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°), $\lambda_{\max}^{\text{alcohol}}$ 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	$\lambda_{\max}$ (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).

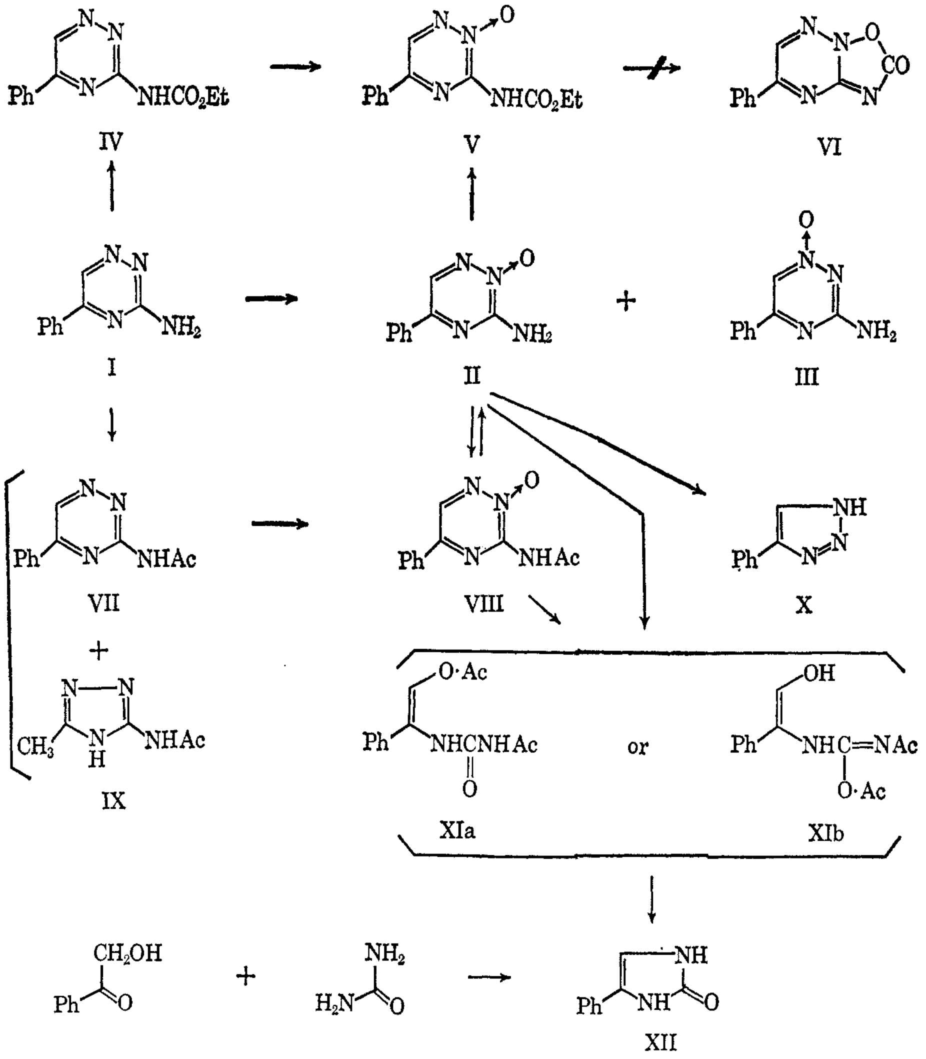
[6] A. R. Katritzky, *ibid.*, 2063 (1956).

[7] M. Ruccia, *Ann. Chim.* (Rome), **50**, 1363 (1960).

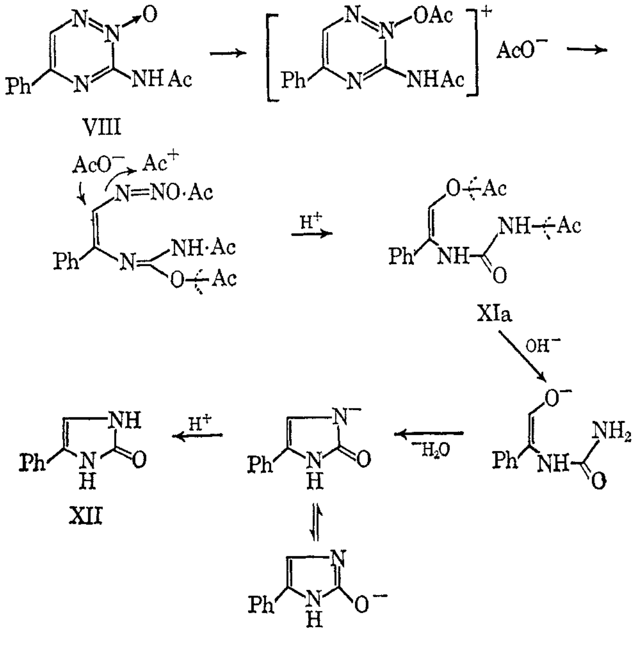
[8] G. B. Brown, *et al.*, *J. Org. Chem.*, **27**, 567 (1962), and other literatures cited there.

[9] J. Thiele, *et al.*, *Chem. Ber.*, **26**, 2599 (1893).

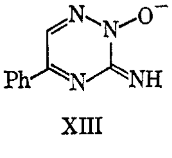
Scheme I



Scheme II



The infrared absorption patterns of II and III are similar, suggesting the skeletal and functional identity of both compounds. Concerning the ultraviolet spectra, II shows a pattern similar to that of V and VIII in neutral medium, suggesting the amino tautomer of II. The difference between the absorption of II in acidic medium and that in neutral medium is small, but in basic medium the longest wavelength absorption is remarkably shifted to the longer wavelength region and a new maximum appears at 450 mμ, presumably due to formation of the anion XIII. In contrast, the minor



XIII

oxide III showed no spectral shift in acid or base, consistent with a structure which precludes interaction of the N-oxide and amino groups.

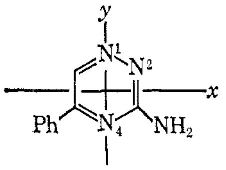
Dipole Moment of the Monoxide II of 3-Amino-5-phenyl-*as*-triazine.—The material utilized here was synthesized and purified according the procedure described in the experimental section and stored in a desiccator containing calcium chloride.

A. Measurement and Results.—The measurement of the dielectric constant was carried out in purified dioxane at 20° by means of a Kamura's apparatus with a stainless steel cell.[10] The specific gravity of an about 0.7% solution was measured by a picnometer with 5 ml

[10] M. Ishidate and Y. Kamura, *Yakugaku Zasshi*, **77**, 407 (1957).

of volume at the same temperature. The dielectric constant of the solvent utilized here was determined anew as ϵ (20°) 2.2253, which was an average of values estimated on several samples of dioxane subjected to the same procedure as the solution itself. From the measured dielectric constant and specific volume was calculated the molar polarization of the solute according the method of Halverstadt and Kumler.[11] The sum of electronic and atomic polarizations of the solute was approximated with the calculated molar refraction for the D line. The results were as follows: α, 12.152; β (g/cc), −0.103; P_∞ (cc), 419.24; $[M]_D$ (cc), 54.26; and μ (D), 4.19. α and β denote, respectively, the changes of the dielectric constant and specific volume of the solution with the weight fraction of the solute; others have their usual significances.

B. Discussion.—For vector analysis, the accepted values of group moments can be conveniently used, *i.e.*, 1.52 D. of aniline[12] for the amino function, 4.24 D. of pyridine N-oxide[13] for the N-oxide group, and 2.22 D. of pyridine[14] for the skelet. One can further use for the present compound the values[2] formerly calculated for 1-, 2-, and 4-oxide of 3-amino-5,6-diphenyl-*as*-triazine [Calcd for 1-oxide, μ = 3.94 D.; 2-oxide, μ = 3.72 D. (3.85 D.); 4-oxide, μ = 0.42 D. (0.61 D.).] as they are, assuming that (1) the mesomeric moment of the 5-phenyl rest is negligible, (2) the plane of the ring is formed hexagonally, and (3) the direction of the amino moment lies in the plane at a distance of 30° from the *x* axis, averaging all angles supposed to be occupied by an amino moment in a free rotatory condition.



The values in parentheses are the ones calculated on the assumption that the amino group is fixed by hydrogen bonding with the oxide oxygen atom and thus the amino moment is apart from the oxide moment by 115° as estimated for the 2-oxide of 5,6-dimethyl analog,[1] whose moment was measured in the same solvent.

In the present case, admittedly, the 1-oxide structure is out of the question because of the positive ferric chloride reaction and the theoretical value for a 4-oxide, 0.42 D. (0.61 D.), is too low. Thus the found moment 4.19 D. indicates the 2-oxide structure of II.

The difference between calculated and found moment, 0.47 D. (0.34 D.), is more attributable to a solvent effect than to possible experimental errors. An appreciable increase in apparent dipole moment has often been observed when measured in dioxane.[15,16] Possibly, some polar structure is stabilized through hydrogen bonding between an amino hydrogen atom of II and an oxygen atom of the dioxane molecule, likewise in our case.

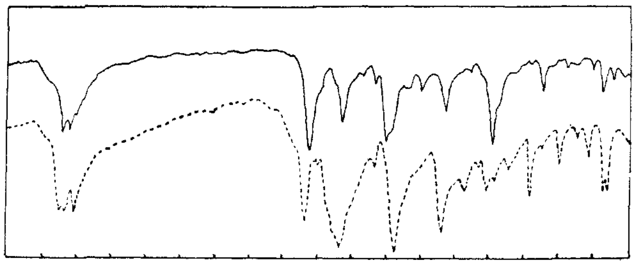


Figure 1.—Infrared spectra in KBr of 3-amino-5-phenyl-*as*-triazine 2-oxide (II) (———) and 3-amino-5-phenyl-*as*-triazine 1-oxide (III) (- - - -).

Experimental Section[17]

Oxidation of 3-Amino-5-phenyl-*as*-triazine (I) with Peroxyacetic Acid.—A solution of I (1.5 g) in acetic acid (20 ml) containing 30% hydrogen peroxide (1.5 ml) was kept at 60° for 4 hr. After this time, a further 30% hydrogen peroxide (0.5 ml) was added and warming was continued at the same temperature for further 3 hr. The reaction mixture was then condensed *in vacuo* below 60° to 0.5 volume under occasional additions of water to remove excess hydrogen peroxide, by which time yellow crystals began to deposit. After filtering this solid, the mother liquor was added with a considerable amount of water to give a large quantity of the second crop. The combined product was dried *in vacuo* in a desiccator, 80 ml of chloroform was added, and it was allowed to stand overnight at room temperature. The insoluble part was filtered (1.2 g, mp 215–217°) and recrystallized once from alcohol to afford 1.1 g of 3-amino-5-phenyl-*as*-triazine 2-oxide (II) as yellow prisms: mp 217–219°; infrared spectrum (KBr), 3325, 3243, 3175 (ν NH), and 1622 cm^{-1} (δ NH); $FeCl_3$ reaction, violet.

Anal. Calcd for $C_9H_8N_4O$: C, 57.44; H, 4.29; N, 29.77. Found: C, 58.05; H, 4.59; N, 29.34.

The foregoing aqueous filtrate was evaporated to dryness below 60° to give a small quantity of residue, which was extracted with 60 ml of chloroform. The chloroform extract was combined with the above chloroform solution separated from II, evaporated to small bulk, and chromatographed in a mixed solvent of EtOH–$CHCl_3$ (1:4) on alumina (200–300 mesh) to afford, from the first, pale yellow fluorescent runnings, substantially pure 3-amino-5-phenyl-*as*-triazine 1-oxide (III) as yellow microcrystalline needles (30 mg): mp 230–231°; infrared spectrum (KBr), 3363, 3302, 3200 (ν_{NH}), and 1628 cm^{-1} (δ_{NH}). This substance gave no color with neutral aqueous ferric chloride solution even under warming.

Anal. Calcd for $C_9H_8N_4O$: C, 57.44; H, 4.29; N, 29.77. Found: C, 57.45; H, 4.41; N, 29.81.

The second runnings gave 0.15 g of yellow prisms, which were identified with II spectroscopically.

3-Acetamido-5-phenyl-*as*-triazine 2-Oxide (VIII).—(1) A mixture of II (0.21 g), acetone (2 ml), and acetic anhydride (2 ml) was gently refluxed on a water bath until the solid was completely dissolved, followed by spontaneous evaporation of the acetone. Then acetic anhydride was distilled off under reduced pressure.

Repeated crystallization of the residue from acetone gave 0.2 g of yellow fine prisms: mp 192–194°, $\nu_{\max}^{\mathrm{KBr}}$ 3306 cm^{-1} (NH) and 1727 cm^{-1} (C=O).

Anal. Calcd for $C_{11}H_{10}N_4O_2$: C, 57.38; H, 4.38; N, 24.34. Found: C, 57.45; H, 4.58; N, 24.19.

(2) To an ice-cold stirred solution of 0.64 ml (4.7 × 10^{-3} mole) of 30% hydrogen peroxide and 5 ml of methylene chloride was added 0.82 g (5.65 × 10^{-3} mole) of maleic anhydride. When the solid had gone into solution, a solution of VII (1.0 g) in 35 ml of methylene chloride was added in one batch. After 2 hr of stirring at room temperature, the separated maleic acid was removed by filtration. The filtrate was, after addition of chloroform, added with diluted sodium hydroxide up to alkalinity to extract the residual maleic acid, when unexpectedly a large amount of orange-yellow crystals separated. The crystals were filtered, thrown into the alkaline solution, separated from the chloroform layer, and

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[11] I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).

[12] Y. Kurita and M. Kubo, *Bull. Chem. Soc.* (Tokyo), **27**, 364 (1954).

[13] E. P. Linton, *J. Am. Chem. Soc.*, **62**, 1945 (1940).

[14] C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, p 253.

[15] M. J. Aroney, *et al.*, *J. Chem. Soc.*, 5115 (1963), and other literatures cited there.

[16] Reference 14, p 342.

[17] The melting points reported were determined on a Hozumi's electric micro melting 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.

again brought into solution by further addition of water. Neutralization of this solution with acetic acid gave a pale yellow precipitate, which was filtered and recrystallized from methanol to give 0.5 g of pale yellow needles, mp 194°. This was identified with the preparation by method 1 infrared spectroscopically. An additional crop (0.15 g) of VIII was obtained from the chloroform layer by silica gel chromatography using the same solvent.

Acid Hydrolysis of VIII to II.—A mixture of VIII (60 mg), alcohol (1 ml) and 2 *N* hydrochloric acid (1 ml) was vigorously refluxed for 1 hr. The reaction mixture was evaporated *in vacuo* to dryness and the residue was basified with ammonia to give a yellow precipitate which was filtered and recrystallized from alcohol to afford 20 mg of yellow prisms, mp 216°. Its infrared spectrum was identical with that of II derived from I.

3-Ethoxycarbonylamino-5-phenyl-*as*-triazine (IV).—A mixture of 3-amino-5-phenyl-*as*-triazine (I, 0.5 g), anhydrous pyridine (10 ml) and ethyl chloroformate (0.4 g) was magnetically stirred at 60° for 1.5 hr. The reaction mixture was condensed *in vacuo* at 60° as thoroughly as possible to give a resinous residue, which was added with water and neutralized with acetic acid. The resulting crystals were filtered by suction, dried, and digested with chloroform. After the major portion (the starting material), sparing soluble in chloroform, was filtered off, the mother liquor was evaporated to small bulk and eluted in chloroform on a silica gel column.

Recrystallization of the main fraction from ether or methylene chloride gave 0.25 g of pale yellow fine plates: mp 101–102°, $\nu_{\max}^{\text{KBr}}$ 1753 cm^{-1} (C=O).

Anal. Calcd for $C_{12}H_{12}N_4O_2$: C, 59.01; H, 4.95; N, 22.94. Found: C, 58.86; H, 4.94; N, 23.08.

3-Ethoxycarbonylamino-5-phenyl-*as*-triazine 2-Oxide (V).—(1) To a cold, stirred mixture of 30% hydrogen peroxide (0.1 ml) and methylene chloride (2 ml) was added maleic anhydride (0.14 g). After 10 min, a solution of IV (0.2 g) in methylene chloride (2 ml) was added to the foregoing solution of permaleic acid. After stirring for 1 hr, the reaction mixture was, in the presence of a considerable amount of chloroform, washed with 10% sodium bicarbonate solution and then with water. The separated organic layer was dried and evaporated *in vacuo* to dryness.

Recrystallization of the residue from chloroform gave 0.15 g of pale yellow needles: mp 151–154°, $\nu_{\max}^{\text{KBr}}$ 3336 cm^{-1} (NH) and 1754 cm^{-1} (C=O).

Anal. Calcd for $C_{12}H_{12}N_4O_3$: C, 55.38; H, 4.65; N, 21.53. Found: C, 55.70; H, 4.43; N, 21.36.

(2) A mixture of II (0.8 g), ethyl chloroformate (0.68 g) and anhydrous pyridine (8 ml) was stirred at 70–80° for *ca.* 10 hr, and then evaporated *in vacuo* to a dark reddish paste. Digestion of the remainder with chloroform made it solidify. The solid portion (0.65 g) was filtered and washed with a small amount of chloroform to give yellow needles, which proved to be practically pure starting material II. The mother liquor, which separated from II, was chromatographed in chloroform on silica gel (100 mesh) to afford about 70 mg of pale yellow needles, mp 150–153°, which were completely identified with the product from method 1 both in infrared and ultraviolet spectrum.

5-Acetamido-3-methyl-1,2,4-triazole (IX).—Compound I (3.0 g) was heated with 15 g of acetic anhydride on a boiling-water bath for 1.5 hr. The excess acetic anhydride was distilled off *in vacuo* and the viscous residue was digested with chloroform. The separating solid (1.0 g) was filtered and, after recrystallization from alcohol, proved to be identical with 3-acetamido-5-phenyl-*as*-triazine (VII). The mother liquor was again condensed under atmospheric pressure to a paste, which, by digestion with a little amount of alcohol, could be brought into crystallization. Recrystallization of the collected solids from alcohol gave 0.5 g of colorless needles which slowly melt above 260°.

The infrared as well as ultraviolet spectrum of this substance proved to be identical with those of an authentic specimen.[9]

Anal. Calcd for $C_5H_8N_4O$: C, 42.85; H, 5.75; N, 39.98. Found: C, 42.36; H, 5.76; N, 39.64.

Alkaline Hydrolysis of II. Formation of 4-Phenyl-1,2,3-triazole (X).—A suspension of II (0.2 g) in 30% aqueous potassium hydroxide solution (3 ml) was strongly heated on a water bath. A steady evolution of ammonia was observed while heating. After 2 hr, during which time the entire solid had gone into solution, the reaction mixture was cooled and neutralized with acetic acid to effect the precipitation of a solid. The collected solid was dried *in vacuo* and repeatedly crystallized from chloroform to give a small quantity of fine lustrous plates, mp 145–147°.

Anal. Calcd for $C_8H_7N_3$: C, 66.19; H, 4.86; N, 28.95. Found: C, 66.71; H, 4.90; N, 29.20.

Identity with an authentic sample[7] was evidenced by mixture melting point determination and spectral comparison.

Acetolysis of II. Formation of XI.[18]—Compound II (0.5 g) was heated with acetic anhydride (5 ml) on a boiling water bath for 2 hr and allowed to stand at room temperature overnight, when a precipitation of needles were observed on the wall of the vessel. After cooling, these crystals were collected by suction and recrystallized from methanol to give star-like, congregated fine needles (0.15 g): mp 185–187°; $\nu_{\max}^{\text{KBr}}$ 3226, 3125 (NH or OH), 2975 (CH), 1749 (C=O, acetoxy), and 1684 cm^{-1} (C=O, ureido); $\lambda_{\max}^{\text{alcohol}}$ 260 mμ (log ε 4.07); nmr spectrum [$CHCl_3$–CCl_4 (4:1)], $2COCH_3$, τ 7.76 (3 H), 8.05 (3 H), and 0.13 (br, unassignable, 1–2 H).

Anal. Calcd for $C_{13}H_{14}N_2O_4$: C, 59.53; H, 5.38; N, 10.68. Found: C, 59.25; H, 5.18; N, 10.90.

When the filtrate was evaporated and digested with methanol, an additional crop (20 mg) of XI was obtained.

4-Phenyl-2-imidazolone (XII).—(1) To a stirred suspension of 60 of mg XI in 2 ml of alcohol was added by drops 2 ml of 10% sodium hydroxide, when the solid went into solution immediately. A slight heating caused the solution to be deep red. The mixture was then cooled with water and neutralized with acetic acid, and separating crystals were filtered. The mother liquor was evaporated *in vacuo* to dryness, little water was added, and the insoluble portion was isolated by filtration. The combined crops were recrystallized from alcohol to give 35 mg of colorless microplates which became red colored slowly near 250° and melted between 280 and 295° (dec), $\lambda_{\max}^{\text{alcohol}}$ 286 mμ (log ε 4.19).

Anal. Calcd for $C_9H_8N_2O$: C, 67.48; H, 5.03; N, 17.49. Found: C, 67.30; H, 5.23; N, 17.36.

(2) Phenacyl alcohol (0.5 g) was thoroughly mixed with urea (0.4 g) and heated at 110° for 2 hr under occasional agitating. The reaction mixture was then cooled up to room temperature and digested with 30 ml of water. The insoluble part was collected by suction, washed with ether, and recrystallized from methanol to give 150 mg of colorless plates, mp above 280°. The infrared as well as ultraviolet spectrum of this substance was proved to be identical with those of a specimen from synthesis 1.

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[18] A few cases were observed where an unspecified yield of VIII was obtained together with XI. The yields of XI were generally extremely low in our several trials, among which the most favorable one is described here.