

Azo-1,3,5-triazines

P. Loew and C. D. Weis

Dyestuffs and Chemicals Department, CIBA-GEIGY Corp., Basel, Switzerland

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The synthesis of variously substituted bis-triazinylhydrazines and their subsequent oxidation preferably with chlorine in a two-phase system to azo-1,3,5-triazines starting from cyanuric chloride is reported. Reaction of ethoxycarbonylhydrazine with cyanuric chloride followed by oxidation gave access to mono- and bis-ethoxycarbonyl-1,3,5-triazines, respectively. Azo-1,3,5-triazines proved to be very reactive dienophiles.

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In the course of synthesizing functionally substituted 1,3,5-triazines we became interested in the properties of the hitherto unknown azo-bridged 1,3,5-triazine rings. Some aspects of the chemistry of an azo group situated between two nitrogen heterocycles and also of the triazine ring as a substituent attached to a nitrogen atom of an azo-carboxylic ester proved to be unusual and form the subject of this paper.

Cyanuric chloride (**1**) reacted with hydrazine hydrate to yield **2a** in over 90% yield (Scheme I). The differing reactivity of the two chlorine atoms in the triazine rings

is attested to by their reaction with isopropylamine or dimethylamine in dioxane solution affording **2a** and **2b**, respectively.

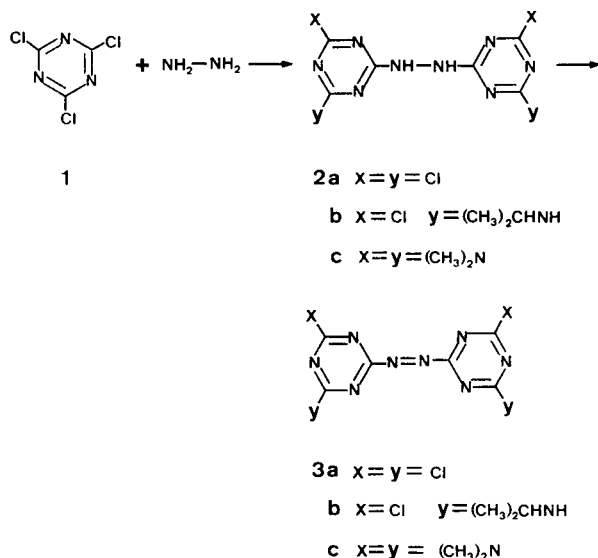
Although oxidations of *N,N'*-diarylhydrazines generally can be carried out with a variety of oxidizing reagents (1), none could be used in this case, due to the ease of hydrolytic cleavage of the carbon-chlorine bond in 1,3,5-triazines. This was found to be particularly true for oxidations with aqueous sodium hypochlorite, sodium bichromate, persulfate salts, nitric acid or with various metal salts of higher oxidation states.

The best procedure for the oxidation of bis-triazinylhydrazines **2a-c** to the corresponding azo compounds proved to be treatment of suspensions of **2a-c** in a two-phase system, comprising an inert organic solvent and aqueous base, either with gaseous chlorine or by adding powdered potassium permanganate to an acetone solution of the hydrazine, as shown for the preparation of **3b**. In particular it was essential for the preparation of **3a** that only slight stirring of the reaction mixture be applied, so that the two phases were still visibly separated, while a current of chlorine was introduced into the organic phase. Compound **2c** was also converted into the azo compound of type **3c** by using bromine instead of chlorine as the oxidizing agent.

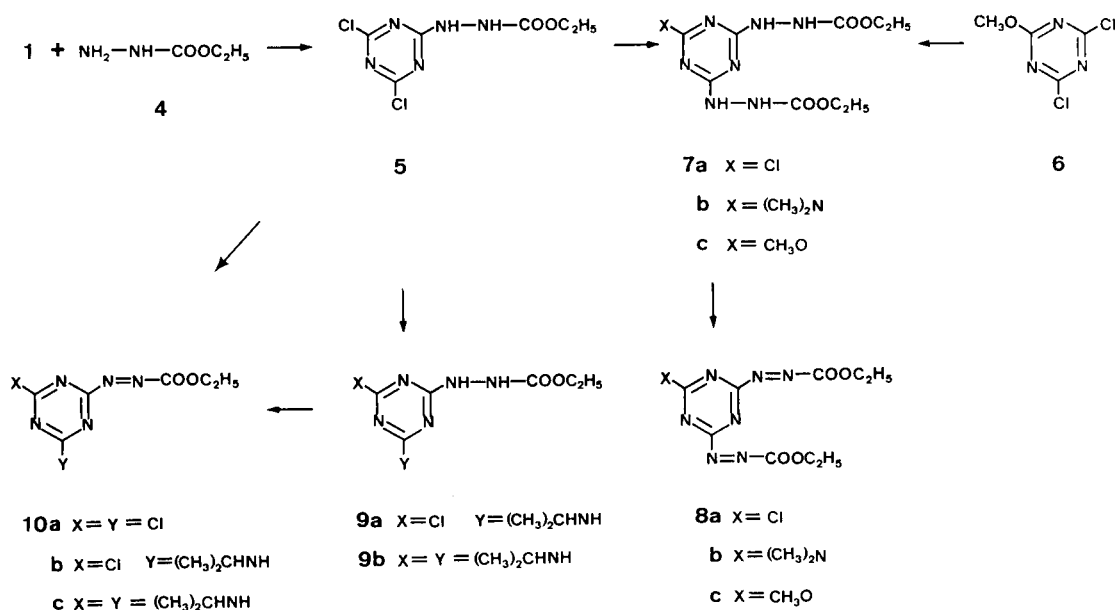
Compounds **3a-c** are stable at room temperature and on heating to the decomposition point no nitrogen evolution was observed with the anticipated formation of a new C-C bond between the two heterocyclic rings.

The reaction of **1** with one mole of ethoxycarbonylhydrazine **4** at 10° afforded the mono substituted dichlorotriazine **5**, whereas the reaction at 25° proceeded

SCHEME I



SCHEME II



further to produce largely the chlorotriazine **7a** containing two ethoxycarbonylhydrazo groups (Scheme 2).

The remaining chlorine atoms of **5** could be easily replaced by amino groups to yield **9a** and **9b**, respectively, and likewise from **7a** the compound **7b** could be obtained. The disubstituted derivative **7c** could be prepared from the known methoxydichlorotriazine (**6**) (2).

Oxidation of the monohydrazines (**5**, **9a**, **b**) and the bis-hydrazotriazines (**7b-c**) with their various substituents by gaseous chlorine in the two-phase system chloroform/aqueous sodium bicarbonate produced again the mono- and bis-azotriazines **10a-c** and **8b-c**, respectively, in good yields. Although **10a** could not be obtained as a pure solid because of its hydrolytic instability, the yield was estimated by isolation of its Diels-Alder adduct with cyclopentadiene.

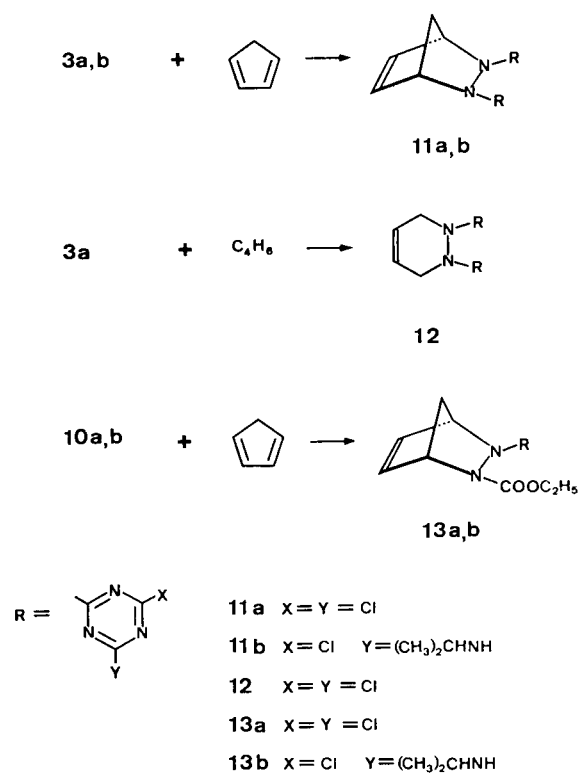
Oxidation of **7a** proceeded readily, but isolation of the bis-azo type **8a** was entirely frustrated again, presumably because of its hydrolytic sensitivity.

The structure of the new compounds described were confirmed by elemental analysis and their spectral data. No attempt was made to determine whether the azo compounds exist in the *syn* or *anti* configuration.

The azo-bis 1,3,5-triazines (**3a,b**) and the 1,3,5-triazinyl-azocarboxylic esters (**10a-b**), respectively, represent the less well known type of disubstituted azo-dienophiles, the substituents of which are *N*-heterocycles (3). They behave as very reactive dienophiles towards such dienes as cyclopentadiene or 1,3-butadiene and formed substituted diazo-norbornenes (**11a,b** and **13a,b**) and tetrahydropyridazines

(**12**), respectively (Scheme 3). The reactions are exothermic and are carried out best in inert solvents, such as benzene or acetone. It may be noted, however, that **3c**

SCHEME III



and **10c** do not exhibit any dienophilic activity.

The 4,4'-dinitroazobenzene seems to be the only representative of an aromatic azo compound which has been used successfully as a dienophile (4), while the corresponding Diels-Alder reactions of the related azo-acyl compounds have been reported by several authors (5).

Characteristic infrared absorption bands of the variously substituted triazinyl hydrazines are centered around 1516-1613 cm^{-1} and 800-823 cm^{-1} , and those of the corresponding azotriazines appear in the region of 1501-1613 cm^{-1} and 810-827 cm^{-1} .

The ester carbonyl absorption band appears for the hydrazinotriazine type at 1709-1751 cm^{-1} and for the corresponding azo compounds at 1770-1789 cm^{-1} . The Diels-Alder addition products show absorptions for the C=N stretching vibration ranging from 1508-1572 cm^{-1} .

EXPERIMENTAL

Melting points are uncorrected. Ir spectra were recorded in nujol or in chloroform solution. Nmr spectra were recorded on a Varian A-60 or HA-100 instrument with TMS as the internal standard.

2,2',4,4'-Tetrachlorohydrazo-1,3,5-triazine (**2a**).

A suspension of 184.5 g. (1 mole) of cyanuric chloride in 500 ml. of tetrahydrofuran was vigorously stirred at -15° to -10° while a solution of 75 g. (1.5 moles) of hydrazine hydrate (100%) in 100 ml. of water was added. After stirring at 0° for an additional 15-30 minutes, the product was precipitated by adding 2 liters of water, filtered, washed with water, dried, affording 154 g. (94%), m.p. $> 250^{\circ}$ dec. Recrystallization could not be achieved without partial decomposition: ir cm^{-1} (potassium bromide): 1572, 1538, 1515, 806, 800.

Anal. Calcd. for $\text{C}_6\text{H}_2\text{Cl}_4\text{N}_8$: C, 21.97; H, 0.61; Cl, 43.24; N, 34.16. Found: C, 22.20; H, 0.71; Cl, 42.98; N, 33.88.

2,2'-Dichloro-4,4'-diisopropylaminohydrazo-1,3,5-triazine (**2b**).

A solution of 12 g. (0.2 mole) of isopropylamine in 50 ml. of dioxane was added with stirring at $15-20^{\circ}$ to a solution of 32.8 g. (0.1 mole) of **2a** in 250 ml. of dioxane, followed by addition of a solution of 8 g. (0.2 mole) of sodium hydroxide in 30 ml. of water at $25-30^{\circ}$. The mixture was stirred for 15 hours at ambient temperature. The product was precipitated by addition of 1.2 liters of water, filtered and dried, affording 36.1 g. (97%), m.p. 250° dec. Recrystallization could not be achieved without partial decomposition; ir cm^{-1} (potassium bromide): 1563, 805.

Anal. Calcd. for $\text{C}_{12}\text{H}_{18}\text{Cl}_2\text{N}_{10}$: C, 38.64; H, 4.86; Cl, 19.01; N, 37.53. Found: C, 39.01; H, 5.02; Cl, 19.20; N, 37.39.

2,2',4,4'-Tetrakis(dimethylamino)hydrazo-1,3,5-triazine (**2c**).

Into a solution of 0.5 g. (0.0012 mole) of **2a** in 15 ml. of dioxane was introduced gaseous dimethylamine until the exothermic reaction subsided. Then 10 ml. of an aqueous trimethylamine solution was added and the mixture refluxed for 1 hour.

Excess solvent was distilled, the precipitated solid filtered, washed with water and dried at 60° under reduced pressure, yielding 0.48 g. (87%) of product, m.p. $196-198^{\circ}$. An analytical sample was obtained by recrystallization from methanol, m.p. $202-204^{\circ}$; ir cm^{-1} (potassium bromide): 1582, 1527, 813, 810.

Anal. Calcd. for $\text{C}_{14}\text{H}_{26}\text{N}_{12}$: C, 46.28; H, 7.20; N, 46.51. Found: C, 46.45; H, 7.30; N, 46.28.

2,2',4,4'-Tetrachloro-azo-1,3,5-triazine (**3a**).

A solution of 1.68 g. (0.02 mole) of sodium bicarbonate in 50 ml. of water was added to a suspension of 3.28 g. (0.01 mole) of **2a** in 100 ml. of chloroform. A slow current of chlorine was introduced at $20-25^{\circ}$ until a red colored homogeneous chloroform layer was formed. The organic phase was separated, washed with water, dried with sodium sulfate and evaporated to dryness. The residue was slurried in ether and filtered, 2.7 g. (83%), m.p. 208° ; visible λ max (chloroform): 439 (199.5); ir cm^{-1} (potassium bromide): 1538, 1471, 824.

Anal. Calcd. for $\text{C}_6\text{Cl}_4\text{N}_8$: C, 22.11; Cl, 43.50; N, 34.37. Found: C, 22.35; Cl, 43.38; N, 34.10.

2,2'-Dichloro-4,4'-diisopropylaminoazo-1,3,5-triazine (**3b**).

A. Oxidation with Chlorine.

A suspension of 3.7 g. (0.01 mole) of **2b** in 100 ml. of dioxane was treated with chlorine at $20-25^{\circ}$ as described for **3a**. The solution was evaporated to dryness and the residue dissolved in a mixture (1:1) of acetone and ether. The solvent was again evaporated yielding 3.7 g. (100%) of **3b**, m.p. 198° . Analytical quantities were obtained by recrystallization from acetone/hexane, m.p. $199-200^{\circ}$. Larger quantities could not be recrystallized without partial decomposition; visible (chloroform): shoulder at 440 ; ir cm^{-1} (potassium bromide): 1538, 821.

Anal. Calcd. for $\text{C}_{12}\text{H}_{16}\text{Cl}_2\text{N}_{10}$: C, 38.85; H, 4.35; Cl, 19.11; N, 37.75. Found: C, 38.81; H, 4.50; Cl, 19.12; N, 37.68.

B. Oxidation with Potassium Permanganate.

To a stirred suspension of 11.7 g. (0.0314 mole) of **2b** in 320 ml. of acetone were added 6.7 g. (0.042 mole) of powdered potassium permanganate at $0-5^{\circ}$. The precipitated manganese dioxide was filtered and extracted with 400 ml. of methylene chloride. The solution was washed with 400 ml. of water, which was then successively extracted with four 50 ml. portions of methylene chloride. The combined extracts were dried over sodium sulfate, followed by evaporation of the solvent, to yield 11.1 g. (96%). The infrared spectrum of the product was shown to be identical with that of the compound obtained from oxidation with chlorine. A mixed m.p. of the two samples showed no depression.

2,2',4,4'-Tetrakis(dimethylamino)azo-1,3,5-triazine (**3c**).

A solution of 1.6 g. (0.01 mole) of bromine in 5 ml. of dry chloroform was added to a suspension of 3.6 g. (0.01 mole) of **2c** in 20 ml. of chloroform, followed by a solution of 1.8 g. (0.021 mole) of sodium bicarbonate in 20 ml. of water, and stirred for 30 minutes at $20-25^{\circ}$. The organic layer was separated, washed with water, dried over sodium sulfate, and evaporated to dryness yielding 3.5 g. of product. Recrystallization from benzene/hexane afforded 3.0 g. (84%), m.p. $242-243^{\circ}$; visible (chloroform): shoulder at 440 ; ir cm^{-1} (potassium bromide): 1527, 814, 810.

Anal. Calcd. for $\text{C}_{14}\text{H}_{24}\text{N}_2$: C, 46.65; H, 6.71; N, 46.64. Found: C, 46.91; H, 6.81; N, 46.49.

2,4-Dichloro-6-ethoxycarbonylhydrazo-1,3,5-triazine (**5**).

To a stirred solution of 18.5 g. (0.1 mole) of cyanuric chloride in 100 ml. of tetrahydrofuran was added in small portions 10.4 g. (0.1 mole) of ethyl hydrazinecarboxylic acid ester at -10° . After the addition had been completed stirring was continued at -10° for an additional 10 minutes, and a solution of 4 g. (0.1 mole) of sodium hydroxide in 20 ml. of water added dropwise at -10° to -5° . The mixture was then stirred for 15 minutes at 0° , poured

into 250 ml. of water and the aqueous solution extracted three times with chloroform. The combined organic extracts were washed with water and evaporated to dryness. The residue was suspended in ether, filtered and dried, yielding 15.1 g. (60%), m.p. 107-108°. An additional 8.5 g. of product crystallized from the filtrate on cooling in ice, m.p. 104-106°; ir cm^{-1} (potassium bromide): 1742, 1592, 809.

Anal. Calcd. for $\text{C}_6\text{H}_7\text{Cl}_2\text{N}_5\text{O}_2$: C, 28.59; H, 2.80; Cl, 28.13; N, 27.79. Found: C, 28.61; H, 2.90; Cl, 27.98; N, 27.82.

2-Chloro-4,6-bis(ethoxycarbonylhydrazo)-1,3,5-triazine (7a).

To a solution of 73.5 g. (0.4 mole) of cyanuric chloride in one liter of tetrahydrofuran was added 83 g. (0.8 mole) of ethyl hydrazinecarboxylate in small portions, followed by a solution of 32 g. (0.8 mole) of sodium hydroxide in 400 ml. of water. The mixture was stirred for 18 hours at 25°, poured into water and extracted with ethyl acetate. The organic phase was separated, dried with sodium sulfate and reduced in volume until crystals began to appear. Filtration yielded 100 g. (79%) of product, m.p. 191°. An analytical sample was obtained by recrystallization from ethyl acetate, m.p. 191°; ir cm^{-1} (potassium bromide): 1751, 1582, 811.

Anal. Calcd. for $\text{C}_9\text{H}_{14}\text{Cl}_2\text{N}_7\text{O}_4$: C, 33.81; H, 4.41; Cl, 11.09; N, 30.67. Found: C, 33.78; H, 4.44; Cl, 11.25; N, 30.62.

2-Dimethylamino-4,6-bis(ethoxycarbonylhydrazo)-1,3,5-triazine (7b).

To a solution of 63.8 g. (0.2 mole) of 7a in 200 ml. of dioxane was added at 25°, 45 g. (0.4 mole) of an aqueous solution of dimethylamine. The temperature rose to 75° during the addition. The mixture was stirred for a period of 2 hours at 70° and then added to 1 liter of water. The suspension was filtered, the residue washed with water and dried, yielding 55.2 g. (84%). An analytical sample was obtained by recrystallization from a mixture of ethyl acetate and hexane (1:1), m.p. 204-205°; ir cm^{-1} (potassium bromide): 1736, 1709, 1613, 1543.

Anal. Calcd. for $\text{C}_{11}\text{H}_{20}\text{N}_8\text{O}_4$: C, 40.24; H, 6.14; N, 34.13. Found: C, 40.18; H, 6.21; N, 33.89.

2-Methoxy-4,6-bis(ethoxycarbonylhydrazo)-1,3,5-triazine (7c).

To a solution of 27 g. (0.15 mole) of 2,4-dichloro-6-methoxy-1,3,5-triazine (6) in 150 ml. of tetrahydrofuran was added 62.5 g. (0.6 mole) of ethyl hydrazinecarboxylate. The temperature rose to 50° and it was stirred for an additional 3.5 hours at this temperature. The solution was then added to 400 ml. of water, the precipitate filtered and dried yielding 39.1 g. (83%), m.p. 175-176°. The filtrate was extracted with chloroform to yield an additional 7.2 g. (total yield 98%) after evaporation of the solvent. An analytical sample was obtained by recrystallization from a mixture of acetone/*n*-hexane, m.p. 171-172°; ir cm^{-1} (potassium bromide): 172, 1605, 1558, 823.

Anal. Calcd. for $\text{C}_{10}\text{H}_{17}\text{N}_7\text{O}_5$: C, 38.09; H, 5.43; N, 31.10. Found: C, 38.20; H, 5.54; N, 30.97.

2-Dimethylamino-4,6-bis(ethoxycarbonylazo)-1,3,5-triazine (8b).

A suspension of 19.7 g. (0.06 mole) of 7b in 250 ml. of methylene chloride was covered with a solution of 20.2 g. (0.24 mole) of sodium bicarbonate in 200 ml. of water. A slow current of chlorine was introduced into the organic layer until a red homogeneous methylene chloride phase was obtained. The two layers were separated and the organic phase washed with water, dried over sodium sulfate and evaporated to dryness. The residue was suspended in ether, the solution filtered to yield 18.4 g. (95%) of

product, m.p. 108°; visible (chloroform): 360 (shoulder); ir cm^{-1} (potassium bromide): 1779, 1613, 1501, 805, 820.

Anal. Calcd. for $\text{C}_{11}\text{H}_{16}\text{N}_8\text{O}_4$: C, 40.74; H, 4.97; N, 34.56. Found: C, 40.71; H, 5.10; N, 34.39.

2-Methoxy-4,6-bis(ethoxycarbonylazo)-1,3,5-triazine (8c).

A slurry of 31.5 g. (0.1 mole) of 7c in a mixture of 500 ml. of chloroform and 16.8 g. (0.2 mole) of sodium bicarbonate in 260 ml. of water was oxidized with chlorine as described for 8b. The residue of the evaporated chloroform phase was extracted with ether, filtered, and yielded after addition of *n*-hexane 22.0 g. (71%) of product, m.p. 67°; visible (chloroform): λ max (ϵ) 433 (218.8); ir cm^{-1} (potassium bromide): 1786, 1587, 1534, 827.

Anal. Calcd. for $\text{C}_{10}\text{H}_{13}\text{N}_7\text{O}_5$: C, 38.59; H, 4.21; N, 31.50. Found: C, 38.70; H, 4.31; N, 31.25.

2-Chloro-4-isopropylamino-6-ethoxycarbonylhydrazo-1,3,5-triazine (9a).

A solution of 1.2 g. (0.02 mole) of isopropylamine in 2 ml. of dioxane was added to a solution of 5 g. (0.02 mole) of 5 in 20 ml. of dioxane at 15-20°, followed by a solution of 0.8 g. (0.02 mole) sodium hydroxide in 3 ml. of water. The mixture was stirred at 25° for a period of 4 hours, and then added to 100 ml. of water. The aqueous phase was extracted 3 times with chloroform, dried over sodium sulfate and evaporated to dryness. The residue was recrystallized from a mixture of ether/hexane, yielding 4.75 g. (87%) of product, m.p. 150-151°; ir cm^{-1} (potassium bromide): 1748, 1597, 812.

Anal. Calcd. for $\text{C}_9\text{H}_{15}\text{Cl}_2\text{N}_6\text{O}_2$: C, 39.34; H, 5.50; Cl, 12.90; N, 30.59. Found: C, 39.54; H, 5.61; Cl, 12.71; N, 30.46.

2,4-Bis(diisopropylamino)-6-ethoxycarbonylhydrazo-1,3,5-triazine (9b).

To a solution of 20 g. (0.0 mole) of 5 in 200 ml. of dioxane were added successively at 25° 20.8 g. (0.35 mole) of isopropylamine and a solution of 6.4 g. (0.16 mole) sodium hydroxide in 40 ml. of water. The mixture was heated under reflux for a period of 8 hours, added to 1 liter of water and extracted 3 times with ethyl acetate. The organic phase was washed with water, dried over sodium sulfate and evaporated to dryness, yielding 23.3 g. (99%) of product. An analytical sample was obtained by recrystallization from ethyl acetate, m.p. 93-95°; ir cm^{-1} (potassium bromide): 1736, 1592, 1511, 814.

Anal. Calcd. for $\text{C}_{12}\text{H}_{23}\text{N}_7\text{O}_2$: C, 48.47; H, 7.80; N, 32.97. Found: C, 48.51; H, 7.88; N, 32.71.

2-Ethoxycarbonylazo-4,6-dichloro-1,3,5-triazine (10a).

The synthesis was carried out by a procedure analogous to that of the preparation of 10b. The yield of crude product was approximately 84%; ir cm^{-1} (chloroform): 1789, 1782, 1538, 1520, 818. The instability of the compound did not allow purification or storage for any length of time, and hence it was used immediately for the preparation of 13a.

2-Ethoxycarbonylazo-4-chloro-6-isopropylamino-1,3,5-triazine (10b).

A solution of 4.0 g. (0.0146 mole) of 9a in 50 ml. of chloroform was added to a solution of 2.6 g. (0.031 mole) of sodium bicarbonate in 35 ml. of water. Chlorine was introduced into the stirred solution until the chloroform layer was deep red. The organic layer was separated, washed with water, dried over sodium sulfate and evaporated to dryness. The residue was a red oil which appeared to be homogeneous by thin layer chromatography. It was distilled at 125°/5.10⁻³ torr in a short path distillation

apparatus; visible (chloroform): shoulder at 430; ir cm^{-1} (potassium bromide): 1786, 1524, 818.

Anal. Calcd. for $\text{C}_9\text{H}_{13}\text{Cl}_2\text{N}_6\text{O}_2$: C, 39.63; H, 4.80; Cl, 13.00; N, 30.82. Found: C, 39.91; H, 5.01; Cl, 13.21; N, 30.62.

2-Ethoxycarbonylazo-4,6-bis(diisopropylamino)-1,3,5-triazine (**10c**).

The synthesis was carried out according to the method described for **10b**. Compound **9b** (8.4 g., 0.0028 mole) yielded after recrystallization from ether 5.7 g. (69%) of **10c**, m.p. 170-172°; visible (chloroform): 420 (shoulder); ir cm^{-1} (potassium bromide): 1616, 1565, 1538, 818.

Anal. Calcd. for $\text{C}_{12}\text{H}_{21}\text{N}_7\text{O}_2$: C, 48.80; H, 7.17; N, 33.20. Found: C, 48.69; H, 7.11; N, 32.98.

2,3-Bis-(4',6'-dichloro-1,3,5-triazinyl)-2,3-diazabicyclo[2.2.1]hept-5-ene (**11a**).

To a stirred solution of 15.3 g. (0.05 mole) of **3a** in 250 ml. of benzene was added 7.3 g. (0.11 mole) of freshly distilled cyclopentadiene at 0-5°. The solvent was then removed under reduced pressure, ether added to the residue and the crystals which precipitated were filtered, yielding 14.1 g. (72%) of product. From the mother liquor were obtained an additional 2.7 g. which combined with the bulk product, gave a total yield of 86%. Recrystallization from an acetone/hexane mixture yielded white crystals, m.p. 165-166°; nmr (deuteriochloroform): δ 2.0 (s, 2H); 5.9 (m, 2H); 6.75 (s, broad, 2H); ir (nujol) cm^{-1} : 1563, 1538, 1508, 1316, 1242, 847, 800, 688.

Anal. Calcd. for $\text{C}_{11}\text{H}_6\text{Cl}_4\text{N}_8$: C, 33.70; H, 1.54; Cl, 36.17; N, 28.58. Found: C, 33.84; H, 1.61; Cl, 35.88; N, 28.49.

2,3-Bis-(2'-chloro-4'-isopropylamino-1,3,5-triazinyl)-2,3-diazabicyclo[2.2.1]hept-5-ene (**11b**).

To a stirred suspension of 14.6 g. (0.039 mole) of **3b** in 220 ml. of benzene were added 5.3 g. (0.078 mole) of freshly distilled cyclopentadiene and the solution stirred at 20° for a period of 15 hours. The solvent was evaporated and the residue recrystallized from a mixture of acetone/hexane (1:1), yielding 13.8 g. (81%) of product, m.p. 148-150°; nmr (deuteriochloroform + DMSO- d_6): δ 1.18 (d, J = 7, 12H); 1.86 (s, 2H); 4.05 (m, 2H); 5.65 (m, 2H); 6.62 (s, broad, 2H); 7.5 (m, 2H); ir (chloroform) cm^{-1} : 3448, 1575, 1590, 1527.

Anal. Calcd. for $\text{C}_{17}\text{H}_{22}\text{Cl}_2\text{N}_{10}$: C, 46.48; H, 5.07; Cl, 16.21; N, 32.03. Found: C, 46.54; H, 5.01; Cl, 16.41; N, 32.04.

1,2-Bis-(4',6'-dichloro-1,3,5-triazinyl)-1,2,5,6-tetrahydropyridazine (**12**).

A slow current of 1,3-butadiene was passed into a slurry of 3.26 g. (0.01 mole) of **3a** in 50 ml. of benzene. The mixture was allowed to stand at 25° for a period of 20 minutes, evaporated to dryness and the residue recrystallized from acetone/hexane, yielding 1.9 g. (51%), m.p. 201-202°; nmr (deuteriochloroform +

DMSO- d_6): δ 4.1 (d, J = 15, 2H); 5.15 (d, J = 15, 2H); 5.95 (s, broad, 2H); ir (nujol) cm^{-1} : 1525, 1538, 1508, 1320, 978, 868, 843, 799, 794.

Anal. Calcd. for $\text{C}_{10}\text{H}_6\text{Cl}_4\text{N}_8$: C, 31.60; H, 1.59; Cl, 37.32; N, 29.49. Found: C, 31.68; H, 1.69; Cl, 37.18; N, 29.52.

2-Ethoxycarbonyl-3-(2',4'-dichloro-1,3,5-triazinyl)-2,3-diazabicyclo[2.2.1]hept-5-ene (**13a**).

To a solution of 15 g. of freshly prepared crude **10a** in 120 ml. of acetone was added a solution of 7.4 g. (0.11 mole) of cyclopentadiene in 18 ml. of acetone at 0-5°. After the strongly exothermic reaction had subsided the solution was stirred for a further 10 minutes and evaporated to dryness. The residue was recrystallized from an acetone/hexane mixture, yielding 12.8 g., 68% of product, m.p. 117°; nmr (deuteriochloroform): δ 1.26 (t, J = 7, 3H); 1.85 (s, 2H); 4.16 (q, J = 7, 2H); 5.22 (s, 1H); 5.66 (s, 1H); 6.53 (s, 2H); ir (chloroform) cm^{-1} : 1475, 1550, 1486, 849.

Anal. Calcd. for $\text{C}_{11}\text{H}_{11}\text{Cl}_2\text{N}_5\text{O}_2$: C, 41.79; H, 3.50; Cl, 22.43; N, 22.13. Found: C, 42.01; H, 3.57; Cl, 22.20; N, 22.12.

2-Ethoxycarbonyl-3-(2'-chloro-4'-isopropylamino-1,3,5-triazinyl)-2,3-diazabicyclo[2.2.1]hept-5-ene (**13b**).

To a solution of 15 g. (0.055 mole) of **10b** in 160 ml. of acetone was added a solution of 7.2 g. of cyclopentadiene in 20 ml. of acetone at 5° and the solution stirred at room temperature for a further period of 4 hours. The solvent was evaporated and the residue recrystallized from a mixture of ether and hexane, yielding 9.5 g. (51%) of product, m.p. 115-116°. The filtrate yielded an additional 2.1 g. of less pure material; nmr (deuteriochloroform): δ 1.22 (d, J = 7, 6H); 1.29 (t, J = 7, 3H); 1.8 (s, 2H); ca. 4.2 (m, 3H); 5.3 (m, 2H); 5.6 (m, 1H); 6.56 (s, 2H); ir (chloroform) cm^{-1} : 3448, 1730, 1515, 1520.

Anal. Calcd. for $\text{C}_{14}\text{H}_{19}\text{ClN}_6\text{O}_2$: C, 49.63; H, 5.65; Cl, 10.46; N, 24.81. Found: C, 49.80; H, 5.74; Cl, 10.41; N, 25.02.

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