1,3,4,6,7,8,9,10,11,11a-Decahydro-1-amino-2H-benzo[*b*]quinolizine (21).—A solution of crude **23** (0.4 g) in ethanol (25 ml) was hydrogenated with platinum oxide (0.1 g) at atmospheric pressure and room temperature. One mole equivalent of hydrogen was absorbed. The catalyst was filtered and the solvent was distilled under reduced pressure to give a yellow oil (0.352 g) which could not be crystallized.

The product was characterized as the **carbobenzoxy derivative** (22). To a stirred and cooled solution of **21** (0.14 g) in anhydrous toluene (10 ml), 2 *N* sodium hydroxide (2.0 ml) was added. Carbobenzoxy chloride (0.12 g) was then added dropwise and the mixture was stirred in an ice bath for 1 hr. The toluene layer was separated and the aqueous layer extracted three times with 25-ml portions of chloroform. The extracts were combined, dried over anhydrous sodium sulfate, and evaporated to dryness under reduced pressure. The crude material was recrystallized twice from acetone–Skellysolve B to yield clusters of colorless crystals (78 mg, 33%), mp 167–169°. Recrystallization gave an analytical sample: mp 168–169°; λ_{max} 2.90 (NH), 3.55, 3.61, 5.78, 5.82, 6.51, 6.60 μ.

Anal. Calcd for $C_{21}H_{28}N_2O_2$: C, 74.08; H, 8.29; N, 8.23. Found: C, 73.90; H, 8.47; N, 7.88.

3,4,6a,7,8,9,10,10a,11,11a-Decahydro-2H-benzo[*b*]quinolizine-6a,10a-diol-1(6H)-one Oxime (8).—In a 50-ml round-bottom flask provided with a water condenser and drying tube were placed 6 (0.1 g, mp 151–152°), hydroxylamine hydrochloride (0.1 g), anhydrous sodium acetate (0.2 g), and anhydrous methanol (10 ml). The mixture was refluxed for 3 hr, cooled, and evaporated to dryness under reduced pressure. Water was added to the residue, followed by several drops of concentrated ammonium hydroxide to pH 9. Upon cooling, the oxime crystallized from solution, was filtered, washed with water, and dried. Several recrystallizations from methanol–ether yielded colorless transparent crystals (68 mg, 67%), mp 242–246° dec. Recrystallization from methanol–ether gave an analytical sample, mp 245–246° dec. The infrared spectrum (mineral oil mull) shows a sharp peak at 2.93 (OH stretching of oxime), a peak at 3.02 attributed to hydrogen-bonded hydroxyl, a *trans*-quinolizidine peak at 3.61, and a sharp peak at 6.09 μ (C=N).

Anal. Calcd for $C_{13}H_{22}N_2O_3$: C, 61.39; H, 8.72; N, 11.02. Found: C, 61.49; H, 8.59; N, 11.10.

The Synthesis of 1,2,4-Triazine

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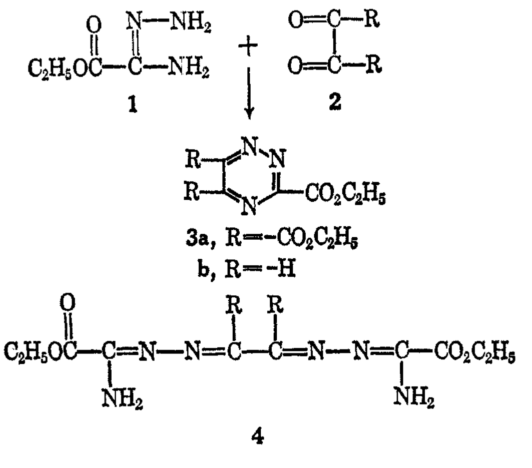
The condensation of glyoxal with ethyl oxalamidrazonate (1) yields ethyl 1,2,4-triazine-3-carboxylate (**3b**). This compound was converted to 1,2,4-triazine by saponification of **3b**, followed by decarboxylation. The nmr spectra of the various triazines are reported.

We have recently[1] been concerned with the study of various heteroaromatic systems, and now wish to report the synthesis of 1,2,4-triazine (*as*-triazine).

During the past few years several attempted syntheses of 1,2,4-triazine have been reported.[2-5] One of these attempts[4] involved the condensation of ethyl oxalamidrazonate (1) (Scheme I) with diethyl diketosuccinate (2, R = $-CO_2C_2H_5$) to yield the triester of 1,2,4-triazine-3,5,6-tricarboxylic acid (**3a**). Hydrolysis to the tricarboxylic acid followed by thermal decarboxylation yielded the anhydride of 1,2,4-triazine-5,6-dicarboxylic acid. Similarly, 5,6-diphenyl-1,2,4-triazine-3-carboxylic acid is readily decarboxylated to 5,6-diphenyl-1,2,4-triazine.[6] These reactions clearly demonstrate the lability of a 3-carboxylate grouping on 1,2,4-triazines.

Scheme I



Previous attempts[4] to obtain 1,2,4-triazine-3-carboxylic acid by condensing ethyl oxalamidrazonate (1) with glyoxal (2, R = –H) did not afford the expected ester **3b**. The only materials obtained were compound **4** (R = –H) and a viscous, presumably polymeric, substance.

It is certainly reasonable to expect that the ester **3b** should be formed in this reaction, especially under the conditions of fairly high dilution as described by Ratz and Schroeder.[4] We consequently repeated this synthesis and examined the nmr spectrum of the crude reaction mixture resulting from the condensation of **1** with glyoxal. This spectrum revealed the presence of a material (A) which shows an AB pattern with H_A and H_B at τ 0.48 and 1.07, respectively. These chemical shifts are typical for H_6 and H_5 in other 1,2,4-triazines (Table I). It thus became clear that an attempt at isolating compound A from the crude reaction mixture would be eminently worthwhile.

Chromatography on neutral alumina afforded material which was considerably enriched in compound A. This substance was finally obtained pure by distillation, followed by recrystallization from a mixture of benzene and hexane. Elemental analysis and molecular weight determination agreed with the formula $C_6H_7N_3O_2$. The nmr spectrum indicates the presence of an ethyl group and of two strongly deshielded, coupled protons (Table I). These data are in agree-

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(1) W. W. Paudler and H. L. Blewitt, *J. Org. Chem.*, **30**, 4081 (1965).

(2) K. Koermendy, P. Sohar, and J. Volford, *Ann. Univ. Sci. Budapest. Rolando Eotvos Nominatae, Sect. Chim.*, **5**, 117 (1963); *Chem. Abstr.*, **60**, 13243*g* (1964).

(3) C. Grundmann and R. Ratz, *Chem. Ber.*, **91**, 1766 (1958).

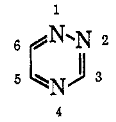
(4) R. Ratz and H. Schroeder, *J. Org. Chem.*, **23**, 1931 (1958).

(5) C. Grundmann, H. Schroeder, and R. Ratz, *ibid.*, **23**, 1522 (1958).

(6) P. Schmidt and J. Druey, *Helv. Chim. Acta*, **38**, 1560 (1955).

TABLE I

PROTON CHEMICAL SHIFTS (τ) AND COUPLING CONSTANTS (CPS) OF SOME 1,2,4-TRIAZINES



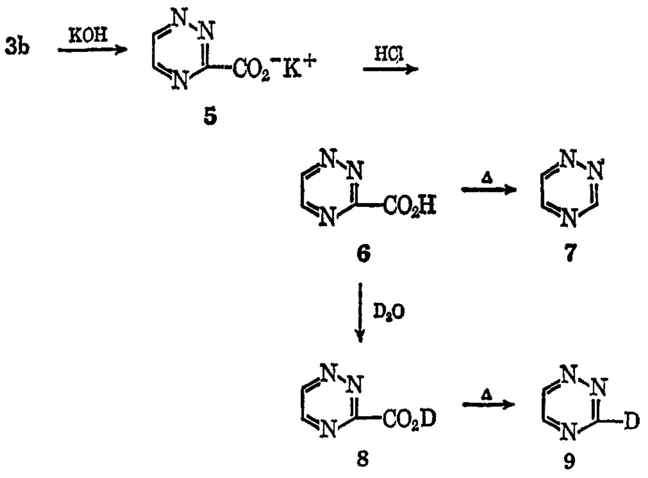
	Parent		3-D	3-$CO_2C_2H_5$	3-$CO_2^-K^+$	3-NH_2[a]	3-NH_2-[b] 5-C_6H_5	3-NH_2-[b] 6-C_6H_5
H_3	0.12	0.37	...	...	...	...	...	...
H_5	1.16	1.47	1.16	1.07	1.00	1.38	...	1.40
H_6	0.52	0.76	0.52	0.48	0.55	0.93	0.87	...
$J_{5,6}$	2.7	2.7	2.7	2.5	2.4	1.8	...	...
$J_{3,6}$	2.2	2.2	...	...	...	...	...	...
Substituent	...	...	...	$-CH_2-5.35$[c] $-CH_3$ 8.48[d] $J = 7.2$	...	...	...	...
Solvent	$CDCl_3$	CCl_4	$CDCl_3$	$CDCl_3$	D_2O	CF_3CO_2D	Dioxane	Dioxane

[a] Prepared by the procedure of J. G. Erickson (*J. Am. Chem. Soc.*, **74**, 4706 (1952)). [b] Taken from ref 8. [c] Quartet. [d] Triplet.

ment with the assigned structure, ethyl 1,2,4-triazine-3-carboxylate (**3b**).

Treatment of **3b** (Scheme II) with alcoholic potassium hydroxide afforded the potassium salt of 1,2,4-triazine-3-carboxylic acid (**5**). The free carboxylic acid was obtained by treatment of the potassium salt with one equivalent of aqueous hydrochloric acid. The carboxylic acid **6** could not be obtained in an anhydrous state. Samples of this acid dried in the presence of phosphorus pentoxide gave elemental analyses approaching the composition expected for a monohydrate. This acid was readily decarboxylated at 110–120° to yield a yellow oil. Gas chromatographic analysis of this oil demonstrates the presence of two compounds in approximately equal amounts. One of these compounds was readily identified as water. Preparative gas chromatography afforded the second component, a solid (mp 16–17.5°) which gave a correct elemental analysis and molecular weight for $C_3H_3N_3$. The nmr spectrum of this compound exhibits three one-proton multiplets at τ 0.37, 0.76, and 1.47, respectively, and is, therefore, consistent with that expected for 1,2,4-triazine (**7**).

SCHEME II



The relative chemical shifts of the various protons of 1,2,4-triazine can be estimated by analogy with other azines. Since H_2 is subject to the N-anisotropy effects of two adjacent nitrogen atoms, we anticipate that it will be the most deshielded proton in 1,2,4-triazine.[7] By analogy with the chemical shifts of H_6 in 3-amino-5-phenyl-1,2,4-triazine (τ 0.87) and of H_5 in 3-amino-6-phenyl-1,2,4-triazine[8] (τ 1.40), we anticipate that H_5 will be the most shielded proton in 1,2,4-triazine.

With these considerations in mind, we can now analyze the nmr spectrum of 1,2,4-triazine (**7**) in detail and arrive at the assignments reported in Table I. Further confirmation of the assignments of the H_3 chemical shift and the long-range coupling of H_3 to H_6 is found by an analysis of the 3-deuterio-1,2,4-triazine (**9**) obtained from the decarboxylation of the deuterated carboxylic acid **8**. The nmr spectrum of the 3-deuterio-1,2,4-triazine is essentially void of the broad doublet at τ 0.37 in **7**, and the "apparent" triplet at τ 0.76, due to H_6, now appears as a simple doublet. Thus, the chemical shift assignments and spin–spin coupling constants reported in Table I are confirmed.

Some aspects of the chemistry of 1,2,4-triazine and an analysis of the vapor phase ultraviolet as well as microwave spectrum of this compound will be described in a forthcoming publication.

Experimental Section[9]

Ethyl 1,2,4-Triazine-3-carboxylate.—A solution of ethyl oxalamidrazonate[6] (16.5 g, 0.126 mole) in 600 ml of absolute ethyl alcohol was added during an 11-hr period to a stirred solution of 48.3 g of 30% aqueous glyoxal in 3 l. of absolute ethyl alcohol. The resulting solution was allowed to stand at room temperature for an additional 36 hr and was finally concentrated *in vacuo* (40–50°) to 300 ml. The precipitated solid was collected by filtration to afford 3.9 g (22% of theory) of compound **4** (R = -H).[6] The filtrate was mixed with 100 g of grade III (Brockman) neutral alumina and the excess solvent was removed *in vacuo* (40–50°). The remaining oily mass was then placed on a column of 300 g of neutral alumina (grade III, Brockman). Rapid elution with a mixture of equal amounts of benzene–ethyl acetate, followed by pure ethyl acetate until the eluate was colorless, yielded, after removal of the solvents, a heavy red oil. This oil was distilled in 1-ml portions at 130–135° (0.25 mm). The combined

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(7) J. H. Reynolds [Ph.D. Thesis, University of Washington, Seattle, Wash., 1964] discusses some of these consideration in great detail for other azines.

(8) J. A. Elvidge, G. T. Newbold, I. R. Senciall, and G. Symes, *J. Chem. Soc.*, 4157 (1964).

(9) Melting points are uncorrected. Nmr spectra were obtained with a Varian A-60 spectrometer. The microanalyses were performed by Mrs. S. DeBoer of this department.

distillates which solidified at room temperature were recrystallized from a mixture of benzene and hexane (3:1). After two recrystallizations, 1.97 g (10.2%) of yellow crystals (mp 72.5–73.8°) was obtained. If the preliminary purification by washing through alumina is omitted, the distilled ester is oily and can be crystallized only with difficulty.

Anal. Calcd for $C_6H_7N_3O_2$: C, 47.05; H, 4.61; N, 27.43; mol wt, 153.1. Found: C, 47.16; H, 4.71; N, 27.43; mol wt, 155 (osmometric).

An increase in the addition time of the ethyl oxalamidrazonate to the glyoxal solution to 36 hr eliminated the formation of compound **4** (R = –H) without increasing the yield of the triazine ester.

1,2,4-Triazine-3-carboxylic Acid (6).—To a stirred solution of 504 mg of ethyl 1,2,4-triazine-3-carboxylate in 8 ml of absolute ethyl alcohol was added a filtered solution of 0.3 g of potassium hydroxide in 15 ml of absolute ethyl alcohol. The resulting solution was allowed to stand at room temperature for 24 hr. The precipitated solid (**5**) (522 mg; 97% of theory) was collected and recrystallized from 95% ethyl alcohol. The small pale yellow crystals melted at 250–280° with decomposition. Additional recrystallizations from the same solvent did not alter the decomposition range.

Anal. Calcd for $C_4H_2KN_3O_2$: C, 29.43; H, 1.23; N, 25.75. Found: C, 29.52; H, 1.22; N, 25.50.

The free carboxylic acid was obtained by dissolving the potassium salt **5** (231 mg; 1.42 mmoles) in 1.0 *N* aqueous hydrochloric acid (1.5 ml). The resulting solution was freeze-dried and the residue was collected, washed with a few drops of water, air dried, and finally dried under vacuum over phosphorus pentoxide.

Anal. Calcd for $C_4H_5N_3O_3$: C, 33.57; H, 3.52; N, 29.37. Found: C, 32.91; H, 3.09; N, 29.15 (see text).

1,2,4-Triazine (7).—Carboxylic acid hydrate (**6**) (200 mg) (1.4 mmoles) was heated at 120° in a Pyrex tube, sealed on one end, for 5 min. The pyrolysis product was washed with a total of 5 ml of chloroform. Vpc analysis of this solution indicated the presence of approximately equal amounts of water and the triazine. The chloroform washings were dried over anhydrous sodium sulfate, filtered, and evaporated to a volume of 1 ml by carefully blowing dry N_2 gas over the solution. The remaining yellow solution was chromatographed by preparative gas chromatography (8-ft silicone gum rubber (10%) on Diatoport S, injection port temperature 200°, column temperature 145°, helium flow rate 150 cc/min). The collected pale yellow oil which gradually solidified (mp 16–17.5°) weighed 46 mg (40% of theory): bp 156 (740 mm) (capillary); $n^{25}\mathrm{D}$ 1.5149.

Anal. Calcd for $C_3H_3N_3$: C, 44.42; H, 3.76; N, 51.82; mol wt, 81.1. Found: C, 44.65; H, 3.40; N, 51.55; mol wt, 85 (osmometric in benzene).

3-D-1,2,4-Triazine (9).—Carboxylic acid **6** (100 mg) was suspended in 15 ml of 98% D_2O, and the suspension was allowed to stand at room temperature, with occasional swirling, for 24 hrs. The carboxylic acid was then recovered by removal of the D_2O by freeze-drying. The deuterated carboxylic acid **8** was then decarboxylated as described for the preparation of 1,2,4-triazine (**7**) to yield 25 mg of 3-D-1,2,4-triazine. The nmr spectrum of this compound is recorded in Table I.

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The Structure of 2-Pyrazolin-5-one Dyes

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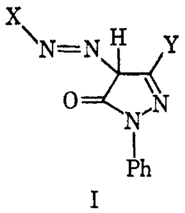
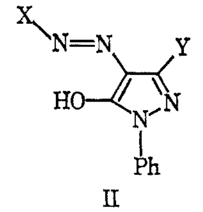
2-Pyrazolin-5-one dyes obtained by the coupling reaction of 1,3-diphenyl-2-pyrazolin-5-one with diazotized anilines exist in the solid state and in solutions as a strongly chelated hydrazone keto structure, IIIb, on the basis of results obtained by the nmr, infrared, and electronic spectral data.

The problem of the tautomeric structure of 4-arylazo-5-one dyes has been source of controversy for a long period. Recently, three groups of investigators have formulated "1-phenyl-3-methyl-4-phenylazo-2-pyrazolin-5-one" as Ia,[1] IIa,[2] and IIIa[3] on the basis of spectroscopic studies. Katritzky and Maine[4] have found that the 4-unsubstituted 2-pyrazolin-5-ones exist as tautomeric mixtures of the 2H and 4H isomers, and the 2H azo keto form (IV), accordingly, may also be considered for these dyes.

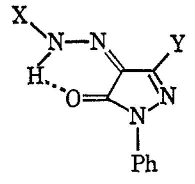
In the present work, the tautomeric structure of "1,3-diphenyl-4-arylazo-2-pyrazolin-5-ones" has been found to be the chelated hydrazone keto form (IIIb), corresponding to that assigned to the 3-methyl derivatives by Jones, *et al.*[3]



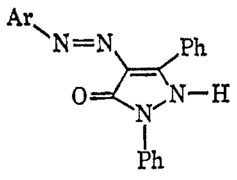
I
Ia, X = Ph; Y = Me
b, X = Ar; Y = Ph



II
IIa, X = Ph; Y = Me
b, X = Ar; Y = Ph



III
IIIa, X = Ph; Y = Me
b, X = Ar; Y = Ph



IV

Nmr Evidence.—The nmr spectrum of the 1,3-diphenyl compound (Va) contained only peaks for aryl protons (δ = 7.34 ppm) and a highly deshielded proton (δ = 13.89 ppm); there was no signal in the 6.4-ppm region[5] corresponding to a proton at C-4. The low-field signal is in a position previously observed for hydrogen-bonded N–H peaks[6] and corresponds closely to the peak at 13.8–14.2 ppm found in the 3-methyl

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(1) F. A. Snavely, W. S. Trahanovsky, and F. H. Suydam, *J. Org. Chem.*, **27**, 994 (1962).

(2) W. Pelz, W. Puschel, H. Schellenberger, and K. Loffler, *Angew. Chem.*, **72**, 967 (1960).

(3) R. Jones, A. J. Ryan, S. Sternhell, and S. E. Wright, *Tetrahedron*, **19**, 1497 (1963).

(4) A. R. Katritzky and F. W. Maine, *ibid.*, **20**, 299 (1964).

(5) D. M. Gale, W. J. Middleton, and C. G. Krespan, *J. Am. Chem. Soc.*, **87**, 657 (1965).

(6) G. O. Dudek and G. P. Volpp, *J. Org. Chem.*, **30**, 50 (1965).