acetonitrile. On standing overnight, 38.5 g of chlorodifluoroacetonitrile distilled out. Hydrolysis and work-up gave 20.5 g (64%) of N,N-diethyl chlorodifluoroacetamidine, bp 80–81° (50 mm), n^{20}D 1.4272.

Anal. Calcd for $C_6H_{11}ClF_2N_2$: N, 15.18. Found: N, 15.09. The infrared spectrum confirmed the structure. Neither triazine nor dihydrotriazine was detected.

Relative Reactivities of Acetonitrile and Chlorodifluoroacetonitrile.—To an ether solution of 25 g of acetonitrile and 67 g of chlorodifluoroacetonitrile at −50° was added 0.2 mole of phenylmagnesium bromide. As addition proceeded, a gelatinous precipitate formed and the mixture was warmed to −25°. On standing for 64 hr, 8 g of chlorodifluoroacetonitrile distilled from the mixture. Hydrolysis, extraction, and distillation gave 9.0 g of a mixture of acetophenone and its imine with a little α,α,α-chlorodifluoroacetophenone, and its imine, bp 80–110° (50 mm), and 6 g of impure α,α,α-chlorodifluoroacetophenone imine, bp 130–134° (10 mm), mp 65–67°.

Anal. Calcd for $C_8H_6ClF_2N$: C, 50.67; H, 3.19; Cl, 18.70; N, 7.39. Found: C, 55.55; H, 3.31; Cl, 13.93; N, 7.21.

Further distillation gave 38 g (46%) of 2-phenyl-2,4,6-tris-(chlorodifluoromethyl)-1,2-dihydro-1,3,5-triazine, bp 144–146° (8 mm). Nmr indicated that there was no incorporation of acetonitrile into the dihydrotriazine.

Acknowledgment.—Appreciation is expressed for the assistance of E. R. Santee, Jr., with nmr spectroscopy and H. L. Joyce with infrared spectroscopy. The encouragement and helpful discussions of J. W. Clark, D. L. Heywood, and W. R. Moore are also gratefully acknowledged.

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as-Triazine Chemistry. III.[1,2] The Structures of the Monoxide of 3-Methoxy- and 3-Phenoxy-5,6-diphenyl-*as*-triazine

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Monoxides of 3-methoxy- and 3-phenoxy-5,6-diphenyl-*as*-triazine were synthesized by oxidation with permaleic acid. The structures of these oxides were determined as 3-methoxy- and 3-phenoxy-5,6-diphenyl-*as*-triazine 2-oxide by chemical methods.

In the previous investigation,[2] we reported the synthesis of the 1-oxides of 3-amino- as well as 3-oxo-5,6-diphenyl-*as*-triazine and of their analogs. Dipole moment measurements were a powerful means for the determination of N-oxide position in these cases.

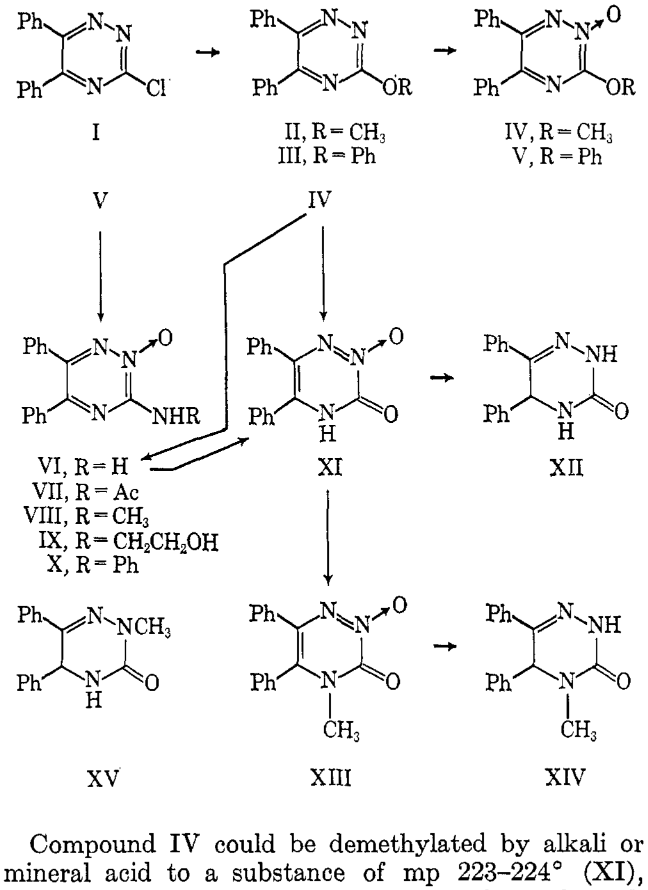
This paper describes the structural elucidation of the N-oxides of 3-methoxy- and 3-phenoxy-5,6-diphenyl-*as*-triazine by simple chemical methods. In the present case, the substituents at the 3 position are capable of chemical modifications, permitting correlation with the previously described N-oxides.

The starting materials, 3-methoxy- (II) and 3-phenoxy-5,6-diphenyl-*as*-triazine (III), were readily obtained from the 3-chloro compound (I)[3] by reaction with sodium methoxide and sodium phenoxide, respectively, as shown in Scheme I. Compound II, isolated previously as a monohydrate of mp 221–222° in unspecified yield,[3] was obtainable in anhydrous state in over 60% yield.

Oxidation of II and III with permaleic acid in methylene chloride led to the monoxides IV and V, respectively. The phenoxy group in compound V was found to undergo facile nucleophilic substitutions by heating with ammonia, aliphatic primary amines, and even with aniline to given VI, VIII, IX, and X. Treatment of IV with 3.6% alcoholic ammonia with subsequent purification by alumina chromatography gave a sample of VI with a slightly different melting point and infrared spectrum from those of a sample prepared from V.

Compound VI was different from the known 3-amino-5,6-diphenyl-*as*-triazine 1-oxide[2] in every respect (melting point, mixture melting point, and infrared and ultraviolet spectra). These data show that IV and V were oxidized at the same position, either at N-2 or N-4.[4]

SCHEME I



Compound IV could be demethylated by alkali or mineral acid to a substance of mp 223–224° (XI), which was also obtainable from VI upon drastic hydrolysis with 30% potassium hydroxide solution. The infrared spectrum (in KBr) of XI showed absorptions at

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(1) Part II: T. Sasaki and K. Minamoto, *Chem. Pharm. Bull.* (Tokyo), **13**, 1168 (1965).

(2) Part IV: T. Sasaki and K. Minamoto, *J. Org. Chem.*, **31**, 3917 (1966).

(3) P. V. Laakso, *et al.*, *Tetrahedron*, **1**, 108 (1957).

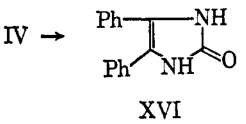
(4) The mass spectrum of IV shows a stronger peak for $(M - 17)^+$, presumed to be generated by elimination of a hydroxyl *via* a cyclic transition state, than for $(M - 16)^+$, formed simply by deoxygenation. This suggests existence of a N-oxide group at either *ortho* position to the methoxyl. Observations in this line will be published later.

1658, 1630 (ν C=O, lactam), 3025, and 3056 cm^{-1} (ν NH or ν OH), the latter two bands being equivocal. Reduction of XI with zinc powder in acetic acid led to the known 5,6-diphenyl-dihydro-*as*-triazin-3(2H,4H)-one (XII),[5] indicating that the *as*-triazine ring in XI remained unaffected. Compound XI showed no color with ferric chloride solution and reacted with methyl iodide to give a monomethylated compound XIII, whose skeletal identity with the former was confirmed by elemental analysis and infrared and ultraviolet spectra.

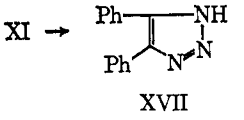
The correct structures of XI and XIII were finally established as 5,6-diphenyl-*as*-triazin-3(4H)-one 2-oxide and 5,6-diphenyl-4-methyl-*as*-triazin-3(4H)-one 2-oxide, respectively, on the basis of the fact that XIII was reduced to 5,6-diphenyl-4-methyldihydro-*as*-triazin-3(2H,4H)-one (XIV), a key substance furnishing the ultimate evidence of position 4 being free from oxidation. The new substance XIV of mp 239–240° derived from XIII by reduction with a Zn–AcOH–EtOH system had the composition $C_{16}H_{15}N_3O$ and its spectral features conformed to a monomethylated derivative of XII; the infrared spectrum showed a lactam band at 1677 cm^{-1} and the ultraviolet curve closely resembled those of XII and the 2-methyl analog XV[6] but was never superimposable on either of these as shown in Figure 1. It is of interest to note that the 4-N-Me group is separated from the major chromophore, thereby contributing to π–π conjugation in less degree than does the 2-N-Me group in XV. In accordance with this, the observed absorption maximum of XIV lay nearer to that of XII than did that of XV, which lacks the contribution by hyperconjugation of a methyl group. A depressed mixture melting point of XIV with XV is an additional proof that XIV is certainly an isomer but not an isomorph of XV. If XI has a 2-N-hydroxy structure, methylation of XI should give a 2-N-methoxy compound whose methoxy function should subsist through the reducing conditions to given an undeoxygenated compound; the formation of XIV as described above clearly reject this structure.

As a conclusion, the oxides, IV and V, must be 2-N-oxides.

It is noteworthy that IV and XI were converted to five-membered heterocycles in drastic degradative conditions: a long heating of IV in aniline, followed by an alumina chromatography, gave 4,5-diphenyl-2-imidazolone (XVI)[7] in contrast with the formation of X from V, while XI, though resistant to cleavage with alkali or mineral acid on a boiling water bath, yielded 4,5-diphenyl-1,2,3-triazole (XVII)[8] when heated with acetic anhydride for a long time. The formation of these five-membered rings seems to involve a degradation of the triazine ring followed by a recombination, the mechanism of which is, however, uncertain at present. Further analogous observations on the formations of five-membered heterocycled from *as*-triazine N-oxides will be published later.



XVI



XVII

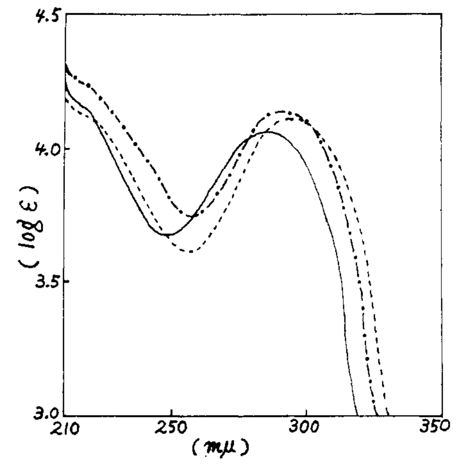


Figure 1.—Ultraviolet absorptions in alcohol of 5,6-diphenyl-dihydro-*as*-triazines, XII (———), XV (- - - -), and XIV (- · · - ·).

Experimental Section[9]

3-Methoxy-5,6-diphenyl-*as*-triazine (II).—To a solution of 0.43 g of sodium in 15 ml of methanol was added a solution of 5.0 g of I in 25 ml of methanol and the mixture was stirred for 1.5 hr at room temperature. The solvent was removed *in vacuo* at room temperature. The residue was dissolved in chloroform and washed with water. The chloroform layer was dried with sodium sulfate and evaporated to dryness.

Recrystallization of the residue from a small quantity of ether gave 3.0 g (61%) of fine needles: mp 75–77°, $\lambda_{max}^{ethanol}$ 257 mμ (log ϵ 4.11) and 328 mμ (log ϵ 3.9).

Anal. Calcd for $C_{16}H_{13}N_3O$: C, 72.98; H, 4.98; N, 15.96. Found: C, 73.04; H, 5.02; N, 15.92.

3-Phenoxy-5,6-diphenyl-*as*-triazine (III).—Ten grams of I and dry sodium phenoxide, which was previously prepared from 3.5 g of phenol and 1.5 g of sodium hydroxide, was mixed in 90 ml of dry benzene and the mixture was refluxed under stirring for a few hours. After cooling, the mixture was washed once with water and the separated organic layer was dried with sodium sulfate and evaporated to dryness under reduced pressure.

Recrystallization of the residue from alcohol afforded 10 g (83%) of straw yellow needles: mp 133°, $\lambda_{max}^{alcohol}$ 258 mμ (log ϵ 4.19) and 327 mμ (log ϵ 3.9).

Anal. Calcd for $C_{21}H_{15}N_3O$: C, 77.52; H, 4.65; N, 12.92. Found: C, 77.73; H, 4.56; N, 13.08.

3-Methoxy-5,6-diphenyl-*as*-triazine 2-Oxide (IV).—To a stirred mixture of 1.3 ml of 30% hydrogen peroxide and 8 ml of methylene chloride was added 1.48 g of maleic anhydride. When the solid had gone into solution, a solution of 2.2 g of II in 10 ml of methylene chloride was added in one portion. After gentle reflux for 1 hr the precipitate was removed by suction and the filtrate was, after addition of chloroform and cracked ice, neutralized with diluted sodium carbonate. The separated organic layer was washed once with water, dried with sodium sulfate, and evaporated to give a viscous residue, which was chromatographed in chloroform on alumina (200–300 mesh). The main fraction (mp 140–150°) was again submitted to alumina chromatography with the same solvent.

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(5) H. Biltz, *Ann.*, **339**, 281 (1905).

(6) H. Biltz, *ibid.*, **339**, 285 (1905).

(7) H. Biltz, *Ber.*, **40**, 4801 (1907).

(8) R. Stollé, *J. Prakt. Chem.*, **70**, 440 (1904).

(9) The melting points were determined on a Hozumi's electric micromelting point apparatus. All the ultraviolet spectra were recorded on a Hitachi Model EPS-2 recording spectrophotometer and infrared spectra were determined on a JASCO Model IR-S infrared spectrophotometer.

Recrystallization of the major fraction from methanol gave 0.84 g (36%) of colorless star-like congregated prisms: mp 157.5–158.5°, $\lambda_{max}^{alcohol}$ 252 mμ (log ϵ 4.21) and 346 mμ (log ϵ 3.89).

Anal. Calcd for $C_{16}H_{13}N_3O_2$: C, 68.80; H, 4.69; N, 15.05. Found: C, 68.71; H, 4.94; N, 15.38.

3-Phenoxy-5,6-diphenyl-*as*-triazine 2-Oxide (V).—Hydrogen peroxide (1.3 ml of 30%) and 1.65 g of maleic anhydride were combined in 10 ml of methylene chloride and the mixture was stirred at room temperature, until the solid anhydride disappeared. A solution of 3.0 g of III in 8 ml of methylene chloride was then added and stirring was continued at room temperature. After 2 hr, the reaction mixture was treated as above to afford a solid crude product.

Repeated crystallization from alcohol gave 1.6 g (51%) of pale yellow needles: mp 208–210°, $\lambda_{max}^{alcohol}$ 250 mμ (log ϵ 4.33) and 343 mμ (log ϵ 3.92).

Anal. Calcd for $C_{21}H_{15}N_3O_2$: C, 73.89; H, 4.43; N, 12.31. Found: C, 74.16; H, 4.15; N, 12.24.

3-Amino-5,6-diphenyl-*as*-triazine 2-Oxide (VI).—(1) A mixture of 0.30 g of V and 5 ml of 3.6% alcoholic ammonia was strongly heated in a pressure tube on a water bath for 10 hr. Then the solvent was distilled off *in vacuo* as thoroughly as possible, during which some sublimation of phenol was observed. The remaining solid was recrystallized from alcohol to give 0.16 g of pale yellow needles: mp 236–238°; $\lambda_{max}^{alcohol}$ 222 mμ (log ϵ 4.25, infl), 257 (4.31), and 365 (3.82).

Anal. Calcd for $C_{15}H_{12}N_4O$: C, 68.17; H, 4.58; N, 21.20. Found: C, 68.62; H, 4.20; N, 21.73.

(2) A mixture of 0.5 g of IV and 5 ml of 3.6% alcoholic ammonia was heated in a pressure tube on a water bath for 13 hr. The reaction mixture was evaporated *in vacuo* to give a brownish paste, which was eluted through alumina column with chloroform. The last main fraction gave 0.16 g of straw yellow prisms after recrystallization from methanol, mp 240–241°. Its ultraviolet spectrum thoroughly coincided with that of the foregoing preparation.

Anal. Calcd for $C_{15}H_{12}N_4O$: C, 68.17; H, 4.58; N, 21.20. Found: C, 68.07; H, 4.28; N, 21.91.

Acetylation with acetic anhydride gave 3-acetamido compound VII in quantitative yield: mp 272–273° (from alcohol); $\lambda_{max}^{alcohol}$ 223 mμ (log ϵ 4.48), 250 (4.46), and 349 (3.90).

Anal. Calcd for $C_{17}H_{14}N_4O_2$: C, 66.65; H, 4.61; N, 18.29. Found: C, 66.38; H, 4.24; N, 18.34.

3-Methylamino-5,6-diphenyl-*as*-triazine 2-Oxide (VIII).—Compound V (1.0 g), 3 ml of 30% aqueous methylamine, and 2 ml of alcohol were combined in a pressure tube and heated on a water bath for 2 days. After cooling, the reaction mixture was poured into water and separating crystals were filtered, dried, and recrystallized from alcohol to give 0.7 g of straw yellow microcrystalline needles: mp 240–241°; $\lambda_{max}^{alcohol}$ 226 mμ (log ϵ 4.29), 262 (4.41), and 374 (3.72).

Anal. Calcd for $C_{16}H_{14}N_4O$: C, 69.05; H, 5.07; N, 20.13. Found: C, 68.86; H, 4.88; N, 20.00.

3-(β-Hydroxyethylamino)-5,6-diphenyl-*as*-triazine 2-Oxide (IX).—Compound V (1.0 g), 0.36 g of ethanolamine, and 6 ml of alcohol were mixed in a pressure tube and heated on a water bath for 8 hr. The mixture was evaporated under reduced pressure to a solid residue, which was, after washing with water and drying, recrystallized from alcohol to give 0.7 g of pale yellow microcrystalline needles: mp 196–197°; $\lambda_{max}^{alcohol}$ 229 mμ (log ϵ 4.35), 262 (4.45), and 374 (3.75).

Anal. Calcd for $C_{17}H_{16}N_4O_2 \cdot {}^1/_2H_2O$: C, 64.34; H, 5.40; N, 17.66. Found: C, 64.47; H, 5.35; N, 17.33.

3-Anilino-5,6-diphenyl-*as*-triazine 2-Oxide (X).—A mixture of 0.7 g of V and 12 ml of aniline was heated at 160–170° in an oil bath for 8 hr and evaporated *in vacuo*. The residue was chromatographed in chloroform on activated alumina (200–300 mesh) to yield 0.35 g of starting material V from the initial fraction and then 0.25 g of yellow solid from the next fraction. The latter was repeatedly crystallized from methanol to give 0.2 g of deep yellow needles: mp 225–227°; $\lambda_{max}^{alcohol}$ 237 mμ (log ϵ 4.24), 293 (4.50), and 384 (3.43).

Anal. Calcd for $C_{21}H_{16}N_4O$: C, 74.10; H, 4.74; N, 16.46. Found: C, 74.36; H, 4.67; N, 16.85.

When the initial reaction mixtue was examined by thin layer chromatography with silica gel, no spots were observed which corresponded to azobenzene and azoxybenzene, oxidation products of aniline.

5,6-Diphenyl-*as*-triazine-3(4H)-one 2-Oxide (XI).—(1) A mixture of IV (0.5 g), concentrated hydrochloric acid (5 ml), and alcohol (3 ml) was heated on a water bath for 30 min. After being cooled, the separated crystals were collected by suction, dried *in vacuo* and recrystallized from alcohol to give 0.35 g (74%) of pale yellow fine needles: mp 223–224°; ν_{max}^{KBr} 3056, 3025 (NH), 1658, and 1630 cm^{-1} (C=O); $\lambda_{max}^{alcohol}$ 255 mμ (log ϵ 4.17) and 354 mμ (log ϵ 3.78).

Anal. Calcd for $C_{15}H_{11}N_3O_2$: C, 67.91; H, 4.18; N, 15.84. Found: C, 68.05; H, 4.26; N, 15.95.

(2) A mixture of IV (0.3 g), 30% potassium hydroxide (2 ml), and alcohol (4 ml) was refluxed on a water bath for 15 min.

After cool, the reaction mixture was neutralized with concentrated hydrochloric acid, added with water. The precipitate was filtered, dried in a desiccator containing calcium chloride, and recrystallized from methanol to colorless needles of mp 223–225°, which proved to be identical with the specimen prepared in 1 by mixture melting point determination and spectral comparison.

(3) A mixture of VI (0.35 g), 30% potassium hydroxide (4 ml), and alcohol (1 ml) was strongly heated on a water bath, until the solid went into solution entirely (1 hr). A steady evolution of ammonia was observed during heating. After cooling, the solidified mixture was dissolved in a large quantity of water, neutralized with concentrated hydrochloric acid. The separating crystals were collected and recrystallized from alcohol to give 0.3 g of needles of mp 223–224°, which were proved to be identical with the substance prepared above in every respect.

Reduction of XI into 5,6-Diphenyldihydro-*as*-triazin-3(2H,4H)-one (XII).—To a suspension of XI (0.2 g) in a mixture of acetic acid (10 ml) and alcohol (10 ml) was added 0.3 g of zinc powder and the mixture was heated at gentle reflux for 1 day. The solution was separated by decantation and evaporated to dryness *in vacuo;* water was added. The insoluble part was collected and recrystallized from alcohol to afford *ca.* 0.1 g of colorless fine needles: mp 278–280° (lit.[5] 275–276°); ν_{max}^{KBr} 3220, 3078 (NH), and 1700 cm^{-1} (C=O); $\lambda_{max}^{alcohol}$ 220 mμ (log ϵ 4.11, infl) and 285 mμ (log ϵ 4.06). The infrared as well as ultraviolet spectrum of this product coincided with that of an authentic sample[5] perfectly.

5,6-Diphenyl-4-methyl-*as*-triazin-3(4H)-one 2-Oxide (XIII).—Compound XI (0.4 g) was dissolved in 1 ml of methanol containing 0.034 g of sodium. After the solvent was distilled off *in vacuo*, the remaining sodium salt was transferred into a pressure tube and dissolved anew in 15 ml of methanol. To this was added 1 ml of methanol which contained 0.21 g of methyl iodide. After prompt sealing, the tube was heated in a water bath for 2 hr, then cooled to 0°. The precipitating crystals were collected and recrystallized from methanol to yield 0.15 g of pale yellow needles: mp above 300°, ν_{max}^{KBr} 1675 cm^{-1} (C=O), $\lambda_{max}^{alcohol}$ 252 mμ (log ϵ 4.11) and 365 mμ (log ϵ 3.79).

Anal. Calcd for $C_{16}H_{13}N_3O_2$: C, 68.80; H, 4.69; N, 15.05. Found: C, 68.99; H, 4.51; N, 15.11.

5,6-Diphenyl-4-methyldihydro-*as*-triazin-3(2H,4H)-one (XIV).—Compound XIII (0.1 g) was dissolved in a mixture of acetic acid (10 ml) and alcohol (5 ml), zinc powder (0.1 g) was added, and this was gently refluxed on a water bath for 70 min. The solution was isolated from zinc and evaporated *in vacuo* to dryness. The residue was washed with water, dried *in vacuo*, and recrystallized from methanol to give *ca.* 60 mg of a colorless powder: mp 239–240°, ν_{max}^{KBr} 1677 cm^{-1}, $\lambda_{max}^{alcohol}$ 220 mμ (log ϵ 4.22, infl) and 290 mμ (log ϵ 4.13).

Anal. Calcd for $C_{16}H_{15}N_3O$: C, 72.43; H, 5.70; N, 15.72. Found: C, 72.33; H, 6.08; N, 15.49.

Conversion of IV into 4,5-Diphenyl-2-imidazolone (XVI).—A mixture of IV (0.5 g) and aniline (10 ml) was heated at 130° for 5 hr. After the solvent was removed by vacuum distillation, the residual tar was eluted through an alumina column with chloroform. Compound IV (0.2 g) was regenerated from the initial fraction. The following main fraction gave, after recrystallization from methanol, 0.1 g of starlike congregated prisms: mp above 300°; ν_{max}^{KBr} 1690 cm^{-1} (C=O); $\lambda_{max}^{alcohol}$ 219 mμ (log ϵ 4.23, infl), 244 (3.83), 260 (3.79), and 308 (4.03).

Anal. Calcd for $C_{15}H_{12}N_2O$: C, 76.25; H, 5.12; N, 11.86. Found: C, 75.73; H, 5.04; N, 11.62.

Identity with an authentic sample[7] was confirmed by infrared and ultraviolet spectra.

Conversion of XI into 4,5-Diphenyl-1,2,3-triazole (XVII).—A mixture of XI (0.5 g) and acetic anhydride (5 ml) was heated at 140–150° for 17.5 hr. The reaction mixture was evaporated under vacuum to a brownish resin, which was submitted to alumina chromatography in chloroform, followed by elution with methanol. The impure elutions were combined, evaporated to dryness, and again heated with 3 ml of acetic anhydride for 1 hr. The solvent was distilled off and the residue was recrystallized from 1:1 mixture of ether and petroleum ether (bp 60–70°) to give *ca.* 0.1 g of colorless needles: mp 140–141° (lit.[8] 139°), $\lambda_{max}^{alcohol}$ 249 mμ (log ϵ 4.10).

Anal. Calcd for $C_{14}H_{11}N_3$: C, 75.99; H, 5.01; N, 18.99. Found: C, 75.82; H, 5.01; N, 18.98.

Identity with an authentic sample[8] was confirmed by infrared and ultraviolet spectra.

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as-Triazine Chemistry. IV. Structural Studies on the Oxidation Products of 3-Amino-5-phenyl-*as*-triazine with Organic Per Acids

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Oxidation of 3-amino-5-phenyl-*as*-triazine with peracetic acid gave the 2-N-oxide II as a major product with a trace of 1-N-oxide III. The orientations of the oxide groups in these compounds were deduced on the basis of spectroscopic investigations and dipole moment measurements. The oxide II was converted to 4-phenyl-1,2,3-triazole (X) and 4-phenyl-2-imidazolone (XII), an additional observation of conversion of *as*-triazine oxides to five-membered heterocycles.

In continuation of our previous work[1-3] on the synthesis of *as*-triazine N-oxides, this paper describes the oxidation of 3-amino-5-phenyl-*as*-triazine (I)[4,5] readily obtained by cyclization of phenylglyoxal guanylhydrazone.[4,5]

Treatment of I with excess hydrogen peroxide in acetic acid gave a mixture of the 2-oxide II and a small amount of the 1-oxide III. These structures are discussed below based upon dipole moment and spectral data.

The reaction of II with ethyl chlorocarbonate afforded, though in poor yield, 3-ethoxycarbonylamino-5-phenyl-*as*-triazine 2-oxide (V), which was also obtainable by oxidation of 3-ethoxycarbonylamino-5-phenyl-*as*-triazine (IV, Scheme I) derived from I. All attempts at cyclization of V to an oxadiazolone derivative VI according to Katritzky[6] failed. Although II is rather stable to mineral acid and alkali, strong heating in 30% potassium hydroxide gave 4-phenyl-1,2,3-triazole (X).[7] Upon acetolysis of II, a new crystalline substance of mp 185–187° was isolated from a resinous mixture. Its structure is, from analysis and spectroscopic findings, assignable to β-(N^1-acetylureido-N^3)-styryl acetate (XIa) or its free alcohol XIb, the former being more acceptable according to a common understanding that an enolized form of an ureidocarbonyl will be rather unstable and further the free alcohol will be less stable than a saturated aldehyde formed by rearrangement of the hydrogen atom of the hydroxyl, as supported by nonexistence of styryl alcohol itself.

Compound XI had an absorption maximum at 260 mμ (log ϵ 4.07) in the ultraviolet spectrum which suggested existence of a double bond conjugated with a phenyl group. Its infrared spectrum showed the absorptions at 1684 (ureido), 1749 (acetoxy), and 3127 and 3226 cm^{-1} (N-H). The proton magnetic resonance spectrum presented two singlet methyl signals at τ 7.76 and 8.05 which are attributable to two nonequivalent acetyl groups.

Compound XI seems to be formed *via* the 3-acetamido compound VIII, since XI is also obtainable upon acetolysis of VIII. Compound VIII was obtained in good yield by treatment of II with acetic anhydride diluted with acetone, and alternatively from VII[4] by oxidation with permaleic acid.

Mild treatment of XI with dilute alkali led to 4-phenyl-2-imidazolone (XII), identical with a sample prepared from the condensation of phenacyl alcohol and urea. Brown, *et al.*,[8] have found that acidic hydrolysis of purine 1-oxide causes cleavage to give an oxime; this reaction can be ascribed to the polarization of the N-oxide bond. A similar effect may operate in the case of II. Scheme II indicates a possible mechanism for the formation of XII.

In the synthesis of VII, a further product was occasionally isolated; this was identified as 5-acetamido-3-methyl-1,2,4-triazole (IX) by spectral comparison with an authentic sample.[9] This compound probably arises by acidic cyclization of a diacetyl derivative of aminoguanidine formed by cleavage of VII.

For comparison, the infrared and ultraviolet spectral data of the oxides are presented in Figure 1 and Table I, respectively.

TABLE I

THE ULTRAVIOLET ABSORPTION SPECTRA OF THE OXIDES OF 3-AMINO-5-PHENYL-*as*-TRIAZINE AND OF THEIR DERIVATIVES

Compd	Solvent	λ_{max} (mμ)	Log ϵ
II	EtOH	229, 288, 398	4.18, 3.96, 3.98
	0.1 *N* HCl-EtOH	229, 291, 385	4.19, 3.96, 3.80
	0.1 *N* NaOH-EtOH	233, 287, 410, 450[a]	4.23, 4.10, 3.74, 3.67
III	EtOH 0.1 *N* HCl-EtOH 0.1 *N* NaOH-EtOH	227,[a] 256, 280,[a] 360	4.18, 4.25, 4.03, 3.85
V	EtOH	235, 296, 384	4.30, 4.18, 4.20
VIII	EtOH	240, 300, 385	4.27, 4.20, 4.18

[a] Inflections.

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[1] T. Sasaki and K. Minamoto, *Chem. Pharm. Bull.* (Tokyo), **12**, 1329 (1964).

[2] T. Sasaki and K. Minamoto, *ibid.*, **13**, 1168 (1965).

[3] Part III: *J. Org. Chem.*, **31**, 3914 (1966).

[4] J. Ekeley, *et al.*, *Rec. Trav. Chim.*, **59**, 496 (1940).

[5] J. A. Elvidge, *et al.*, *J. Chem. Soc.*, 4157 (1964).

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