichloroacetonitrile in the presence of hydrogen chloride,[7] (3) ethyl acetylbenzimidate with ethyl acetimidate in the presence of acetic acid,[8] and (4) cyanobenzoyl chloride with trichloroacetonitrile in the presence of aluminum chloride.[9] Selective oxidation by potassium permanganate of the benzylic methyl group of **3a,b** to yield **6a,b** did not realize success nor did the oxidation of all three methyl groups followed by decarboxylation of the carboxyl groups on the triazine ring[5] to give the parent compounds, *m*- and *p*-triazinylbenzoic acid.

Table I
pK$_a$'s of Substituted Benzoic Acids[a]

Compd	pK_a[b]
m-Toluic acid	5.62
Benzoic acid	5.49
m-Methoxybenzoic acid	5.39
m-Bromobenzoic acid	5.00
m-Nitrobenzoic acid	4.46
6a	5.15
6b	4.94

[a] 0.05 *M* in LiCl. [b] Reference 18a.

Taft[10] has successfully separated the Hammett substituent constants for a large number of meta substituents into two parameters, one which represents the inductive or field effect, σ_I, and the other which represents a resonance effect, $\sigma_R{}^m$. In the case of para substituents the Hammett substituent constant is separated into the inductive parameter and a resonance parameter, $\sigma_R{}^p$, or an effective resonance parameter, σ_R. The latter includes both the resonance polar effect[10b] as well as the direct conjugative or through resonance effect between the substituent and the reaction center.

Another and independent approach to the determination of the inductive effect, σ_I, has also been developed by Gutowsky[11] and Taft[12] through the utilization of the chemical shifts of the ^{19}F nmr signals of substituted fluorobenzenes relative to the unsubstituted fluorobenzene. In the case of meta-substituted fluorobenzenes, the resonance parameter, $\sigma_R{}^m$, apparently makes no significant contribution to the ^{19}F chemical shift, as evidenced by the wide applicability of eq 1 in a given solvent.[13] For

$$\int_{H}^{m\text{-X}} = -7.10\sigma_I + 0.60 \tag{1}$$

many para substituents which are electron donating *via* a resonance effect (−R), the ^{19}F chemical shift relative to fluorobenzene was found to correlate well with the inductive parameter and a resonance parameter, $\sigma_R{}^0$, as expressed by the equation[14]

$$\int_{H}^{p\text{-X}} = -29.5\sigma_R{}^0 + \int_{H}^{m\text{-X}} = -29.5\sigma_R{}^0 - 7.10\sigma_I + 0.60 \tag{2}$$

where $\sigma_R{}^0$ represents a resonance contribution which is free of any direct conjugative or through resonance.[15] However, for para substituents having an electron-withdrawing effect (+R) where through resonance is possible, linearity with respect to a resonance parameter is not realized. However, assuming identical inductive effects within the meta and para isomers,[16] an effective resonance parameter may be solved for from eq 2 by replacing $\sigma_R{}^0$ by $\bar{\sigma}_R$ to give eq 3.[14]

$$\bar{\sigma}_R{}^p = -0.0339\left(\int_{H}^{p\text{-X}} - \int_{H}^{m\text{-X}}\right) \tag{3}$$

Results and Discussion

The procedure used for the determination of the Hammett σ values for the *m*- and *p*-4,6-dimethyl-s-triazin-2-yl (**1**) substituent was that recommended by Taft.[17] The pK_a's for the acids listed in Table I were determined in 50% (v/v) ethanol-water having a constant ionic strength of 0.05 *M*.[18] A Hammett plot of the log K_a's of the five reference acids against the recommended corresponding σ values[17] gave, by the method of least squares, a ρ value of +1.47 (reported value 1.464[18a]) and a log K_0 of −5.52.[19] The σ values for the known substituents obtained from the calculated values of ρ and log K_0 did not differ from the recommended σ values by more than ±0.03 and gave a standard deviation of ±0.02. These values fall well within the limits established by Taft of ±0.07 and ±0.03, respectively.[17] Using the experimental values of log K_a obtained for **6a** and **6b**, the Hammett σ values for *m*-**1** and *p*-**1** are calculated as +0.25 and +0.39, respectively. These σ values may then be further separated into the inductive parameter and a resonance parameter.[10,16,20] This separation is achieved by assuming (1) that the inductive effect and field effect of the substituent are identical for the meta and para isomers,[16a] (2) that within a given reaction series the resonance effect of the substituent in the meta position is a constant proportion (α) of its resonance effect in the para position,[16a,17] and (3) that $\rho_I = \rho^m$.[17] These assumptions enable the inductive parameter, σ_I, to be solved for by eq 4.[17] Taft and Lewis have determined the

$$\sigma_I = \left(\frac{1}{\rho(1-\alpha)}\right)(\log K^m/K_0 - \alpha \log K^p/K_0) \quad (4)$$

value of α for the ionization of benzoic acids in 50% aqueous ethanol at 25° as 0.42.[17] Based upon this value of α, the calculated values for the inductive parameter and the resonance parameter for the substituent **1** are given in Table II.

Table II
σ Values for 1 from Ionization Data

σ_I	+0.15
σ_R^p	+0.24

In an attempt to confirm the above value for the inductive parameter, σ_I, for **1** by another independent method, the ^{19}F chemical shifts of fluorobenzene, **3c**, and **3d** were measured relative to external *p*-difluorobenzene (20% solution in CCl_4),[13] and then the chemical shifts of **3c** and **3d** were calculated relative to fluorobenzene. The use of *p*-difluorobenzene, rather than fluorobenzene, as an experimental reference was necessitated because the signal from the meta isomer, **3c**, was close to or superimposed upon that of fluorobenzene. The chemical shifts were measured in carbon tetrachloride, methanol, and dimethyl sulfoxide, and are given in Table III together with the values for σ_I calculated with eq 1, and $\bar{\sigma}_R^p$ calculated with eq 3. The use of the dual substituent parameter (DSP) equation[21] instead of eq 3 for carbon tetrachloride and dimethyl sulfoxide gave somewhat lower values for $\bar{\sigma}_R^p$, namely, 0.15 and 0.13, respectively. As indicated in Table III, and in accord with Taft's findings in aprotic solvents,[21] the σ_I values are larger in the more polar solvents, but the $\bar{\sigma}_R^p$ values remain essentially unchanged. The σ_I value in methanol (0.18) agrees quite well with the value obtained from the pK_a data in 50% aqueous ethanol (0.15). Likewise, the $\bar{\sigma}_R^p$ values calculated from the ^{19}F chemical shift data (0.18–0.19) agree within acceptable limits[17] with that obtained from the pK_a data (0.24). It might have been anticipated that the $\bar{\sigma}_R^p$ value from the chemical shift data would be larger than that from the pK_a data in view of the possibility that, for an electron-withdrawing group, such as **1**, direct conjugation or through resonance might be realized more fully in the *p*-triazinylfluorobenzene, **3d**, than between the ground states of the corresponding para-substituted benzoic acid, **6b**, and its anion in comparably polar solvents. Indeed, a comparison of the values for $\bar{\sigma}_R^p$ from ^{19}F chemical shift data and pK_a data for six other +R substituents[13,14,19b] does show that the values for $\bar{\sigma}_R^p$ from the chemical shift data do in general exceed or equal those from the pK_a data (+0.12 to −0.03; average +0.03). However, the enhancements are small, and rightly so, in view of the relatively small difference of −0.13 between σ^+ and σ (Hammett) for fluorine. Infrared intensities of para-substituted fluorobenzenes also support the existence of direct conjugation between fluorine and strong electron-withdrawing substituents, but the resulting increase in the σ value is estimated as only 0.03 unit.[22] Thus, the above values for $\bar{\sigma}_R^p$ for **1** from the ^{19}F chemical shift data might be adjusted downward to 0.15–0.16. It would seem somewhat untenable to postulate that the σ_R^p value for **1** from the pK_a data is abnormally high relative to that from the ^{19}F chemical shift data because of the existence of the conjugate acid of **6b**, namely **7**. Two factors would speak against any significant amount of **7**. First, the basicity of the triazine ring is low, approximately of the order

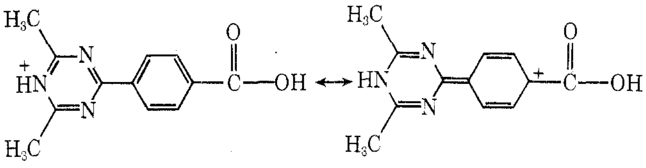


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Table III
^{19}F Chemical Shifts and Calculated Substituent Constants

Solvent	$-\int_{p\text{-F}}^{\text{H}^a}$	$-\int_{p\text{-F}}^{m\text{-}1^a}$	$-\int_{p\text{-F}}^{p\text{-}1^a}$	$-\int_{\text{H}}^{m\text{-}1^b}$	$-\int_{\text{H}}^{p\text{-}1^b}$	σ_I	$\bar{\sigma}_R^p$
CCl_4	7.11	7.10	12.34	−0.01	5.23	0.08	0.18
CH_3OH	3.39	4.07	9.69	0.68	6.30	0.18	0.19
DMSO	6.08	6.63	11.78	0.55	5.70	0.16	0.18

[a] Approximately 3–5% solution (wt/vol) of unsubstituted or substituted fluorobenzene relative to external *p*-difluorobenzene (20%, CCl_4). Negative sign indicates downfield shift. Values not corrected for bulk susceptibility. [b] $\int_{p\text{-F}}^{-x} - \int_{p\text{-F}}^{\text{H}}$.

Table IV
Comparison of Substituent Constants for +R Substituents

Substituent	$\sigma_p{}^a$	$\sigma_I{}^b$	$\sigma_R{}^p$
p-NO_2	+0.78	+0.64	+0.14
p-SO_2CH_3	+0.72	+0.55	+0.17
p-CN	+0.66	+0.56	+0.10
p-CF_3	+0.54	+0.41	+0.13
p-CH_3CO	+0.50	+0.28	+0.22
p-CO_2Et	+0.45	+0.31	+0.14
p-**1**	+0.39	+0.15	+0.24

[a] Reference 19b. [b] From reactivities, ref 13.

10^{-11},[23] and second, if **7** were to exist in any significant amount, a much larger σ_I would be anticipated. Thus, the value of 0.24 for $\sigma_R{}^p$ from the pK_a data for the substituent **1** is probably the more reliable value, although an average value of 0.20 might be appropriate.

It is worth noting that a comparison of the substituent constants for **1** with those of other +R groups as illustrated in Table IV shows **1** to have the lowest σ_I value, but the largest $\sigma_R{}^p$ value.

Experimental Section

Instrumentation. All melting points are corrected and were taken in a stirred silicone oil bath using calibrated Anchuetz thermometers with the sample in an open capillary tube unless noted otherwise. All ir spectra were obtained on a Beckman IR-8 infrared spectrophotometer. All proton nmr spectra were obtained on a Hitachi Perkin-Elmer R-20 spectrometer. The ^{19}F nmr spectra were also taken on a Hitachi Perkin-Elmer R-20 spectrometer having an internal lock-on and equipped with a ^{19}F RF unit, Model R-203F operating at 56.456 MHz. The chemical shifts were counted with a Takeda Riken frequency counter, Model TR-3824X. The ^{19}F spectra were run at 34° with an external reference of *p*-difluorobenzene [20% (v/v) in CCl_4]. The solutions of the fluorine compounds in carbon tetrachloride were approximately 5% (wt/vol), whereas those in methanol and dimethyl sulfoxide were approximately 3%.[21] The spectra for the 4,6-dimethyl-2-(*m*-fluorophenyl)-*s*-triazine (**3c**) and fluorobenzene were recorded with a sweep width of 10 ppm and a sweep time of 500 sec in all solvents. The spectra for the 4,6-dimethyl-2-(*p*-fluorophenyl)-*s*-triazine (**3d**) were recorded with a sweep width of 10 ppm in methanol and 20 ppm in carbon tetrachloride and dimethyl sulfoxide, and a sweep time of 500 sec. Each spectrum was swept three times in each direction, and the chemical shifts were recorded from the centers of the signals with a precision of ±2 Hz (±0.035 ppm).

pK_a determinations were obtained at 25 ± 0.2° by potentiometric titrations using an IL Deltamatic Model 245 pH meter and an IL 14063 combination pH electrode system. The electrode system was balanced at its isoelectric point with a 6.86 ± 0.01 buffer, and then the pH slope control was adjusted with a 4.01 ± 0.01 buffer.

Solution Preparations. The sodium hydroxide solution was prepared by diluting Hellige concentrate with freshly boiled water and then storing under nitrogen.

The aqueous 1 *M* lithium chloride solution was prepared by quickly weighing the AR grade lithium chloride (vacuum dried several weeks) and dissolving it in freshly boiled water in a volumetric flask. This solution contained no detectable hydroxide as determined by a blank titration. The 0.1 *M* solutions were obtained by dilution of the 1.0 *M* solution with freshly boiled water.

The ethanolic lithium chloride solution was prepared in a manner similar to the preparation of aqueous solution.

The reference benzoic acids were obtained commercially and were recrystallized at least twice to obtain compounds whose melting points were within 2° of literature values.

pK_a Determination.[18] Approximately 0.25 mmol of the substituted benzoic acid was dissolved in 50 ml of distilled, carbonate-free, absolute ethanol. To this solution was added 50 ml of carbonate-free 0.1 *M* aqueous lithium chloride and the resulting solution was titrated under nitrogen, with stirring at 25 ± 0.2°, with equal volumes of 0.02 *N* carbonate-free sodium hydroxide and carbonate-free 0.08 *M* ethanolic lithium chloride. The pK_a of the acid was determined from the pH of the solution at the half-neutralization point. The neutralization point or end point was determined to be the point where the ΔpH was the greatest for the addition of a 0.1-ml aliquot of base.

4,6-Bis(trichloromethyl)-2-(*p*-tolyl)-*s*-triazine (2b). *p*-Tolunitrile (56.3 g, 0.48 mol) and trichloroacetonitrile (138.4 g, 0.96 mol) were combined in a cylindrical reaction flask, and dry hydrogen chloride was bubbled through the mixture *via* a sintered glass bubbler for 7 hr (25°) after which the contents were permitted to stand for 5 days (25°). The resulting solid was removed with difficulty, dissolved in ether, and washed with 2% sodium hydroxide and then with water to pH 6. The ether was dried ($MgSO_4$) and evaporated to yield yellow crystals which were recrystallized from absolute ethanol to yield 101 g (52%) of white crystals: mp 123.7–124.4°; ir (Nujol) 1550 cm^{-1} (triazine).

Anal. Calcd for $C_{12}H_7N_3Cl_6$: C, 35.48; H, 1.74; N, 10.34; Cl, 52.44. Found: C, 35.72; H, 1.70; N, 10.37; Cl, 52.73.

4,6-Dimethyl-2-(*p*-tolyl)-*s*-triazine (3b). To a stirred solution of **2b** (60 g, 0.15 mol) in 2.1 l. of methanol was added approximately 0.5 g of cupric acetate followed by the slow addition of 10 mesh zinc (300 g, 4.6 g-atoms, activated with dilute nitric acid) over a period of 30 min. The stirred solution was refluxed from the beginning of the addition of the zinc, and the color of the solution changed from green to dark gray during the addition and remained dark gray during the course of the reaction. The mixture was stirred and refluxed for 6 days, after which the reaction mixture was cooled and decanted into 2.5 l. of ice water to give a gray precipitate. The mixture was acidified to Congo Red with dilute nitric acid and the precipitate was filtered. The filtrate was extracted with ether and the latter was used to dissolve the precipitate. The ether solution was washed with 5% sodium carbonate and with water to neutrality, dried ($MgSO_4$), and evaporated to yield 21 g (74%) of a yellow-brown solid. This solid was recrystallized from absolute ethanol to yield white crystals: mp 78.5–79.5°; ir (Nujol) 1530 cm^{-1} (triazine); nmr (CCl_4) τ 1.68 (d, 2 H, aromatic H ortho to triazine), 2.85 (d, 2 H, aromatic H meta to triazine), 7.42 (s, 6 H, $-CH_3$ on triazine), and 7.61 (s, 3 H, benzylic $-CH_3$).

Anal. Calcd for $C_{12}H_{13}N_3$: C, 72.34; H, 6.58; N, 21.08. Found: C, 72.40; H, 6.59; N, 20.90.

4,6-Dimethyl-2-(4-bromomethylphenyl)-*s*-triazine (4b). To a stirred solution of **3b** (13.8 g, 0.069 mol) in 75 ml of carbon tetrachloride was added slowly (1 hr) a pulverized mixture of *N*-bromosuccinimide (15.2 g, 0.085 mol) and benzoyl peroxide (2.6 g, 0.011 mol). The solution was refluxed for 5 hr, after which time all the solid was floating. The hot solution was filtered, the solid was discarded, and the filtrate was cooled and filtered again to yield a yellow solid. Second and third crops were also obtained from the filtrate by the same method. The combined crops were triturated with hot water to dissolve any succinimide and filtered to yield 10.6 g (55%) of light colored crystals. A portion of this solid was recrystallized from carbon tetrachloride and sublimed to yield a white powder: mp 145.0–146.0°; ir (CH_2Cl_2) 1530 cm^{-1} (triazine); nmr (CCl_4) τ 1.60 (d, 2 H, aromatic H ortho to triazine), 2.62 (d, 2 H, aromatic H meta to triazine), 5.56 (s, 2 H, benzylic $-CH_2-$), and 7.41 (s, 6 H, $-CH_3$ on triazine).

Anal. Calcd for $C_{12}H_{12}N_3Br$: C, 51.82; H, 4.35; N, 15.10; Br, 28.73. Found: C, 52.13; H, 4.62; N, 14.97; Br, 28.75.

***p*-(4,6-Dimethyl-*s*-triazin-2-yl)benzyl Alcohol (5b).** To a stirred solution of **4b** (10.1 g, 0.036 mol) in 235 ml of glyme was added 235 ml of 5% aqueous potassium carbonate. The resulting cloudy solution was refluxed for 3 hr (the solution was clear after 0.5 hr), after which time the glyme was distilled. The brown oil which had separated from solution was physically removed and discarded. The remaining solution was cooled (0°) overnight to yield 4.88 g (63%) of yellow crystals. The yellow crystals were recrystallized from benzene and then sublimed to yield 2.34 g of white powder: mp 152.5–153.3°; ir (Nujol) 3230 (OH), 1520 (triazine), and 1065 cm^{-1} (CO); nmr ($CDCl_3$) τ 1.63 (d, 2 H, aromatic H ortho to triazine), 2.64 (d, 2 H, aromatic H meta to triazine), 5.32 (s, 2 H, benzylic $-CH_2-$), 6.88 (s, 1 H, alcoholic H), and 7.36 (s, 6 H, $-CH_3$ on triazine); nmr after shaking with D_2O, τ 5.32 (s, sharper) and 6.88 (negligible).

Anal. Calcd for $C_{12}H_{13}N_3O$: C, 66.96; H, 6.09; N, 19.52. Found: C, 67.14; H, 6.73; N, 19.23.

***p*-(4,6-Dimethyl-*s*-triazin-2-yl)benzoic Acid (6b).** To a stirred solution (0°) of potassium permanganate (2.25 g, 0.014 mol, in 225 ml of freshly boiled water) was added slowly **5b** (2.02 g, 0.0093 mol), followed by 11.2 ml of 5% sodium hydroxide. The solution was stirred at 0° for 3 hr, after which time the solution was filtered and acidified to Congo Red with 6 *N* nitric acid. The resulting precipitate was filtered to yield a white solid which was recrystallized from diethylene glycol and then sublimed to yield 0.75 g (35%) of a white powder: mp 297.2–299.3° (sealed capillary); ir (Nujol) 1700 (C=O), 1525 (triazine), and 1240 cm^{-1} (CO); nmr (DMSO-d_6) τ 0.69 (s, broad, 1 H, carboxyl H), 1.48 (d, 2 H, aromatic H ortho to triazine), 1.90 (d, 2 H, aromatic H meta to triazine), and 7.39 (s, 6 H, $-CH_3$ on triazine).

Anal. Calcd for $C_{12}H_{11}N_3O_2$: C, 62.87; H, 4.84; N, 18.32. Found: C, 62.88; H, 4.88; N, 17.92.

4,6-Bis(trichloromethyl)-2-(*m*-tolyl)-*s*-triazine (2a). *m*-Tolunitrile (44.0 g, 0.38 mol) and trichloroacetonitrile (106.0 g, 0.74 mol) were combined in a cylindrical reaction flask and dry hydrogen chloride was bubbled through the mixture *via* a sintered bubbler for 5 hr (25°), after which the contents were permitted to stand for 7 days (25°) with no apparent results. Dry hydrogen chloride was again bubbled through the solution for 5 hr (25°) and for 0.5 hr (40°) after which the contents were cooled (0°) for 9 days. The unreacted liquid nitriles were decanted from the resulting solid product and the latter was dissolved in ether and washed with 5% sodium hydroxide and with water to pH 6. The ether was dried (MgSO$_4$) and evaporated to yield a whitish solid which was recrystallized from absolute ethanol to yield 41.6 g (28%). Additional dry hydrogen chloride (10 hr, 25°) was added to the decanted nitriles and the resulting solution was permitted to stand for 24 hr (0°). The resulting solid was treated as above to yield 35.7 g (24%): mp 87.4–88.6°; ir (Nujol) 1550 cm^{-1} (triazine); nmr (CCl$_4$) τ 1.62 (m, 2 H, aromatic H ortho to triazine), 2.64 (m, 2 H, aromatic H meta to triazine), and 7.50 (s, 3 H, benzylic -CH$_3$).

Anal. Calcd for $C_{12}H_7N_3Cl_6$: C, 35.48; H, 1.74; N, 10.34; Cl, 52.44. Found C, 35.75; H, 1.81; N, 10.28; Cl, 52.06.

4,6-Dimethyl-2-(*m*-tolyl)-*s*-triazine (3a). Compound **3a** was prepared in 86% yield from **2a** by the same method as described above for the preparation of **3b**. A portion of the product was recrystallized from absolute ethanol and sublimed to yield a white powder: mp 76.0–77.2°; ir (Nujol) 1528 cm^{-1} (triazine); nmr (CCl$_4$) τ 1.78 (s, 2 H, aromatic H ortho to triazine), 2.80 (d, 2 H, aromatic H meta to triazine), 7.43 (s, 6 H, -CH$_3$ on triazine), and 7.60 (s, 3 H, benzylic -CH$_3$).

Anal. Calcd for $C_{12}H_{13}N_3$: C, 72.34; H, 6.58; N, 21.08. Found: C, 72.24; H, 6.41; N, 21.01.

4,6-Dimethyl-2-(3-bromomethylphenyl)-*s*-triazine (4a). Compound **4a** was prepared in 56% yield from **3a** by the same method described above for the preparation of **4b**. A portion of the product was recrystallized from 95% ethanol and sublimed to yield a white powder: mp 76.7–78.0°; ir (CH$_2$Cl$_2$) 1525 cm^{-1} (triazine); nmr (CCl$_4$) τ 1.48 (m, 2 H, aromatic H ortho to triazine), 2.48 (m, 2 H, aromatic H meta to triazine), 5.47 (s, 2 H, benzylic -CH$_2$–), and 7.36 (s, 6 H, -CH$_3$ on triazine).

Anal. Calcd for $C_{12}H_{12}N_3Br$: C, 51.82; H, 4.35; N, 15.10; Br, 28.73. Found: C, 51.68; H, 4.73; N, 15.01; Br, 28.67.

***m*-(4,6-Dimethyl-*s*-triazin-2-yl)benzyl Alcohol (5a).** Compound **5a** was prepared in 35% yield from **4a** by the same method described above for the preparation of **5b**. A portion of the light yellow product was recrystallized from benzene and sublimed to yield a white powder: mp 100.0–100.7°; ir (CH$_2$Cl$_2$) 3450 (OH), 1538 (triazine), and 1062 cm^{-1} (CO); nmr (CDCl$_3$) τ 1.55 (m, 2 H, aromatic H ortho to triazine), 2.48 (m, 2 H, aromatic H meta to triazine), 5.24 (s, 2 H, benzylic -CH$_2$–), 6.50 (s, 1 H, alcoholic H), and 7.36 (s, 6 H, -CH$_3$ on triazine).

Anal. Calcd for $C_{12}H_{13}N_3O$: C, 66.96; H, 6.09; N, 19.52. Found: C, 66.89; H, 5.90; N, 19.10.

***m*-(4,6-Dimethyl-*s*-trianzin-2-yl)benzoic Acid (6a).** Compound **6a** was prepared in 73% yield from **5a** by the same method described above for the preparation of **6b**. The off-white product was recrystallized from diethylene glycol and sublimed to a white powder: mp 263.8–264.9° (with darkening); ir (Nujol) 2200–3500 (broad, OH), 1523 (triazine), 1695 (C=O), and 1240 cm^{-1} (CO); nmr (DMSO-d_6) τ 0.92–2.40 (m, 4 H, aromatic H), 4.0 (s, 1 H, very broad, carboxyl H), and 7.32 (s, 6 H, -CH$_3$ on triazine).

Anal. Calcd for $C_{12}H_{11}N_3O_2$: C, 62.87; H, 4.84; N, 18.32. Found: C, 63.11; H, 4.93; N, 17.96.

4,6-Bis(trichloromethyl)-2-(*p*-fluorophenyl)-*s*-triazine (2d). *p*-Fluorobenzonitrile (9.6 g, 0.079 mol) and trichloroacetonitrile (22.9 g, 0.16 mol) were combined in a cylindrical reaction flask and dry hydrogen chloride was added *via* a sintered glass bubbler for 5 hr (25°) per day for 4 consecutive days, after which the reaction was permitted to stand for 2 days at 25° and 8 days at 0° to yield a solid which was filtered, dissolved in ether, and washed with 5% sodium hydroxide and with water to pH 6. The ether was dried (MgSO$_4$) and evaporated to yield 5.84 g (18%) of a white solid. A portion of this solid was recrystallized from absolute ethanol and sublimed to yield a white powder: mp 129.0–130.6°; ir (Nujol) 1548 cm^{-1} (triazine).

Anal. Calcd for $C_{11}H_4N_3Cl_6F$: C, 32.24; H, 0.98; N, 10.25; Cl, 51.90. Found: C, 32.46; H, 1.11; N, 10.22; Cl, 52.34.

4,6-Dimethyl-2-(*p*-fluorophenyl)-*s*-triazine (3d). Compound **3d** was prepared from **2d** by the same method described above for the preparation of **3b**. The yellow-brown product was thrice sublimed to give 123 mg (4.7%) of a white powder: mp 98.4–100.2°; ir (CH$_2$Cl$_2$) 1530 cm^{-1} (triazine); nmr (CCl$_4$) τ 1.40 (m, 2 H, aromatic H ortho to triazine), 2.83 (m, 2 H, aromatic H meta to triazine), and 7.39 (s, 6 H, -CH$_3$ on triazine).

Anal. Calcd for $C_{11}H_{10}N_3F$: C, 65.01; H, 4.97; N, 20.67. Found: C, 65.57; H, 5.14; N, 20.60.

4,6-Bis(trichloromethyl)-2-(*m*-fluorophenyl)-*s*-triazine (2c). *m*-Fluorobenzonitrile (10.0 g, 0.083 mol) and trichloroacetonitrile (23.9 g, 0.17 mol) were combined in a cylindrical reaction flask and dry hydrogen chloride was added *via* a sintered glass bubbler for 10 hr (25°) per day for 5 consecutive days with no visible results. A portion (1.7 g) of the reaction mixture was then chromatographed on silica gel to yield 430 mg of product which was recrystallized from absolute ethanol and sublimed to yield a white powder: mp 75.1–76.2°; ir (CH$_2$Cl$_2$) 1550 cm^{-1} (triazine).

Anal. Calcd for $C_{11}H_4N_3Cl_6F$: C, 32.24; H, 0.98; N, 10.25; Cl, 51.90. Found: C, 32.30; H, 1.05; N, 10.53; Cl, 51.62.

4,6-Dimethyl-2-(*m*-fluorophenyl)-*s*-triazine (3c). Compound **3c** was prepared from crude **2c** by the same method described above for the preparation of **3b**. The off-white solid was recrystallized from absolute ethanol and sublimed to yield 250 mg of a white powder: mp 120.5–121.3°; ir (CH$_2$Cl$_2$) 1538 cm^{-1} (triazine); nmr (CDCl$_3$) τ 1.75 (m, 2 H, aromatic H ortho to triazine), 2.65 (m, 2 H, aromatic H meta to triazine), and 7.35 (s, 6 H, -CH$_3$ on triazine).

Anal. Calcd for $C_{11}H_{10}N_3F$: C, 65.01; H, 4.97; N, 20.67. Found: C, 65.57; H, 5.04; N, 20.71.

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